Successful Pathways Through Anaerobic Digestion

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How do we achieve high SRT in anaerobic treatment systems?

- AD configuration for municipal waste water is typically continuous stirred tank reactor (CSTR) for which HRT closely coupled to SRT (HRT ≈ SRT)
- Designs are based on volatile solids (VS) loading rate (OLR), HRT/SRT, and or CFR 40 503 Regulations
- Primary goal has been for solids reduction and stabilization
- Used as a pretreatment strategy
- Recent priority on optimizing for energy production
- Anaerobic treatment of wastewaters requires a long SRT of active biomass to achieve needed treatment efficiency
- A ratio of SRT/HRT ~ 10-100 is needed to allow for sufficient yield of methanogens
Anaerobic Waste Treatment

Anaerobic digestion is a biological process carried out in the absence of O\textsubscript{2} for the stabilization of organic materials by conversion to CH\textsubscript{4}, CO\textsubscript{2}, NH\textsubscript{3}, etc.

\[
\text{Organic materials} + \text{Nutrients} \xrightarrow{\text{Anaerobic microbes}} \text{CH}_4 + \text{CO}_2 + \text{NH}_3 + \text{Biomass}
\]

Anaerobic processes

- Anaerobic fermentation
- Anaerobic respiration
**Anaerobic fermentation**

An enzymatically controlled breakdown of an energy-rich compound (as a carbohydrate to carbon dioxide and alcohol or to an organic acid)

![Diagram of anaerobic fermentation of glucose to ethanol]

Anaerobic fermentation of glucose to ethanol
Anaerobic respiration

- Anaerobic respiration requires external electron acceptor. The electron acceptors in this case could be $\text{SO}_4^{2-}$, $\text{NO}_3^-$ or $\text{CO}_2$. The energy released under such a condition is higher than anaerobic fermentation.

Anaerobic respiration of glucose, preference for electron acceptors

$\text{O}_2 > \text{NO}_3^- > \text{SO}_4^{2-} > \text{CO}_2$
Advantages of anaerobic processes

- Energy generation in the form of methane gas
- 1.16 kWh energy is produced for every 1 kg of COD in anaerobic process
- Less biomass (sludge) generation - only 20% of sludge production as compared with aerobic process
- Application of higher organic loading rates ~ 5-10 times higher than that of aerobic processes are possible
- Higher loading rates require smaller reactor volumes – lower CAPEX
- Ability to transform several hazardous solvents including chloroform, trichloroethylene and trichloroethane to an easily degradable form
Limitations of anaerobic digestion

- Long start-up and recovery times due to lower yield rates
- Specific nutrients/trace metal requirements
- Anaerobic microorganisms, especially methanogens, have specific nutrients e.g. Fe, Ni, and Co requirement for optimum growth.
- More susceptible to changes in environmental conditions
- Need to pay attention to temperature, pH, redox potential, etc.
- Treatment of sulfate-rich wastewater
- Effluent quality of treated wastewater
- The minimum substrate concentration ($S_{min}$) from which microorganisms are able to generate energy for their growth and maintenance is much higher for anaerobic treatment systems.
- Treatment of high protein & nitrogen containing wastewater
The anaerobic degradation of complex organic matter is carried out by a series of bacteria and archaeae as indicated in the following figures (with numbers).

There exists a coordinated interaction among these microbes. The process may fail if certain organisms are inhibited.

Conversion of substrates is typically described in three (3) steps; hydrolysis, acidogenesis, and methanogenesis.

**Process Goal:** Create acetate.

**Process Goal:** Maintain appropriate balance of hydrogen.

**Process Goal:** Minimize use of anaerobic respiration which has a preferential use of Nitrates (NO$_3$/NO$_2$) and Sulfates (SO$_4$) as compared to CO$_2$.

**Process Goal:** Have a well balanced diet!
Fermentative bacteria (1)

- This group of bacteria is responsible for the first stage of anaerobic digestion - hydrolysis and acidogenesis. These bacteria are either facultative or strict anaerobes.
This group of bacteria metabolizes propionate and other fatty acids (>C-2), alcohols and certain aromatic compounds (i.e. benzoate) into acetate and CO₂

\[ \text{CH}_3\text{CH}_2\text{COO}^- \rightarrow \text{CH}_3\text{COO}^- + \text{CO}_2 + \text{H}_2 \]

Syntrophic association of acetogenic organisms with methanogenic H₂-consuming bacteria helps lower the concentration of H₂ below inhibitory level so that propionate degrading bacteria are not suppressed by excessive H₂ level - H₂ partial pressure 10⁻² (100 ppm)
Homoacetogenesis (3)

- Homoacetogenesis has gained much attention in recent years in anaerobic processes due to its final product: acetate, which is the important precursor to methane generation.
- Homoacetogenic (HAG) bacteria have a high thermodynamic efficiency; as a result there is no accumulation H₂ and CO₂ during growth on multi-carbon compounds – helps in the balance of pH of overall reactor.

\[
\text{CO}_2 + \text{H}_2 + \text{HAG organisms} \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}
\]

\[
\text{Acetate} \rightarrow \text{Hydrogen, Carbon dioxide}
\]
Methanogens (4 and 5)

- Methanogens are obligate anaerobes and typically considered as a rate-limiting species in anaerobic treatment of wastewater.

- Methanogens co-exist and compete with sulfate-reducing bacteria for the substrates in anaerobic treatment of sulfate-laden wastewater.
Organics conversion in anaerobic systems

- **COMPLEX ORGANIC MATTER**
  - Proteins
  - Carbohydrates
  - Lipids

**Acidogenesis**

- **Hydrolysis**
  - Amino Acids, Sugars
  - Fatty Acids, Alcohols

**Acetogenesis**

- **INTERMEDIARY PRODUCTS** (C>2; Propionate, Butyrate etc)

**Methanogenesis**

- **Acetotrophic Methanogenesis**
- **Hydrogenotrophic Methanogenesis**

- **Homoacetogenesis**
  - Acetate
  - Methane
  - Carbon dioxide
  - Hydrogen
  - Carbon dioxide
Successful Pathways to CH₄ hydrogenotrophs via CO₂ and H gas

- Approximately 70% of biogas formed via the use of acetate (Zinder 1993)
- Today there are only two known groups of methanogens that break down acetate: Methanoseta and Methanosarcina
- Balance of biogas is produced via other hydrogenotrophs such as Methanobacterium, Methanococcus, Methanogenium and Methanobrevibacter (Garcia et al 2000, Liu and Withman 2008)

<table>
<thead>
<tr>
<th>Methanogens</th>
<th>Doubling time</th>
<th>Lowest acetate concentration used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanosarcina</td>
<td>1 day</td>
<td>~ 20 mg/L</td>
</tr>
<tr>
<td>Methanoseta</td>
<td>2-12 days</td>
<td>~ 4 mg/L</td>
</tr>
</tbody>
</table>
## How much biogas can I expect?

Theoretical quantity and composition of biogas formed from carbohydrate, fat and protein (Berglund and Börjesson 2003)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>~ Biogas formed (m³/kg VS)</th>
<th>Biogas composition: CH₄ : CO₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbohydrates</td>
<td>0.38</td>
<td>50:50</td>
</tr>
<tr>
<td>Fat</td>
<td>1.0</td>
<td>70:30</td>
</tr>
<tr>
<td>Protein</td>
<td>0.53</td>
<td>60:40</td>
</tr>
</tbody>
</table>
Cellulosic materials will take longer to digest!

15 days - Class B
## Degrees of Degradation

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Degradation ratio (% of VS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cattle manure</td>
<td>30-40</td>
</tr>
<tr>
<td>Pig manure</td>
<td>40-45</td>
</tr>
<tr>
<td>Forage crops</td>
<td>60-70</td>
</tr>
<tr>
<td>Grease trap waste</td>
<td>75-90</td>
</tr>
<tr>
<td>Fruit and vegetable waste</td>
<td>80-95</td>
</tr>
</tbody>
</table>
## Anaerobic digester configurations

<table>
<thead>
<tr>
<th>Digestion Type</th>
<th>Organic Loading</th>
<th>Industry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete mix</td>
<td>High Rate</td>
<td>Ag, Muni, Industrial</td>
</tr>
<tr>
<td>Upflow Anaerobic Sludge Bed (UASB) and variants</td>
<td>High Rate</td>
<td>Industrial</td>
</tr>
<tr>
<td>Lagoon</td>
<td>Low Rate</td>
<td>Ag, Industrial (slaughter houses)</td>
</tr>
<tr>
<td>Fluidized Bed</td>
<td>High Rate</td>
<td>Industrial</td>
</tr>
<tr>
<td>Membrane</td>
<td>High Rate</td>
<td>Industrial</td>
</tr>
<tr>
<td>Fixed Media</td>
<td>High Rate</td>
<td>Industrial</td>
</tr>
<tr>
<td>Plug Flow</td>
<td>Low Rate</td>
<td>Ag</td>
</tr>
</tbody>
</table>
Conditions for efficient anaerobic treatment

- Avoid excessive air/O₂ exposure
- Maintain pH between 6.8 –7.8
- Sufficient alkalinity present (mainly bicarbonates)
- Low volatile fatty acids (VFAs)
- No rapid changes in temperature
- No toxic/inhibitory compounds present in the influent
- Enough nutrients (N & P) and trace metals especially, Fe, Co, Ni, etc.

COD:N:P = 350:7:1 (for highly loaded system) 1000:7:1 (lightly loaded system) SRT/HRT >> 1 (use high rate anaerobic reactors)
Affect of pH

- The properly operating pH for anaerobic cultures is 6.8-7.8
- Acceptable enzymatic activity of methane forming bacteria does not occur below pH of 6.2
- Since methanogenesis is considered as a rate limiting step, it is necessary to maintain the reactor pH close to neutral.
- Low pH reduces the activity of methanogens (and increases the activity of acidogens) causing accumulation of VFA and H₂.
- At higher partial pressure of H₂, propionic acid degrading bacteria will be severely inhibited thereby causing excessive accumulation of higher molecular weight VFAs such as propionic and butyric acids and the pH drops further. If the situation is left uncorrected, the process may eventually fail. This condition is known as going “SOUR”.
- Remedial measures: Reduce the loading rates and supplement chemicals to adjust the pH: alkaline chemicals such as NaOH, Na₂CO₃
pH dependence of methanogens

Relative activity of methanogens to pH

Ammonia and H₂S inhibition can occur
Natural buffering

- An anaerobic treatment system has its own buffering capacity against pH drop because of alkalinity produced during waste treatment: e.g. the degradation of protein present in the waste releases NH$_3$, which reacts with CO$_2$ and water forming ammonium carbonate as alkalinity.

\[ NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3 \]

- The degradation of salt of fatty acids may produce some alkalinity.

\[ CH_3COONa + H_2O \rightarrow CH_4 + NaHCO_3 \]

- Sulfate and sulfite reduction also generate alkalinity.

\[ CH_3COO^- + SO_4^{2-} \rightarrow HS^- + HCO_3^- + 3H_2O \]

- When pH starts to drop due to VFA accumulation, the alkalinity present within the system neutralizes the acid and prevents further drop in pH. If the alkalinity is not enough to buffer the system pH, we need external additions.
Accumulation of VFAs

Sum of all VFAs

Potential process failure indicator
Effect of sulfate on methane production

- When the waste contains sulfate, part of COD is diverted away from methane production to sulfate reduction.
- In this case, total COD available for methane production would be reduced greatly.

\[
\text{SO}_4^{2-} + \text{COD} \rightarrow \text{HS}^- + \text{CO}_2
\]

Sulfate + Substrates \rightarrow Sulfide + Carbon Dioxide

Sulfate Reducing Bacteria

Sulfide will also impose toxicity on methanogens at a concentration of 50 to 250 mg/L as free sulfide.
Flow of Nutrients

- Nitrogen concentrations typically remain unchanged through digestion.
- The forms of nitrogen are changed from organic to ammonia or ammonium depending on pH.
- Anaerobic microorganisms are ~ 12% nitrogen by mass.
- 12 g of nitrogen is needed for every 100 g of anaerobic biomass produced.
- Anaerobic conditions are likely to release soluble P from BioP sludges.
- Anaerobic microorganisms are ~ 2% phosphorous by mass.
- 2 g of phosphorous is needed for every 100 g of anaerobic biomass produced.
- Insure that there are adequate residual concentrations in digester effluent.

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Micronutrient</th>
<th>Macronutrient</th>
<th>Minimum Recommended (% of COD)</th>
</tr>
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<tbody>
<tr>
<td>Cobalt</td>
<td>x</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>Iron</td>
<td>x</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Nickel</td>
<td>x</td>
<td></td>
<td>0.001</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td>x</td>
<td>3-4</td>
</tr>
<tr>
<td>Phosphorous</td>
<td></td>
<td>x</td>
<td>0.5-1</td>
</tr>
<tr>
<td>Sulfur</td>
<td></td>
<td>x</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Process Control

- Perform testing of biogas, digestate, and substrates
- Leads to better understanding of process “health”
- Optimization of system (lower operating costs, better results)
- Inhibition of methanogens can be detected by:
  - decrease in gas production
  - increase in CO$_2$ and hydrogen
- Determine H$_2$S (who is winning in the fight of substrates?)
- Siloxane concentrations
Why Co-Digest?

- Enhanced overall degradation of solids
- Economic Balance:
  - Tipping fees
  - Electrical generation
  - Higher utilization of existing infrastructure
  - Recycle streams
  - Additional solids disposal cost
Questions?

THANK YOU

BioWorks Energy LLC
Advanced organics processing

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