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 %).

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Liquid</th>
<th>Char</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow heating rates, large particles, large residence time of vapors</td>
<td>30 - 45 %</td>
<td>25-35 %</td>
<td>25-35 %</td>
</tr>
</tbody>
</table>
Introduction

Slow Pyrolysis

SLOW PYROLYSIS 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).

How to make sequestration profitable?
Develop low cost adsorbents for course treatment of waste water

Soil amendments
Load with nutrients for slow release fertilizers

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

Introduction

Integrated Pyrolysis - AD System

Combustion

Pyrolysis

Char Oxidation

Fiber

Lagoon Storage

Ion Exchange Filtration

Steam turbine

Low Pressure steam

Dairy manure

Water

Char

High CEC char

Electricity

Low Pressure steam

 Electricity, heat and/or fuel

Aqueous phase rich in acetic acid from fast pyrolysis and torrefaction

Electricity, heat and/or fuel

Electricity

Steam

Vapor

Solids

Liquid rich in N and P

N & P loaded char

Clean water

Aqueous phase rich

Dairy manure

Steam

Electricity

Low Pressure steam

Dairy manure

Water

Electricity

Low Pressure steam

Combustion Gases

Vapor

Combustion

Pyrolysis

Char Oxidation

Fiber

Lagoon Storage

Ion Exchange Filtration

Introduction
Introduction

Integrated Pyrolysis - AD System

Combustion Gases → Steam turbine → Electricity → Low Pressure steam

Steam → Dairy manure → Biogas

Electricity, heat and/or fuel

Aqueous phase rich in acetic acid from fast pyrolysis and torrefaction

Combustion

Pyrolysis → Vapor → Steam

Fiber

Pyrolysis

Char Oxidation

Char → Lagoon Storage

Solids

Liquid rich in N and P

Low Pressure steam

Steam turbine

Electricity

Lagoon Storage

 Ion Exchange Filtration

N & P loaded char

Clean water

Dairy manure

Introduction
Introduction

Integrated Pyrolysis - AD System

Combustion Gases → Steam turbine → Electricity

Steam → Low Pressure steam → Dairy manure → Biogas → Electricity, heat and/or fuel

Combustion → Water

Pyrolysis → Vapor

Char Oxidation → char

Char → High CEC char

Fiber → 1

Solids → Liquid rich in N and P

Lagoon Storage

Aqueous phase rich in acetic acid from fast pyrolysis and torrefaction

Ion Exchange Filtration

N & P loaded char

Clean water

Dairy manure

Steam turbine

Electricity

Low Pressure steam

Water

Vapor

1

1a
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. This treatment was selected for further studies.
Phosphorous Removal

Pre-pyrolysis $\text{CaCl}_2$ modification of AD fiber

**Experimental**

AD fiber was impregnated with calcium by immersion in a $\text{CaCl}_2$ solution followed by pH adjustment to 6, 8, 9.35, 11 and 12.

Modified fiber samples were then dried and pyrolyzed at 500$^\circ$C for 30 minutes using a spoon reactor.

*Spoon Reactor Diagram*
Phosphorous Removal

Pre-pyrolysis CaCl$_2$ modification of AD fiber

![Graph showing calcium concentration and pH relationship](image)

- **Calcium Concentration (mg / g fiber)**
- **Final pH of CaCl$_2$ Solution**
- **Char fraction (%)**
- **Total AAEM fraction mg / g fiber**

- **Raw Fiber**
Phosphorous Removal

Pre-pyrolysis $\text{CaCl}_2$ 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

![Graph showing the relationship between phosphate adsorption and contact time at different pH levels.](image-url)
Phosphorous Removal

Phosphate Adsorption

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

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

- \(dq/dt\) = 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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- \(q_e\) = equilibrium constant
- \(q\) = concentration at time \(t\)

Plateau, followed by increase after 24 hours suggests multilayer adsorption or slow mineralization is occurring.
Phosphorous Removal

Phosphate Adsorption

Equilibrium Adsorption mmol/g
1st order rate constant (1/hr)
Calcium Concentration (mmol/g)
Phosphorous Removal

Phosphate Adsorption

Raw

\[ Y = 0.0765x - 0.0886 \]

1 mol PO$_4^{3-}$ adsorbed per 13 mol Ca + Mg
Phosphorous Removal

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

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na</th>
<th>Ca</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>0.07</td>
<td>0.38</td>
<td>0.00</td>
</tr>
<tr>
<td>pH 6</td>
<td>0.01</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>pH 8</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>pH 9.35</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>pH 11</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>pH 12</td>
<td>0.06</td>
<td>0.02</td>
<td>0.13</td>
</tr>
</tbody>
</table>
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 fiber was pyrolized at 500°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
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)
# Oxidation for Nitrogen Removal

## Mass loss due to oxidation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass Loss (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>N/A</td>
</tr>
<tr>
<td>AW</td>
<td>N/A</td>
</tr>
<tr>
<td>O₃-30 min</td>
<td>2</td>
</tr>
<tr>
<td>CP-20 min</td>
<td>2</td>
</tr>
<tr>
<td>O₂-250 °C-2hr</td>
<td>6</td>
</tr>
<tr>
<td>O₂-275 °C-2hr</td>
<td>11</td>
</tr>
<tr>
<td>O₂-300 °C-2hr</td>
<td>21</td>
</tr>
</tbody>
</table>

## Carboxylic Group Formation

![Bar chart showing carboxylic group formation](chart.png)

- Cold Plasma
Oxidation for Nitrogen Removal

Correlation between CEC, Ammonium Adsorption and Carboxylic groups

\[ \Delta \text{Carboxyl groups} \]
\[ \Delta \text{Total Acid Groups (\(\mu\text{mol/g}\))} \]
\[ \text{CEC/NH}_4^+ \text{-N (\(\mu\text{mol/g}\))} \]
Oxidation for Nitrogen Removal

Changes in soluble matter due to oxidation

[Bar chart showing metal leached from during acid wash (mg/g) for different treatments: Na, Mg, K, Ca, Fe. Treatment groups include Raw, AW, O3, CP, O2-250, O2-275, O2-300, O2-350.]
Oxidation for Nitrogen Removal

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

- Raw
- AW
- O3
- CP
- O₂ treated 275-350 °C
Oxidation for Nitrogen Removal

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

Ozone (O3) treated samples exhibit different colors compared to the raw sample (Raw), indicating changes in the soluble matter due to oxidation.
All oxidation methods tested resulted in varying degrees of acid group formation and carbon gasification.

Air at temperatures of 250-300 °C was effective at generating carboxylic acid groups, at 350 °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 should be further studied.
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Steam turbine

Low Pressure steam

Dairy manure

Biogas

Combustion Gases

Electricity

Steam

Solids

Liquid rich in N and P

Lagoon Storage

N & P loaded char

Clean water

Electricity, heat and/or fuel

Solids

High CEC char

Aqueous phase rich in N and P

Electricity

Steam

Water

Vapor

Electricity, heat and/or fuel
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

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

![Graph showing gas yield versus acetic acid concentration over time. The graph illustrates the optimal concentration for maximum gas yield.](image)
Anaerobic Digestion of Pyrolytic C1-C4 Compounds

Bio-Methane Production from Acetol

![Graph showing gas yield vs. acetol concentration over time. The graph illustrates the optimal concentration for methane production.]
Anaerobic Digestion of Pyrolytic C1-C4 Compounds

Bio-Methane Production from Pyrolytic Aqueous Phase rich in 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

- Pyrolysis
  - Char Oxidation
    - Char
    - High CEC char
  - Vapor
- Combustion
  - Steam turbine
  - Electricity
  - Low Pressure steam
- Steam
- Fiber
  - Solids
    - Liquid rich in N and P
    - N & P loaded char
  - Char
  - High CEC char
- Lagoon Storage
- Ion Exchange Filtration
  - Clean water
- Biogas
  - Electricity, heat and/or fuel
  - Aqueous phase rich in acetic acid from fast pyrolysis and torrefaction
Conclusions - Summary

Integrated Pyrolysis - AD System

- Combustion Gases → Steam turbine → Electricity
- Low Pressure steam → Dairy manure → Biogas → Electricity, heat and/or fuel
- Steam → Anaerobic digester → Gas and solids
  - Solids: Raise pH to 9 → Liquid rich in N and P → Lagoon Storage → N & P loaded char → Ion Exchange Filtration → Clean water
- Vapor → Combustion
- Pyrolysis → Char
- Char Oxidation → High CEC char
- Pyrolysis → Fiber
- Fiber → Ion Exchange Filtration
- Char Oxidation → Char

Aqueous phase rich in acetic acid from fast pyrolysis and torrefaction
Conclusions - Summary

Integrated Pyrolysis - AD System

Combustion

Pyrolysis

Char Oxidation

Electricity

Steam turbine

Low Pressure steam

Steam

Water

Dairy manure

Aqueous phase rich in acetic acid from fast pyrolysis and torrefaction

Electricity, heat and/or fuel

Biogas

Anaerobic digester

Solids

Lagoon Storage

Ion Exchange Filtration

N & P loaded char

Clean water

Liquid rich in N and P

Vapor

Combustion Gases

Pyrolysis Fiber Char Oxidation

Raise pH to 9

Expose to air at 250°C for 1-2 hours during cooling

High CEC char

Exposure to air at 250°C for 1-2 hours during cooling
Conclusions - Summary

Integrated Pyrolysis - AD System

- **Combustion**
  - Combustion Gases
  - Steam turbine
  - Electricity
  - Low Pressure steam

- **Pyrolysis**
  - Vapor
  - char

- **Char Oxidation**
  - High CEC char

- **Anaerobic digester**
  - Dairy manure
  - Solids
  - Raise pH to 9
  - Liquid rich in N and P
  - Aqueous phase rich in acetic acid from fast pyrolysis and torrefaction

- **Ion Exchange Filtration**
  - N & P loaded char
  - Clean water

- **Lagoon Storage**
  - Electric, heat and/or fuel

- **Fiber**
  - Water
  - Steam

- **Electricity**

**Conclusions - Summary**

- Raise pH to 9
- Expose to air at 250°C for 1-2 hours during cooling
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QUESTIONS ?