ANAEROBIC DIGESTION PROCESSES

Functional definition of "Anaerobic" = absence of oxygen or nitrate.

Role of anaerobic processes in wastewater treatment

1. Enhanced biological phosphate removal (EBPR)
2. **Sludge stabilization = reduction in volatile (bioreactive) solids from primary, biofilm, and waste activated sludge**
3. **Reduction in pathogens in sludge**
4. **Energy recovery as biofuels production, primarily methane (CH_4)**

For 2-4, the unit process is the anaerobic digester.

General characteristics: mixed suspended solids, complex microorganism communities, long hydraulic and solids residence time (30-60 days), mesophilic temperature (~35 C)

Dominant Microbial populations:

Bacteria and Archaea

Rate and extent of stabilization and methane production depend strongly on population interactions.

Three groups of anaerobic microorganisms in digester populations:

- Group I: hydrolytic fermentative bacteria
- Group II: Syntrophic acetogenic bacteria (SAB)
- Group III: Archaea (methanogens)

Populations, substrates, products and reaction stoichiometries are shown in Figure 1 and Table 1, following.

Fig 1. PARTICULATE HYDROLYSIS: HYDROLYTIC FERMENTATIVE BACTERIA (X_f)

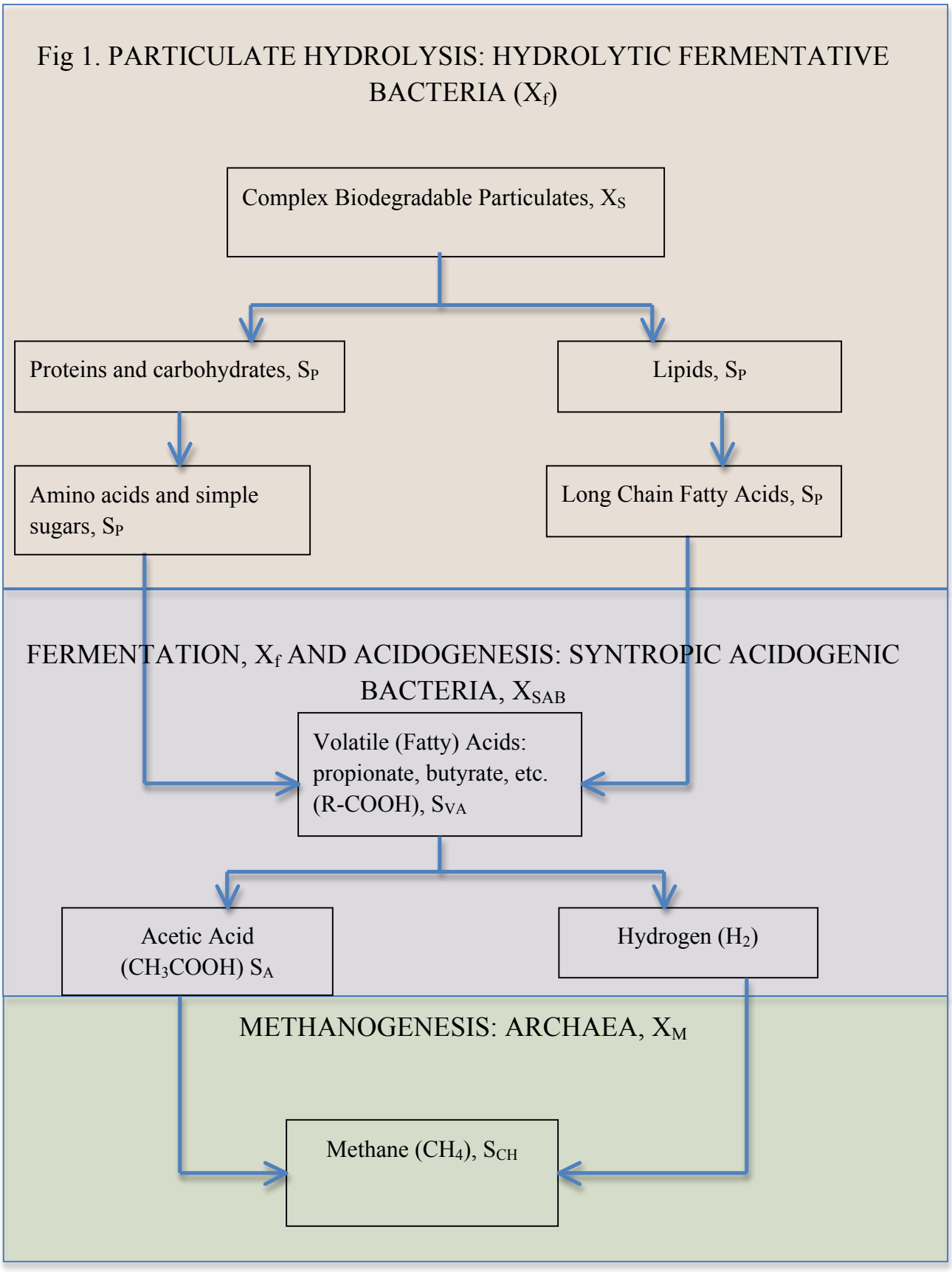


Table 1. MICROBIAL REACTIONS (MOLAR STOICHIOMETRIES)

I. Fermentation reaction examples (glucose substrate, various VA products)

Product	Reaction	ΔG (kJ/mole glucose)
Lactate	$C_6H_{12}O_6 \rightarrow 2CH_3CH(OH)COO^- + 2H^+$	-198.1
Butyrate	$C_6H_{12}O_6 + 2H_2O \rightarrow CH_32(CH_2)COO^- + 2HCO_3^- + 2H_2 + 3H^+$	-254.4
Propionate + acetate	$1.5C_6H_{12}O_6 \rightarrow 2CH_3CH_2COO^- + CH_3COO^- + HCO_3^- + 3H^+$	-109.9

Genera: *Bacteroides, Clostridium,* etc.

II. Syntropic acetogenic reaction examples (various VA substrates, acetate, H_2 products)

Substrate	Reaction	ΔG (kJ/mole substrate)
Lactate	$CH_3CH(OH)COO^- + 2H_2O \rightarrow CH_3COO^- + HCO_3^- + 2H_2 + H^+$	- 3.96
Butyrate	$CH_32(CH_2)COO^- + 2H_2O \rightarrow 2CH_3COO^- + 2H_2 + H^+$	+ 48.1
Propionate	$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + 3H_2 + H^+$	+ 76.1

Genus: *Acetobacter*

III. Methanogenic reaction examples (various substrates, CH_4 product)

Substrate	Reaction	ΔG (kJ/mole substrate)
Acetate	$CH_3COO^- + 2H_2O \rightarrow CH_4 + HCO_3^-$	- 31.0
Hydrogen	$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$	- 33.9
Formate	$4COO^- + H_2O + H^+ \rightarrow CH_4 + 3HCO_3^-$	- 32.6

Genera: *Methanococcus, Methanosarcina, Methanospirillum,* etc.

Group I. Hydrolytic and Fermentative bacteria (X_f)

Reactions:

a. Hydrolysis of particulate COD (X_S) primarily by anaerobic bacteria (not facultative, generally): *Bacteroides, Clostridium, Bifidobacteria* to produce amino acids, simple sugars, lipids and fatty acids. Hydrolysis reactions are not considered to be growth related:

$$-X_S + S_P = 0 \qquad \text{(COD basis)}$$

Where X_f = population of hydrolytic/fermenting bacteria and S_P = soluble hydrolysis products

$$-r_{XS} = r_{SP}$$

$$r_{XS} = -k_h \left[\frac{X_S / X_f}{\left(K_X + X_S / X_f \right)} \right] X_f$$

b. Fermentation of hydrolysis products by same strains of anaerobic bacteria (reactions are growth linked). Products are volatile fatty acids (lactate, propionate, butyrate, formate), alcohols, in addition to cells.

$$- S_P + Y_f X_f + Y_{VA} S_{VA} = 0 \qquad \text{(COD basis)}$$

Where Y_f = fermenting bacteria cell growth/hydrolyzed products consumed and Y_{VA} = volatile acids produced/hydrolysis products consumed, and S_{VA} = soluble volatile acids

Rearranging so X_f is reference component:

$$- S_P/Y_f + X_f + (Y_{VA}/Y_f) S_{VA} = 0 \qquad \text{(COD basis)}$$

Relative rates from stoichiometry:

$$\frac{r_{SVA}}{\left(Y_{VA} / Y_f \right)} = r_{Xf} = \frac{-r_{SP}}{\left(\frac{1}{Y_f} \right)}$$

Reference Monod growth rate expression for fermenting bacteria:

$$r_{Xf} = \hat{\mu}_f \frac{S_P}{(K_P + S_P)} X_f$$

Fermenting bacteria produce protons (acid). Important factor in keeping digester environment balanced and stable is that consumption of VA's and available alkalinity matches proton production by fermenters.

Group II. Syntropic acetogenic bacteria (X_{SAB}).

SAB reduce protons to H_2 and produce acetate and formate from fermentation products, as well as CO_2. Note that some of these reactions are not thermodynamically favored ($\Delta G > 0$). They rely on product consumption (interspecies hydrogen or acetate transfer) by Group III Archaea to drive the reaction. SAB produce alkalinity, which is useful for buffering digester pH. Some SABs are inhibited by product (acetate) accumulation.

$$- S_{VA} + Y_{SAB}X_{SAB} + Y_A S_A = 0 \qquad \text{(COD basis)}$$

Where Y_{SAB} = SAB cell growth/volatile acids consumed and Y_A = acetate produced/volatile acids consumed, and S_A = soluble acetate. Rearranging so reference component is X_{SAB}:

$$- S_{VA}/Y_{SAB} + X_{SAB} + (Y_A/Y_{SAB})S_A = 0 \qquad \text{(COD basis)}$$

Relative rates from stoichiometry:

$$\frac{r_A}{\left(Y_A/Y_{SAB}\right)} = r_{SAB} = \frac{-S_{VA}}{\left(\frac{1}{Y_{SAB}}\right)}$$

Reference Monod growth rate expression for acetogenic bacteria:

$$r_{SAB} = \hat{\mu}_{SAB} \left(\frac{S_{VA}}{(K_{VA} + S_{VA})}\right) \left(\frac{K_A}{(K_A + S_A)}\right) X_{SAB}$$

Product (acetate) inhibition switching function (when $S_A >> K_A$, $\mu_{SAB} << \hat{\mu}_{SAB}$)

Group III. Archaea (X_M).

Methane producing microorganisms. Approximately 2/3 of methane is produced from acetate and 1/3 from hydrogen.

Acetoclastic methane production (using acetate as substrate) is important because acid is removed and alkalinity is formed. Bicarbonate also acts as electron acceptor for both SAB and Archaea. Acetoclastic *Archaea* strains: *Methanosarcina, Methanothrix*.

$$- S_A + Y_M X_M + Y_{CH} S_{CH} = 0 \qquad \text{(COD basis)}$$

Rearranging so X_M is reference component:

$$- S_A/Y_M + X_M + (Y_{CH}/Y_M) S_{CH} = 0 \qquad \text{(COD basis)}$$

Where Y_M = archaea cell growth/acetate consumed, Y_{CH} = methane produced/acetate consumed, and S_{CH} = methane.

Reference Monod growth rate expression for Archaea using acetate:

$$\frac{r_{CH}}{\left({}^{Y_{CH}}/_{Y_M}\right)} = r_{XM} = \frac{-r_{SA}}{\left(\frac{1}{Y_M}\right)}$$

$$r_{XM} = \hat{\mu}_M \left(\frac{S_A}{(K_A + S_A)}\right)\left(\frac{1}{\left(log\left(\frac{H^+}{10^{-7}}\right) + 1\right)}\right) X_M$$

Note pH switching function as H^+ gets larger than 10^{-7} (more acidic), pH switching function gets smaller and growth rate decreases.

Another group, not particularly valued, but always active, are sulfate reducing bacteria (SRB). SRB respire sulfate anaerobically to produce H_2S species using soluble organic compounds, especially acetate and H_2, as electron donors.

ANAEROBIC DIGESTION STOICHIOMETRIC AND KINETIC MATRIX

	Components								Rates
Process	Acetate, S_A (mg/L COD)	Particulate COD, X_S (mg/L COD)	Fermenting Bacteria, X_F (mg/L COD)	Volatile Acids, S_{VA} (mg/L COD)	Soluble Substrate, S_P (mg/L COD)	Syntrophic Acetogenic Bacteria, X_{SAB} (mg/L COD)	Methanogen Archaea, X_M (mg/L COD)	Methane, S_{CH} (mg/L COD)	ρ_j
Hydrolysis		-1			1				q_H*X_F
Fermentation			1	Y_{VA}/Y_F	$-1/Y_F$				μ_F*X_F
Acetogenesis	Y_A/Y_{SAB}			$-1/Y_{SAB}$		1			$\mu_{SAB}*X_{SAB}$
Methanogenesis	$-1/Y_M$						1	Y_{CH}/Y_A	μ_M*X_M

Y_{VA} = g-volatile acids (COD) produced/g-particulate COD consumed
Y_F = g-fermenting biomass (COD) grown/g-hydrolysis products
Y_A = g-acetate produced/g-volatile acid COD consumed
Y_{SAB} = g-SAB cell growth (COD)/g-volatile acids (COD) consumed
Y_M = g-archaea cell growth (COD)/g-acetate (COD) consumed
Y_{CH} = g-methane produced (COD)/g-acetate (COD) consumed

$$q_H = k_H\left(\frac{X_S/X_F}{K_{XS}+X_S/X_F}\right)$$ (mg-COD-S_P/mg-COD-X_F/d) Hydrolysis product formation rate

$$\mu_F = \hat{\mu}_F\left(\frac{S_P}{K_P+S_P}\right)$$ (mg-COD-X_F/mg-COD-S_P/d) Fermenting bacteria growth rate

$$\mu_{SAB} = \hat{\mu}_{SAB}\left(\frac{S_{VA}}{K_{VA}+S_{VA}}\right)\left(\frac{K_A}{K_A+S_A}\right)$$ (mg-COD-X_{SAB}/mg-COD-S_{VA}/d) Acetogenic bacteria growth rate

$$\mu_M = \hat{\mu}_M\left(\frac{S_A}{K_A+S_A}\right)\left(\frac{1}{log\left(\frac{[H+]}{10^{-7}}\right)+1}\right)$$ (mg-COD-X_M/mg-COD-S_A/d) Methanogenic archaea growth rate

Summary of microbial process issues:

1. Anaerobic digestion depends on coordination of three trophic groups of microorganisms.
2. The rate determining step depends on digester conditions: carbon substrates, temperature, pH, etc. Often, it is hydrolysis.
3. Metabolite inhibition (especially pH, acetate) can determine process performance. Methanogens need neutral pH.
4. Spatial organization of populations is important, especially SAB and archaea for interspecies metabolite transfer. Flocculant and mixed suspensions favor optimal spatial organization.
5. Speculation that significant hydrogen resides in micro-environment rather than bulk liquid or gas phases and may not be measurable even though it is a substrate.

Example. Anaerobic digester is CSTR, T = 35 C, Q = 3,000 m^3/d, influent is COD_{XS} = 10,000 g/m^3. Overall yield for mixed population, Y = 0.04 g cells produced/g-COD destroyed, 50% of influent COD is destroyed, 70% of the digester gas produced is methane (CH_4) and 30% is CO_2.

Find the rate of methane production in **m^3/day** under steady-state condition.

Steady-state mass balance for COD on digester CSTR:

$0 = COD_{XS,IN} - COD_{XS,OUT} - COD - COD_{CH4,OUT}$

$0 = Q(COD_{XS,IN}) - Q(0.5\ COD_{XS,IN}) - QY(1\text{-}0.5)COD_{XS,IN} - R_{COD\text{-}CH4}$

$R_{COD\text{-}CH4} = Q\ COD_{XS,IN}\ (1 - 0.5\ \text{-}0.02) = 3{,}000(10{,}000)(0.48)$

$= 1.44 \times 10^7$ g-COD-CH_4/day

Assume CH_4 is ideal gas p = 1 atm, T = 35 C.

$$\frac{V}{n} = \frac{RT}{p} = \frac{0.082057(273 + 35)}{1\ atm} = 25.3\ \frac{L}{mole}$$

$$\frac{V}{m} = 25.3 \frac{L}{mole}\left(\frac{1\ mole CH_4}{64 g COD_{CH4}}\right) = 0.4 \frac{L_{CH4}}{g COD_{CH4}}$$

$R_{V,\ COD\text{-}CH4} = 1.44 \times 10^7$ g COD_{CH4}/day (0.4 L_{CH4}/g COD_{CH4})10^{-3} m^3/L

= 5,800 m^3/day CH_4

Total volume of gas produced/d = 5,800/0.7 = **8,200 m^3/day digester gas.**

GENERAL ANAEROBIC DIGESTER PROCESS CHARACTERISTICS

1. Suspended growth, mixed system (CSTR no recycle. Feed rate is too low compared with process volume to bother with batch or semi-batch simulation)
2. Low growth rate and low cell yields for bacteria and archaea, compared with aerobic heterotrophs.
3. Heated: 35 C for mesophilic, 55 C for thermophilic
4. Reducing environment: ORP = -200 to -400 mV
5. Floating cover for gas separation and storage
6. Mixing and heating operation often use same equipment

Typical design parameters for typical mesophilic high rate digester:

$$15 \text{ d} < \Theta = \tau < 20 \text{ d}$$

Process Control:

1. Consistency in sludge feed (primary and secondary fractions) and feed rate. Spikes in COD loading can produce excess acid due to rapid growth of fermenting bacteria.
2. Alkalinity, typically 2 to 5 g-$CaCO_3$/L. Source is biological reactions, but can be added if pH drops too low.

Typical high rate mesophilic digester performance

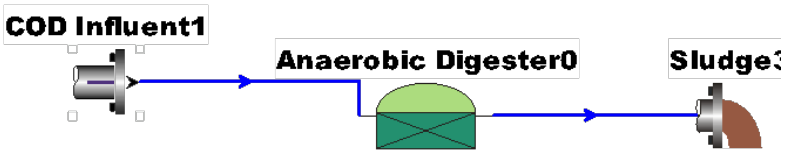
1. Typical TS reduction range = 45 – 50%
2. Typical VS reduction range = 55 – 65%
3. Biogas production $\cong$ 0.5 m^3/kg-COD consumed
4. Methane production $\cong$ 0.35 m^3/kg-COD consumed

BioWin Anaerobic Digester Example

Steady state solution

SRT: 20 days
Temperature: 35.0

Flowsheet



Configuration information for all Anaerobic Digester units

Physical data

Element name	Volume [m3]	Area [m2]	Depth [m]	Head space volume
Anaerobic Digester0	60000	10000.	6.0	20000.

Operating data Average (flow/time weighted as required)

Element name	Pressure	pH
Anaerobic Digester0	103.0	7.0

Element name	Average Temperature
Anaerobic Digester0	35.0

Configuration information for all COD Influent units

Element name	Flow (m^3/d)	COD mg/L	TKN mg N/L	Total P mgP/L		pH	Alk mM	Inorg S.S. mgTSS/L	Ca mg/L	Mg mg/L	DO mg/L
COD in	3000	10000	600.	50.		7.30	10	2000.	160	25.	0.

Anaerobic Digester Effluent,
BioWin Simulation

Water Quality Components	Conc. (mg/L)	Mass rate (kg/d)	Notes
Volatile suspended solids	*2237.18*	6711.53	
Total suspended solids	*4253.85*	12761.54	
Particulate COD	3544.99	10634.98	
Filtered COD	1172.99	3518.96	
Total COD	4717.98	14153.94	
Soluble PO4-P	17.56	52.68	
Total P	50.00	150.00	
Filtered TKN	478.94	1436.82	All NH4-N
Particulate TKN	113.88	341.65	
Total Kjeldahl Nitrogen	592.82	1778.47	
Filtered Carbonaceous BOD	122.13	366.39	
Total Carbonaceous BOD	899.51	2698.52	
Nitrite + Nitrate	0.00	0.00	
Total N	592.82	1778.47	
Total inorganic N	476.72	1430.17	
Alkalinity	16.28	48.83	mmol/L, kmol/d
pH	6.49		A bit low
Volatile fatty acids	134.95	404.85	
Total precipitated solids	0	0.00	
Total inorganic suspended solids	2016.67	6050.01	
Ammonia N	476.72	1430.17	
Nitrate N	0.00	0.00	

Operation and Performance	Value	Units	
Hydraulic residence time	480.00	hours	Compare with
Flow	3000.00	m3/d	Pg 9 example
Gas flow rate (dry)	8368.77	m3/d	8,200 m3/d
Methane content	72.63	%	70%
Carbon dioxide content	26.31	%	30%
Hydrogen content	0.09	%	
Ammonia content	0.46	%	
VSS destruction	44.96	%	50%