# Biomass: biogases

# BIOGAS

## Source

- Solid (wood, straw)
- Wet (waste, manure)
- Sugar/starch
- Oil crops

## Process

- Combustion
- Gasification
- Pyrolysis
- Methanation
- Fermentation
- Extraction + esterification

## Product

- Heat
- Woodgas
- Woodoil
- Biogas
- Bioethanol
- Biodiesel

## Service

- Heat / CHP
- Electricity
- (Transport) Fuels
- Chemicals

# Sources for biogas generation

*=> essentially wet wastes, too inefficient too burn:*

| | |
|---|---|
| • organic industrial effluents | <5% organic dry matter |
| • sewage | 5% |
| • farming residues | 10% |
| • solid wastes (digesters, landfill) | >20% |
| – municipalities (≈20 $m^3$/yr.person) | MSW |
| – industry | ISW |

- >100 $m^3$ biogas produced per tonne 'solid' waste (≈20% org. solids) (ca. 500 L biogas per kg organic dry matter)

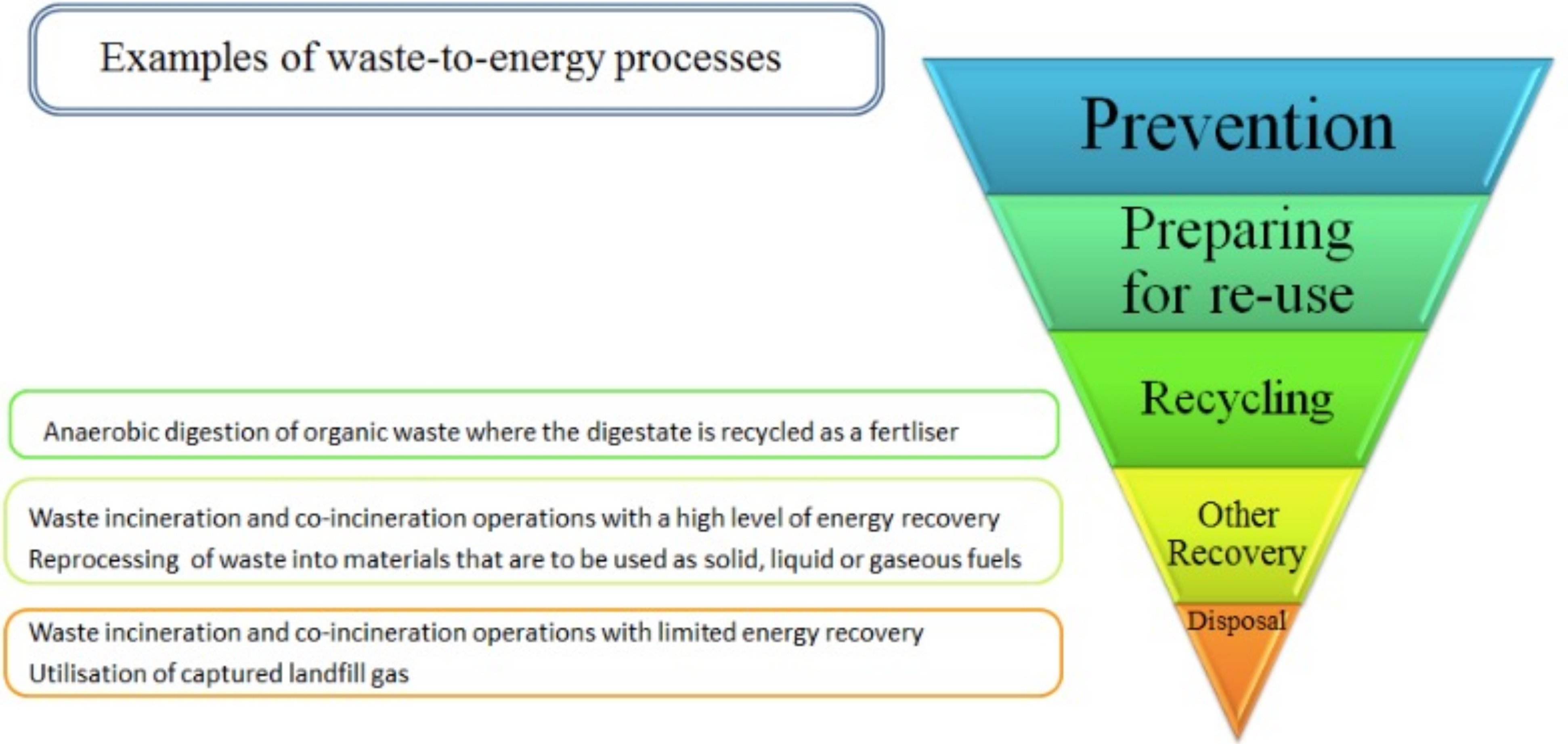
# When to *digest* waste?

Waste disposal scheme options, in particular for organics :

- incineration: for **solid** wastes
- composting: = aerobic; for farming (fertilising)
- **methanisation: = anaerobic digestion**
- landfill: as a lesser option, when none of the other options apply…; landfilling, however, is restricted in the case of organic wastes

**=>** most appropriate for **liquid** wastes with an organic fraction

# EU ''waste-to-energy hierarchy''




**''The role of waste-to-energy in the circular economy'',**
Brussels, 26.1.2017 COM(2017) 34 final

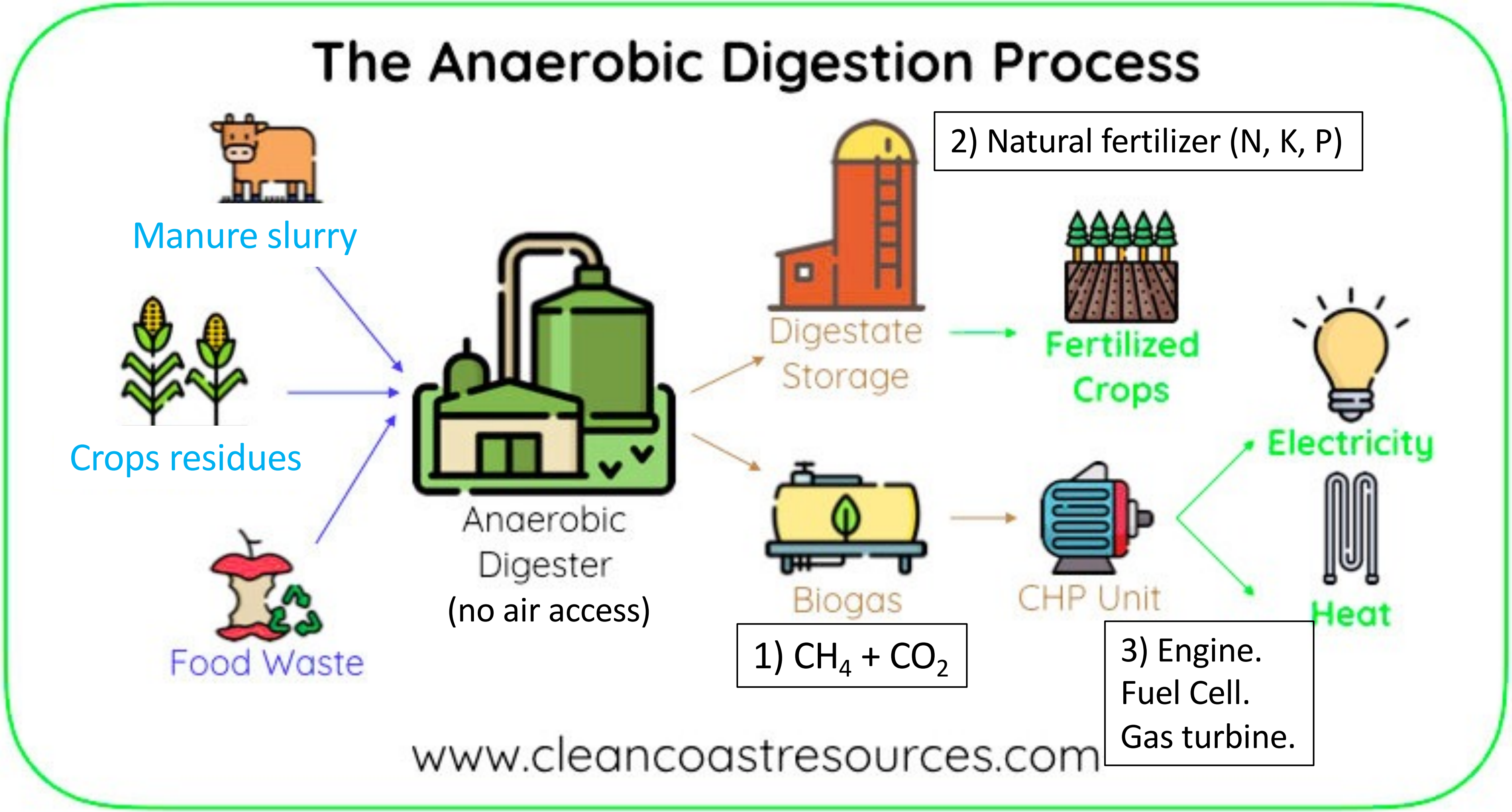
# Anaerobic digestion - AD (1)

- =transformation of organic matter by microorganisms (bacteria) in absence of $O_2$
- internal reduction + oxidation breakdown of the biomass polymers (C-H-O) to the simplest building blocks :

  **$CH_4$** (fully reduced) + **$CO_2$** (fully oxidized ) => biogas
- mature market technology
- drawback: lignine is nearly undigestable, cellulose is difficult to digest

  => AD is a slow process (10-20 days residence time), occurring at ≈35-55°C

# Anaerobic digestion (AD) of biowaste




https://www.cleancoastresources.com/industry-resources/what-is-anaerobic-digestion

# Digestion process (2)

4 distinct steps in time; using 3 different bacterial groups

1. **Hydrolysis** (uses exo-enzymes)

   = the ***slowest*** of the 4 steps (rate-determining)

   breaks solid org. matter down to liquified monomeres & dimeres:

   cellulose → cellobiose + glucose

   starch → maltose + glucose

2. **Digestion**

   = formation of organic **acids**

   acetic / propionic / butyric acid (=$C_2$/$C_3$/$C_4$-OOH), lactic acid, ethanol, and little $H_2$ and $CO_2$

# Digestion process (3)

3. '**Acidogenesis**'

   higher acids break down to $CH_3COOH$ (**acetic acid**), $H_2$ and $CO_2$, approximatively as in the overall reaction:

   $C_6H_{12}O_6 + 2H_2O \rightarrow 2\ CH_3COOH + 2\ CO_2 + 4\ H_2$

4. '**Methanogenesis**':

   a. $2CH_3COOH \rightarrow 2\ \mathbf{CH_4} + 2\ CO_2$ (**70-80%** of $CH_4$ product)

   b. $CO_2 + 4\ H_2 \rightarrow \mathbf{CH_4} + 2\ H_2O$ (**20-30%** of $CH_4$ product)

   Reactions a & b take place upon different bacterial actions.

   These 2 parallel $CH_4$-synthesis reactions explain why biogas compositions typically are (60±5)% $CH_4$ and (40±5%) $CO_2$

Overall approximation: $C_6H_{12}O_6$ -> $3\ CH_4 + 3\ CO_2$

# Anaerobic digestion - AD (4)

- The main objective for sewage and similar effluents (e.g. food industry) is waste **treatment**, i.e. **depollution** of liquid streams that are too heavily charged in organics, which cannot be discharged directly into the aquatic ecosystem; hence biogas is here mainly a **by-product** (energy recovered to power the ''depollution plant'')
- However, in the case of largely untapped farm waste (manure, crop residues) and MSW/ISW, biogas is not a by-product but an active **energy vector** (and especially for valorisation into electricity production, in gas **engines** or **fuel cells**)

# Advantages of AD

1. Biowastes become an energy source (=> biogas), not a burden.
2. Biogas is a local universal versatile fuel similar to natural gas, and therefore reduces (fossil) energy import (e.g. in agriculture).
3. Digesting the biowastes in a sealed tank, especially manure, instead of letting them freely rot (compost) in open air, will recover the $CH_4$ as fuel in a controlled way.
4. Biodigestate is a natural fertilizer of superior quality (better absorbed by the soil) than synthetic fertilizer (made from fossil fuels through e.g. industrial ammonia-synthesis)
5. The installation brings revenue to e.g. farmers, who become producers of biogas (renewable energy suppliers instead of fossil energy importers) and of natural fertilizer.

# Chemical formulae for biogas generation

'Buswell' formula:

$$C_a H_b O_c + \left[a - \tfrac{1}{4}b - \tfrac{1}{2}c\right] H_2O \rightarrow \left(\tfrac{1}{2}a + \tfrac{1}{8}b - \tfrac{1}{4}c\right) CH_4 + \left(\tfrac{1}{2}a - \tfrac{1}{8}b + \tfrac{1}{4}c\right) CO_2$$

e.g. for **manure**, approximated as $C_4H_8O_2$ (butyric acid):

$$C_4 H_8 O_2 + [4 - 2 - 1] H_2O \rightarrow \left(2 + 1 - \tfrac{1}{2}\right) CH_4 + \left(2 - 1 + \tfrac{1}{2}\right) CO_2 = \tfrac{5}{8} CH_4 + \tfrac{3}{8} CO_2$$

'Buswell-Boyle' (with N, S):

$$C_a H_b O_c N_d S_e + \frac{1}{4}\left[4a - b - 2c + 3d + 2e\right] H_2O$$

$$\rightarrow \frac{1}{8}\left(4a + b - 2c - 3d - 2e\right) CH_4$$

$$+ \frac{1}{8}\left(4a - b + 2c + 3d + 2e\right) CO_2$$

$$+ dNH_3 + eH_2S$$

Remark: $CO_2$, $NH_3$, $H_2S$ dissolve better in $H_2O$ than $CH_4$, hence the recovered gas is actually methane-enriched

# Digestion is a batch process

- once a day, fresh organic substrate is filled in, and digested matter is removed from a batch reactor

- mean residence time (days):
  - saturation after 20 days

$$\theta = \frac{V_{reactor}\left[m^3\right]}{\dot{V}_{org}\left[m^3/d\right]}$$

- daily specific load (kg/m$^3$.d)
  - M can designate fresh or dry organic matter

$$M_{day} = \dot{V}_{org} \cdot \frac{M}{V} = \frac{M}{\theta}$$

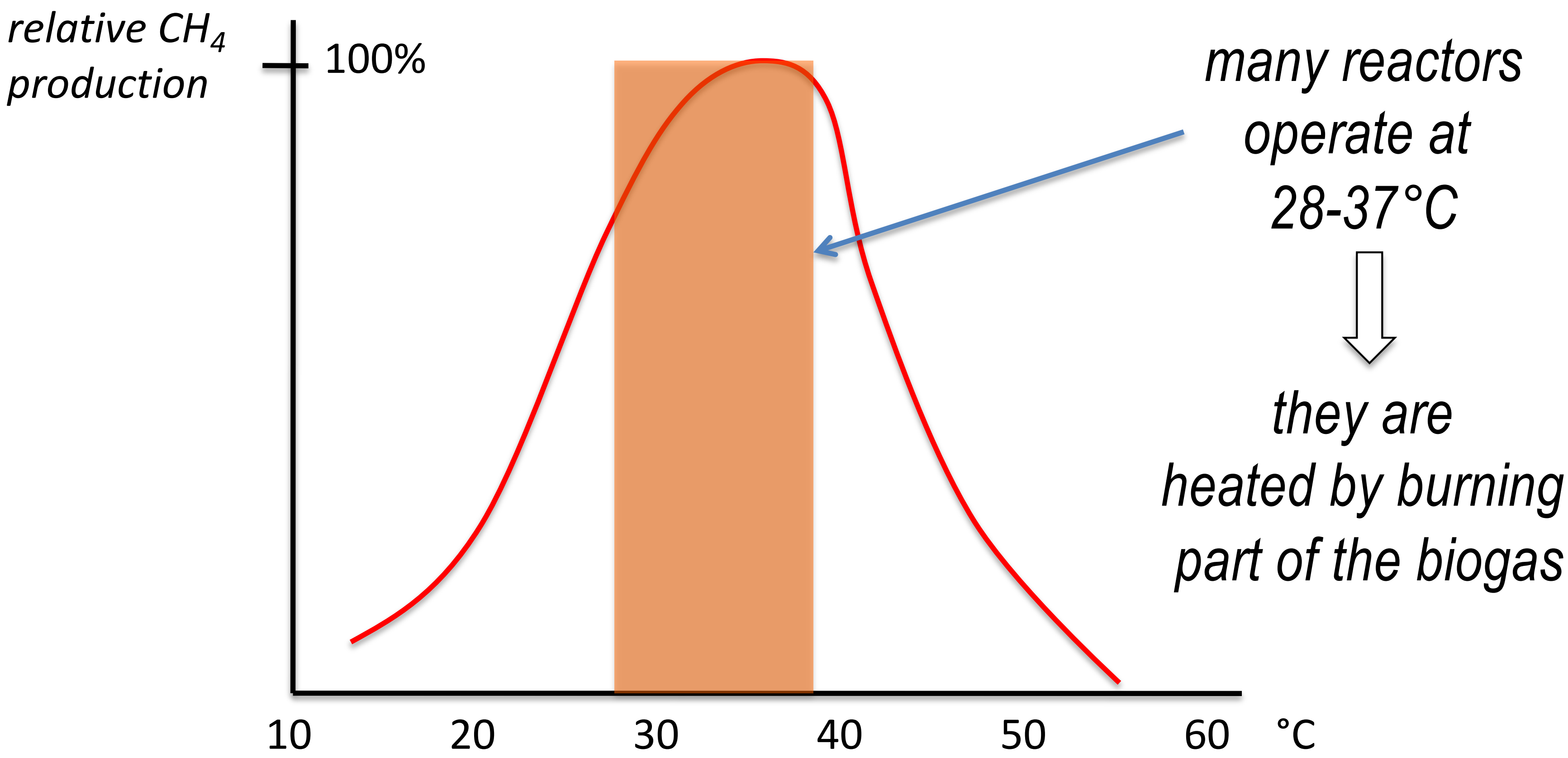
- biogas production can be expressed as:

$$m^3_{biogas} / m^3_{reactor}$$

$$m^3_{biogas} / kg_{org.matter}$$

# Digestor reactor temperature

| Enzyme | Optimal T range |
|---|---|
| ‘Psychrophilic’ | 20°C |
| ‘Mesophilic’ | 20-45°C |
| ‘Thermophilic’ | >45°C |



# Experience values

- The determining factors in biogas production are:
  - **temperature**; part of the biogas is used to heat the reactor; the biogas production rate saturates at 40°C
  - **residence time** (days); saturates at 20 days
  - **organic** matter **charge** (usually 3-10%)

| Production | Unit | Cows | Pigs |
|---|---|---|---|
| per animal and day | $m^3_{biogas} / head.day$ | 1.3 ± 0.3 | 1.5 ± 0.6 |
| per mass | $m^3_{biogas} / kg_{org.matter}$ | 0.3 ± 0.05 | 0.5 ± 0.05 |

→1.5 $m^3$/day @ 20 MJ/$m^3$ = 30 MJ/day ≈ 8 kWh/day

= equivalent to 2 $m^2$ of thermal solar collectors

Any farm animal produces ca. 18-20 kg of manure per year per kg of its own body weight

# Biogas vs. natural gas

| Property | Unit | NG | BG (60% $CH_4$) |
|---|---|---|---|
| LHV | MJ / $m^3$ | 36 | 21.5 |
| Density | kg/$m^3$ | 0.82 | 1.21 |
| Ignition T | °C | 620 | 700 |
| Ignition speed in air | m/s | 39 | 0.25 |
| Air factor | - | 9.5 | 5.7 |
| Exhaust, max $CO_2$ | Vol% | 11.9 | 17.8 |
| Exhaust, dew point | °C | 59 | 60-160 |

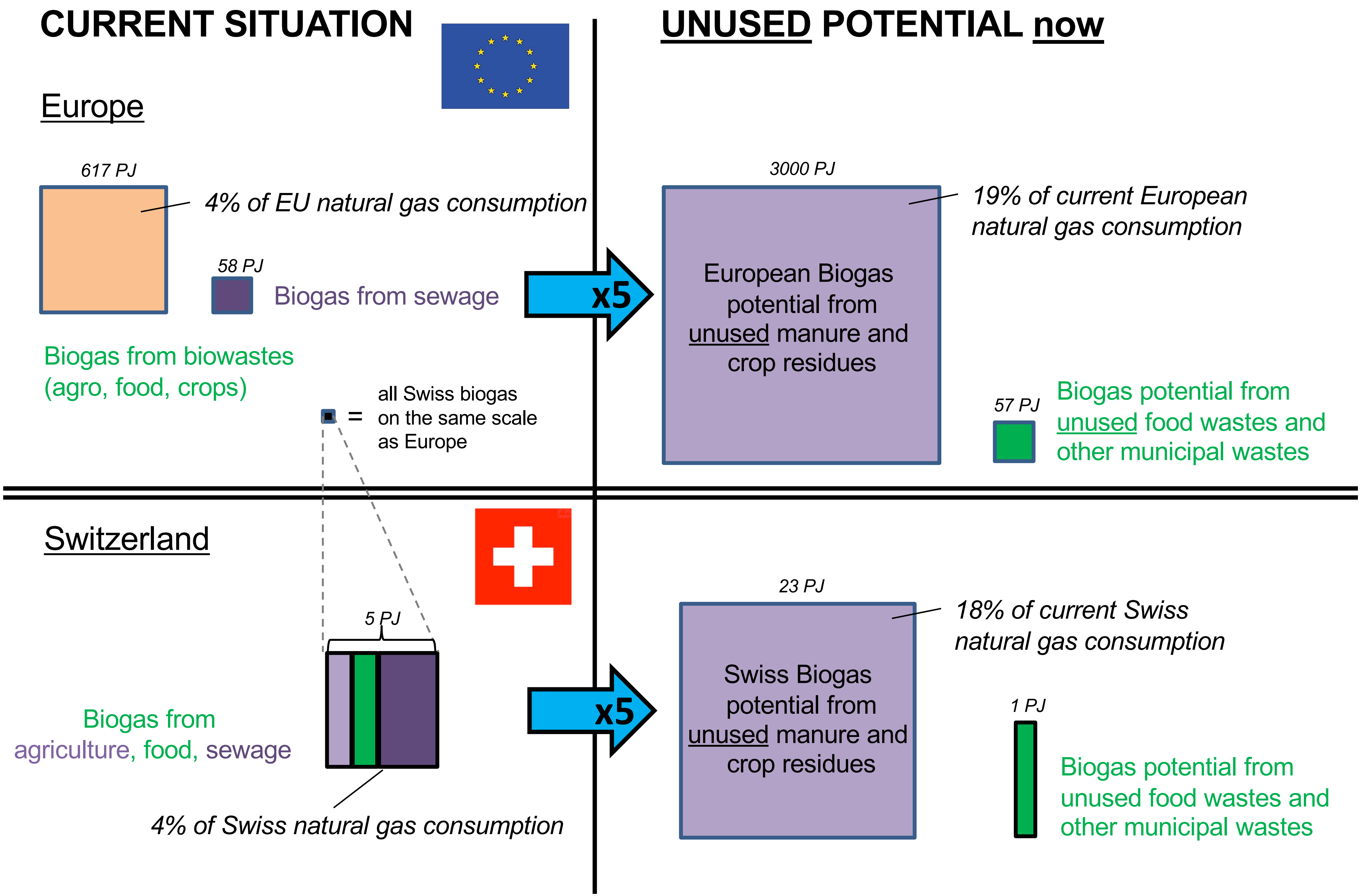
# Some characteristics of biogas production

- the digestate is a good quality **fertilizer** (2% nitrogen)
  - better than (air-)composted waste (<1% nitrogen)
- else N-fertilizer has to be imported, which is made from natural gas in huge plants (1.5% of global energy consumption).
- a significant part of the produced biogas is used for **heating of the digester** and the installation itself (farm,…)
- (cold) **desulfurisation** of the biogas is done with $FeCl_3$ solution (to precipitate FeS); sulfur is removed as it is poisonous (for the atmosphere but also in downstream CHP engines or fuel cells)

# Biogas application examples (CH)

| Source | Biogas $m^3$/day | % $CH_4$ | % yr load | Installed power | Effi-ciency |
|---|---|---|---|---|---|
| Farm 37 cattle | 70 | 57 | 60 | **5 $kW_{el}$** | **18%** |
| Sewage 30'000 p. | 1000 | 65 | 65 | **130 $kW_{el}$** | **28%** |
| MSW 80'000 p. | 1300 | 60 | 95 | **90 $kW_{el}$** | **25%** |

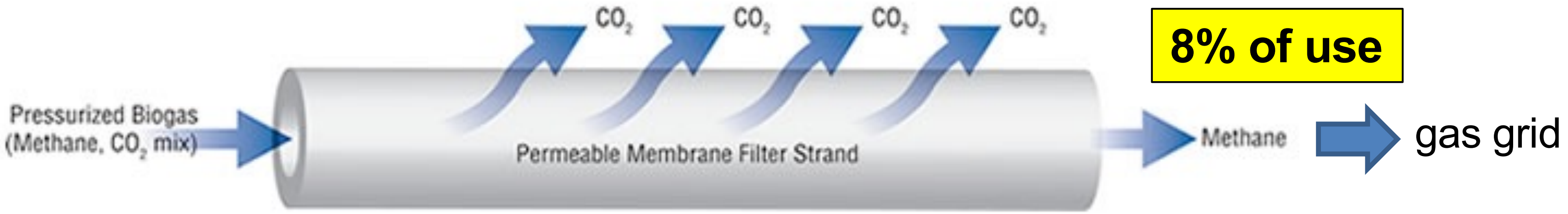
*=> small power sites (gas engines); low (electrical) efficiency*


CURRENT SITUATION
UNUSED POTENTIAL now
Europe
617 PJ
4% of EU natural gas consumption
58 PJ
Biogas from sewage
Biogas from biowastes
(agro, food, crops)
= all Swiss biogas on the same scale as Europe
x5
3000 PJ
19% of current European natural gas consumption
European Biogas potential from unused manure and crop residues
57 PJ
Biogas potential from unused food wastes and other municipal wastes
Switzerland
5 PJ
Biogas from
agriculture, food, sewage
4% of Swiss natural gas consumption
x5
23 PJ
18% of current Swiss natural gas consumption
Swiss Biogas potential from unused manure and crop residues
1 PJ
Biogas potential from unused food wastes and other municipal wastes

# Current uses of biogas

There are presently 2 main ways to valorise biogas ($CH_4/CO_2$) as fuel:

1) Separate $CH_4$ from $CO_2$ and inject the $CH_4$ into the natural gas grid.



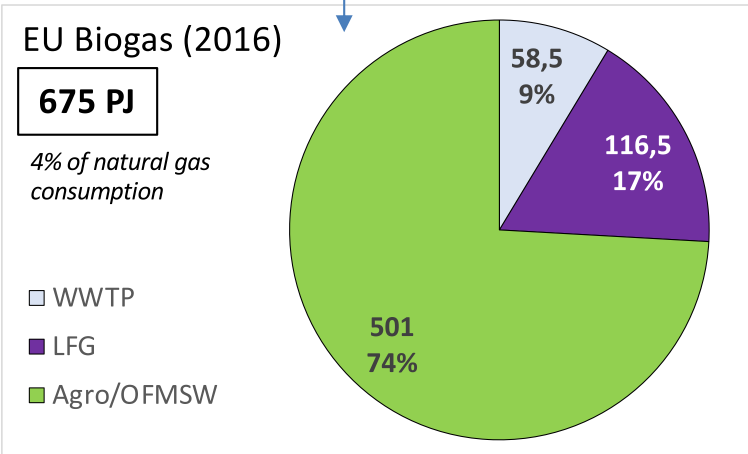

2) Burn the biogas into a large engine to generate electricity and heat.

500 $kW_{el}$
biogas engine

**92% of use**

*Part is used in burners only*

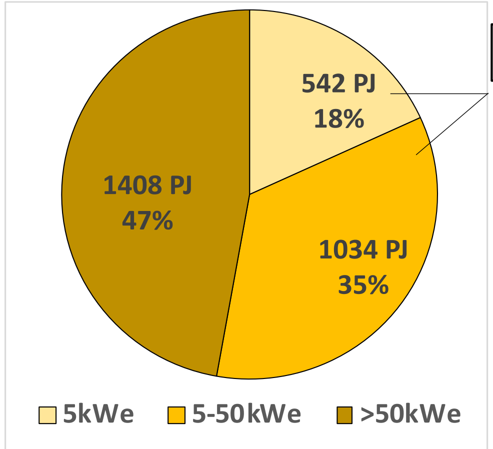
# Status and potential in Europe




Unused potential in agriculture:

**3000 PJ**

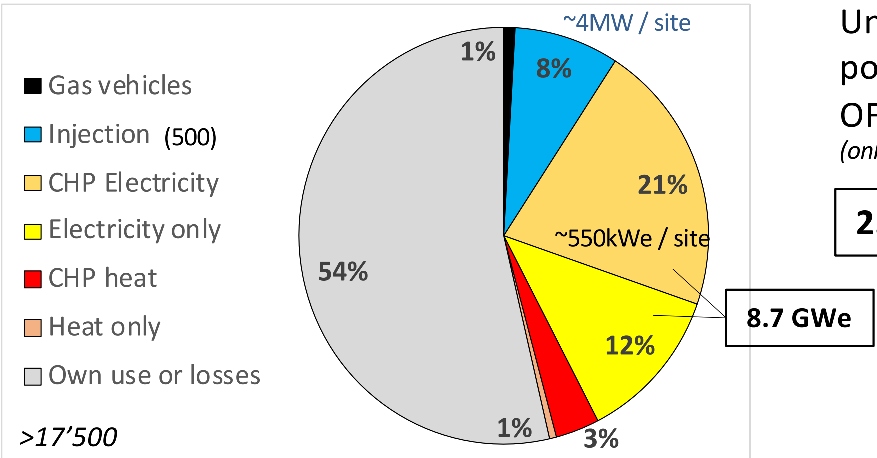
*18% of natural gas consumption*




**25 GWe**

*500'000 installations of 50 kWe*

use:




*>17'500 installations*

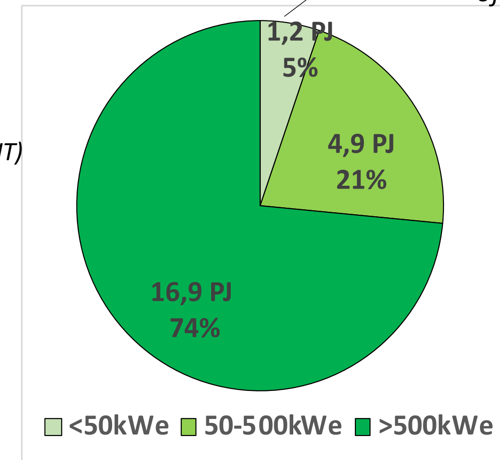
Unused potential in OFMSW:

*(only for CH/D/F/IT)*

**23 PJ**

**19 MWe**

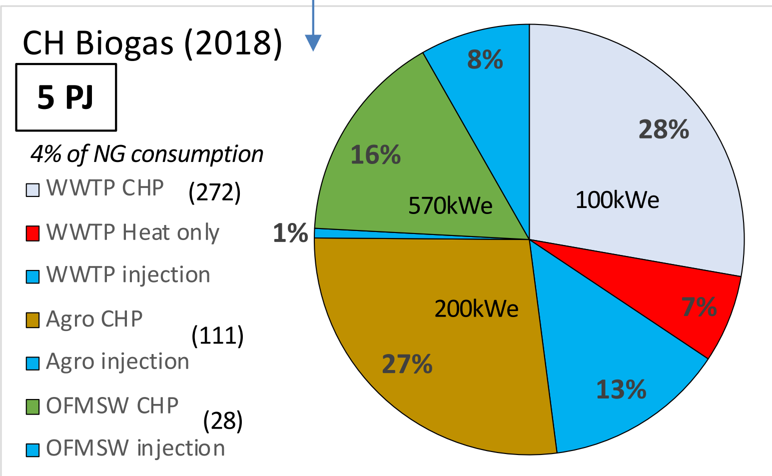
*400 installations of 50 kWe*




Use : mainly large installations >200m³/h (>1 $MW_{CH4}$)

The unused potential lies in small scale installations of <20 m³/h

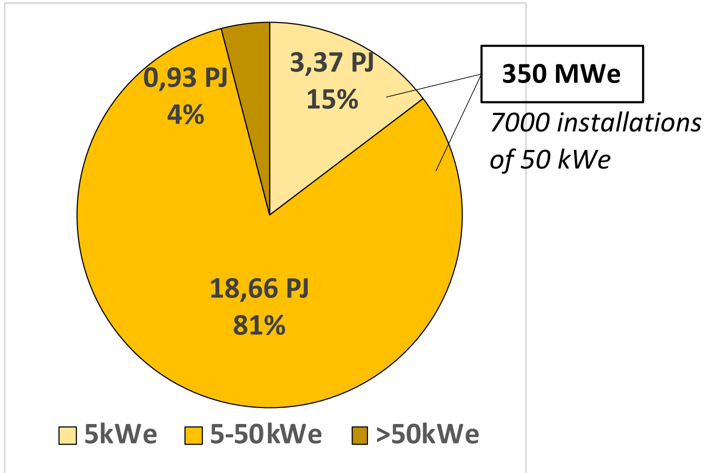
# Status and potential in Switzerland



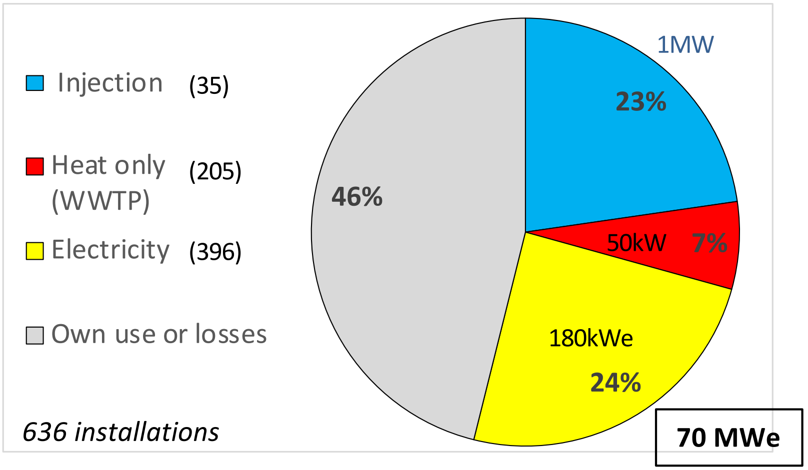

Unused potential in agriculture:

**23 PJ**

*18% of natural gas consumption*

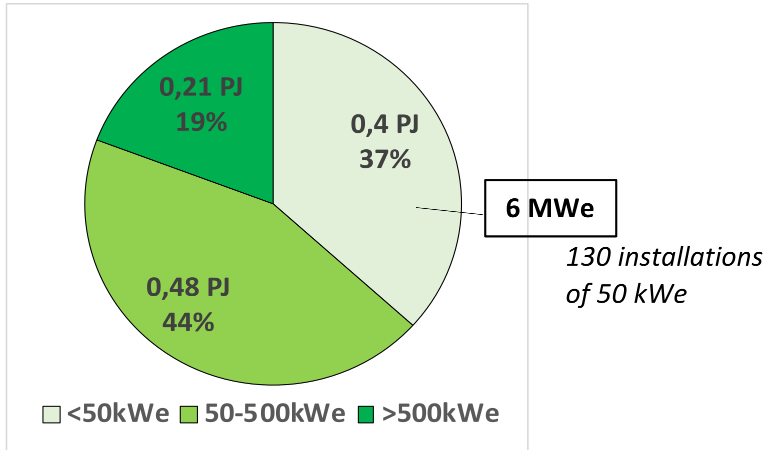



use:




Unused potential in OFMSW:

**1.1 PJ**



# The issues

- The current use technologies of biomethane injection and CHP engines impose a **scale** of biogas production in large digesters to generate biogas flows of 100-1000 $m^3/h$ (0.6-6 $MW_{CH4}$), because at lower scale:
  - $CH_4/CO_2$ separation becomes expensive
  - Engines (and turbines) are electrically inefficient:
    - at 500 kWe, a biogas engine reaches up to 40% electrical efficiency*
    - at <50 kWe, a biogas engine does not reach 30% electrical efficiency

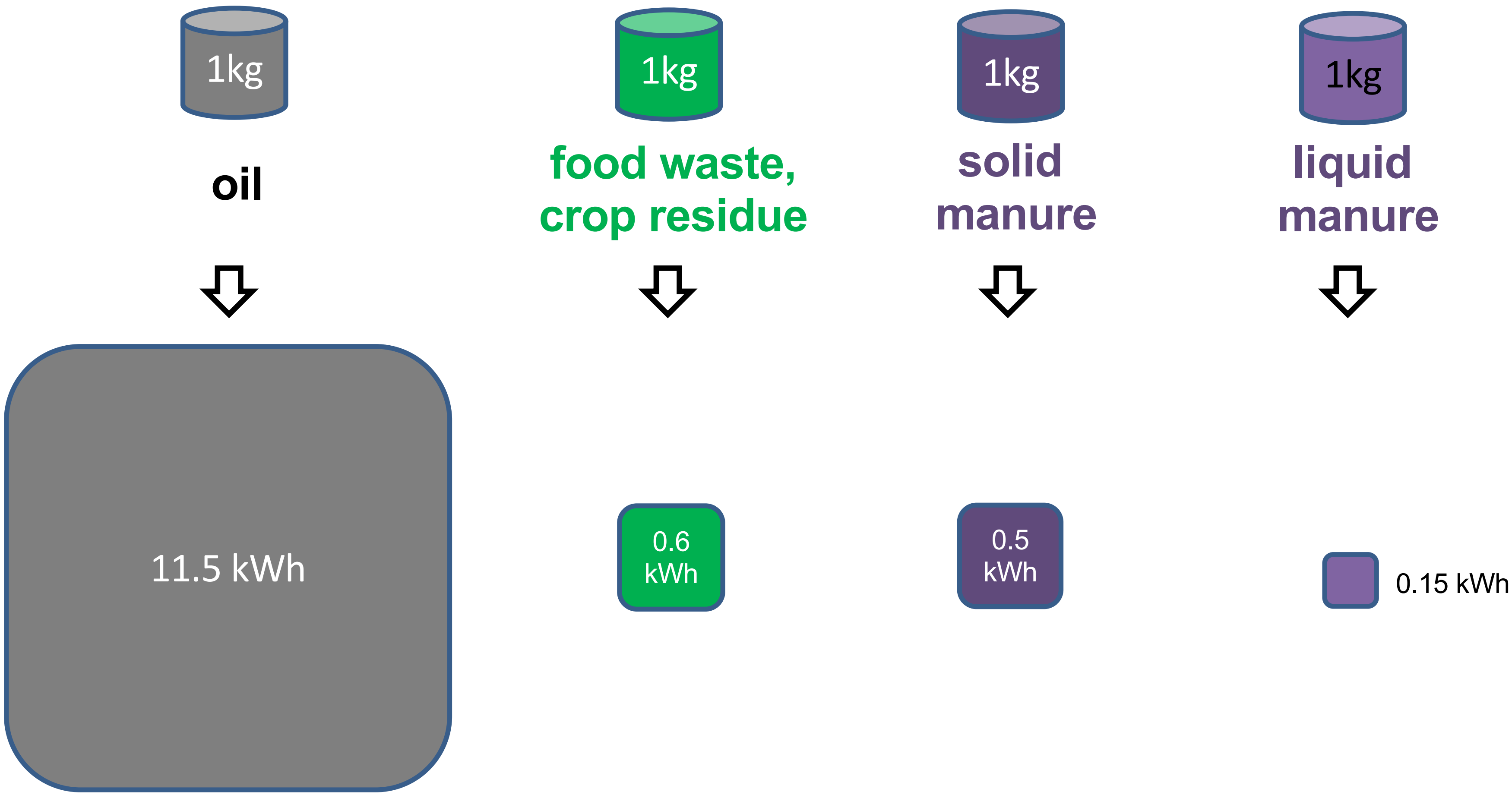
**=> as a consequence, small-scale biogas generation remains unused, whereas this represents the majority of the resource**

- Biogas engines **pollute** (they generate NO, CO, $SO_2$), are noisy, and expensive in maintenance (need regular replacement of parts). In fact small engines are replaced almost yearly.

**presently, average biogas engine efficiency is 38% in Europe and 34% in Switzerland*

# The issue of scale (1)

Biowastes are a dilute energy source



# The issue of scale (2)

food wastes collected over **1 km²** of urban centers

5000 people*

⇩

2 kg / week / person

⇩

300’000 kWh/year

⇩ *8000h/yr*

| 40 $kW_{CH4}$ |
|---|

⇩

| 12 $kW_{el}$ engine |
|---|

crop residues collected from **1 km²** farmland

*average farmsize*

*1 hectare*

⇩

20 kg / day / hectare

⇩

400’000 kWh/year

⇩ *8000h/yr*

| 50 $kW_{CH4}$ |
|---|

⇩

| 15 $kW_{el}$ engine |
|---|

manure collected from animals that occupy **1 km²** farmland

200 large animals (cows)

⇩

25 kg / day / cow

⇩

400’000 kWh/year

⇩ *8000h/yr*

| 50 $kW_{CH4}$ |
|---|

⇩

| 15 $kW_{el}$ engine |
|---|

**5000 people/km² is a dense city (Lausanne: 3400 hab / km²)*

# Transporting biowaste fuel

- A tractor consumes 50 L diesel/100km = 500 kWh/100km
- 1 ton biowaste contains
  - 500 kWh for solids (crop residues, solid manure)
  - 150 kWh for liquid manure
- => it is not very sensical to transport a few tonnes of biowaste over more than 5-10km.

# Special case of landfill gas (LFG)

- (multi)$MW_{el}$-size sites (with gas engines, gas turbines)
- an important fraction of world biogas (20 Mtoe)
- 3 Mtoe in EU-27

- often heavily contaminated (with F, Cl, $NH_3$, $H_2S$, Si,…)
- often of low calorific value (diluted with $N_2/O_2$)
  - engines stop running <45% $CH_4$
  - fuel-assisted flaring or venting !

# Summarised:

- Biowaste is best used <u>locally</u>, over a few $km^2$
- The available energy is then a few 100 $kW_{CH4}$, in biogas flows of 10-50 $m^3/h$*

This requires:

1. cost-effective small-scale AD (digesters)
2. a valorisation technology that is more efficient and cleaner than engines, on small-scale

⇒**Solid Oxide Fuel Cells** : **>50% electrical efficiency**

**no pollution (~~NO~~, ~~CO~~, ~~$SO_2$~~)**

*1.6 $m^3/h$ biogas (60%$CH_4$-40%$CO_2$) = 1 $m^3/h$ $CH_4$ = 10 kWh_$CH_4$ = 3 kWe in a 30% efficient engine

# Demo biogas fuel cell

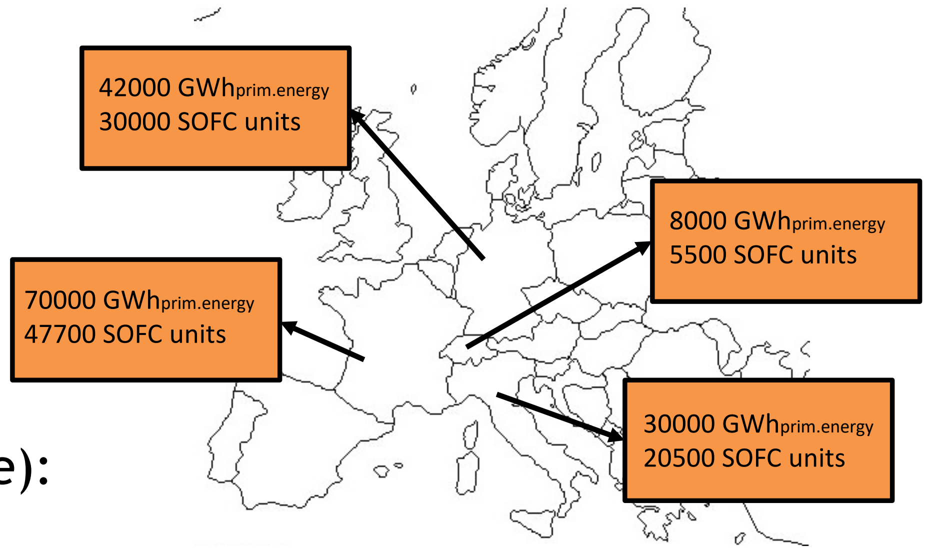


Initial result
52% elec efficiency.
Test to continue 2 years.
New sorbents to clean the biogas from sulfur.

=> Semester or master project

# Biogas potential

For 🇩🇪 + 🇫🇷 + 🇮🇹 + 🇨🇭 :
**>100’000 sites of 50 kWe equiv.**
from <u>agrowaste</u> presently <u>not-used</u>, assuming only 50% of potential sites would be equipped

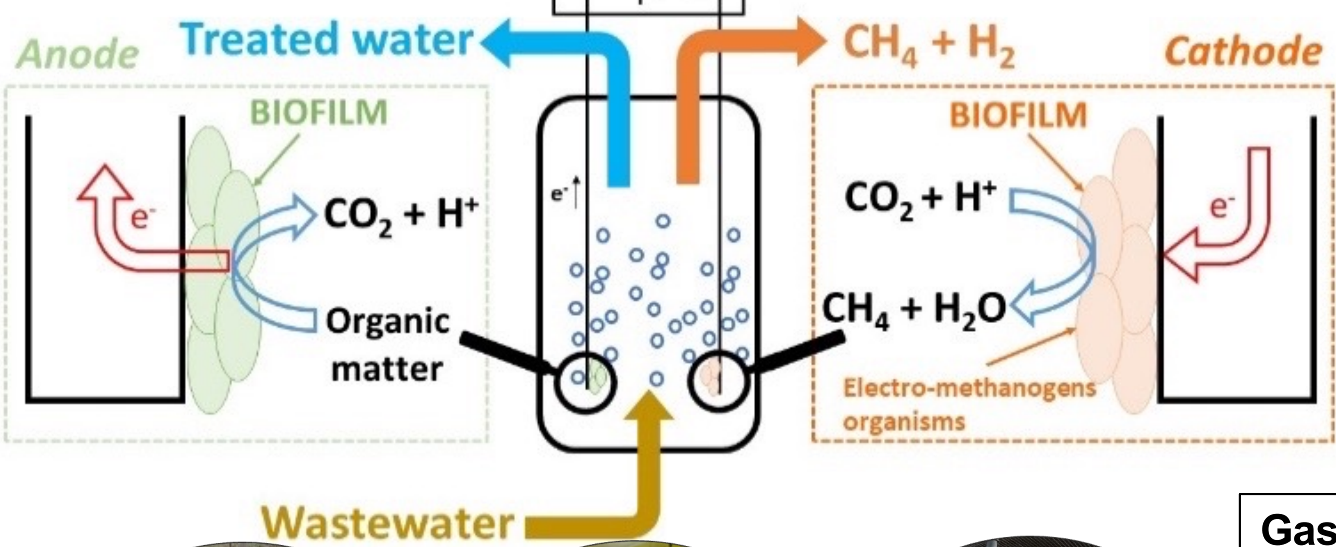


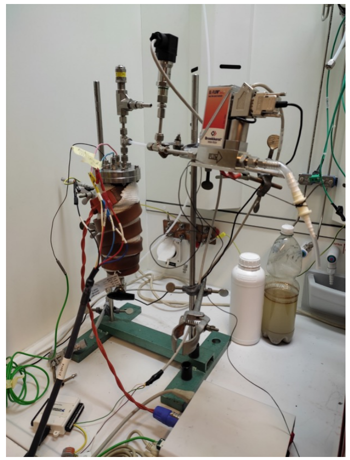

- For Switzerland (5500 units of 50 kWe):
- 275 MWe * 8000 h => 2.2 TWhe
- = **4% of CH electricity**
- = as much as the solid waste incineration plants (2.2 TWhe from 13 TWh solid wastes, electrical efficiency <20%)

# Bio-electrical systems (BES)

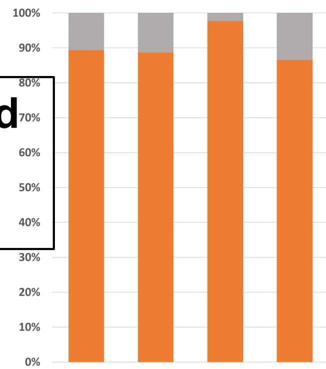
- In BES, the **biological methanation of $CO_2$** is electrocatalyzed **in a single step at ambient P & T, using microbes as renewable catalyst**.
- The microbes - **methanogenic bacteria** (*Archaea*) - act as electron bridges to reduce the high energy step from $CO_2$ to $CH_4$. Only a small amount of electrical energy is needed to maintain microbial conversion.

$$CO_2 + 8\,H^+ + 8\,e^- \rightarrow CH_4 + 2\,H_2O$$



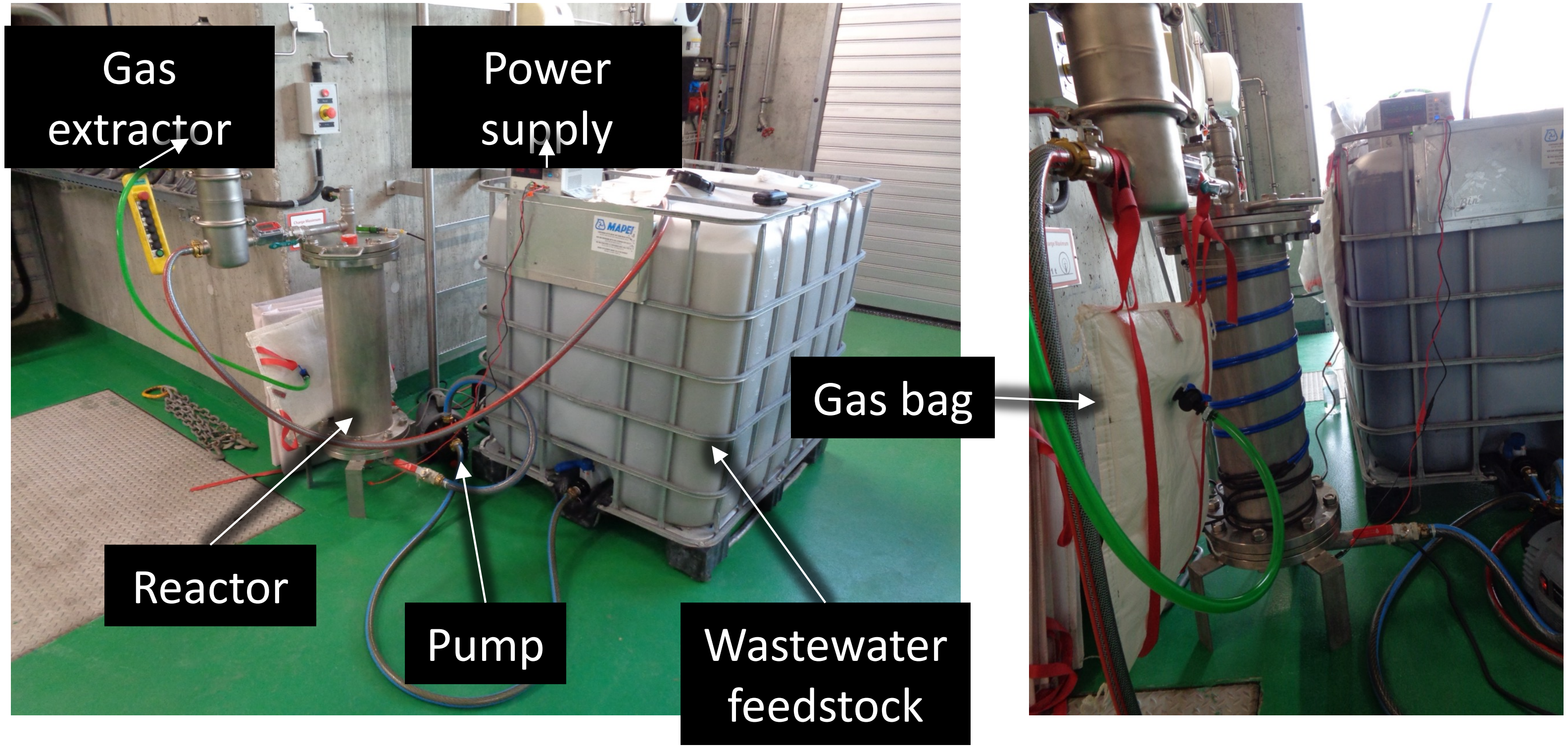
**Gas produced in 1 step: 99% $CH_4$**




The business case is lowering the **COD** (**chemical oxygen demand**) of the WW treatment

# BES prototype tested

- 30 L (10 bar) microbial electrolysis reactor was operated at a  local wastewater treatment plant producing 90% $CH_4$ gas:




1. In laboratory conditions, we achieve >99% CH4 gas
2. The process can also convert $NH_4^+$ to $N_2$, to meet new strict regulations

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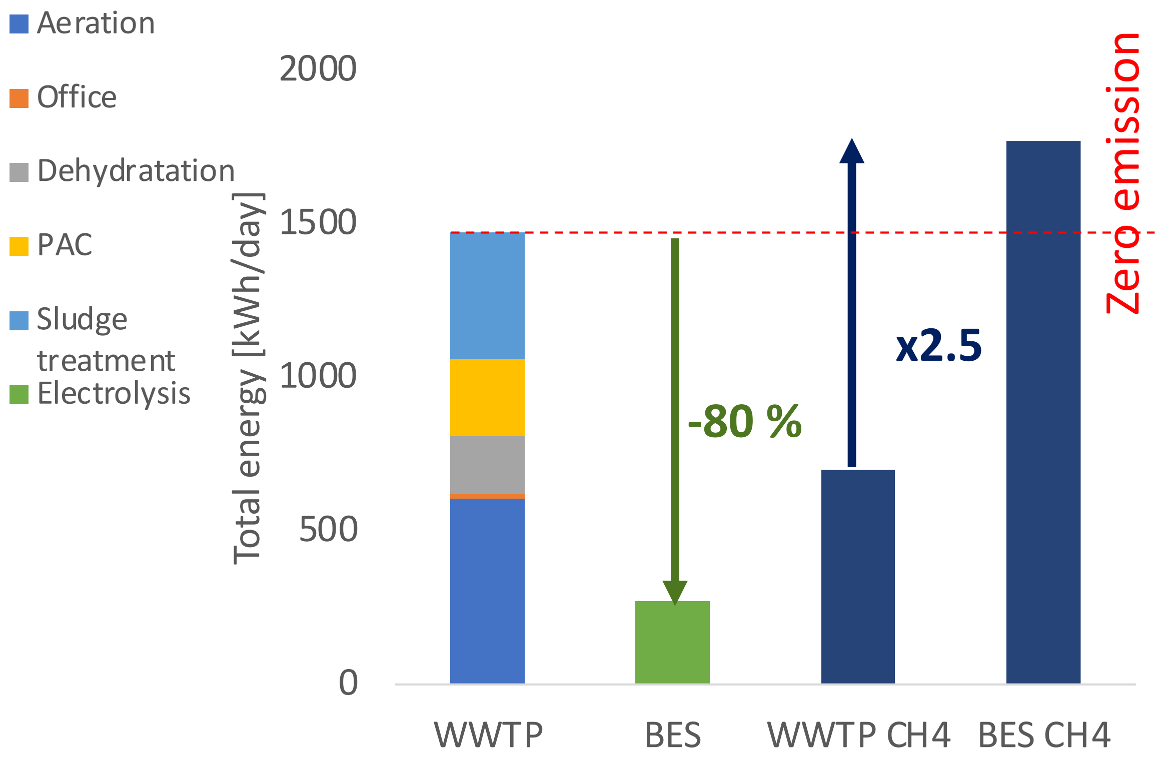
# Waste water treatment with BES

- WWTP data :




**Potential impact:**

**80% of energy** consumption **reduction** using BES

**2.5 more $CH_4$ production**

**Savings and production:**

**Savings: 167 kCHF/yr** in electricity

**Production: +13 kCHF/yr in $CH_4$ sale**

**Perspective : turning a WWTP from energy-negative to energy-positive**

$CH_4$ potential from waste waters = replace 2% of natural gas import

**=> Semester or master project**