ENVE 424
Anaerobic Treatment

Lecture 5
Influence of Environmental/Desing Factors

2012 – 2013 Fall

18 Oct 2012

Assist. Prof. A. Evren Tugtas

Marmara Üniversitesi

Environmental/Desing Factors

1. Temperature
2. Substrates / Nutrients
3. Presence of alternative electron acceptors (SO_4^{2-}, NO_3^-, etc.)
4. pH-Buffer capacity
5. Mixing
6. Solids Retention Time

Environmental factors affect ...

- Specific growth rate
- Decay rate
- Gas production rate
- Substrate utilization rate
- Start-up
- Response to change in input

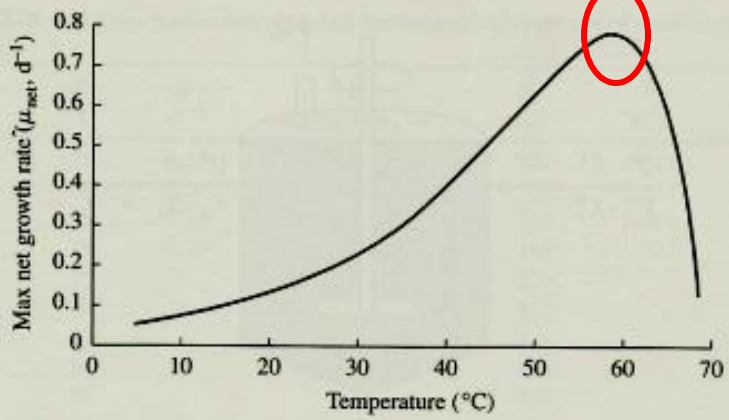
Temperature

- Temperature affects reaction rates
- The most influential environmental factors as it controls the activity of all microorganisms.
- Anaerobic treatment – slow growth rate – significantly affected by the temperature changes
- Growth rates generally double for each 10°C rise in temperature

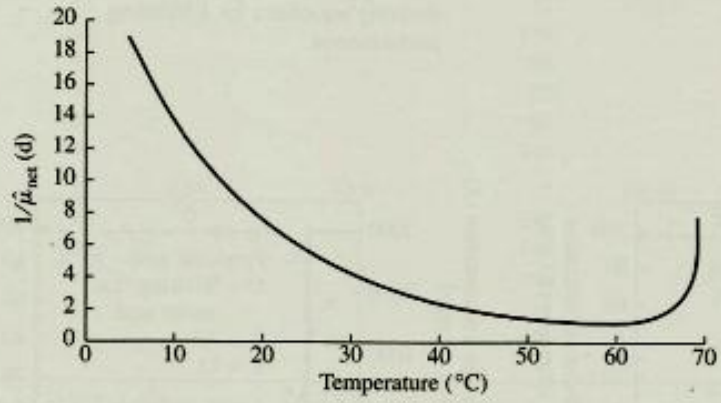
Temperature

- A *rise* in *temperature* leads to an increase in the rate of biochemical and enzymatic reactions within cells, causing *increased growth rates*.
- Above a optimum temperatures, cell decay occurs.

Temperature and Growth



a.



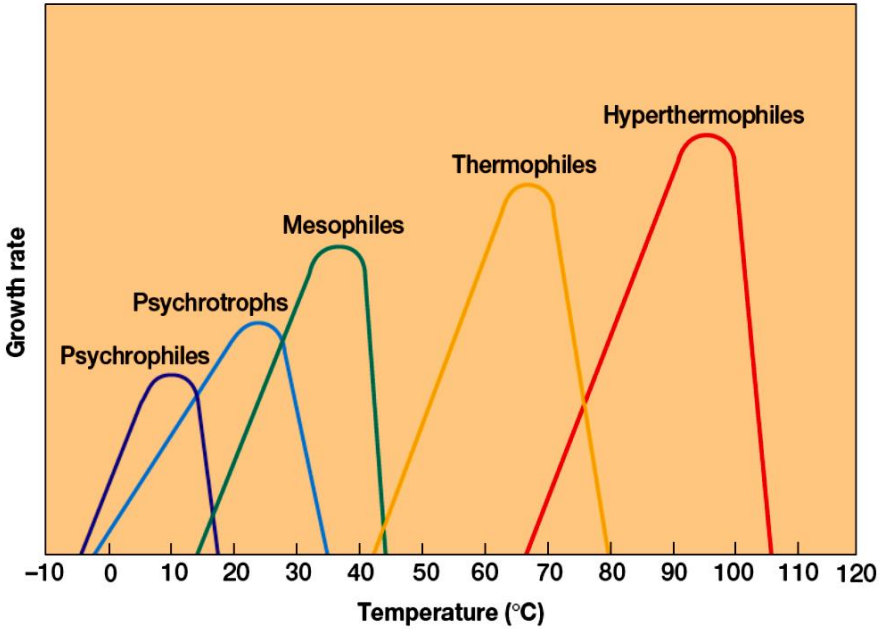
b.

Figure 13.6 Effect of temperature on the maximum growth rate and its reciprocal for volatile acid using methanogenic mixed cultures. SOURCE: Using formulation after Buhr and Andrews, 1977b.

Ref: Rittmann, B. E., McCarty P. Environmental Biotechnology: Principles and Applications. McGraw Hill. 2001.

Classification of Bacteria Based on Temperature

Temperature Class	Normal Temperature Range for Growth (^{o}C)
Psycrophile	-5 – 20
Mesophile	8 – 45
Thermophile	40 – 70
Hyperthermophile	65 - 110

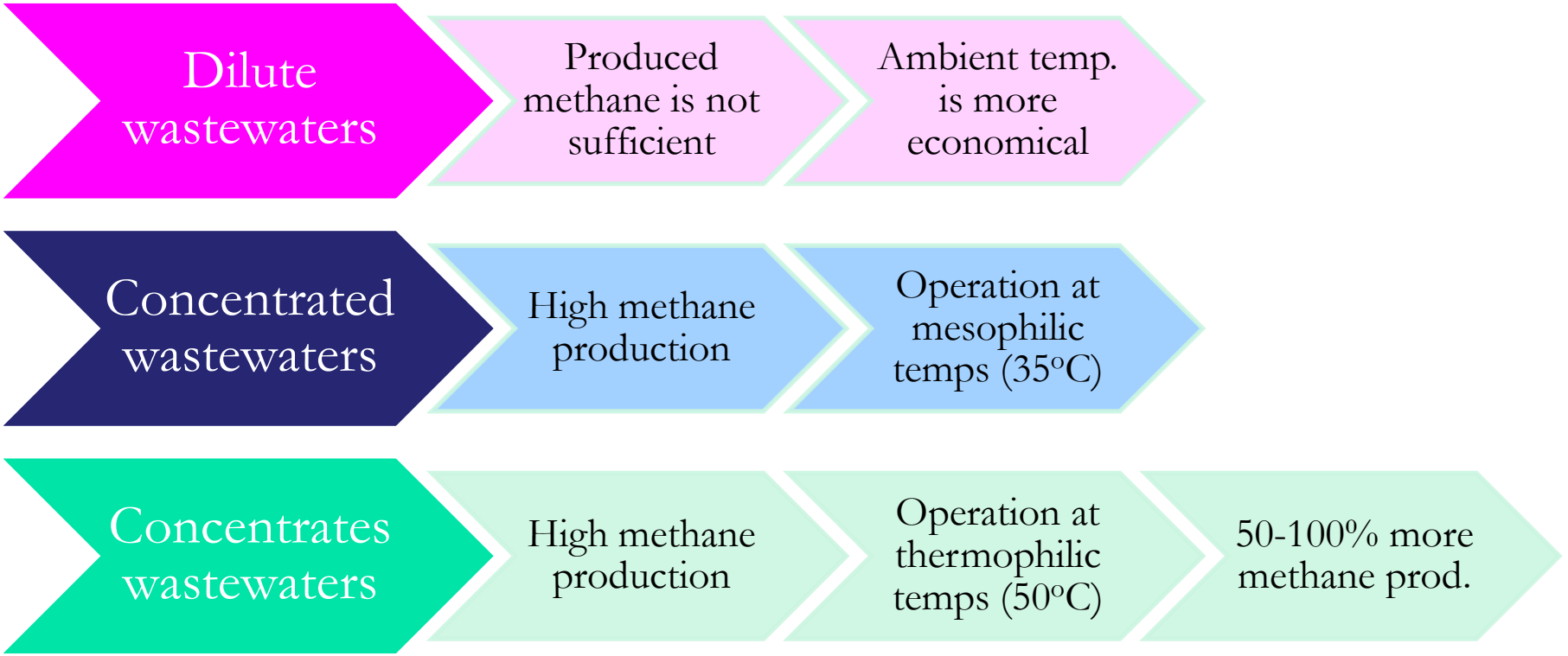


Marmara Üniversitesi

Temperature

- Mesophiles: Growth rates do not change between 35-40^{o}C. However, protein denaturation occurs above 45^{o}C
- Thermophiles do not function well at 35-40^{o}C. Optimum thermophilic temperatures are 55-65^{o}C
- Psychrophilic microorganisms have optimum temperatures of 15-20^{o}C. They are not as efficient as mesophilic and thermophilic AD
- In terms of efficiency psychrophilic<mesophilic<thermophilic

Temperature



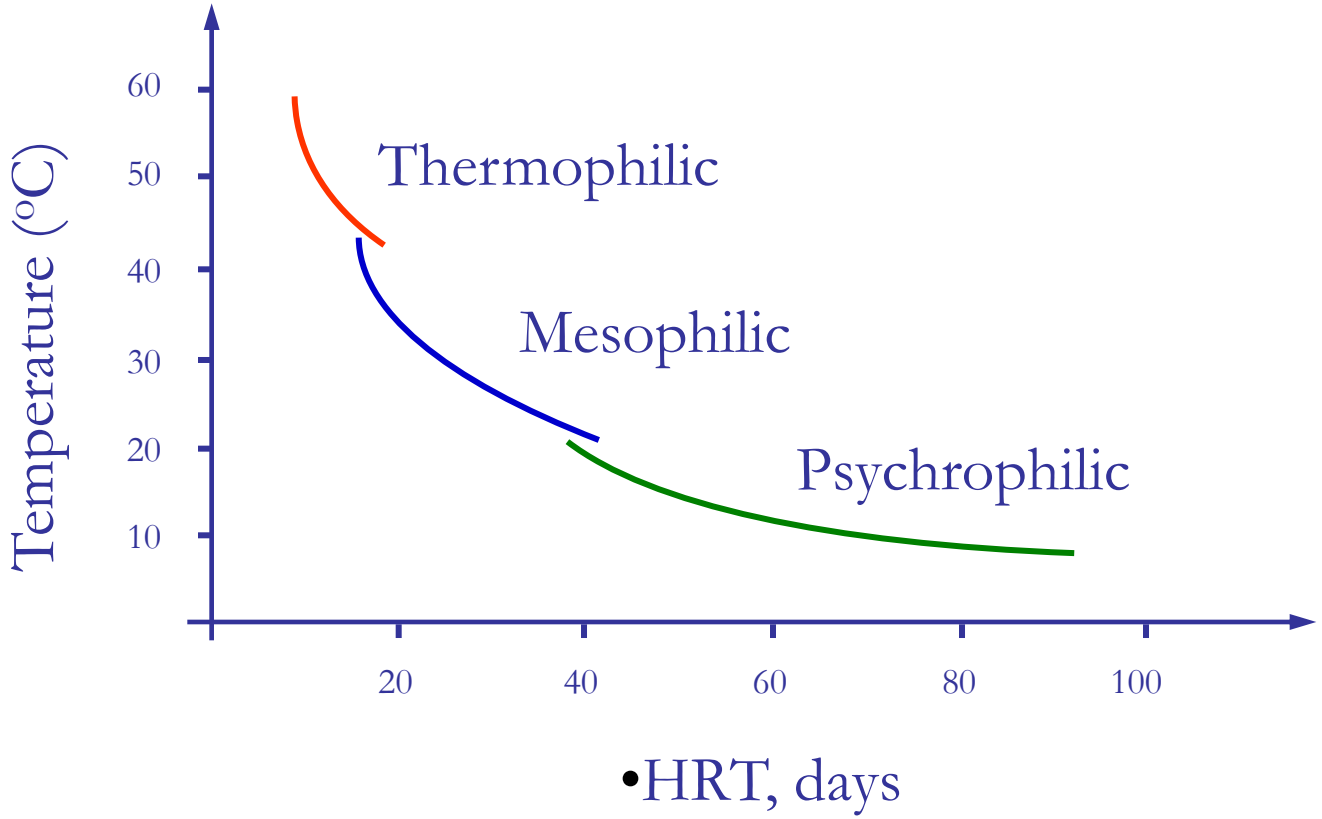
Mesophilic vs Thermophilic

- Thermophilic reactors can accept higher organic loading rates and produce lower quantities of sludge.
- Mesophilic reactors are often more stable.
- Thermophilic reactors require more energy to heat the reactor
- Thermophilic reactors produce high concentrations of VFA in their effluent.
- Thermophilic AD is an attractive option for treating warm industrial effluents and slurries of relatively constant composition.

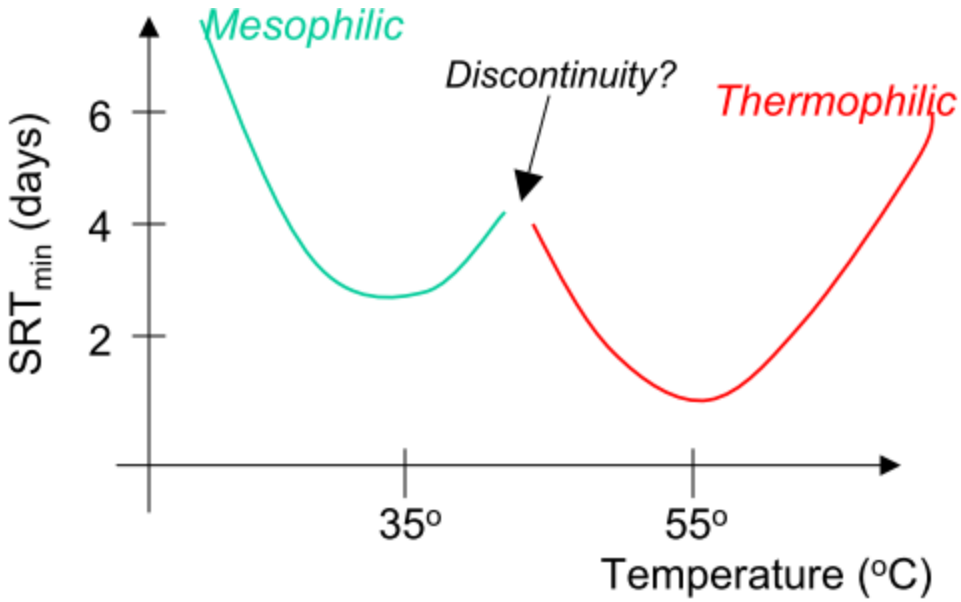
Temperature

- Higher temperature → faster reaction rate → smaller tank volume
- Higher temperatures → greater energy cost → rapid loss in treatment efficiency due to heater failure

Anaerobic Sludge Digestion



Mesophilic vs. Thermophilic



Mesophilic digestion: ~ 35°C (95°F) optimum
Thermophilic digestion: ~ 55 – 60°C (130 – 140°F) optimum

Most municipal digesters are mesophilic, because the energy cost of heating to thermophilic temperatures may be more than the cost savings of being able to use a smaller digester, taking advantage of faster kinetics.

Pathogen de-activation and control may be a plus for thermophilic digestion.

Microbial diversity is lower in thermophilic digesters, which means less stability

Temperature

- The change in rate of a chemical reaction with temperature is expressed with the Arrhenius eqn.

$$\frac{dlnk}{dT} = \frac{E_a}{RT^2}$$

- integrate from T_1 to T_2

$$ln\frac{k_2}{k_1} = \frac{E_a(T_2 - T_1)}{RT_2T_1} \quad \phi$$

$$k_2 = k_1 e^{\phi(T_2 - T_1)} \qquad k_2 = k_1 \phi'^{(T_2 - T_1)}$$

Temperature

Table 13.7 Temperature coefficient ϕ for determining the effect of temperature on various rate constants for anaerobic treatment

Rate Constant	Substrate	ϕ	Temperature Range °C	Reference
$\hat{\mu}$	volatile acids	0.06	15–70	(Buhr and Andrews, 1977)
$\hat{q}$	volatile acids	0.077	15–35	(Lin et al., 1987)
	acetate	0.11	37–70	(van Lier et al., 1996)
	primary sludge	0.035	20–35	(O'Rourke, 1968)
b	volatile acids	0.14	15–70	(Buhr and Andrews, 1977)
	acetate	0.30	37–70	(van Lier et al., 1996)
	primary sludge	0.035	20–35	(O'Rourke, 1968)
K	volatile acids	−0.077	25–35	(Lawrence and McCarty, 1969)
	volatile acids	−0.061	15–35	(Lin et al., 1987)
	primary sludge	−0.112	20–35	(O'Rourke, 1968)

Ref: Rittmann, B. E., McCarty P. Environmental Biotechnology: Principles and Applications. McGraw Hill. 2001.

Temperature

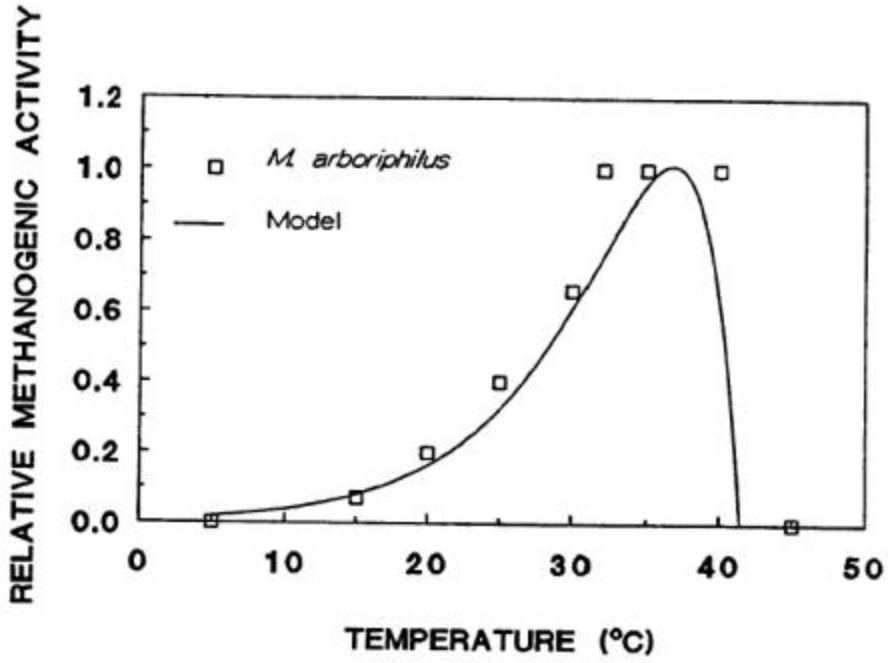
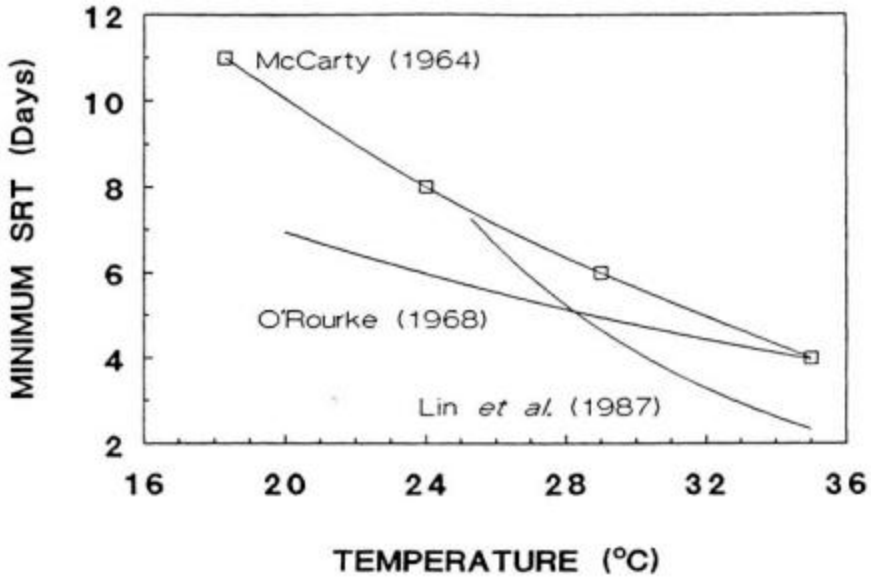


FIGURE 6. Effect of temperature on methanogenic activity: (□) experimental data; line according tc Equation 29 (see text). (Data from Reference 104.)

Pavlostathis and Giraldo-Gomez, 1991



Influence of temperature

- Compared to aerobic processes which are relatively robust to temp. variations, AD is sensitive to sudden temperature fluctuations
- Temp. changes as small as 1-2^{o}C have significant adverse effects on process performance particularly when changes occur rapidly (<2 hrs).
- If bacteria become adversely affected by temperature variations, several days or even weeks may be required to restore a healthy population once again.

Nutrients

- Nutrients supply the basic *cellular building blocks* for growth and ensure the cell is able to *synthesize the enzymes and cofactors* that drive the biochemical and metabolic reactions.
- According to the relative quantities required by the cell, nutrients can be divided into two groups;
  - Macro-nutrients
  - Micro-nutrients

Macronutrients

- Both macro- and micronutrients have to be present in an available form in the growth environment to allow effective uptake.
- Ideally, nutrient levels should be in excess of the optimum concentrations required.
- Anaerobic bacteria can be severely inhibited by even slight nutrient deficiencies.
- Essential nutrients can become toxic when present in high concentrations.

Table 13.3 Nutrient requirements for anaerobic treatment

Element	Requirement mg/g COD	Desired Excess Concentration mg/l	Typical Form for Addition
Macronutrients			
Nitrogen	5–15	50	NH_3, NH_4Cl, NH_4HCO_3
Phosphorus	0.8–2.5	10	NaH_2PO_4
Sulfur	1–3	5	$MgSO_4 \cdot 7\,H_2O$
Micronutrients			
Iron	0.03	10	$FeCl_2 \cdot 4\,H_2O$
Cobalt	0.003	0.02	$CoCl_2 \cdot 2\,H_2O$
Nickel	0.004	0.02	$NiCl_2 \cdot 6\,H_2O$
Zinc	0.02	0.02	$ZnCl_2$
Copper	0.004	0.02	$CuCl_2 \cdot 2\,H_2O$
Manganese	0.004	0.02	$MnCl_2 \cdot 4\,H_2O$
Molybdenum	0.004	0.05	$NaMoO_4 \cdot 2\,H_2O$
Selenium	0.004	0.08	Na_2SeO_3
Tungsten	0.004	0.02	$NaWO_4 \cdot 2\,H_2O$
Boron	0.004	0.02	H_3BO_3
Common Cations			
Sodium		100–200	NaCl, $NaHCO_3$
Potassium		200–400	KCl
Calcium		100–200	$CaCl_2 \cdot 2\,H_2O$
Magnesium		75–250	$MgCl_2$

SOURCE: Speece, 1996.

Ref: Rittmann, B. E., McCarty P. Environmental Biotechnology: Principles and Applications. McGraw Hill. 2001.

Macronutrients: Nitrogen

- A rough estimate of the theoretical amount of macro-nutrients (N, P and S) can be derived from elemental composition of bacterial cells within anaerobic sludge.
- Emprical formula of biomass: $C_5H_7O_2N$ then;
  - 3 - 6 kg N /1000 kg of COD consumed or
  - 0.5 -10 kg N /60 m^3 of CH_4 produced

Macronutrients: Nitrogen

- Most common nitrogen forms; ammonia (NH_3), nitrate (NO_3^-), nitrite (NO_2^-), nitrogen gas (N_2).
- NH_3 is the most readily utilized inorganic forms of nitrogen, existing in the *reduced state* that is required for anabolic metabolism and an uncharged state that facilitates *cellular uptake*.

Macronutrients: Phosphorus

- N:P ratio ~ 7:1 (Recommended)
- Then COD/N/P ratio ~ 300:7:1
- The usual forms of 'P' in aqueous solution include orthophosphate, polyphosphate & organic phosphate.
- The orthophosphates are immediately available for biological metabolism without further modification.
- Organic phosphates must generally be hydrolysed by the cell to release inorganic phosphate before use.

Macronutrients: Sulfur

- In addition to N and P, the sulfur (S) requirement of anaerobic bacteria should also be satisfied and this can be supplied as sulfur, sulfide, sulfite, thiosulfate, sulfate or amino acids (cysteine and methionine).
- Optimum anaerobic digester concentrations of S have been reported between 0.001 and 1.0 mg/l.

Micronutrients

Nutrient	Concentration required (mg/l)	Effects on digestion
Ca	100-200	Granulation and increase in activity
Mg	75-150	Granulation and increase in activity
Na	100-200	Increase in activity
Fe	20-100	Increase in activity and precipitation of sulphide
K	200-400	Increase in activity
Ba	0.01-0.1	Divalent cation effect hence good granulation
Co	20	Vitamin B12 dependent
W	-	Formate dehydrogenase
Se	0.8	Formate dehydrogenase, glycine reductase, hydroxylase, and dehydrogenase dependent
SO_4^{2-}	0.1-10	Sulfur source of cell synthesis

Presence of alternative electron acceptors

- Under anaerobic conditions sulfate (SO_4^{2-}) and sulfite (SO_3^{2-}) is reduced to sulfide (S^{2-}) by SRB.
- The SRB utilize electron-donating substrates present in wastewater for the reduction of sulfate.
- The substrates are either partially oxidized to acetate or fully oxidized to CO_2.

Presence of alternative electron acceptors

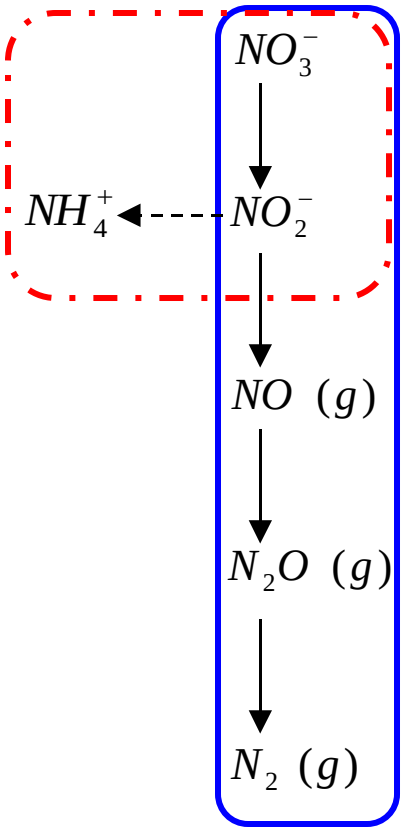
- Sulfate behaves as an alternative electron acceptor to support anaerobic respiration.
- Sulfate redution lower the CH_4 yield per kg organic waste
- Biogas treatment is required to remove corrosive H_2S

Presence of alternative electron acceptors

- Denitrification is an anoxic process in which either an organic or inorganic electron-donating substrates are oxidized at the expense of reducing nitrate (NO_3^-) or nitrite (NO_2^-) to dinitrogen gas (N_2).
- Denitrifiers have the ability to utilize a variety of fermentative/methanogenic substrates therefore these microorganisms compete for the same substrate(s) such as glucose, VFAs and H_2.
- Propionate is the most preferred VFAs as carbon source by denitrifiers.

Nitrate Reduction

Occurs in two distinct pathways:

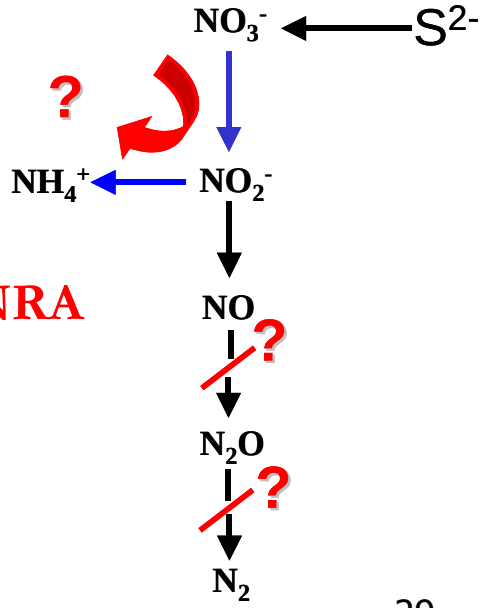


- Dissimilatory nitrate reduction to nitrogen gas (Denitrification)
- Dissimilatory nitrate reduction to ammonia *(DNRA)*
- Denitrification is the dominant pathway in engineered systems

However,

- Low redox potential
- Presence of sulfide
- High COD/N ratios

} **favor DNRA**



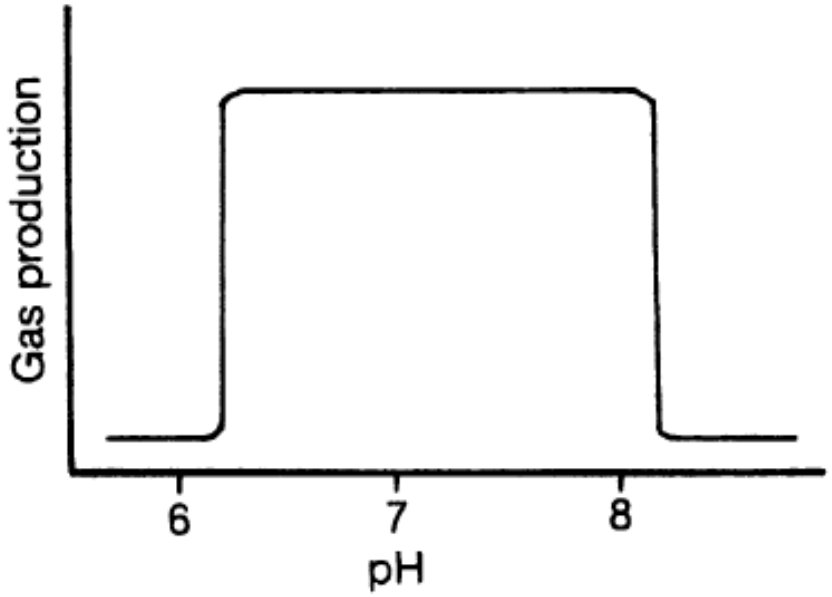
Marmara Üniversitesi

pH-Buffer capacity

- For an efficient methanogenic digestion a suitable and stable pH has to be maintained within the digester.
- pH has critical influences on;
  - Microorganisms (esp. Methanogens) responsible for AD
  - Biochemistry of AD process
  - Alkalinity buffering and
  - Chemical reactions affecting the solubility and availability of dissolved ions.

Effect of pH

- Best pH range appears to be around neutrality, while 6.5-8.0 is generally believed to be optimal.



•The effect of pH on biogas production.

pH and Alkalinity

Optimum pH 6.6 – 7.6 (lethal < 6.0)

Because typical p_{CO2} in gas is 0.25 – 0.40, there must be sufficient bicarbonate alkalinity to allow pH to remain in neutral range:

$$K_1 = \frac{[HCO_3^-]\,[H^+]}{[HCO_3^*]} = 10^{-6} \text{ @ } 38^oC \text{ and } I = 0.2$$

$[HCO_3^*] = K_H\, p_{CO2}$ where K_H = Henry's law constant = 0.0246 mole/L-atm @ 38°C and I = 0.2

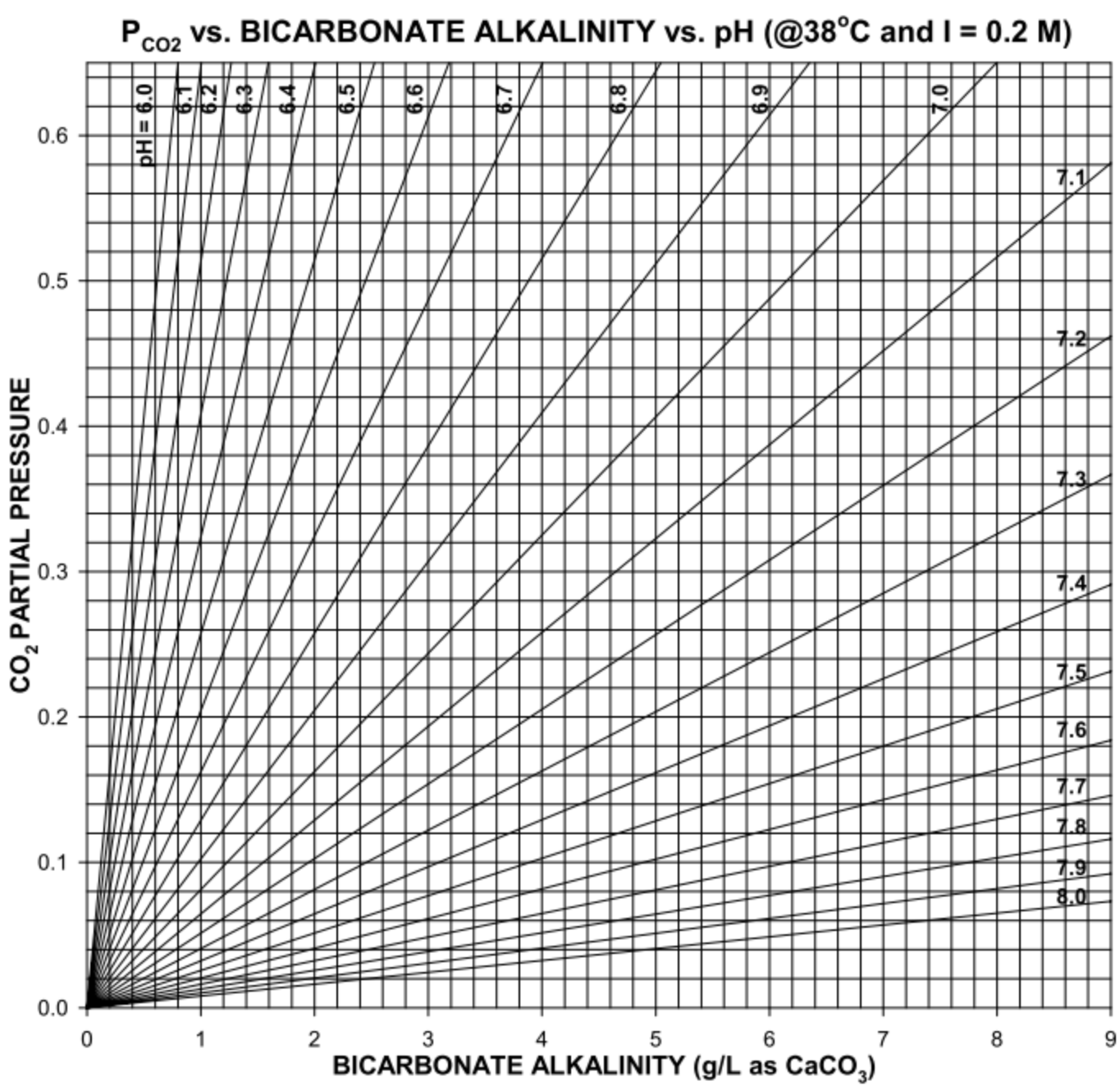
$$[H^+] = \frac{K_1\, K_H\, p_{CO2}}{[HCO_3^-]}$$; Between pH 6 and 8, [Alk] (eq/L) ≈ $[HCO_3^-]$

NOTE: For the pH range of interest (pH 6 to 8), buffering capacity of volatile fatty acids and ammonia are negligible. Also, the concentrations of orthophosphoric and hydrosulfuric acid systems are too low to provide significant buffering capacity.

Therfore: $[H^+] \approx \frac{K_1\, K_H\, p_{CO2}}{[BAlk]}$ where [BAlk] = bicarbonate alkalinity only

Substitute K_1 and K_H: $[H^+] \approx \frac{1.23 \times 10^{-3}\, p_{CO2}}{BAlk}$ for pH = 6 – 8

where: p_{CO2} = atm and BAlk = mg/L as $CaCO_3$



Based on (@ 38°C and I = 0.2 M):

$K_H = [H_2CO_3^*]/P_{CO2} =$

$= 2.46 \times 10^{-2}$ moles/L-atm

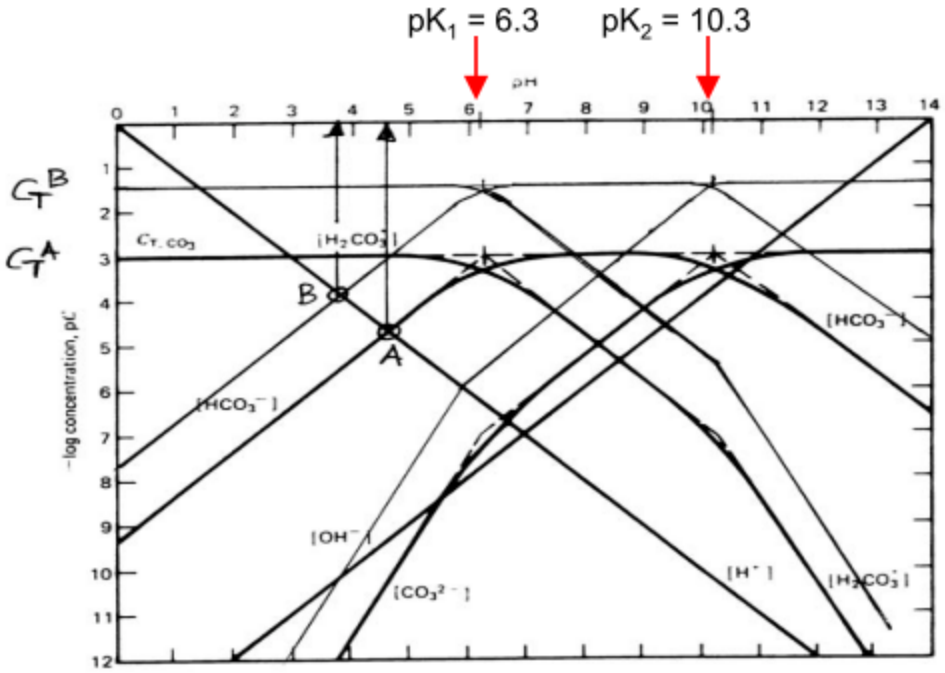
$K_1 = \{[H^+]\ [HCO_3^-]\}/[H_2CO_3^*] = 10^{-6}$

$BAlk = 1.23 \times 10^{-3}\ (P_{CO2}/10^{-pH})$

where BAlk: mg/L as $CaCO_3$

P_{CO2}: atm

The normal end-point in an alkalinity titration (CO_2 equivalent point) for digester liquor is approx. pH 4.0 (it is actually a function of C_T)



Proton Condition:

$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

or for pH < 7 ==> $[H^+] \approx [HCO_3^-]$

But at this end-point, some of the VFAs will have been titrated (e.g., pK_a for acetic acid is approx. 4.5, corrected for ionic strength).

Bicarbonate alkalinity is calculated as:

BAlk ≈ Total Measured Alk – (0.85) (0.833) (VFA)

(mg/L as $CaCO_3$) (mg/L as $CaCO_3$) (mg/L as acetic acid)

where: 0.85 ≈ 85% of VFAs titrated by pH 4.0

0.833 = conversion factor (50/60); (50 mg/L $CaCO_3$/meeq; 60 mg/mmole acetic acid

pH Control

When digesters become "upset" it is usually because methanogens and some fermenters of short-chain VFAs are inhibited. Thus, VFAs build up and bicarbonate alkalinity is destroyed:

$$HAc + HCO_3^- \rightarrow H_2CO_3^* + Ac^-$$

Total measured alkalinity may not decrease much because VFAs get partially measured as total alkalinity.

When VFAs build up, pH drops and it can cause further problems if it gets below 6 – 6.5.

Several techniques can be used to control pH, such as:

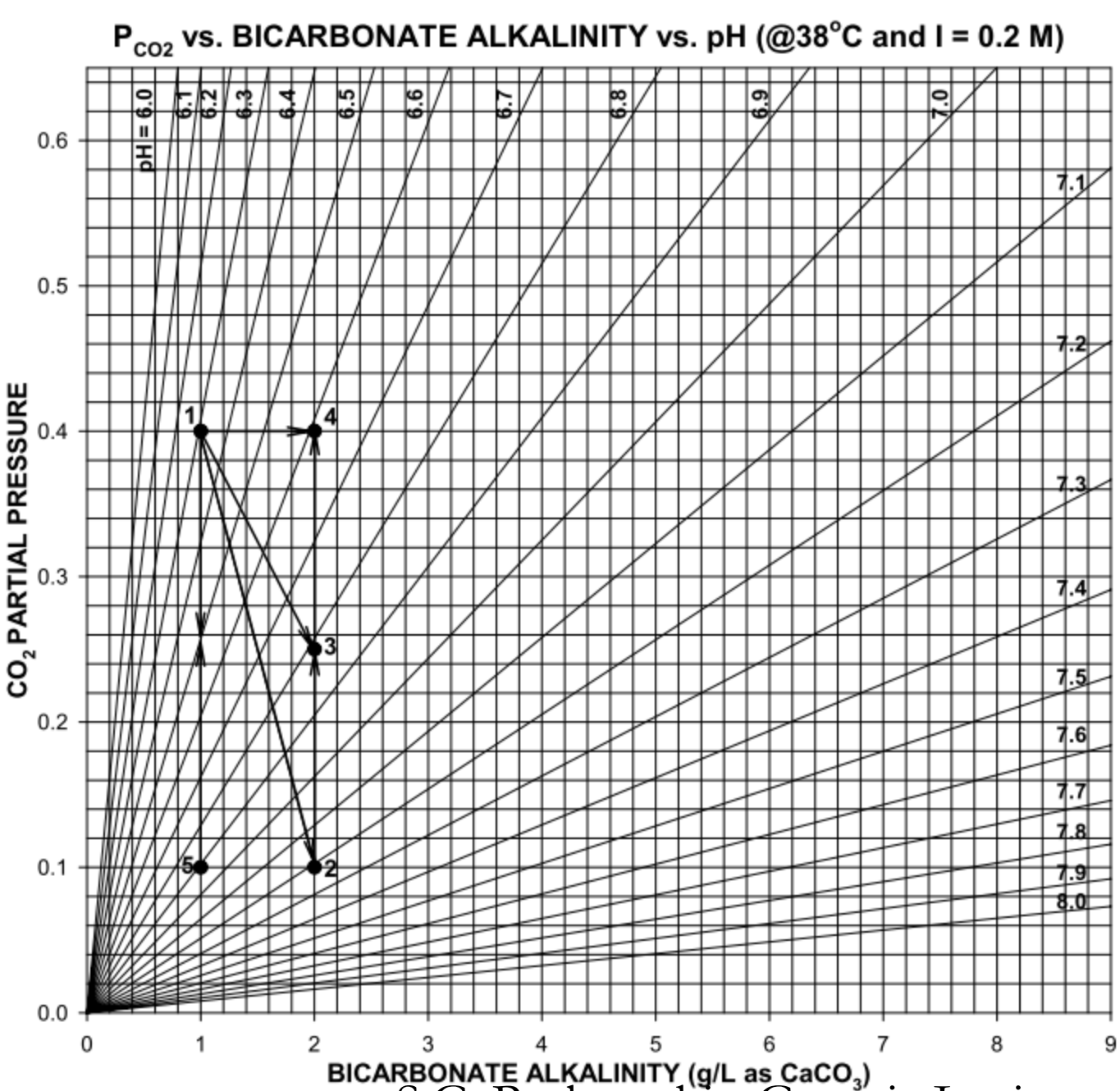
- Addition of strong bases to the digester mixed liquor
- Addition of bicarbonates and carbonates to the digester mixed liquor
- Removal of carbon dioxide from the digester gas

If a strong base (e.g., NaOH or NH_3) or a carbonate salt (Na_2CO_3) is added, ionic equilibrium occurs very rapidly and CO_2 is removed from the gas phase to form the required bicarbonate alkalinity:

$$NaOH + CO_2 \rightarrow NaHCO_3$$

$$Na2CO3 + CO2 + H2O \rightarrow 2NaHCO_3$$

The effect of each pH control technique can better be understood by use of the p_{CO2} vs. BAlk vs. pH diagram.



pH Control Strategies

1. Addition of strong base:
   points 1-->2, then -->4
   Addition of carbonate salt:
   points 1-->3, then -->4
   Addition of bicarbonate salt:
   points 1-->4

2. CO_2 scrubbing:
   points 1-->5, then -->1

Reactions affecting pH

- Four major chemical and biochemical reactions that influence the pH of an AD are:
  - Ammonia (NH_3) consumption and release
  - Volatile fatty acid production and consumption
  - Sulfide (S^{2-}) release by dissimilatory reduction of sulfate (SO_4^{2-}) or sulfite (SO_3^{2-})
  - Conversion of neutral carbonaceous organic carbon to methane (CH_4) and carbon dioxide (CO_2)

Controlling the pH

- In AD, pH reduction can be countered by formation of bicarbonate alkalinity and consumption of VFAs by methanogens.
- Consumption of VFAs is dependent on the equilibrium between rapid growing acidogens and slow growing methanogens.
- This equilibrium can be easily upset by changes in the operational or environmental conditions.

Controlling the pH

- If the balance is disturbed and therefore pH starts to drop because of VFAs accumulation.
  - Stop feeding the reactor to give the methanogens sufficient time to consume excess VFAs and raise the pH value to an acceptable level. OR
  - Dose the reactor with alkali, i.e. NaOH, Na_2CO_3 or $NaHCO_3$ in order to raise the pH or provide additional buffering capacity.
- In some cases both options are used simultaneously.

Controlling the pH

- The amount of alkalinity required to accommodate VFA increases in AD depends on many factors.
- Well- established anaerobic reactors treating typical organic loads are likely to contain alkalinity in the range 2000 to 3000 mg/l as $CaCO_3$.
- This level of alkalinity will impart an improved resistance to acidification caused by short-term fluctuations in feed composition.

pH Control

Two kinds of chemicals for pH control:

a) Those which add bicarbonate alkalinity directly

b) Those which trap CO_2 and convert it to bicarbonate

The choice of the chemical to be added to a digester for pH control should be based on two factors:

1) Type of effect that the chemical has upon the system: Chemicals that trap CO_2, make the pH overshoot the desired value because of the time lag associated with CO_2 equilibrium. If the chemical dose is large, pH could rise to very high values, causing inhibition. Bicarbonate salts have no such effects on pH and pH control can be achieved more precisely.

2) Chemical solubility: For example, Na-salts are more soluble than Ca-salts

Lime [$Ca(OH)_2$] is often added for pH control:

$$Ca(OH)_2 + 2CO_2 \rightarrow Ca_2^{+} + 2HCO_3^{-}$$

Initial additions of lime increases bicarbonate alkalinity and decrease pCO2, which cause the pH to rise initially. However, there is an equilibrium relationship between HCO_3^- and CO_3^{2-} that is pH-dependant, and that $CaCO_3$ is very insoluble. For a digester with 500 to 1000 mg/L BAlk, once the pH has been raised to approx. 6.5 – 6.8, the solubility of CaCO3 will be exceeded with further lime addition:

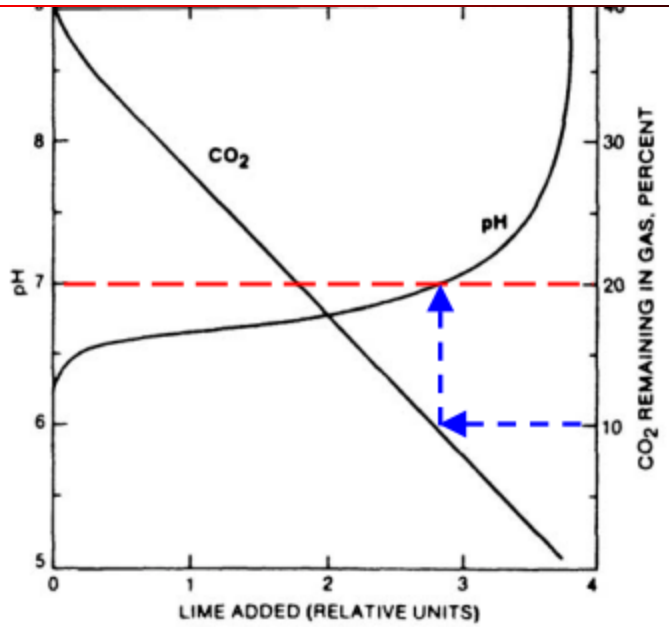
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow$$

pH Control

Another way of looking at the effect of adding lime beyond this point is:

$Ca(OH)_2 + CO_2 \rightarrow \underline{CaCO_3}\downarrow + H_2O$

All that happens when lime is added beyond the solubility point of $CaCO_3$ is that the CO_2 content of the digester gas decreases, but no increase in soluble bicarbonate alkalinity occurs, and very little pH increase is achieved. pH remains between 6.5 – 7.0 until p_{CO2} has dropped to ~ 10%, then pH shoots up.



NOTE: you should not try to reach pH = 7; be satisfied with pH 6.5 – 6.7. As the pH shoots up to 8.9 or so, then organisms produce CO_2 that drops the pH down to 6.5 (even without VFA production!). Then, the operator adds more lime, etc., etc. and the digester get "concreted" with $CaCO_3$.

Suggestion: Do not add lime inless the pH drops below 6.5, and only add enough to reach pH ~ 6.7.

Another problem: in case of lime overdose, CO_2 consumption can lead to vacuum in the digester head space, O_2 can leak in resulting in an explosive CH_4/O_2 mixture → Explosion!

$NaHCO_3$ is easier to use (better control), but more expensive. It does not consume CO_2, and cannot raise the pH > 8.5.

Mixing

- AD comprises an inherent degree of mixing from the continuous rise of biogas bubbles within the reactor,
- This mixing is not sufficient for efficient mass transfer.
- Mixing enhances the AD process by distributing microorganisms, substrate, and nutrients throughout the digester as well as equalizing temperature.
- Mixing also provides for rapid hydrolysis of wastes by allowing the hydrolytic bacteria to attack a much larger surface area

Types of Mixing

- The level and type of mixing also affects;
  - Growth rate and distribution of bacteria within the sludge
  - Substrate availability and utilization rates
  - Granule formation and
  - Biogas production.
- Mixing can be enhanced using;
  - Mechanical devices (paddles, turbines and propellers)
  - Hydraulic shear force (feed recycle)
  - Biogas recirculation

Advantages of Mixing

- Eliminating or reducing scum build-up
- Eliminating thermal stratification or localized pockets of depressed temperature
- Maintaining digester sludge chemical and physical uniformity throughout the tank
- Rapid dispersion of metabolic wastes (products) produced during substrate digestion
- Rapid dispersion of any toxic materials entering the tank (minimizing toxicity)
- Prevent deposition of grit

Excessive Mixing

- Excessive mixing may lead to a reduction in reactor performance by disrupting the flocs and granules containing active anaerobic microorganisms.
- Result in short-circuiting of the reactor, leading to unconverted substrate appearing in the reactor effluent.
- Lead to the formation of smaller flocs, which have poor settling characteristics.
- The kind of mixing equipment and amount of mixing varies with the type of reactor and the solids content in the digester.

Solids Retention Time

- Solid retention time controls the types of microorganisms that can grow in a system
- Very stable reactor operation can be obtained in some anaerobic digestors with long SRT

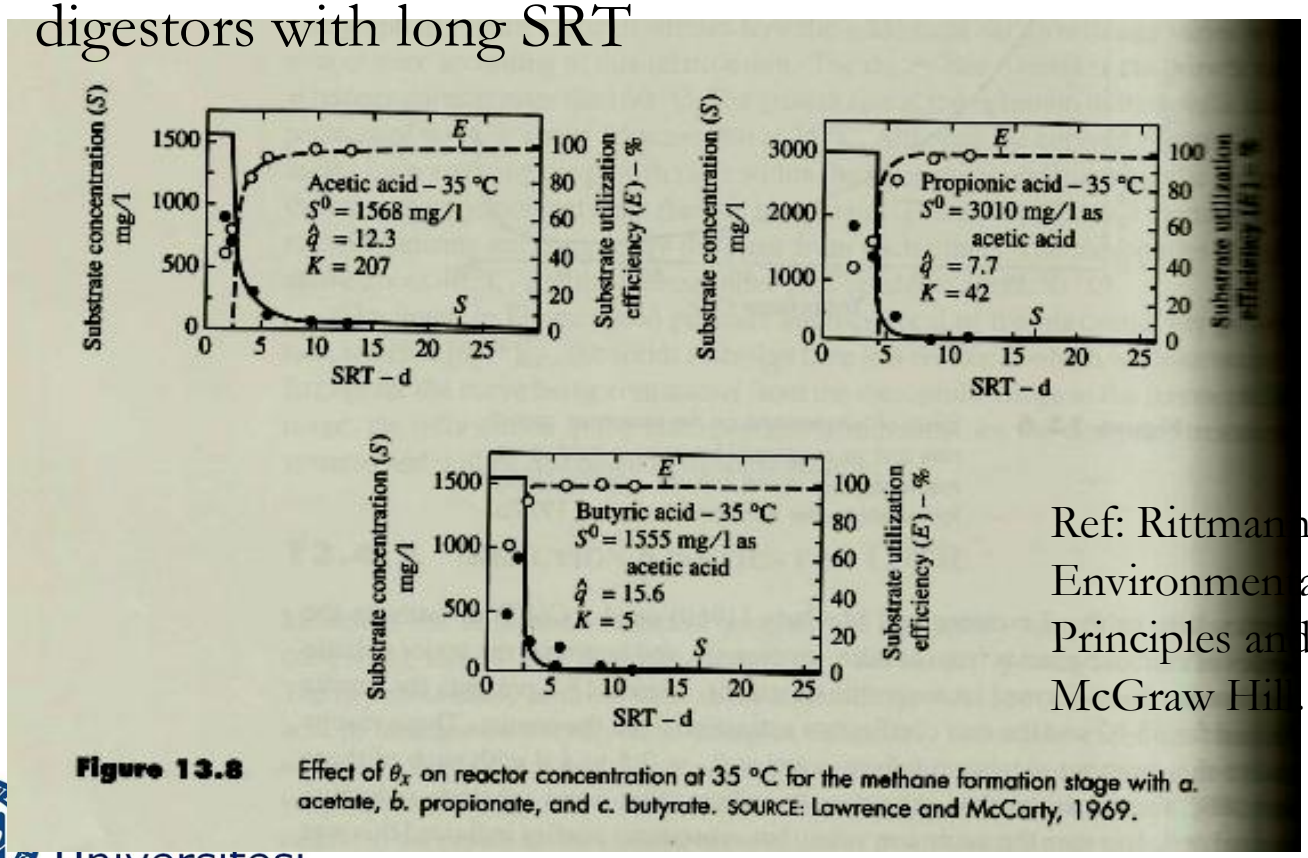


Figure 13.8 Effect of θ_x on reactor concentration at 35 °C for the methane formation stage with a. acetate, b. propionate, and c. butyrate. SOURCE: Lawrence and McCarty, 1969.

Ref: Rittmann, B. E., McCarty P. Environmental Biotechnology: Principles and Applications. McGraw Hill, 2001.

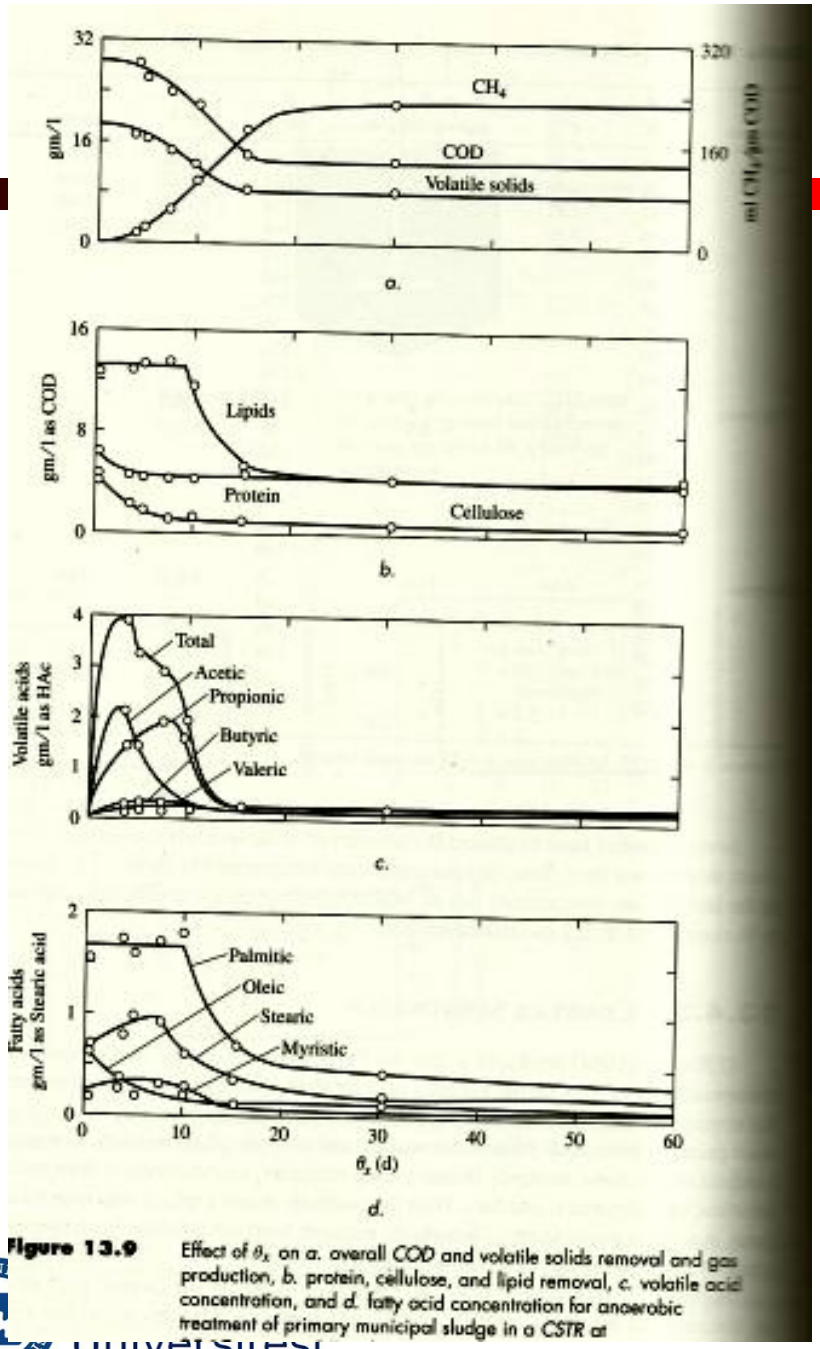


Figure 13.9 Effect of θ_x on *a.* overall COD and volatile solids removal and gas production, *b.* protein, cellulose, and lipid removal, *c.* volatile acid concentration, and *d.* fatty acid concentration for anaerobic treatment of primary municipal sludge in a CSTR at

Ref: Rittmann, B. E., McCarty P. Environmental Biotechnology: Principles and Applications. McGraw Hill. 2001.