WASTE-TO-ENERGY: ASSETS & LIMITS OF ANAEROBIC DIGESTION

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Waste-to-RNG: anaerobic digestion / gasification

Biomass

90% Water content

15%

Fermentation

Anaerobic digestion & derived applications

Wet biochemical

EtOH ButOH

Gasification

Dry thermochemical

Pyrolysis

Incineration

syngas: CO, H₂, CO₂

oil, char gases, CO₂

CO₂, H₂O heat

biogas

CH₄, CO₂

catalytic methanation

CH₄
Anaerobic digestion (AD)

- AD converts complex organics into biogas (CH$_4$ + CO$_2$) through the concerted work of diverse microbial groups.

- Fundamentally, the reducing power of the pollution or waste is transferred from one microbial group to the other, to end up into the final product, CH$_4$.

**Theoretical biochemical methane potential, from elemental formulas:**

**CARBOHYDRATES:**

$$\text{C}_x\text{H}_y\text{O}_z + \text{H}_2\text{O} \rightarrow 3 \text{CH}_4 + 3 \text{CO}_2$$

$$Y_{\text{CH}_4} = 0.42 \text{Nm}^3 / \text{kg sugar}$$

**PROTEINS:**

$$\text{C}_{x.12}\text{H}_{4.94}\text{O}_{0.82}\text{N}_{0.03} + 2 \text{H}_2\text{O} \rightarrow 1.61 \text{CH}_4 + 1.51 \text{CO}_2 + 0.82 \text{NH}_3 + 0.03 \text{H}_2\text{S}$$

$$Y_{\text{CH}_4} = 0.51 \text{Nm}^3 / \text{kg protein}$$

**FATS:**

$$\text{C}_y\text{H}_{15}\text{O} + 3.74 \text{H}_2\text{O} \rightarrow 5.62 \text{CH}_4 + 2.38 \text{CO}_2$$

$$Y_{\text{CH}_4} = 1 \text{Nm}^3 / \text{kg fat}$$
Biomethane vs bioethanol

Cel 35%
Lign 19%
Hemicel 26%
Lip 4%
Prot 6%
Oth 4%
Lign 19%
Ash 6%

Fraction convertible in EtOH 35-61%

CH₄ 75%

SENSITIVE ISSUES
AD yields: in practice

In practice, degradation efficiency hardly exceeds 60%, and $Y_{\text{CH}_4}$, 0.3 Nm$^3$/kg VS added (except some residues (agro-food, slaughterhouse, FOG ... > 80%)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Conversion</th>
<th>Methane Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>Nm$^3$ CH$^4$/wet t. (/dry t.) add</td>
</tr>
<tr>
<td>MSW-OF</td>
<td>50-70</td>
<td>100 (350)</td>
</tr>
<tr>
<td>Secondary sludge</td>
<td>30-60</td>
<td>70 (318)</td>
</tr>
<tr>
<td>Slaughterhouse residue</td>
<td>60-85</td>
<td>140 (550)</td>
</tr>
<tr>
<td>FOG</td>
<td>&gt; 80</td>
<td>ND (1010)</td>
</tr>
<tr>
<td>Bovine manure</td>
<td>33</td>
<td>25 (~115)</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>30-75</td>
<td>162 (377)</td>
</tr>
</tbody>
</table>


$\Rightarrow$ Limiting step = Hydrolysis
$\Rightarrow$ pre-treatment

Nutrient balance

<table>
<thead>
<tr>
<th>Substrates</th>
<th>C:N</th>
<th>C:P</th>
<th>Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>OF-MSW</td>
<td>40:1 to 100:1</td>
<td>200:1</td>
<td>Small C, P surplus</td>
</tr>
<tr>
<td>Primary, secondary sludges</td>
<td>5:1 to 10:1</td>
<td>13:1 to 27:1</td>
<td>Large N, P surplus</td>
</tr>
<tr>
<td>FOG</td>
<td>&gt;50 to 100:1</td>
<td>200 to 300:1</td>
<td>C surplus</td>
</tr>
<tr>
<td>Manure (pig, cow)</td>
<td>14:1 to 20:1</td>
<td>25:1 to 110:1</td>
<td>N, P surplus</td>
</tr>
<tr>
<td>Energy crop (switchgrass)</td>
<td>92:1 to 491:1</td>
<td>624:1 to 2344:1</td>
<td>Large C surplus</td>
</tr>
</tbody>
</table>

$\Rightarrow$ co-digestion

$\Rightarrow$ S.R. Guiot 2011
Inhibition

- Inhibition by accumulation of acid, pH (organic overload/unbalance fermentation/methanogenesis)

- Inhibition by ammonia in case of nitrogen surplus, ou production during digestion of proteins (slaughterhouses, manure)

\[
\begin{align*}
\text{HAc} & \rightleftharpoons \text{Ac}^- \\
\text{NH}_4^+ & \rightleftharpoons \text{NH}_3
\end{align*}
\]

The non-ionic form of the acid or ammonia is inhibitory

- pH control and neutralization

- Other inhibitors: copper sulphate and antibiotics

H₂S

- Ubiquitous in anoxic systems
- From the reduction of sulfates and sulfites (SO₄²⁻, SO₃²⁻) by SRB to sulfides (S²⁻)
- Foul smell: detectable at 0.001 ppm in air
- Highly toxic
- Highly corrosive in humid biogas
- Complete inhibition of methanogens at [H₂S] > 200 ppm

⇒ removal at the source

- D.O. is the most effective inhibitor of H₂S formation: returns almost all sulfides to their initial oxidized form
- Small [O₂] are not detrimental to AD
AD ex situ enhancement

• Pre-treatment (vast array of options)
  • Thermochemical options (steam explosion; ammonia explosion, pulsed-electric-field, ultrasound ….)
  • Soft chemical options (dilute acid, sulfur dioxide, soda, lime, ozone, peroxide ….)
  • Enzymatic pre-treatment
    ✓ alkaliization alone : $Y_{\text{CH}_4/Y_{\text{SAD}}} + 19\%$
    ✓ alkaliization at high temperature (120 °C) : + 64 %
    ✓ microwave irradiation (10 min at 120 °C) : + 10 %
    ✓ peroxidases : lignin (LiP) or manganese peroxidase (MnP) : + 29 & + 42 %
    ✓ combination of alkali and MnP : + 91%
    ✓ combination of pectinases (pectate-lyase and poly-galacturonase) : + 101 %
    ✓ cellulases + 21%

Model feedstock : switchgrass

Enzyme pre-treatment seems promising, whereas they are not yet commercially available at a competitive cost
Conventional
- On-line control
- Temperature
- Retention of limiting microorganisms (dissociate liquid RT from solid and microbes RTs)

Advanced (consolidated bio-processing ~ CBP)

On-line control

On-line control VFA/liquid / multiwavelength spectrofluorimetry (ex. cheese factory, Agropur, Notre-Dame du Bon Conseil)

Multiwavelength light source
- UV-LED
- 370nm
- 380nm
- 400nm
- 420nm
- US Patent 7,474,400

Spectrofluorimter
- Linear array of CCD photodiodes
- 200-1100 nm
- Complete scan in 13 ms
- Integration time 3ms – 65s

Compact
Low cost compared to NIR systems and titration
Temperature

Temperature ranges: psychrophilic (7-25 °C), mesophilic (27-37 °C), thermophilic (55-60 °C)

- Digestion rate increases with temperature (higher growth rate of microorganisms => higher loads or reduced retention time)
- Efficiency of digestion (% degradation) increases with temperature

Biodegradability improvement

Biosolids (WAS): +20%


OF-MSW: +7% to 35%


 egret: proteins(++), lipids(+)

Hydrolysis & fermentation/1 step

Microbial consolidation of naturally occurring consortia

- e.g. co-digestion
- e.g. bioaugmentation → adding protozoa and fungi (anaerobic, aerobic) (cellulases, xylanases and lignases)
- e.g. controlled micro-aerobic conditions (stimulation of added or indigenous hydrolytic aerobic or facultative microorganisms)
- e.g. electrochemically-assisted AD (e.g. electrolysis integrated within AD)

Mata-Herrera, Meul & Labbé. 2000. Bioresource Techn. 74:3-16
Co-digestion

<table>
<thead>
<tr>
<th>D 1: dairy manure</th>
<th>D 2: manure + switchgrass (20% wet ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLR kg TVS/m³rx.d</td>
<td>2.1</td>
</tr>
<tr>
<td>TVS degradation efficiency</td>
<td>35%</td>
</tr>
<tr>
<td>Yield Nm³CH₄/kg TVS added</td>
<td>0.12</td>
</tr>
<tr>
<td>Q₇CH₄ Nm³CH₄/m³rx.d</td>
<td>0.32 (+63%)</td>
</tr>
</tbody>
</table>

At a 500 m³ scale, co-digestion would yield a surplus of 7 GJ/d (i.e. + $30K/yr)

Other advantages: nutrients balance (C:N:P 100:1.6:0.54 for switchgrass versus C:N:P 100:3.6:1.15 for mix); dilution

Co-digestion: microbial consolidation

Co-digestion = enhance bacterial cooperation

<table>
<thead>
<tr>
<th>Substrate (C:N:P balanced, 100:4:1)</th>
<th>Yield (NL₇CH₄/kg TVS added)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Switchgrass (mulched)</td>
<td>152 ± 1</td>
</tr>
<tr>
<td>Cattle manure</td>
<td>315 ± 19</td>
</tr>
<tr>
<td>Switchgrass/manure mix (49%/51% dry wt)</td>
<td></td>
</tr>
<tr>
<td>Weighted sum / separately</td>
<td>235 ± 9</td>
</tr>
<tr>
<td>Actual mix in co-digestion</td>
<td>288 ± 31 (+23%)</td>
</tr>
</tbody>
</table>

Adapted microorganisms-rich substrates → re/co-inoculate the digester & help to digest target substrate. Cattle manure (cellulolytic & fermentative bacteria, methanogens). Silage (lactic acid bacteria, fermentation bacteria).
Micro-aeration

Model feedstock: switchgrass

- Lab scale CSTR: HRT 23 days / OLR 3 g VSS/L-1rxr.d
- Microaerobic conditions at <0.5% O2 / headspace
- Biogas production: 2.2 L.d-1 in the microaerobic digester against 1.8 L.d-1 in the control digester
- Stimulation of enzyme activities:
  - Cellulase: 155 in the microaerobic digester vs 131 U.L-1 i.e. +15%
  - Feruloyl esterase: 4.85 in the microaerobic digester vs 3.82 U.L-1 i.e. +27%
- Facultative populations slightly triggered by microaerobic conditions

Electrolysis-enhanced-AD (eAD)

Concept: integration of electrolysis → O2 + H2

- Microaerobic conditions:
  - Stimulation of indigenous hydrolytic, aerobic or facultative microorganisms
  - H2S removal from biogas
  - Partial CO2 sequestration (through CO2+H2 conversion to CH4)
  - Higher CH4 yield

The eAD process uses water electrolysis at low applied voltages and current densities to facilitate biomethanization of complex organic materials. Electrodes can be installed directly in the anaerobic digester (reactor) or in the reactor external recirculation loop.

Feedstock: mixture of switchgrass and cow manure / 6 L reactor
two pairs of electrodes, 100-200 mA
methane content, 40-48%, H₂ 7-15%, oxygen 0-1.8%

Significant increase in methane production rate because of:
• exogenous H₂
• improved hydrolysis of solid organic matter
• H₂S inhibition (from 0.3% to < 100 ppm) alleviated
• catalytic effect of microbes on the electrochemical reactions (electromethanogenesis) less power consumption (16-24 WH/L CH₄ eq i.e. 4.8 Wh/LH₂ vs > 7 Wh/LH₂ w/H₂O electrolysis)

net energy gain (ΔCH₄ produced vs energy consumed)
GHG reduction thanks to AD

- GHG production
  - GHG generated/landfill: 4.3 t eCO₂/wet ton OSW landfilled (based on UNEP baseline w/o LFG collect)
  - Baseline in Canada: 2.35 t eCO₂/wet ton landfilled w/LFG collected and flared 8.4 t eCO₂/dry ton (dt) OSW
  - GHG generated/AD (w/E @ 50%): 0.34 t eCO₂/dt OSW (w/80% VS)
    (considering that AD w/CH₄ recovery generates 0.86 t eCO₂/t VS degraded)

- Reduction GHG emissions with AD (@ E 50% and 80% VS/OSW)
  - Direct: ≈ 3 t eCO₂/dt OSW (considering that non-digested fraction, 5 t eCO₂/dt as if landfilled)
  - GHG reduction by fossil fuel displaced: 2 kg eCO₂/Nm³ CH₄ combusted
  - Total reduction: 3.4 t eCO₂/dt OSW (could be 8.5 non-digested fraction composted)

GHG: greenhouse gas
eCO₂: CO₂-equivalent
OSW: organic solid waste (dt: dry ton)
LFG: landfill gas
E: VS degradation efficiency of AD
VS: volatile solids

AD COST/PROFIT

Per tonne of MSW-OF

<table>
<thead>
<tr>
<th>Conversion by AD (%)</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane potential (Nm³/tonne)</td>
<td>56</td>
</tr>
<tr>
<td>Electricity generated (kWh/tonne)</td>
<td>161</td>
</tr>
<tr>
<td>Commercial value ($/kWh)</td>
<td>0.17</td>
</tr>
<tr>
<td>Co-generation (45% heat) $/GJ NG displaced</td>
<td>5</td>
</tr>
<tr>
<td>Revenue from energy produced ($/tonne)</td>
<td>30</td>
</tr>
<tr>
<td>Tipping fees ($/tonne)</td>
<td>+ 46</td>
</tr>
<tr>
<td>Capital &amp; operation AD ($/tonne)</td>
<td>– 75</td>
</tr>
<tr>
<td>(Deficit)/benefit ($/tonne)</td>
<td>1</td>
</tr>
</tbody>
</table>

Conversion: 9.6 kWh/Nm³ CH₄
Efficiency/electricity: 30% - Cost: 0.8 ¢/kWh
Efficiency/heat: 45% (value $5/GJ)

Digestion: Dryness: 28% - VS/TS: 80% - Yield: 0.5 Nm³ CH₄ / kg SV degraded

AD unit cost (capital [7 yr] + operation): 30 $/tonne → 75 $/ton (50 000 tonne/yr capacity)
Dry biomass
‘gasification / biomethanation’

90% Water content 15%

Biomass

Fermentation

Anaerobic digestion & derived applications

EtOH ButOH

Wet biochemical

Dry thermochemical

Gasification

Pyrolysis

Incineration

syngas: CO, H₂, CO₂

oil, char gases, CO₂ heat

Methanogenic bioconversion of syngas

CH₄, CO₂

Dry biomass

Gasification

Syngas methanogenic bio-upgrading

SYNGAS

Biocatalyzed conversion

BIOGAS

CH₄, CO₂

Gasification

CO 30-48%
H₂ 40-25%
CO₂ 35-15%
CH₄ 10-1%
C₂+, NH₃, H₂S, N₂, HCN ...

Biocatalyzed conversion

Carboxydotrophic methanogenesis, to convert syngas compounds into methane
- CO₂ + 4 H₂ → CH₄ + 2 H₂O (ΔG°' = -245 kJ/mol CO₂)
- CO + 3 H₂ → CH₄ + H₂O (ΔG°' = -150 kJ/mol CO)
- 4 CO + 2 H₂O → CH₄ + 3 CO₂ (ΔG°' = -53 kJ/mol CO)

Engineering challenge: to significantly improve gas-to-liquid mass transfer rate

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MUNICIPAL SOLID WASTE Composition

An approach close to industrial application: to use industrial waste/water-treating anaerobic populations (that have the potential to consume CO) and to retrofit AD facilities

MUNICIPAL SOLID WASTE Composition

per tonne MSW

AD

70 Nm³ CH₄

15 Nm³ CH₄

Gasification

Syngas

85 Nm³ CH₄ i.e. \( \times 5x \)

“There should be little doubt that by placing the focus of AD on the production of green energy and clean nutrients, the future of AD will be assured.”

W. Verstraete, AD10, Montreal - 2004