Anaerobic Wastewater Treatment

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Content

1. Anaerobic wastewater treatment for sustainable development

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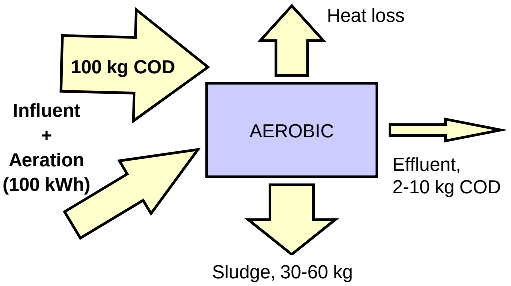
Sustainability criteria for wastewater treatment systems

1. High treatment efficiency (according specifications) for: COD/BOD, suspended solids, N, P, etc.
2. Robust technology: high stability towards power cuts, peak loads, toxicants, etc.
3. Flexible with respect to future amendments (extensions, improvement)
4. Simple in operation maintenance and control
5. Limited number of treatment steps
6. Absence of disposal problems (e.g. sludge)
7. No malodour nuisance
8. Applicable at any size, also inside city sections for a decentralised approach
9. Availability of local experience
10. Designed for (by)products recovery

Why Anaerobic Treatment ?



100 kg COD

Influent
+
Aeration
(100 kWh)

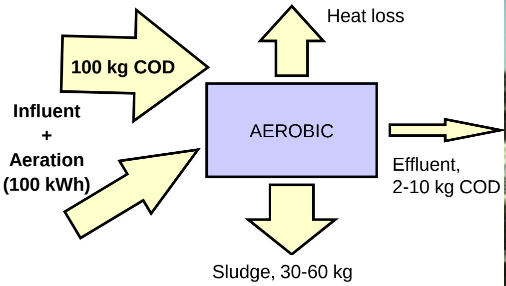
Heat loss

AEROBIC

Effluent,
2-10 kg COD

Sludge, 30-60 kg

Why Anaerobic Treatment ?



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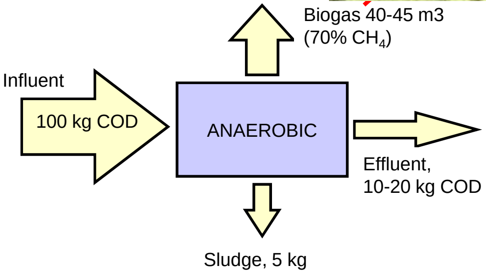


Biogas 40-45 m3
(70% CH_4)

Influent

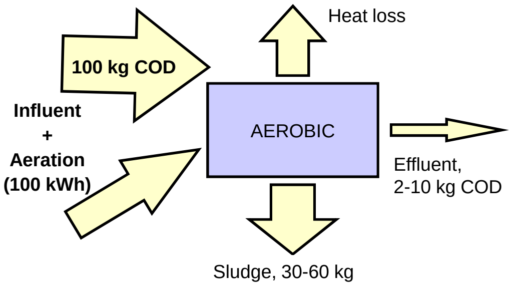
100 kg COD

ANAEROBIC

Effluent,
10-20 kg COD

Sludge, 5 kg

Why Anaerobic Treatment ?



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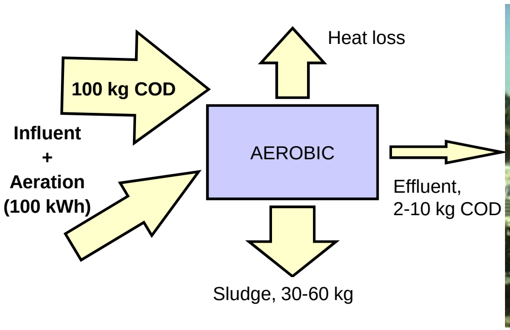

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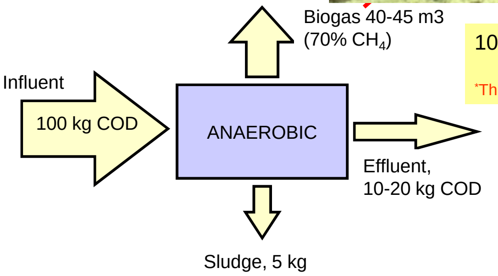


Biogas 40-45 m3
(70% CH_4)

Influent

100 kg COD

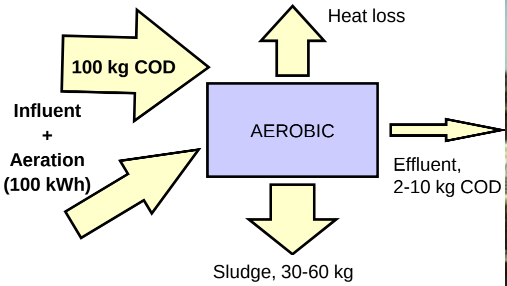
ANAEROBIC

Effluent,
10-20 kg COD

Sludge, 5 kg

100 kg COD ≅ 35 m^3 CH_4
≅ 382 kWh*
*Theoretical energy equivalent

Why Anaerobic Treatment ?



Comparison Aerobic - Anaerobic

	Aerobic	Anaerobic
Reaction	$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$	$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$
Energy release	$\Delta G°' = -2840$ kJ/mol glucose	$\Delta G°' = -393$ kJ/mol glucose
Carbon balance	50% → CO_2 50% → biomass	95% → $CH_4 + CO_2$ (= biogas) 5% → biomass
Energy balance	60% → biomass 40% → heat production	90% retained in CH_4 5% → biomass 5% → heat production
Biomass production	Fast growth of biomass, Resulting in a sewage sludge problem	Slow growth of biomass
Energy input for aeration	Yes	No

Anaerobic versus Aerobic

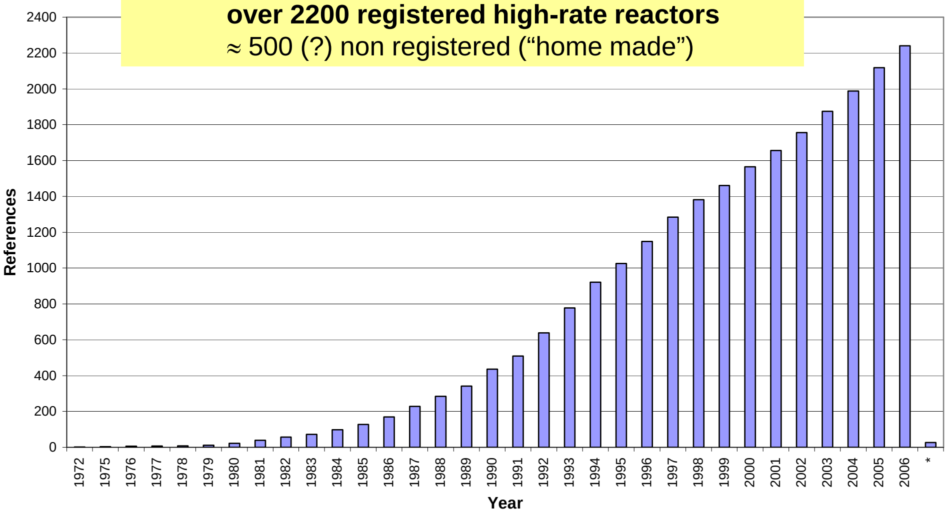
Yesterday

Anaerobic versus Aerobic

Today

Worldwide cumulative anaerobic references 2007

Anaerobic Industrial Wastewater Reactors, census **2007**
over 2200 registered high-rate reactors
≈ 500 (?) non registered (“home made”)



High-rate Anaerobic Applications in Industries

Number of installed reactors, N= 2266 (Jan. 2007)

AGRO-FOOD INDUSTRY 36%		**BEVERAGE 29%**	**ALCOHOL DISTILLERY 10%**	**PULP & PAPER 11%**	**MISCELLANEOUS 14%**
Sugar	**Cannery**	**Beer**	**Sugar cane juice**	**Recycle paper**	**Chemical**
Potato	**Confectionery**	**Malting**	**Sugar cane molasses**	**Mechanical pulp**	**Pharmaceutical**
Starch	**Fruit**	**Soft drink**	**Sugar beet molasses**	**NSSC**	**Sludge liquor**
Yeast	**Vegetable**	**Fruit juice**	**Grape wine**	**Sulphite pulp**	**Municipal sewage**
Pectin	**Dairy**	**Wine**	**Grain**	**Straw**	**Landfill leachate**
Citric acid	**Bakery**	**Coffee**	**Fruit**	**Bagasse**	**Acid mine water**


Yeast, Italy


Beer, Brazil


Distillery, Japan


Paper, Netherlands


Chemical, Netherlands

High-rate Anaerobic Wastewater Treatment 2007

- Reduction of excess sludge production by 90% !
- Up to 90% reduction in space requirements !
- High loading rates (up to 35 kg COD.m^{-3}.day^{-1}), smaller reactors
- No use of fossil fuels for treatment (saving ≈ 0.5-1 kWh / kg COD)
- Production of energy as CH4 (3.8* kWh / kg COD converted)
- Rapid start up with granular sludge (1 week)
- No or very little use of chemicals (e.g. nutrients)
- Plain technology with high treatment efficiencies
- Anaerobic sludge can be stored unfed → campaign industries
- Excess sludge has a market value
- Compact high-rate systems facilitate in-house loop closure
- Perspectives for nutrients recovery (agricultural reuse, struvite)
- Bleed of sulphur as H_2S via produced biogas

Potentials of carbon credits with AD projects?

CO_2 emissions with conventional electricity production:

Coal powered electricity plant: **0.86 ton CO_2/MWh-e**
Natural gas powered plant: **0.44 ton CO_2/MWh-e**

If bio-CH_4 is used as renewable fuel:
CO_2 emission reduction !!

Expected stabilised price:
20 €/ton CO_2

Energy & carbon credits in anaerobic wastewater treatment:

- Loading capacity AWWT: **10 – 35** kg COD/(m^3.d)
- Energy output: **0.5 – 1.7** kW-elec/m^3 (80% CH_4 rec., 40% CHP eff.)
- CO_2 emission reduction: **3.8 – 13** ton CO_2/(m^3.y) (coal PP)

PARAMETER	UNIT	Brewery
Flow	m³/d	2720– 5780
COD average	mg/l	4043
COD range	mg/l	2020– 5790
SS	mg/l	260– 2160
Temperature	°C	21– 40
pH		2.6– 7.0

Reactor:
COD-load: 17 ton/day
Loading: 35 kg COD/(m3.d)
Reactor: V = 500 m3
(h=25 m, d=5 m)
Excess sludge:
≈ 0.6 ton DM/d

Brewery Effluent: Energy & Carbon Credits benefit

Energy recovered:
17 ton COD x 0.8 (eff) x 3820 kWh* x 40% CHP eff. = 21 MWh-e/d ≈ 0.9 MW

No energy consumption:
Assumed energy requirement activated sludge: ≈ 0.5-1 kWh-e/kg $COD_{rem.}$
Saved: 17 ton COD x 0.8 (eff.) = 7-14 MWh-e/day

Total energy benefit: 21 + (7-14) = 28-35 MWh-e/day ≅ 1680-2100 €/d
(with 0.06 €/kWh) or: **700.000 €/year**

CO_2 emission reduction
Recovered: 21 MWh-e/d x 0.86 ton CO_2/MWh-e ≈ **18 ton CO_2/day (coal)**
Prevented: 7-15 MWh-e/d x 0.86 ton CO_2/MWh-e ≈ **6-13 ton CO_2/day (coal)**

Potential benefit: 18 x 20 x 365 = **130.000 €/year**

Importance for developing countries:

Energy recovery & CO_2 credits as an incentive to implement environmental technologies in developing countries

Treatment alcohol distillery effluents Cuba (Santa Clara):
- 800 $m^3.d^{-1}$,
- 65 kg $COD.m^{-3}$

Anaerobics: 13,500 m^3 $CH_4.d^{-1}$
or: about **2.2 MW-electric** (40% eff.)
At a price of 0.12 US$ $.kWh^{-1}$ this equals: **2.300.000 US$.$y^{-1}$**
CO_2 credits: 330.000 US$.$y^{-1}$ (coal)

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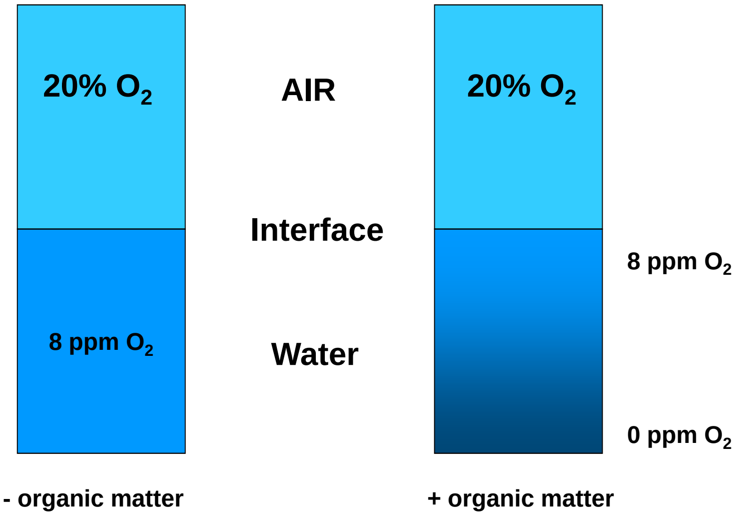
2. Microbial aspects of anaerobic conversions

Natural Anaerobic Environments



20% O_2

AIR

20% O_2

Interface

8 ppm O_2

8 ppm O_2

Water

0 ppm O_2

- organic matter

+ organic matter

History of anaerobic microbiology

- Volta (1776) discovery of CH_4 in swamp-gas
- Early microbiologist: Béchamp (1868), Popoff (1875)
- Microbiology of methane bacteria:
  - Söhngen (1906) *Methanothrix soehngenii* (in defined mix) (renamed *Methanosaeta soehngenii*, Patel)
  - Schnellen (1947): first pure cultures (*Methanosarcina barkeri, Methanobacterium formicium*)

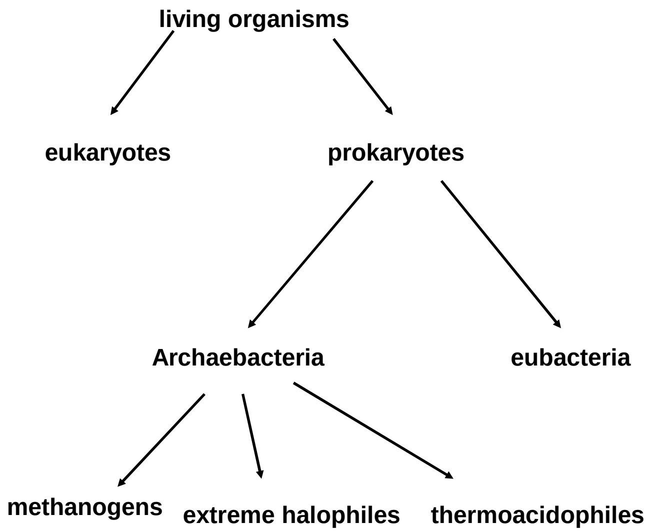
Bryant (1967) very important discovery:

Methanobacterium Omelianski (fermenting EtOH) exist of 2 bacteria !!
EtOH =>Acetate + H_2 (not directly to CH_4 !!)

Description of the new kingdom of Archeabacteria

- methane bacteria
- sulphate reducer
- halophilic bacter,etc.

Classification of methanogens



living organisms

eukaryotes

prokaryotes

Archaebacteria

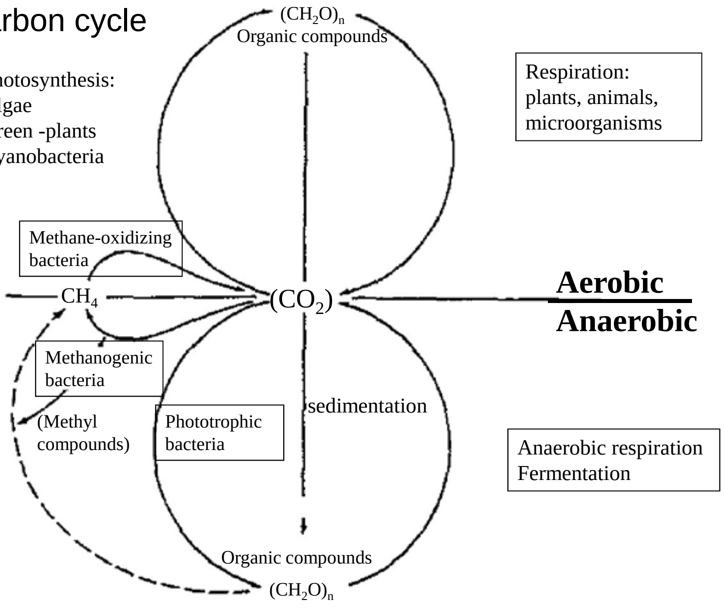
eubacteria

methanogens

extreme halophiles

thermoacidophiles

Carbon cycle



$(CH_2O)_n$
Organic compounds

Photosynthesis:
Algae
Green -plants
Cyanobacteria

Respiration:
plants, animals,
microorganisms

Methane-oxidizing bacteria

CH_4

(CO_2)

Aerobic

Anaerobic

Methanogenic bacteria

(Methyl compounds)

Phototrophic bacteria

sedimentation

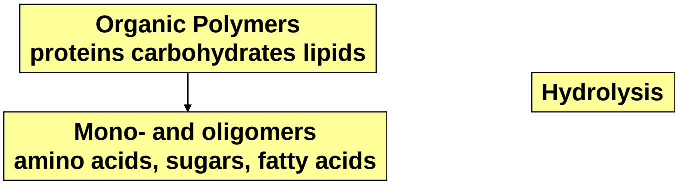
Anaerobic respiration
Fermentation

Organic compounds
$(CH_2O)_n$

Anaerobic Conversion of Organic Matter

Organic Polymers
proteins carbohydrates lipids

Anaerobic Conversion of Organic Matter

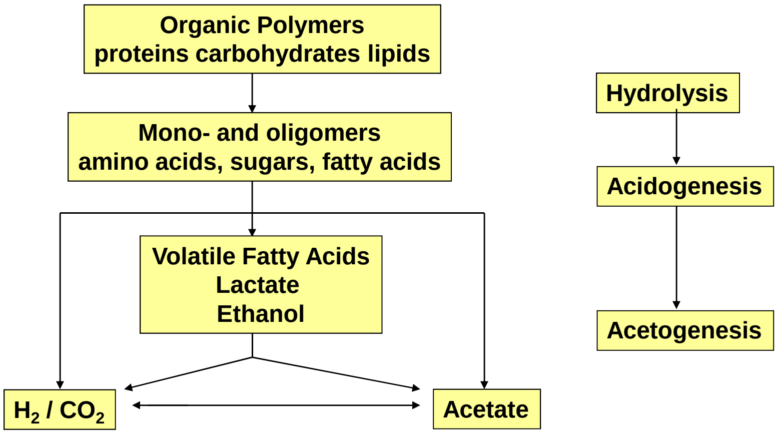


Organic Polymers
proteins carbohydrates lipids

Mono- and oligomers
amino acids, sugars, fatty acids

Hydrolysis

Anaerobic Conversion of Organic Matter



Organic Polymers
proteins carbohydrates lipids

Mono- and oligomers
amino acids, sugars, fatty acids

Volatile Fatty Acids
Lactate
Ethanol

H_2 / CO_2

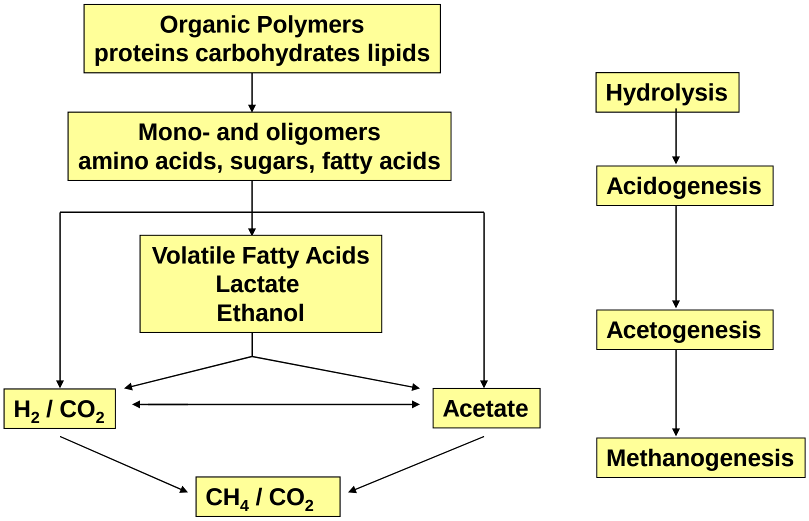
Acetate

Hydrolysis

Acidogenesis

Acetogenesis

Anaerobic Conversion of Organic Matter



Organic Polymers
proteins carbohydrates lipids

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Volatile Fatty Acids
Lactate
Ethanol

H_2 / CO_2

Acetate

CH_4 / CO_2

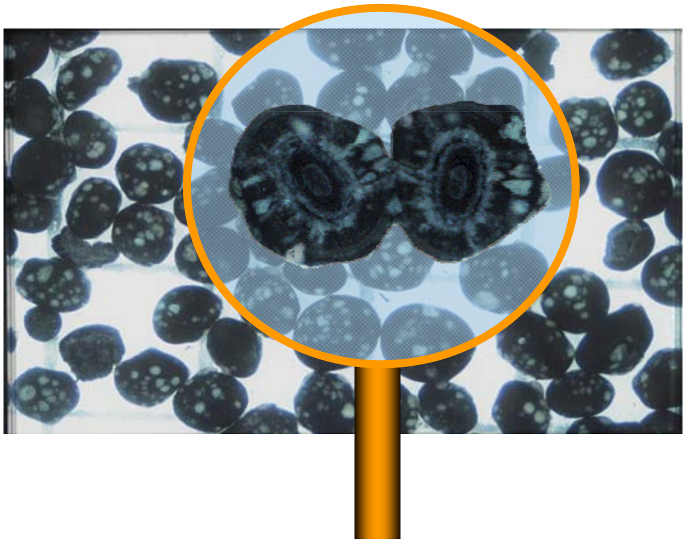
Hydrolysis

Acidogenesis

Acetogenesis

Methanogenesis

Anaerobic granular sludge



Hydrolysis

- slow process (generally rate limiting): $dS/dt = -K_h \cdot S$
- optimum pH = 6
- retention time and particle size are rate determining parameters
- cellulose/hemicellulose degradation depends on lignin fraction
- hydrolysis of fats hardly proceeds < 15-20 °C (rate limiting step)

(product) inhibition by:

- LCFA
- NH3
- amino acids
- H_2 ?

Hydrolytic enzymes

Hydrolysis

Sugars

sucrose $(C_6H_{10}O_5)_2$ $\xrightarrow{\text{saccharase}}$ glucose $C_6H_{10}O_6$

starch $(C_6H_{10}O_5)_n$ $\xrightarrow{\text{amylase}}$ glucose

cellulose $(C_6H_{10}O_5)_n$ $\xrightarrow{\text{cellulase}}$ glucose

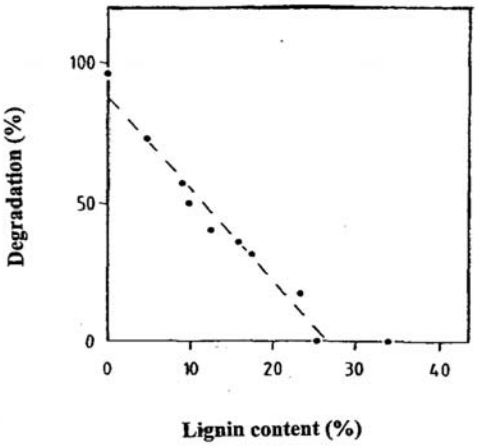
Protein

protein $\xrightarrow{\text{protease}}$ VFA's+NH_3

Fat

fat $\xrightarrow{\text{lipase}}$ glycerol + Long Chain Fatty Acids (LCFA)

Bio-degradation of cellulytic matter *versus* lignin content



	% lignin
Cellulose	**0**
Hay	**5**
Barley straw	**9**
Alfalfa	**10**
Bagasse	**12**
Rye straw	**16**
Reed	**17**
Newspaper	**23**
Saw dust	**25**
Coconut fibre	**34**

Acidogenesis / Fermentation - Sugars

- Release of protons (H^+) and reaction products (proton acceptors)
- H_2 formation (catalyzed by the enzyme hydrogenase)
- Performed by a very large group of bacteria (about 1% of all bacteria facultative fermenters)

$$C_{12}H_{22}O_{11} + 9\ H_2O \rightarrow 4\ CH_3COO^- + 4\ HCO_3^- + 8\ H^+ + 8\ H_2$$

$$C_{12}H_{22}O_{11} + 5\ H_2O \rightarrow 2\ CH_3CH_2CH_2COO^- + 4\ HCO_3^- + 6\ H^+ + 4\ H_2$$

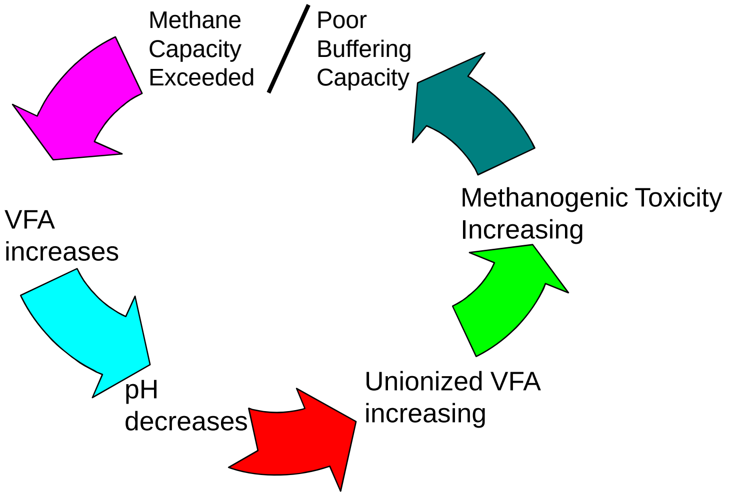
- End products depend on circumstances, e.g.
  - glucose fermentation in a two-step system: more reduced products like ethanol, lactate, propionate, butyrate, CO_2 and H_2
  - glucose fermentation in a one-step system: acetate, H_2 and CO_2
- production of acids proceeds up to pH = 4 (product inhibition)

Acidogenesis of sugars: most rapid step!

Kinetic Properties Acidifiers / Methanogens

Process	R_x gCOD/gVSS /d	Y g VSS/g COD	Ks mg COD/l	μ-max Day^{-1}
Acidogenesis	13	0.15	200	2.0
Methanogenesis	3	0.03	30	0.12
Overall	2	0.03 –0.18	-	0.12

Overloading may lead to process deterioration:



Methane Capacity Exceeded / Poor Buffering Capacity

Methanogenic Toxicity Increasing

Unionized VFA increasing

pH decreases

VFA increases

Inhibition by VFA

Concentrations of VFA that correspond to the 50% inhibition of methanogenic activity. Calculated from 16 and 6 mg COD/l of unionized acetic and propionic acids, respectively

pH	50% Inhibiting concentration	
	acetate	propionate
	--------mg COD L^{-1}-----------	
5.0	44	13
5.5	106	30
6.0	300	80
6.5	912	241
7.0	2851	745
7.5	8976	2358
8.0	28368	7398

$$[VFA]_{unionized} = [VFA] * \alpha_0$$

$$\alpha_0 = \{10^{(pH-pKa)} + 1\}$$

$$pKa = 4.75$$

Acidogenesis / Fermentation - Proteins

- organically bound N (amino acids) is released as NH4$^+$ (stickland reaction: oxidation-reduction)

Alanine: $CH_3CHNH_2COO^- + 3\ H_2O \rightarrow CH_3COO^- + HCO_3^- + NH_4^+ + 2\ H_2$

Glycine: $2\ CH_2NH_2COO^- + 2\ H_2 \rightarrow 2\ CH_3COO^- + 2\ NH_3$

$$\text{alanine} + \text{glycine} + 3\ H_2O \rightarrow 3\ \text{acetate} + 2\ NH_3 + NH_4^+ + HCO_3^-$$

$$(2\ NH_3 + 2\ H_2O + 2\ CO_2 \rightarrow 2\ NH_4^+ + 2\ HCO_3^-)$$

Acidogenesis / Fermentation – Long Chain Fatty Acids

- anaerobic degradation of LCFA proceeds via β-oxidation

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COO^-$

palmitic acid: $CH_3\text{-}(CH_2)_{14}\text{-}COO^- + 14\ H_2O \rightarrow 8\ CH_3COO^- + 7\ H^+ + 14\ H_2$

With uneven numbers: acetate + propionate is formed:

$CH_3\ (CH_2)_{14}\text{-}CH_2COO^- + 14\ H_2O \rightarrow 7\ CH_3COO^- + CH_3CH_2COO^-\ 7\ H^+ + 14\ H_2$

- unsaturated LCFA are firstly hydrogenated before degradation

Acetogenesis (Acetate formation)

Conversion of fermentation products into acetic acid, CO_2 , and H_2

Mainly formation of propionic acid, butyric acid and ethanol

propionate$^-$ + $3H_2O$ → acetate$^-$ + HCO_3^- + H^+ + $3H_2$ $\Delta G_0' = +76.1$ kJ/mole

butyrate$^-$ + 2H2O → 2 acetate$^-$ + H^+ + $2H_2$ $\Delta G_0' = +48.1$ kJ/mole

ethanol + $2H_2O$ → acetate$^-$ + H^+ + $2H_2$ $\Delta G_0' = +9.6$ kJ/mole

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$4H_2 + CO_2$ → $CH_4 + 2H_2O$ $\Delta G_0' = -138.9$ kJ/mole

➡ Need for syntrophic associations !!!

GIBB's FREE ENERGY

$$aA + bB \Leftrightarrow cC + dD$$

$$\Delta G' = \Delta G'_0 + RT \ln \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

$\Delta G'$ = Actual Gibb's free energy change [kJ/mole]

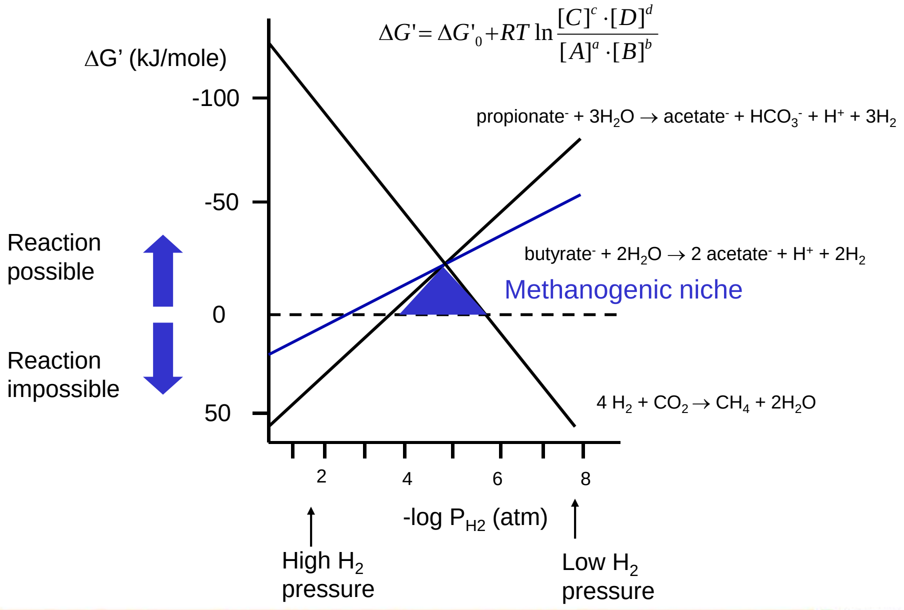
$\Delta G'_0$ = Standard Gibb’s free energy change [kJ/mole] under standard conditions (pH = 7, T = 25 °C, p = 1 atm., the activity of all compounds present in solution is 1 mole/kg

R = gas constant (8.28 J)

T = absolute temperature [K]

Impact of $P(H_2)$ on thermodynamics

$$\Delta G' = \Delta G'_0 + RT \ln \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$



Methanogenesis

→ Substrates

		ΔG^0 (kJ/mole CH_4)
$4H_2 + CO_2$	=> $CH_4 + 2H_2O$	-130.4
4HCOOH	=> $CH_4 + 3CO_2 + 2H_2O$	-119.5
$4CO + 2H_2O$	=> $CH_4 + 3CO_2$	-185.5
$4CH_3OH$	=> $3CH_4 + CO_2 + 2H_2O$	-103.0
$CH_3OH + H_2$	=> $CH_4 + H_2O$	-112.5
$4CH_3NH_3 + 2\ H_2O$	=> $3CH_4 + CO_2 + 4NH_4^+$	- 74.0
$2(CH_3)_2NH_2 + 2H_2O$	=> $9CH_4 + 3CO_2 + 4NH_4^+$	- 74.0
CH_3COOH	=> $CH_4 + CO_2$	- 32.5

Most important substrates: hydrogen and acetate

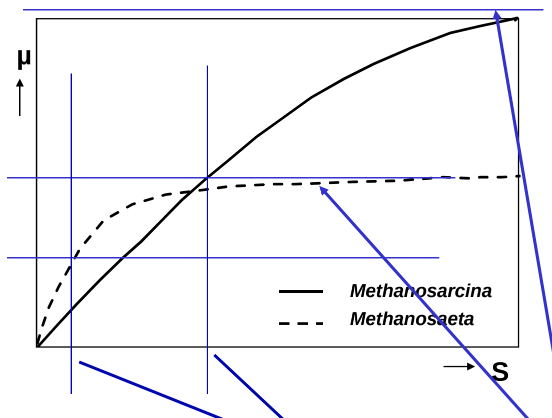
furthermore: formate, carbon monoxyde, methanol and methylamines

Kinetic parameters

Substrate	Product	μ_{max} (d^{-1})	t_d (d)	K_S (mg COD • l^{-1})
acetate*	methane	0.12 0.71	5.8 1.0	30 300
hydrogen	methane	2.85	0.2	0.06
propionate	acetate	0.22	3.2	48
butyrate	acetate	0.55	1.3	9

*** two different acetate consuming methanogens**

Impact of kinetics on bacterial selection



The Monod equation for bacterial growth:

$$\frac{dX}{dt} = \mu \cdot X$$

with:

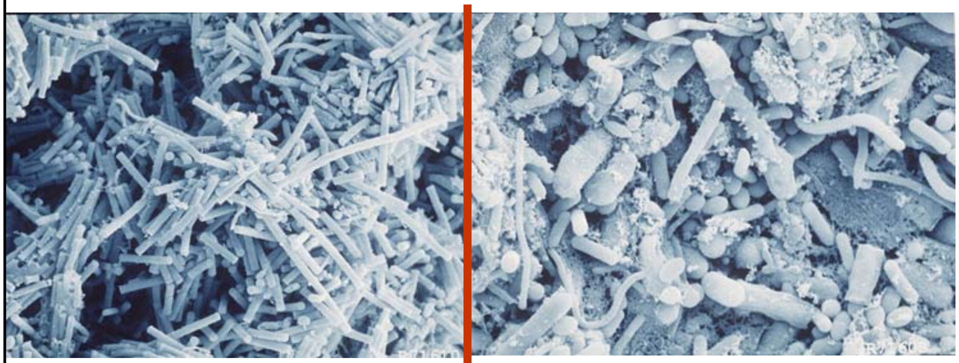
$$\mu = \mu_{max} \cdot \frac{S}{K_s + S}$$

$K_s = S$ when $\mu = ½\, \mu_{max}$

	K_S	μ_{max}
Methanosaeta	**30**	**0.12**
Methanosarcina	**300**	**0.71**

Anaerobic granular sludge

SEM pictures

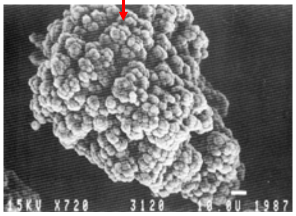


Acetate as Substrate
(Methanosaeta)

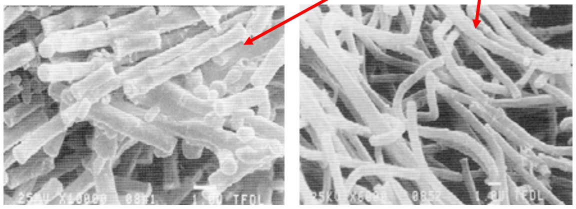
Sucrose as Substrate
(mixed population)

Bacterial composition of methanogenic sludge granule

1. 20-50% consist of methanogenic bacteria: acetotrophic (Methanosaeta, Methanosarcina) and hydrogenotrophic (e.g. Methanobacterium)



- Coccoid
- Excretion ECP → clumps
- Substrate: Ac^-, H_2/CO_2, MeOH, methylamines
- Low substrate affinity
- Relatively high μ



- Rod-shaped (4-10 cells) or filaments
- Hydrophobic surface
- Substrate: Acetate
- High substrate affinity
- Low μ, low Y
- Generally predominant !!

Bacterial composition of methanogenic sludge granule

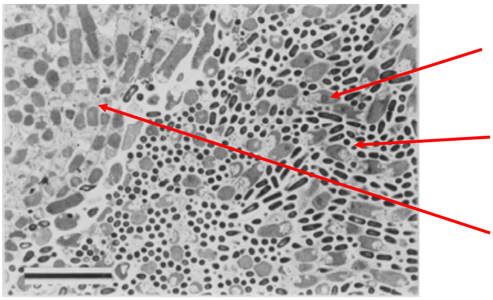
2. Close association between hydrogen producing and hydrogen consuming organisms (syntrophic associations)

$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + 3H_2 + HCO_3^- + H^+$ ΔG °'= +76.1 kJ (1)

$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$ ΔG °'= –135.4 kJ (2)

$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$ ΔG °'= –31.0 kJ (3)

$CH_3CH_2COO^- + 0.75\ H_2O \rightarrow CH_3COO^- + 0.75CH_4 + 0.25\ HCO_3^- + 0.25H^+$ ΔG °'= –25.45 kJ



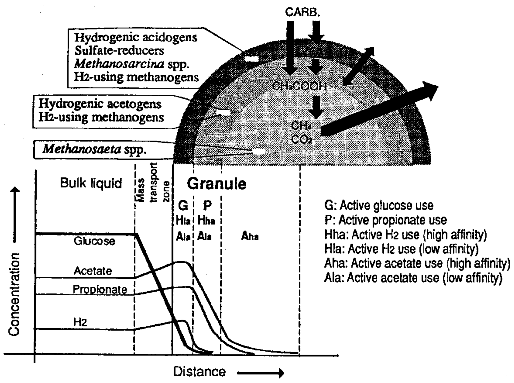
(1) *Syntrophobacter*

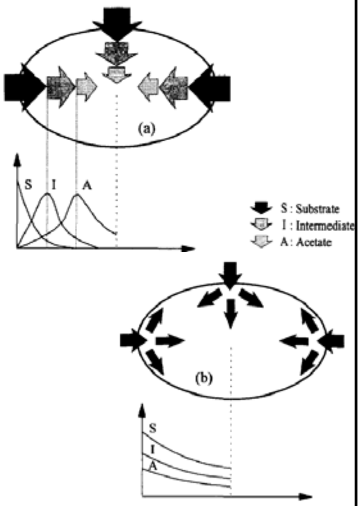
(2) *Methanobrevibacter*

(3) *Methanosaeta*

Bacterial composition of methanogenic sludge granule

3. Presence of acidifiers or fermentative bacteria.
   Depending on the substrate a uniform or layered structure is observed





Macro nutrients requirement of anaerobic sludge

The requirement for N and P can be calculated from the cell composition.

(i.e. 10-12% N and appr. 2% P)

substrate = mixture of **volatile fatty acids**

growth yield = 0.02 - **0.05** g/g

COD : N : P = 1000 : 5 : 1

C : N : P = 330 : 5 : 1

substrate = **non-acidified carbohydrates**

→ growth yield = 0.10 - **0.15** g/g

COD : N : P = 350 : 5 : 1

C : N : P = 130 : 5 : 1

Level of micro-nutrients mostly sufficient in agro-industrial wastewater

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Micro nutrients (heavy metals) requirement

Based on elemental composition of methane bacteria (Scherer, 1983)

Element	Concentration mg kg^{-1} dried cell	Element	Concentration mg kg^{-1} dried cell
Macronutrients:		Micronutrients:	
N	65000	Fe	1800
P	15000	Ni	100
K	10000	Co	75
S	10000	Mo	60
Ca	4000	Zn	60
Mg	3000	Mn	20
		Cu	10

Conversion factors for methane bacteria cell:
g VSS*1.4= g COD
g TS*0.825= g VSS

Important notes

- Anaerobic microbial conversion differs from aerobic
- Ultimate COD removal via production of CH_4
- Anaerobic bacteria have a narrow substrate spectrum: complex consortia are needed for complete COD removal
- Anaerobic bacteria form bacterial aggregates (anaerobic granular sludge). Proper bacterium should be selected.