Integrating Pyrolysis and Anaerobic Digestion

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Outline

Introduction

Phosphorous Removal

Oxidation for Nitrogen Removal

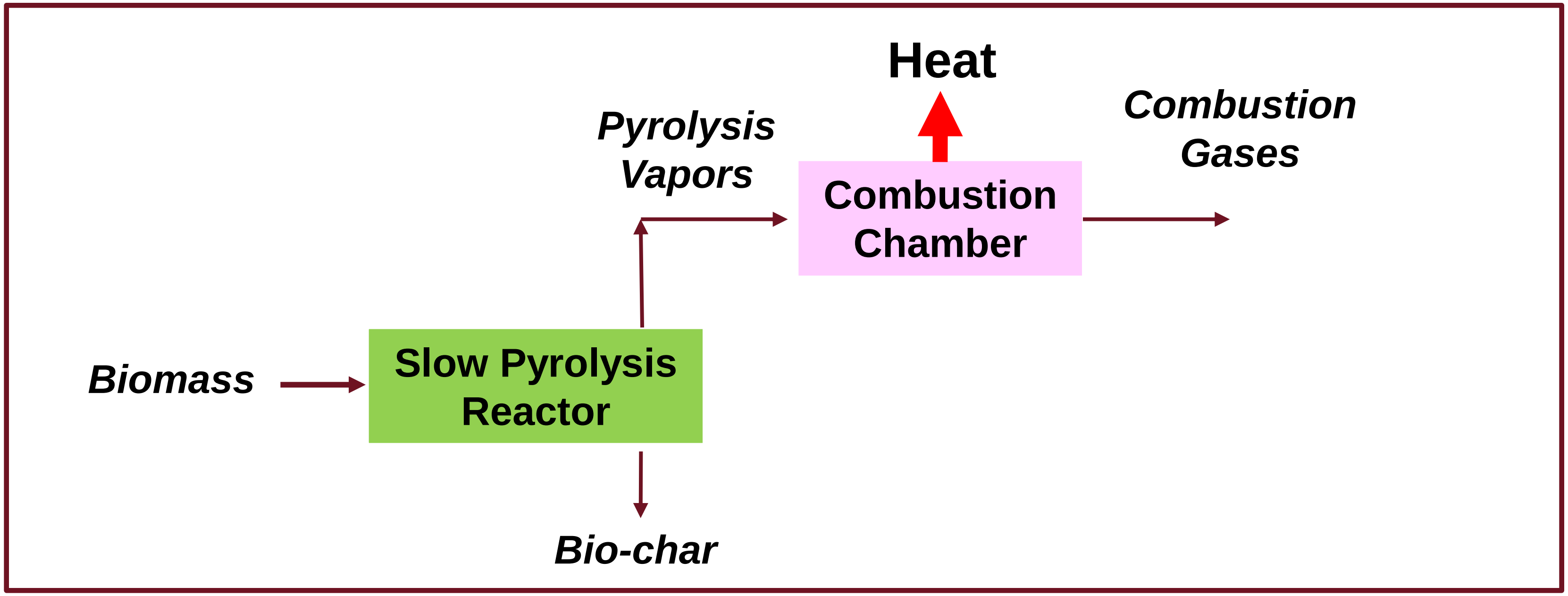
Anaerobic Digestion of Pyrolytic C1-C4 Compounds

Conclusions

Introduction

Slow Pyrolysis

Slow pyrolysis is a process in which large biomass particles (more than 2 mm diameter) are heated at 450 – 600 °C in the absence of *air/oxygen to* produce high bio-char yield (25-35 mass %).

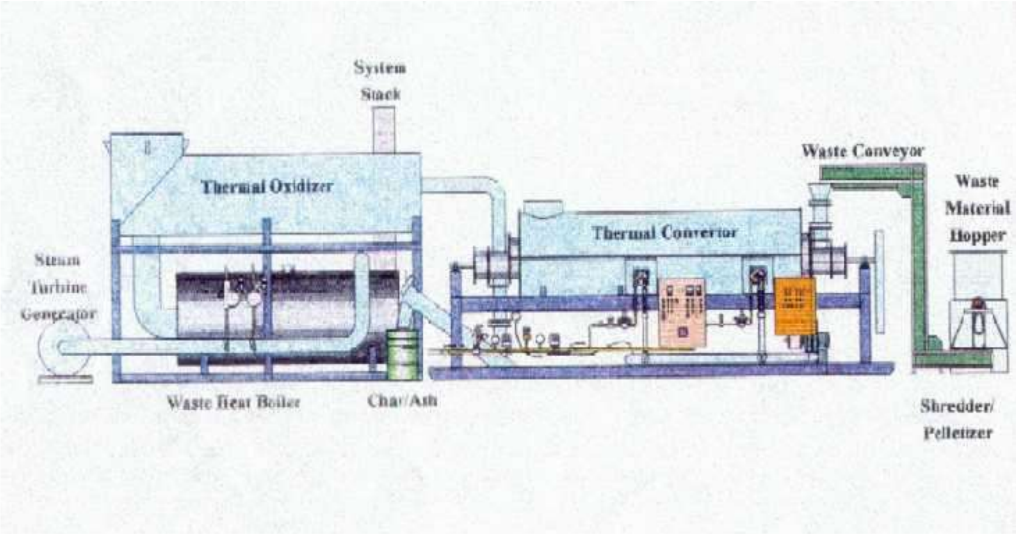


Conditions	Liquid	Char	Gas
Slow heating rates, large particles, large residence time of vapors	30 - 45 %	**25-35 %**	25-35 %

Introduction

Slow Pyrolysis

SLOW PYROLSYSIS is well suited for producing bio-char and heat/electricity from agricultural wastes with a high content of alkalines that are generated by the State. This is one of the most promising concepts for carbon sequestration.



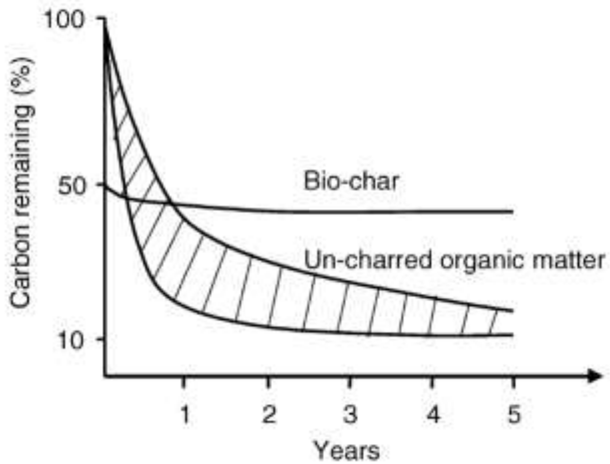
Primary Challenge:

Higher value products from Bio-char have to be developed while minimizing production costs

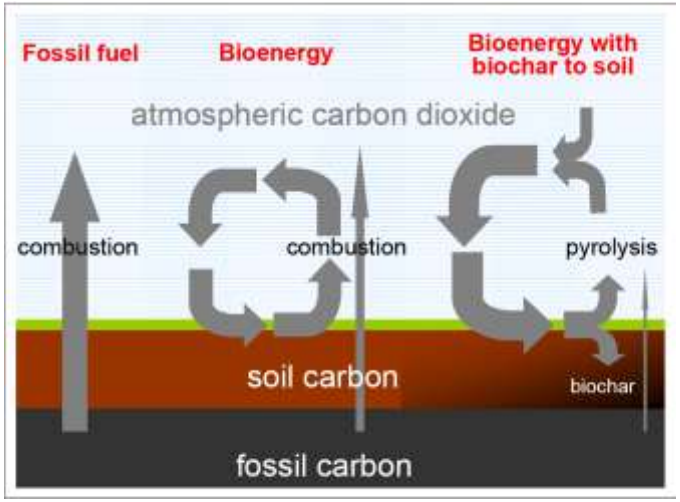
Introduction

Bio-char: Potential for Carbon Sequestration

The application of bio-char to soil is proposed as a novel approach to establish a significant, long term sink for atmospheric carbon dioxide in terrestrial ecosystems.



Biomass Carbon Remaining in the soil (Bio-char vs. Un-charred organic matter).



Bio-char can result in a net removal of carbon from the atmosphere, with net energy production.

How to make sequestration profitable?

Develop low cost adsorbents for course treatment of waste water

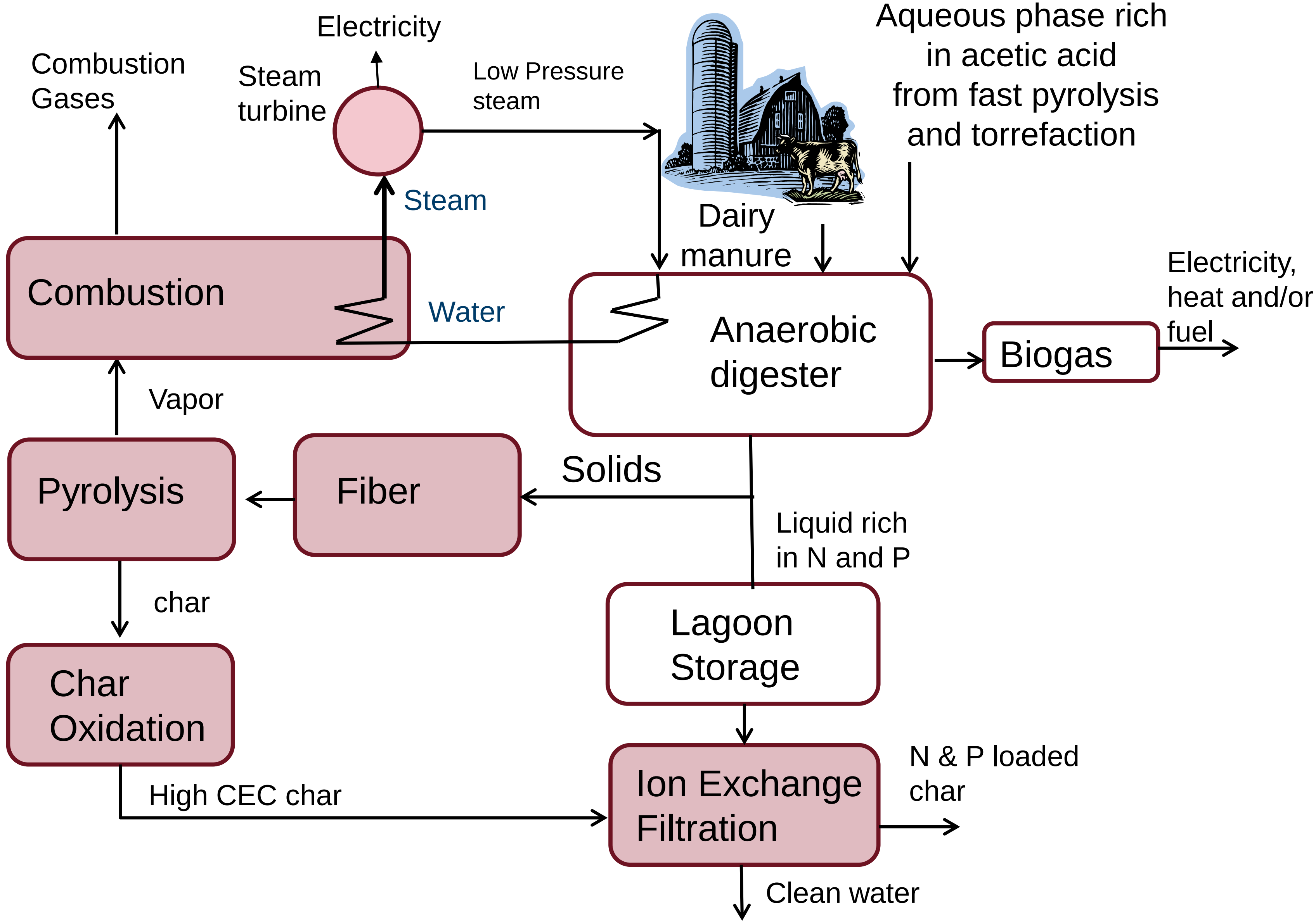
Soil amendments

Load with nutrients for slow release fertilizers

Lehmann J, Gaunt J, Rondon M: Bio-char sequestration in terrestrial ecosystems – a review. Mitigation and Adaptation Strategies for Global Change (2006) 11: 403-427.

Introduction

Integrated Pyrolysis - AD System



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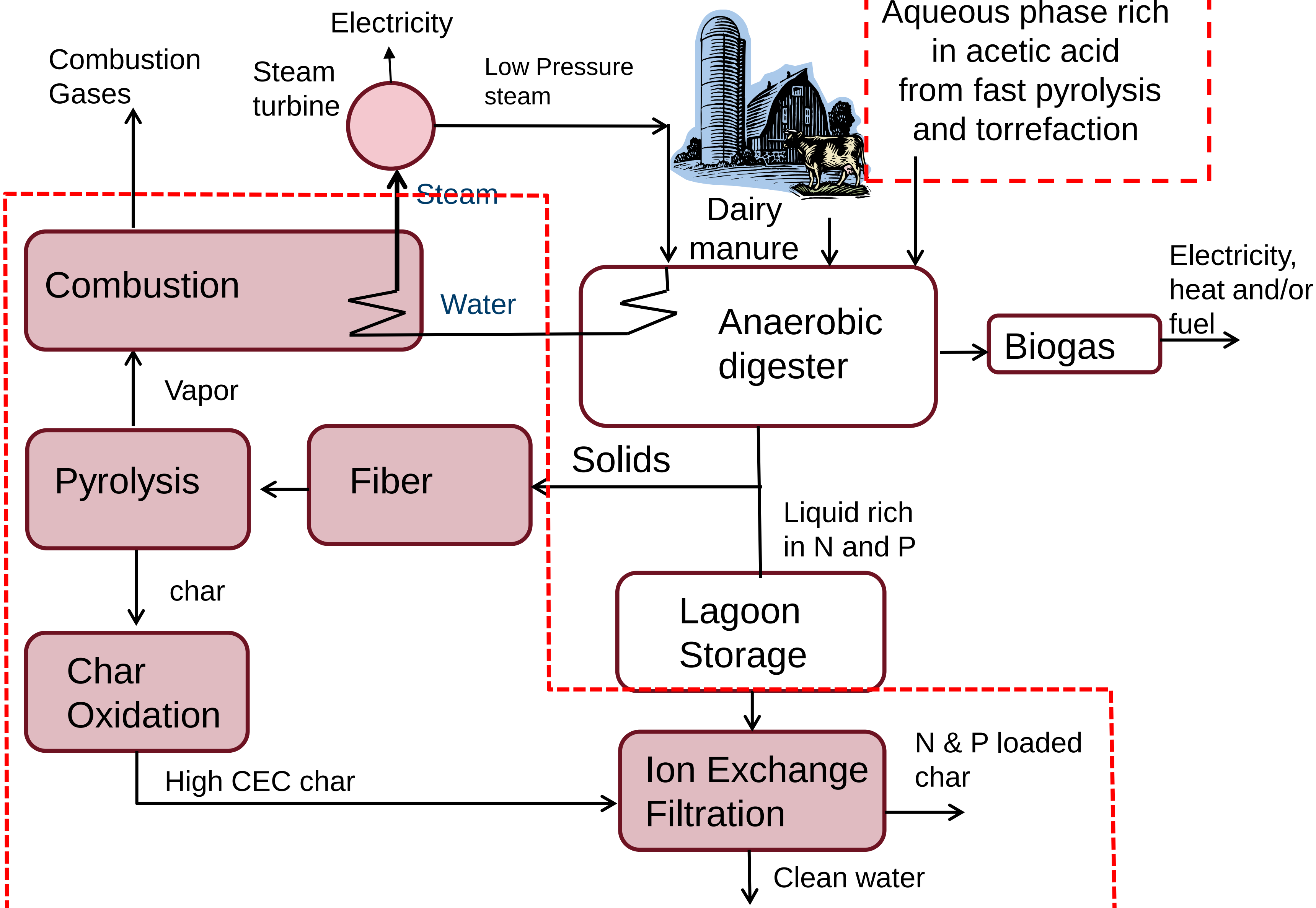

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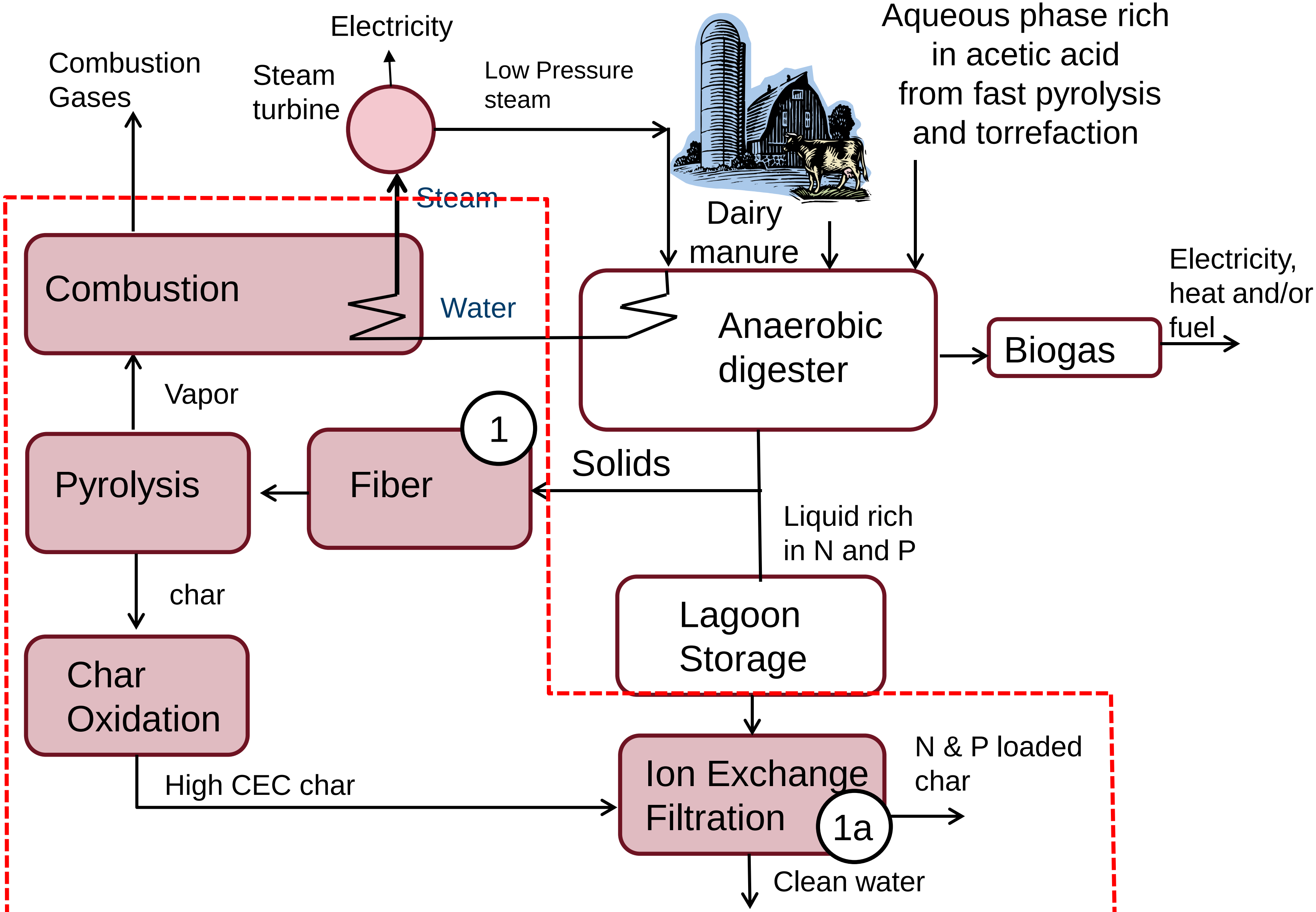


Phosphorous Removal

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 prior to pyrolysis is an effective method to INCREASE CHARCOAL YIELD AND PHOSPHATE ADSORPTION. <u>This treatment was selected for further studies.</u>

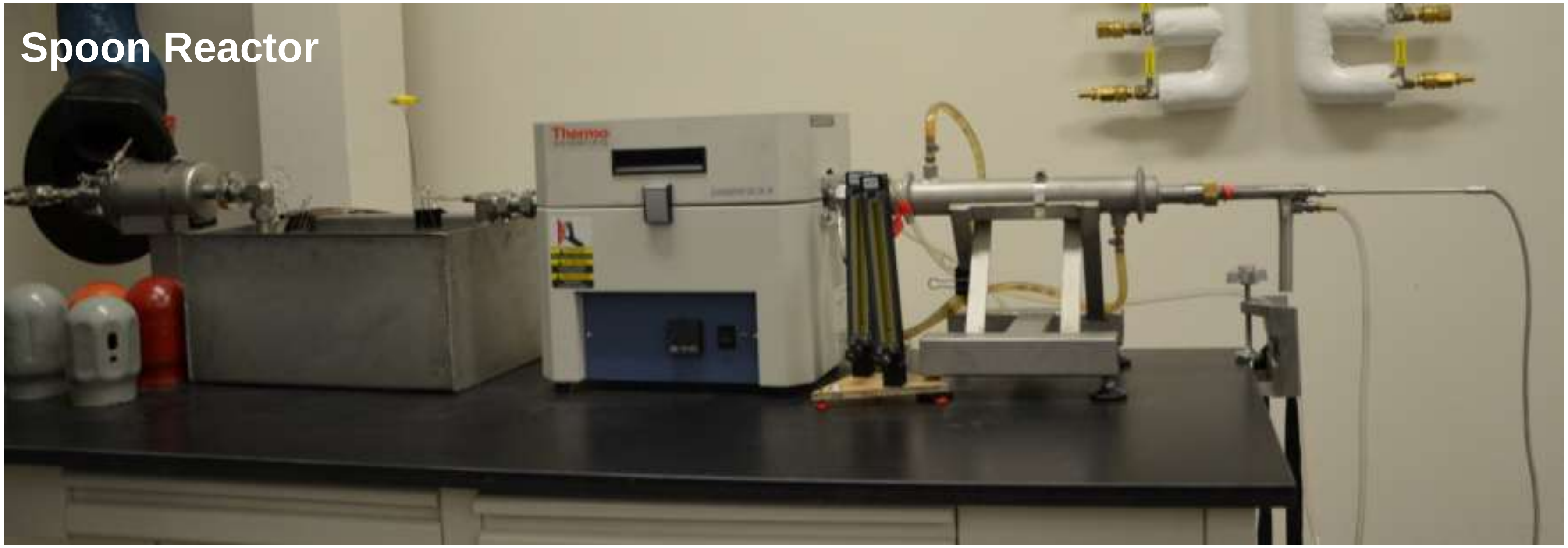
Phosphorous Removal

Pre-pyrolysis $CaCl_2$ modification of AD fiber

Experimental

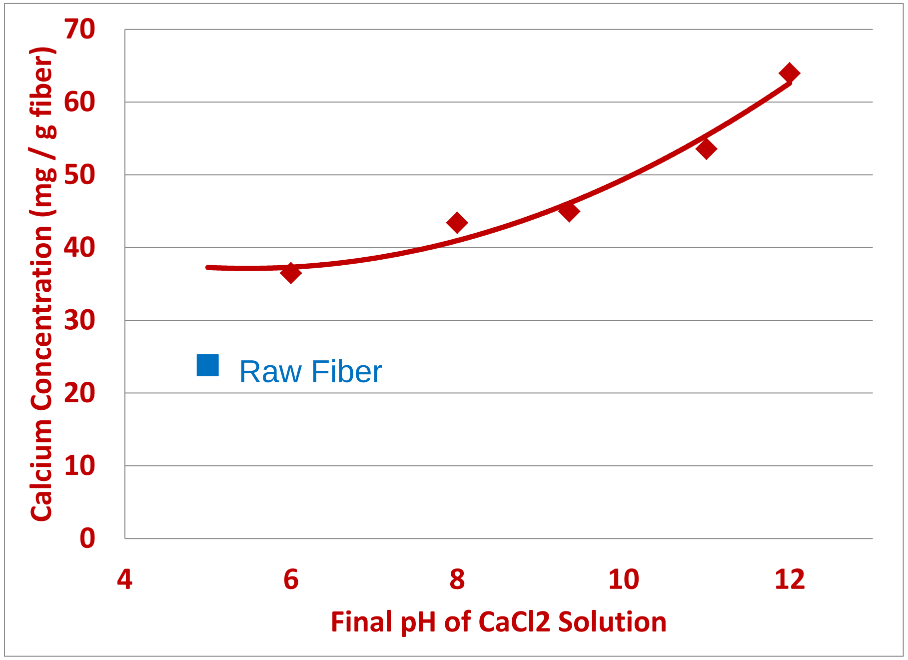
AD fiber was impregnated with calcium by immersion in a $CaCl_2$ solution followed by pH adjustment to 6, 8, 9.35, 11 and 12

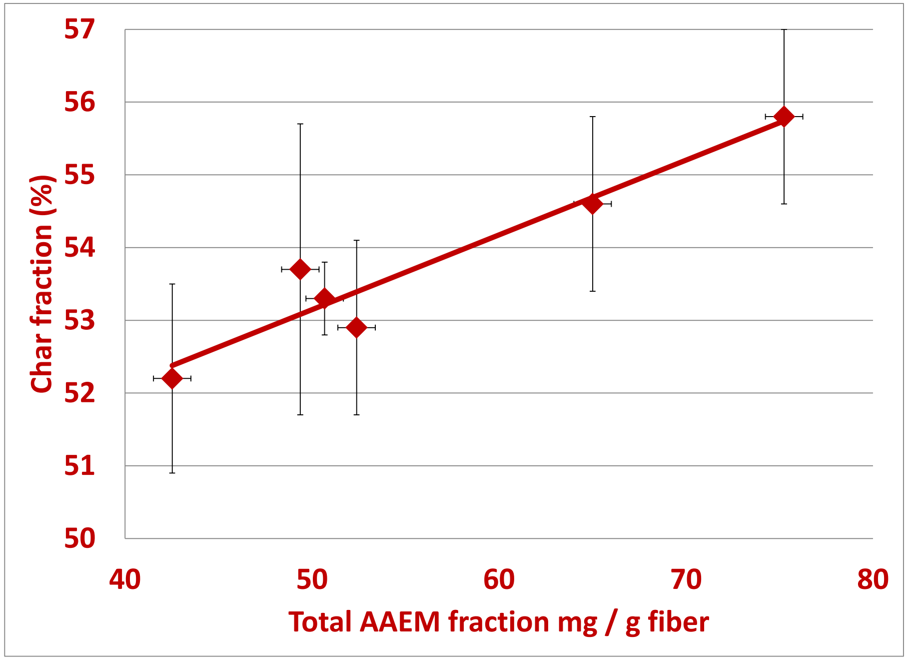
Modified fiber samples were then dried and pyrolized at 500°C for 30 minutes using a spoon reactor



Phosphorous Removal

Pre-pyrolysis $CaCl_2$ modification of AD fiber





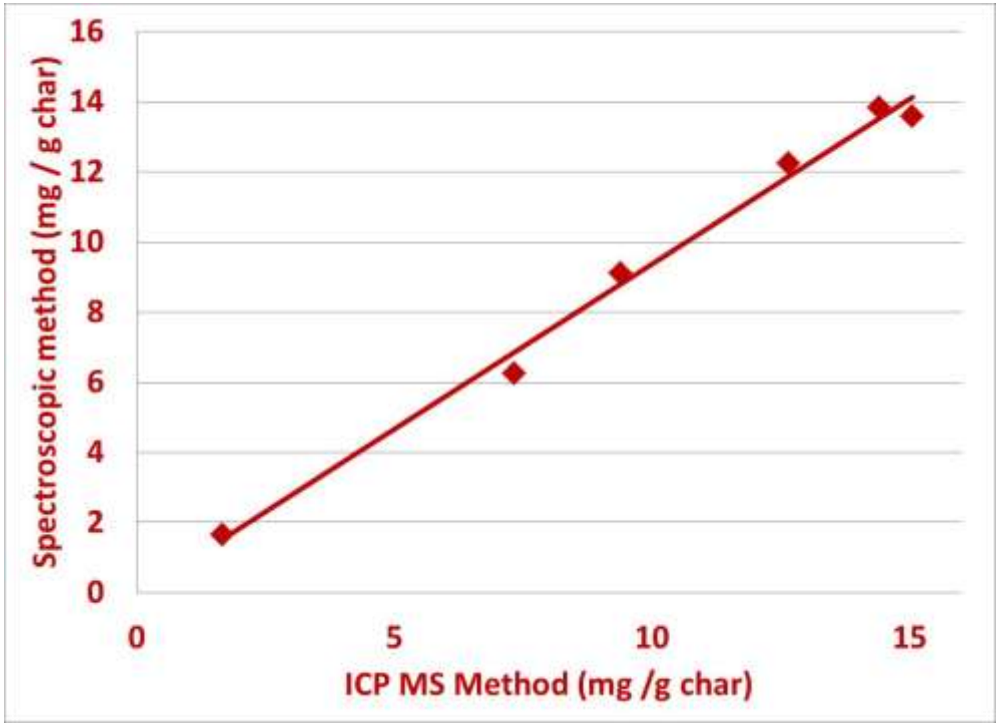
Phosphorous Removal

Pre-pyrolysis $CaCl_2$ modification of AD fiber

Phosphate Adsorption

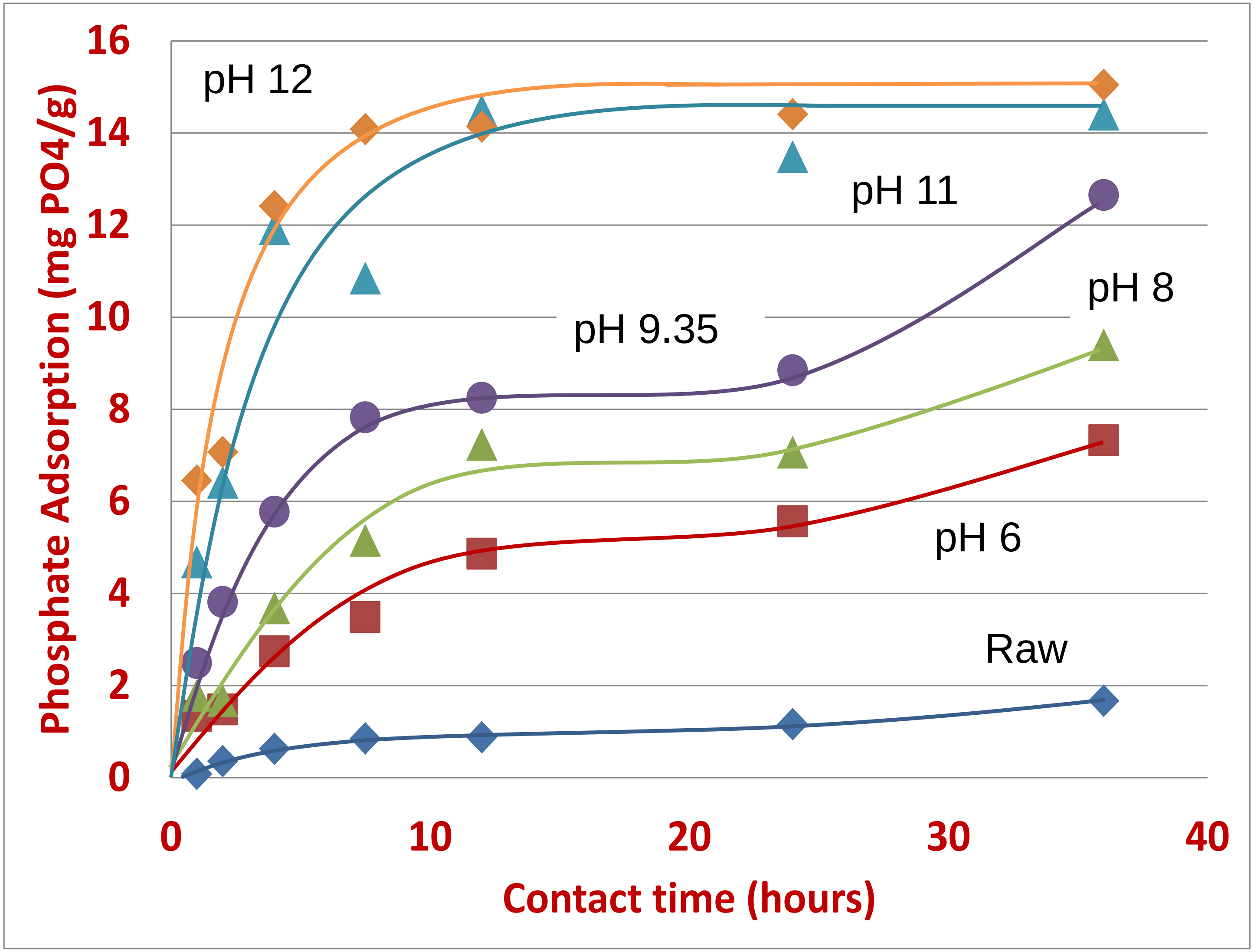
50 mg of each modified char was suspended in 10 ml of a 75 mg/L sodium phosphate for 1-36 hrs.

Comparison of Phosphate Detection Methods (36 hrs)



Phosphorous Removal

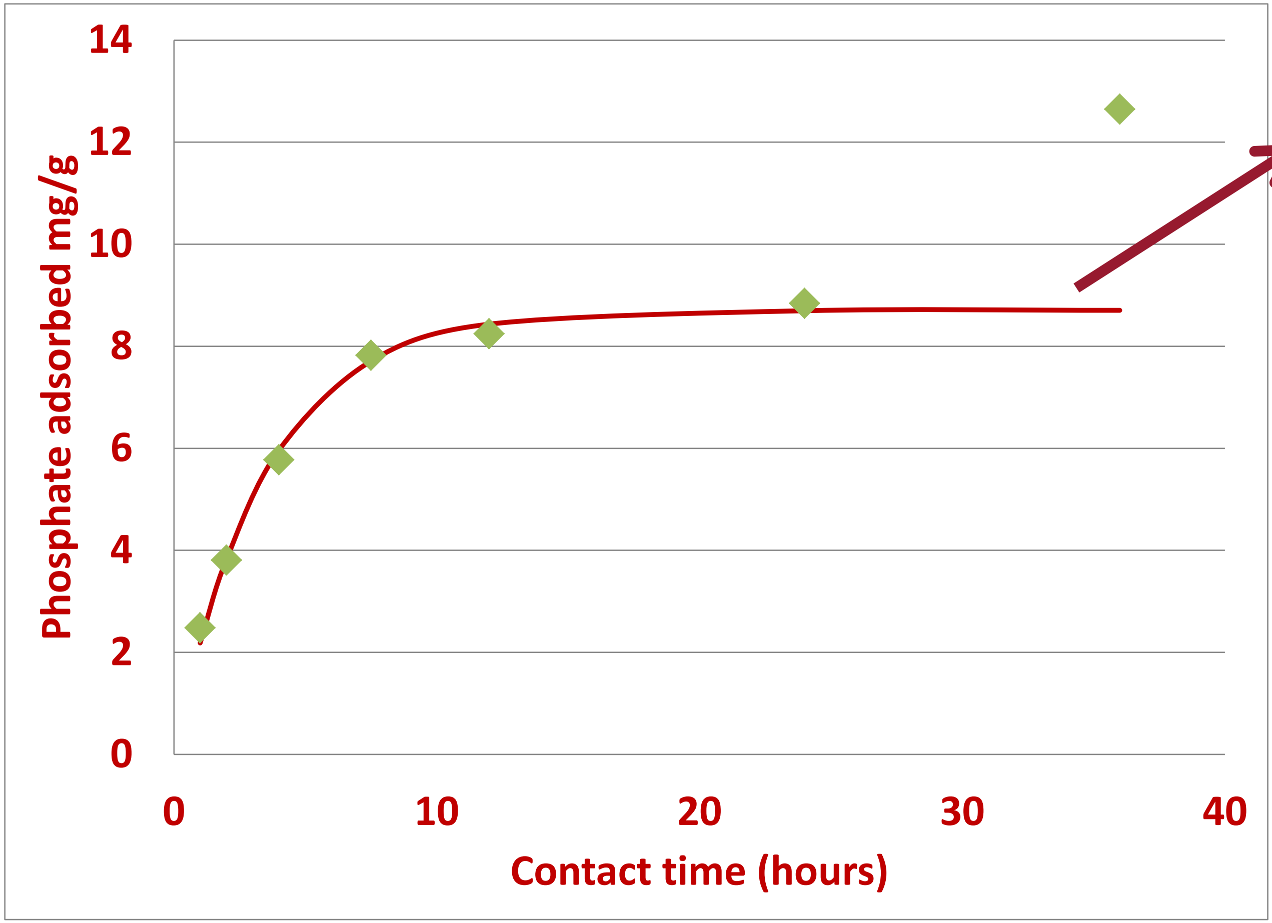
Phosphate Adsorption



Phosphorous Removal

Phosphate Adsorption

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



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

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

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

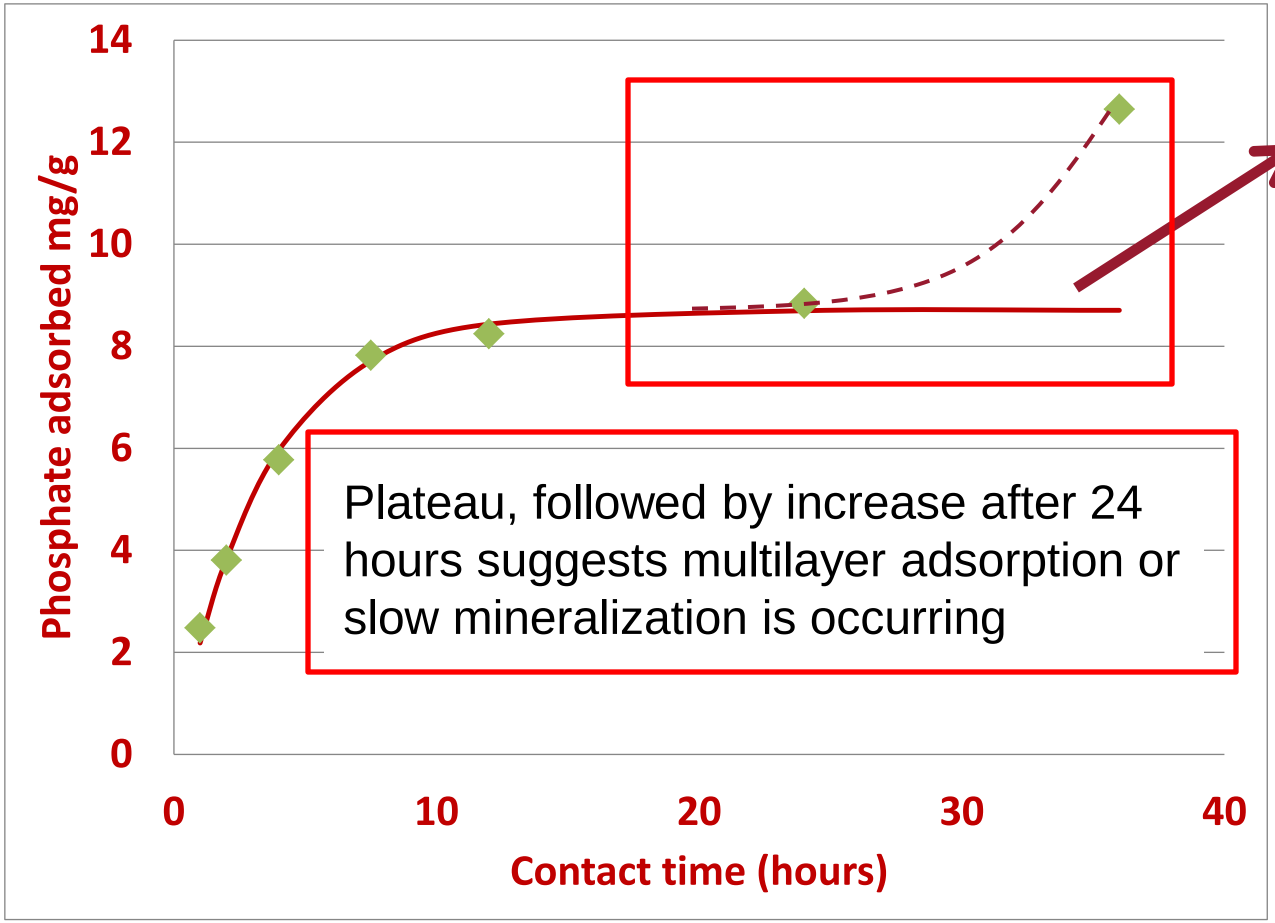
$q_e = equilibrium$ $constant$

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

Phosphorous Removal

Phosphate Adsorption

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



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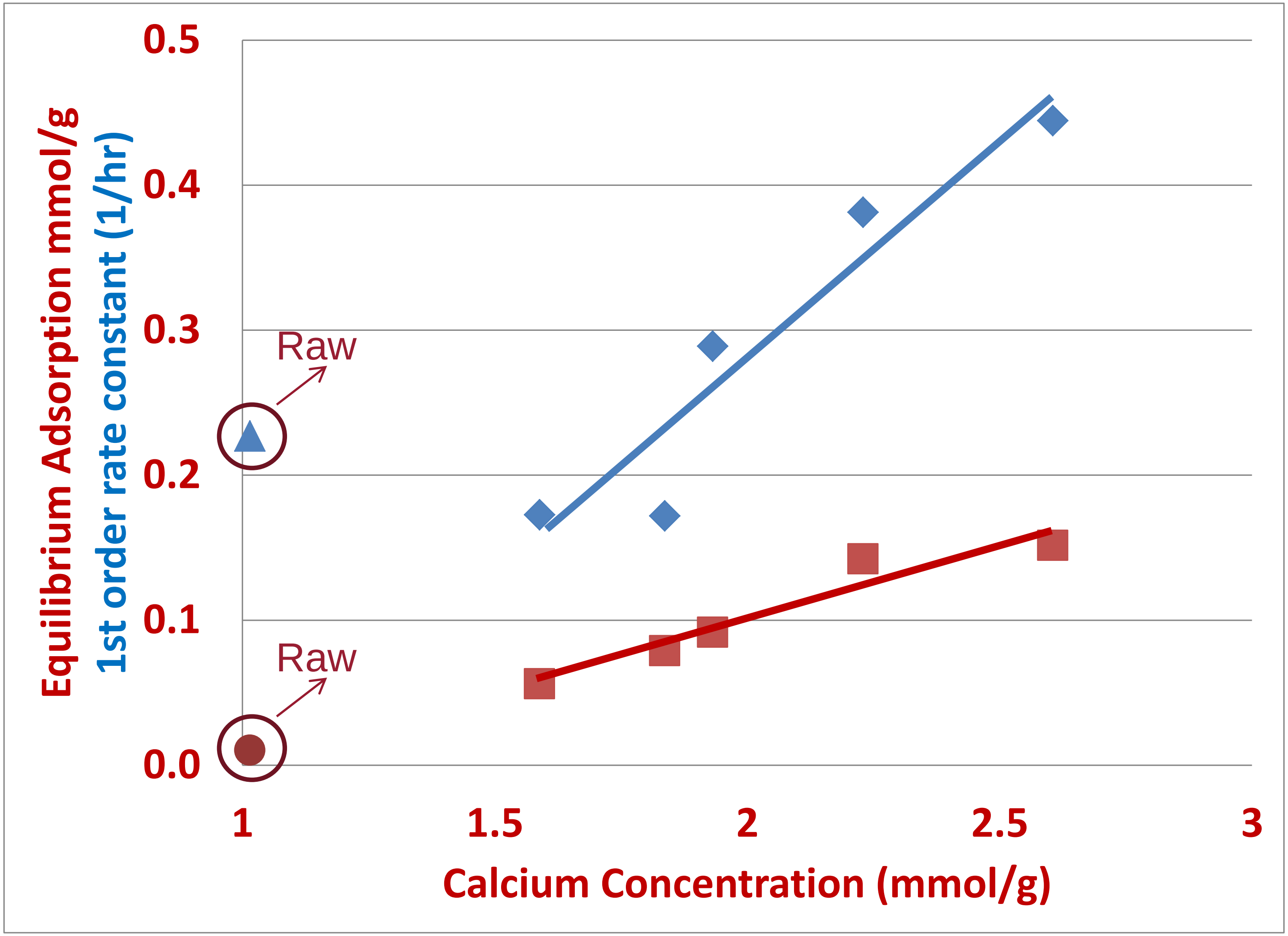
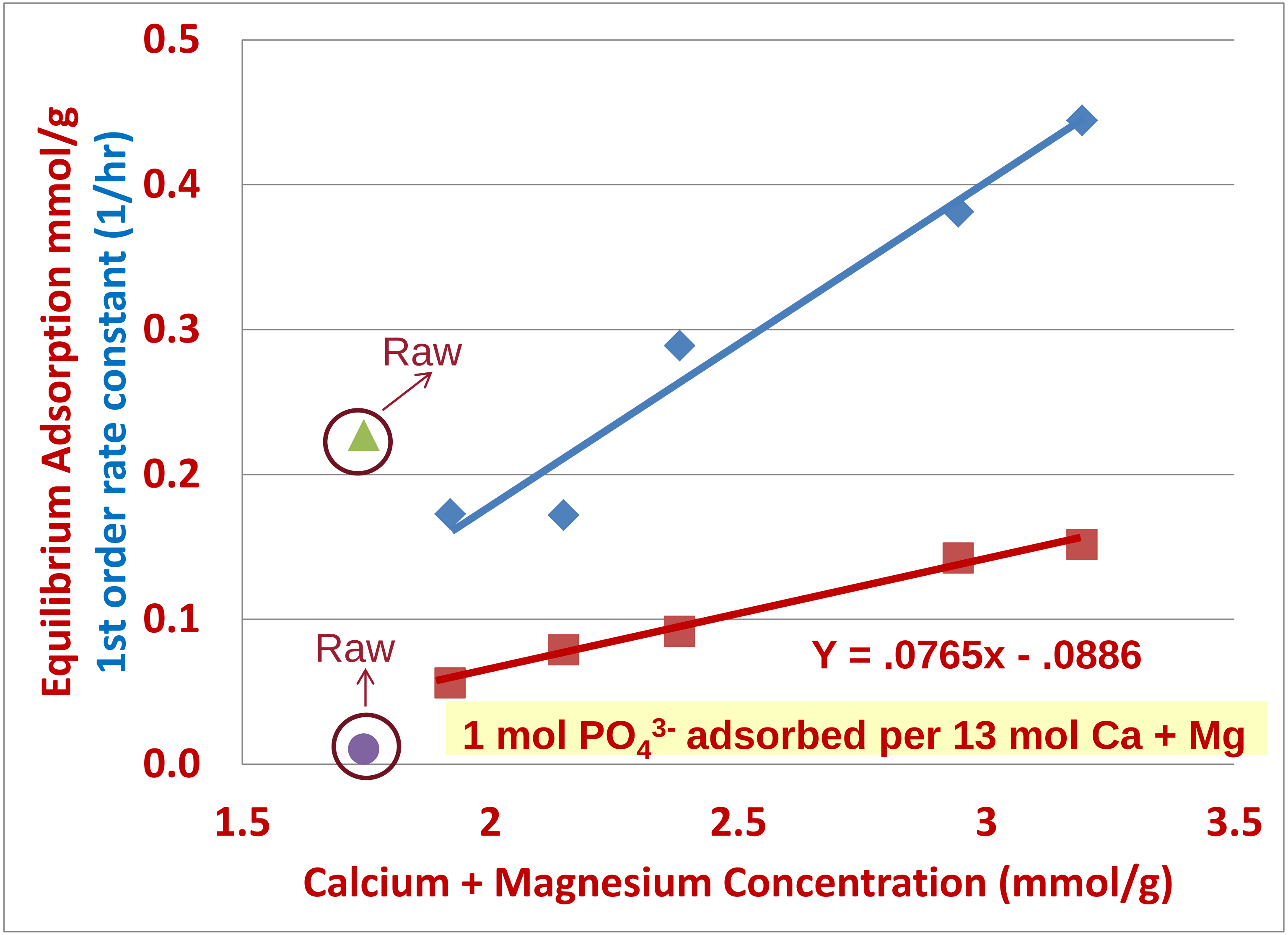
Phosphorous Removal

Phosphate Adsorption



Phosphorous Removal

Phosphate Adsorption



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

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.

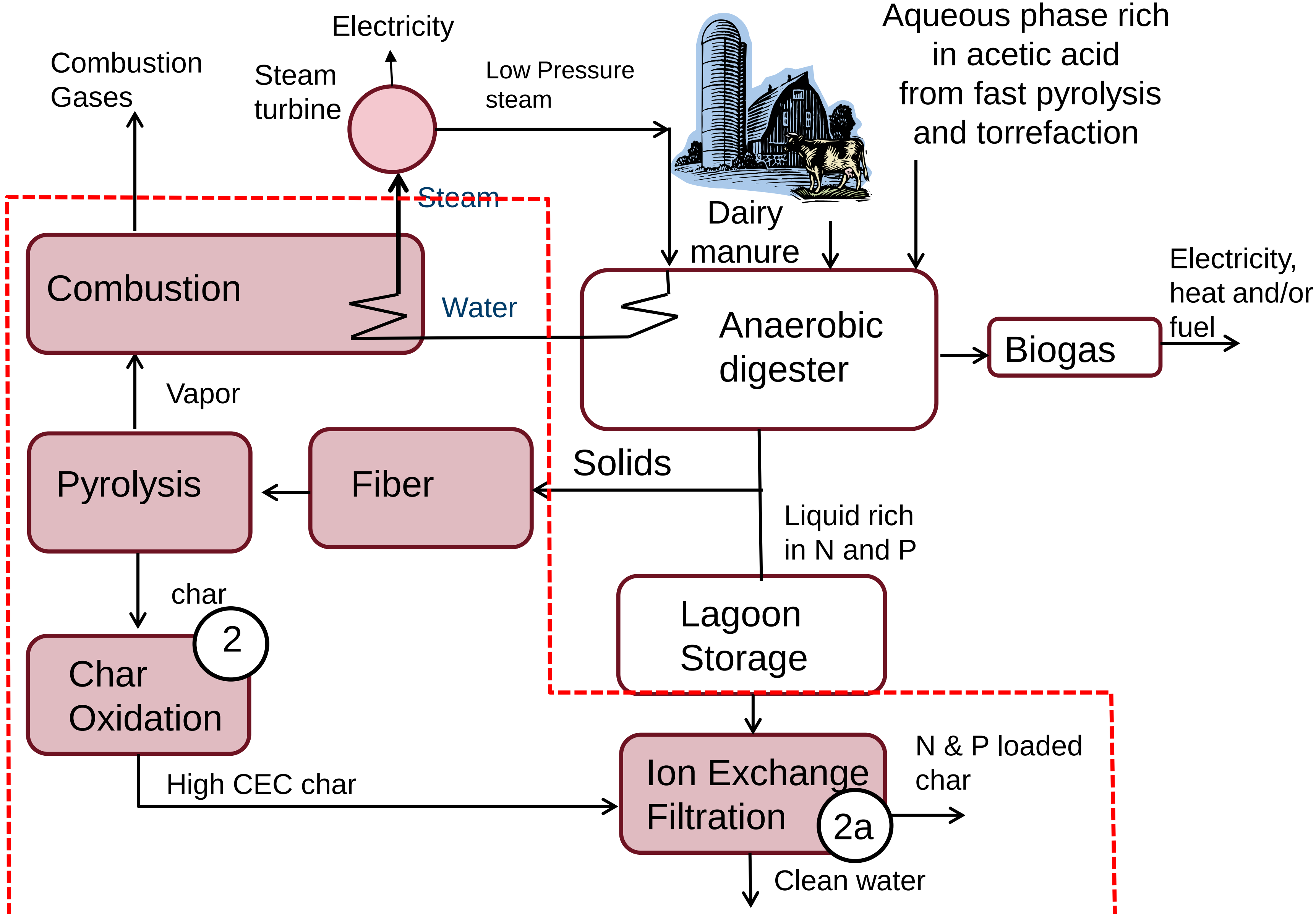
Chars prepared from fiber equilibrated at pH 9.35 effectively removed more than 50% of ionic phosphate after 7.5 hours and 80% after 36 hours.

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.

Introduction

Integrated Pyrolysis - AD System

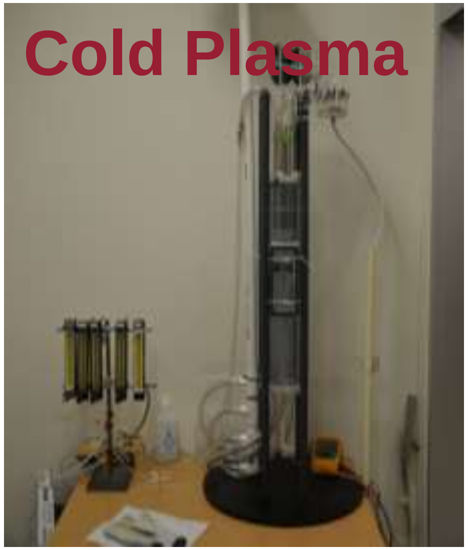


Oxidation for Nitrogen Removal

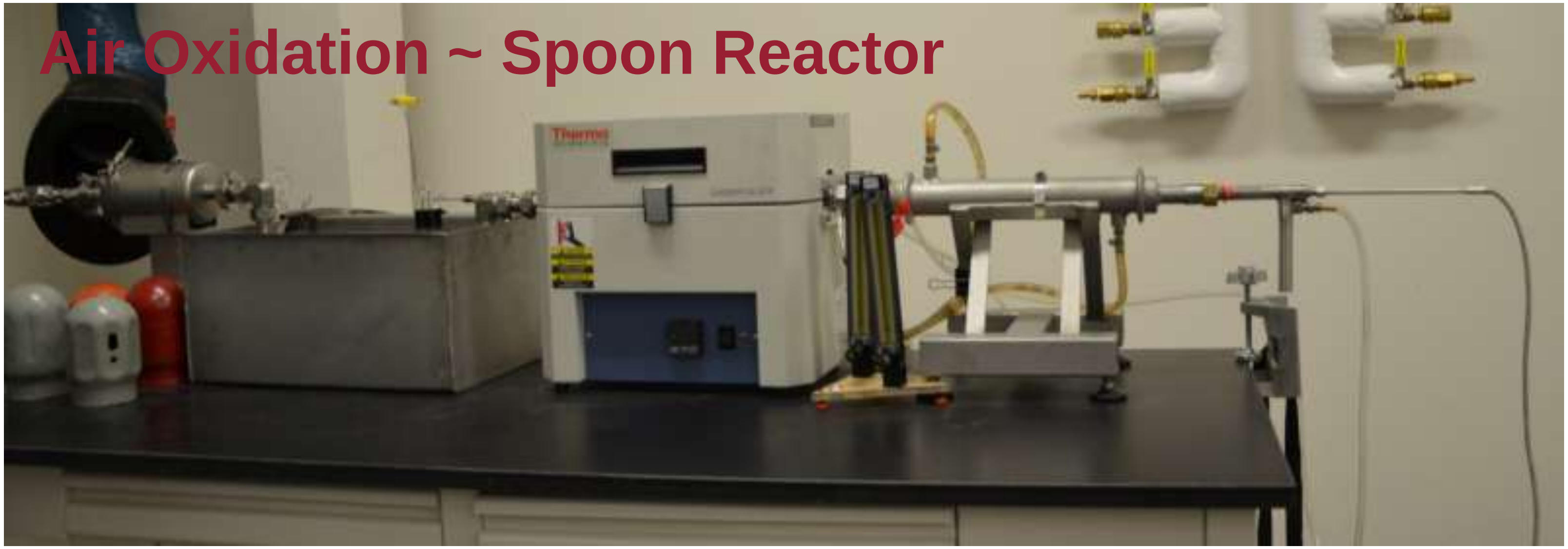
Experimental Equipment

Ozone

Cold Plasma



Air Oxidation ~ Spoon Reactor



Oxidation for Nitrogen Removal

Experimental

Untreated fiber was pyrolized at 500^{o}C for 30 minutes to generate all char samples studied.

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

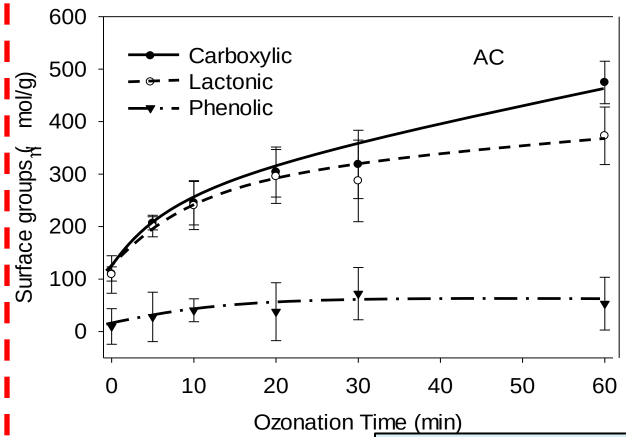
The change in functional groups were evaluated by Boehm titration

Oxidation for Nitrogen Removal

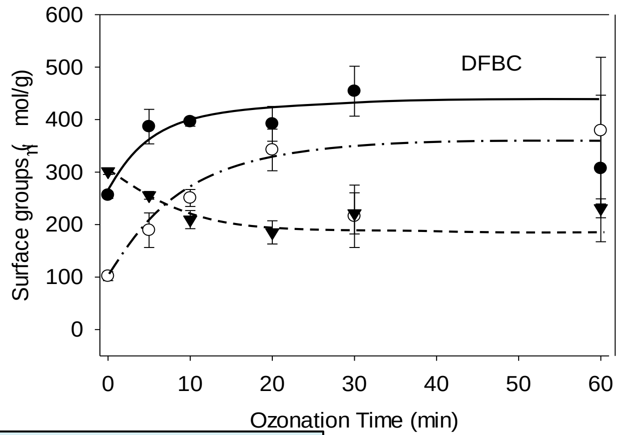
Ozone

In previous studies ozone was found to be an excellent oxidizing agent for highly aromatic chars, such as those from activated carbons (AC) and Douglas Fir Bar Char (DFBC) but had limited effect on Douglas Fir Wood Char (DFWC)

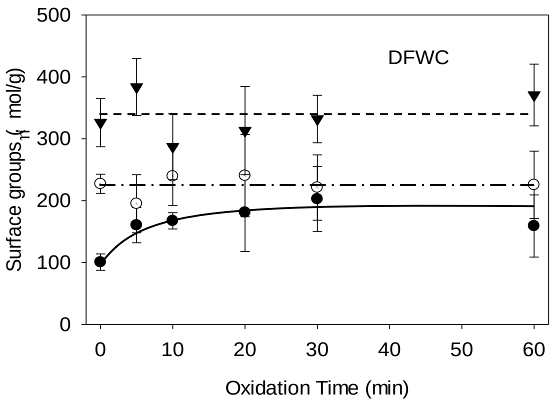
Activated Carbon



DF Bark Char



DF Wood Char



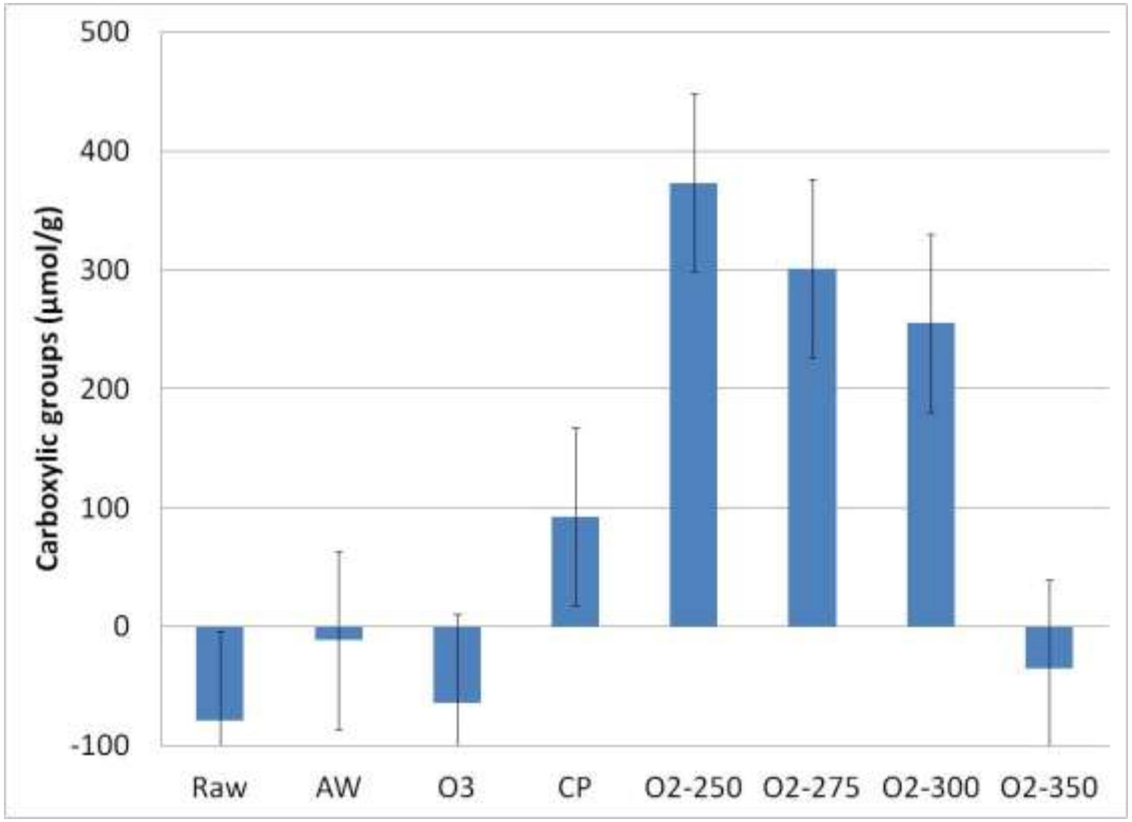
Strong ozonation effect

Oxidation for Nitrogen Removal

Mass loss due to oxidation

Sample	Mass Loss (mass %)
Raw	N/A
AW	N/A
O_3-30 min	2
CP-20 min	2
O_2-250 ^oC-2hr	6
O_2-275 ^oC-2hr	11
O_2-300 ^oC-2hr	21

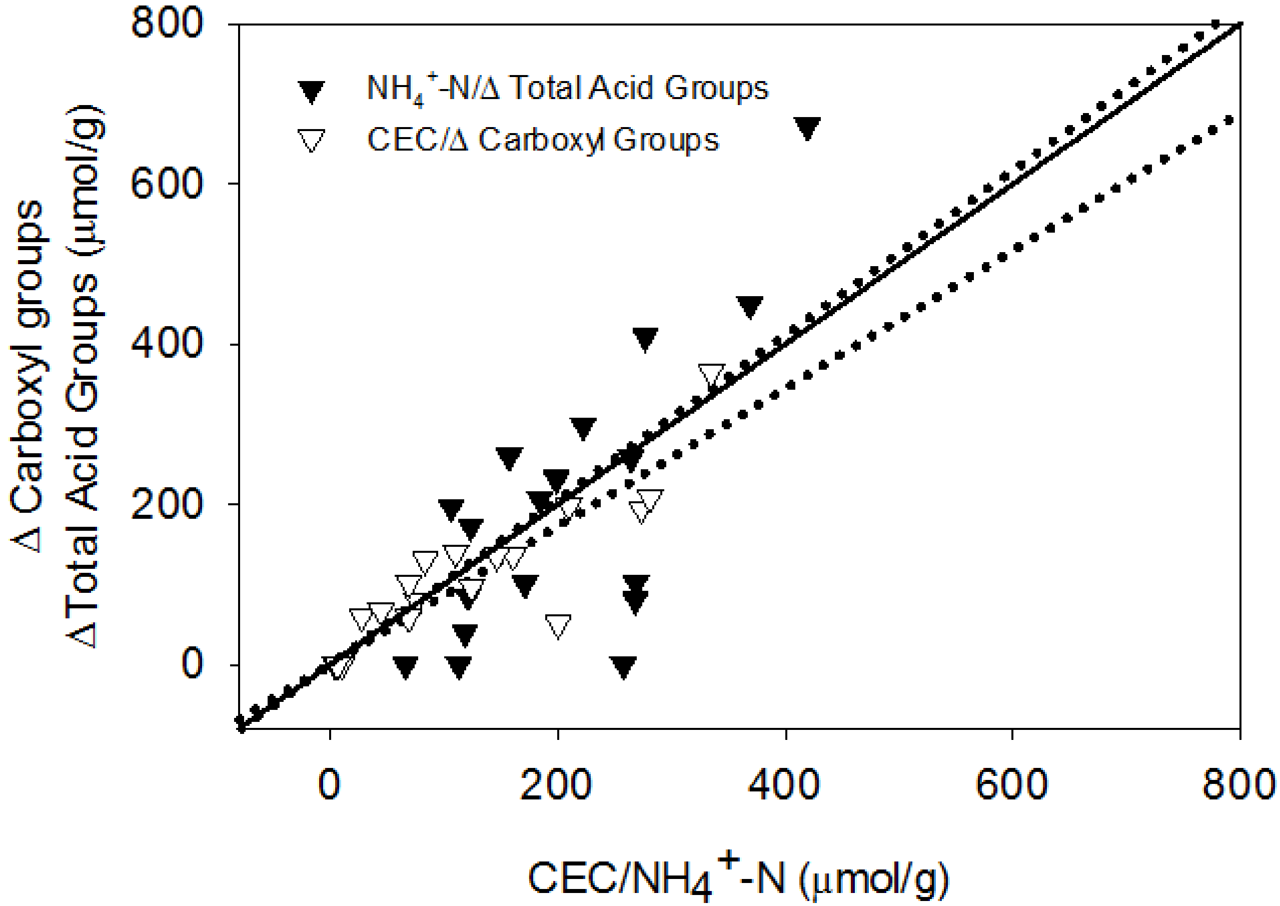
Carboxylic Group Formation



Cold Plasma

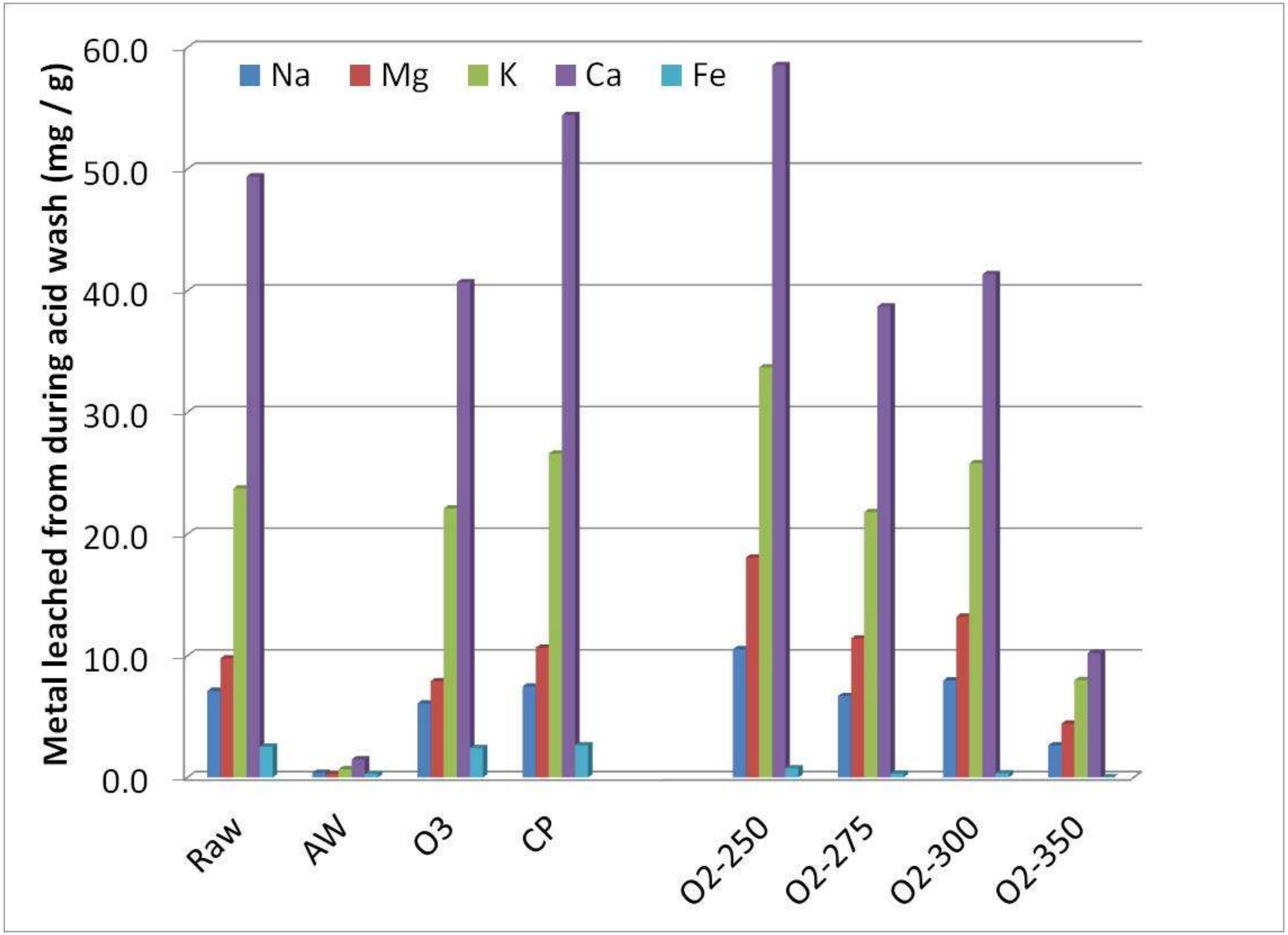
Oxidation for Nitrogen Removal

Correlation between CEC, Ammonium Adsorption and Carboxylic groups



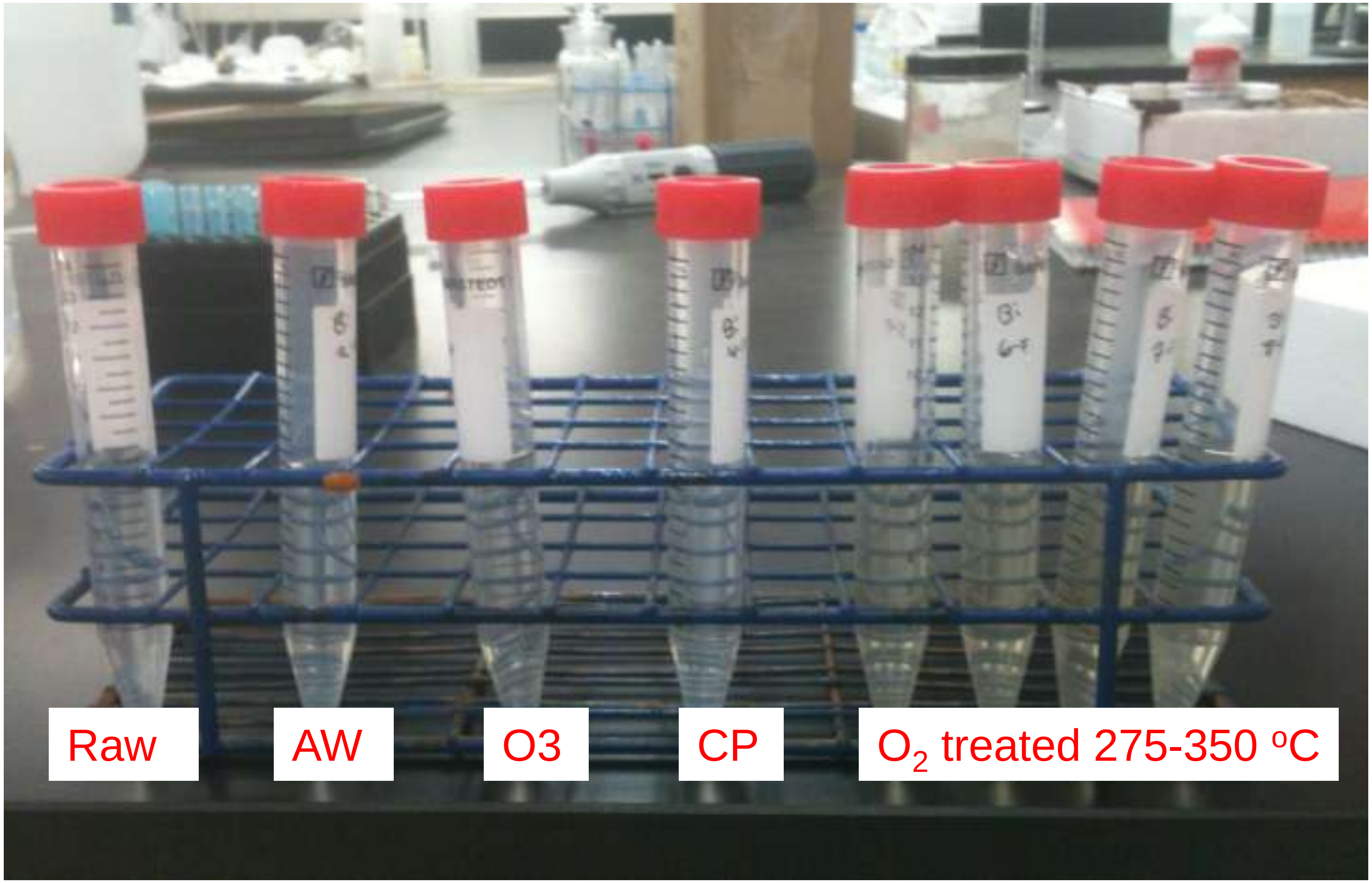
Oxidation for Nitrogen Removal

Changes in soluble matter due to oxidation



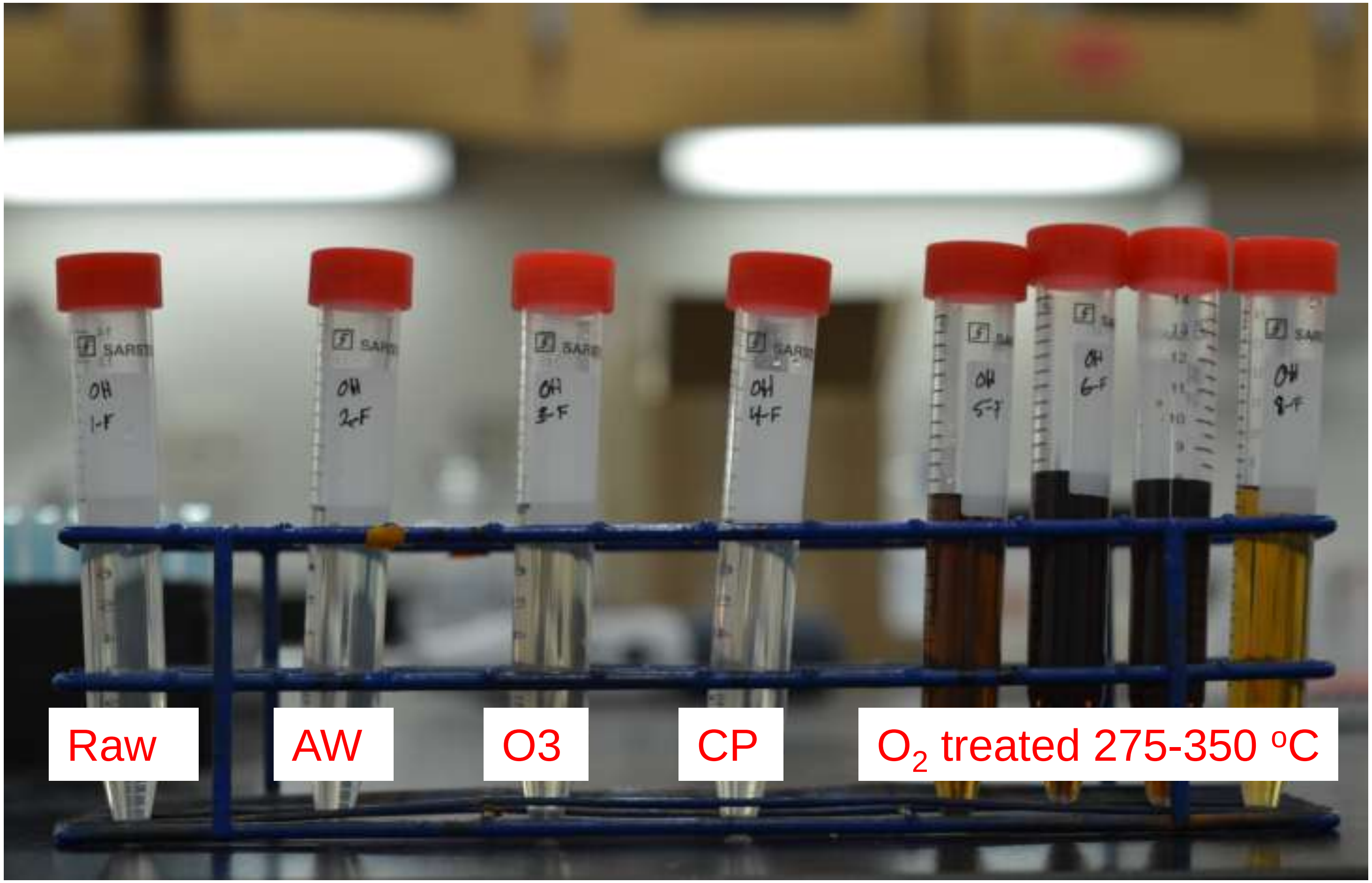
Oxidation for Nitrogen Removal

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

Conclusions

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

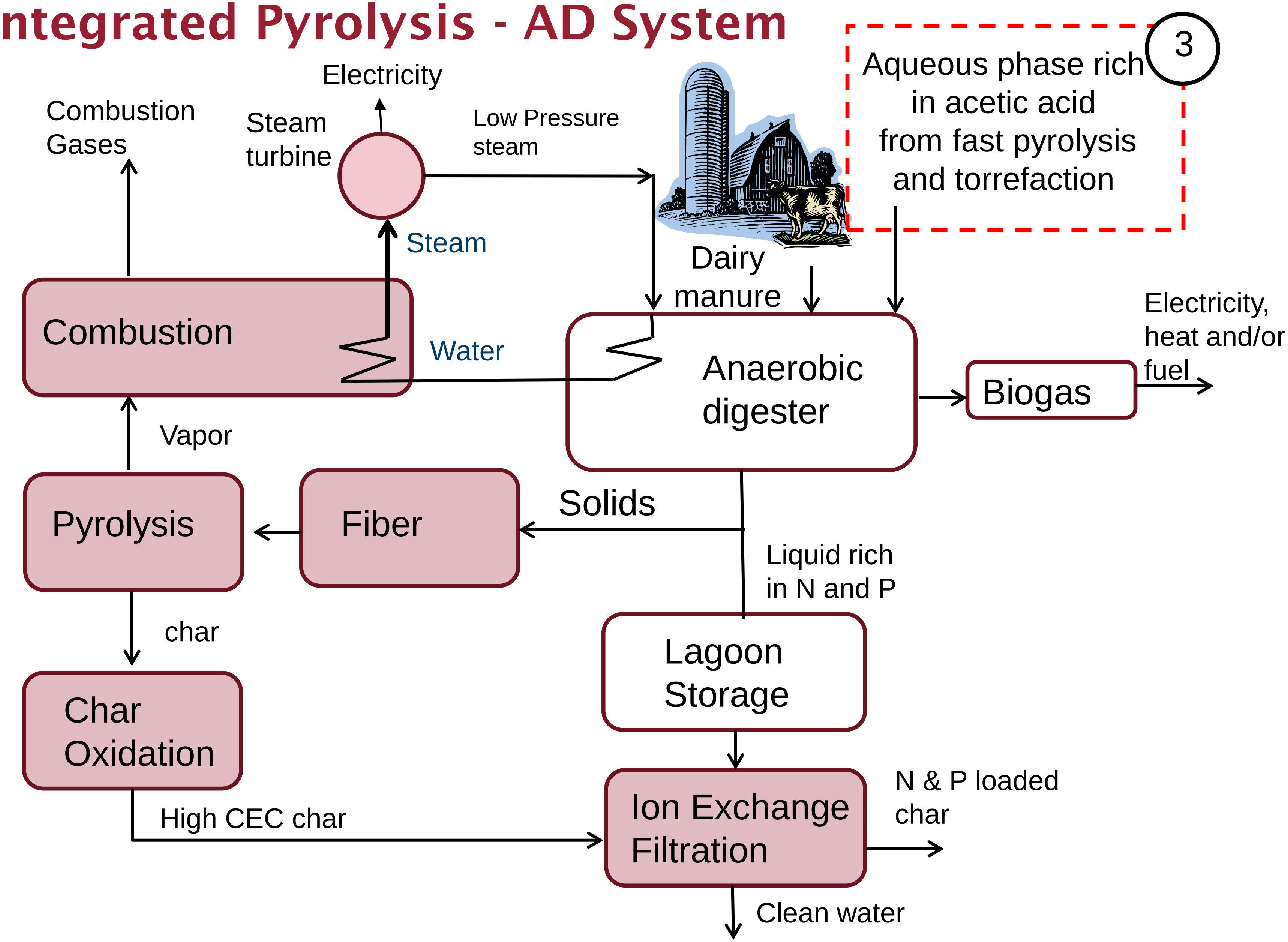
Air at temperatures of 250-300 ºC was effective at generating carboxylic acid groups, at 350 ºC carboxylic groups were not detected. This process can be easily integrated to a pyrolysis units during bio-char cooling.

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 should be further studied.

Introduction

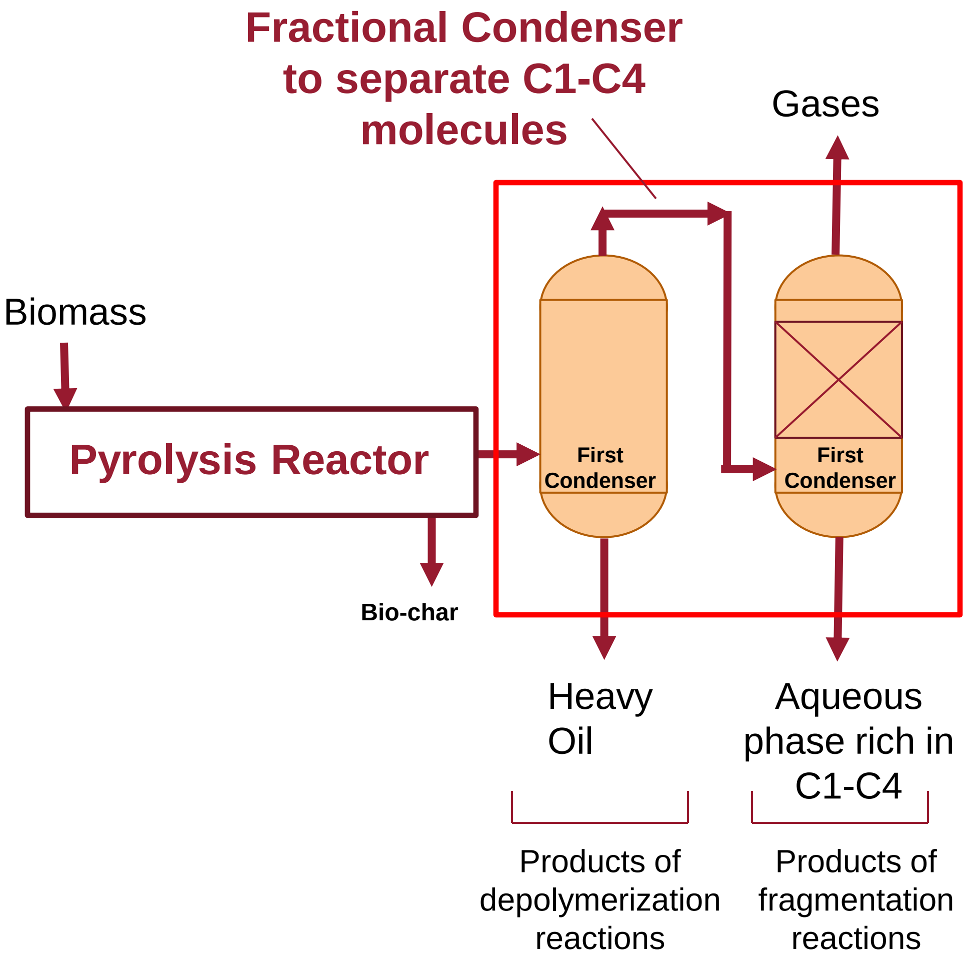
Integrated Pyrolysis - AD System



Anaerobic Digestion of Pyrolytic C1-C4 Compounds

Challenge

The Pyrolytic C1-C4 molecules are responsible for many of the undesirable properties of bio-oil (acidity, low thermal stability). Thus, separating and developing products from this fraction is critical for the success of the biomass pyrolysis industry.

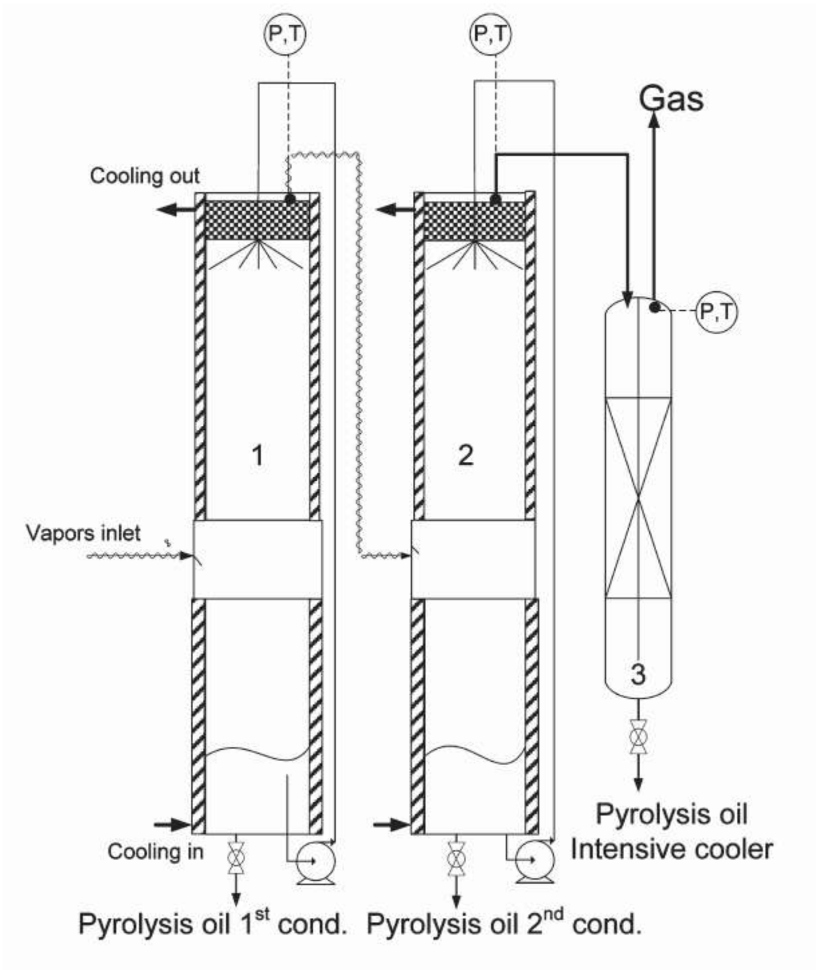


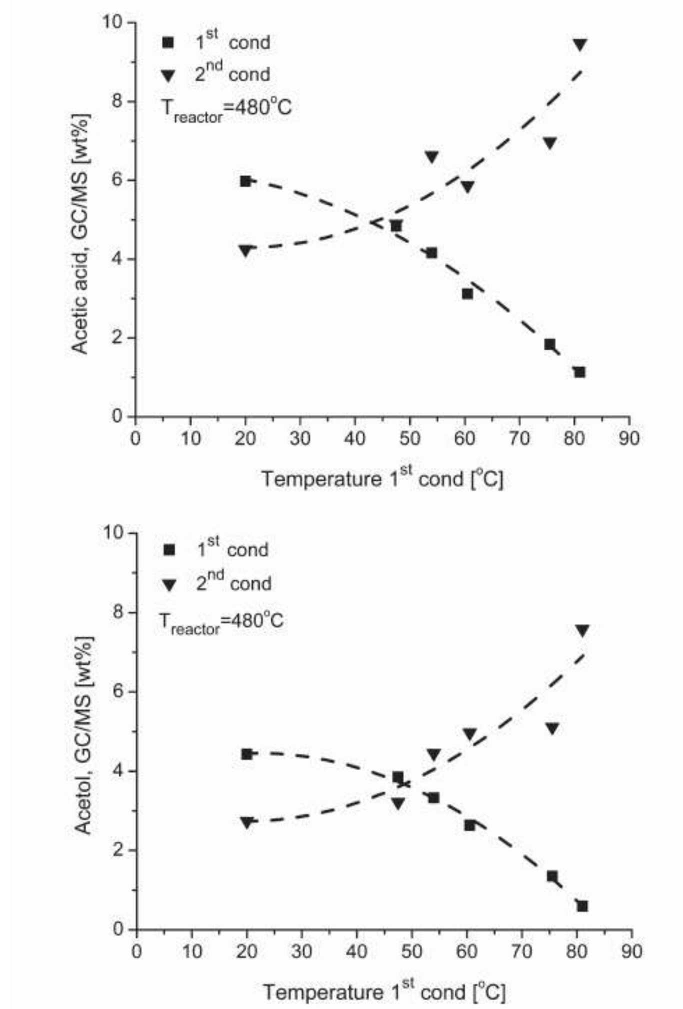
Possible use

Many of the C1-C4 products can be converted to methane through anaerobic digestion.

Anaerobic Digestion of Pyrolytic C1-C4 Compounds

Fractional Condenser to Separate C1-C4 molecules from Precursors of Transportation Fuels





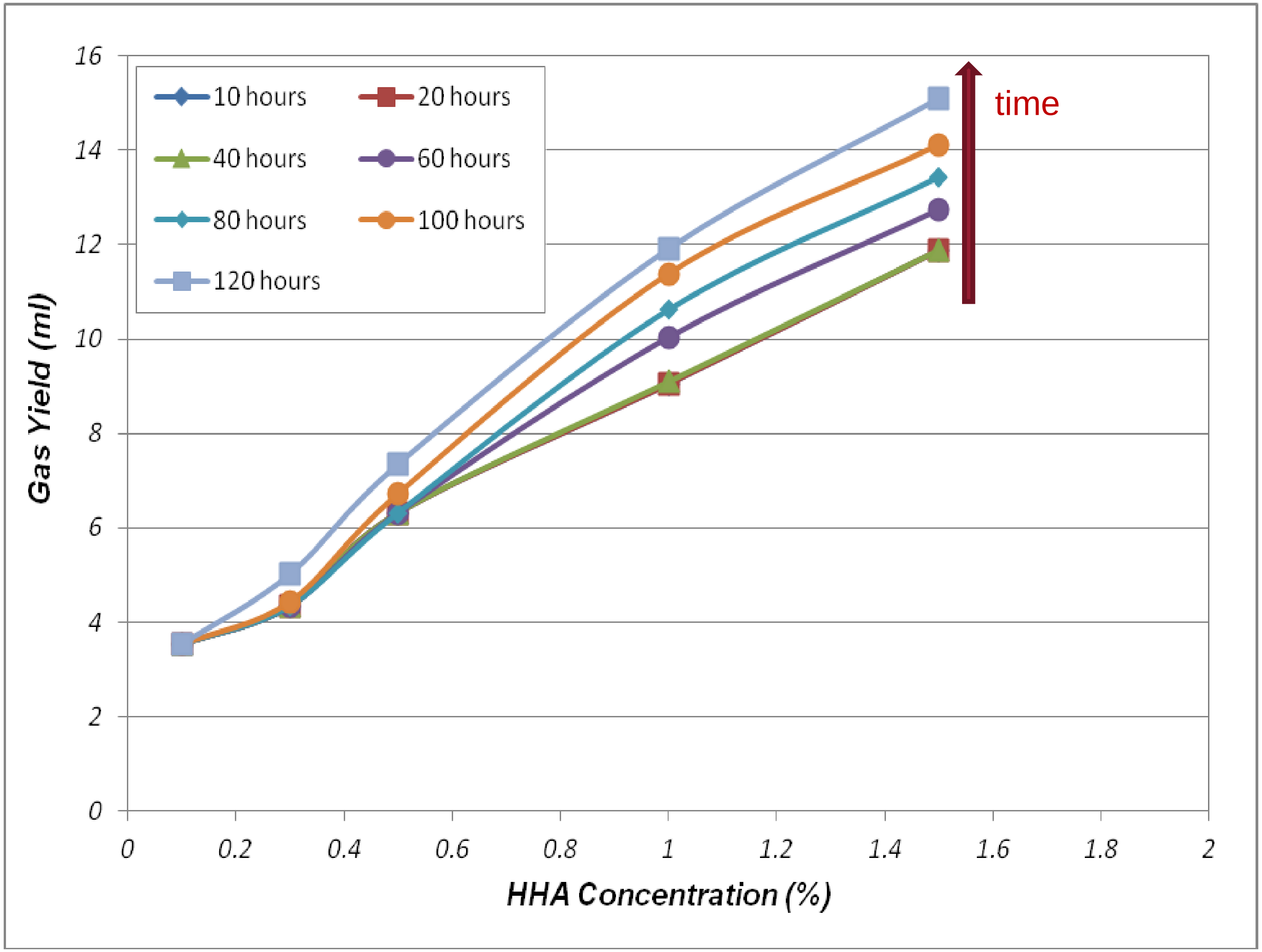
Westerhof RM, Brilmant DW, Garcia-Perez M, Wang Z, Oudenhoven SRG, van Swaaij WPM, Kersten SRA: Fractional Consensation of Biomass Pyrolysis Vapors. Energy Fuels, 2011, 25 (4), 1817-1829

Anaerobic Digestion of Pyrolytic C1-C4 Compounds

Bio-Methane Production from C1-C4 Pyrolytic Products

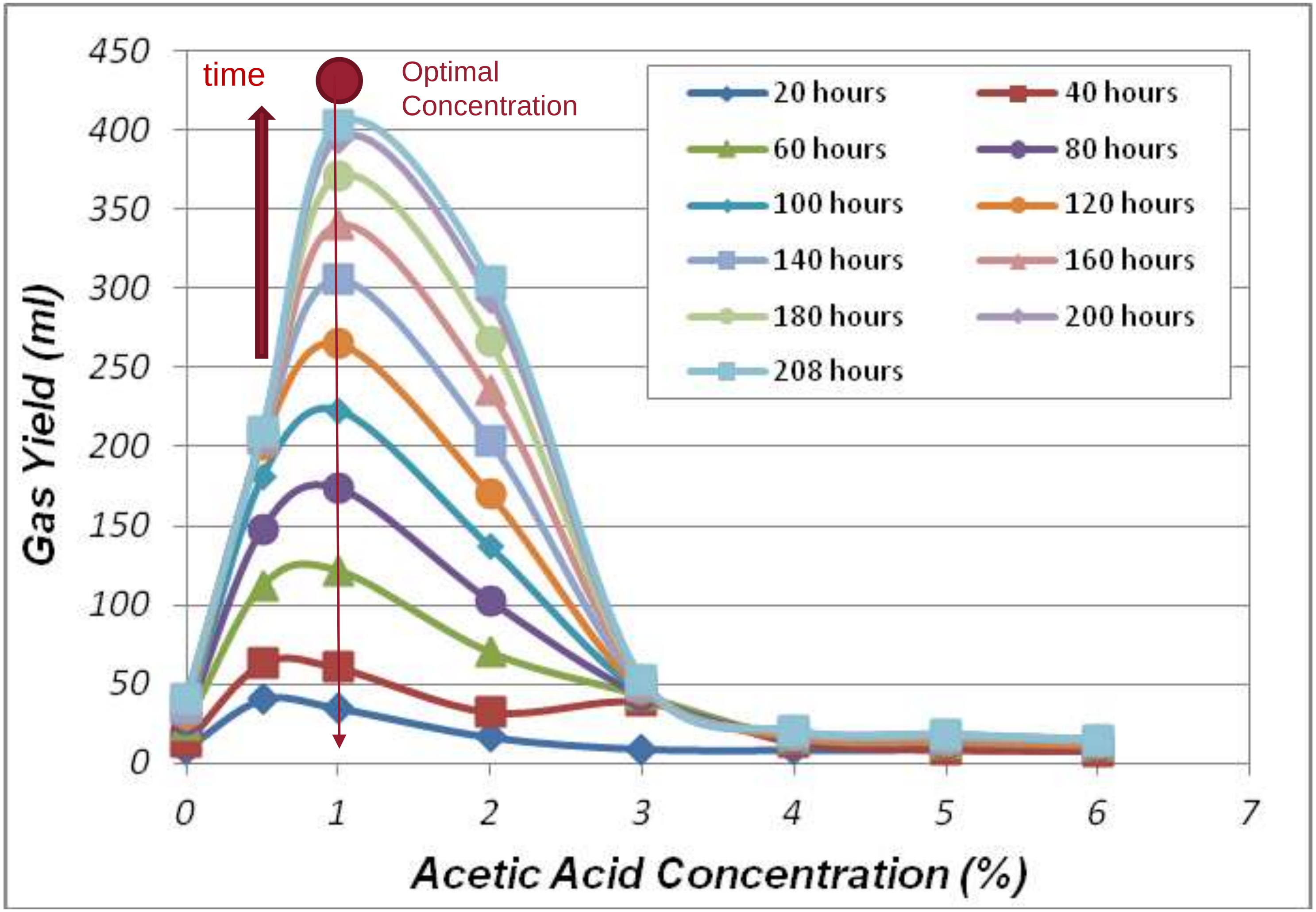
Anaerobic Digestion of Pyrolytic C1-C4 Compounds

Bio-Methane Production from Hydroxy-acetaldehyde



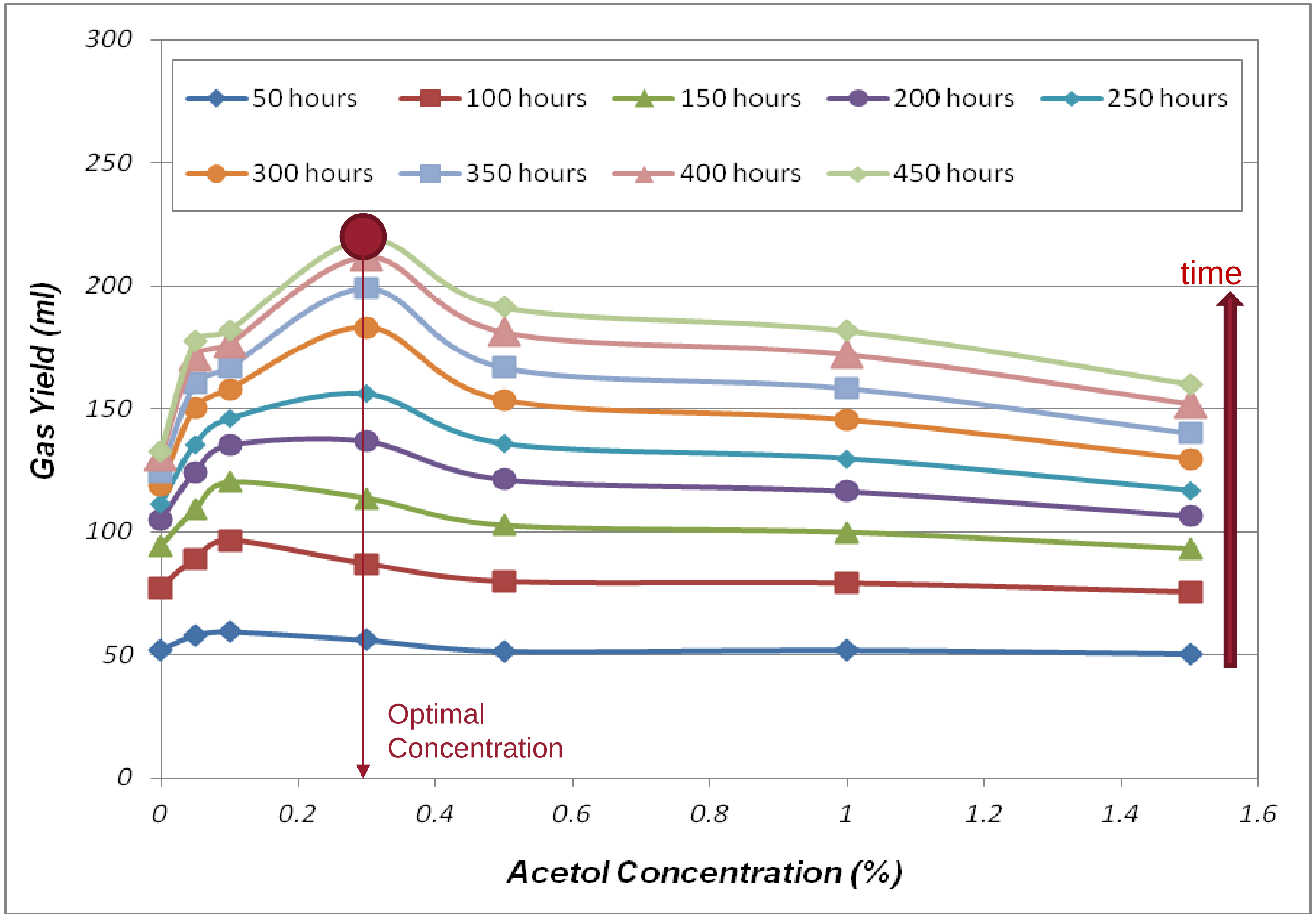
Anaerobic Digestion of Pyrolytic C1-C4 Compounds

Bio-Methane Production from Acetic Acid



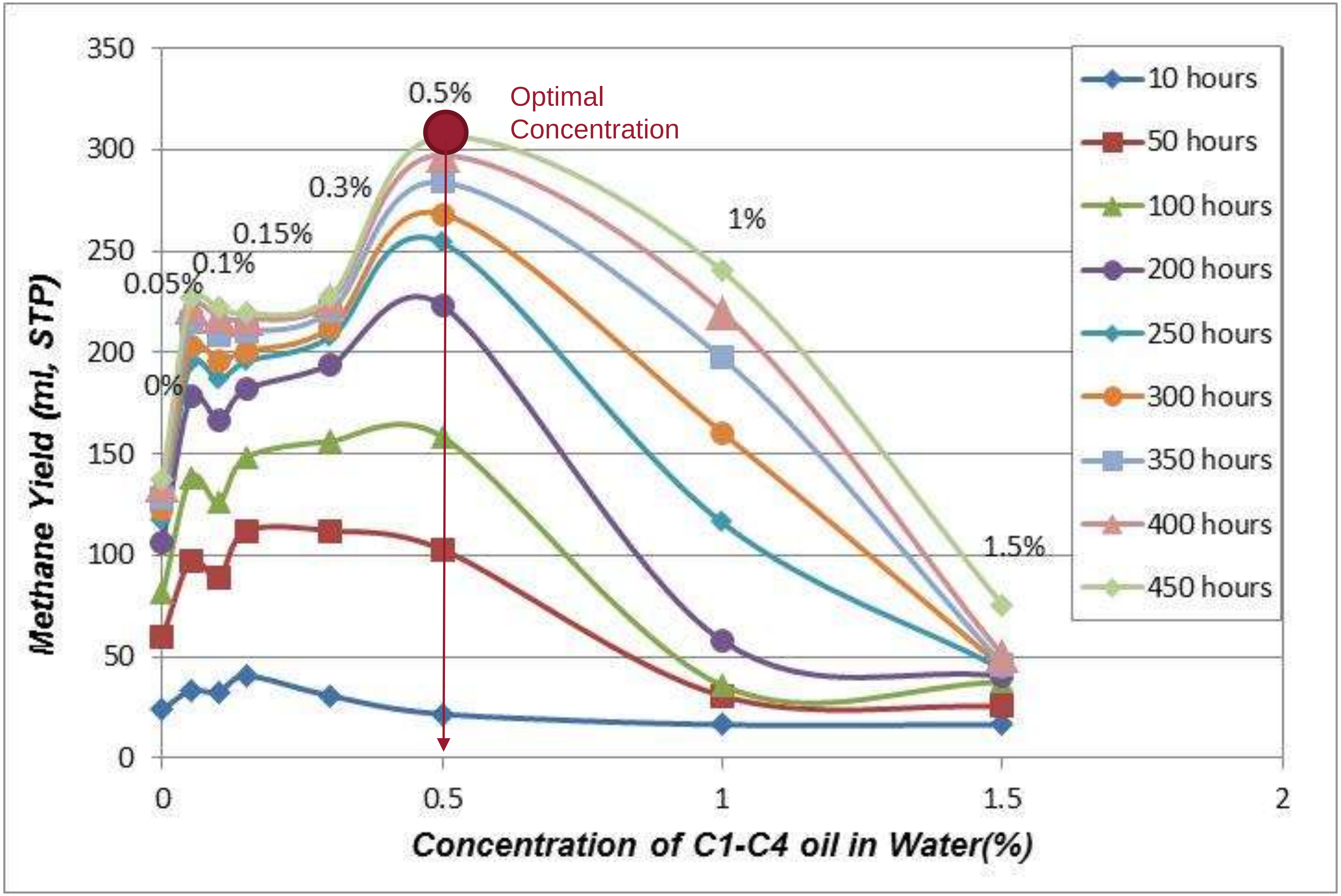
Anaerobic Digestion of Pyrolytic C1-C4 Compounds

Bio-Methane Production from Acetol



Anaerobic Digestion of Pyrolytic C1-C4 Compounds

Bio-Methane Production from Pyrolytic Aqueous Phase rich in C1-C4 compounds



Anaerobic Digestion of Pyrolytic C1-C4 Compounds

Conclusions

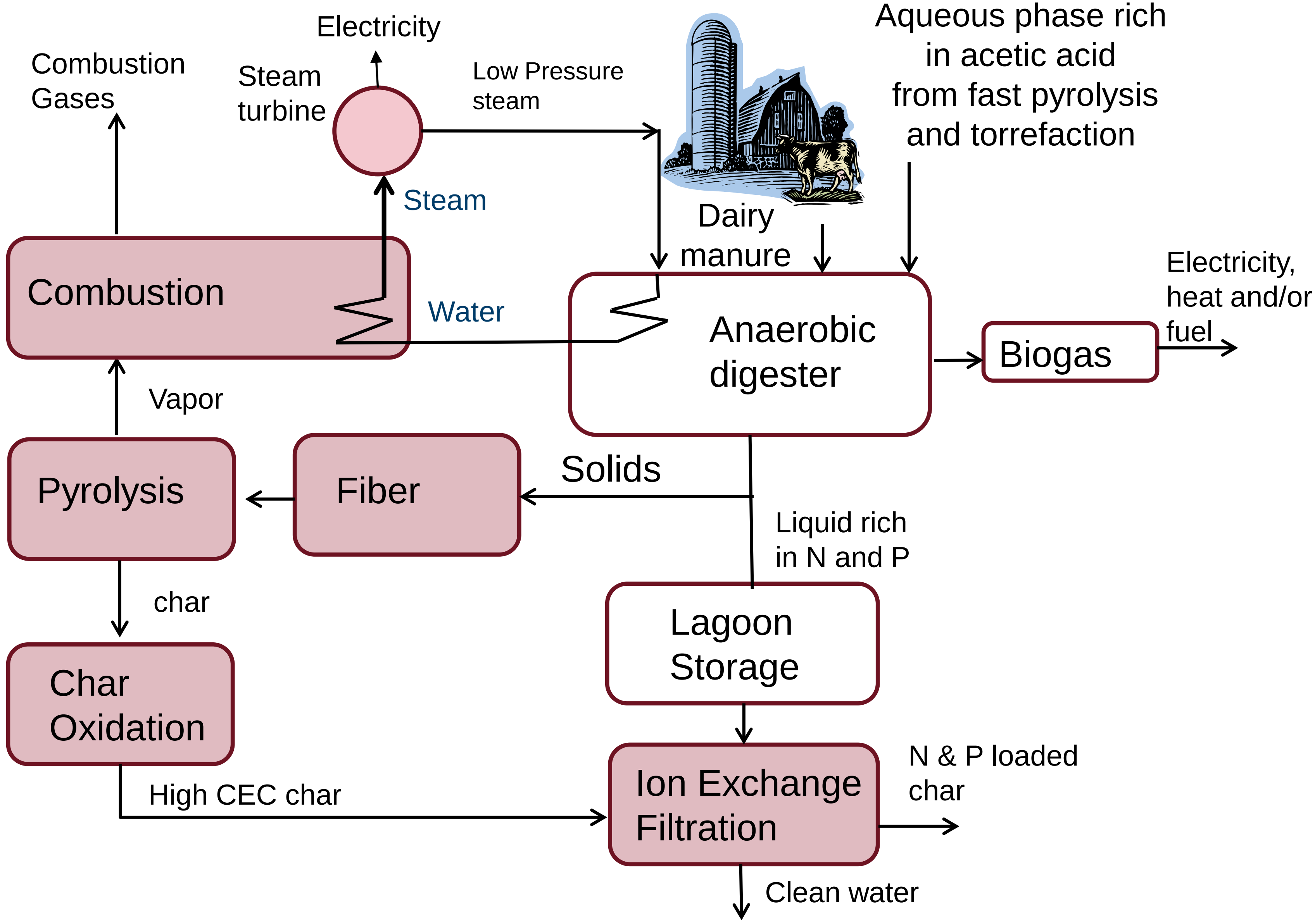
Microbes are highly sensitive to elevated concentrations of acetic acid, and mildly sensitive to acetol concentration.

Low concentration of the aqueous phase rich in C1-C4 molecules, 0.5 mass %, can be effectively converted to methane through anaerobic digestion

Higher concentrations of aqueous phase rich in C1-C4 molecules could be digested if the concentration of toxic compounds (mainly phenolic compounds) is reduced.

Conclusions - Summary

Integrated Pyrolysis - AD System



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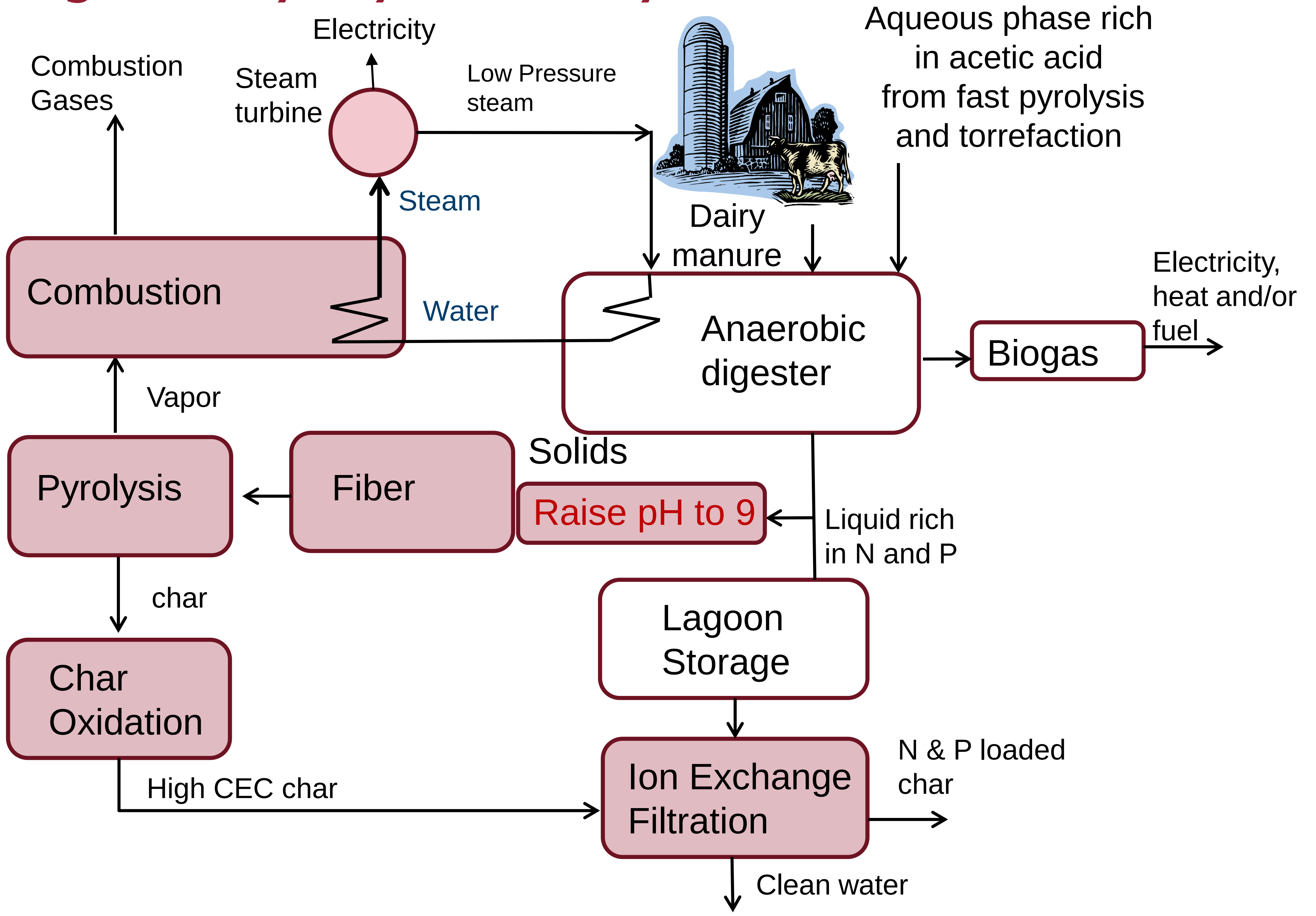

Conclusions - Summary

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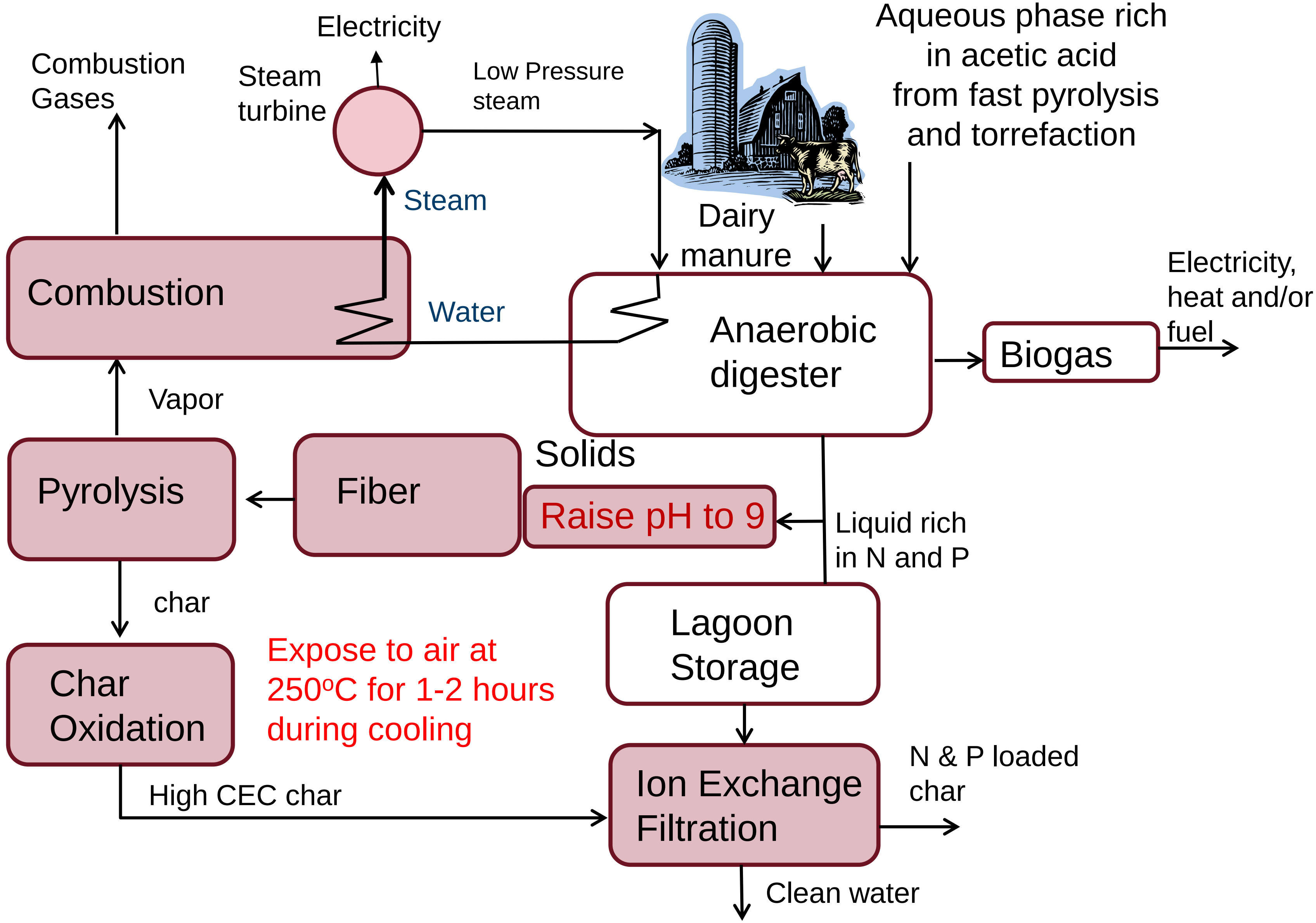

Conclusions - Summary

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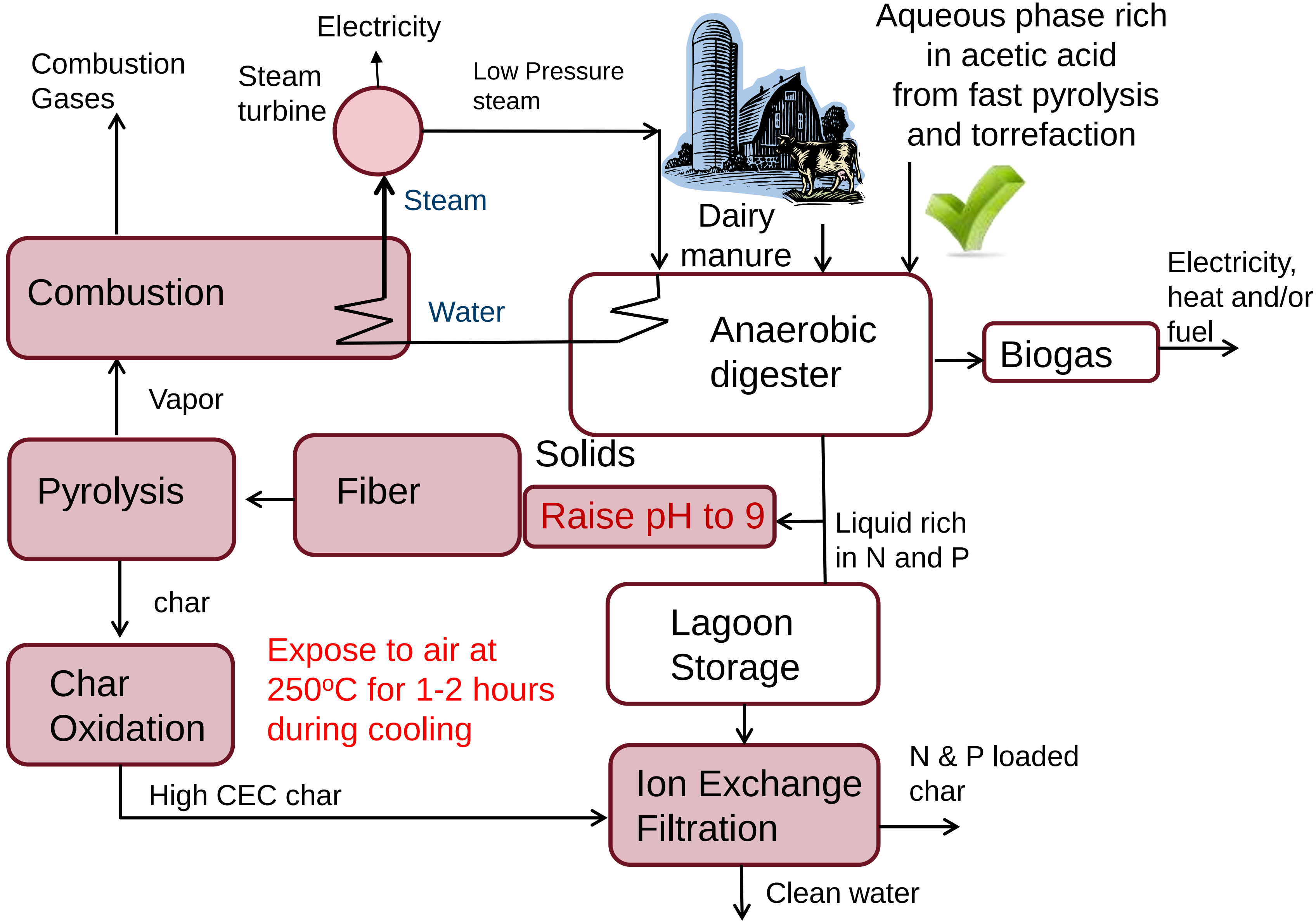
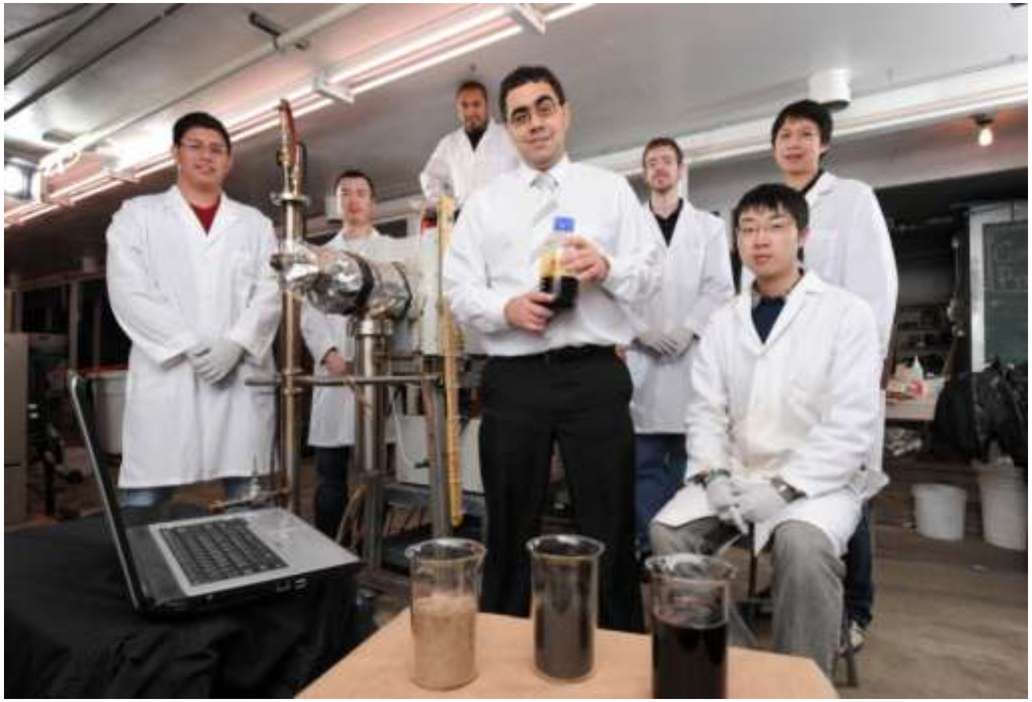


Acknowledgements



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QUESTIONS ?