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# Anaerobic treatment of wastewater and solid waste

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# Content

- Basics of anaerobic treatment
- Possible feedstocks
- Important parameters
- Reactor types
- Examples of anaerobic treatment

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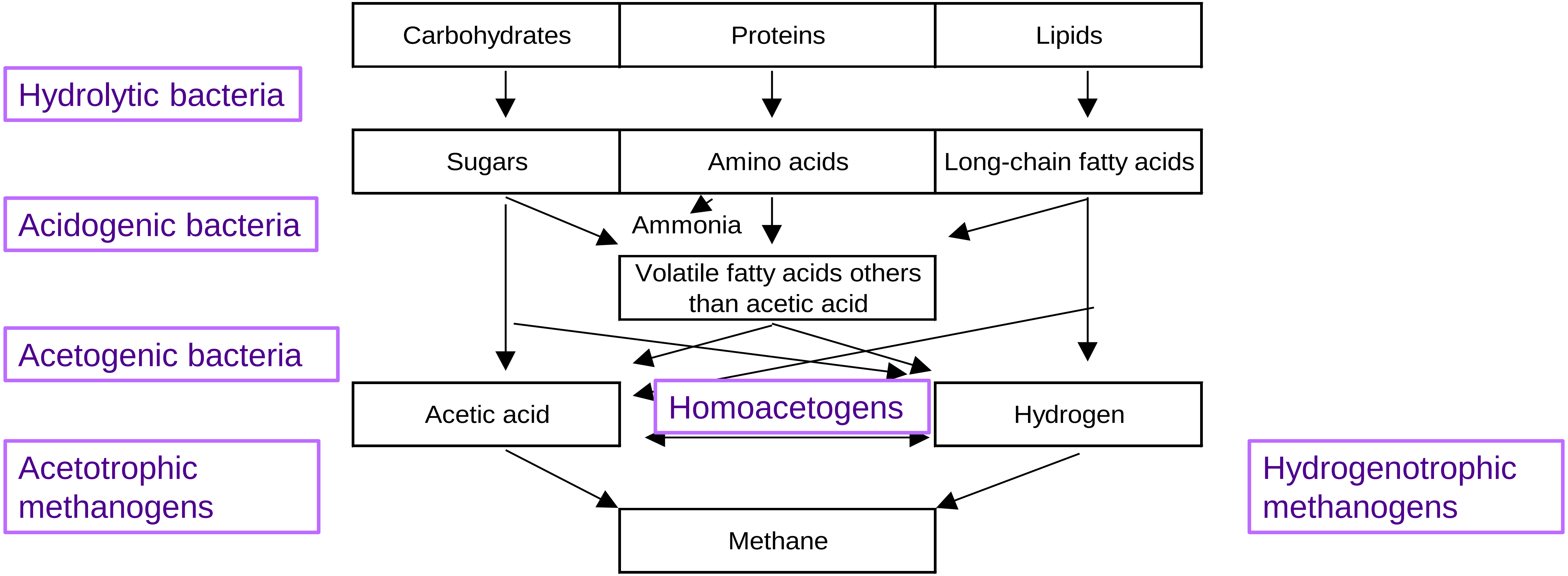
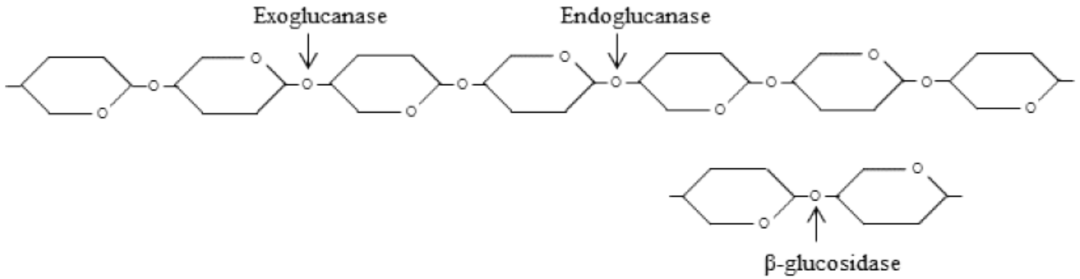
# Comparison of aerobic and anaerobic wastewater treatment

| | Aerobic | Anaerobic |
|---|---|---|
| **Energy requirement** | $C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$<br>$\Delta G°' = -2826$ kJ | $C_6H_{12}O_6 \rightarrow 3\ CH_4 + 3\ CO_2$<br>$\Delta G°' = -394$ kJ |
| **End-product** | | 85% of the substrate´s energy is stored in methane (theoretically: 1 kg COD = 350 L $CH_4$) |
| **Substrate concentration** | Also treats low concentrations | |
| **Nutrient reguirements (BOD:N:P)** | 100:5:1 | 100:2:0.5 |
| **Biomass holdup** | 1-3 kg/$m^3$ | 10-30 kg/$m^3$ (faster treatment rates) |
| **Sludge production** | 0,25-0,5 kg/kg $BOD_{5\text{-removed}}$<br>(requires stabilisation) | 0.05-0.1 kg/kg $BOD_{5\text{-removed}}$<br>(stable sludge) |
| **Sensitivity** | Not sensitive (microbes work independently/in parallel) | Sensitive (microbes interact with each other/work in series) |

# Microorganisms in anaerobic treatment






Cellulase enzymes
(individual enzymes)

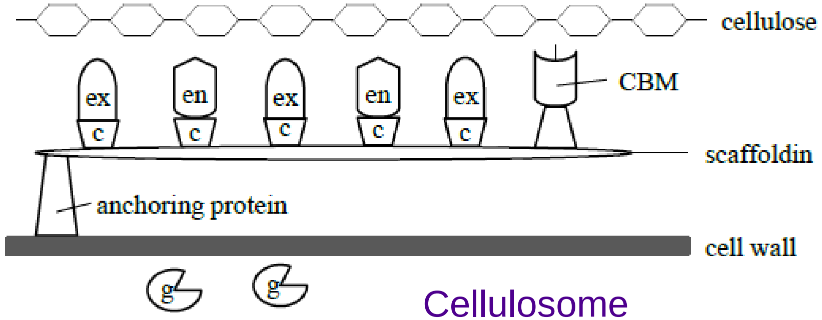
# Hydrolytic bacteria

- 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 |




Cellulosome
(multi-enzyme complex)

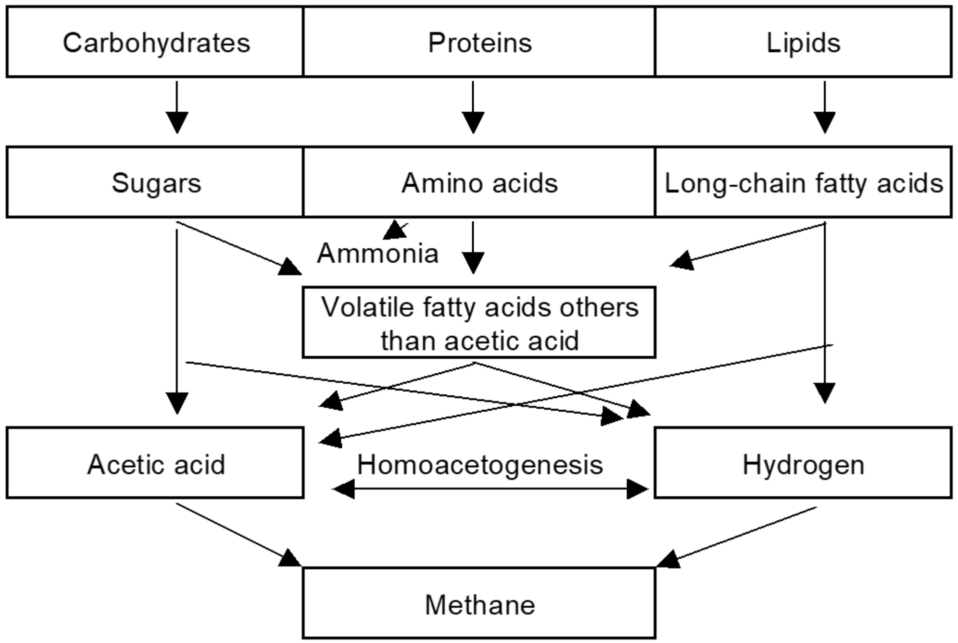
- Dissolved smaller molecules are transferred through the bacterial cell wall and they are used as a source of carbon and energy

# 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



# Acetogenic bacteria

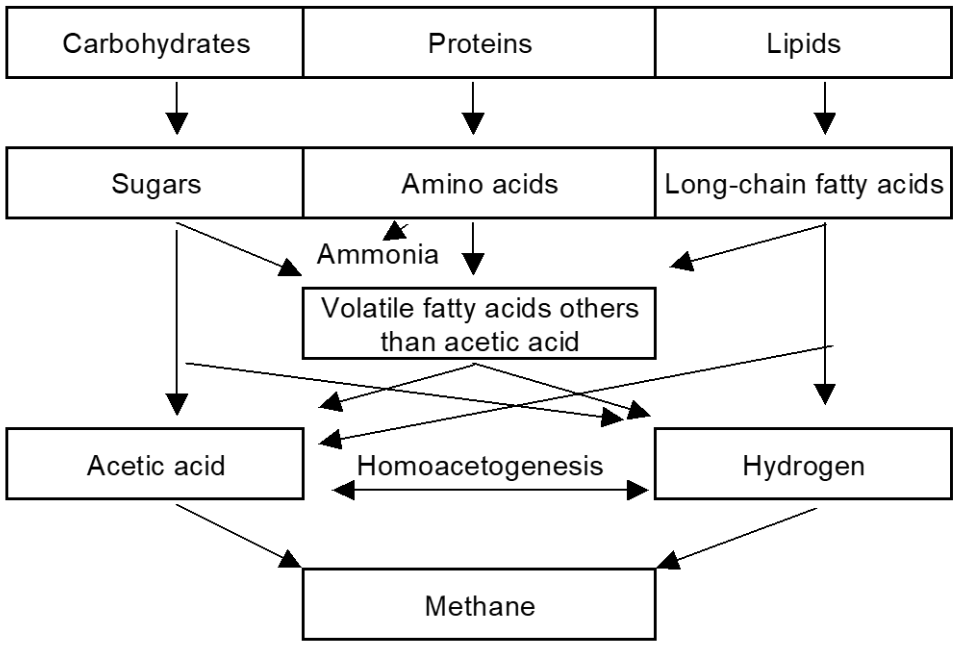
- Acetogenesis = reaction producing acetate

- Hydrogen consuming acetogenic bacteria

$$4\ H_2 + 2\ HCO_3^- + H^+ \rightarrow CH_3COOH + 4\ H_2O$$

- Hydrogen producing acetogenic bacteria

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



# Methanogens

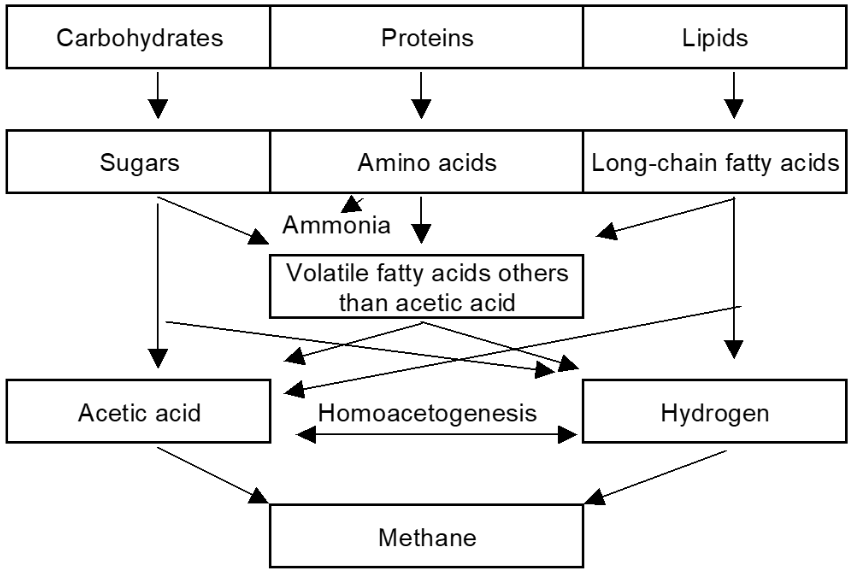
- Hydrogen oxidizing methanogens

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

  - 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

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



# Sulphate reducing bacteria (SRB)

- Competing process with methanogenesis in anaerobic environments
- Sulphate is the terminal electron acceptor
  1. Incomplete oxidizers: oxidise organic acids and alcohols to acetate

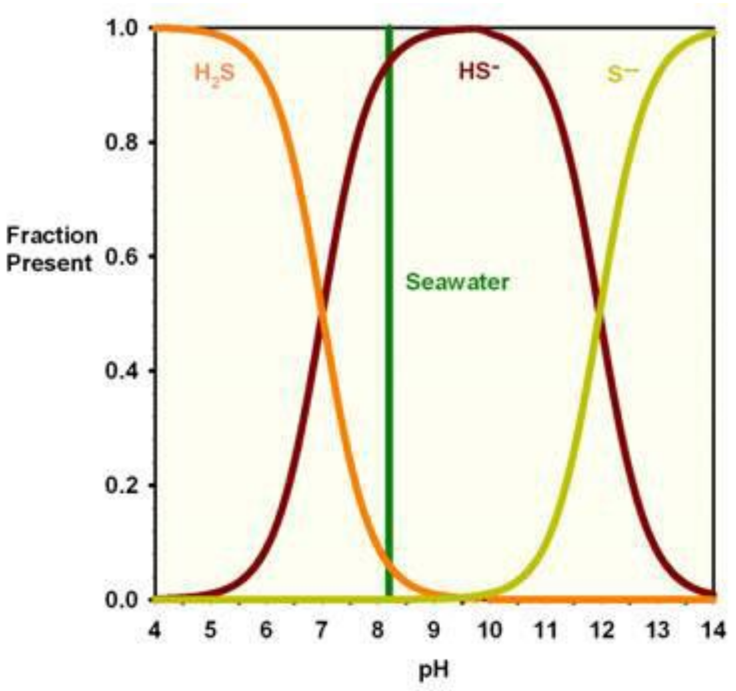
     $4\ C_2H_5COO^- + 3\ SO_4^{2-} \rightarrow 4\ CH_3COO^- + 4\ HCO_3^- + 3\ HS^- + H^+$

  2. Complete oxidizers: oxidise organic acids to carbon dioxide

     $2\ C_6H_{12}O_6 + 6\ SO_4^{2-} + 9\ H^+ \rightarrow 12\ CO_2 + 12\ H_2O + 3\ H_2S + 3\ HS^-$

     $CH_3COO^- + SO_4^{2-} \rightarrow 2\ HCO_3^- + HS^-$

- $H_2S$ inhibits methane production



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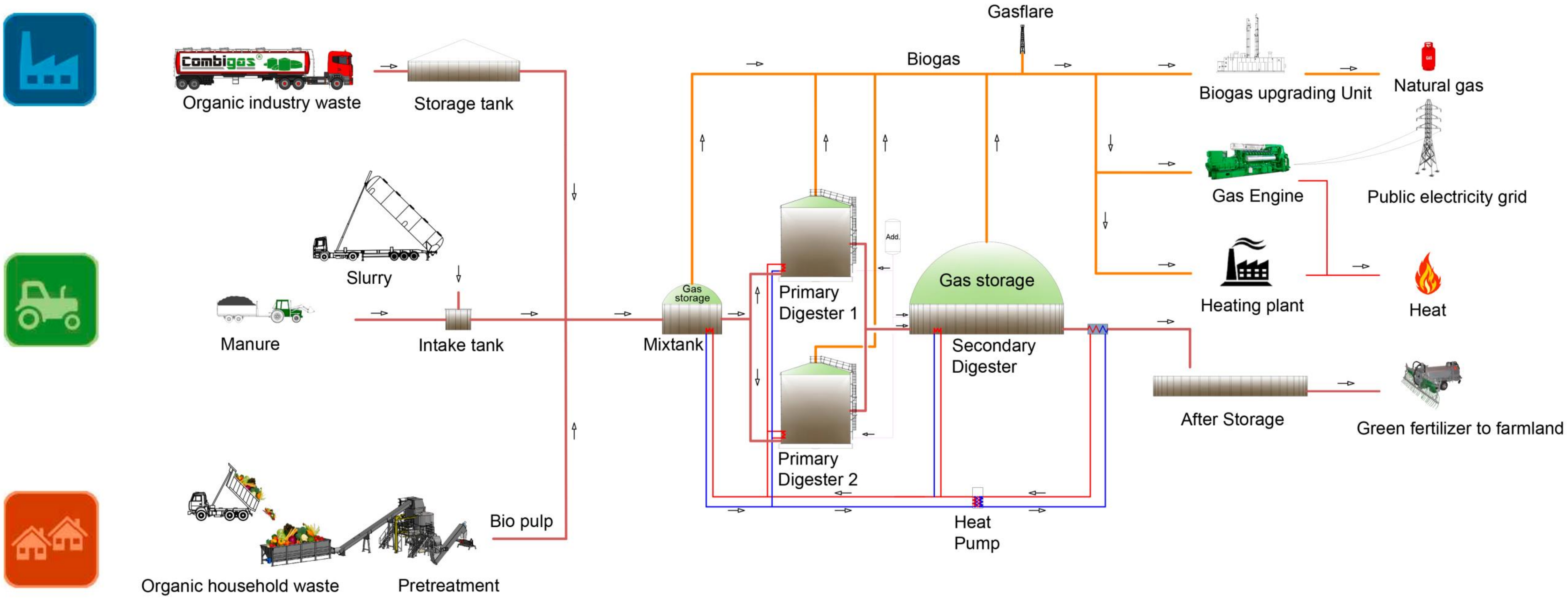
# Biogas process




https://www.combigas.com/biogas-2/

# 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

# Possible feedstocks

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

- Varioations in feedstock characteristics
- Industrial wastes and by-products
  - Changes in process
  - Seasonal variation
  - Changes in raw materials
- Municipalities
  - Population increase / decrease
  - Consumption changes
  - Changes in waste management system, e.g. collection
  - Season, temperature

# 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

| | 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 |

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# 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 organic loading rates (OLRs)

# 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

# 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…
- Requirements for **hygienisation**
  - Before or after biogas process (1 h, 70°C)
  - Thermophilic AD process (55 °C) more efficient for pathogen removal than mesophilic (35 °C)
- Traceability of each digestate or digestate product important

- Heavy metals, traces from medicines, microplastics?

# Municipal and industrial sewage sludges

- Municipal sewage sludge
  - Anaerobic digestion traditional technology to treat sewage sludge
  - In wastewater treatment plants sewage sludge can be used at 2-4 % TS or dewatered (e.g. 10-15% TS)
  - When transported to biogas plant, dewatered to 20-30 % TS

- Industrial sludge
  - Characteristics vary depending on the industry
  - Sludge from food industry is often easily degradable
  - 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 %

www.etappi.com

# Industrial wastes and by-products

- **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 of digestate

- **Industrial wastewaters**
  - Often for strong (COD > 1000 mg/L) and warm industrial wastewaters that do not contain inhibiting compounds
  - Food industry, breweries, distilleries, pulp and paper industry wastewaters

# 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

https://www.manuremanager.com

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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
  - Nitrogen 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

- Phosphorous 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, Mo...)
  - 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 are possible solutions

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

- Process technology / reactor design
- Population of microorganisms in the process
- Process stability
- Biogas composition and yield
- Digestate characteristics
- Digestate processing
- Hygienisation

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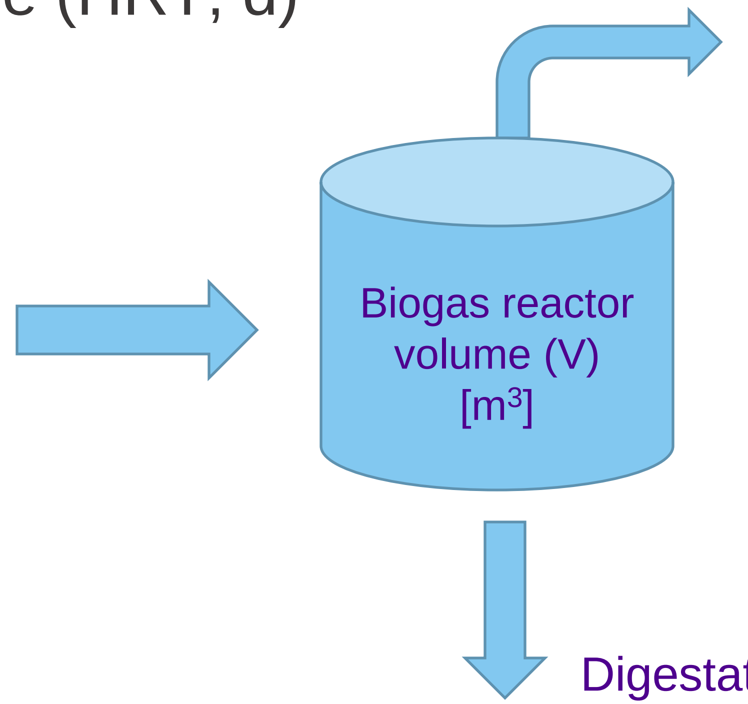
# Process operation – important parameters

- Organic loading rate (OLR; kg-VS/m$^3$d)
- Hydraulic retention time (HRT; d)

Feed flow rate (Q) [m$^3$/d]

Feed concentration (C) [kgVS/m$^3$]




$CO_2$ & $CH_4$

Digestate

## Process parameters

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

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

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# OLR and HRT

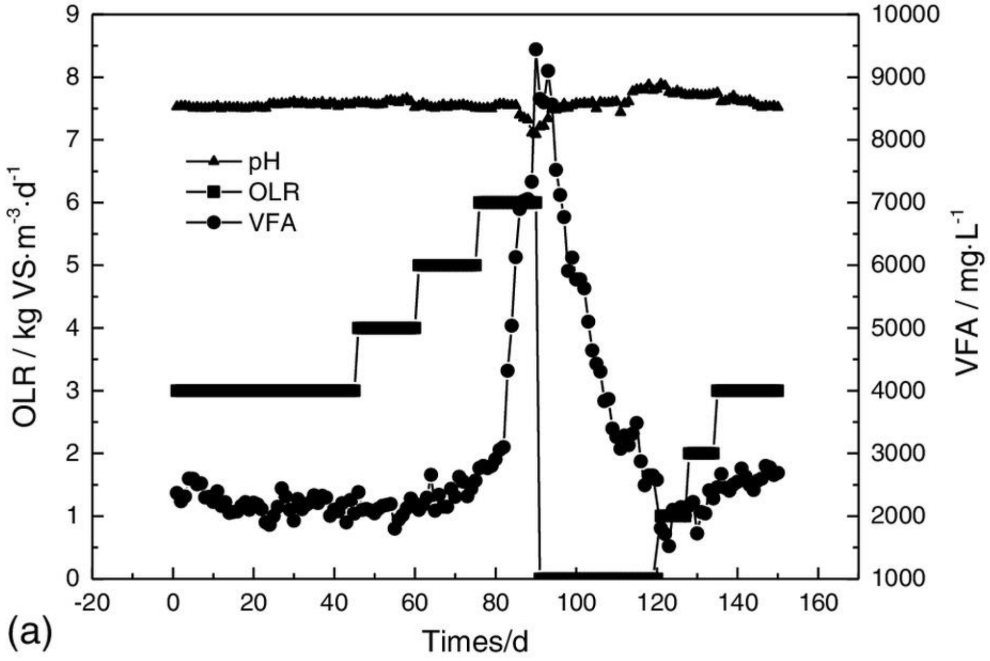
- OLR determines the size of the reactor
- The aim is to maximize the OLR, while keeping the process stable and controlling the amount of methane produced in the reactor
- The OLR (usual OLR 1-8 kgVS/m$^3$d) is maximized by
  - Choosing reactor type
  - Composition and homogenity of the feed
  - Enrichment and adaptation of microbial community (done by increasing OLR step by step)
- HRT can be between 10-150 d in anaerobic digestion
- The reactor content should change 2-3 times (2-3 times the HRT) before the process performance can be seen

# OLR and overload

- If OLR changes fast and significantly, it can result in overload

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

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

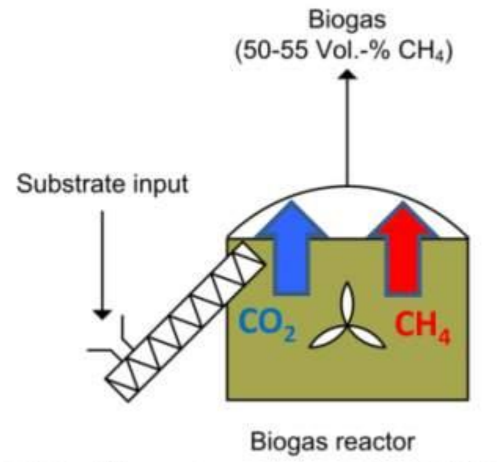


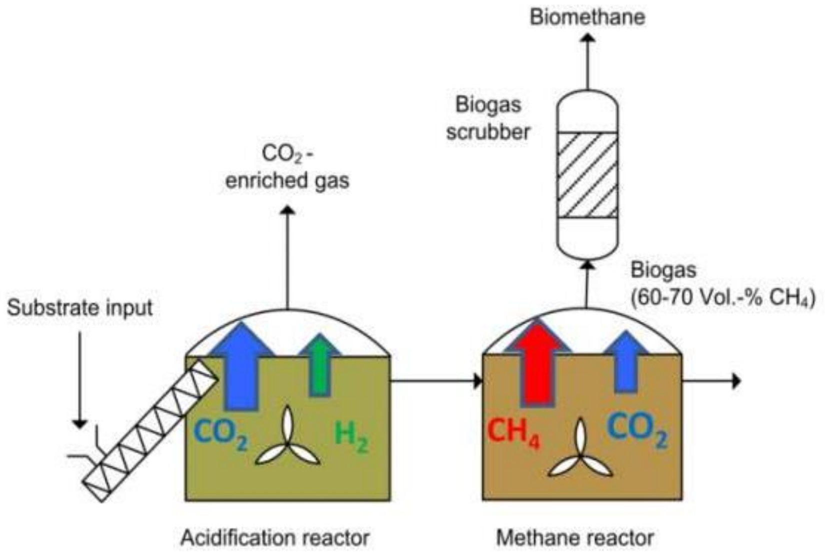

https://ascelibrary.org/doi/10.1061/%28ASCE%29EE.1943-7870.0001280

# 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

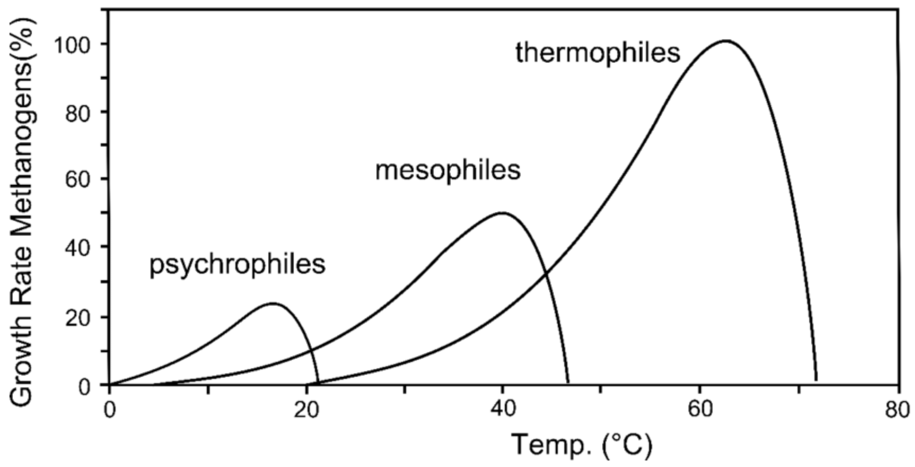
- Combination of these




Example: one-stage vs. two-stage process (anaerobic-digestion.com)

# 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, but 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

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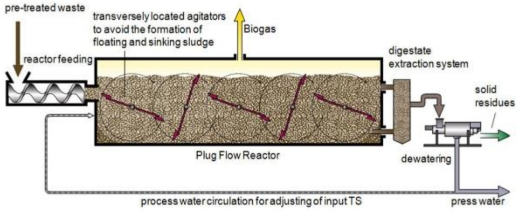
# Solids (TS) and organic matter (VS) content

- **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//

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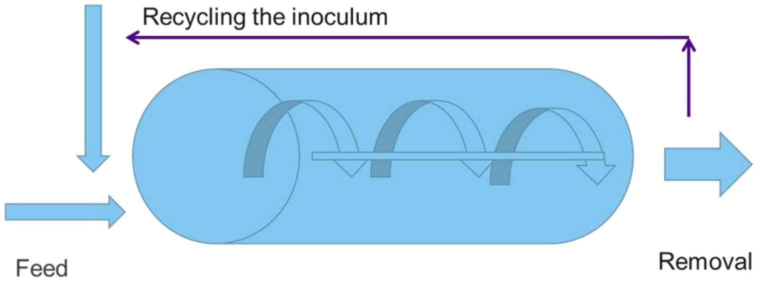
# Dry vs. wet process

## 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



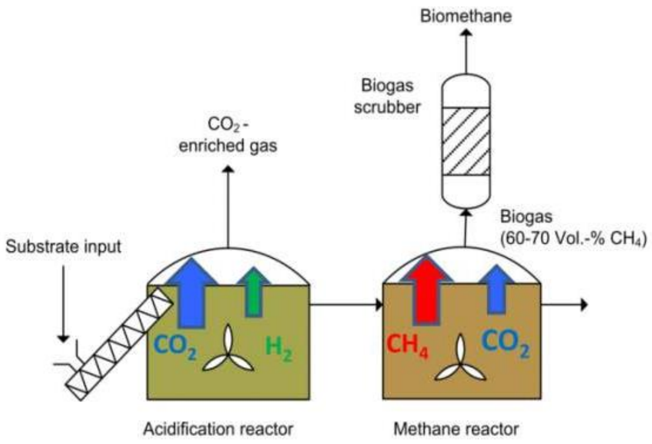

## Wet process

- TS < 10%, 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 (contains e.g. ammonium-N)

# 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




Example: one-stage vs. two-stage process (anaerobic-digestion.com)

## 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 $H_2$-process
- More structures required than one stage process → More expensive, if the enhanced methane production does not compensate the costs

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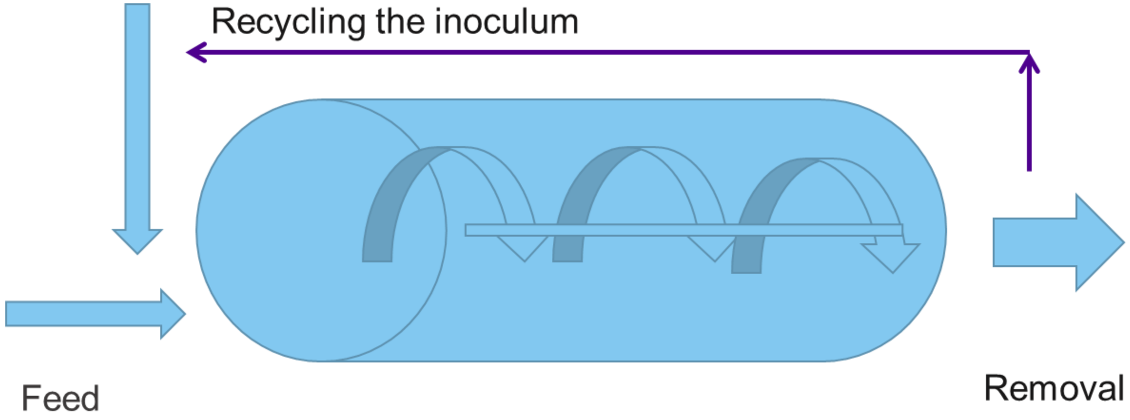
# Plug flow reactor




- Often dry processes

- Horizontal
  - Inoculum can be added to the feed before the reactor
  - Produces 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, in which case the accumulation of certain compounds (e.g. $NH_4^+$) has to be taken into account

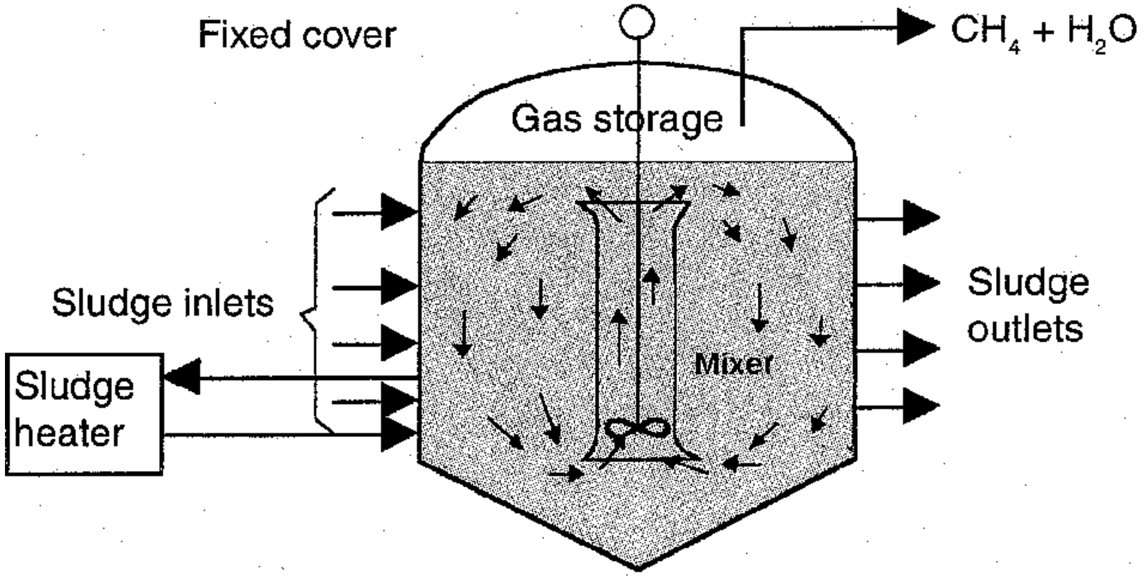
- Design parameters
  - 35ºC
  - Sludge retention time (SRT): 15-30 d
  - Ogranic loading rate (OLR): 4 kg COD/m³d

# 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



# Design of anaerobic wastewater treatment

- Design parameters available for anaerobic sewage 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, nutrients
  - 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)

# 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
- 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

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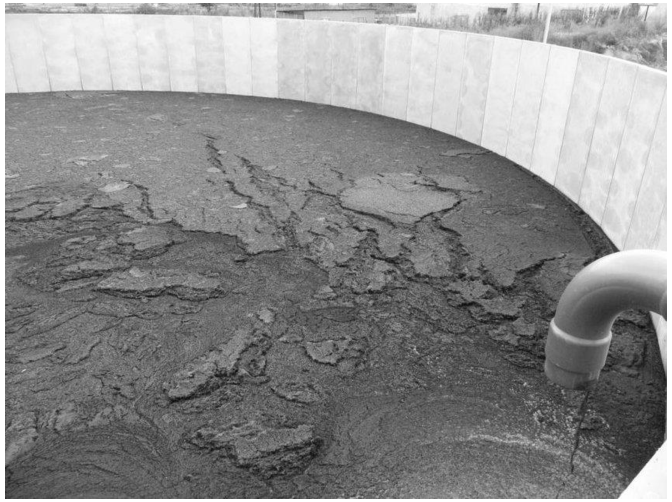
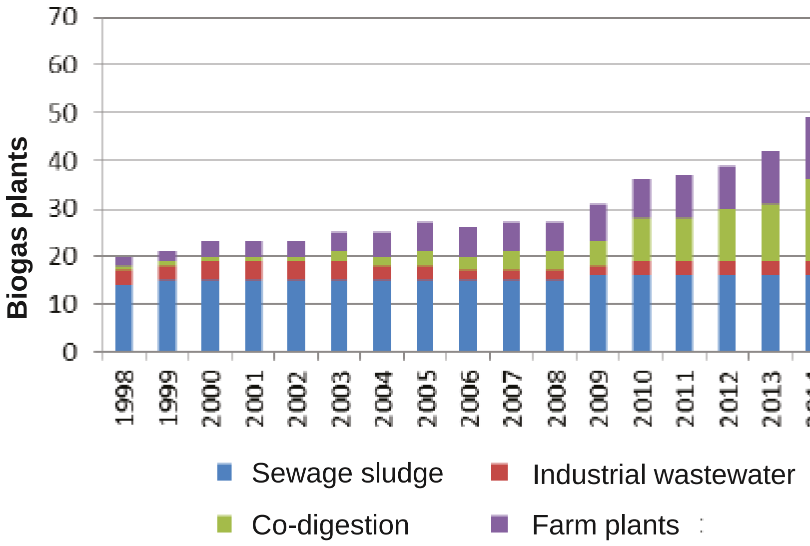
# The effect of biogas process on the digestate

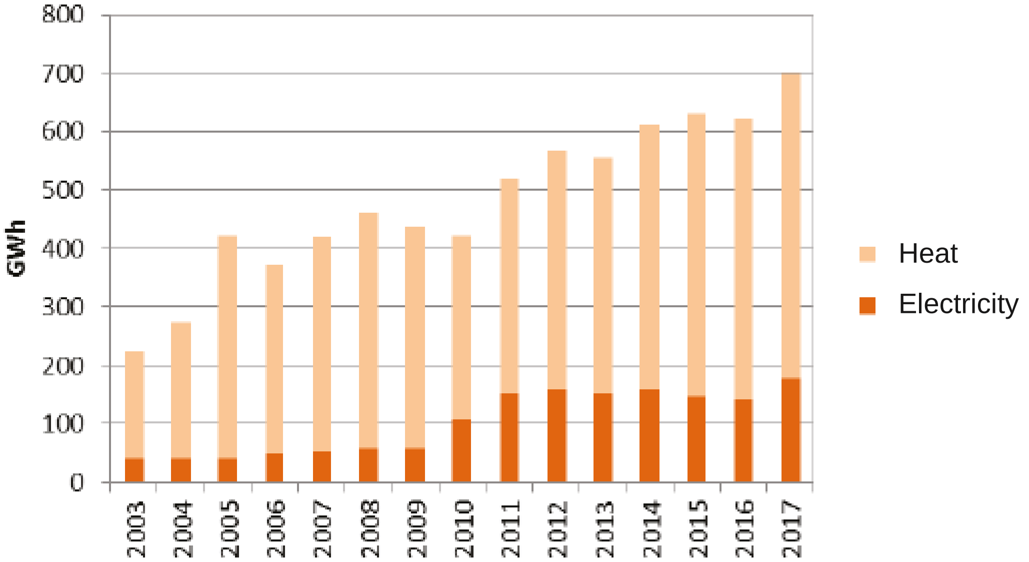
- Hygienisation
- Some detrimental compounds are degraded
- Better nutrient balance
  - The share of ammonium-N increases, usually 50-60% as ammonium-N (depends on feed and process conditions)
  - C:N –ratio decreases
  - Recycling of other nutrients, e.g. P, K. Ca, Mg
- The amount of organic matter 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

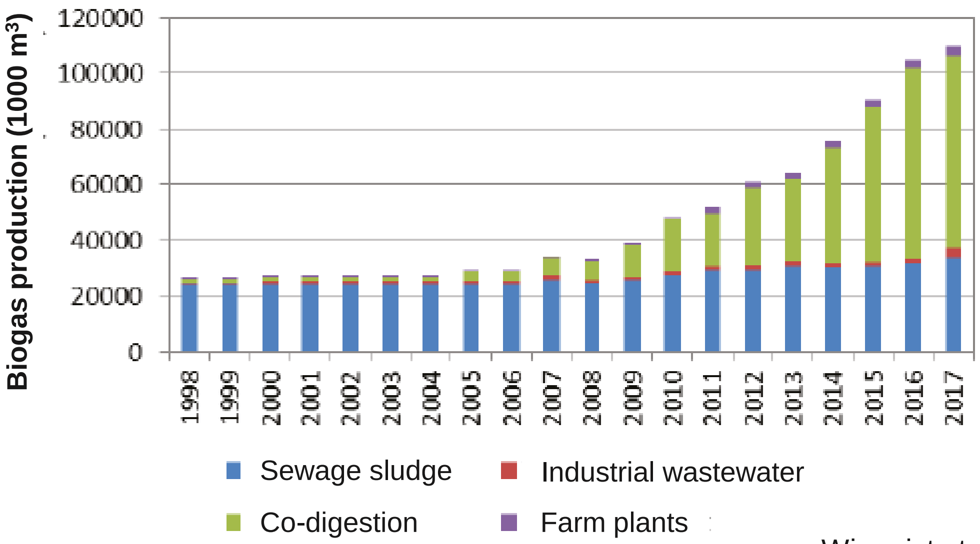


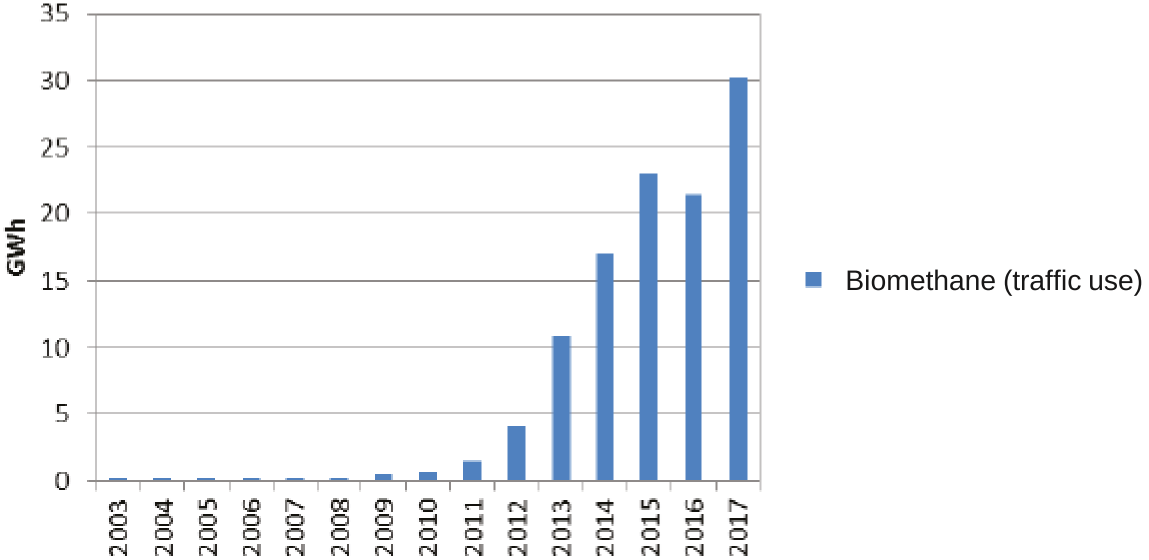
Digestate storage tank
DOI: 10.5593/SGEM2015/B41/S17.046

# Statistics




Winquist et al. (2018) Suomen biokaasualan haasteet ja mahdollisuudet. Luonnonvara- ja biotalouden tutkimus 47/2018.

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# Biogas plants in Finland (2021)


https://biokierto.fi/biokaasu/tuotanto/

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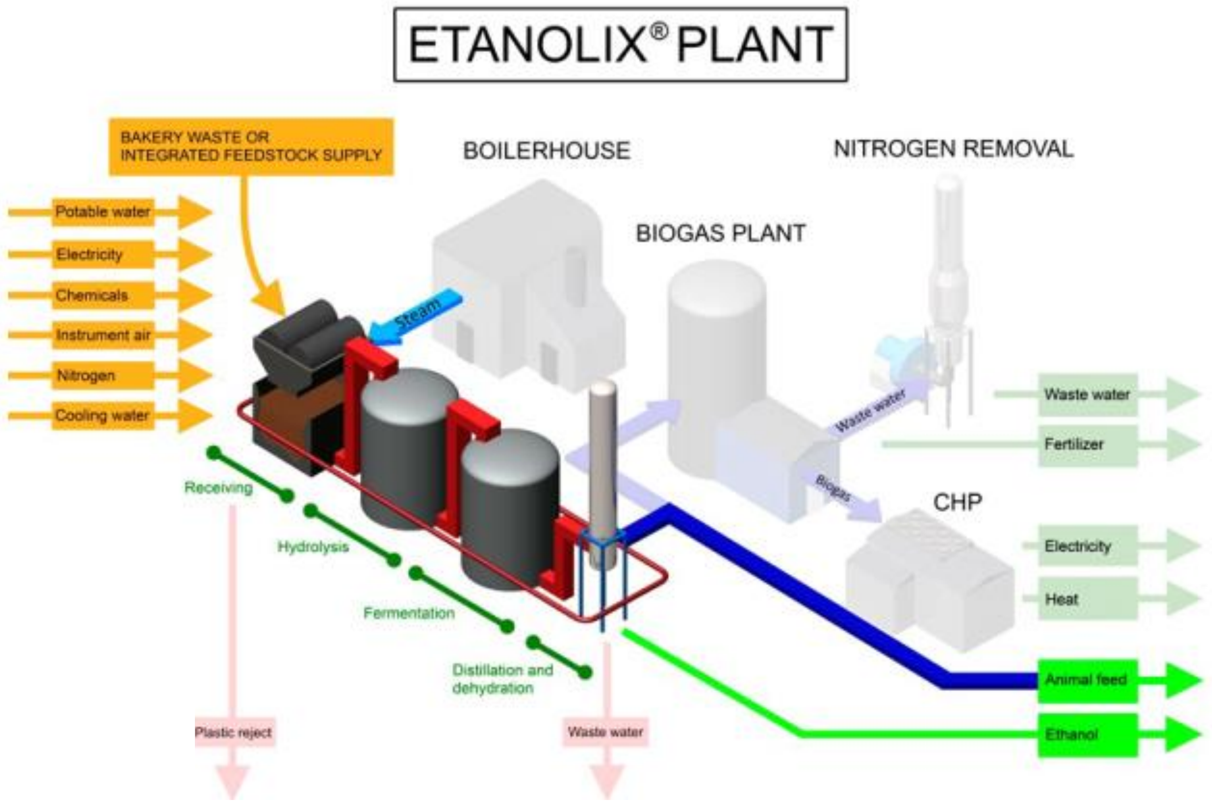
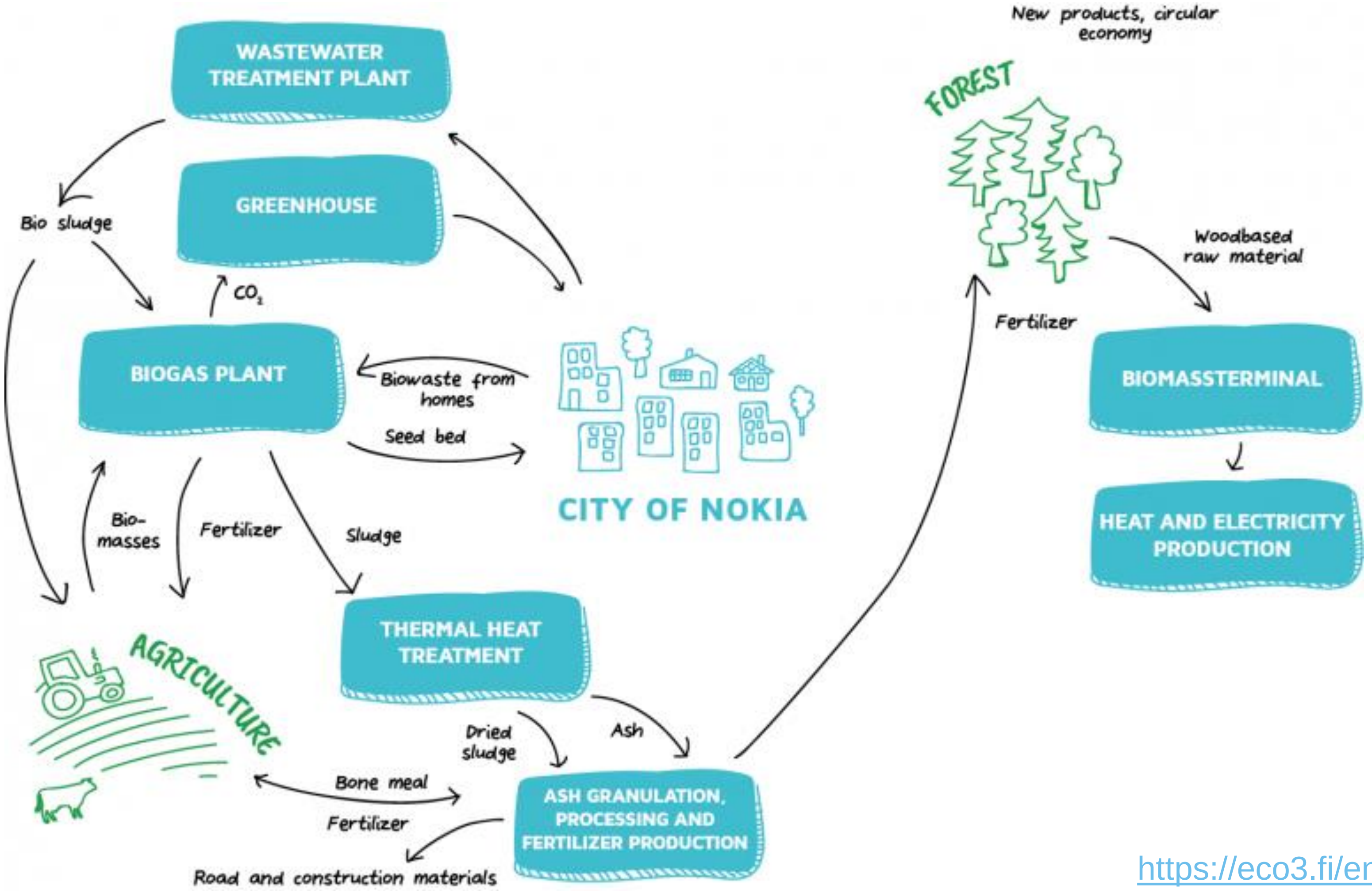
# Biogas from industrial wastewater

- Ethanol distillation process generates liquid high-protein stillage that can be used as feedstock for the biogas plants.




https://www.st1.eu/about-st1/company-information/areas-operations/advanced-fuels-waste

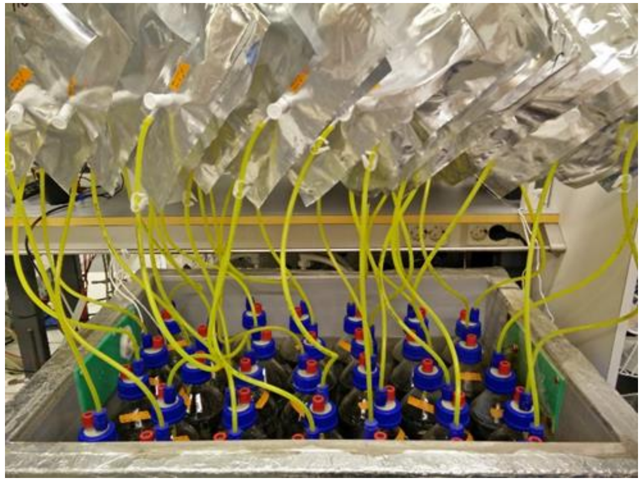
# Biogas plants in the center of nutrient recycling; Example of ECO3 area

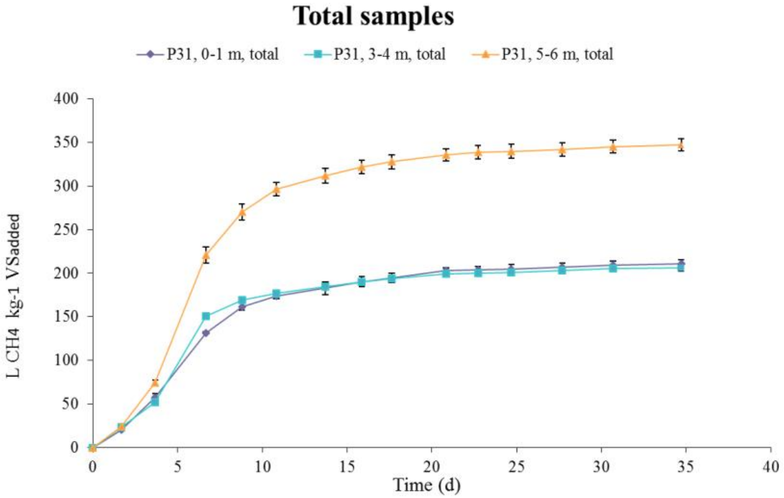


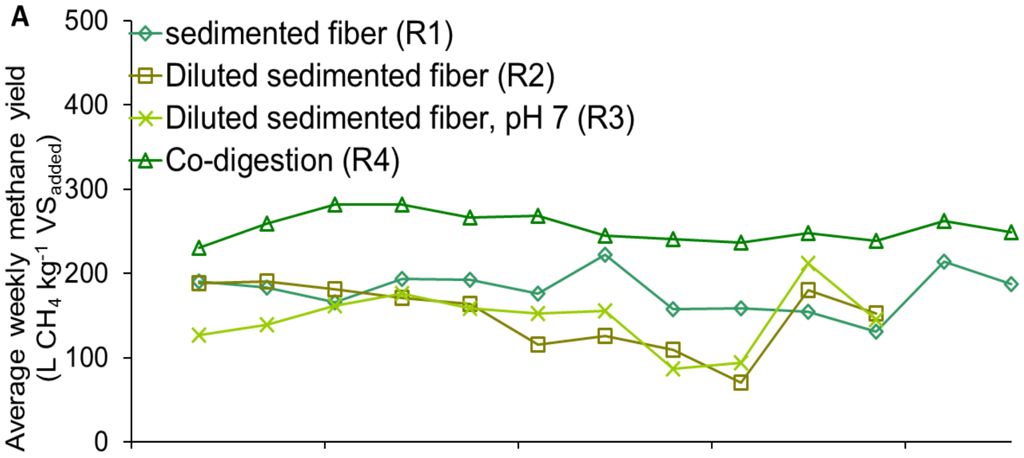

https://eco3.fi/en/ravinnekierto/

Chatterjee et al. (2018) Water Research 143, 209-217
Kokko et al. (2018) Water Research 133, 218-226

# Biological methane potential of sedimented fibers – tests in laboratory scale





# Anaerobic treatment of sedimented fibers in pilot scale

- 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

# Conclusions

- Anaerobic treatment and anaerobic digestion requires four different microbial groups

- The reactor design and process technology is chosen e.g. based on
  - Substrate type (e.g. wastewater vs. more solid waste)
  - Substrate composition (e.g. solid content, possible inhibiting compounds)

- The (end-)use of the digestate has to be considered
  - The volume does not decrease considerably
  - Contains most of the nutrients in the substrate