Linkages: Water and Renewable Energy

Recovering Ammonia for Hydrogen Biofuel Production during Anaerobic Digestion

Donna E. Fennell
Rutgers University, New Brunswick, NJ, USA

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• Contributors

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• Collaborators

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[Images of Prof. Shaurya Prakash from The Ohio State University]
Renewable energy efforts may have unforeseen environmental consequences for local water supplies and wastewater treatment systems.
Ensuring neutral environmental consequences for renewable energy applications is critical for moving these technologies forward. We need to be (more) sustainable...
Anaerobic Digestion

Advantages
• Established technology for many wastes
  — sludges, solid waste, manures, food and crop wastes
• Scalable
• Methane has existing infrastructure/end uses

Disadvantages
• Conversion efficiency is low
• Process can be finicky
• N and P are liberated
• Residuals need further treatment and disposal
How Does It Work?

Biomass Feedstock → anaerobic digester

Methane (Biogas)

Residual
(Undigested Biomass plus Microbial Cells)
Anaerobic Digestion of Biomass

Complex Polymers
- Polysaccharides
- Lipids
- Proteins

Hydrolysis
- Hydrolytic and cellulolytic bacteria

Monomers
- Sugars, fatty acids, amino acids
- Fermentative bacteria

Fermentation

Acetate
- H₂ + CO₂
- Homo-acetogens
- Acetogenesis
- Acetotrophic Methanogens
- Methanogenesis

CH₄ + CO₂

Propionate
- Butyrate
- Succinate
- Alcohols
- Obligate Proton-Reducing Bacteria (syntrophs)
- Fermentation
- Anaerobic Oxidation

Acetate
- H₂ + CO₂
- Acetotrophic Methanogens
- Methanogenesis

Ammonia
- Urea
- Ureolytic bacteria
- Ammoniogenesis
Ammonia and C:N Ratio

- Ammonia released is a function of the organic nitrogen in the feedstock.
- The C:N ratio is the ratio of carbon to nitrogen (g/g).

C:N Ratio and Ammonia Toxicity

- As C:N ratio \( \downarrow \) the total ammonia nitrogen (TAN) \( \uparrow \)
- TAN as low as 1.5 g/L may inhibit digester microbial communities
- To control ammonia toxicity
  - Increase feedstock C:N
  - Remove ammonia

\[
\text{Ammonia/Ammonium} \\
\text{NH}_3 + H^+ \leftrightarrow \text{NH}_4^+ \\
\text{Total Ammonia-N (TAN)} \\
\text{NH}_3 + \text{NH}_4^+ 
\]
Ammonia

• Ammonia causes eutrophication and is toxic to aquatic life, so it must be carefully managed
  – Used as a fertilizer
  – Treated/removed
• In population centers far from agricultural systems, use as fertilizer may not be economical or energy efficient
  – Net food importers
  – Net nutrient importers
• Traditional treatments are aerobic, energy intensive processes
To remove NH₃, energy/mass inputs are required.

C-source in

O₂ energy in

Image modified from © 2010 Nature Education
Aerobic Treatment to Remove Ammonia
Is There Another Way?

Our work considers NH₃ an energy output.
Approach

Anaerobic Digestion
Bioammonia to Hydrogen (ADBH) System

• Could bioammonia liberated during anaerobic degradation of biomass be converted to hydrogen, as part of an integrated anaerobic digestion system?
• Is the energy balance favorable for this process?
• Establish theoretical design and conduct energy balance
ADBH System: Three Integrated Systems

- **Anaerobic Digester System**
- **Ammonia Recovery System**
- **Ammonia Reforming System**

Diagram includes steps and processes such as:
- Anaerobic Digester (3)
- Solid/Liquid Separator (5)
- pH Shift (7-11)
- Stripper (9)
- pH Shift (11-7)
- Ammonia Reformer (Microcombustor) (10, 13, 15)
## Trial Variable Inputs

<table>
<thead>
<tr>
<th>Parameter Description</th>
<th>Input Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry-Solids Flow</td>
<td>1,000 kg/hr</td>
</tr>
<tr>
<td>Degradable Organic Fraction (DOF)</td>
<td>0.80</td>
</tr>
<tr>
<td>Moisture Content (wt.% water)</td>
<td>90.0%</td>
</tr>
<tr>
<td>Aqueous Ammonium Loading</td>
<td>100 mg NH$_4^+$-N/L</td>
</tr>
<tr>
<td>Percent Recycle</td>
<td>65.0%</td>
</tr>
<tr>
<td>Ambient-Digester Temperature Difference</td>
<td>40.0 K</td>
</tr>
<tr>
<td>Internal Heat and Power Efficiency</td>
<td>0.35</td>
</tr>
<tr>
<td><strong>C:N Ratio</strong></td>
<td>Variable (3.0 to 136)</td>
</tr>
</tbody>
</table>
ADBH System: Anaerobic Digester

Inputs and Outputs

- (1) Organic Feedstock
- (2) Additional Liquid
- Heat (kJ/hr)
- Mixing (kJ/hr)

Anaerobic Digester

- (3) Digestate Slurry
- Biogas (11)
- (12) Liquid Recycle

• Energy
  - Heat
    o Influent heating
    o Heat loss across the digester boundary
  - Mixing
Stoichiometry of Biomass Conversion

Overall Stoichiometry

\[ C_a H_b O_c N_d + (2a + d - c - 0.45 \cdot e \cdot f_s - 0.25 \cdot e \cdot f_e) \cdot H_2O \rightarrow \]
\[ (0.125 \cdot e \cdot f_e) \cdot CH_4 + (a - c - 0.2 \cdot e \cdot f_s - 0.125 \cdot e \cdot f_e) \cdot CO_2 + (0.05 \cdot e \cdot f_s) \cdot C_5H_7O_2N \]
\[ + (d - 0.05 \cdot e \cdot f_s) \cdot NH_4^+ + (d - 0.05 \cdot e \cdot f_s) \cdot HCO_3^- \]
C:N Ratio and TAN

Feedstock C:N Ratio vs. TAN (mg/L)
ADBH: Ammonia Recovery System

Inputs and Outputs

- Energy
  - Stripping power
  - Mixing enthalpy in pH-shift reactors
  - Velocity gradient mixing in pH-shift reactors

(5) Digestate leachate $\text{NH}_4^+_{(aq)}$ and $\text{NH}_3_{(aq)}$

(6) $\text{NH}_3_{(aq)}$

(7) Stripping Liquid to vaporizer

(8) Alkaline leachate N removed

(9) Condensed Stripping Steam

(10) $\text{NH}_3_{(g)}$

(11) Biogas from digester

(12) Liquid Recycle to digester

(13) Enhanced Biogas

(14) Liquid Discharge

$V = \text{Vaporizer}$

$C = \text{Condenser}$

$Q = -16.73 \text{ kJ/mol-Ca(OH)}_2$

Power = 1.574 \text{ kJ/kg-(aq.)}$

$Q = -97.1 \text{ kJ/mol-Ca(OH)}_2$
ADBH: Ammonia Reforming System

- **Chemistry**
  - Combustion: \( \text{CH}_4 + 2 \text{O}_2 (\text{Air}) \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \)
    - Consume some methane from biogas...
  - Reforming: \( 2 \text{NH}_3 (g) \rightarrow \text{N}_2 (g) + 3 \text{H}_2 (g) \)
    - ...to remove ammonia and
    - ...produce hydrogen biofuel
Conclusions

Conclusion

• The bioammonia to hydrogen process could increase the total energy recovery compared to the methane potential alone for digesters operated with feedstocks with C:N ratios less than ~17
Ammonia Release During Digestion

Ammonia is released rapidly from proteins and urea.
Implications

Methane

Manures

Crops, residues

Human waste

Waste food, msw

Anaerobic digestion

Biomass

Ammonia

Nitrification-denitrification

Crop application

Precipitate

Residual
Implications

• Traditional treatment is expensive
• For urban/suburban centers far from land/crop nutrient demand, fertilizer use may not be energetically or economically favorable

[Diagram showing methane, nitrification-denitrification, crop application, and precipitate with residual waste food, msw]
A new paradigm considers waste ammonia as an energy source.