ENVE 424
Anaerobic Treatment

Lecture 7
Process monitoring and control in anaerobic treatment

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Operational Conditions

- The rate limiting step in anaerobic digestion is the conversion of VFAs to methane (easily biodegradable substrate)
- Methanogens have low growth rate
- Therefore, optimum conditions should be met
- Methane formers are strict anaerobes and are extremely sensitive to changes in alkalinity, pH, and temperature
- Process control of anaerobic digesters is often difficult

Operational Conditions

TABLE 10.1 Operational Conditions for Acceptable Activity of Methane-forming Bacteria and Methane Production

Condition	Optimum	Marginal
Alkalinity, mg/l as $CaCO_3$	1500–3000	1000–1500
		3000–5000
Gas composition		
Methane, % volume	65–70	60–65 & 70–75
Carbon dioxide, % volume	30–35	25–30 & 35–40
Hydraulic retention time, days	10–15	7–10 & 15–30
pH	6.8–7.2	6.6–6.8 & 7.2–7.6
Temperature, mesophilic	30–35°C	20–30° & 35–40°C
Temperature, thermophilic	50–56°C	45–50° & 57–60°C
Volatile acids, mg/l as acetic acid	50–500	500–2000

Ref: Gerardi M.H. The microbiology of anaerobic digesters. Wiley Interscience. 2003

Process Optimization and Control

- In AD, it is necessary to evaluate the process status by observing the important process inputs and outputs.
- Optimally, the process outputs should be easily measurable and have a pronounced response to the changes in loading and stability.
- However, some outputs respond in an almost on/off or stepwise manner when certain process instabilities occur.
- Process outputs are also called "process indicators".

Process Upsets

- There are seven basic conditions responsible of upset in anaerobic digesters
  1. Hydraulic overload
  2. Organic overload
  3. pH changes
  4. Temperature fluctuations
  5. Toxicity
  6. Large withdrawal of sludge
  7. Air contamination and other sudden changes

Process Upsets

TABLE 19.1 Conditions Responsible for Upsets and Unstable Anaerobic Digesters

Condition	Example
Hydraulic overload	Overpumping of dilute feed sludge
Organic overload	Overpumping of concentrated feed sludge
pH changes	Drop in pH (<6.8) and loss of alkalinity
Temperature fluctuations	Overpumping of feed sludge
Toxicity	Specific inorganic and organic wastes
Large withdrawal of sludge	Excess withdrawal of sludge and reduced retention time
Sudden changes	Rapid increase in nitrate ion concentration

Ref: Gerardi M.H. The microbiology of anaerobic digesters. Wiley Interscience. 2003

Indicators of Unstable Anaerobic Digester

TABLE 19.2 Indicators of Unstable Anaerobic Digesters

Indicator	Decrease	Increase
Biogas production	X	
Methane production	X	
Alkalinity	X	
pH	X	
Volatile solids destruction	X	
Volatile acid concentration		X
Percent CO_2 in biogas		X

Ref: Gerardi M.H. The microbiology of anaerobic digesters. Wiley Interscience. 2003

Hydraulic Overload

- HRT is reduced to a value, which methanogens cannot reproduce (washed out).
- Hydraulic overload may be due to sudden increase in flow
- Also grit accumulation and scum formation decreases digester volume and causes hydraulic overload
- Washout of alkalinity also results in hydraulic overload

Hydraulic Overload

- Hydraulic overload also causes;
  - Increased heating requirements
  - Increased sludge dewatering and disposal cost
  - Decreased methane production
  - Decreased VFA utilization

Organic Overload

- Organic overload usually accompanied by a relatively high concentration of nitrogenous wastes in municipal ww.
- The release of ammonia during digestion causes toxicity

Foam and Scum Formation

TABLE 20.1 Operational Conditions Associated with Foam Production

Condition	Contributing Factor
Alkalinity increase	Lysis of large numbers of strict aerobic bacteria including Nocardioforms
	High percentage of activated sludge feed
Carbon dioxide increase	Change in digester fermentation reactions
Fatty acid increase	Excess grease
	Excess triglycerides
	Lysis of large numbers of strict aerobic bacteria including Nocardioforms
Mixing	Insufficient stripping of gases
	Excessive entrapment of gas from fine bubble mixing
Polymers	Excess cationic polymers from dewatering units
	Excess cationic polymers from thickening units
Solids, fine	Excessive particulate surfactants
Solids, total	Low level of total solids
Temperature fluctuations	Intermittent feeding of sludge
	Slug feeding of sludge
Scum	Rapid breakdown of scum in mature digester
Feed sludge	High organic content

Ref: Gerardi M.H. The microbiology of anaerobic digesters. Wiley Interscience. 2003

Foam and Scum

TABLE 20.2 Control Measures for Foam and Scum Production

Measure	Description
Activated sludge	Feed sludge to one digester at a relatively low feed rate, e.g., <0.05 lb VS/ft^3/day
Digester foam/scum	Manually remove foam and scum
	Treat foam and scum with an appropriate defoaming agent
	Break bubbles by passing foam through impeller
Mixing	Produce homogenized sludge, i.e., prevent stratification of solids
Primary clarifier scum	Do not waste to digester, i.e., find alternate means of disposal
	Treat with bioaugmentation products or enzymatic products to degrade lipids
Solids loading	Avoid high or slug loadings
	Avoid intermittent loadings
	If possible, feed continuously
Temperature	Maintain stable temperature
	Avoid temperature fluctuations >2°C

Ref: Gerardi M.H. The microbiology of anaerobic digesters. Wiley Interscience. 2003

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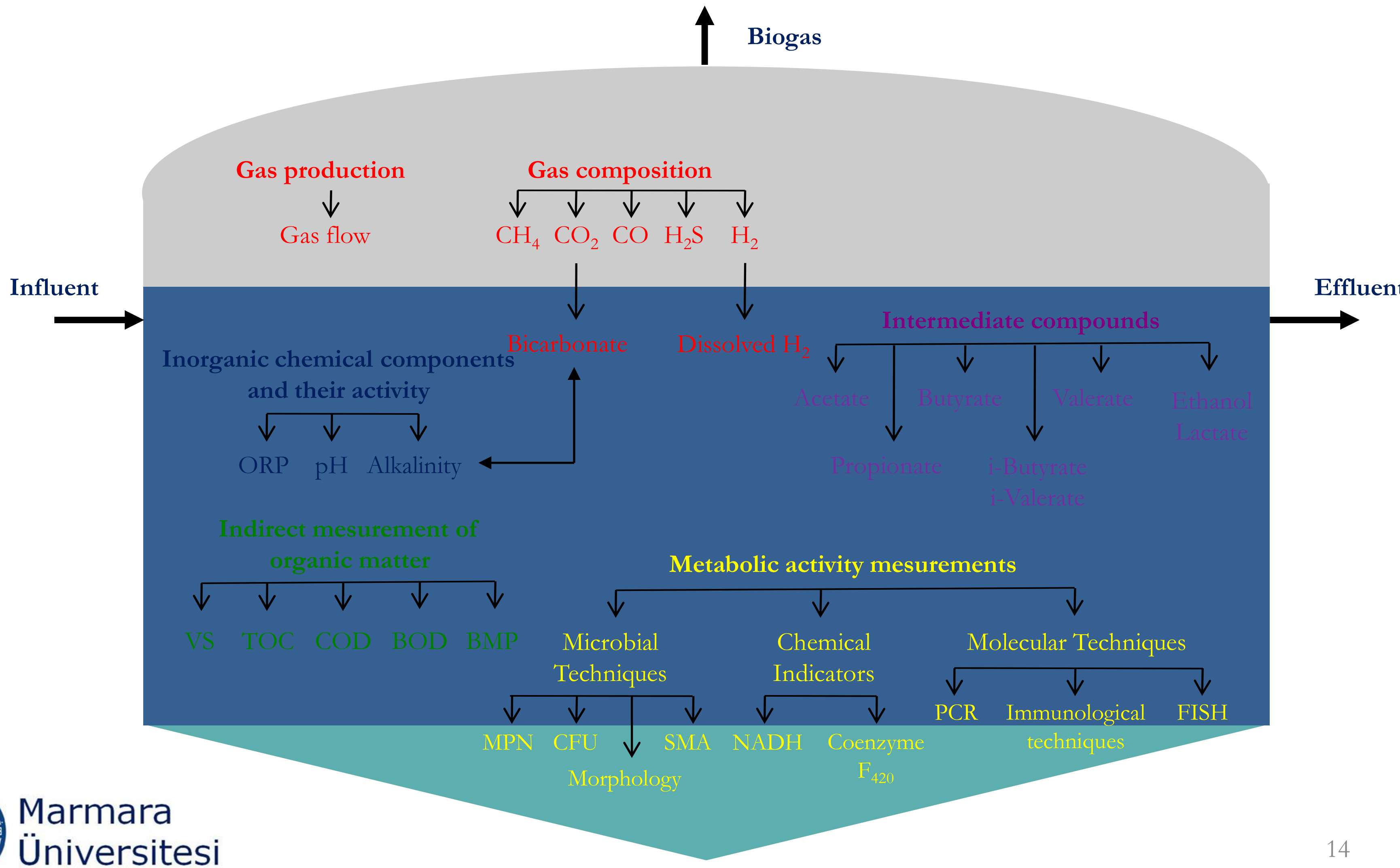
Process Measurements

Common process measurements used for monitoring anaerobic reactors are;

1. Gas production and gas composition
2. Intermediate compounds
3. Inorganic chemical components and their activity
4. Indirect measurements of organic matter
5. Metabolic activity measurements

Process Measurements



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1. Gas production and composition

- ***Gas Flow***
- Gas production is the earliest and most commonly used parameter for monitoring and control of ADs.
- Use of gas flow as an on-line measured parameter in control systems is widespread.
- Inhibition or overloading of methanogenesis can cause build-up of intermediate compounds such as VFAs, giving a lower gas production.

1. Gas production and composition

- ***Methane***
- Redox potential of the degraded waste controls the ratio between CH_4 and CO_2 being produced.
- pH and alkalinity inside the reactor control the solubility of CO_2 and so the percentage of CO_2 in the biogas.
- Therefore, it is desirable to use the production rate of CH_4 alone, since it is not disturbed by pH and alkalinity.

1. Gas production and composition

- ***Methane***
- By passing the biogas through a column/bed of soda lime, CO_2 can be scrubbed off, and a simple volumetric measurement of CH_4 can be conducted.
- Alternatively, CH_4 percentage can be measured using;
  - Gas chromatographic methods or
  - Infrared measurements

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1. Gas production and composition

- ***Carbon Dioxide and Bicarbonate***
- Bicarbonate (HCO_3^-) is usually the predominant buffer in ADs affecting the alkalinity due to the production of CO_2.
- Therefore, it is interesting to follow the evolution of CO_2 production if alkalinity or pH control is desired.
- Measurements of bicarbonate in liquid phase can be accomplished by controlled stripping of CO_2 followed by measurement of the amount of CO_2 stripped.

1. Gas production and composition

Hydrogen Gas

- Oxidation of propionate into acetate is energetically favorable only if the H_2 partial pressure is less than 6 Pa (60 ppm) at 35 °C.
- Assuming that the microorganisms producing and utilizing H_2 are well balanced in a stable reactor, overloading would rise H_2 concentration in biogas.
- However, the H_2 gas concentration does not reflect the degree of loading very well.

1. Gas production and composition

- ***Dissolved Hydrogen***
- Inconsistency in H_2 gas measurements is due to highly dynamic and non-linear air-liquid transfer of H_2.
- Therefore H_2 gas concentrations could not reflect the stability of AD process alone.
- Dissolved H_2 as a process variable, does not suffer from the same limitations and shows better correlation to organic loaading.

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1. Gas production and composition

- ***Hydrogen Sulfide***
- The concentration of H_2S in biogas reflects the current presence and degradation of sulfide containing compounds, if the pH is known.
- When dealing with concentrations below inhibiting levels, H_2S is not an interesting parameter to monitor.
- Since it can cause corrosion, measurements using electronic sensors or GC may be necessary.

1. Gas production and composition

- ***Carbon Monoxide***
- Presence of CO in concentrations of 10-100 ppm has also been reported to be of interest, due to the low solubility and easy measurement.
- However, use of CO concentration for process control has not yet been reported

2. Intermediate compounds

- ***Acetate***
- Monitoring the specific concentration of VFAs can give vital information on the status of AD process.
- After an overloading, HAc concentration often increases.
- However, if CH_4 production increases as well, process can find a new balance at a higher concentration level.
- So, increase in acetate concentration should not be seen as a sure sign of process failure, but more as a change in process balance that potentially could lead to failure.

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2. Intermediate compounds

- ***Propionate and Butyrate***
- Accumulation of propionate and butyrate is often seen as an imbalance between fermentation and acetogenesis.
- Propionate, butyrate and higher VFAs require very low H_2 concentrations for degradation to be energetically favorable.
- Propionate degradation requires 5-6 times lower concentrations of H_2 than butyrate degradation,

2. Intermediate compounds

- ***Propionate and Butyrate***
- Accumulation of propionate is often seen during feed composition changes due to short-time increases in dissolved H_2 levels & sudden fluctuations in temperature.
- If H_2 increase is more severe, butyrate will also build up.
- As the stress factor on the reactor is removed and process can stabilize itself, it will often be observed that butyrate is removed before propionate as a consequence of the difference in H_2 sensitivity.

2. Intermediate compounds

- ***iso-Butyrate and iso-Valerate***
- Due to the low concentrations of iso-butyrate and iso-valerate in a stable process, the relative change in these components will be higher when imbalance occurs.
- Therefore isoforms of butyrate and valerate are the best indicators of changes in the process balance.

3. Inorganic chemical components and their activity

- ***Redox Potential (ORP)***
- One of the simplest measurements is the ORP, which can reflect changes in oxidizing or reducing agents.
- ORP monitoring could detect inhibition by O_2.
- Applicability of ORP is very limited, since the anaerobic process is only energetically favorable at stable redox potentials below app. -400 mV, so that only inhibition by oxidizing matter can be detected by this measurement.

3. Inorganic chemical components and their activity

- ***pH***
- pH can indicate changes in the chemical balance, when acids, bases, anions and cations are being produced or removed as a consequence of metabolic activity.
- Monitoring is essential if pH is not kept constant by the process itself, however interpreting the pH data is complicated.

3. Inorganic chemical components and their activity

pH

- Dominating buffers such as bicarbonate, NH_3 & VFAs can stabilize the pH, or at least affect it considerably.
- Therefore, pH measurements cannot be used as indirect measurements of specific components or activities alone.
- However it should be used as a significant additional measurement that describes the state of AD.

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3. Inorganic chemical components and their activity

- ***Alkalinity***
- Total alkalinity (TA) is measured by titrating the sample to pH 3.7 and using the total number of moles added as the measurement.
- This measurement would normally include both bicarbonate and all VFAs.
- TA, therefore, reflects the liquid’s capability to withstand acidification without lowering the pH.
- It is commonly expressed in units of mgCaCO3/L and and preferably be in the range of 2000–3000 mg/L.

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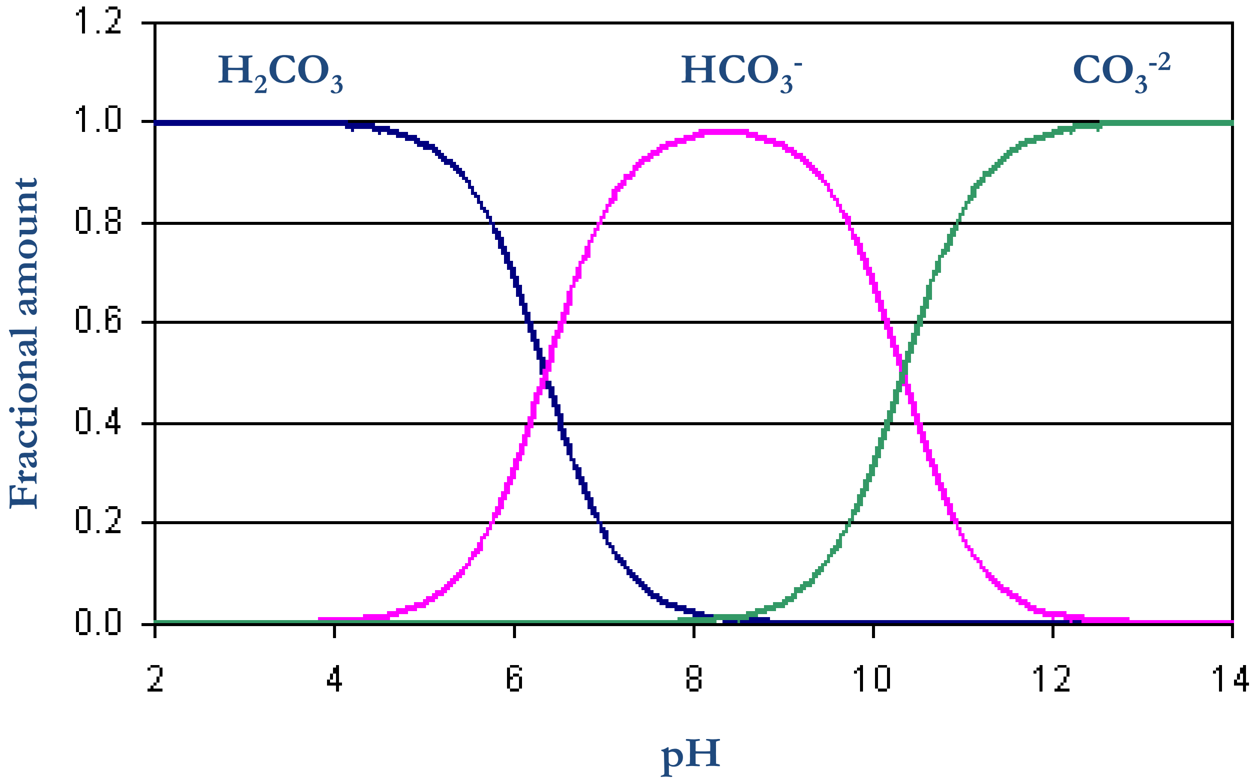
3. Inorganic chemical components and their activity

Components of carbonate system



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3. Inorganic chemical components and their activity

- ***Alkalinity***
- A decrease in TA below the normal operating level is used as an indicator of pending failure.
- A decrease in TA can be caused by;
    - An accumulation of organic acids due to the failure of methanogens to convert the VFAs to CH_4
    - A slug discharge of organic acids to the anaerobic digester, or
    - The presence of wastes that inhibit the activity of methanogens.

3. Inorganic chemical components and their activity

Chemicals commonly used for alkalinity addition

Chemical	Formula	Buffering Cation
Sodium bicarbonate	$NaHCO_3$	Na^+
Potassium bicarbonate	$KHCO_3$	K^+
Sodium carbonate (soda ash)	Na_2CO_3	Na^+
Potassium carbonate	K_2CO_3	K^+
Calcium carbonate (lime)	$CaCO_3$	Ca^{2+}
Calcium hydroxide (quick lime)	$Ca(OH)_2$	Ca^{2+}
Anhydrous ammonia (gas)	NH_3	NH^{4+}
Sodium nitrate	$NaNO_3$	Na^+

4. Indirect mesurement of organic matter

- ***Volatile solids (VS)***
- Measuring the content of organic matter before and after the process can reflect the efficiency AD.
- However, organic matter includes both solid and dissolved different types of organic matter, so no precise and simple method exists that can include all of this in one unit.
- Instead, a simple and indirect method called volatile solids (VS) is used.

4. Indirect mesurement of organic matter

- ***Volatile solids (VS)***
- Prior to VS measurement the content of total solids (TS) has to be determined.
- TS is measured as the dry matter content after drying the sample for at least 1 hour at app. 105°C, and includes both inorganic and organic matter.
- VS are measured as the amount lost when inginating the dry matter at app. 550 °C for 1 hour.
- VS amount reflects the organic matter in the sample.

4. Indirect mesurement of organic matter

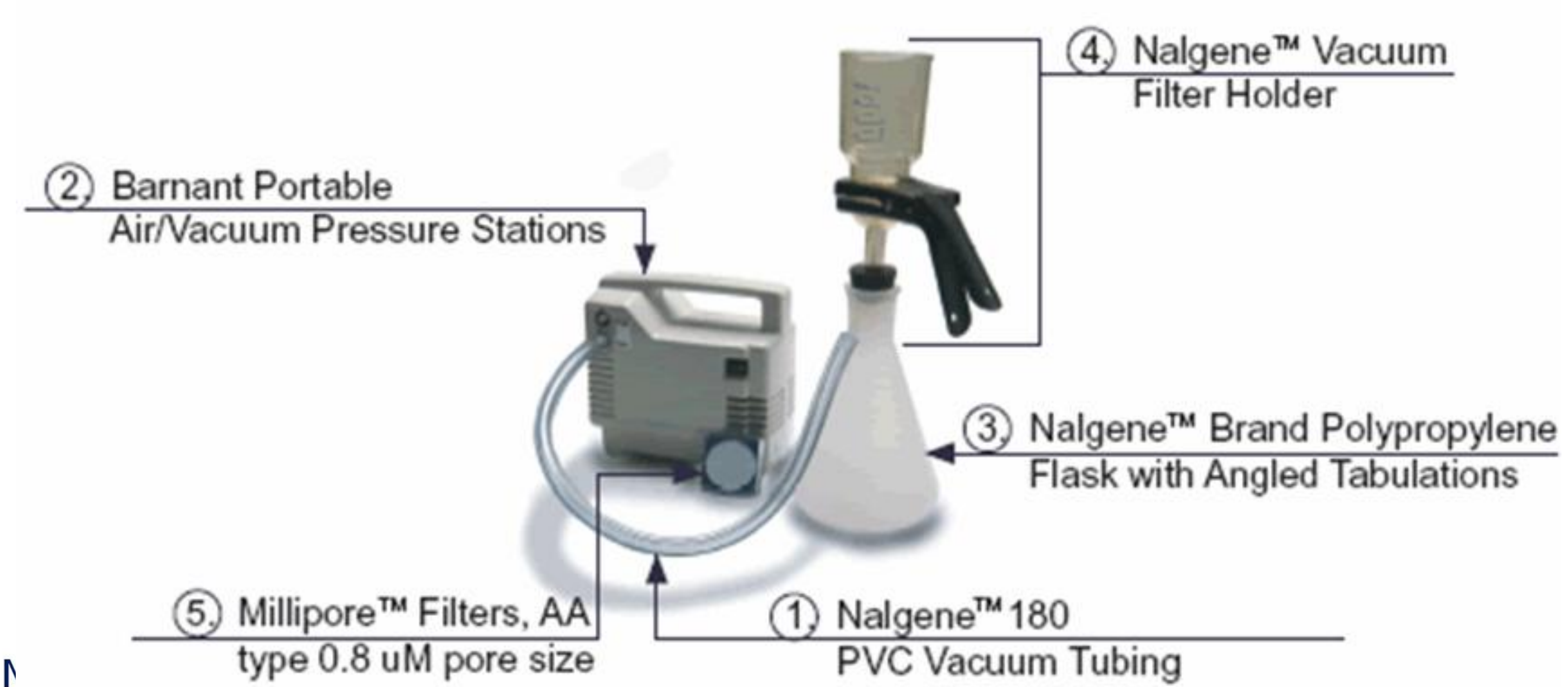
- ***Volatile solids (VS)***
- In practice, the actual yield is always lower than the theoretical yield of CH_4 given as (ml/gVS) due to effluent losses, VS spent for biomass synthesis and the presence of non-degradable complexes.
- VS is a good parameter for all types of organic matter, but the analysis time and method makes it unsuitable for on-line measurement and the application is mostly conducted manually for low-rate reactors.

4. Indirect mesurement of organic matter

- ***Volatile suspended solids (VSS)***
- If it is desirable to distinguish between dissolved (DS) and suspended solids (SS), filter the sample using a 1.2 mm pore-size filter.
- Solids left on the filter is characterized as the total suspended solid (TSS) or,
- Volatile suspended solid (VSS) by the same igniting process.

4. Indirect mesurement of organic matter

Total and Volatile suspended solids (TSS/VSS)



4. Indirect mesurement of organic matter

- ***Total Organic Carbon (TOC)***
- TOC is a suitable method, when dealing with dissolved organics at low concentrations.
- Determines the amount of organic matter by chemically oxidizing all carbon to CO_2, which is measured by an infrared analyzer.
- Not suitable for particulate matter, therefore mostly used in systems treating completely dissolved organics.

4. Indirect mesurement of organic matter

- ***Chemical Oxygen Demand (COD)***
- COD is another way of estimating all organic matter, by chemical oxidation at destructive temperatures.
- An advantage of COD is the fixed conversion factor of 0.35 m^3CH_4/kgCOD for all types of organic matter.
- However, COD also includes organic matter, which is not biologically degradable in anaerobic processes.

4. Indirect mesurement of organic matter

- ***Bio-chemical Oxygen Demand (BOD)***
- Therefore, BOD analysis is preferable for estimating the biodegradable organic matter in the waste.
- BOD is determined by measuring the O_2 used during aerobic degradation of the sample over a fixed period, normally 5 days; then it is termed BOD_5.
- However, BOD does not necessary reflect all the possibly biodegradable organic compounds under anaerobic conditions.

4. Indirect mesurement of organic matter

- ***Bio-chemical Methane Potential (BMP)***
- A better evaluation of anaerobic biodegradability can be achieved by BMP assays.
- BMP represent the amount of organic matter which can potentially be converted to CH_4.
- Whereas in BOD test the depletion of O_2 is measured, in BMP assay the production of biogas is evaluated.
- BMP is given as $mLCH_4/gVS_{added}$ or $mLCH_4/gVS_{degraded}$

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5. Metabolic activity measurements

- ***Microbial Techniques***
- Traditional techniques such as morphological studies are found to be insufficient for characterizing the micro-organisms in ADs.
- Other cultivation based methods, such as most probable number (MPN) or cell-forming unit (CFU) are selective, due to choice of media and other growth conditions.
- Although these techniques cannot be considered suitable for exact characterization or quantification of bacteria in ADs, they are still widely used.

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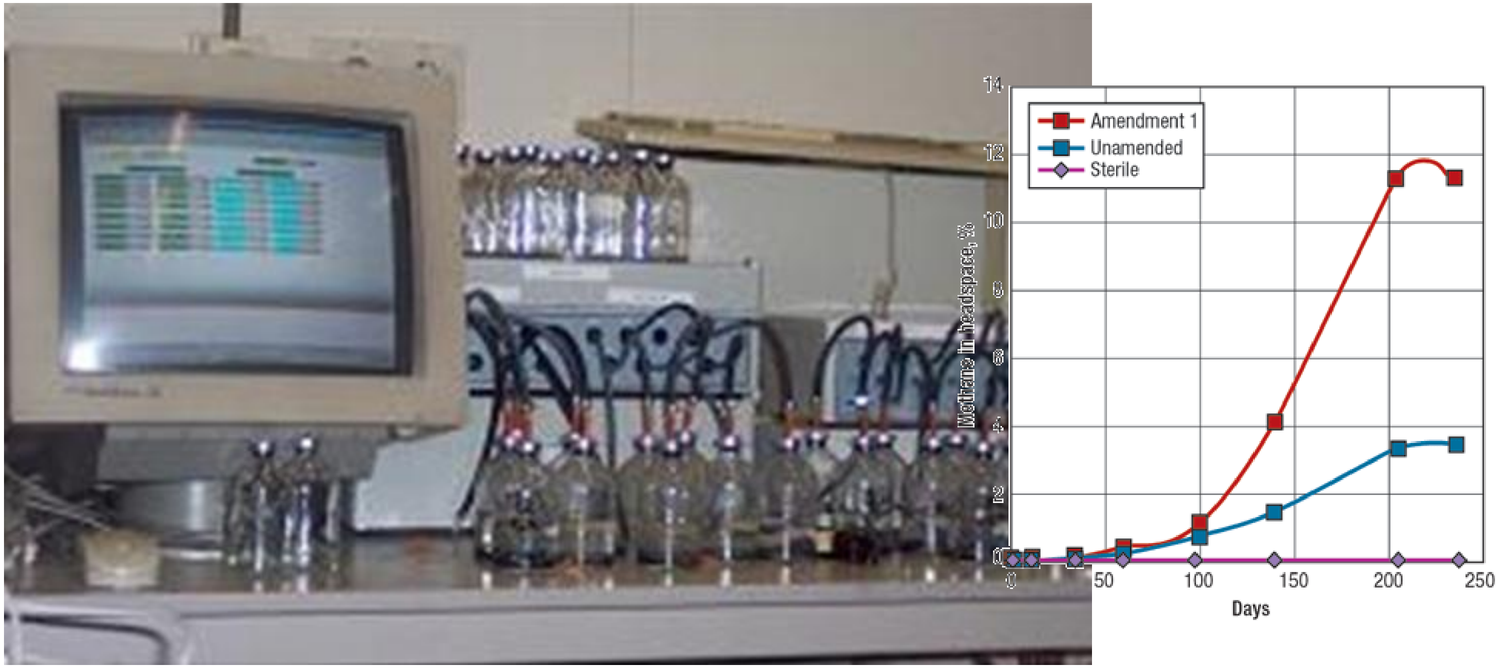
5. Metabolic activity measurements

- ***Microbial Techniques***
- Specific methanogenic activity (SMA), a test specifically developed for anaerobic conditions, estimates the potential gas production rate in a reactor system.
- It is mostly used to follow start up of anaerobic reactors.
- SMA, MPN and CFU techniques all require several measurements over a time span of hours to days to obtain usable results.

5. Metabolic activity measurements

Specific methanogenic activity (SMA) test



5. Metabolic activity measurements

- ***Molecular Techniques***
- Both immunological techniques and techniques based on RNA and DNA probing are used for both identification and quantification of microorganisms in ADs.
- All molecular techniques are only off-line methods and require tremendous amount of laboratory work.
- These techniques are, therefore, primarily used for obtaining better process understanding rather than actual monitoring.

5. Metabolic activity measurements

- ***Chemical Indicators***
- Cell-produced indicators, such as Coenzyme F420 and NADH have gained interest because of their easy detectability by fluorescence monitoring.
- A clear transient response in NADH and coenzyme F420 was observed as a reflection of the daily loading.
- The levels of NADH and coenzyme F420 increases instantly when feeding took place, followed by slow decrease in the level.