

**Anaerobic processes
Toxic & recalcitrant organic
compound removal**

Anaerobic fermentation & oxidation

- **Applications**

- Treatment of waste sludge & high-strength organic wastes
- Pretreatment step for conventional biological treatment

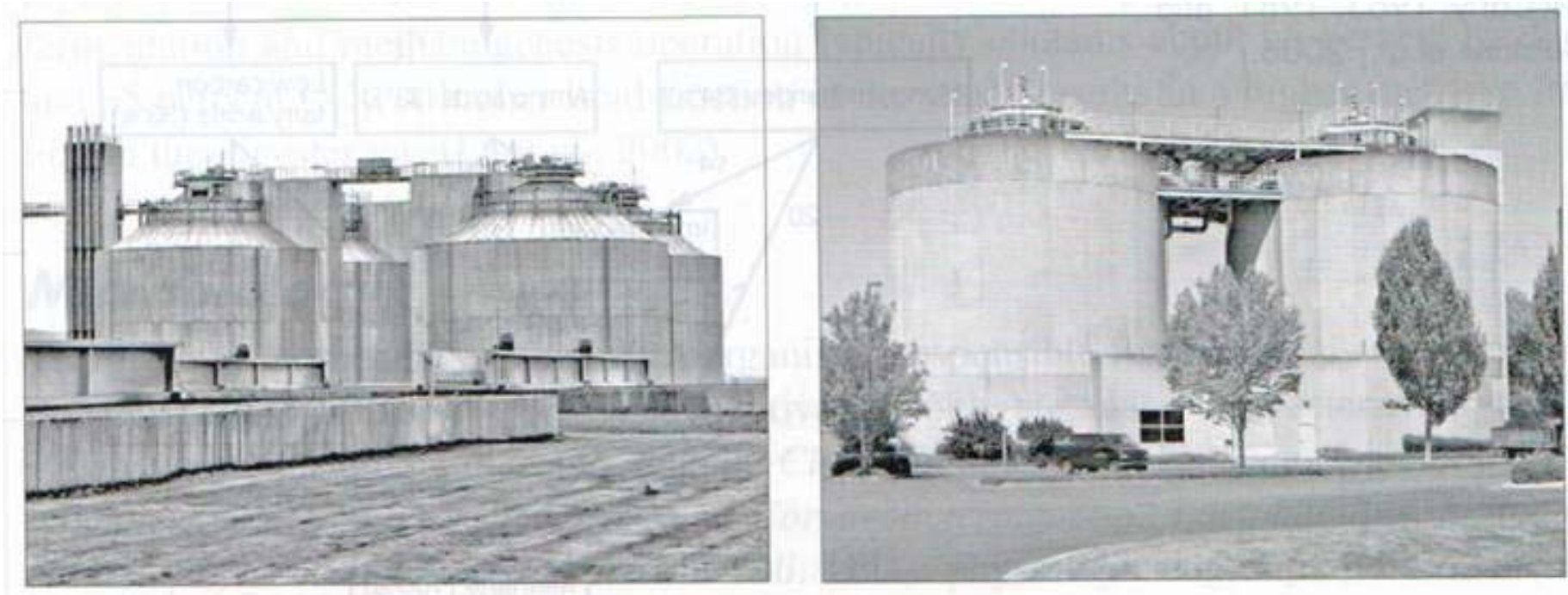
- **Advantage**

- Low biomass yield
- Energy production in the form of methane (of recent interest!)
 - WWTP -- ~3% of total energy cost in USA
 - Target on energy positive treatment of wastewater

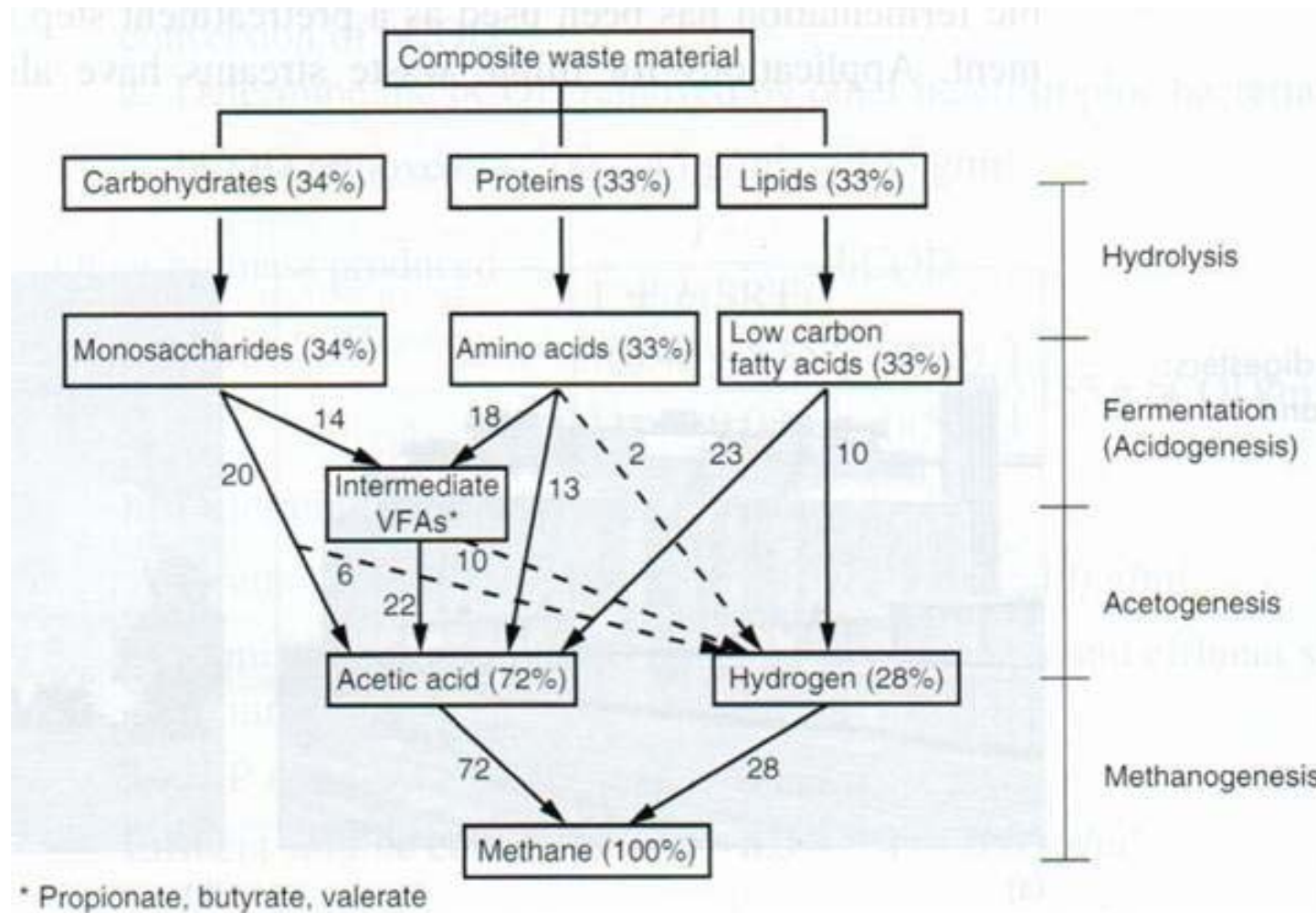
- **Disadvantage**

- Effluent quality usually not as good as aerobic treatment

Anaerobic fermentation & oxidation



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Anaerobic fermentation & oxidation

- **Hydrolysis**

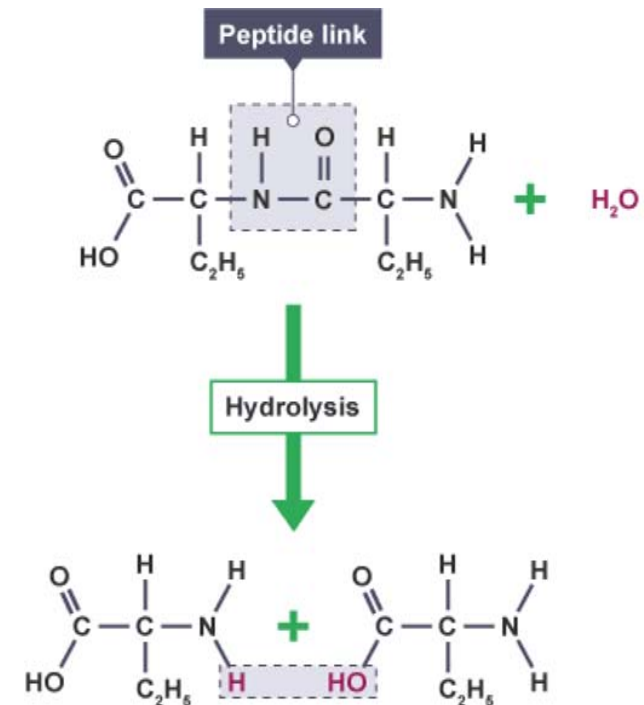
- Particulates - - - - → Soluble molecules - - - - → Monomers
- By extracellular enzymes

- **Acidogenesis (fermentation)**

- Use: sugars, amino acids, fatty acids (both e- donor & acceptor)
- Produce: VFAs, CO₂, H₂

- **Acetogenesis**

- Use: VFAs other than acetate
- Produce: acetate, H₂, CO₂



Anaerobic fermentation & oxidation

- **Methanogenesis**

- By methanogens (belongs to domain Archaea)
- Two groups of methanogens
 - *acetoclastic* methanogens: acetate \rightarrow CH₄ + CO₂
 - *hydrogenotrophic* methanogens: H₂ + CO₂ \rightarrow CH₄
- In anaerobic digestion process, ~72% methane from acetic acid & ~28% from H₂ (\rightarrow gas production of ~65% CH₄ & ~35% CO₂)

- **Syntrophic relationship**

- Methanogens – acidogens & acetogens
 - Acidogens & acetogens: produce H₂, acetate, etc.
 - Methanogens: cleans up the acido/acetogenesis end products
- “*Interspecies hydrogen transfer*”

Process kinetics

- Low yield coefficients
 - Low energy gain by chemical transformation
 - Fermentation: $Y \sim 0.06 \text{ g VSS/g COD}$; $b \sim 0.02 \text{ d}^{-1}$
 - Methanogenesis: $Y \sim 0.03 \text{ g VSS/g COD}$; $b \sim 0.008 \text{ d}^{-1}$
- Consider two steps :
 - Hydrolysis
 - Soluble substrate utilization for fermentation and methanogenesis
 - Methanogenesis usually slower than fermentation
 - Hydrolysis or methanogenesis a rate limiting step
- High SRT is needed (around 40 d) due to slow degradation rate

Process stability

- Kinetics of VFA production is faster than utilization (methanogenesis)
- At steady state, sufficient methanogen population is established to maintain low VFA concentration ($<200 \text{ g/m}^3$) & $\text{pH} \geq 7.0$
- Unstable digester operation may develop under transient loading conditions (VFA production $>$ utilization): VFA accumulation & pH drop
- Low pH leads to decline in methanogenic activity: process failure
- Methanogenic inhibition can also occur by acetate accumulation (acetate conc. $> 3000 \text{ g/m}^3$)

Toxic & recalcitrant organic cmpd removal

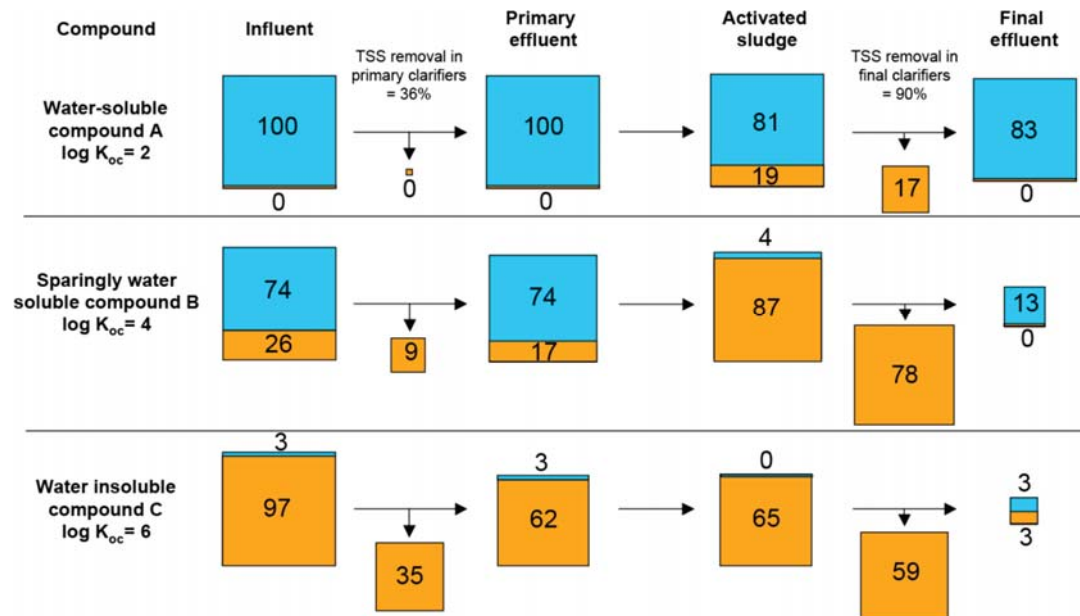
- **Xenobiotic compounds: man-made**
 - Many are resistant to biodegradation and have potential toxicity to ecosystem & human health
- **Refractory, recalcitrant – not easily biodegradable**
- Some specific microorganisms may have the ability to degrade toxic and recalcitrant compounds

Examples of toxic & recalcitrant organics

Type of waste	Types of organic compounds
Petroleum	alkanes; alkenes; polyaromatic hydrocarbons; monocyclic aromatics – benzene, toluene, ethylbenzene, xylenes; naphthenes
Non-halogenated solvents	alcohols; ketones; esters; ethers; aromatic and aliphatic hydrocarbons; glycols; amines
Halogenated solvents	chlorinated methanes – methylene chloride, chloroform, carbon tetrachloride; chlorinated ethenes – tetrachloroethene, trichloroethene; chlorinated ethanes – trichloroethane; chlorinated benzenes
Insecticides, herbicides, fungicides	organochloride compounds; organophosphate compounds; carbamate esters; phenyl ethers; creosotes; chlorinated phenols
Munitions and explosives	nitroaromatics – trinitrotoluene; nitramines; nitrate esters
Industrial intermediates	phthalate esters; benzene; phenol; chlorobenzenes; chlorophenols; xylenes
Transformer and hydraulic fluids	polychlorinated biphenyls
Production byproducts	dioxin, furans

Abiotic losses

- May be significant for many toxic & recalcitrant compounds
- Adsorption to biomass in secondary treatment
 - Removed from wastewater as sludge
 - Issues with sludge application and disposal
- Volatilization: released to the atmosphere



Fate of non-biodegradable and non-volatile organic compounds during conventional wastewater treatment

Heidler & Halden (2008) ES&T 42:6324-6332.