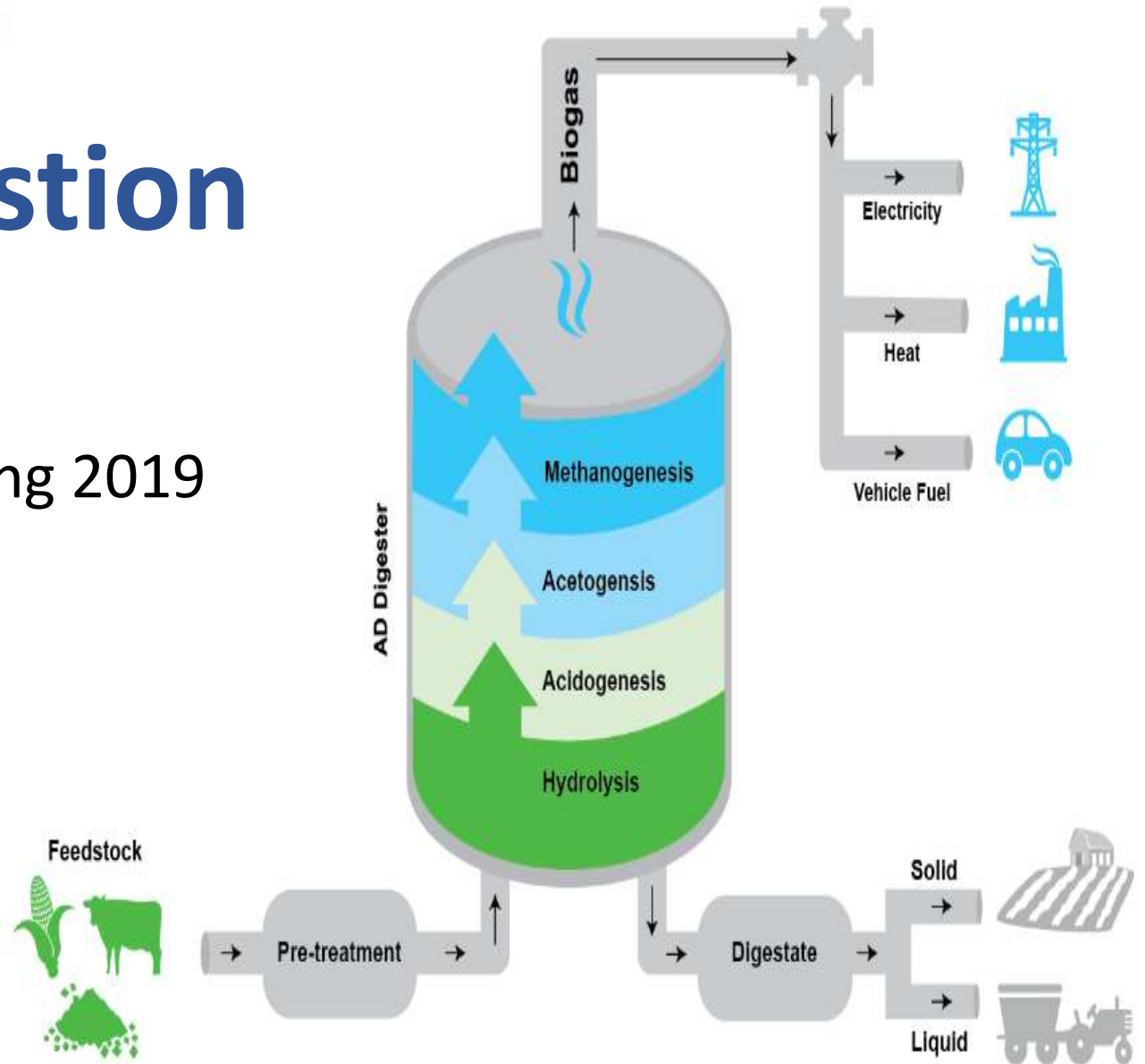


Basics of Anaerobic Digestion

ABC UW-OshKosh Operator Training 2019
OshKosh, WI
June 10-14

Bernie Sheff, PE



Biological Process

Natural and Engineered Process

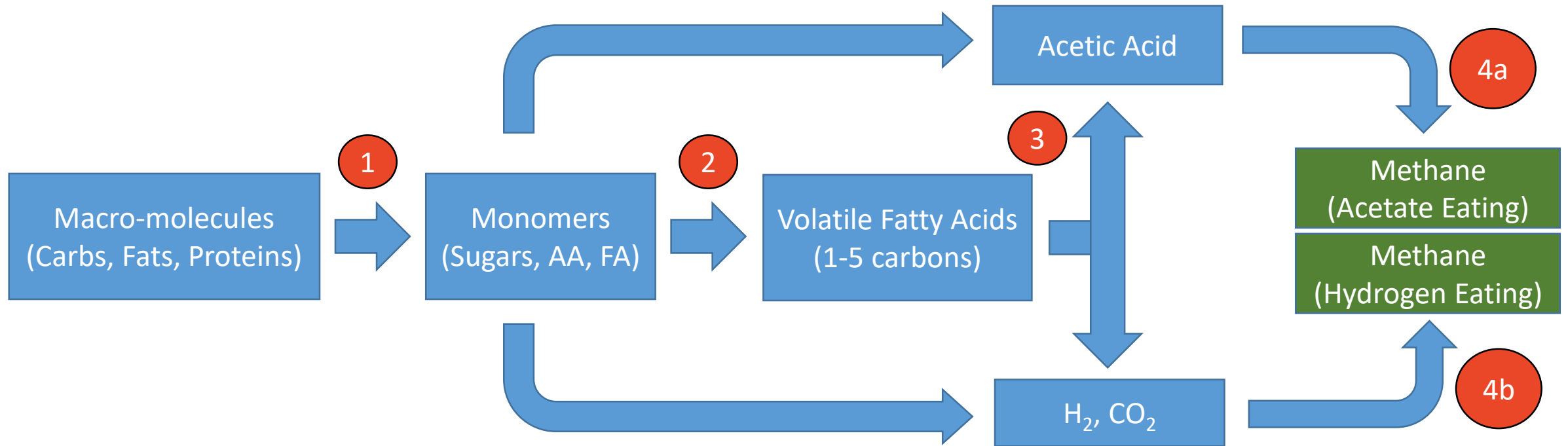


Natural Systems: Swamp; Manure Lagoon



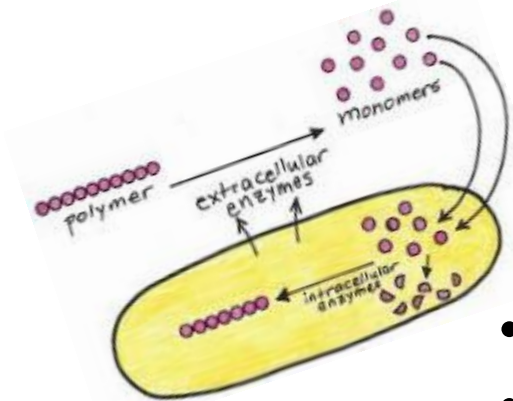
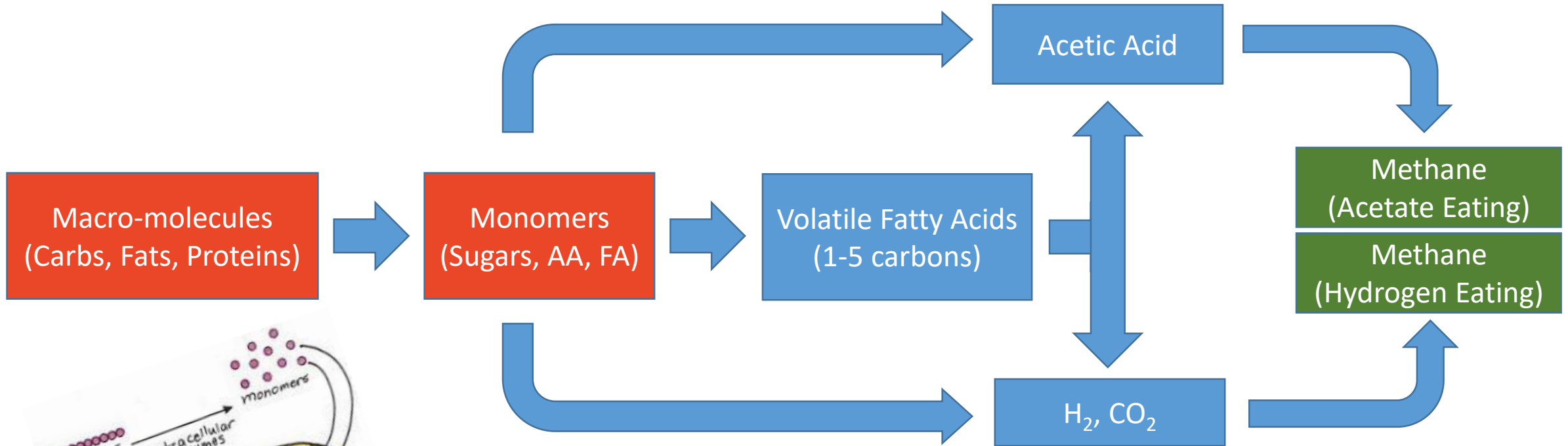
Engineered Systems: Mixed-plug flow;
Complete-Mix; Covered Lagoon

Anaerobic Digestion: 4-Step Process



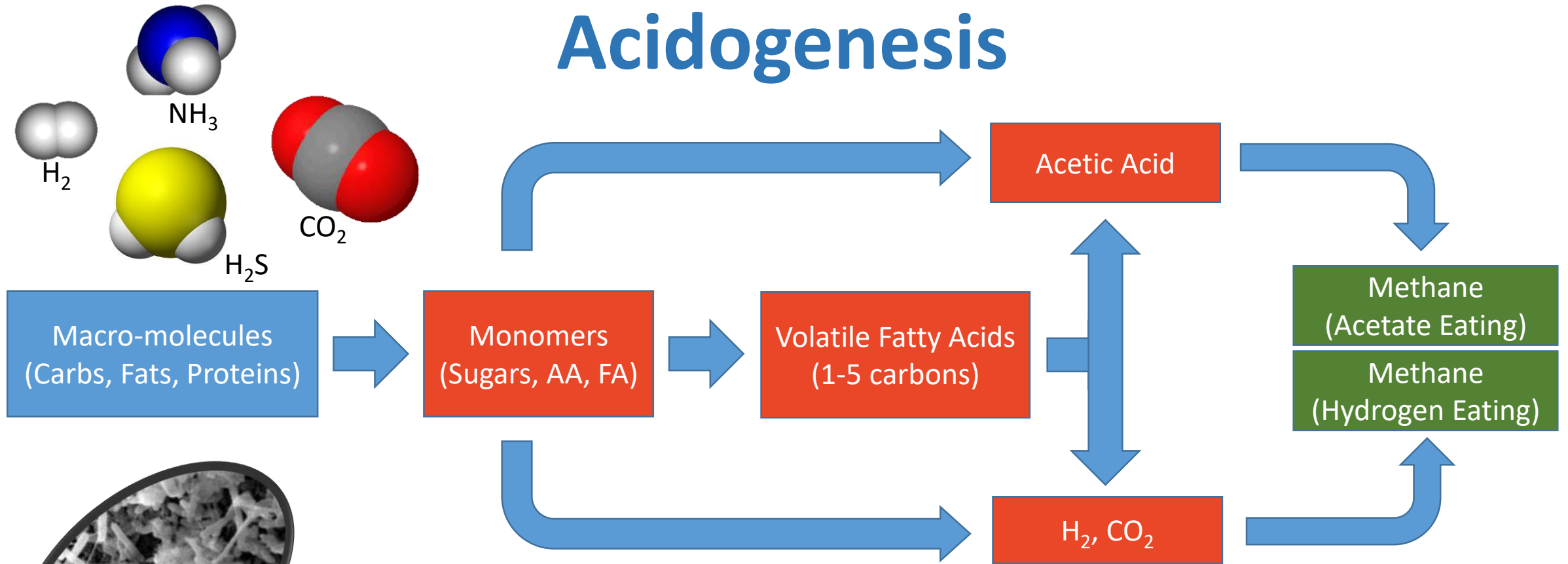
① Hydrolysis ② Acidogenesis ③ Acetogenesis ④ Methanogenesis

Hydrolysis



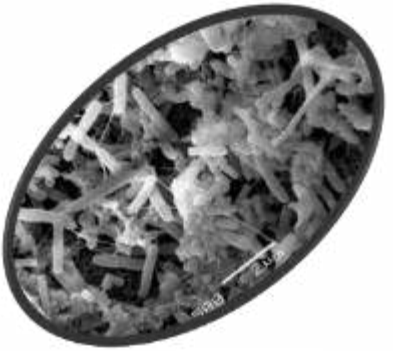
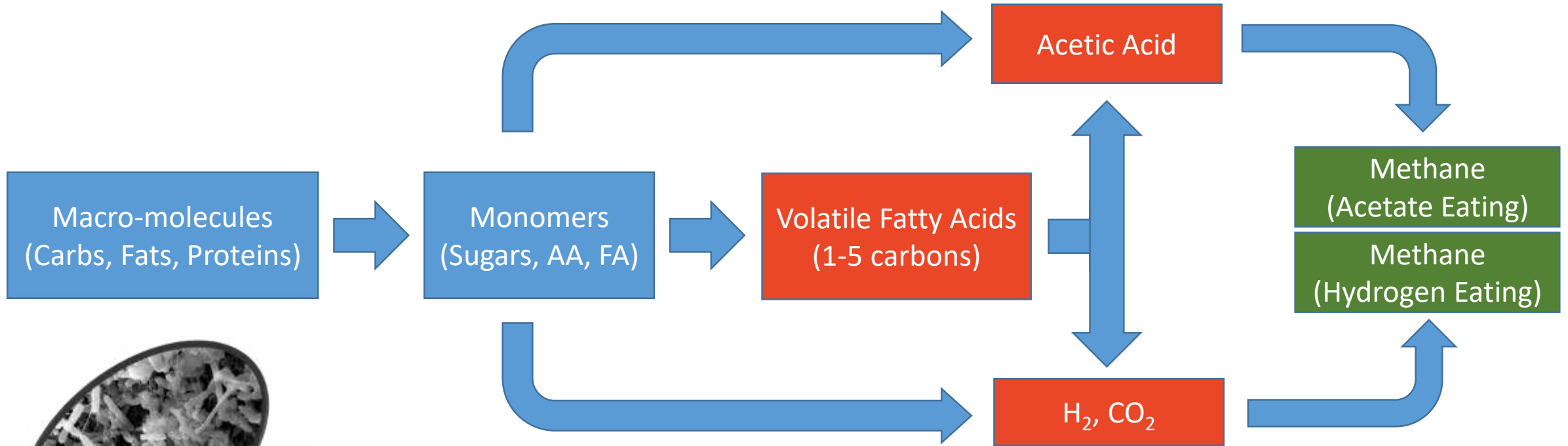
- Liquify basic food groups into smaller monomers
- Uses suite of extracellular enzymes excreted by bacteria
- Relatively fast step; except with lignocellulosic material (then difficult)

Acidogenesis



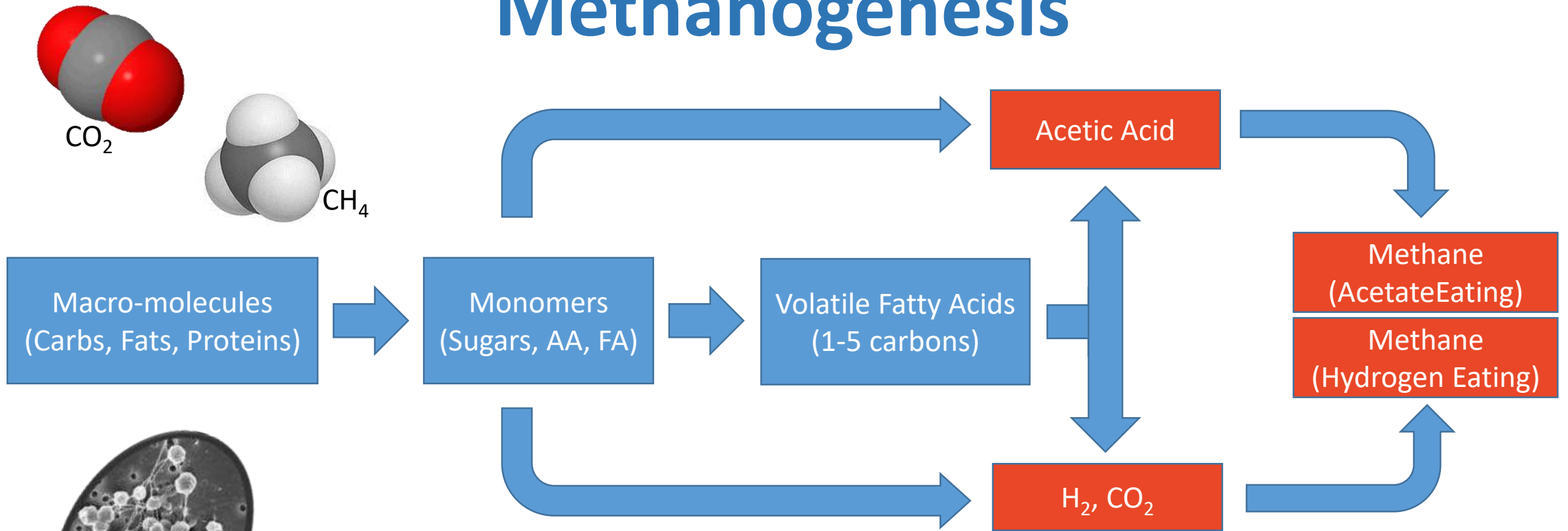
- Convert monomers to VFA with hydrogen and carbon dioxide as waste
- Bacterial intracellular conversion
- Relatively fast step
- Also produce hydrogen sulfide (H₂S) and ammonia (NH₃)

Acetogenesis



- Convert VFA to a particular form—acetic acid
- Bacterial intracellular conversion
- Relatively fast step

Methanogenesis



- Acetate-eating methanogens (~75%) eat acetate
- Hydrogen-eating methanogens (~25%) eat H_2 and CO_2
- Slow growing, most sensitive step; hate presence of oxygen
- Not bacteria—older, called archae

Synergistic Community

All of the micro-organisms in the 4-step process work together synergistically—making and removing feeds/wastes to maintain stable environment for all to thrive

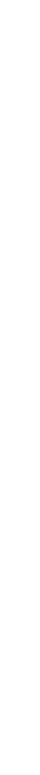


Figure: FISH Image (a) bacteria; (b) archaea; (c) both and (d) sludge visual

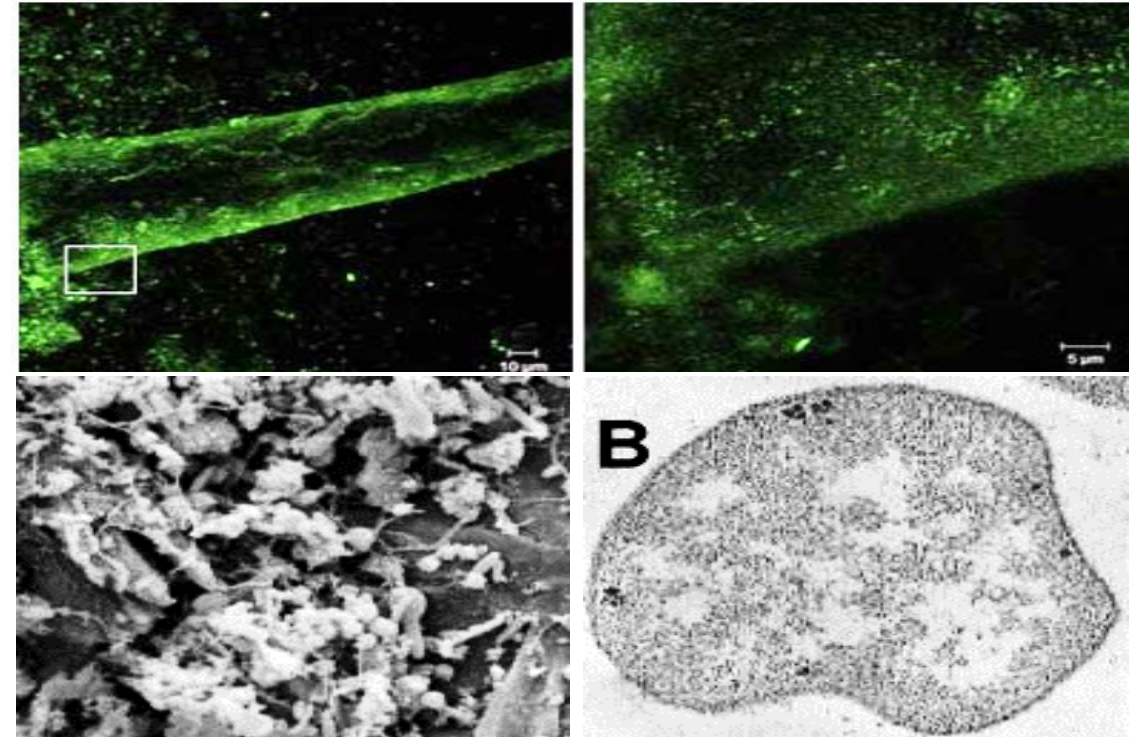
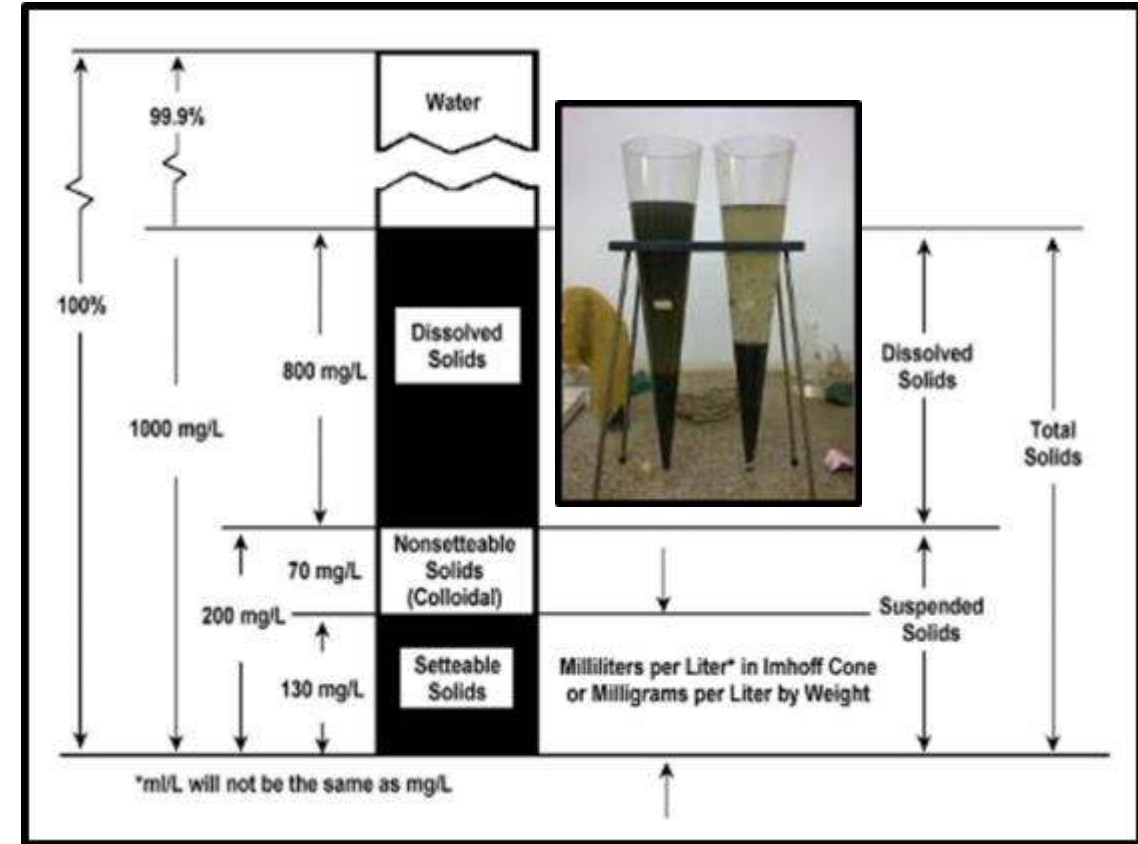


Figure: Methanosarcina (a) confocal on dairy fiber; (b) blow-up; (c) SEM; (d) blow-up

Chemistry and Chemistry Terms

Total Solids/Volatile Solids

- **Total Solids (TS)**—Weight of dry solids in slurry, reported as % or g/L.
 - Settleable Solids
 - Suspended Solids
 - Dissolved Solids
- **Volatile Solids (VS)**—Weight of combustible solids (~organic solids) in slurry, reported as % of TS or g/L.
 - Fraction of TS that is approximately organic and can be used as feed to organisms to produce biogas



Column: Water; Solids (Dissolved, Suspended, and Settleable)

Biological and Chemical Oxygen Demand

- While AD typically uses VS as measurement of organic content, can also use other common ones including BOD, COD.
- Biological Oxygen Demand (BOD)**—amount of food or organic carbon that biological organisms can oxidize.
 - Total, 5-day, Soluble forms—measured in g/L
- Chemical Oxygen Demand (COD)**—Is total weight of chemicals that can be oxidized
 - Total or Soluble forms—measured in g/L

BOD	COD
Measures biodegradable organics	Measures biodegradable and non biodegradable organics
Uses oxidizing microorganism	Uses a strong chemical agent
Affected by toxic substance	Not affected
Affected by temperature	Not affected
5 days incubation	2 hrs
Accuracy $\pm 10\%$	Accuracy $\pm 2\%$

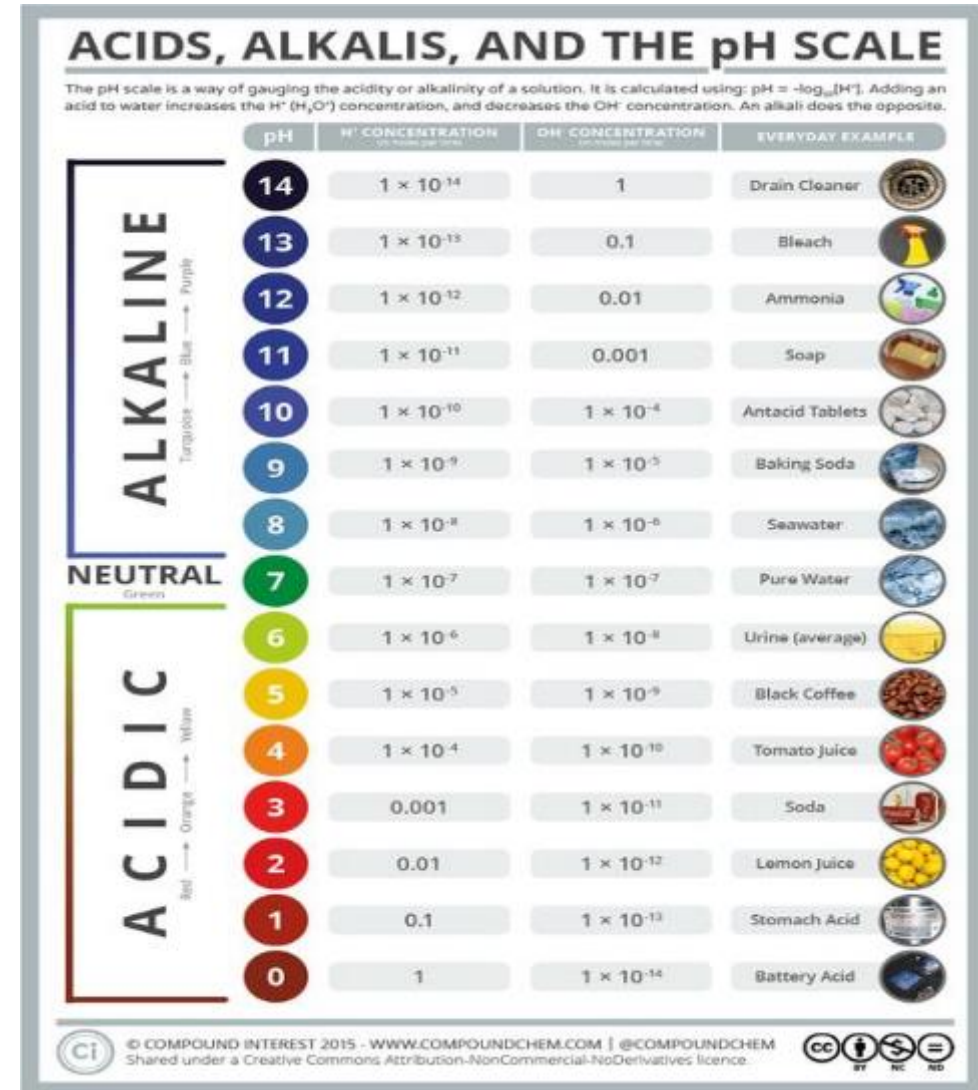
(Metcalf and Eddy, 2003)

Table 1
Physical and biochemical characteristics of the mono-digestion samples.

Mono-digestion samples	BOD (g/kg)	COD (g/kg)	TS (g/kg)	VS (g/kg)	BOD/COD	VS/TS	VS/COD
<i>Raw manures</i>							
Raw dairy manure	45.8	128.9	124.0	102.1	0.36	0.82	0.79
Manure separated liquid	33.2	71.0	57.5	40.5	0.47	0.71	0.57
<i>Food residues</i>							
Cheese whey	64.9	128.3	71.4	59.8	0.53	0.84	0.53
Plain pasta	188.7	934.3	422.6	407.7	0.20	0.97	0.44
Meat pasta	205.8	562.8	381.8	340.6	0.37	0.89	0.61
Used vegetable oil	ND	2880.0	991.0	988.8	ND	1.00	0.34
Ice cream	ND	266.8	113.8	109.1	ND	0.96	0.41
Fresh dog food	ND	530.4	132.2	125.6	ND	0.95	0.24
Cola beverage	ND	121.5	93.6	88.7	ND	0.95	0.73
Cabbage, raw	ND	90.9	78.6	72.0	ND	0.92	0.79
Potatoes, raw	53.5	261.8	177.4	163.5	0.20	0.92	0.63

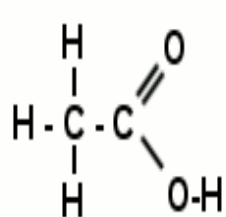
Acids/Bases/pH

- **pH scale is 0-14**, with acids on the low end, bases on the high end of **7, which is neutral**.
- The scale is a **log-scale** so difference between a single number is actually **10x**.
- Always equilibrium of **acid group (H^+)** and **base group (OH^-)**—acids have higher amount of H^+ , less OH^- and vice versa.
- Biological organisms in GENERAL, content in **pH range of 6-8**—higher or lower, and you risk viability/death.

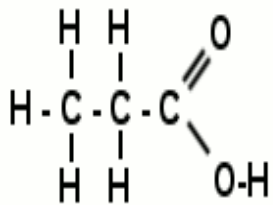


Volatile Fatty Acids (VFA)

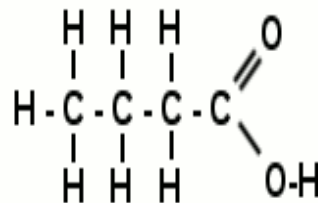
- Acids come in many forms, but acids formed in AD are small-sized organic acids (1-7 carbons; especially 2 carbons) that are relatively weak on the pH scale and evaporate readily (hence they smell).
- Rate at which they form, amount that accumulates, and the ratio of each impacts the anaerobic digestion process



Acetic acid
Vinegar



Propionic acid
Sour/Acid



Butyric acid
Vomit



OTHERS

AD
VFAs

AD
Produced

AD
Produced

Aroma Chemistry
THE SMELL OF GARBAGE

WHAT MAKES GARBAGE STINK?

H_2S ? NH_3

Lots of different things can end up in your bin, including packaging, food, and garden waste. The degradation of these, followed by their consumption by bacteria, mites, fungi, and parasites, can produce a large number of chemical compounds, many of which contribute the characteristic stench of garbage. Below are some of the stinky culprits!

A SELECTION OF ODOROUS COMPOUNDS IN GARBAGE

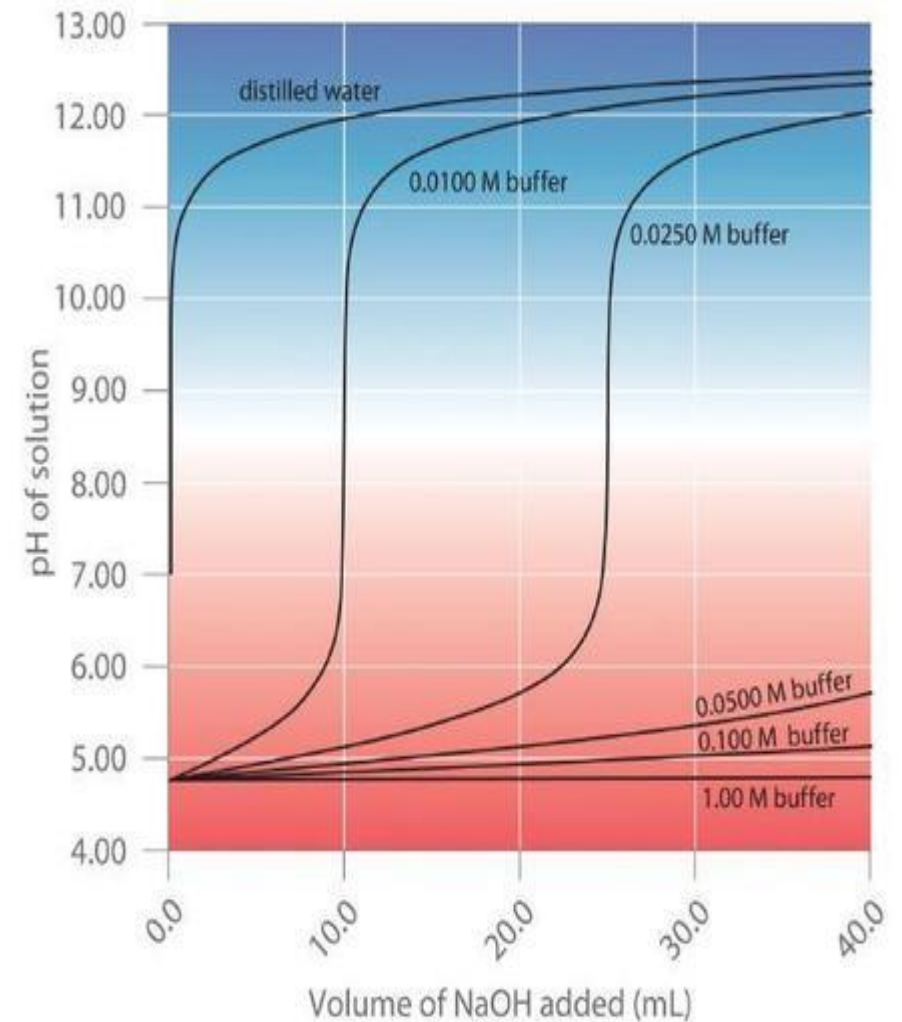
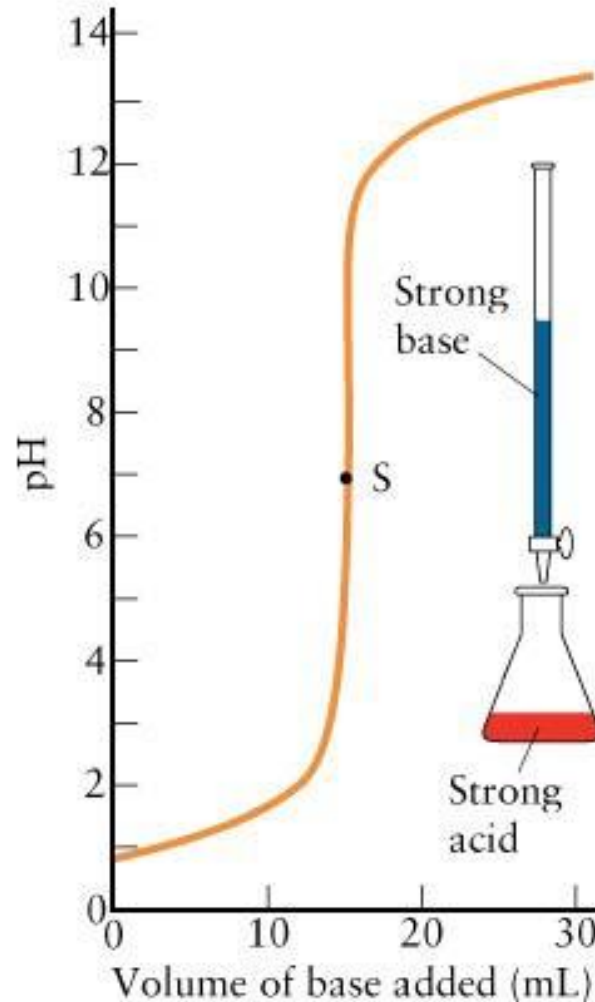
SULFUR-CONTAINING		
$\text{H}-\text{S}-\text{H}$	$\text{H}_3\text{C}-\text{S}-\text{CH}_3$	$\text{H}_3\text{C}-\text{SH}$
HYDROGEN SULFIDE rotten eggs	DIMETHYL SULFIDE rotten cabbage	METHANETHIOL rotten cabbage
NITROGEN-CONTAINING		
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$	$\text{H}_3\text{C}-\text{N}(\text{CH}_3)_2$
PUTRESCINE rotting meat	CADAVERINE rotting meat	TRIMETHYLAMINE fishy
OTHER COMPOUNDS		
$\text{H}-\text{N}-\text{H}$	$\text{H}_3\text{C}-\text{CHO}$	$\text{H}_3\text{C}-\text{COOH}$
AMMONIA medicinal, pungent	ACETALDEHYDE fruity, pungent	ACETIC ACID sour, vinegary

Many other compounds contribute, including aldehydes, carboxylic acids, and terpenes. Often these compounds, and those mentioned above, are produced during anaerobic decomposition (where there is not an adequate supply of oxygen). Some smell good in isolation, but bad when mixed with other odour compounds!

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Buffers/Alkalinity

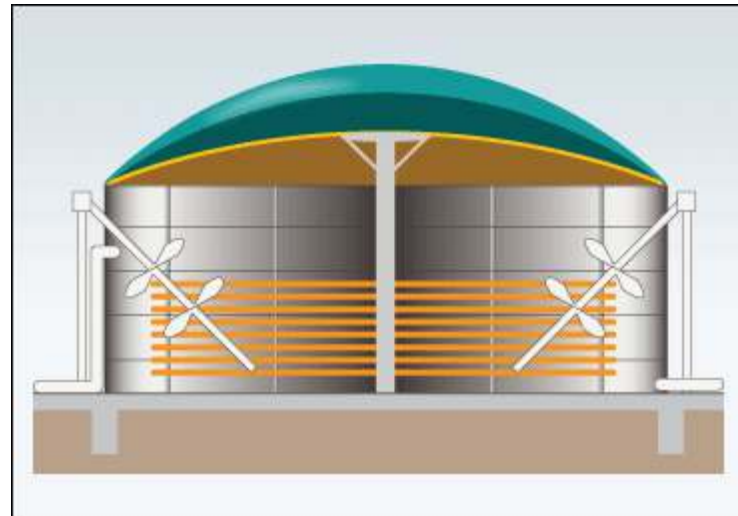
- If you add a base to an acid, the high pH of the base starts to **neutralize** the low pH of the acid. The curve is an important one! The pH will slightly change until you get to what is called the **equivalency point**, and then suddenly pH changes rapidly.
- ***pH can be a delayed indicator, being too late to tell you, there is a problem***
- ***When a buffer system or alkalinity is present, this curve changes.*** As the buffer gets stronger, the time where pH holds roughly constant before equivalency points increases, to the point of not even getting to the point.



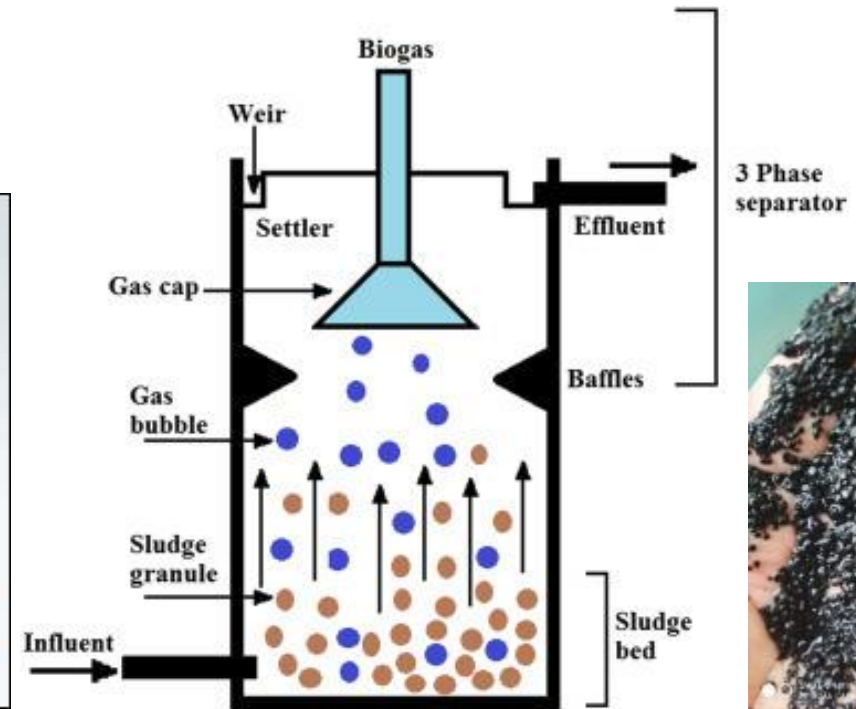
Hydraulic and Solids Retention Times

- Hydraulic Retention Time (HRT) is the time liquid or mixed-liquor stays within the vessel.
- Solids Retention Time (SRT) is the time solids/bacteria stay within the vessel
- **SRT and HRT are not always equal**

WHY (HRT \neq SRT)
Move lots of liquid
but not wash out bacteria
and still get good gas production



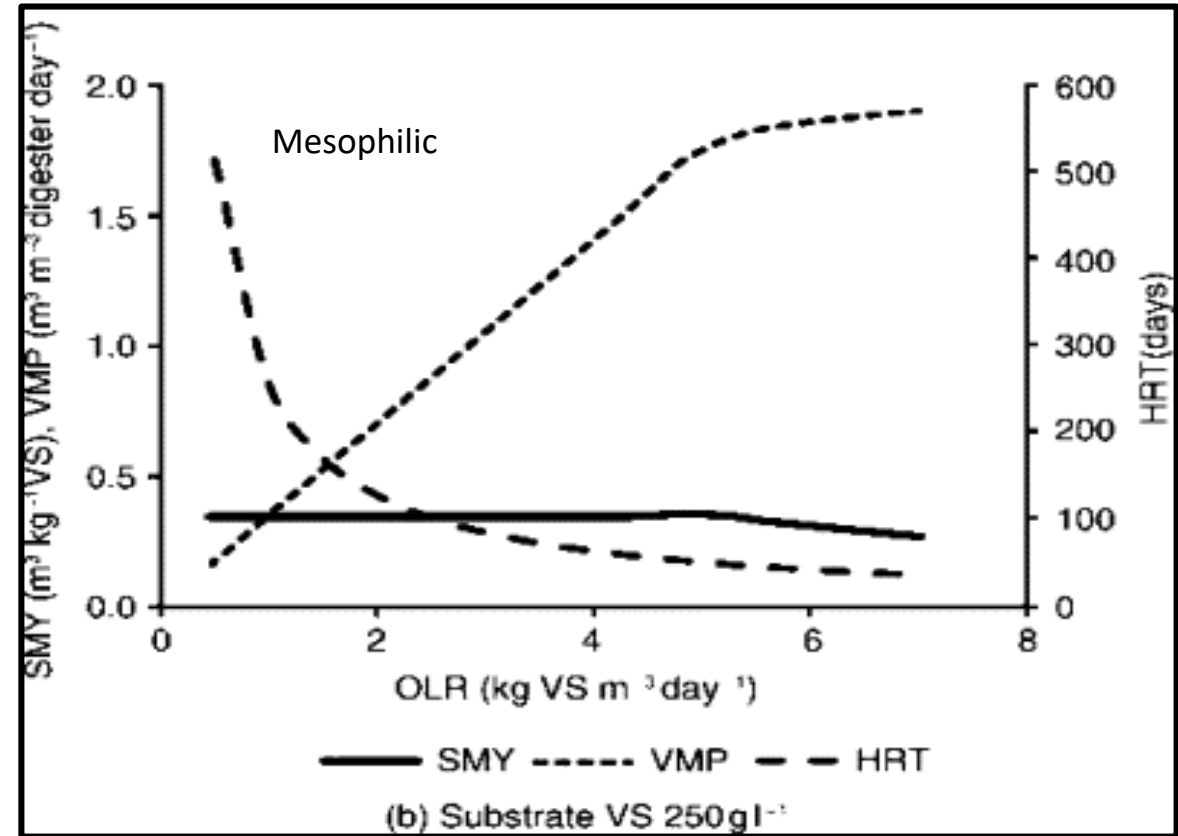
Complete-Mix (HRT = SRT)



UASB (HRT \neq SRT)

Organic Loading Rate (OLR)

- **Organic Loading Rate (OLR)** is a ratio of how much VS you feed divided by the HRT of the digester vessel.
 - Measured in **g VS/L/day**
 - Feed a **lot of VS** into a small digester with **low HRT** and you have a **high OLR**
 - *i.e. small child stomach eating multiple big-macs*
 - **Don't want to be > 4-5 for typical mesophilic slurry digesters**



As OLR increase of HRT decrease, will exceed ability to properly operate and gas production decreases
($< 4\text{-}5 \text{ g VS/L/day}$ or $< 15 \text{ days slurry}$)

VA/Alk Ratio

- Indicates the progress of digestion, its stability, and is used for process control.
- The results of the volatile acids and alkalinity tests are expressed as a ratio. Example:
 - Volatile acids = 300 mg/l
 - Alkalinity = 2,000 mg/l
 - $VA/Alk = 300 / 2,000 = 0.15$
- The range of VA/Alk ratio is 0.1 to 0.35, 0.1 to 0.25 is ideal.
- VA/Alk ratio of 0.5 indicates a sour digester
- Parameters must be sampled and tested daily at start-up, no less than a minimum of three times per week during stable operation.
 - If unstable conditions are beginning to occur, or are present (trending above 0.25), test daily.

What is the proper ratio of volatile acids to alkalinity?

1. Ideally, the VA/ALK ratio should range between 0.1 and 0.25, once it goes beyond 0.25 the operator is cautioned to back off on the feed and monitor very closely.
1. Within this range, the digester is considered healthy with good digestion taking place.
2. When the ratio begins to change, it is an indication of a potential digester upset. Trending towards 0.35 is entering the danger zone. A ratio of 0.5 indicates a sour digester.

VA/Alk Ratio

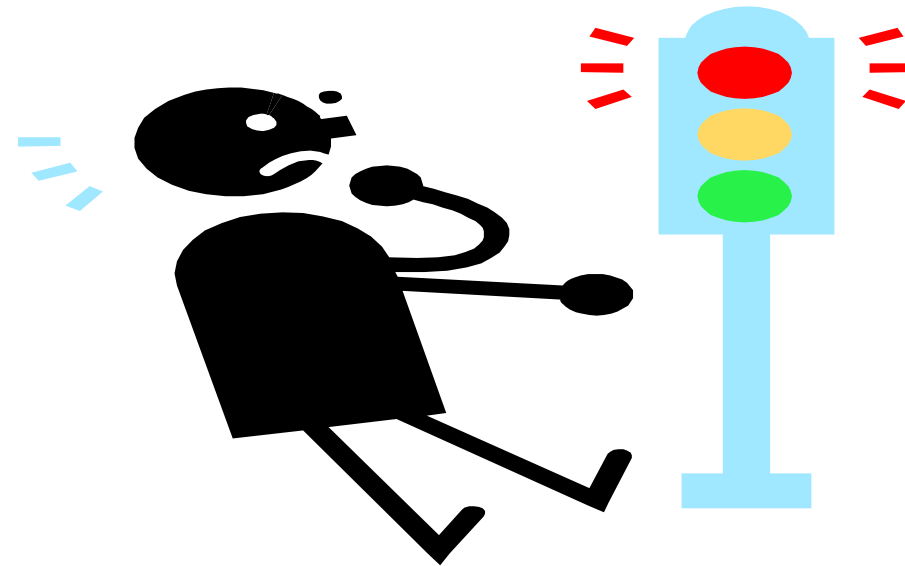
0.1 – 0.25 **green light**

0.25 + **yellow caution light**

0.35 + **red warning danger light**

0.5 **FLASHING RED LIGHT!**

SOUR DIGESTER !!!



**AMERICAN
BIOGAS
COUNCIL**

Since the VA/ALK ratio is the first indicator of potential digester upset, what are some other signs which follow?

1. The process of sludge digestion generates methane and carbon dioxide gas and other trace gases.
2. Under normal circumstances, the production of methane represents 65 to 70 percent of the digester gas; carbon dioxide being 30 percent and the remaining 1 or 2 percent various trace gases.
3. Since an increase in the VA/ALK ratio is the first sign of digester trouble, an increase in this ratio will ultimately lead to an increase in carbon dioxide and a decrease in methane.

Since the VA/ALK ratio is the first indicator of potential digester upset, what are some other signs which follow?

4. Methane production will represent less than 65 percent of the contents of the digester gas and carbon dioxide will exceed 30 percent.
5. Finally, the pH of the digester sludge will begin to drop.
6. Temperature also affects the work of the methane bacteria.

Since the VA/ALK ratio is the first indicator of potential digester upset, what are some other signs which follow?

7. The best temperature range for the digester contents should be between 93° - 100°F and variations in temperature should **not exceed 1°F per day.**
8. In general, the detention time needed to obtain complete digestion decreases with increasing temperature since organism activity increases as temperature increases.

Gases

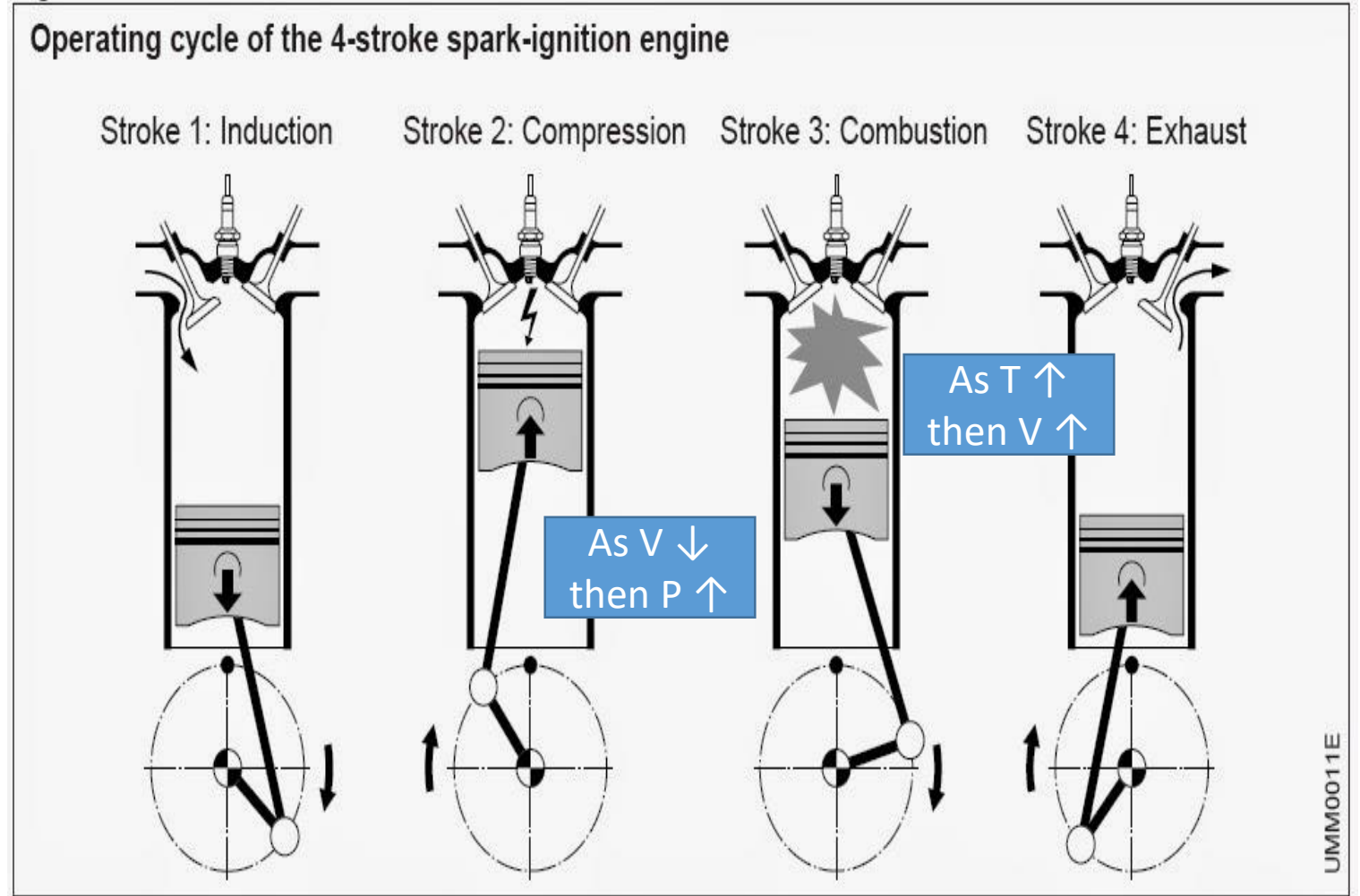
Ideal Gas Law describes the relationship between pressure, volume, amount of gas, and temperature.

- Can explain much of nature and world around us, **including AD**

Pressure (atm) Number of Moles Temperature (K)

$$P V = n R T$$

Volume (L) Gas Constant (0.082 $\frac{\text{mol} \cdot \text{L}}{\text{atm} \cdot \text{K}}$)

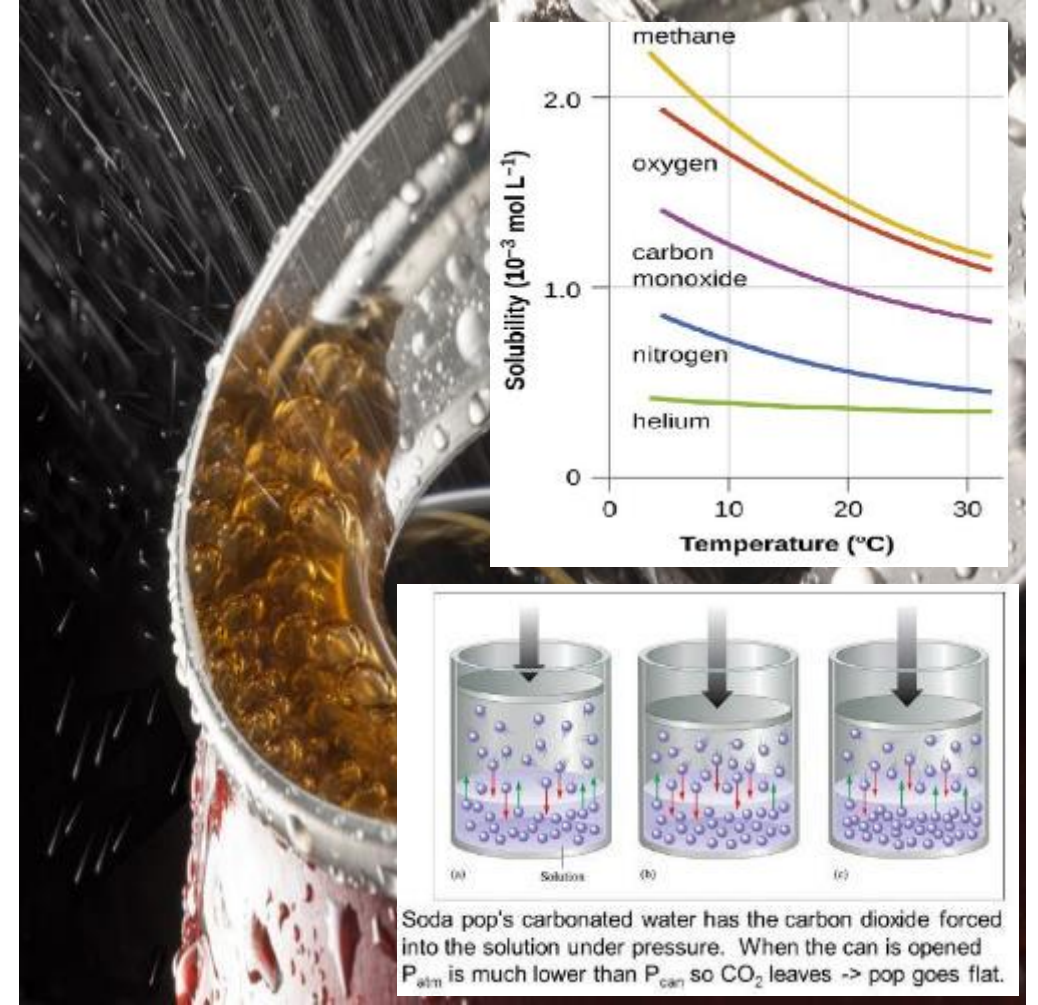


Example: AD/Car Engine

Gases—Continued

Gas Solubility and Henry's Gas Laws describe the extent to which gases can dissolve in solution AND how there is a dynamic equilibrium between gases being dissolved in solution and not (free) which is in-part controlled by P, T, and pH.

- AD has numerous gases in headspace.
 - Some dissolve well (CO_2 , NH_3), others not
 - Dynamic equilibrium between free form in headspace and dissolved in the liquid
- Can impact biological process, pH, buffers, etc.



Anaerobic Digestion Tests

Solids Analysis (TS, VS, FS)

A common analysis done on-site at AD facilities is determination of solids content.

- **Tare Weighing**—empty sample dish is weighed and recorded using the **analytical scale**.
- **Determination of TS**—Sample placed in dish and weighed again, then put in oven for drying and then reweighed. Calculate.
- **Determination of VS/FS**—TS sample placed in furnace for ignition, then reweighed. Calculate.
Difference between TS and VS = **Fixed Solids (FS, Ash)**



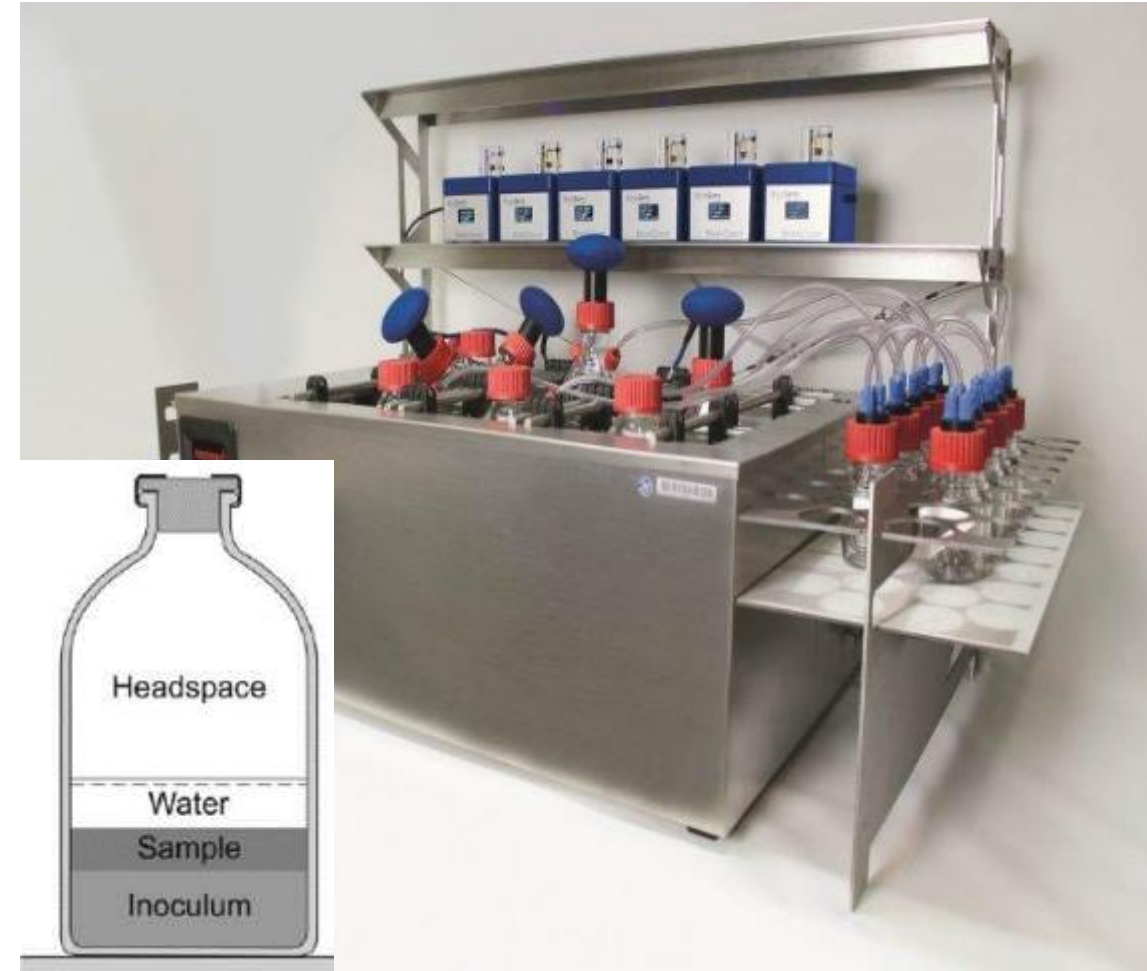
Weighing dish and scale as well as oven for drying (TS) and muffle furnace for Ignition (VS)



Bio-Chemical Methane Potential (BMP)

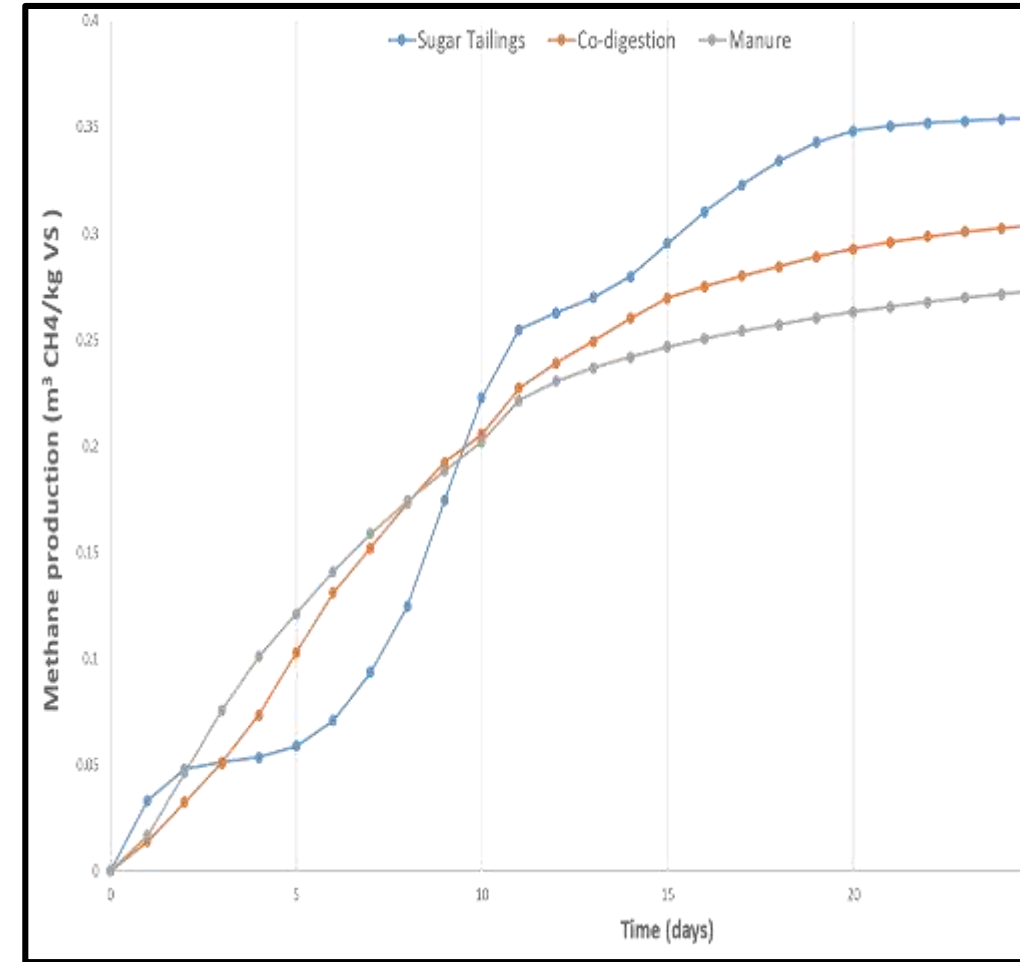
A **Bio-chemical Methane Potential (BMP)** test is an excellent way to predict the biogas production from a particular waste stream—using controlled conditions.

- **Ideal conditions**—bacteria, mixing, temperature, loading conditions.
- Calculates an important ratio—**Specific Methane Potential** (SMP)
 - Metric: $\text{m}^3 \text{CH}_4/\text{Biogas}/\text{kg VS input}$
 - US: $\text{ft}^3 \text{CH}_4/\text{Biogas}/\text{lb. VS input}$



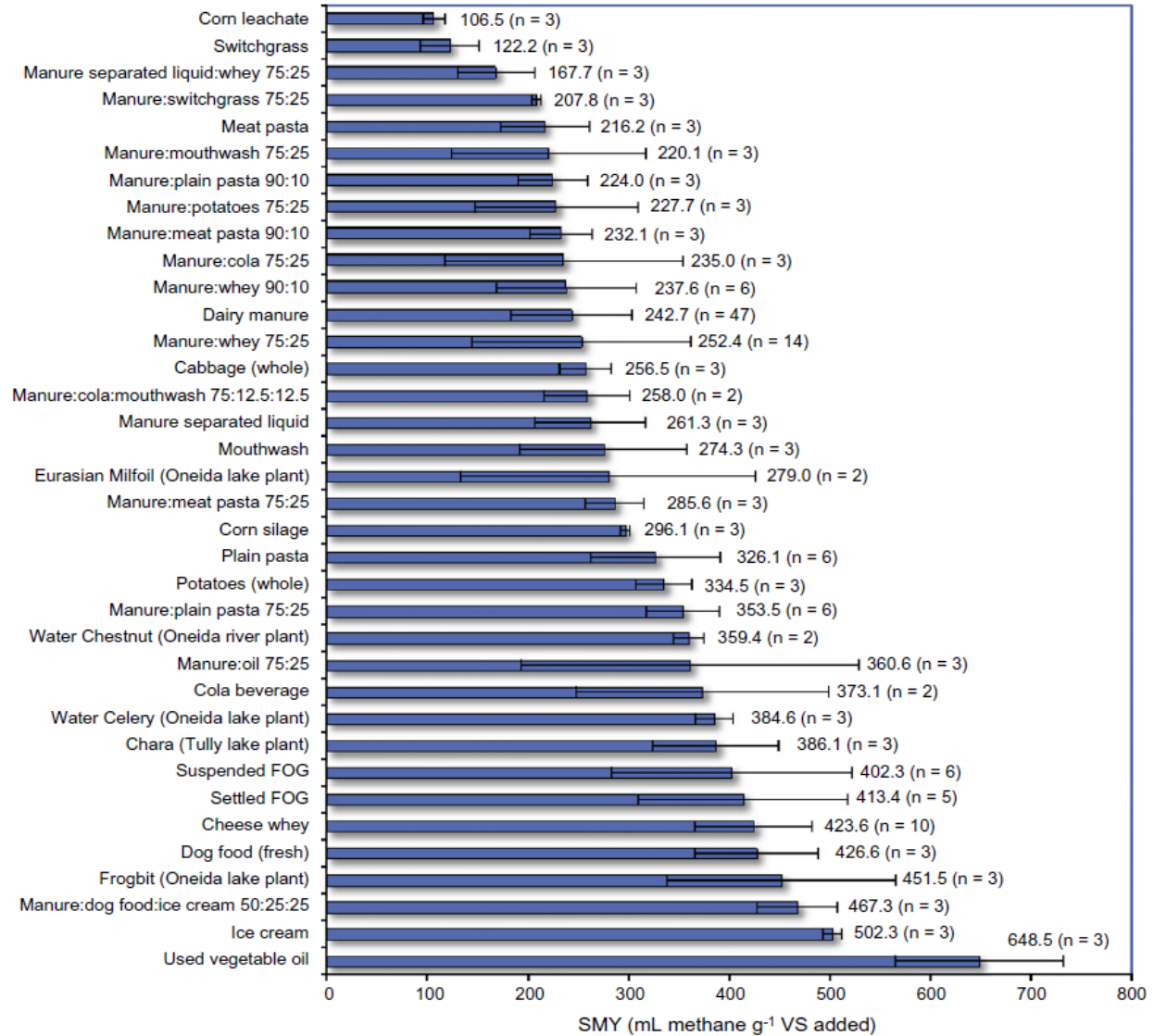
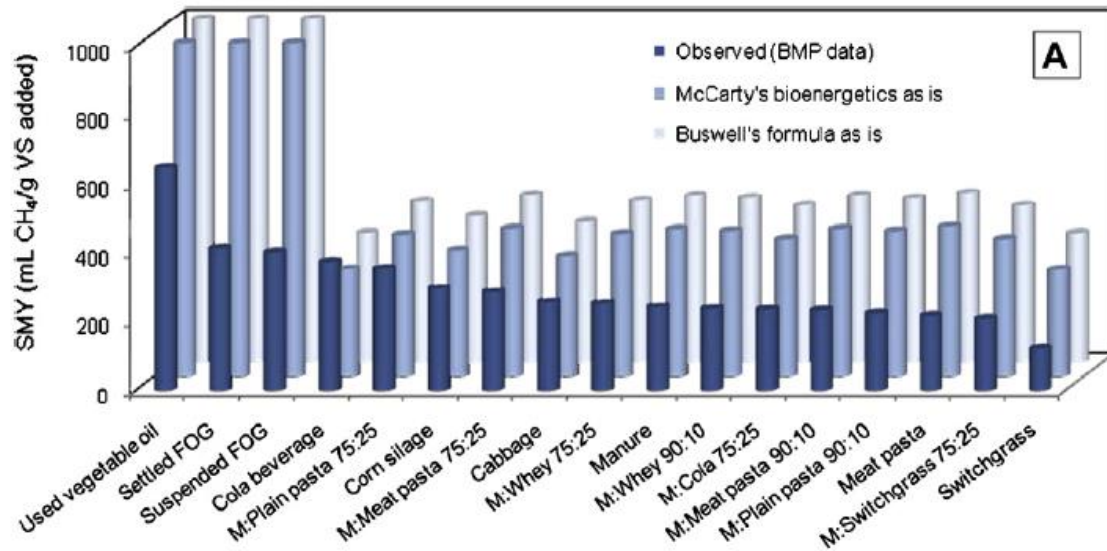
Bio-Chemical Methane Potential (BMP)

- Smooth curve—with 3-sections
 - **Lag**—bacteria acclimating/growing
 - **Exponential**—bacteria multiplying rapidly and eating
 - **Flat**—running out of *digestible* food
- If NOT smooth, represents some type of upset worth noting
 - Sugar Tailings—**Readily Biodegradable Organics**
 - Co-digestion with manure—alkalinity/buffer
- **95% Mark/Final SMP/Ideal Conditions**



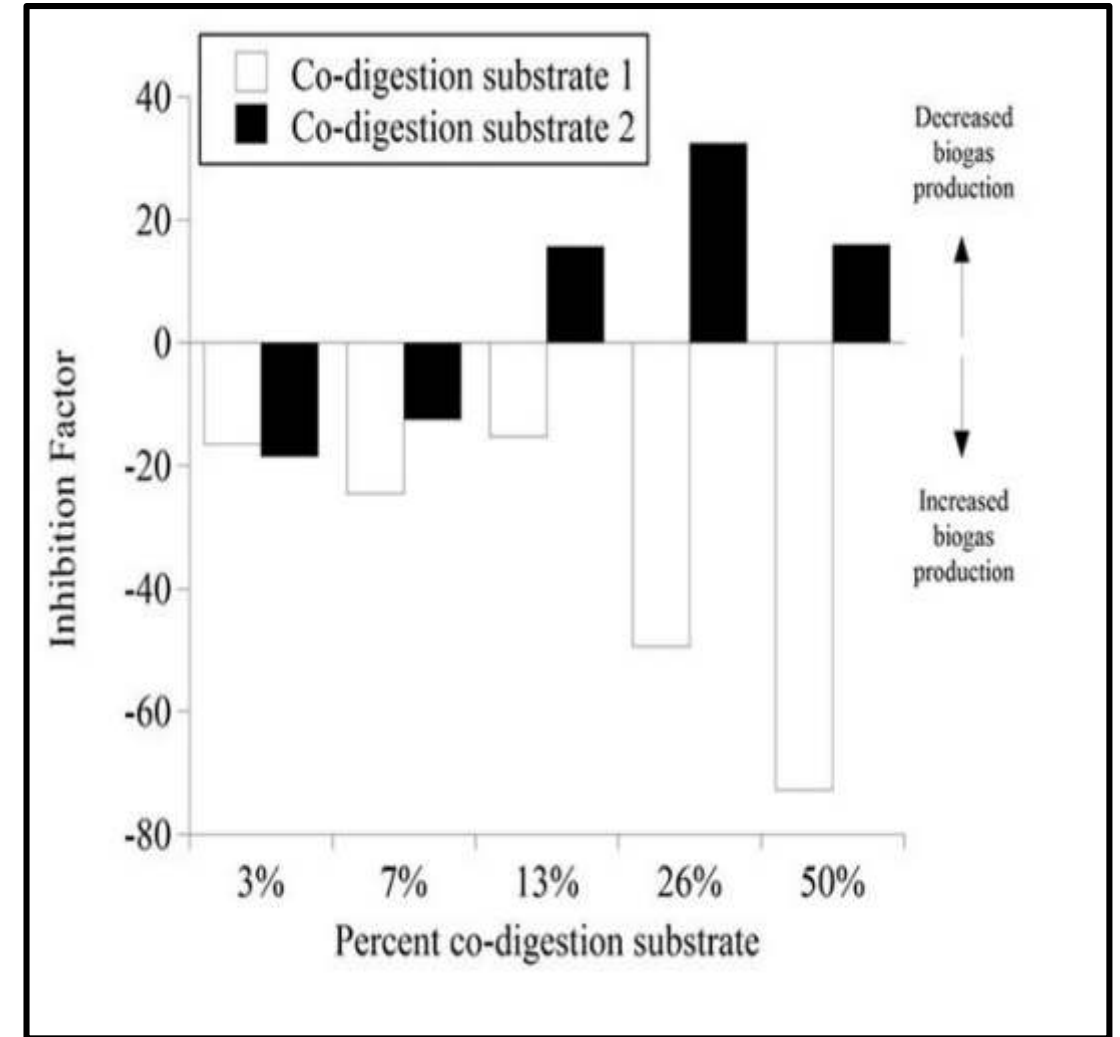
Bio-Chemical Methane Potential (BMP)

- Each feedstock produces its own BMP value
- Not all VS is digestible—some recalcitrant
 - $B_o/B_u = f_D$
 - Dairy Manure = 0.44 or 44%



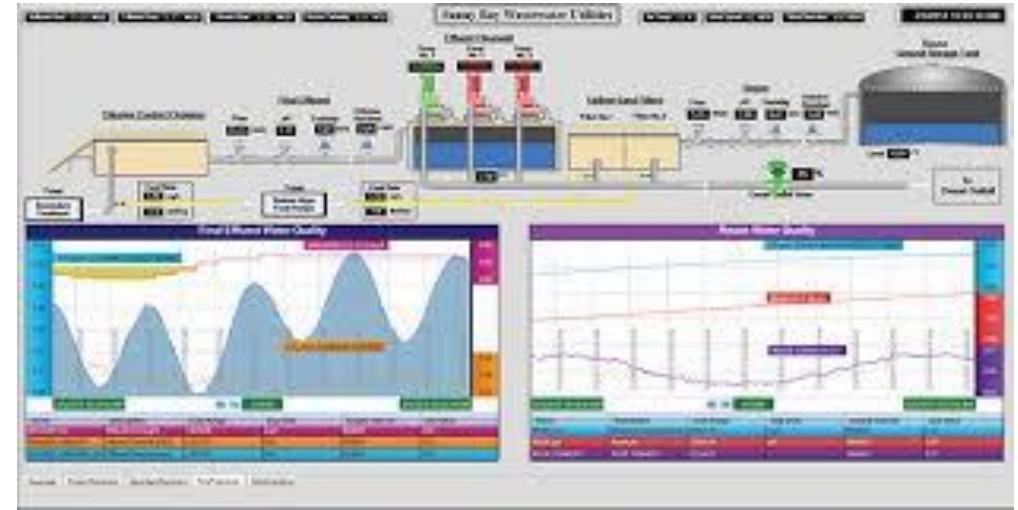
Anaerobic Toxicity Assay (ATA)

- Assesses deviation from exponential slope, using several different test conditions
- In example, is there – or + impacts to changing the percentage of a substrate (OLR)—by type of substrate?
 - Substrate 1—**As you increase its % in feed, you get + impact—more biogas**
 - Substrate 2—**As you increase its % in feed, you get – impact—less biogas**
- Useful not just for OLR, but toxins, unknowns**



Process/Gas Analyzers

- **Control Panels/SCADA**—Monitoring of AD system and unit operations
- **In-line Gas Flow Meters**—Measure biogas and/or RNG flow
- **Gas Species Analyzer**—Analysis of gas constituents, such as methane, carbon dioxide, hydrogen sulfide in biogas
- **Gas Chromatograph**—More detailed gas analysis for RNG pipeline projects

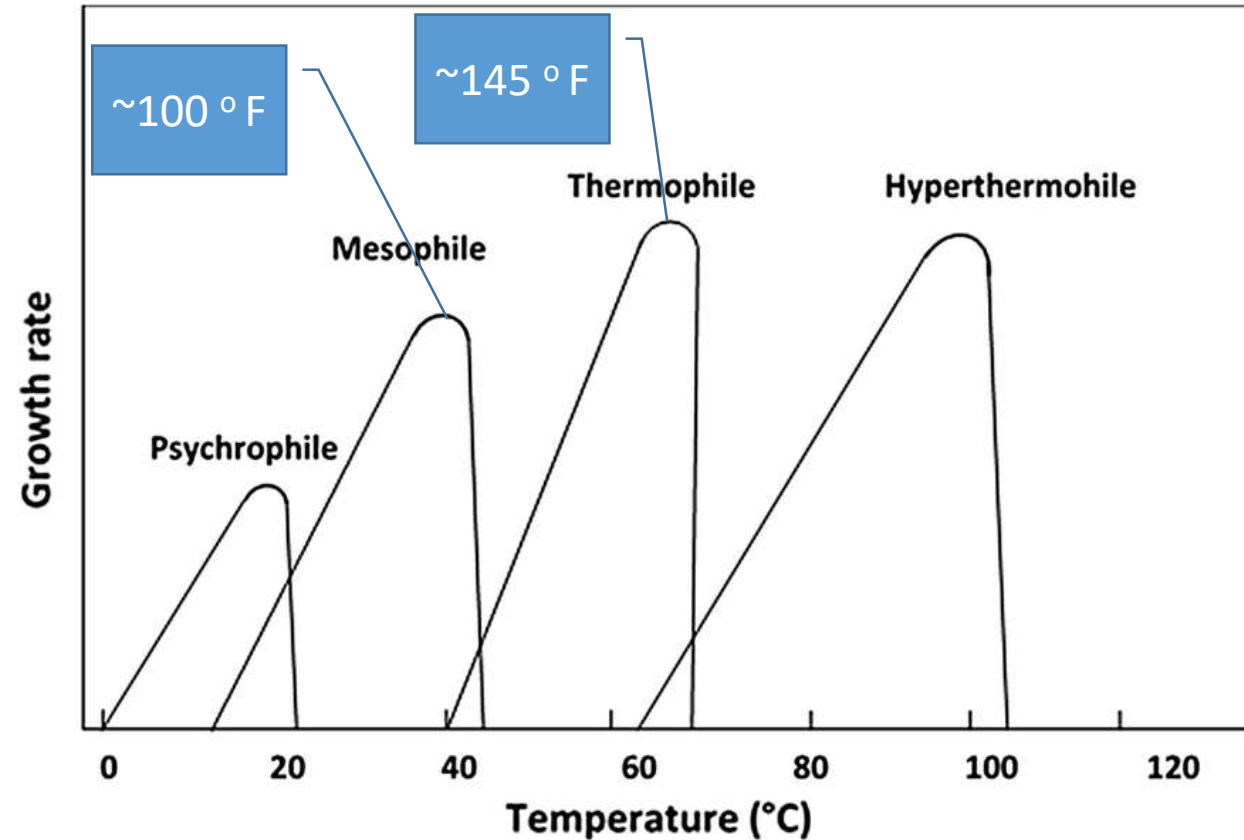


Reactor Types

Temperature Regimes

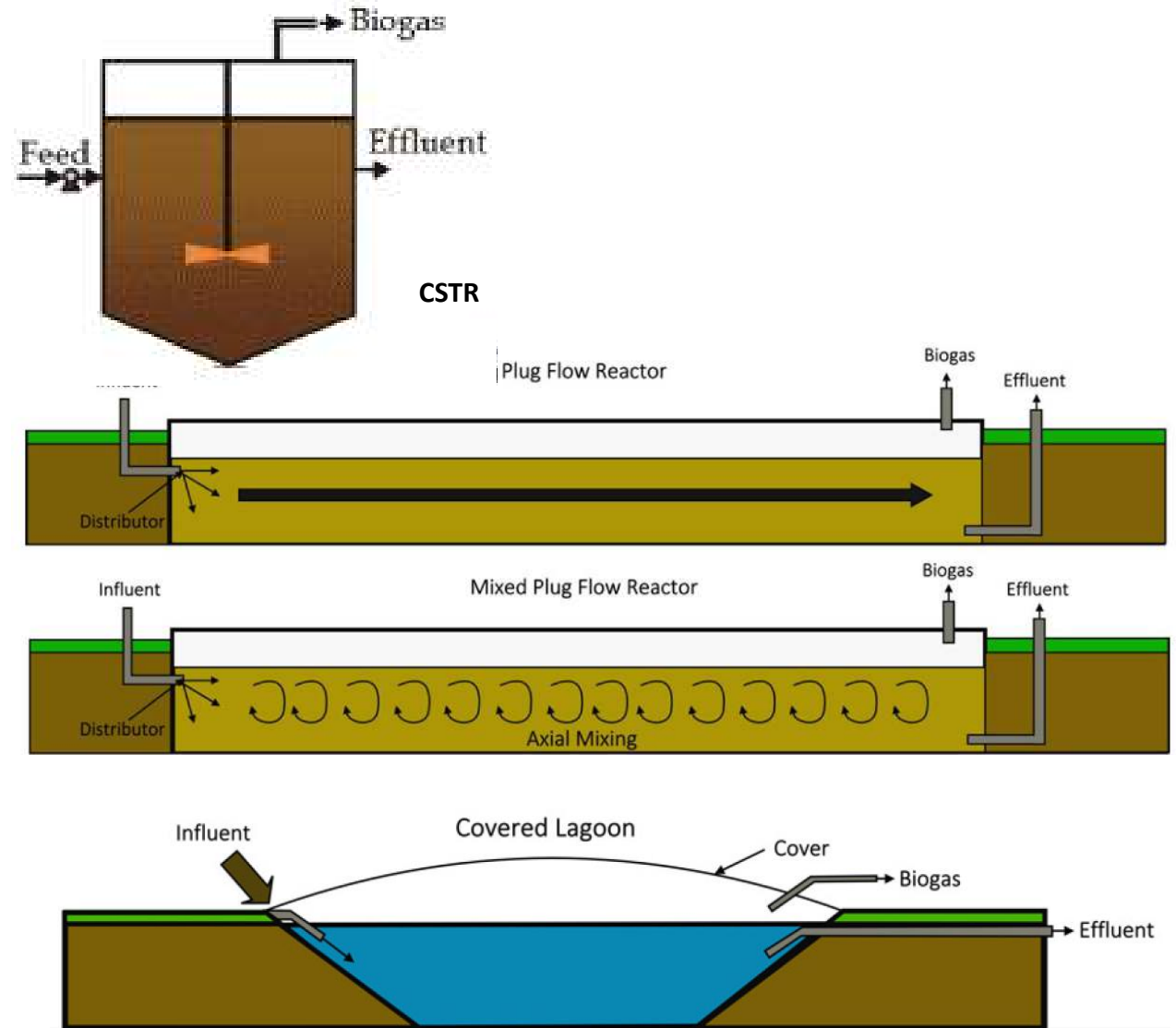
Anaerobic digestion can occur at various temperature regimes, using different consortia of micro-organisms that are adapted for the particular temperature ranges. Within each regime is a more specific temperature where their growth rate is optimized. The regimes are:

- **Psychrophilic**
 - Often ambient AD—covered lagoons
- **Mesophilic**
 - Most common
- **Thermophilic**
 - Several advantages, but also concerns
- **Hyper-thermophilic**
 - Little active research/utilization



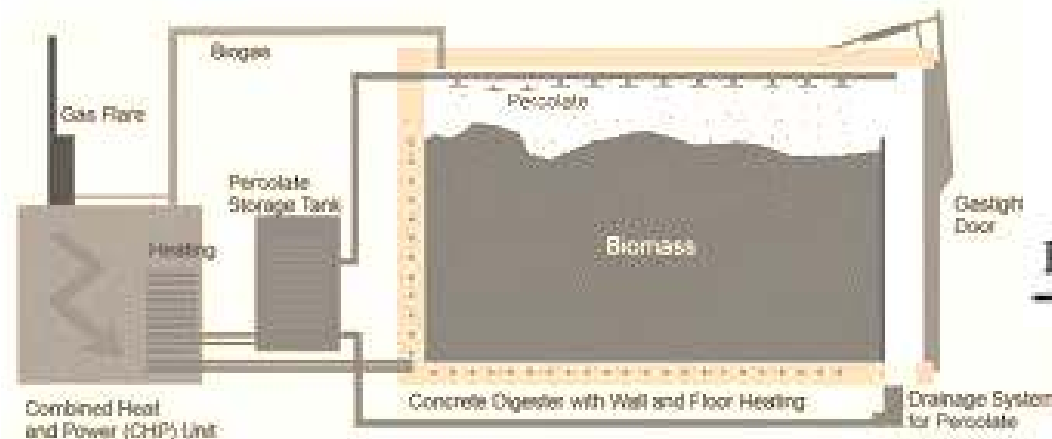
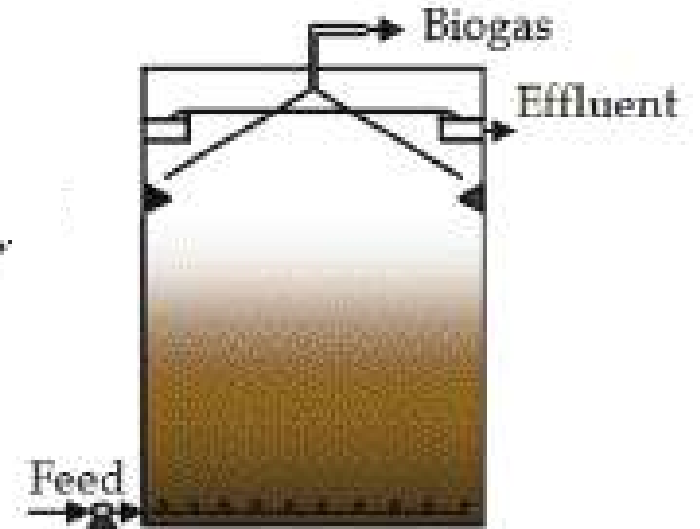
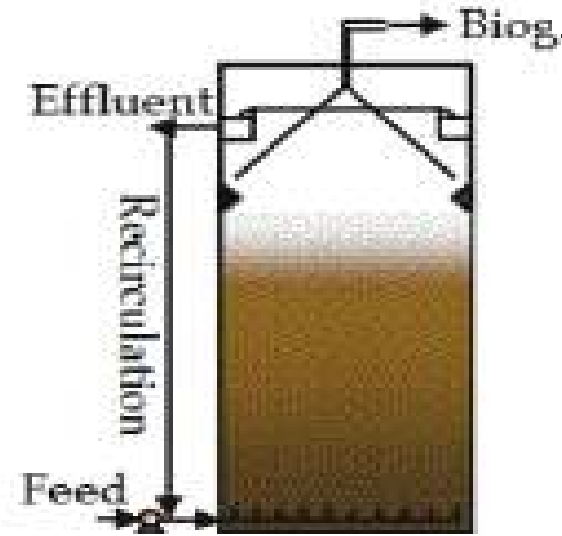
Reactor Types

- **CSTR—Complete Mix Stir Reactor**
 - Slurry digester— $HRT = SRT$
- **Mixed-Plug Flow Reactor**
 - Slurry digester— $HRT = SRT$
 - High-Solids digester— $HRT = SRT$
- **Covered Lagoon**
 - Non-mixed, no-heat— $HRT \neq SRT$
 - Heated



Reactor Types

- **UASB—Up-flow Anaerobic Sludge Blanket**
 - Fixed Film—HRT \neq SRT
 - Other forms of Fixed Film—Media
- **EGSB—Expanded Granular Sludge Blanket**
 - Fixed Film—HRT \neq SRT
- **SBR—Sludge Bed Reactor**
 - Phased STR—HRT \neq SRT
- **Garage-Style**
 - High Solids—Batch
 - HRT \neq SRT; Trickling-Filter



Pre-Treatment

Several steps are commonly used or in active-research relating to pre-treatment of feedstock prior to entry to the digester vessel. These pre-treatments are mainly to accentuate bacterial access for greater gas production/stabilization and/or greater pathogen control. Some examples include:

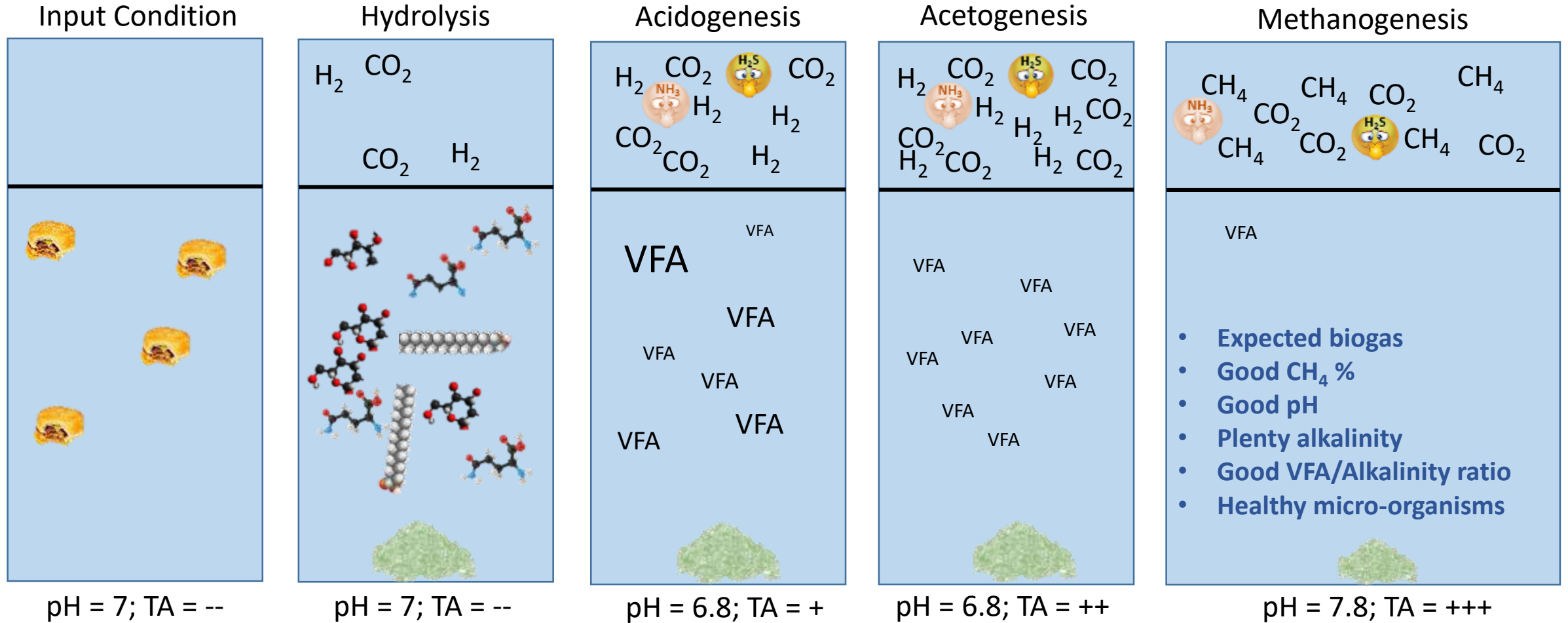
- **Pasteurization/Hygienization**
- **Maceration other Physical**
- **Thermal Hydrolysis**
- Enzymatic
- Chemical
- Sonication
- Cavitation
- Extrusion
- Steam Explosion

(a) Pasteurizers; (b) thermal hydrolyzers; and (c) macerator pumps



Digester Upset Examples

Healthy Digester



- Expected biogas
- Good CH₄ %
- Good pH
- Plenty alkalinity
- Good VFA/Alkalinity ratio
- Healthy micro-organisms

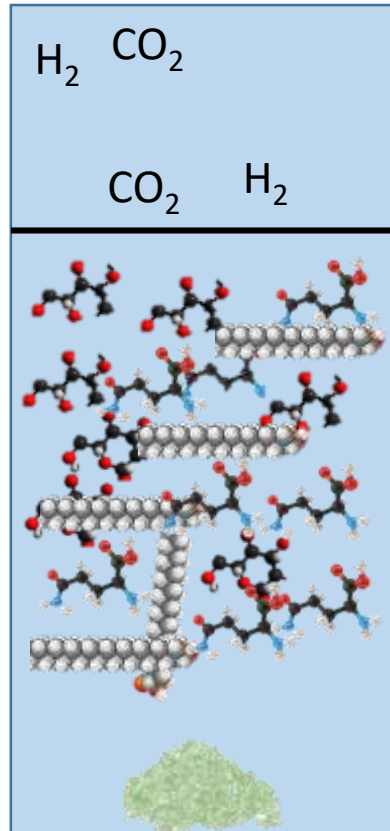
Overloaded (OLR > 4)

Input Condition



pH = 7; TA = --

Hydrolysis



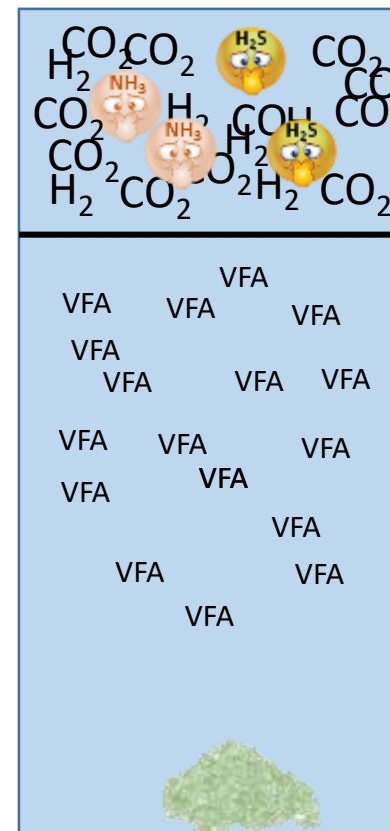
pH = 7; TA = --

Acidogenesis



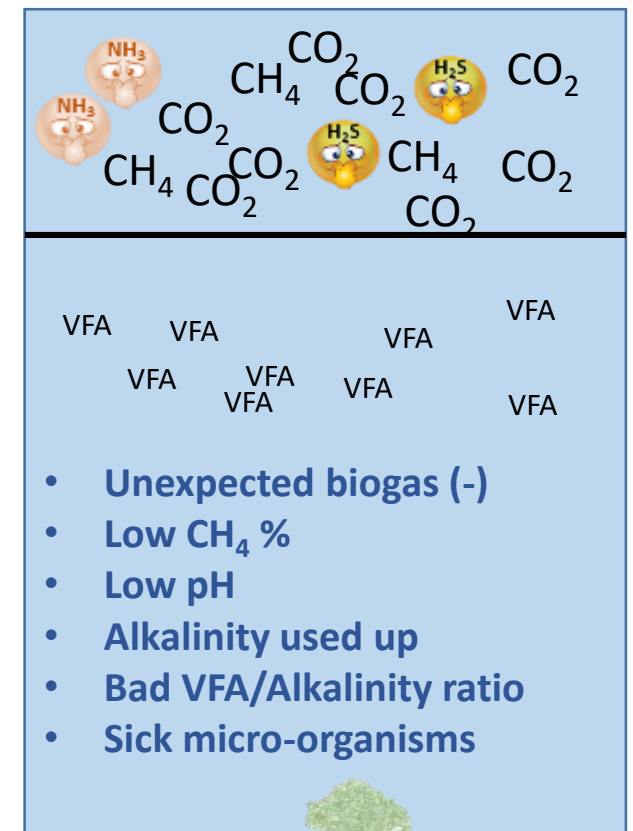
pH = 6.2; TA = +

Acetogenesis



pH = 5.5; TA = ---

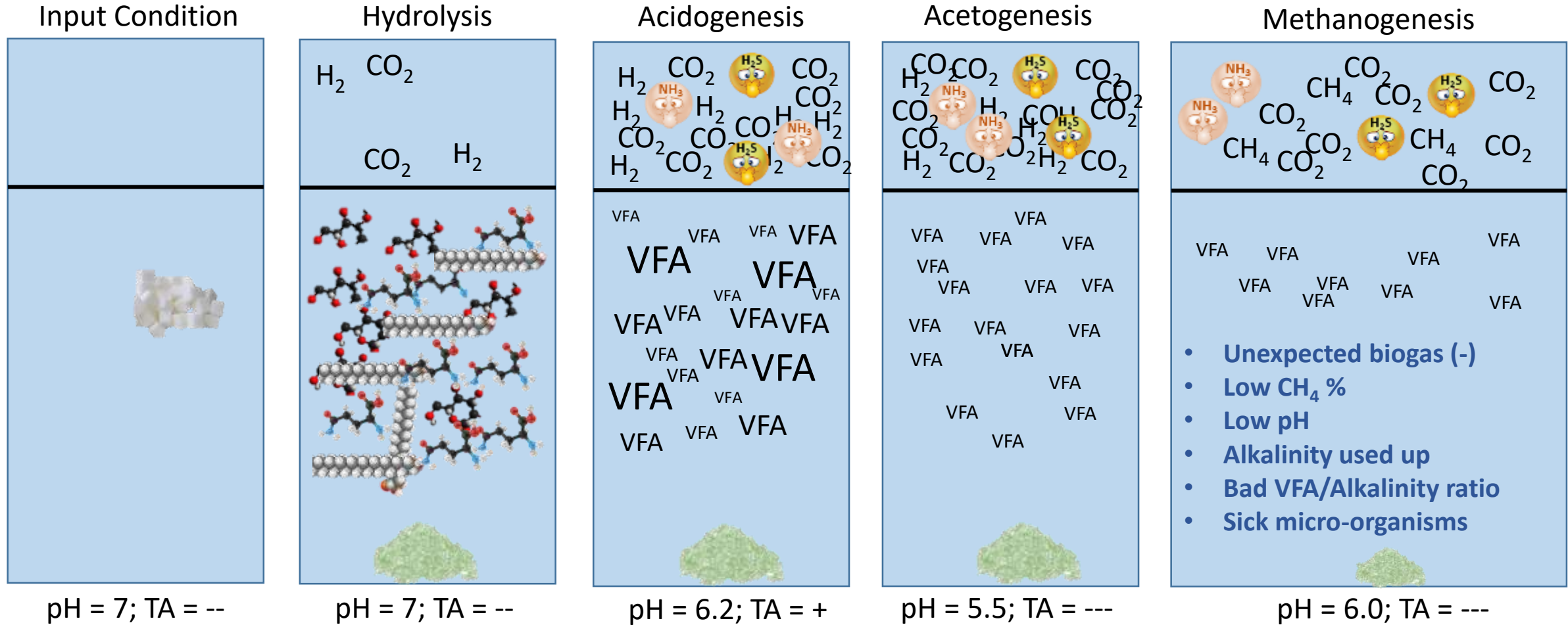
Methanogenesis



pH = 6.0; TA = ---

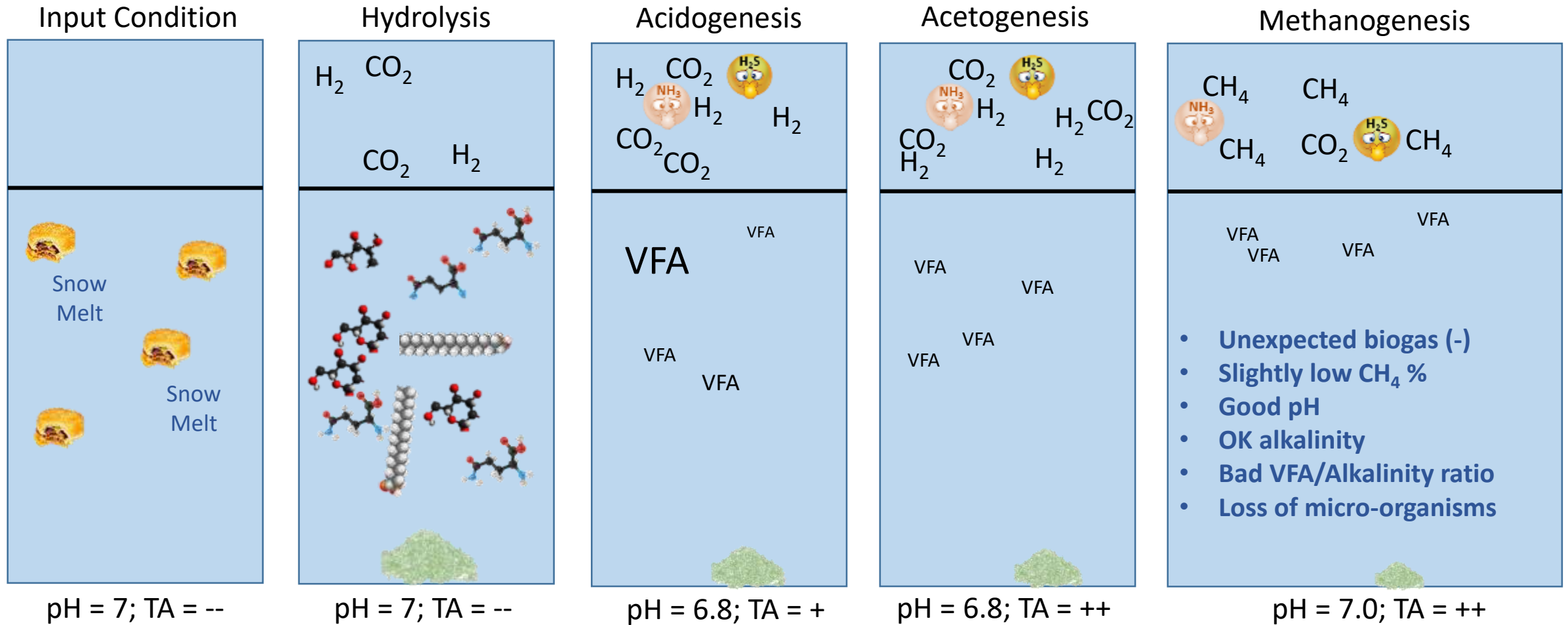
- Unexpected biogas (-)
- Low CH₄ %
- Low pH
- Alkalinity used up
- Bad VFA/Alkalinity ratio
- Sick micro-organisms

Highly Biodegradable (OLR < 4, but too easy)



- Unexpected biogas (-)
- Low CH₄ %
- Low pH
- Alkalinity used up
- Bad VFA/Alkalinity ratio
- Sick micro-organisms

Too High Flow (HRT < 12 days)



Math for Digester Operators

Math for Digester Operators

- TS and VS
- The BMP
- How much Biogas Can I make?
- Is this a Good Substrate?
- Exercise – Show what you know.

Typical BMP Graph

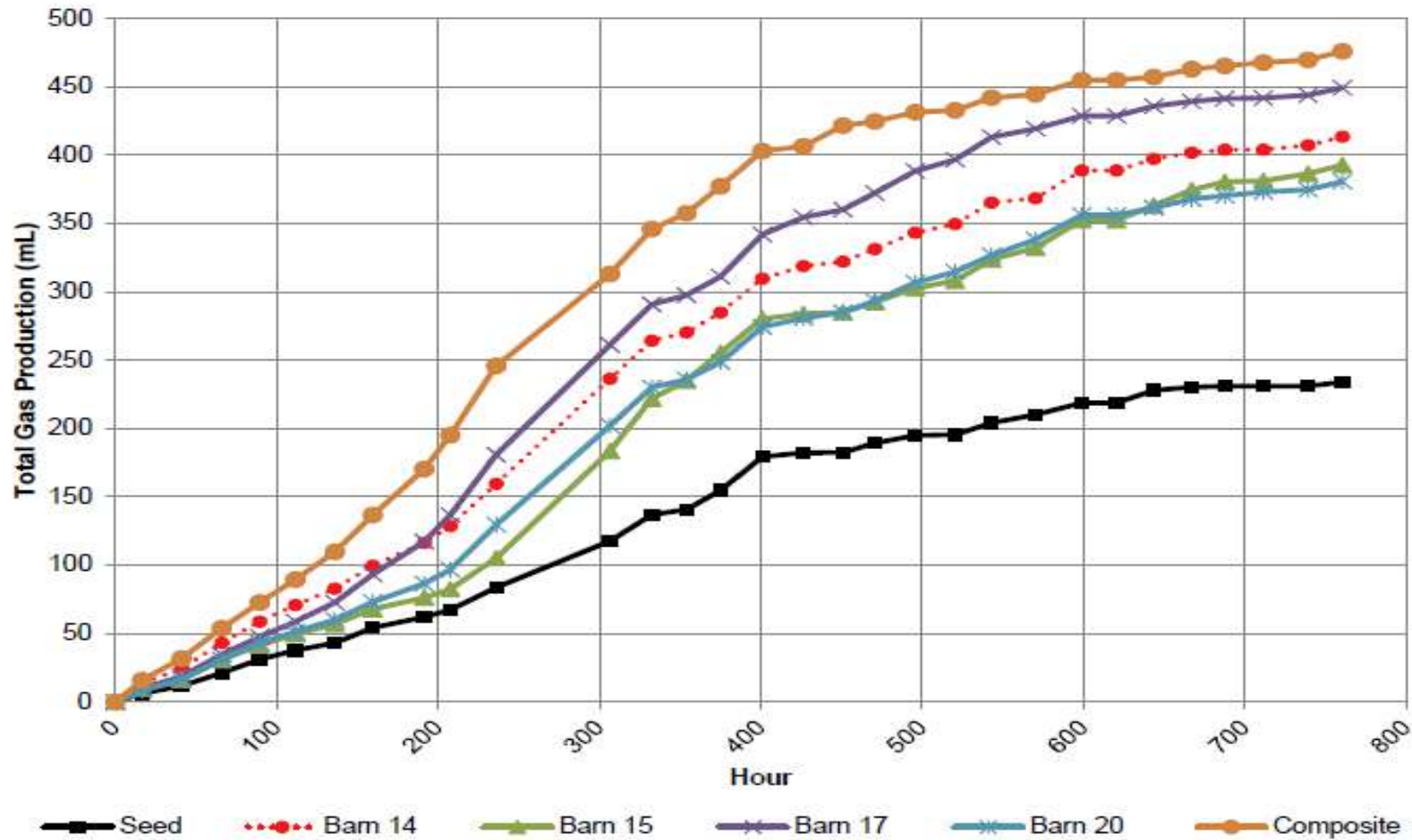


Figure 1. Cumulative Biogas Volume (Average of Triplicates)

*Gas volumes are corrected for change in temperature. Gas is counted at 22 C and corrected to STP (0 C, 1 atm).

Biogas Analysis BMP Summary

Flaskzz	Initial VS (mg/L)	Normalized VS (mg)	Total Gas Produced (mL) ²	*Normalized Gas Produced (mL)	Average Methane (%)	Max Methane (%)	*Biogas / Initial VS (L/kg) ¹
Seed 1	5,040		226		49	57	
Seed 2	5,127		236		53	62	
Seed 3	6,152		241		55	66	
Barn 14 (1)	10,168	709	394	160	65	73	238±11
Barn 14 (2)	10,330	734	415	181	65	70	
Barn 14 (3)	10,885	817	431	197	65	70	
Barn 15 (1)	9,617	627	381	147	59	68	248±32
Barn 15 (2)	9,607	625	374	140	61	73	
Barn 15 (3)	9,873	665	423	189	61	68	
Barn 17 (1)	8,938	525	448	214	62	69	392±24
Barn 17 (2)	9,085	547	455	221	61	68	
Barn 17 (2)	9,307	580	446	212	62	70	
Barn 20 (1)	9,418	597	390	156	62	71	237±35
Barn 20 (2)	9,922	672	367	133	63	72	
Barn 20 (3)	9,462	603	386	152	61	72	
Composite (1)	9,560	618	460	226	65	70	398±28
Composite (2)	9,327	583	477	243	64	69	
Composite (3)	9,615	626	492	258	63	69	

± Standard Deviation

*Normalized to seed control samples

¹ Average/Standard deviation of triplicate samples

² Biogas is counted in a lab maintained @ 22°C. Biogas is corrected to STP (0°C, 1 atm) and assumed to be saturated.