Biogas Production from Biological Sludge

D. J. Lee
Department of Chemical Engineering
National Taiwan University
Sludge?

Influent → Primary settler → Aeration tank → ASM → Recycled activated biomass → Secondary settler → Effluent

Primary sludge → Secondary sludge (waste activated sludge)

Filtration → Digester → Thickener → Settling

Dry sludge dewatering
Biological Sludge Floc

Floc is a common form of bioaggregates appearing in the wastewater treatment process.

- Irregular shape;
- Highly porous;
- Compressible and fragile;
- Inhomogeneous distribution of internal mass.
A group of symbiotic microorganisms “embedded” in the extracellular polymers.
Aerobic treatment

biosolids

organic matter + O₂

CO₂ + H₂O

Anaerobic treatment

biosolids

organic matter

CH₄ + CO₂

Biogas

1. hydrolysis
2. fermentation
3. acetogenesis
4. methanogenesis

complex organic matter

- carbohydrates, proteins, fats

soluble organic molecules

- sugars, amino acids, fatty acids

volatile fatty acids

acetic acid

pH 5-6

CH₄ + CO₂

pH 7-8

H₂ + CO₂
Anaerobic digestion

Complex biopolymers
(Carbohydrate/ protein/ lipids)

Organic monomers
(sugar/ amino acids/ fatty acids)

Long chain VFA(C3/C4/i-C4/C5/C6)
alcohol/methanol/lactate/formate/butanol/acetone

H₂/CO₂

Acetogen B. 17%

Acetoclastic B. 28%

H₂O/CO₂/CH₄

Acetate

Acetogenic B. 75%

Homoacetogenic B. 30%

Hydrogenophilic B. 72%

Acetate

Acetogen B. 10%

Acetogenic B. 75%

Homoacetogenic B. 30%

Hydrogenophilic B. 72%

Acetate

Acetogen B. 10%

Acetogenic B. 75%

Homoacetogenic B. 30%

Hydrogenophilic B. 72%

Acetate

Acetogen B. 10%

Acetogenic B. 75%

Homoacetogenic B. 30%

Hydrogenophilic B. 72%

Acetate
\[ \Delta G^0' \]

**Step**

**Fermentation**

\[ C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^- + 2HCO^- + 4H^+ + 4H_2 \quad -207 \]

\[ C_6H_{12}O_6 + 2H_2O \rightarrow CH_3(CH_2)_2COO^- + 2HCO^- + 3H^+ + 2H_2 \quad -135 \]

\[ 3C_6H_{12}O_6 \rightarrow 4CH_3CH_2COO^- + 2CH_3COO^- + 2CO_2 + 2H_2O + 2H^+ + H_2 \quad -922 \]

**Acetogenesis**

\[ CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2H_2 \quad +10 \]

\[ CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + H^+ + 3H_2 + HCO_3^- \quad +76 \]

\[ CH_3(CH_2)_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2 \quad +48 \]

\[ 2HCO^- + 4H_2 + H^+ \rightarrow CH_3COO^- + 4H_2O \quad -105 \]

**Methanogenesis**

\[ CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad -130 \]

\[ 4HCOO^- + 4H^+ \rightarrow CH_4 + 3CO_2 + 2H_2O \quad -120 \]

\[ 4CO + 2H_2O \rightarrow CH_4 + 3CO_2 \quad -186 \]

\[ CH_3COO^- + H^+ \rightarrow CH_4 + CO_2 \quad -33 \]

\[ 4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O \quad -309 \]

\[ 4(CH_3)_3NH^+ + 6H_2O \rightarrow 9CH_4 + 3CO_2 + 4NH_4^+ \quad -666 \]
Step

Denitrification

\[ 12NO_3^- + C_6H_{12}O_6 \rightarrow 12NO_2^- + 6CO_2 + 6H_2O \]  
\[ -1946 \]

\[ 8NO_2^- + C_6H_{12}O_6 \rightarrow 4N_2O + 6CO_2 + 6H_2O \]  
\[ -632 \]

\[ 12N_2O + C_6H_{12}O_6 \rightarrow 12N_2 + 6CO_2 + 6H_2O \]  
\[ -134 \]

Sulphate reduction

\[ 4H_2 + SO_4^{2-} + H^+ \rightarrow 4H_2O + HS^- \]  
\[ -152 \]

\[ CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^- \]  
\[ -48 \]

\[ 4CH_3CH_2COO^- + 3SO_4^{2-} \rightarrow 4CH_3COO^- + 4HCO_3^- + H^+ \]  
\[ -151 \]
Phase

- Fermenting Bacteria
  - pH = 5.2~6.3
  - $Y_x = 0.2 \text{ g-VS g-COD}^{-1}$
  - Faculative anaerobic

- Acedogenesis and Methadogenesis
  - pH = 6.8~7.2
  - $Y_x = 0.03~0.05 \text{ g-VS g-COD}^{-1}$
  - Obligate anaerobic
  - Syntrophic reaction
    - Interspecies hydrogen transfer
Propionate and H₂

Propionate: account for over 30% of the electron flow
Deterioration of propionate degradation
→ Decrease in VFA removal efficiency

McCarty, P.L. and Smith, D.P. 
Anaerobic wastewater treatment 
Through enzymes
Enhanced Hydrolysis
Pre-hydrolysis of sludge is often applied in prior to the anaerobic digestion to:

- Disintegrate the suspended particles
- Decompose the insoluble organic molecules.

Alkaline treatment and ultrasonication were reported as effective pre-hydrolytic treatments.
Enhancing Digestion
Waste Activated Sludge

- Sampling from the recycled stream in the secondary treatment stage in St. Marys sewage treatment plant in Sydney, Australia.
- \( \text{pH} = 7.50 \)
- \( \text{TSS} = 10,700 \text{ mg/L} \)
- \( \rho_S = 1,612 \text{ kg/m}^3 \)
Strains in inoculum K8: (a) *bacillus*; (b) *cocci*. 
Flocculation retards Digestion; while Ultrasonication Enhances it.
Before sonication
- Original
- Flocculated

After sonication
- Original
- Flocculated

Poor digestion
Ori, 0 & 30 d

Floc, 0 & 30 d
Insufficient Challenge

![Graph showing floc size (µm) vs. sonication time (min) for different watt densities.]

- 0.11 W/cm³
- 0.22 W/cm³
- 0.33 W/cm³
Full-Scale Landfill Site
Sustainable Landfill

Simulative rainfall

Fresh layer

Leacahte recycling

Fresh layer

Leacahte recycling

Fresh layer

Pretreatment

Column No.1

No. 2

No.3-5
Internal Circulation
Biogas production
天子岭Site in HangZhu

气体收集
——天子岭现场
The diagram illustrates the process of microbial degradation of complex organic matter (carbohydrates, proteins, fats) into volatile fatty acids, acetic acid, and eventually into methane ($CH_4$) and carbon dioxide ($CO_2$).

1. **Hydrolysis**: The initial step involves the breakdown of complex organic matter into simpler forms.

2. **Fermentation**: Soluble organic molecules (sugars, amino acids, fatty acids) are converted into volatile fatty acids.

3. **Acetogenesis**: Volatile fatty acids are converted into acetic acid.

4. **Methanogenesis**: Acetic acid is further converted into methane ($CH_4$) and carbon dioxide ($CO_2$).

The pH levels indicated in the diagram are:
- pH 5-6 for hydrolysis and fermentation stages.
- pH 7-8 for acetogenesis and methanogenesis stages.
Hydrogen from waste

Hydrogen production by pure substance or mixture

- molasses (Tanisho and Ishiwata, 1994)
- glucose (Kataoka et al., 1997; Lin and Chang, 1999)
- crystalline cellulose (Lay, 2001)
- peptone (Bai et al., 2001)
- starch (Lay, 2001)

Hydrogen production by concentrated wastewater

(Bolliger et al., 1985; Liu et al., 1995; Ueno et al., 1996; Zhu et al., 1999)

Hydrogen production by solid waste

- municipal solid waste (Lay et al., 1999)
- bean curd manufacturing waste (Mizuno et al., 2000)

Hydrogen production by biological sludge

???
### Min-sheng Sludge

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Concentration of wet solids</td>
<td>10,000~12,000 mg/L</td>
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<tr>
<td>Concentration of dry solids</td>
<td>1,429 kg/m³</td>
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<td>pH value</td>
<td>6.4</td>
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<td>Neutron particle size</td>
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<td>Zeta potential</td>
<td>-19.1 mV</td>
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<tr>
<td>TCOD</td>
<td>24,800 mg/L</td>
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<tr>
<td>SCOD</td>
<td>435 mg/L</td>
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<tr>
<td>Alkalinity</td>
<td>325 mg/L</td>
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<td>Elemental composition</td>
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<tr>
<td>C</td>
<td>34.3%</td>
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<tr>
<td>H</td>
<td>5.3%</td>
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<tr>
<td>N</td>
<td>5.4%</td>
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<tr>
<td>O</td>
<td>55%</td>
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63 µm
**Tong-yi Sludge**

<table>
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<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Concentration of wet solids</td>
<td>10,000 mg/L</td>
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<td>Concentration of dry solids</td>
<td>1,450 kg/m³</td>
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<td>Neutron particle size</td>
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<tr>
<td>Zeta potential</td>
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<tr>
<td>TCOD</td>
<td>16,000 mg/L</td>
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<td>SCOD</td>
<td>86.7 mg/L</td>
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<td>alkalinity</td>
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<td>H</td>
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<td>N</td>
<td>5.4%</td>
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<tr>
<td>O</td>
<td>46.7%</td>
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Strains screening

DNA sequencing

Finding optimal dealing parameters

Concentration

Pretreatment methods

Inhibitors

Measuring time points

Continuous anaerobic experiments

Gas production

Hydrogen productive substrates

Composition analysis
Strains screening (2)

Add them individually

M-B M-D M-F M-G

Test the ability of hydrogen production

The ability of hydrogen production is about 0.65-1.11 H₂/kg DS
Species identification

Extract DNA → PCR

Compare to the gene library

purification

Continuous sequencing

GCGGGNGNGTNCC
TAACACATGCAAGT
CGTAACANGGTATT
CCACANCAGNGNGC
TGGACGGACNNGNA
ACAGAGG......
DNA Sequence

M-B  M-D
M-F  M-G

Clostridium bifermentans
Clostridium bifermmentans
Pretreatment flow chart

Original sludge

Ultrasonication

Acidification

Pasteurization

Add BESA

Freeze-thaw treatment

Original sludge filtrate

Ultrasonicated filtrate

Acidified filtrate

Pasteurized filtrate

BESA adding filtrate

Freeze-thawed filtrate
**Sludge fermentation test - COD**

**COD**<sub>0</sub> - COD of original biosolid

**SCOD** - Soluble COD

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**Min-sheng sludge**

- Original
- Sonicated
- Acidified
- Pasteurized
- Frozen/thawed
- BESA-inhibited

**Tong-yi sludge**

- Original
- Sonicated
- Acidified
- Pasteurized
- Frozen/thawed
- BESA-inhibited
Sludge fermentation test - Hydrogen production

COD\textsubscript{i} - COD of the substrate before testing

**Min-sheng sludge**

**Tong-yi sludge**

Yield of hydrogen (mg/g-COD\textsubscript{i})

- Original
- Sonicated
- Acidified
- Pasteurized
- Frozen/thawed
- BESA-inhibited

Time (hours)

8hr 24hr

8hr 24hr
Sludge fermentation test - methane production

Min-sheng sludge

Tong-yi sludge

No CH₄!!
Sludge fermentation test - pH measuring

Min-sheng sludge

Original
Sonicated
Acidified
Pasteurized
Frozen/thawed
BESA-inhibited

Tong-yi sludge

Original
Sonicated
Acidified
Pasteurized
Frozen/thawed
BESA-inhibited

Time (hours)

pH

0 2 5 25 50 75 100

6

5.5

Time (hours)

pH

0 2 5 25 50 75 100

6.5

5.5
Sludge fermentation test - ORP

Min-sheng sludge

Tong-yi sludge

-300

-350
**Sludge fermentation test - Zeta potential**

Min-sheng sludge

![Graph showing zeta potential over time for Min-sheng sludge](image)

- Original
- Sonicated
- Acidified
- Pasteurized
- Frozen/thawed
- BESA-inhibited

Tong-yi sludge

![Graph showing zeta potential over time for Tong-yi sludge](image)

- Original
- Sonicated
- Acidified
- Pasteurized
- Frozen/thawed
- BESA-inhibited

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Zeta potential (mV)</th>
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<td>75</td>
<td>-32</td>
</tr>
<tr>
<td>100</td>
<td>-20</td>
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</tbody>
</table>
Sludge fermentation test - Particle size distribution

**Min-sheng sludge**

- Original
- Sonicated
- Acidified
- Pasteurized
- Frozen/thawed
- BESA-inhibited

**Tong-yi sludge**

- Original
- Sonicated
- Acidified
- Pasteurized
- Frozen/thawed
- BESA-inhibited
Filtrate fermentation test - COD

Min-sheng filtrate

Time (hours)

SCOD/COD₀

Original
• Sonicated
○ Acidified
▼ Pasteurized
▲ Frozen/thawed
□ BESA-inhibited

Tong-yi filtrate

Time (hours)

SCOD/COD₀

Original
• Sonicated
○ Acidified
▼ Pasteurized
▲ Frozen/thawed
□ BESA-inhibited
**Filtrate fermentation test**

**Hydrogen production**

![Graphs showing hydrogen production over time for Min-sheng and Tong-yi filtrates with different treatments: Original, Sonicated, Acidified, Pasteurized, Frozen/thawed, BESA-inhibited.](image)

- **Min-sheng filtrate**
  - 8hr
  - 24hr

- **Tong-yi filtrate**
  - 8hr
  - 24hr

Time (hours) vs. Yield of hydrogen (mg/g-COD)
Filtrate fermentation test - pH measuring

**Min-sheng filtrate**

- Original
- Sonicated
- Acidified
- Pasteurized
- Frozen/thawed
- BESA-inhibited

**Tong-yi filtrate**

- Original
- Sonicated
- Acidified
- Pasteurized
- Frozen/thawed
- BESA-inhibited

Time (hours) vs pH graph for Min-sheng filtrate and Tong-yi filtrate.
Filtrate fermentation test - ORP

Min-sheng filtrate

Tong-yi filtrate

-360
Filtrate fermentation test - Zeta potential

Min-sheng filtrate

Tong-yi filtrate

Zeta potential (mV)

Time (hours)

Original
Sonicated
Acidified
Pasteurized
Frozen/thawed
BESA-inhibited

Min-sheng filtrate

Tong-yi filtrate

Zeta potential (mV)

Time (hours)

Original
Sonicated
Acidified
Pasteurized
Frozen/thawed
BESA-inhibited

-12
-15
-24
-18
Clostridium inoculum
All pretreatments can assist hydrolysis of organic materials effectively. But not all of them help in producing hydrogen.

The production of hydrogen increases markedly over 8-24 hr, and is consumed afterward.

Freezing-thawing, pasteurization, and acidification assist hydrogen production. But adding BESA and ultrasonication retard it.

Hydrogen production reaction occurs in liquid phase, while the existence of sludge would in some sense consumes the hydrogen.
Co-Production of H$_2$ and CH$_4$
Twin Fermentors
K8 inoculum

產 氫 消耗氫氣

累積甲烷

0  8  16  24  32  40  48  72  96  120  144  168  192  216
厌氧消化

Clostridium

K8

240hr 厌氧消化

96hr 厌氧消化

至240hr 厌氧消化
Co-Production

Hydrogen content (g/kg DS)

- sludge
- sludge + clo
- frozen/thawed
- acidified
- alkalized

Yield of CH4 (g/kg DS)

- original sludge
- sludge + clostridium
- frozen/thawed
- acidified
- alkalized

Time (hrs)
TCOD

Time (hrs)

0 100 200 300 400

TCOD (mg/L)

0 10000 20000 30000 40000 50000

sludge
sludge+clo
frozen/thawed
acidified
alkalized
noodle

SCOD

Time (hrs)

0 100 200 300 400

SCOD (mg/L)

0 2000 4000 6000 8000 10000

sludge
sludge+clo
frozen/thawed
acidified
alkalized
noodle
Time (hrs)

NH₃-N (ppm)

- original sludge
- sludge+clo
- freeze/thawed +clo
- acidified+clo
- alkalized+clo
- alkalized noodle+clo
Frozen/thawed

Basified sludge

Sludge+clo

Alkalized

Ori+clo

Time (hrs)

ppm

lactic acid
acetic acid
propionic acid
butyric acid
Acidified

Original

<table>
<thead>
<tr>
<th>lactic acid</th>
<th>acetic acid</th>
<th>propionic acid</th>
<th>butyric acid</th>
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<tr>
<td>400</td>
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</table>
Original sludge

Time (hrs) vs. Methane (g/kg DS)

- Time (hrs): 0, 100, 200, 300, 400, 500
- Methane (g/kg DS): 0, 10, 20, 30, 40, 50, 60, 70
SUMMARY

1. Hydrolysis
2. Fermentation
3. Acetogenesis
4. Methanogenesis

1. Complex organic matter
   Carbohydrates, proteins, fats

2. Soluble organic molecules
   Sugars, amino acids, fatty acids

3. Volatile fatty acids

4. Acetic acid

5. Methane and carbon dioxide

pH 5-6

pH 7-8