Spring 6-12-2013

Integrating Pyrolysis and Anaerobic Digestion in a Novel Biorefinery Concept

Matthew Smith
Washington State University

Manuel Garcia Perez
Washington State University

Integrating Pyrolysis and Anaerobic Digestion in a Novel Biorefinery Concept

Matthew Smith, Manuel Garcia-Perez

Bioenergy IV
June 12th, Otranto Italy

WASHINGTON STATE UNIVERSITY
World Class. Face to Face.

Motivation for Integration

Adoption of anaerobic digestion is currently proceeding at a slower than desired pace in the United States

Adoption is hindered by currently marginal economics of operations

Pyrolysis offers an effective means to treat recalcitrant fiber remaining after digestion and develop potentially valuable co-products

Fields surrounding numerous dairy and CAFOs are overloaded with N and P (36% and 55%). Char based filters may be effective in reducing effluent concentrations and limiting further over application

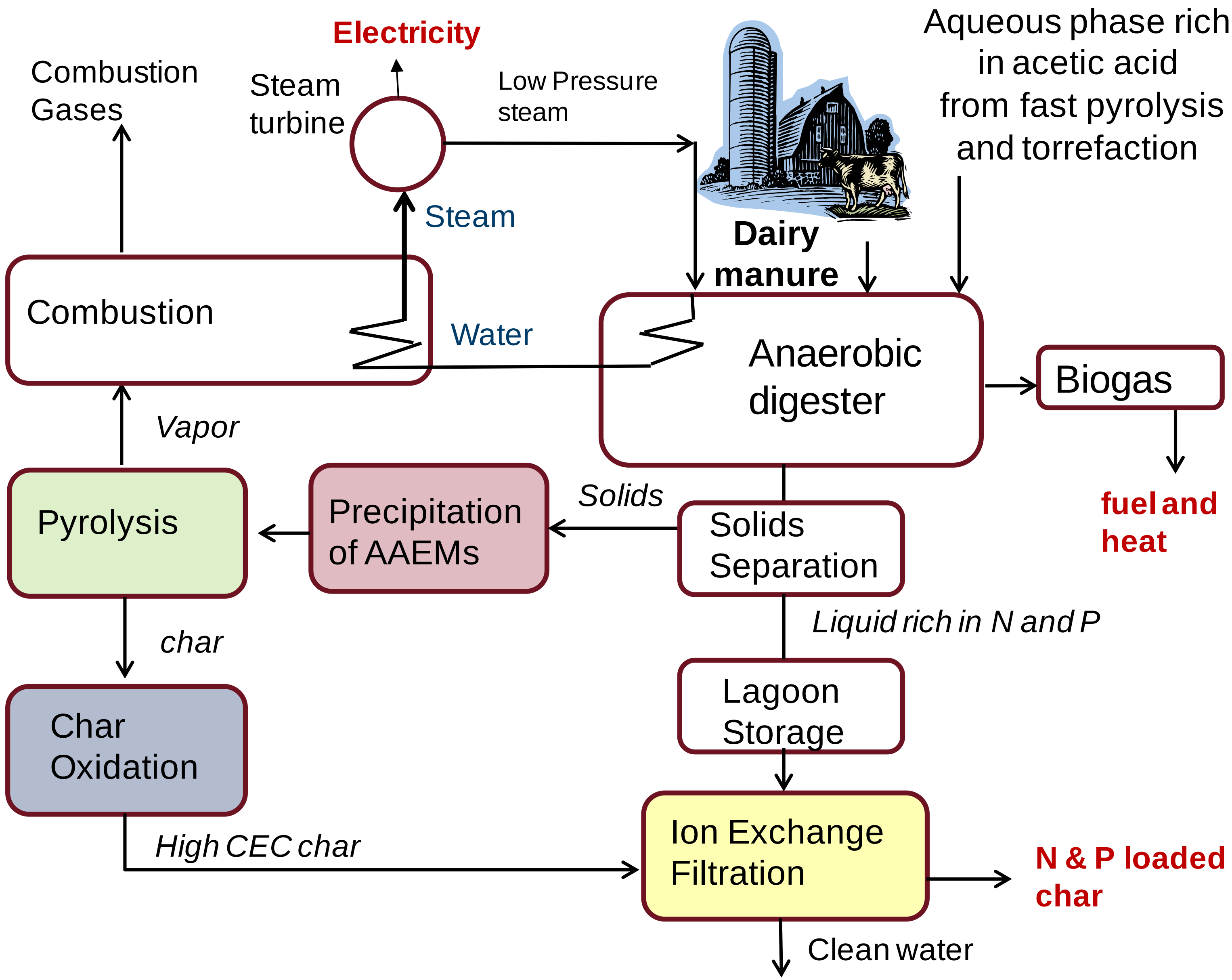
Desired Design Properties

Pyrolysis unit should be able to operate with little maintenance using AD fiber

Char modification should not require an abundance of purchased chemicals or generate significant waste water

Filter media should be able to reduce phosphates and ammonium to near zero levels in the effluent

Filter media should not contaminate the treated effluent stream



Electricity
Combustion Gases
Steam turbine
Low Pressure steam
Aqueous phase rich in acetic acid from fast pyrolysis and torrefaction
Steam
Dairy manure
Combustion
Water
Anaerobic digester
Biogas
Vapor
fuel and heat
Solids
Pyrolysis
Precipitation of AAEMs
Solids Separation
Liquid rich in N and P
char
Lagoon Storage
Char Oxidation
High CEC char
Ion Exchange Filtration
N & P loaded char
Clean water

Phosphorous Removal

Exploratory Study Results

Char produced from unaltered AD fiber has relatively poor phosphate adsorption characteristics.

Post-pyrolysis calcium addition was effective at reducing phosphates but resulted in higher metal leaching

Post-pyrolysis iron addition was not effective at reducing phosphate in solution

Addition of Calcium to the fiber to pyrolysis is an effective method to phosphate adsorption. This treatment was selected for further studies.

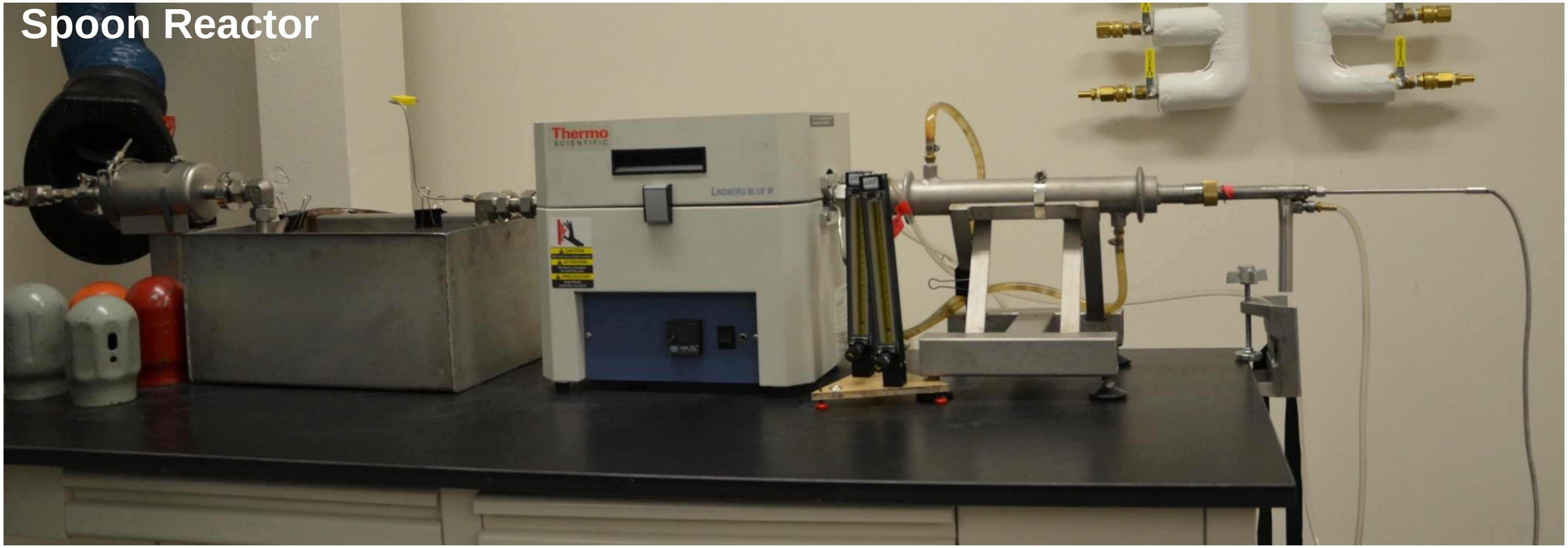
Phosphorous Removal

Pre-pyrolysis $CaCl_2$ modification of AD fiber

Experimental

AD fiber was acid washed in 2% nitric acid and impregnated with calcium by immersion in a $CaCl_2$ solution followed by pH adjustment to 6, 8, 9.35, 11 and 12

Modified fiber samples were then dried and pyrolized at 500^{o}C for 30 minutes using a spoon reactor



Spoon Reactor

Phosphorous Removal

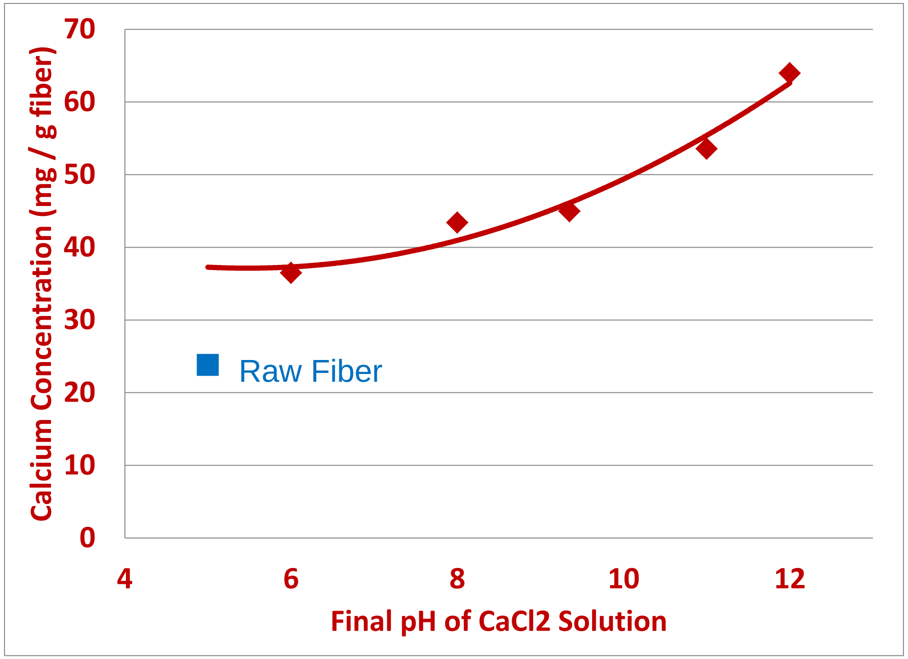
Pre-pyrolysis $CaCl_2$ modification of AD fiber

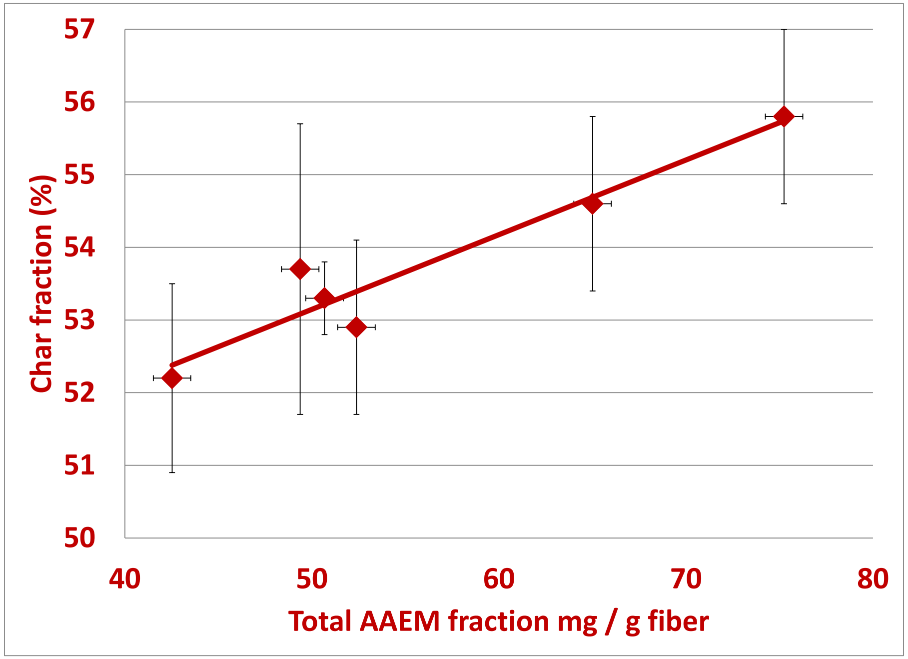
Elemental Analysis

	C	H	N	Ash	O
AD1	39.8	4.4	3.3	25.5	27.0
AD1AW	43.1	4.7	3.5	18.9	29.8
AD1AWC	42.8	2.2	2.9	40.2	11.8
pH6	43.6	2.6	2.9	38.4	12.5
pH8	42.5	2.5	2.8	37.3	14.8
pH9.35	42.2	2.5	2.8	39.8	12.7
pH11	39.1	2.4	2.6	41.3	14.6

Phosphorous Removal

Pre-pyrolysis $CaCl_2$ modification of AD fiber





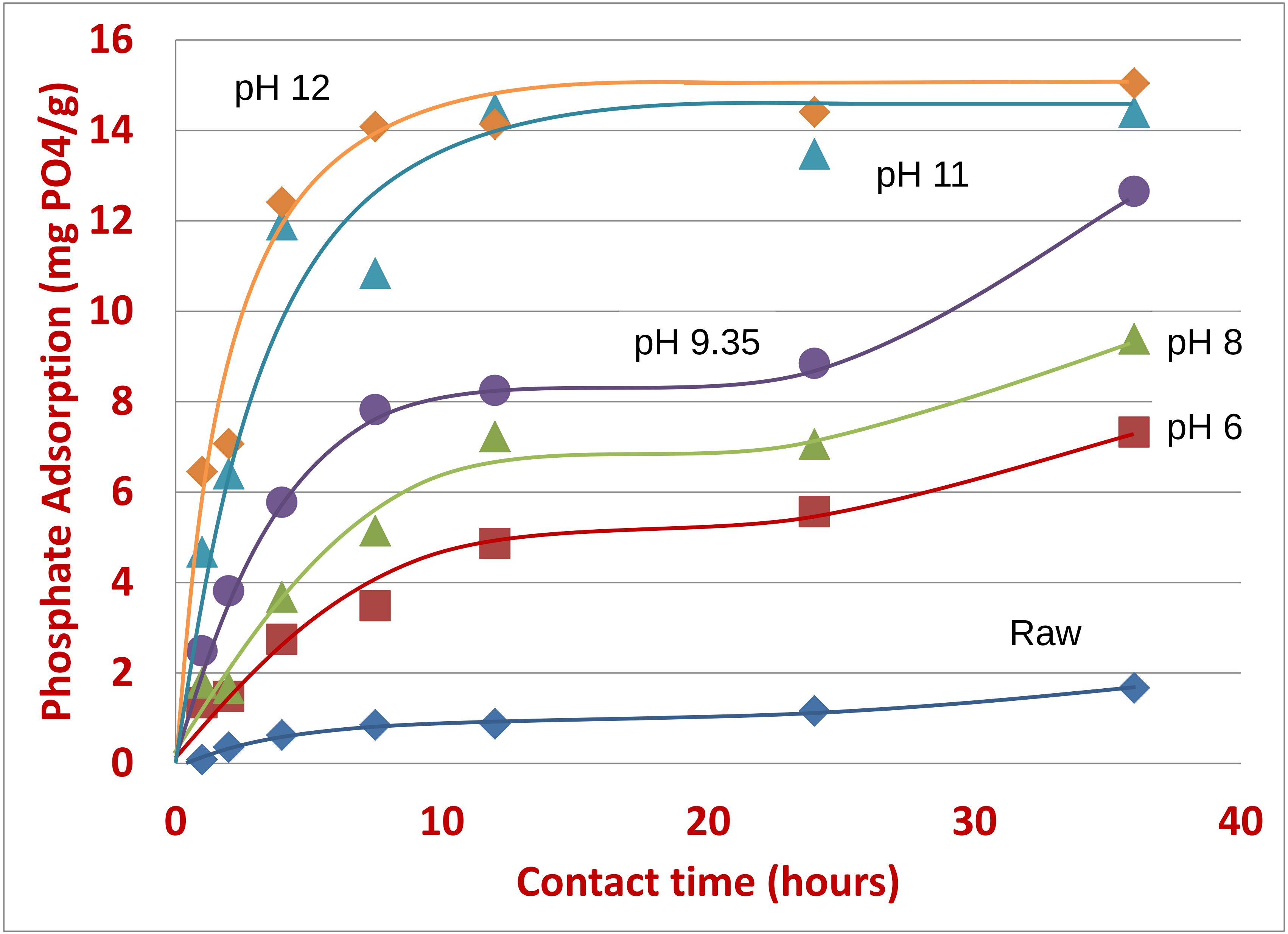
Phosphorous Removal

Na, Ca, K show possible metal leaching, other metals showed no significant loss

Metal leaching, mg X / g char. Error ± 0.1

Sample	Na	Ca	K
Raw	0.07	0.38	0.00
pH 6	0.01	0.02	0.06
pH 8	0.00	0.02	0.01
pH 9.35	0.01	0.01	0.01
pH 11	0.01	0.02	0.01
pH 12	0.06	0.02	0.13

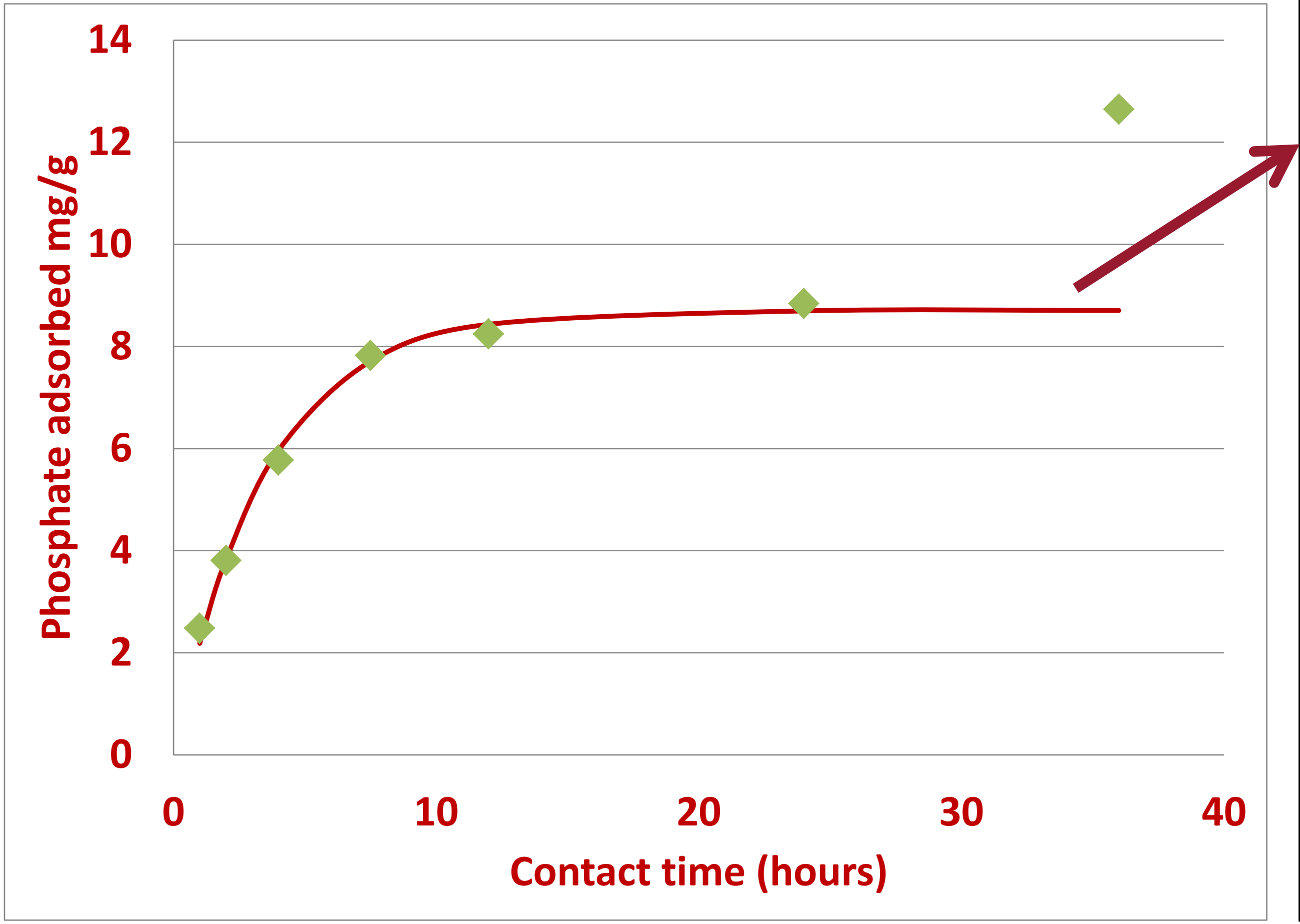
Phosphorous Removal



Phosphorous Removal

Phosphate Adsorption

Sample 'pH 9.35' phosphate adsorption compared to first order model



$$\frac{dq}{dt} = k(q_e - q)$$

$\frac{dq}{dt}$ = change in concentration

k = 1st order rate constant

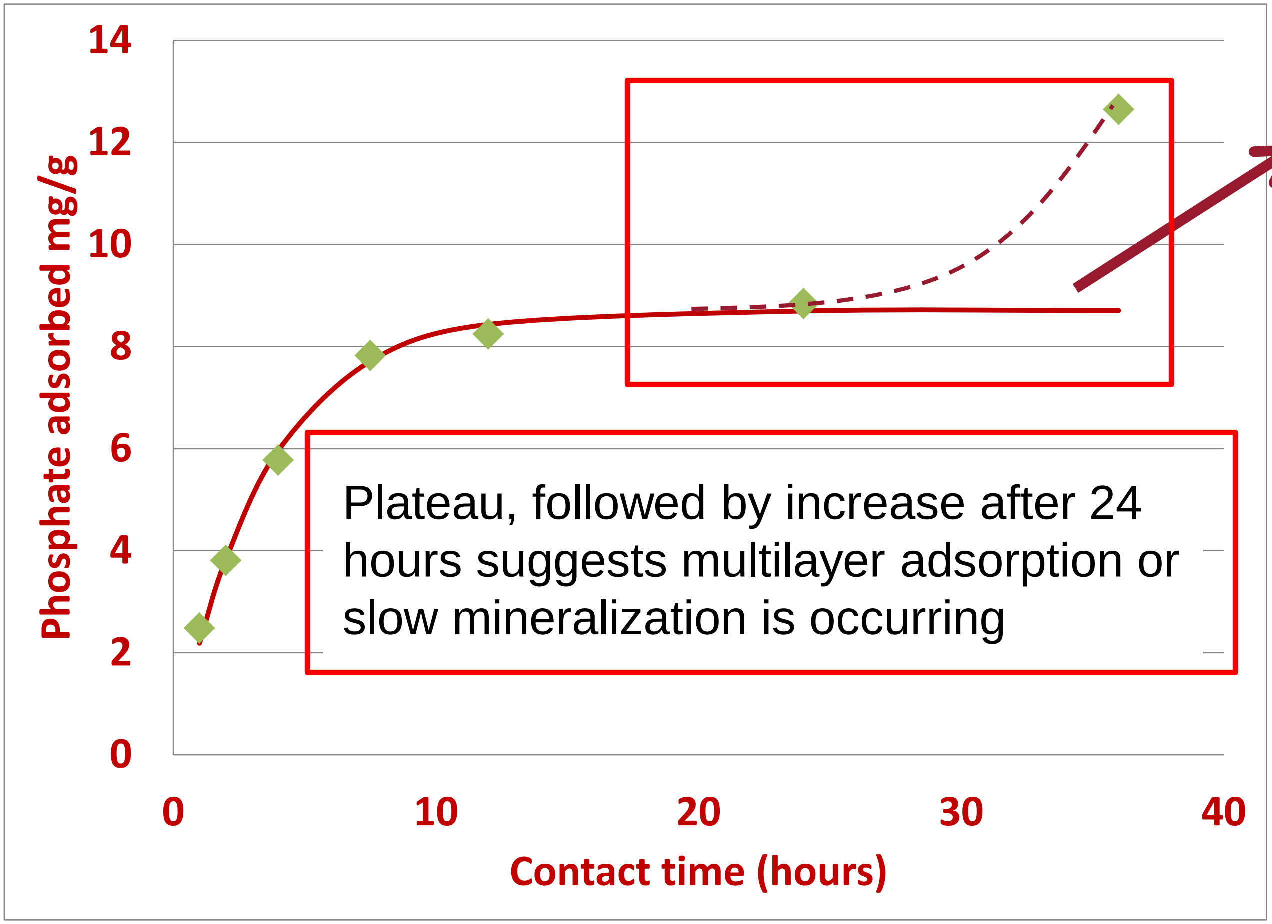
q_e = equilibrium constant

q = concentration at time t

Phosphorous Removal

Phosphate Adsorption

Sample ‘pH 9.35’ phosphate adsorption compared to first order model



$$\frac{dq}{dt} = k(q_e - q)$$

$\frac{dq}{dt} = change$ $in\ concentration$

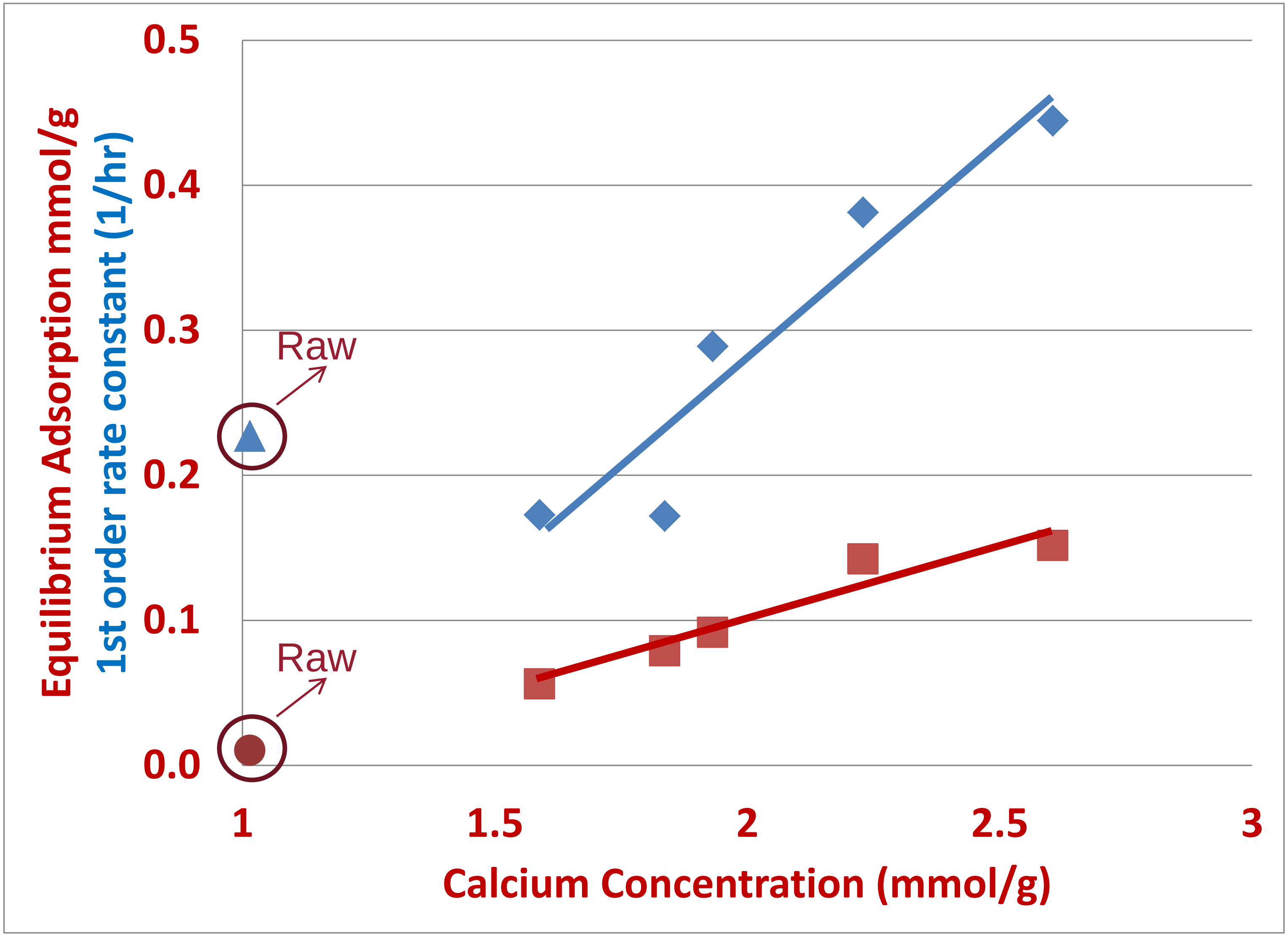
$k = 1st\ order\ rate$ $constant$

$q_e = equilibrium$ $constant$

$q = concentration$ $at\ time\ t$

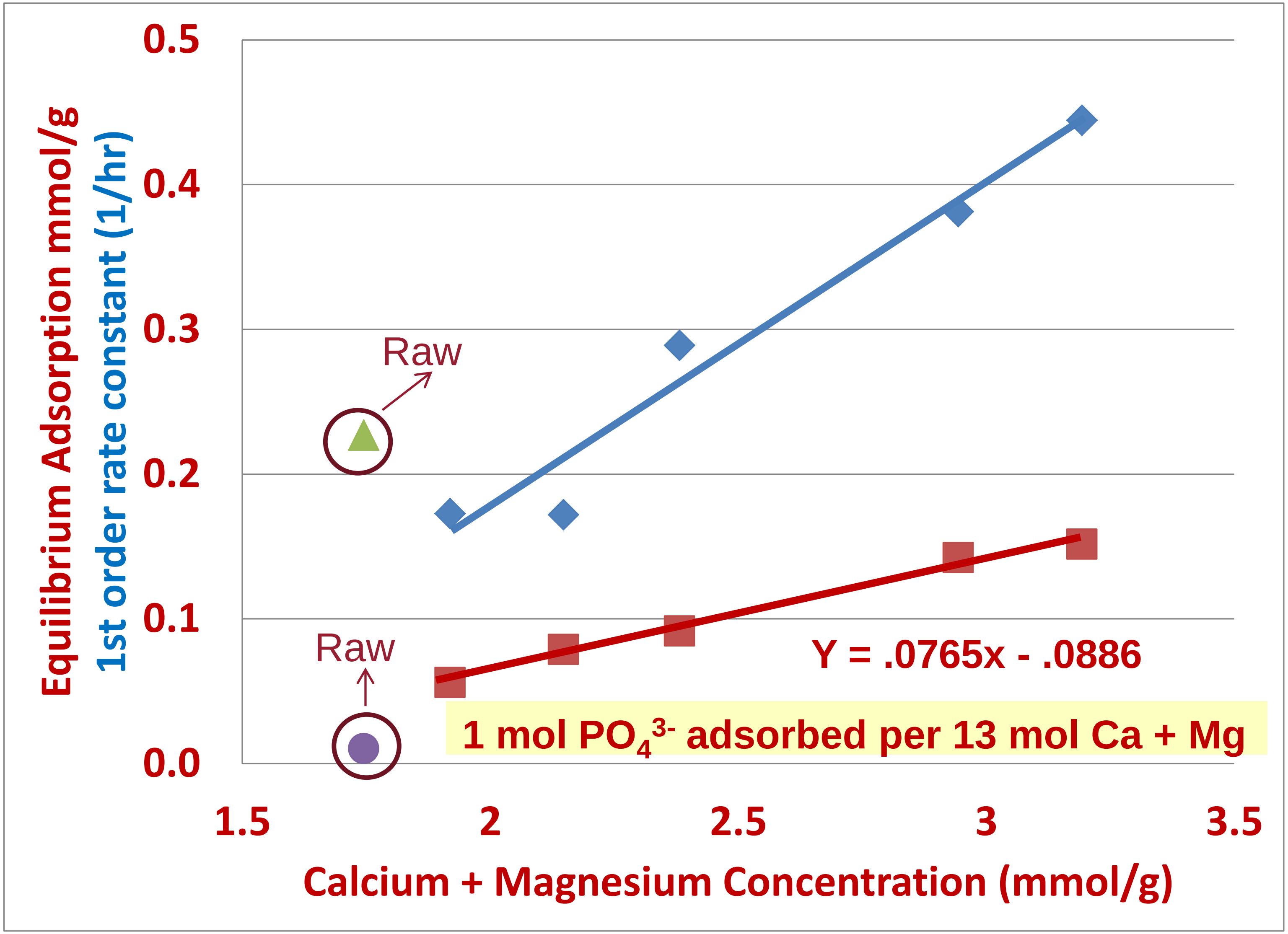
Phosphorous Removal

Phosphate Adsorption



Phosphorous Removal

Phosphate Adsorption



Phosphorous Removal

Conclusions

Contacting fiber with a $CaCl_2$ solutions prior to pyrolysis significantly increased the adsorption capacity of resulting chars.

Increasing the equilibrium pH of solutions during contacting further increased both the rate and equilibrium adsorption capacity of the char.

Chars prepared from fiber equilibrated at pH 9.35 effectively removed more than 50% of ionic phosphate after 7.5 hours and 80% after 36 hours.

Minerals of both calcium and magnesium are involved in the adsorption of phosphates

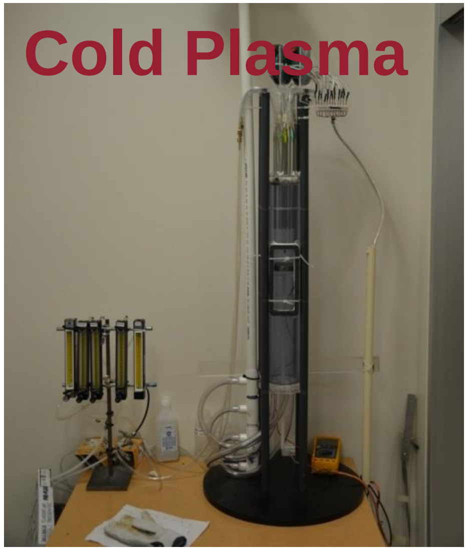
Chars modified with calcium did not show high levels of leaching during the adsorption tests, indicating that the mineral matter was converted to a stable form.

Oxidation for Nitrogen Removal

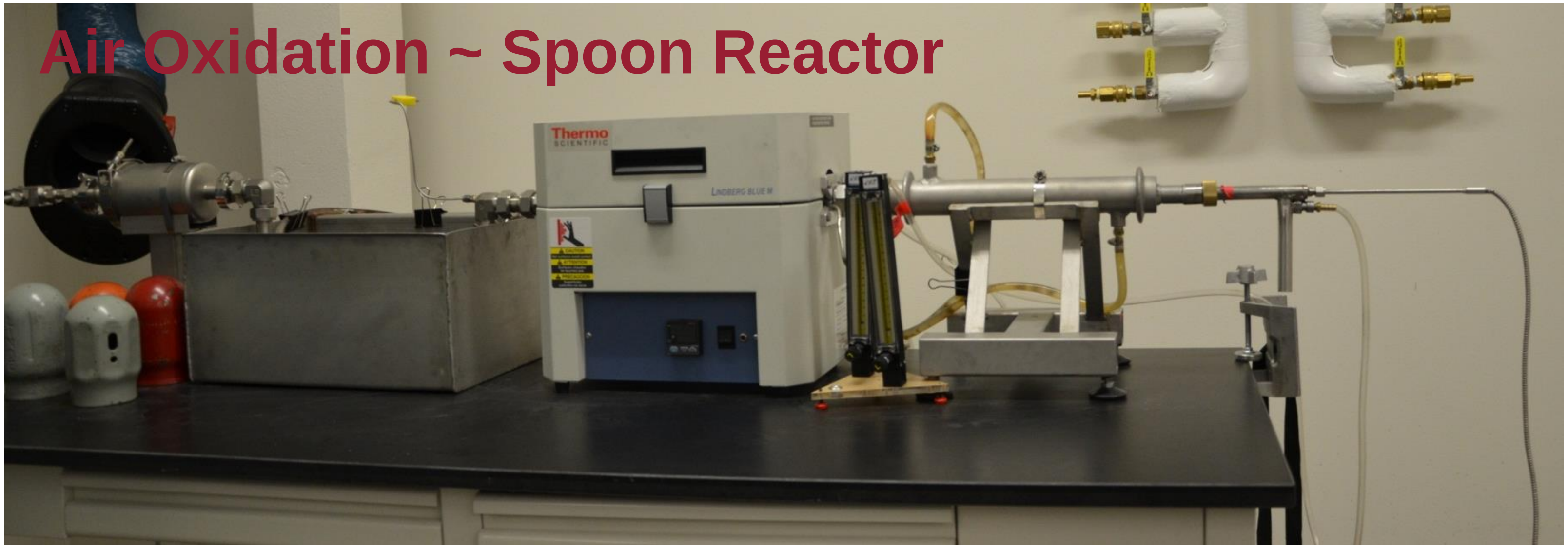
Experimental Equipment

Ozone

Cold Plasma



Air Oxidation ~ Spoon Reactor



Oxidation for Nitrogen Removal

Experimental

Untreated AD fiber was pyrolized at 500^oC for 30 minutes to generate all char samples studied, Pine wood and bark chars were produced in an auger reactor at 500^oC

Untreated fiber char was oxidized by three different mechanisms

1) Ozone at 70 mg/L (4%) at 2 SLPM for 30 minutes

2) Cold plasma using a 4.2 kV RMS arc potential for 20 minutes

3) Air at elevated temperature for 1.5-2 hours

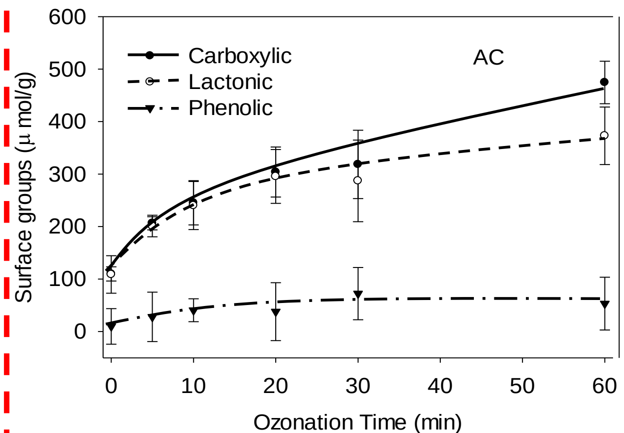
The change in functional groups were evaluated by Boehm titration

Oxidation for Nitrogen Removal

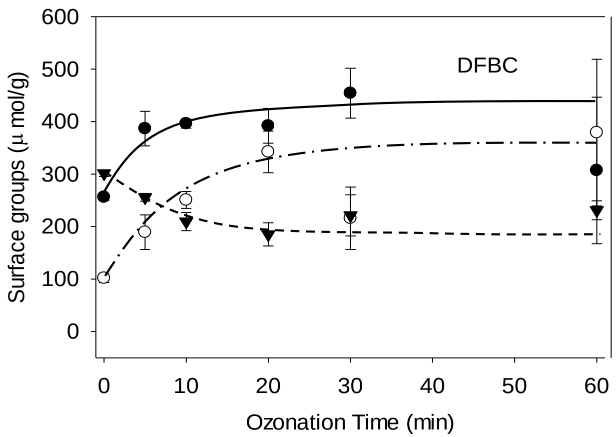
Ozone

Studies using ozone showed to it be an excellent oxidizing agent for activated carbons and chars from Douglas Fir Bark(DFBC) but had limited effect on Douglas Fir Wood Char (DFWC)

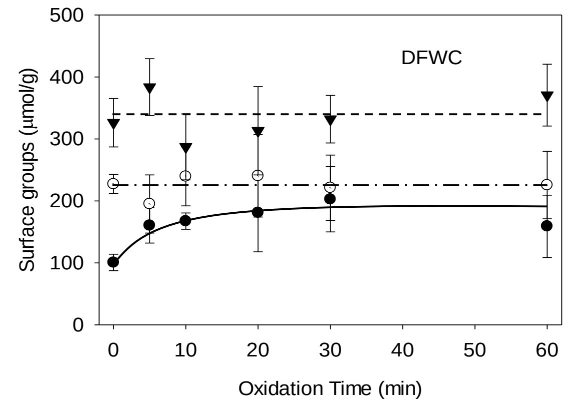
Activated Carbon



DF Bark Char



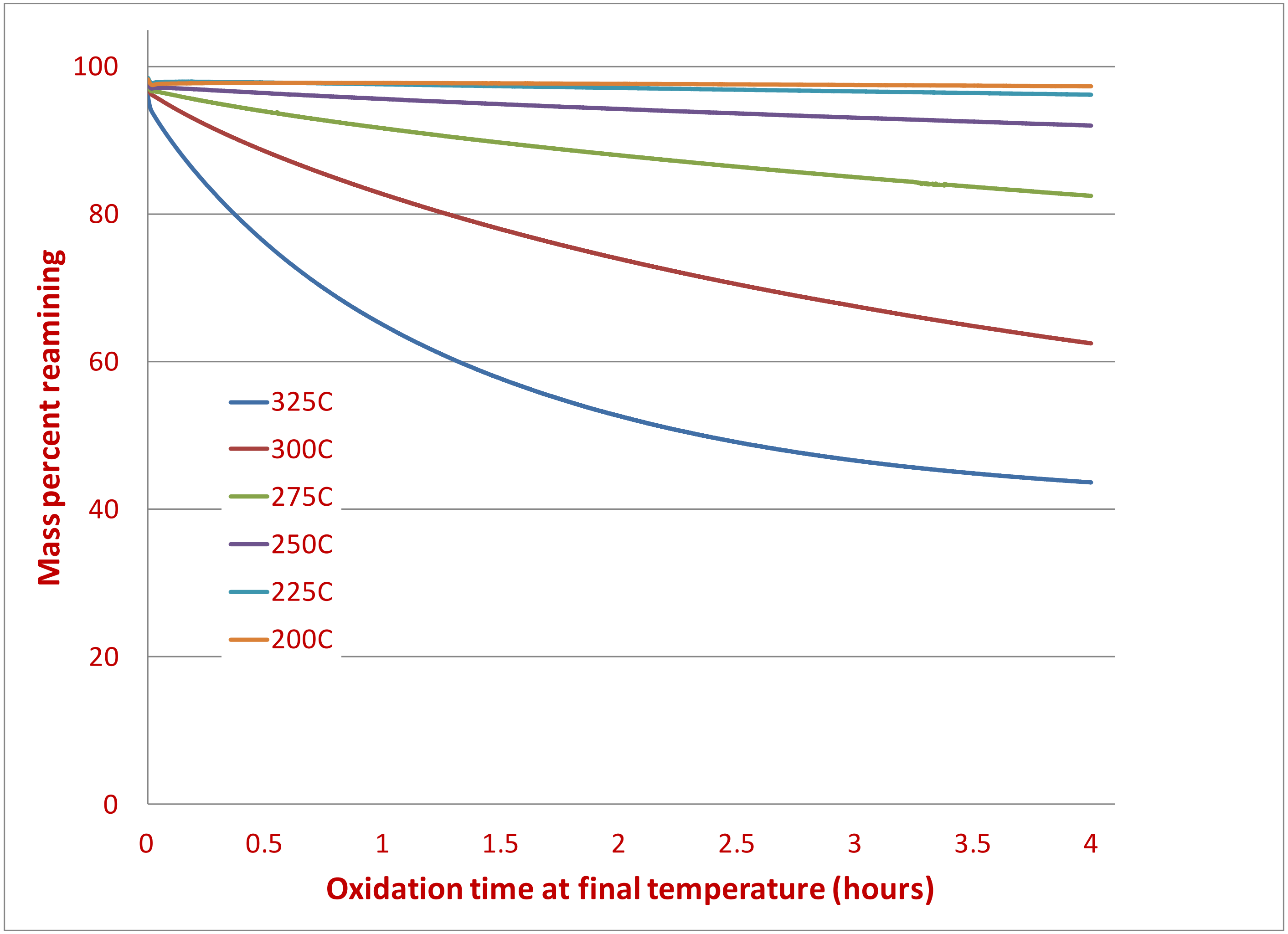
DF Wood Char



Strong ozonation effect

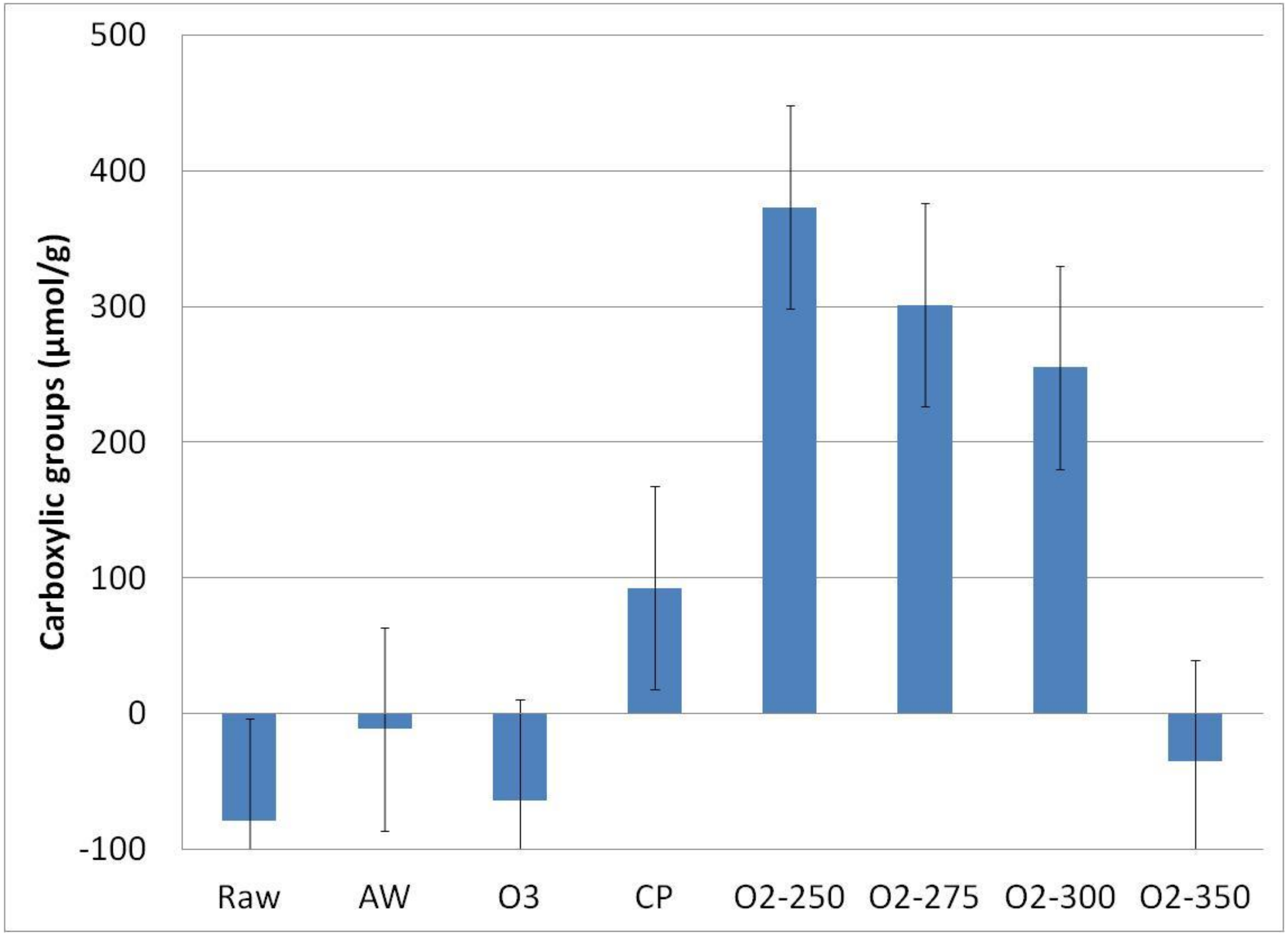
Oxidation for Nitrogen Removal

Mass loss due to oxidation



Oxidation for Nitrogen Removal

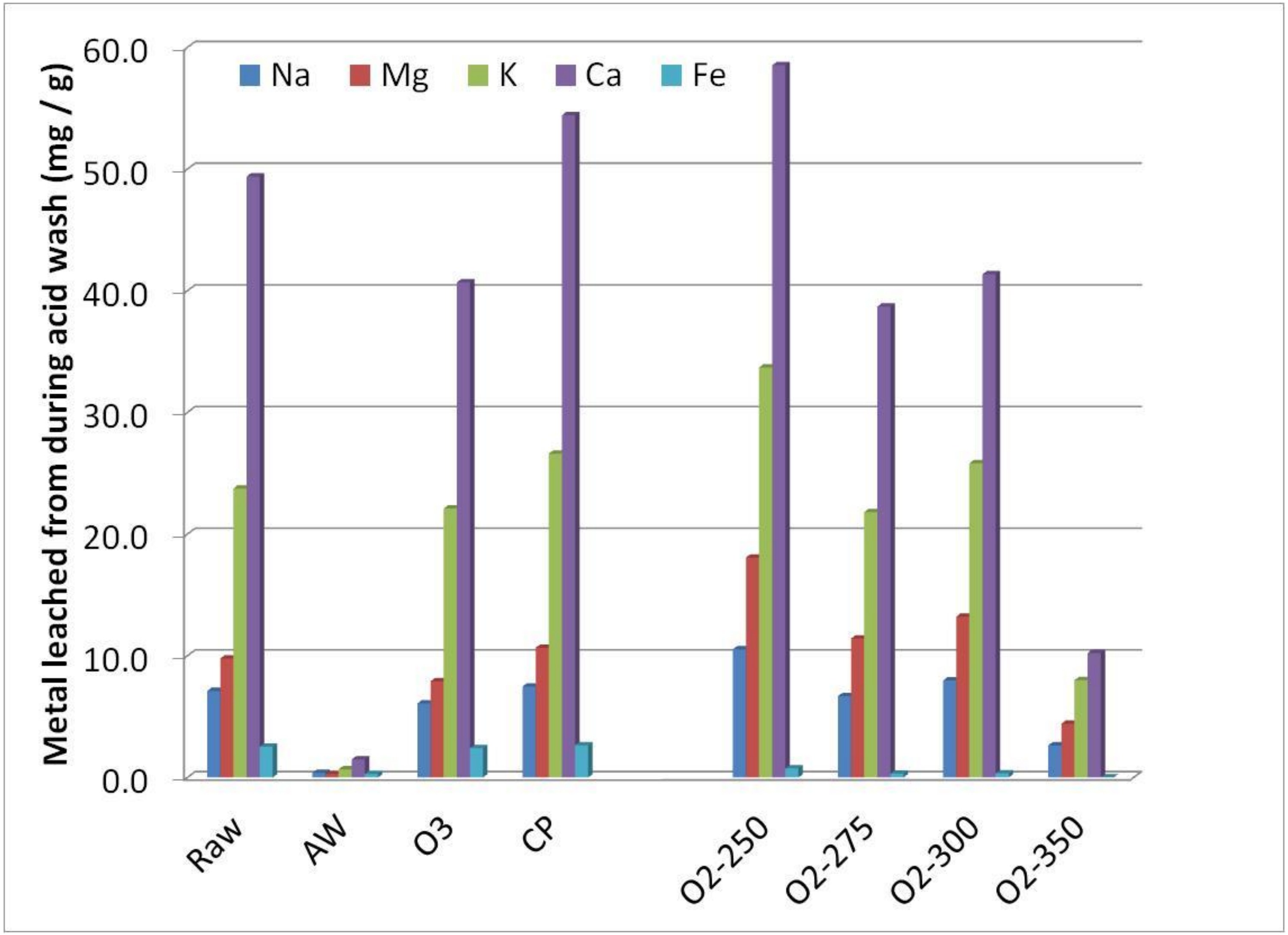
Carboxylic Group Formation



Cold Plasma

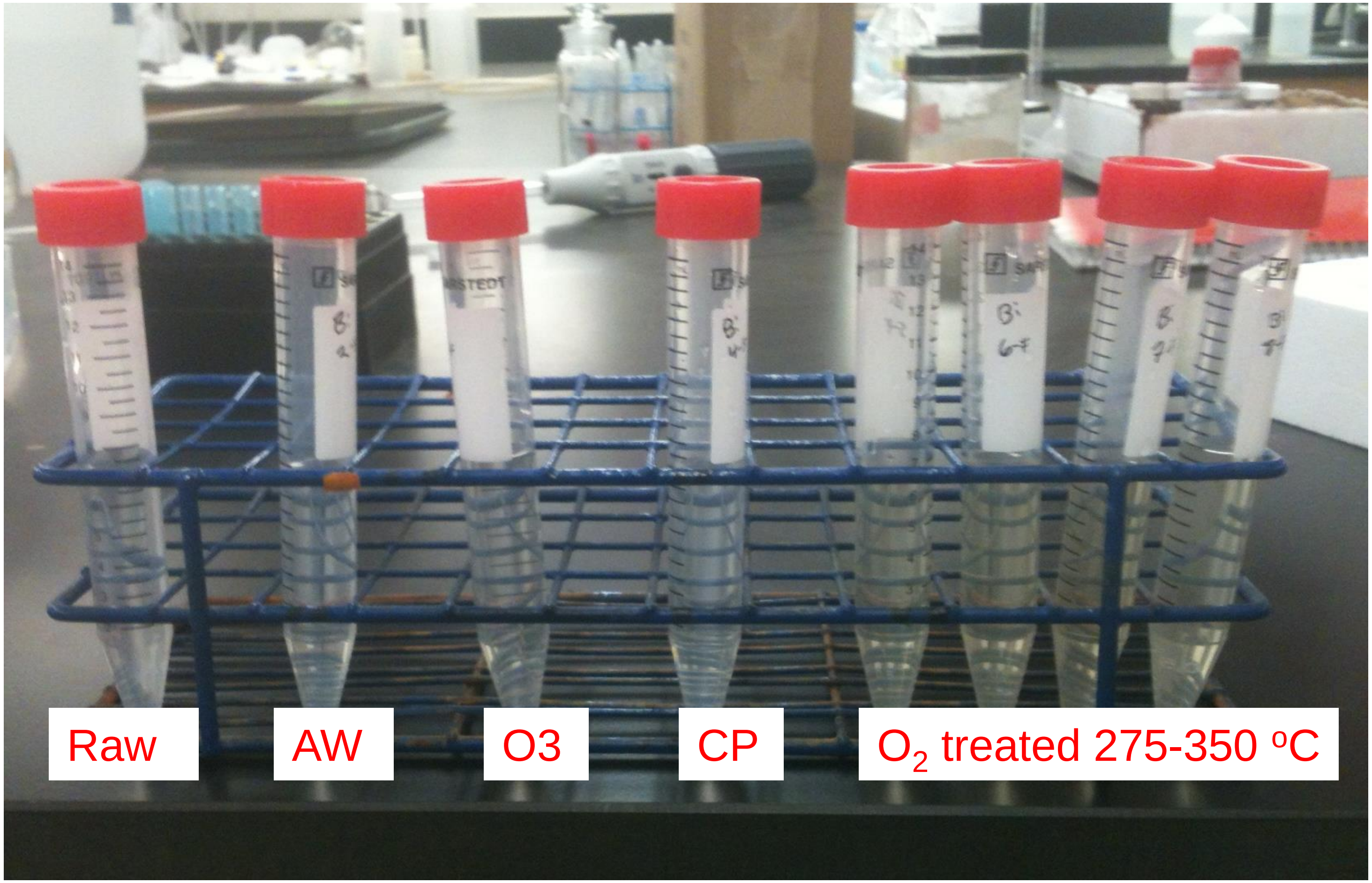
Oxidation for Nitrogen Removal

Changes in soluble matter due to oxidation



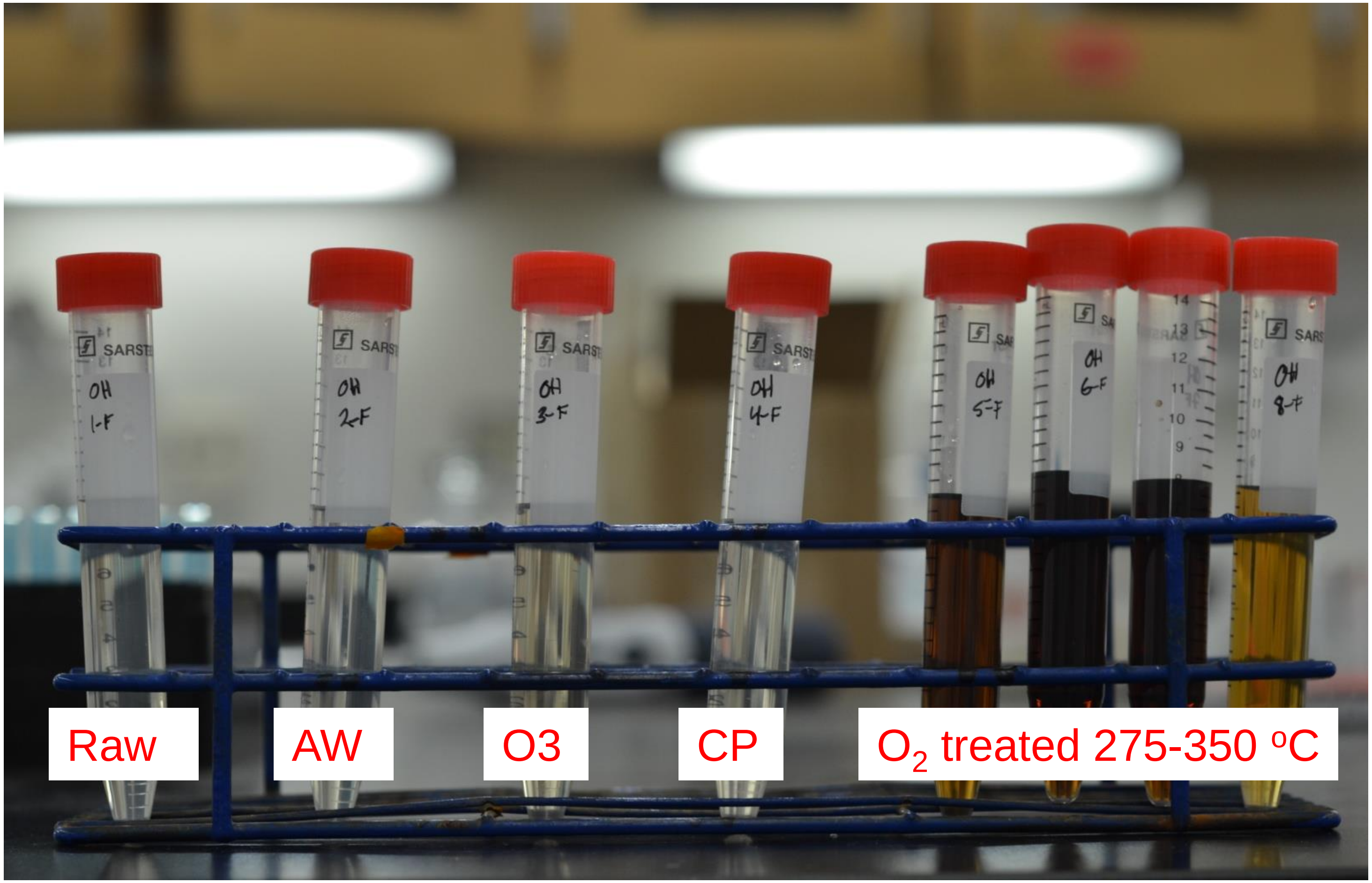
Oxidation for Nitrogen Removal

Changes in soluble matter (pH 8-9) due to oxidation



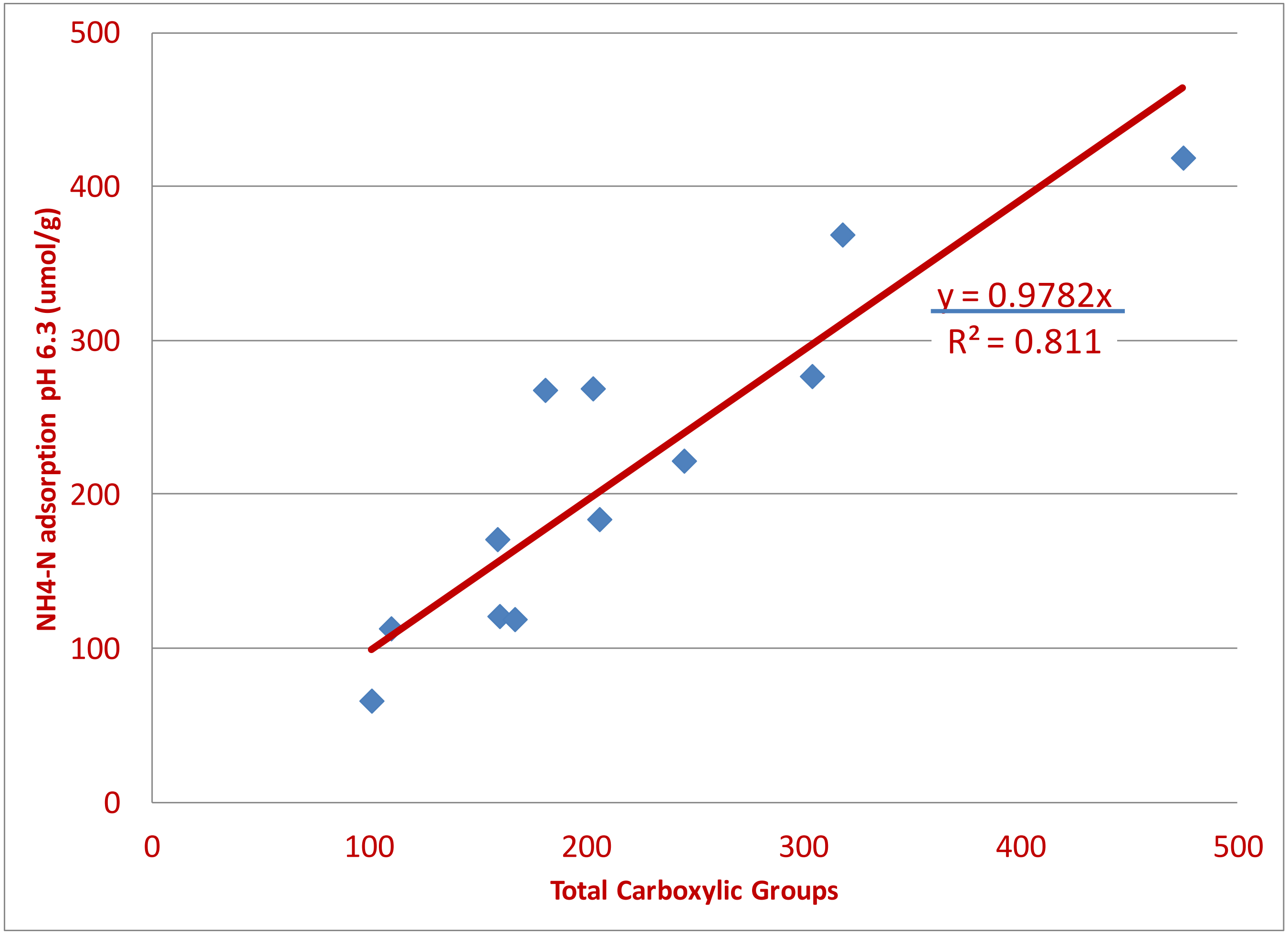
Oxidation for Nitrogen Removal

Changes in soluble matter (pH ~ 12) due to oxidation



Oxidation for Nitrogen Removal

Correlation between Ammonium Adsorption and Carboxylic groups (acid washed chars)



Oxidation for Nitrogen Removal

Conclusions

All oxidation methods tested resulted in varying degrees of acid group formation and carbon gasification.

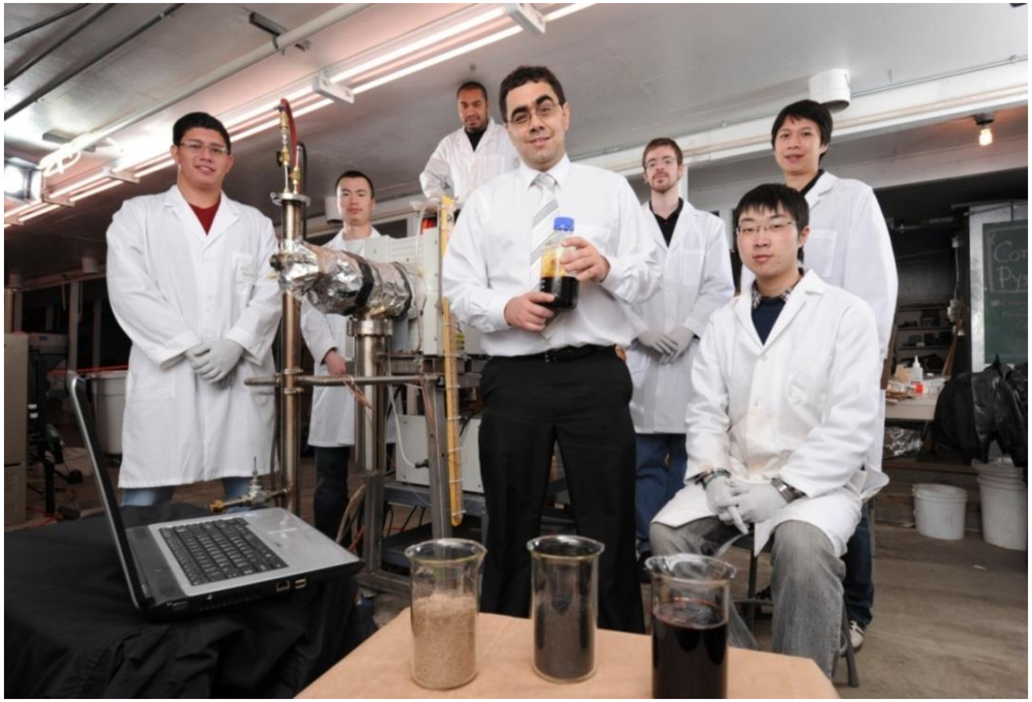
Air at temperatures of 250-300 ^{o}C was effective at generating carboxylic acid groups, at 350 ^{o}C carboxylic groups were not detected. This process can be easily integrated to a pyrolysis units during bio-char cooling.

Increasing the number of carboxylic groups on various char surfaces was found to have a near 1:1 correlation with CEC and ammonium adsorption

Oxidation by air results in the formation of a significant fraction of small molecules and particles soluble in basic solutions that require further study

Shorter oxidation times and possibly lower oxygen concentration are required to mitigate destruction of the surface

Acknowledgements



We would like to thank the funding agencies supporting our Research Program

WASHINGTON STATE UNIVERSITY AGRICULTURAL RESEARCH CENTER

WASHINGTON STATE DEPARTMENT OF ECOLOGY

WASHINGTON STATE DEPARTMENT OF AGRICULTURE

SUN GRANT INITIATIVE, U.S. DEPARTMENT OF TRANSPORTATION, USDA

U.S. NATIONAL SCIENCE FOUNDATION

U.S. DEPARTMENT OF ENERGY

QUESTIONS ?