Anaerobic treatment of water and waste

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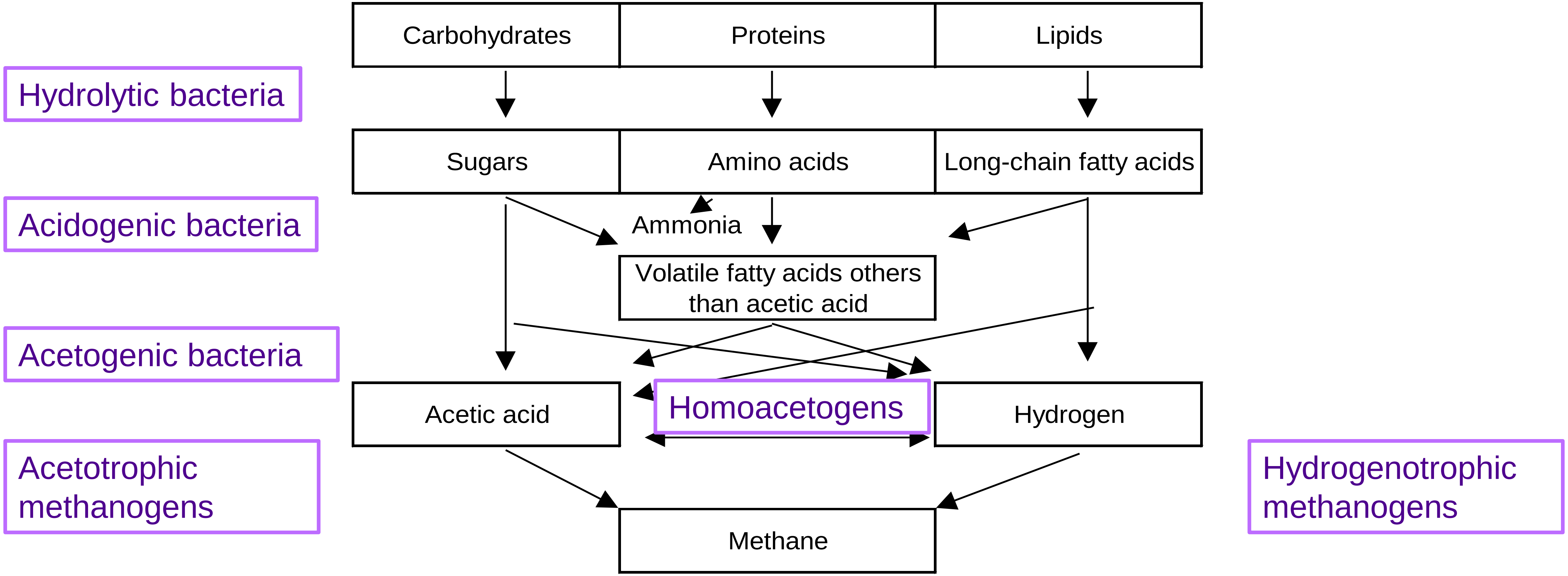
Content

- Basics of anaerobic treatment
- Possible feedstocks
- Process technology and important parameters
- Process types
- Examples of anaerobic treatment

Microorganisms in anaerobic treatment



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Hydrolytic bacteria

- Polymeric compounds do not access the cell membrane

  → Bacteria excrete enzymes that degrade polymers to smaller units

- Enzymes degrading different polymers

Polymer	Enzyme
Cellulose	Cellulase
Protein	Protease
Lipid	Lipase
Starch	Amulase
Chitin	Chitinase

- Dissolved smaller molecules are transferred through the bacterial cell wall and they are used as a source of carbon and energy

Acidogenic bacteria

- Acidogenic bacteria oxidize the amino acids, sugars and long chain fatty acids formed in hydrolysis (= fermentation)

- The end products consist of
  - Volatile fatty acids (VFAs)
  - Alcohols
  - H_2 and CO_2

- There are various different acidogenic bacteria
  - Obligate and facultative anaerobes
  - *Clostridia* are important group of acidogenic bacteria

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Acetogenic bacteria

- Acetogenesis = reaction producing acetate

- Hydrogen consuming acetogenic bacteria

$$4\ H_2 + 2\ HCO_3^- + H^+ \rightarrow CH_3COOH + 4\ H_2O, \qquad \Delta G° = -104{,}6\ \text{kJ/reaktio}$$

- Hydrogen producing acetogenic bacteria

$$\text{Butyrate}^- + 2\ H_2O \rightarrow 2\ \text{acetate}^- + H^+ + 2\ H_2$$
$$\text{Propionate}^- + 3\ H_2O \rightarrow \text{acetate}^- + HCO_3^- + 3\ H_2 + H^+$$

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Methanogens

- Hydrogen oxidizing methanogens

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$$

  - Remove hydrogen from the system, i.e. keep the hydrogen partial pressure low due to which hydrogen producing reactions become energetically beneficial

- Acetate degrading methanogens

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$$

Possible feedstocks

- Agricultural residues
  - Manure
  - Crop residues
- Municipalities
  - Sewage sludge
  - Biowaste
- Industrial biowaste and by-products
  - Food industry
  - Pulp and paper industry
- Energy crops

Important feedstock characteristics

- Solids content (total solids, TS)
- Organic matter content (volatile solids, VS)
- Chemical oxygen demand (COD)
- Composition: lipids, carbohydrates, proteins, lignin
- Methane production potential
- Nutrient content: nitrogen, phosphorous, potassium, micronutrients
- Physical and chemical characteristics: size, pH, potential toxins/inhibitive substances, impurities, non-degradable organic matter, fibers
- Pathogens, organic pollutants

Important feedstock characteristics

- Feedstock charcteristics may vary because of various reasons
  - Industrial wastes and by-products
    - Changes in process
    - Seasonal variation
    - Changes in raw-materials
  - Municipalities
    - Population increse/decrase
    - Consumption changes
    - Changes in waste management system, e.g. collection
    - Season, temperature

Pathogens and contaminants in feedstock

- When the feedstock is human or animal originated waste (e.g. slaughterhouse waste, sewage sludge) strict regulations for digestate use
- Salmonella, foot and mouth disease, mad cow disease…
- Indicator organisms usually analyzed (bacterial coliforms, *E.coli*, salmonella)
- Thermophilic AD process (55 °C) more eficient for pathogen removal than mesophilic (35 °C)
- Traceability of each digestate or digestate product important

- Heavy metals, traces from medicines, microplastics?

Composition of the feedstock

- Detemines the methane production potential
- Affects the degradation mechanism and rate
- Affects to potential process inhibition
  - Long chain fatty acids (LCFA) from lipids
  - Ammonia from proteins (nitrogen rich)

	Biogas (m^3/t)	Methane (m^3/t)	Methane conc. (%)
Carbohydrates	830	415	50.0
Lipids	1444	1014	70.2
Proteins	793	504	63.6

Inhibiting compounds in anaerobic treatment

- Mechanisms
  - Nonionized form of a compound penetrates the cell wall and affects the cell growth and functions (NH_3, H_2S, acetic acid, propionic acid)
  - Mechanical: prevents transfer of compounds to the microbes (e.g. LCFA)
- Anaerobic processes are more sensitive to inhibition than aerobic processes
  - Growth of methanoges is slow (especially acetate degrading methanogens)
- Due to inhibition, microbial growth slows down
  - Does not necessarily prevent wastewater treatment, but leads to decrased OLRs

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Examples of inhibiting compounds and their concentrations

Compound	Inhibiting concentration (mg/L)	Inhibiting effect (activity % from control sample)
Sulfite	125	50
Sulfide	50	10-50
Pentachlorophenol	0.2	50
2,5-dichlorophenol	600	100
Resin acids	40-90	50
Tannins	350-700	50
Dithionate	1500	99

Decreasing problems related to inhibition

- Removing inhibiting compound
  - Removing the waste fraction
  - Removing the inhibiting compounds in pretreatment
  - Precipitation or stripping in the process

- Diluting the inhibiting compound
  - Co-treatment of waste fractions
  - Dilution of wastewater, i.e. recirculation

- Adaptation of microbes
  - Adding inhibiting compounds gradually
  - Using specific microbial populations

Feedstock and its characteristics will affect to the whole biogas process design

- Affects
  - Process technology
  - Population of microorganisms in the process
  - Process stability
  - Biogas composition and yield
  - Digestate characteristics
  - Digestate processing
  - Hygienization

Municipal and industrial sewage sludges

- Municipal sewage sludge
  - Anaerobic digestion traditional technology to treat sewage sludge
  - Pathogens and heavy metals (Cd) may hinder the digestate use
  - In wastewater treatment plants sewage sludge is at 2-4 % TS
  - When transported to biogas plant, dewatered to 20-30 % TS

- Industrial sewage sludge
  - Characteristics vary depending on the industry
  - Sewage sludge from food industry is often easily degradable, e.g. sludge from fat separation process
  - Sewage sludge from forest industry difficult to degrade because of lignin and cellulose

Municipal biowaste

- Kitchen and gardening waste
- Biowastes can be different, e.g. in central Europe a lot of gardening waste included
- The aim of source separation is to obtain pure waste fraction (however, impurities are always included)
- Typically: TS 25-30 %, VS/TS 60-90 %

- Conventionally composted (consumes energy)

Industrial wastes and by-products

- Large variety of different wastes

- Food industry
  - Plant originated: vegetables, fruits, etc. → good degradability, no contaminants
  - Dairy industry: production of e.g. milk, butter, yoghurt, cheese
  - Brewing industry: bioethanol production

- Meat processing: slaughterhouses, rendering plants
  - Fats and proteins, high methane production but potential inhibition (LCFA, ammonia)
  - Animal by-product regulates the use

Manure

- Cow manure
  - Low methane production potential (already degraded in rumen)
  - Good buffer capacity
  - Methane and N_2O emissions can be reduced in anaerobic digestion process (GHGs)

- Pig manure
  - Higher methane production potential
  - Often quite large units
  - Low C:N ratio (~6)

- Poultry manure
  - Dry, up to 60% TS
  - High nitrogen content, danger to inhibition

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Anaerobic wastewater treatment

- Often for strong (COD > 1000 mg/L) and warm industrial wastewater that do not contain inhibiting compounds
  - Food industry, brewerys, distilleries

- Also for
  - Wastewater that are more difficult to treat, e.g. pulp and paper industry wastewaters
  - Municipal wastewaters in warm countries, mainly in developing countries where it enables wastewater treatment

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Nutrients in the feed – nitrogen

- Important growth nutrient for plants

- In anaerobic digestion process, organic nitrogen is mineralized to ammonium (in digestate >50 % as NH_4), which is readily available for plants
  - However, specially the unionized form (NH_3) is one of the most common inhibitors of anaerobic digestion process
  - If ammonium from digestate cannot be utilized, may result in high load to wastewater treatment

- Safe C/N ratio for feedstock ~20–30
  - Co-digestion of nitrogen rich substrate with other (low N) feedstocks may be needed
  - Nirtogen rich feedstocks include e.g.; slaughterhouse and rendering plant wastes, fish waste (protein rich feedstocks), manures

Nutrients in the feed - phosphorus

- Important growth nutrient for plants
- Phosphorus resources are decreasing?
  - Biogas technology could be one way to recover and recycle phosphorus from waste streams
- Not causing inhibition in biogas process in usual concentrations
- Phosphorus rich feedstocks include: Manures, wastewaters, sewage sludges…

Nutrients in the feed – potassium and micronutrients

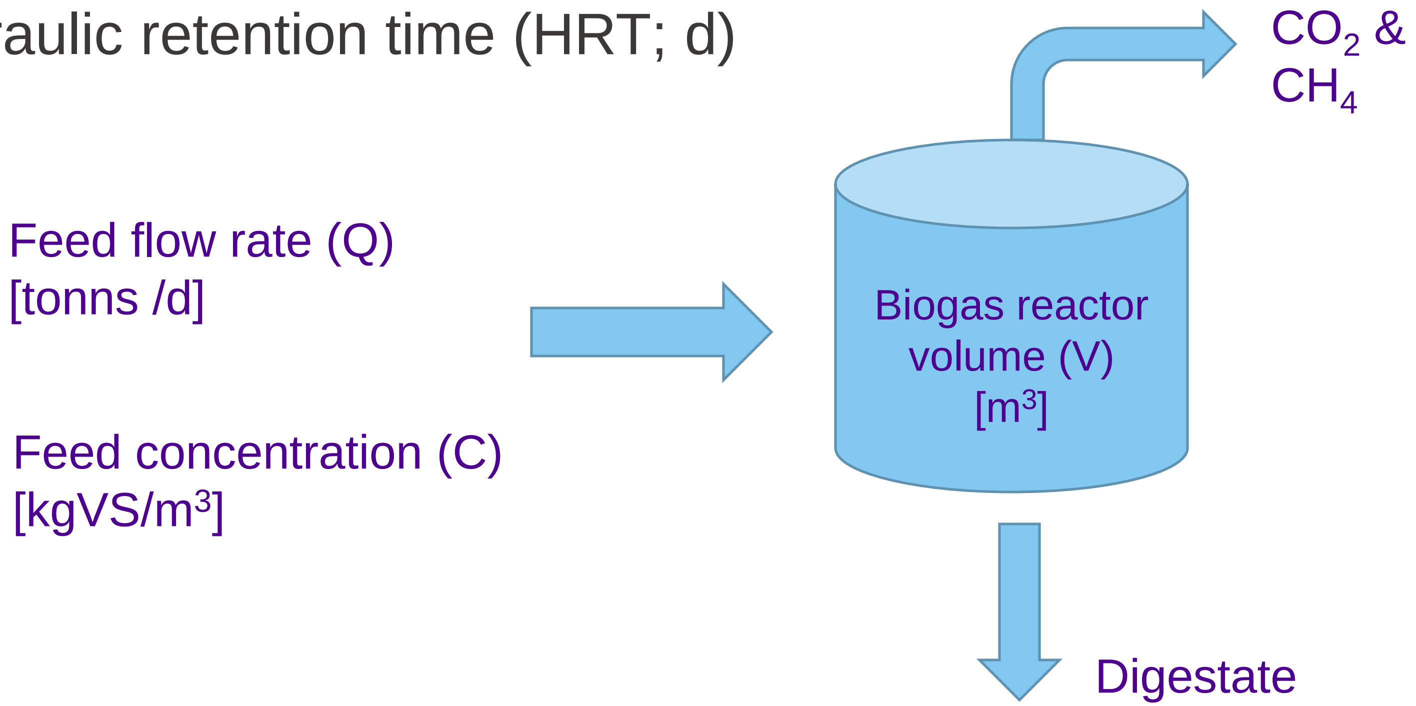
- Potassium
  - Also an important nutrient, possible to recover in digestates

- Micronutrients (e.g. Fe, Mg, Co, Na...)
  - Necessary for anaerobic micro-organisms, but also inhibitive in too high concentrations
  - Some feedstocks may lack of micronutrients, or nutrients are not bioavailable
    - E.g. Rendering plant wastes, crops, municipal biowaste
    - Co-digestion or additives is a possible solution

Process operation – important parameters

- Organic loading rate (OLR)
  - Treatment of waste: kgVS/m^{3}d

- Hydraulic retention time (HRT; d)



Process parameters

$$OLR = \frac{Q\,C}{V} \quad [\text{g VS/m}^3\text{d}]$$

$$\text{HRT} = \frac{V}{Q} \quad [\text{d}]$$

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OLR and HRT

- OLR determines the size of the reactor
- The aim is to maximize the OLR, while keeping the process stable and controlling the amount of methane produced after the reactor
- The OLR (usual OLR 1-8 $kgVS/m^3d$) is maximized by
  - Choosing reactor type
  - Composition and homogenity of the feed
  - Enrichment and adaptation of microbial community (done by increasing OLR step by step)

- The reactor content should change 2-3 times (2-3 times the HRT) before the process performance can be seen
- HRT can be between 10-150 d

OLR and overload

- OLR changes fast and significantly → the OLR increases, which can result in overload

- Possible effects
  - Production of VFAs
  - Decrease or termination of methane production

- Actions
  - Stopping the feed
  - Adding inoculum
  - Diluting the feed

Process technology options

- Mesophilic vs. thermophilic
- Batch vs. continuous process
- Completely mixed vs. plug flow process
- One stage vs. multi-stage process
- Wet vs. dry process

- Combination of these

Parameters affecting anaerobic treatment

- pH
  - Methanogens 6.6-7.6
  - Acidogenic bacteria 5.2-6.3
  - High OLR → Decrease in pH → Decrease in methane production
  - Disturbances in feeding → Increase in pH → Disturbance in acidogenic bacteria

- Temperature
  - Mesophilic microorganisms (35-40°C): Not sensitive for temperature fluctuations, hygienisation is not as effective
  - Thermophilic microorganisms (55-65°C): More sensitive for fluctuations in pH and temperature as well as for inhibiting compounds, requirement for additional heating, better hygienisation, possibility to use higher OLR, faster treatment of wastewater

Batch vs. continuous

Batch

- Reactor is filled and the anaerobic degradation proceeds from hydrolysis to methane production
- Various batch reactors, where degradation proceeds in different steps
- Often dry processes
- So called ”carage model”

Continuous

- More often used
- Ofter semi-continuous, where feed is added periodically
- Better result, if continuous feeding
- More stable quality of the digestate and methane production

Dry vs. wet process

Dry process

- Transfer with screw conveyers, belts, etc.
- Gas removal can be difficult
- Often plug flow
- The inoculum has to be recycled
- Substrate gradients, i.e. the substrate concentrations and anaerobic degradation phases vary
- Small need for heating

Wet process

- TS 10-13%, but can be even higher if the biodegradability is high
- The feed is pumped
- Reactor content can be mechanically mixed
- Completely mixed reactor with homogenous content
- Liquid fraction is often separated from the digestate (conteins e.g. ammonium-N)
- If used for dry feed, the feed is diluted with the liquid part of the digestate (risk for inhibition)

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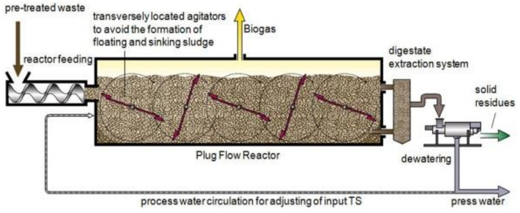
Solids (TS) and organic matter (VS) content

- **TS <1 %**
  - Wastewaters
  - Sludge bed reactors (upflow anaerobic sludge bed, UASB)
  - Chemical oxygen demand (COD) usually used as loading parameter instead of VS
- **TS <10 %**
  - **Wet process**
  - Usually possible to use pumps
  - Needs more energy for heating than dry process
  - Water separation from effluent, if needed, consumes energy
  - Manure ~4-6 % TS, concentrated sludge from wastewater treatment ~ 2-4 %

- **TS >10 %**
  - **Dry process** (e.g. plug flow) or dilution needed
  - Material transported in the system using e.g. screw feeders
  - Solubilisation less effective, mixing consumes more energy
  - Municipal biowaste ~ 30 %, grass ~ 20-40%



http://enermac.com//

One vs. multi-stage process

One stage

- All the reactions occur in one reactor
- The reactor is optimized according to the slowest phase and methane production
- Does not necessarily lead to maximum methane production
- Often the process is completely stirred

Multi-stage

- Degradation occurs in many reactors
- Hydrolysis and acidogenesis in one reactor, methane production in another
- The stages can be optimized separately
- Examples
  - Spontaneous hydrolysis and acidogenesis can occur in storage tank
  - Methane can be produced in post storage of digestate
  - First stage can also be H2-process
- More structures required than one stage process → More expensive, if the enhanced methane production does not compensate the costs

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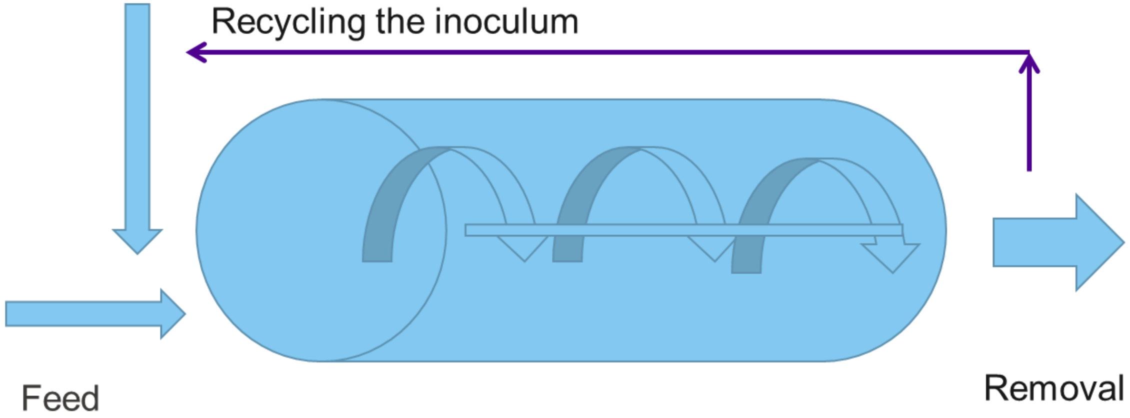
Plug flow reactor



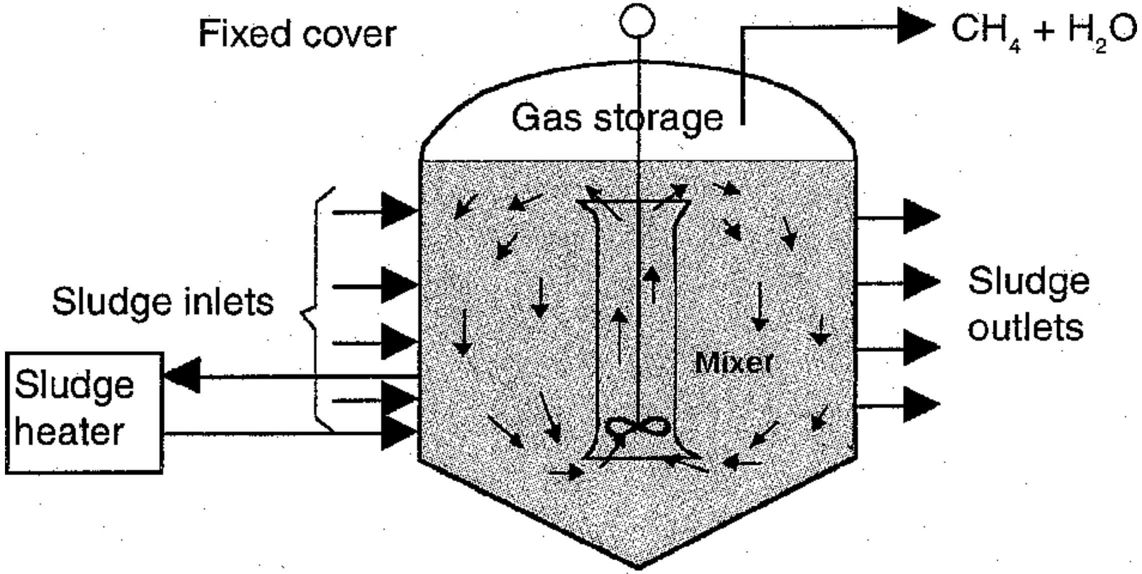
- Often dry processes

- Horizontal
  - Inoculum can be added to the feed before the reactor
  - Produced methane along the whole reactor volume
  - Mass transfer mechanically

- Vertical
  - Feed from the top of the reactor
  - Degradation products are transferred towards the bottom, when the methane production is enhanced
  - Screw axis is used for mass transfer

Completely stirred tank reactor (CSTR)

- Mainly anaerobic digestion of sludge
- Often wet processes
  - The liquid fraction of the digestate can be recycled, here the accumulation of certain compounds (e.g. NH_4^+) has to be taken into accoung
- Design parameters
  - 35ºC
  - Sludge retention time (SRT): 15-30 d
  - Ogranic loading rate (OLR): 4 kg COD/m³d



Completely stirred tank reactor (CSTR)

- Mechanical mixing
  - Picket fence stirrer (blades at different heights)
  - The surface can be mixed separately
  - Continuous or intermittent
  - To be considered: energy consumption, corrosion resistance

- Gas mixing
  - Nozzles at the bottom of the reactor, where the gas is recycled to

- Hydraulic mixing
  - Using pumps to recycle the reactor content
  - The pump can contain a shredder to decrease the particle size

Upflow anaerobic sludge blanket (UASB) reactor

- Operation is based on the good settling characteristics of the sludge
- Biomass retention due to formation of granules
  - Mainly microbial biomass
  - Diameter 1-5 mm, compact aggragates
  - Sludge granules can be obtained as preprepared granules or they are grown upon start-up

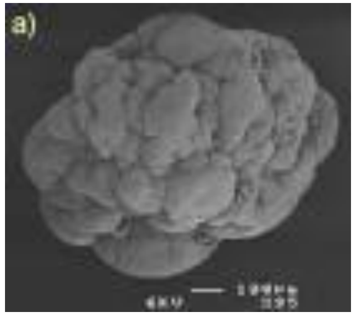
  → Microbes are close to each other → Transfer of metabolites is fast

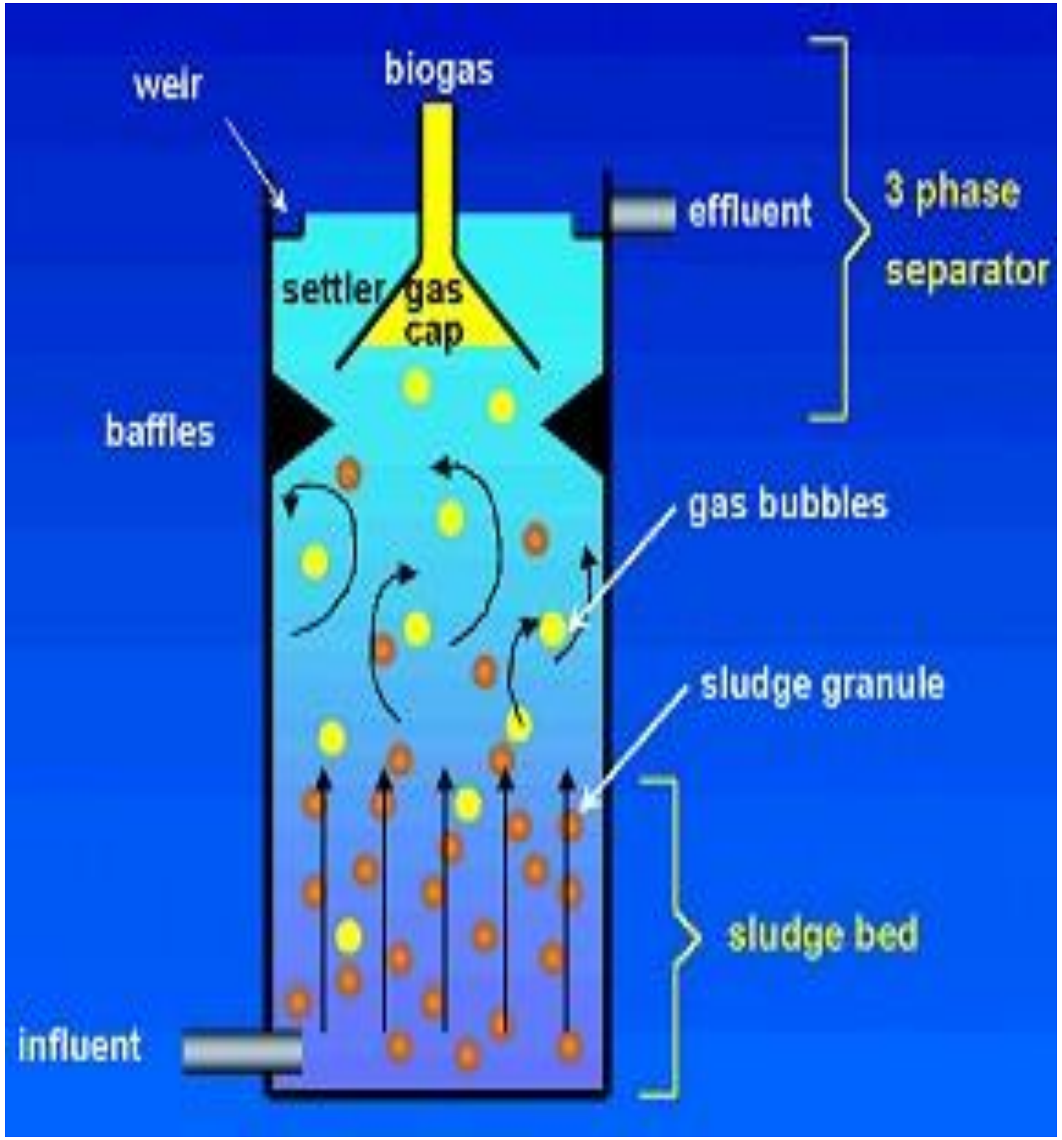
- Upflow of liquid and gas bubbles fluidize the sludge and cause hydraulic mixing

UASB

- Especially for
  - Food industry
  - Pulp and paper factories
  - Chemical industry

- Design parameters
  - Hydraulic retention time (HRT): 4-8 h
  - SRT ≥ 15-30 d
  - OLR: 5-20 kg COD/m^3d

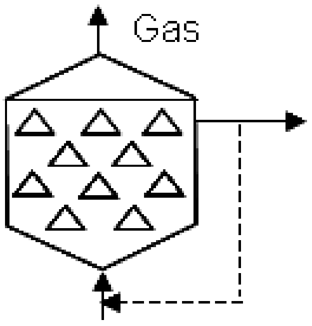




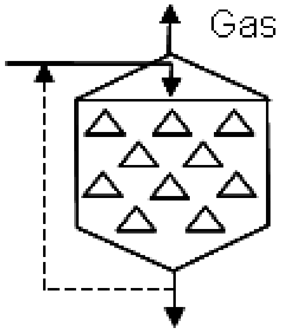
Anaerobic filter and hybrid reactors

- Anaerobic biofilters
  - Upflow or downflor filters
  - Bacteria form a biofilm on carrier materia
  - Excellent retention of biomass
  - HRT: 1-3 d
  - OLR: 5-20 kg COD/m^{3}d

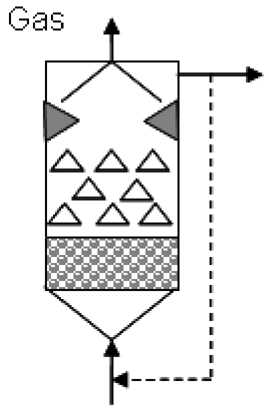
- Hybrid reactors
  - Combination of filter and sludge bed reactors
  - HRT: 12-40 h
  - OLR: 1-10 kg COD/m^{3}d



Upflow filter



Downflow filter



Anaerobic hybrid reactor

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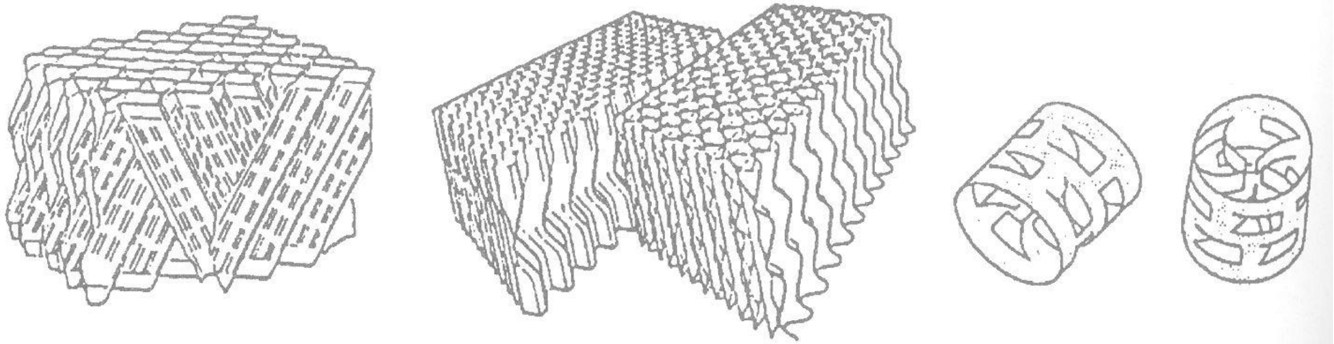
Anaerobic filter materials

www.sequencertech.com

- Plastic particles or matrixes
- Part of the biomass can retain as aggregates in the voids of filter material
- Problems: clogging
- Different rinsing processes have been developed to remove the biomass

- Typical specific surface area: 100 m^2/m^3
- Void space 90-95% of the overall volume

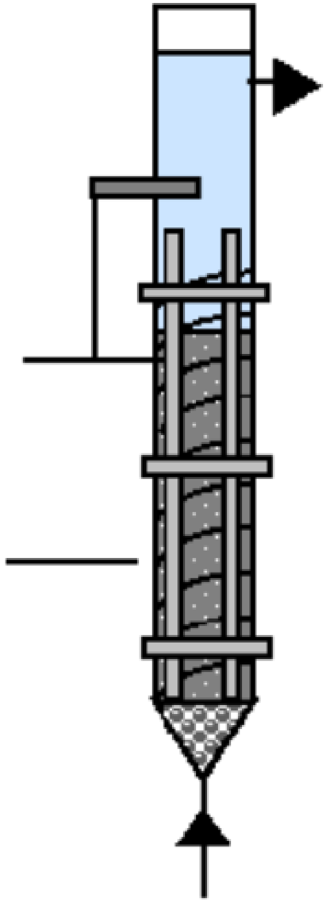


A. B. C.

Rittman & McCarty (2001)

Anaerobic fluidised bed reactor (FBR)

- High upflow velocity fluidizes the carrier materials, which is achieved with recirculation flow
- Biomass forms a biofilm on the carrier material (15-35 g VSS/L)
- Carrier material
  - 0.2-0.55 mm sand particles/activated carbon
  - Typical specific surface area: 5000-10000 m^2/m^3
- Good mass transfer
- Design parameters
  - HRT: 0.2-2 g
  - OLR: 20-40 kg COD/m^3d



Fluidised bed

Design of anaerobic wastewater treatment

- Design parameters available for anaerobic sludge treatment

- Not specific design parameters for anaerobic wastewater treatment → industrial wastewaters have large variations

- Has to be considered
  - Organic content and concentration of wastewater (loading)
  - Inhibiting compounds
  - Temperature and pH
  - Changes in loading

- Aim
  - Fast growth of active biomass and good retention in the reactor
  - Long SRT
  - Short HRT
  - Short treatment time

- Before design
  - Laboratory experiments (biodegradability, inhibition)
  - Pilot-scale experiments (reactor type, optimization of environmental parameters)

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Digestate

- The end product of the biogas process
- The aim is to utilize the digestate, e.g. in crop production
- Treatment of digestate
  - The quality of the digestate has to be controlled considering the end-use
  - Important factor is the control of emissions (incl. greenhouse gas emissions)
- Digestate processing can produce a liquid fraction that also requires treatment

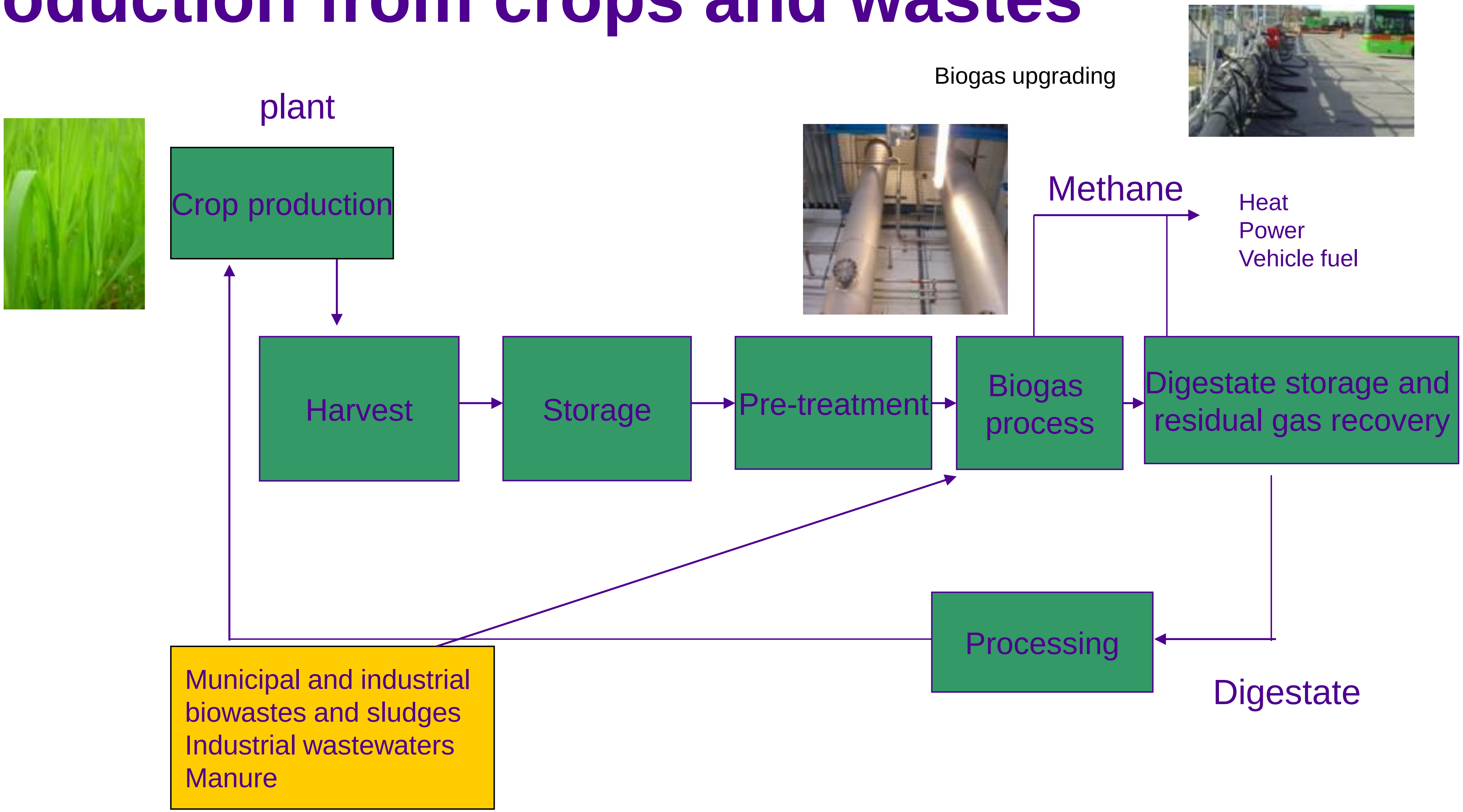
Digestate quality

- Nutrients available for plant growth
- No pathogens
- No heavy metals
- Also the concentrations of organic detrimental compounds are regulated
- The digestate (or nutrient product) has to be spread with the existing equipment
- High enough nutrient content

The effect of biogas process on the digestate

- Hygienisation
- Some detrimental compounds are degraded
- Better nutrient balance
  - The share of ammonium-N increases, usually 50-60% as ammonium-N (depends on feed and process conditions)
  - C:N –ratio decreases
  - Recycling of other nutrients, e.g. P, K. Ca, Mg
- The amount of organic matter in the soil increases
- The use of inorganic fertilizers decreases
- More homogenous material compared to the feed
  - Easier and more controlled spreading
  - Transfers more easily to the soil

Overview – Concept for methane and fertilisers production from crops and wastes



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Anaerobic treatment of sedimented fibers

- New city district, Hiedanranta, of 115 ha for 25 000 people
- Sulphite/CTMP pulp mill discharged effluents to the nearby bay area from 1910s to 1980s
  Ca. 1.5 million m^3 sedimented fibers from a pulp mill, up to 10 m, ca. 20 ha