Biomass: biogases

BIOGAS

Source	Process	Product	Service
Solid (wood, straw)	Combustion	Heat	Heat / CHP
Wet (waste, manure)	Gasification	Woodgas	Electricity
Sugar/starch	Pyrolysis	Woodoil	(Transport) Fuels
Oil crops	Methanation	Biogas	Chemicals
	Fermentation	Bioethanol	
	Extraction + esterification	Biodiesel	

Sources for biogas generation

=> essentially wet wastes, too inefficient to 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)

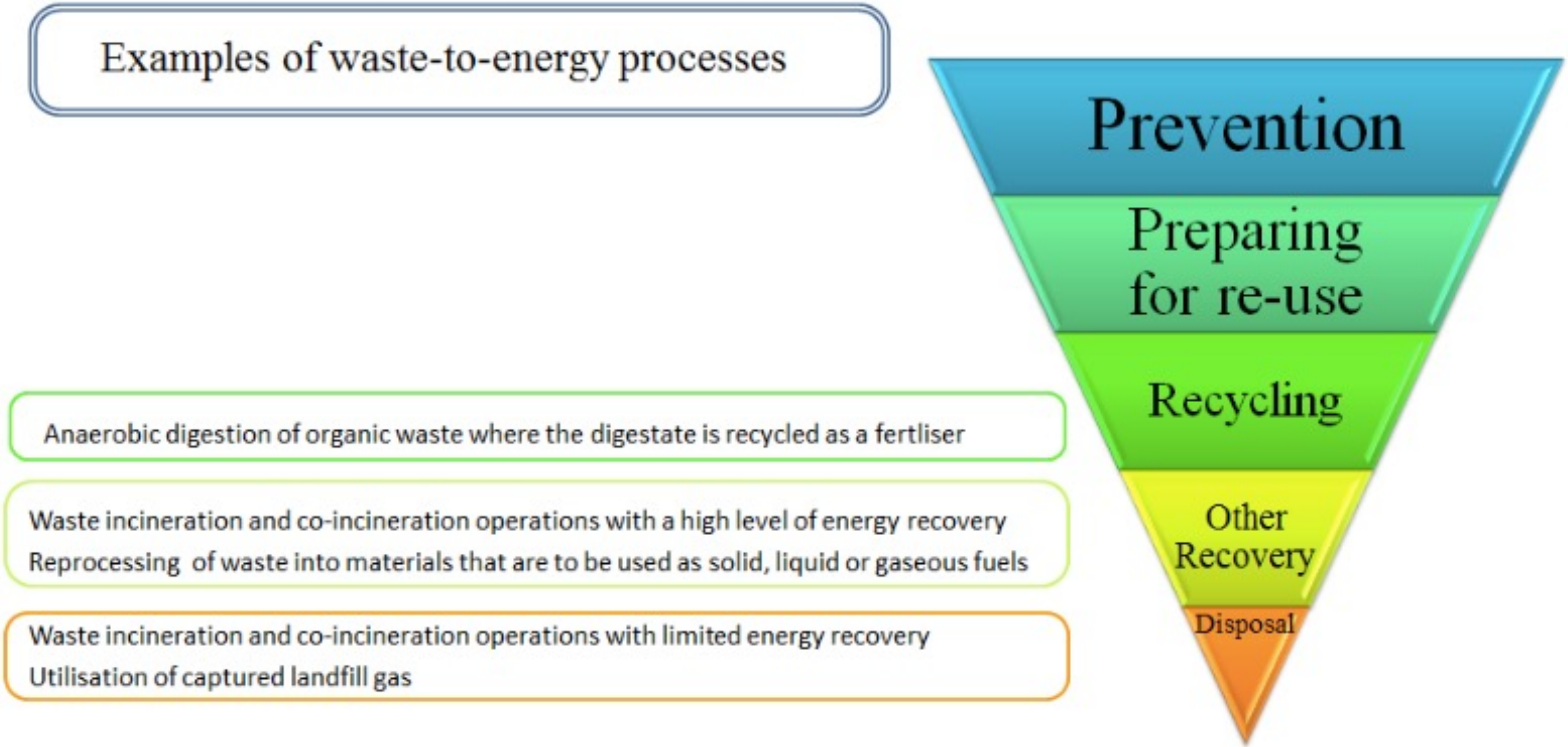
When to *digest* waste?

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

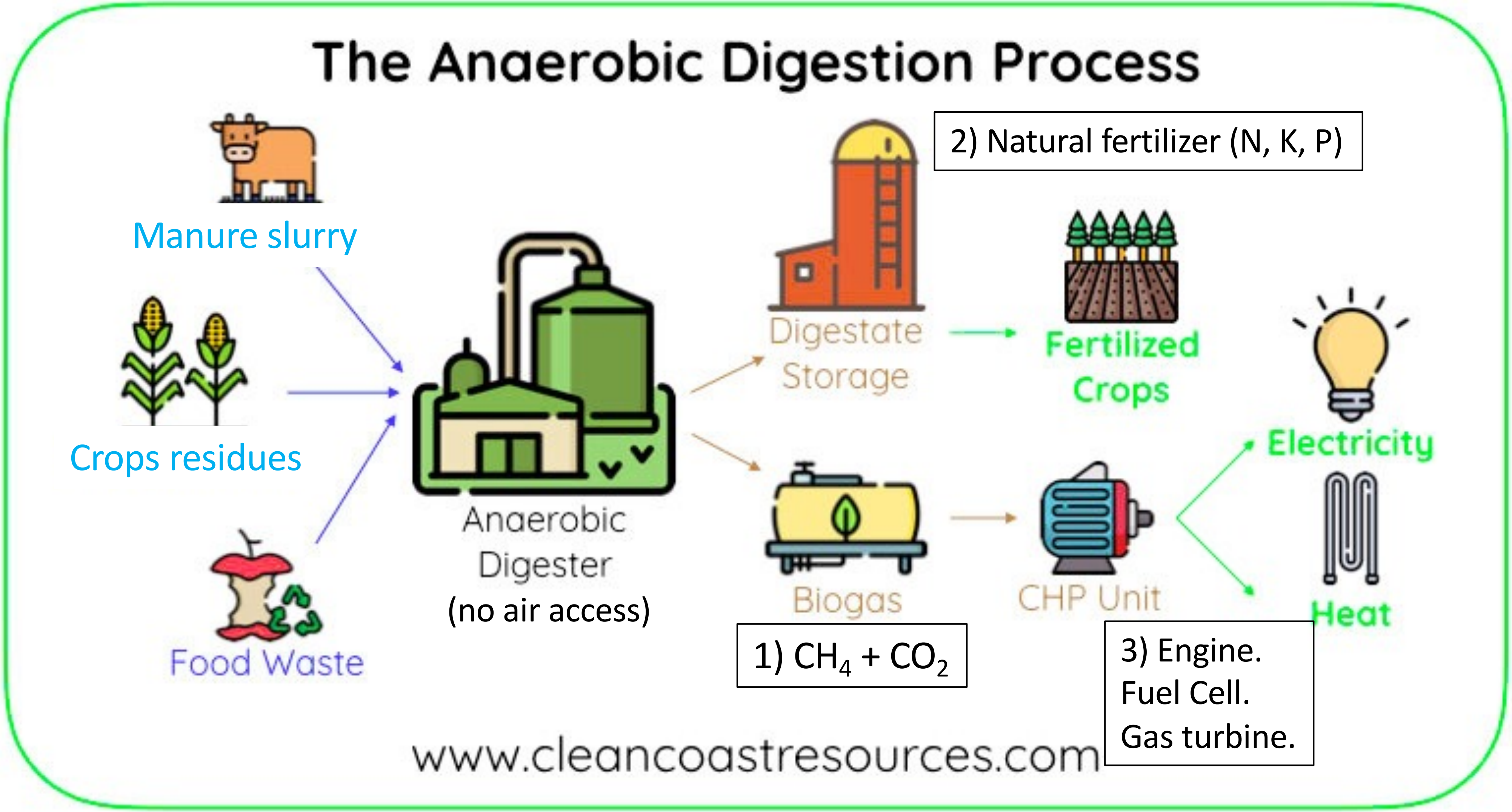
Anaerobic digestion - AD (1)

- =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

<u>'Buswell' formula:</u>

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

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

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

<u>'Buswell-Boyle'</u> (with N, S):

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

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

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

$$+ \; dNH_3 \; + \; eH_2S$$

<u>Remark</u>: 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 <u>batch</u> 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

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

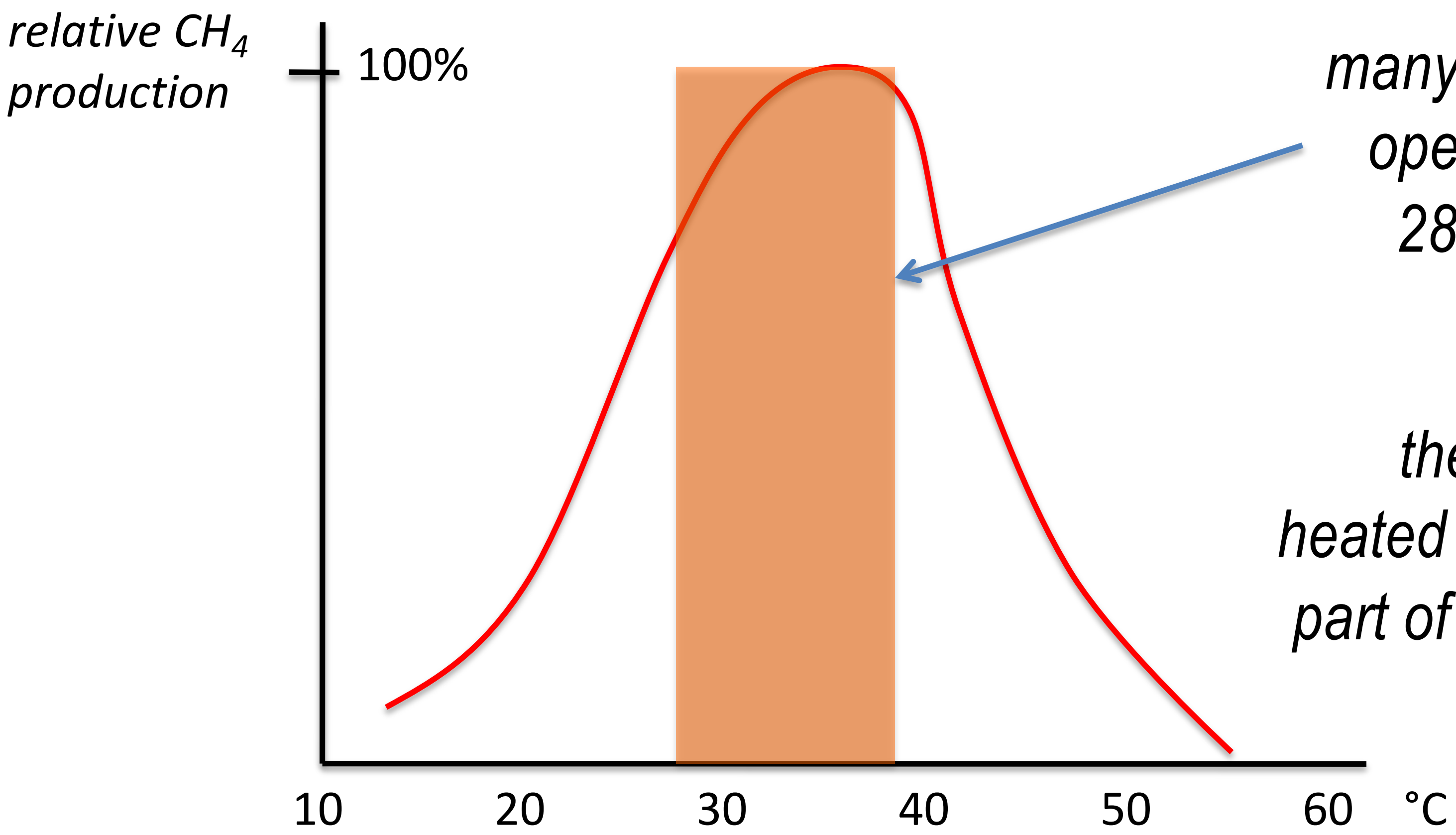
- biogas production can be expressed as:

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

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

Digestor reactor temperature

Enzymes / bacteria	Optimal T range
'Psychrophilic'	20°C
'Mesophilic'	20-45°C
'Thermophilic'	>45°C



many reactors operate at 28-37°C

⇩

they are heated by burning part of the biogas

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 $\pm$ 0.3	1.5 $\pm$ 0.6
per mass	$m^3_{biogas} / kg_{org.matter}$	0.3 $\pm$ 0.05	0.5 $\pm$ 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 is 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)

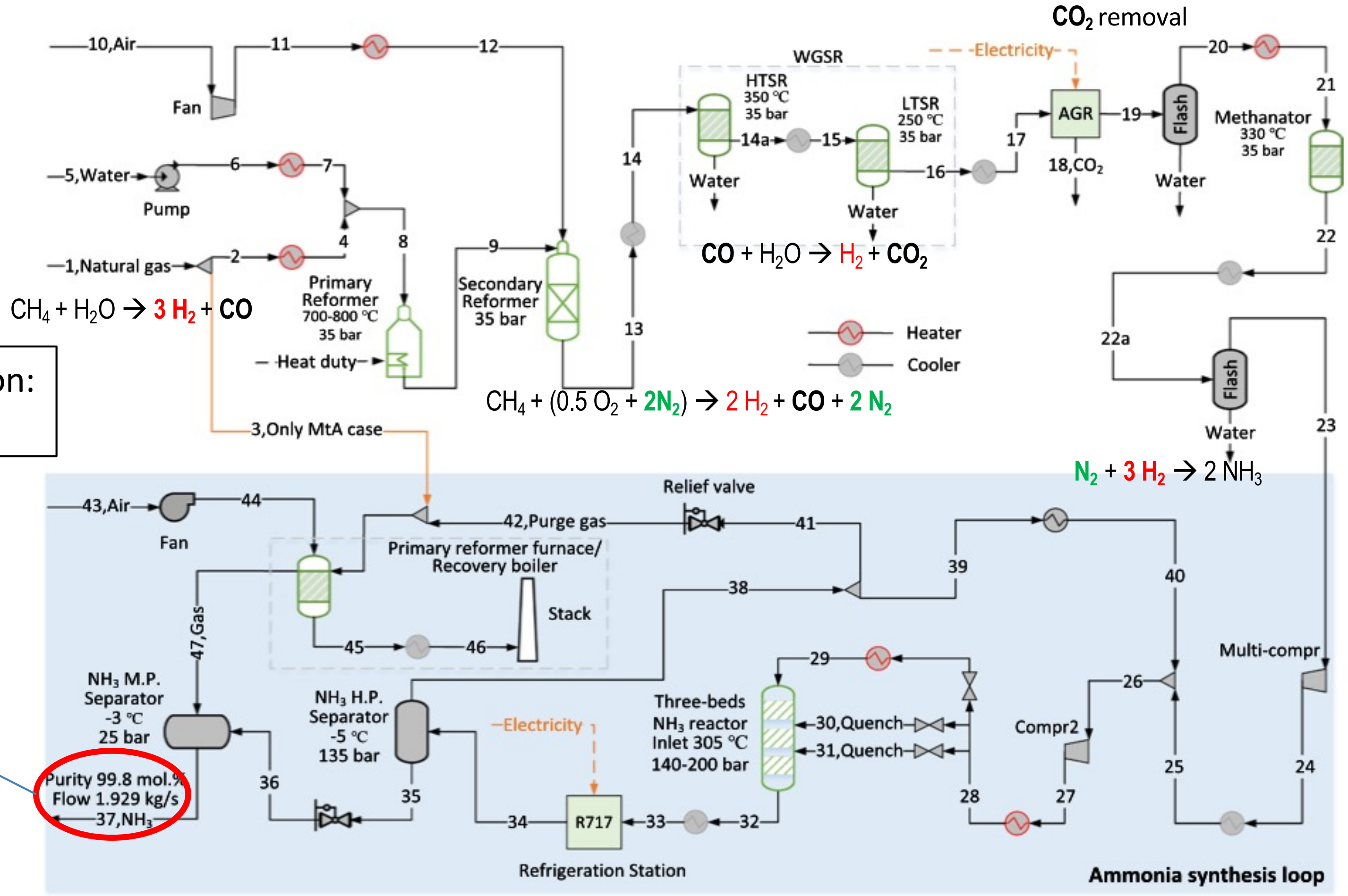
Ammonia synthesis plant

requires
41.5 Mt H_2
(5 EJ or 1382 TWh)
~500 GWe

World ammonia production:
235 Mt / yr

just 60 kt NH_3/yr
(1 small plant)

1.93 kg/s NH_3
$\Rightarrow$ 3.8 Nm³/s H_2
= 13725 Nm³/h
= 30 tonne H_2/day
= 45 MW_{chem}

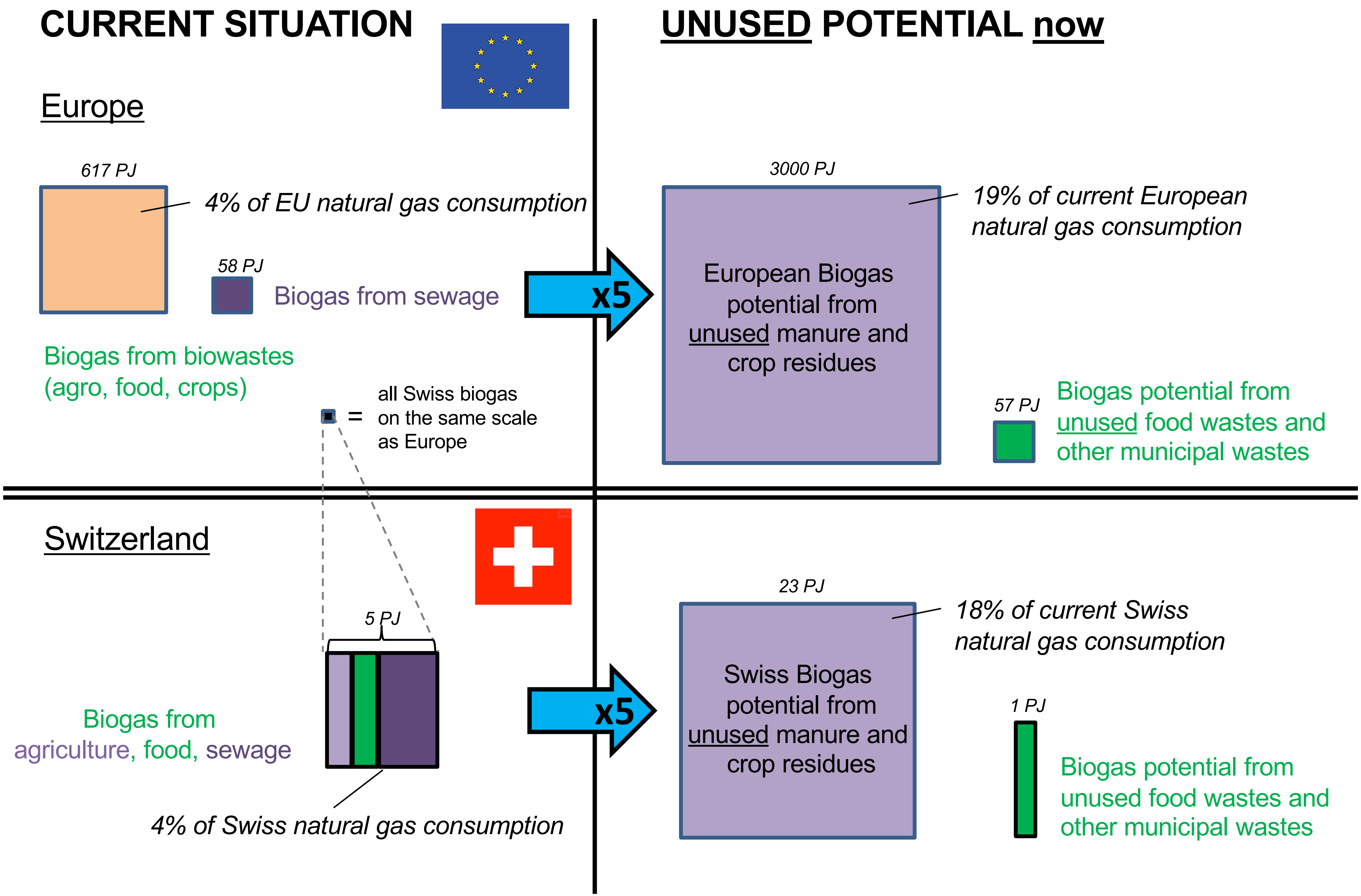


Techno-economic comparison of green ammonia production processes, Fig. 1
H Zhang, L Wang, J Van herle, F Maréchal, U Desideri, *Applied Energy* **259, 114135 (2020)**

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%**

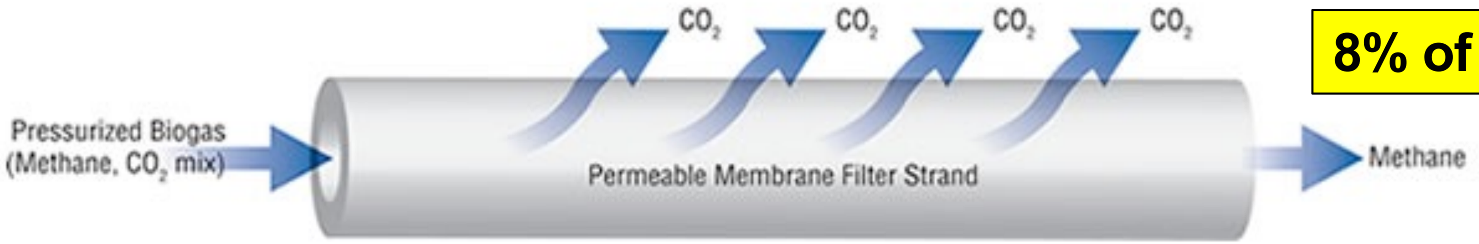
=> small power sites (gas engines); low (electrical) efficiency


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
European Biogas
potential from
unused manure and
crop residues
19% of current European
natural gas consumption
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
Swiss Biogas
potential from
unused manure and
crop residues
18% of current Swiss
natural gas consumption
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.



8% of use

gas grid

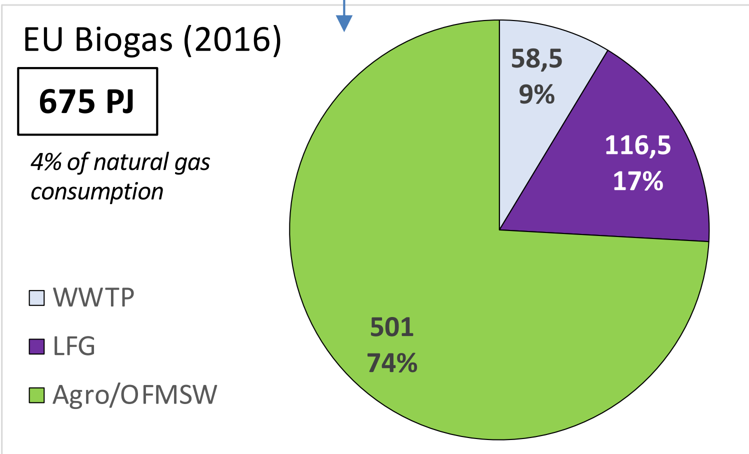
2) Burn the biogas into a large engine to generate electricity and heat.

500 kW_{el}
biogas engine

92% of use

Part is used in burners only

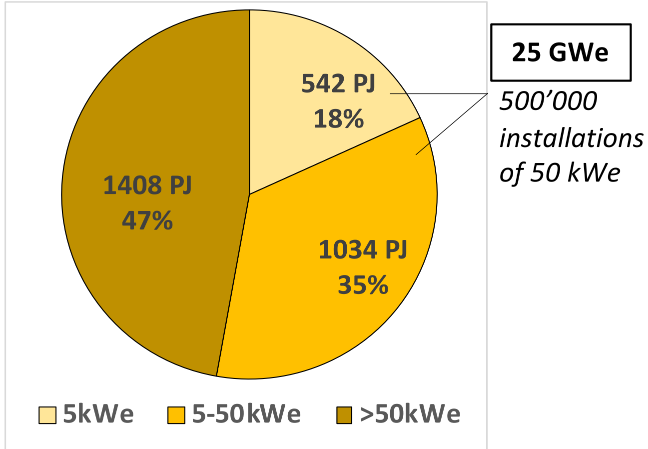
Status and potential in Europe



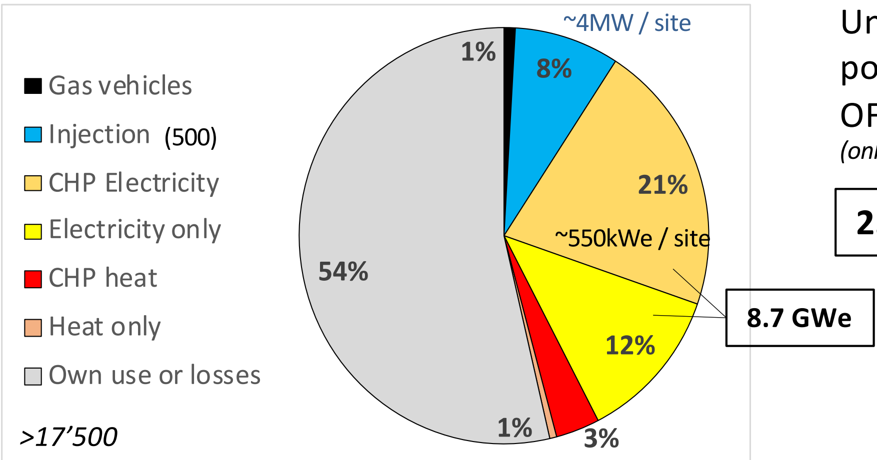
Unused potential in agriculture:

3000 PJ

18% of natural gas consumption



use:

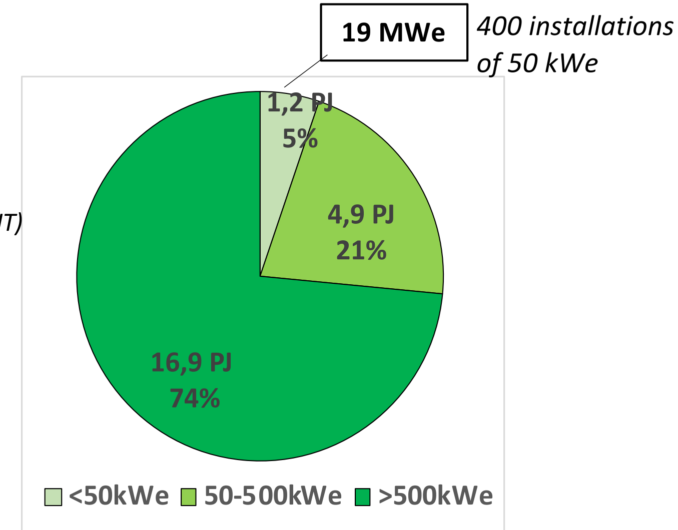


>17'500 installations

Unused potential in OFMSW:

(only for CH/D/F/IT)

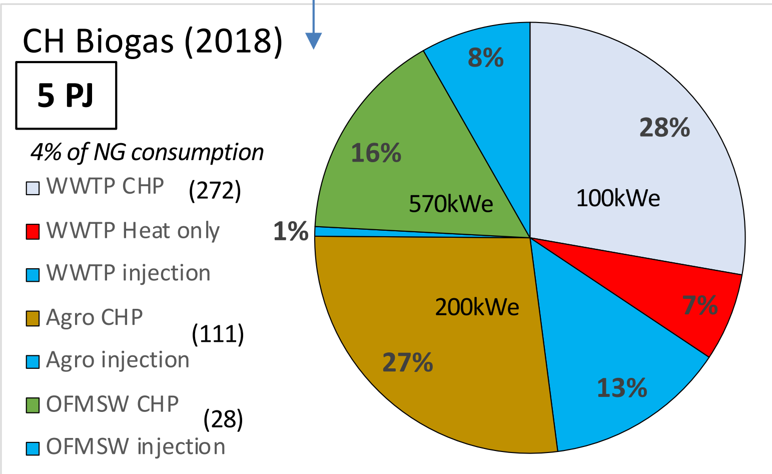
23 PJ



Use : mainly large installations > 200 m^3/h (>1 MW_{CH4})

The unused potential lies in small scale installations of <20 m^3/h

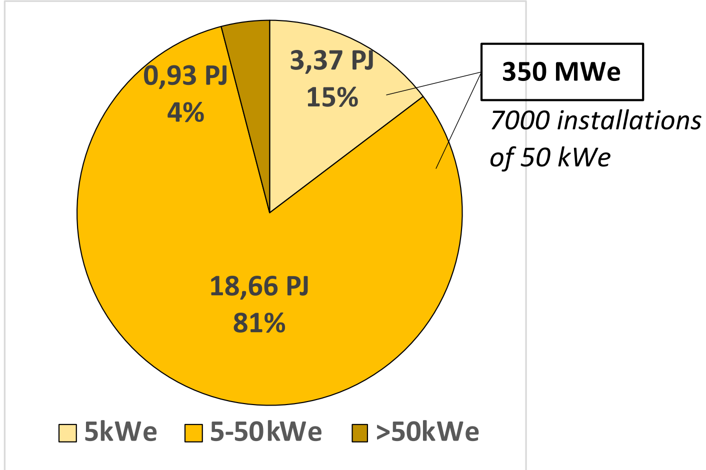
Status and potential in Switzerland



Unused potential in agriculture:

23 PJ

18% of natural gas consumption



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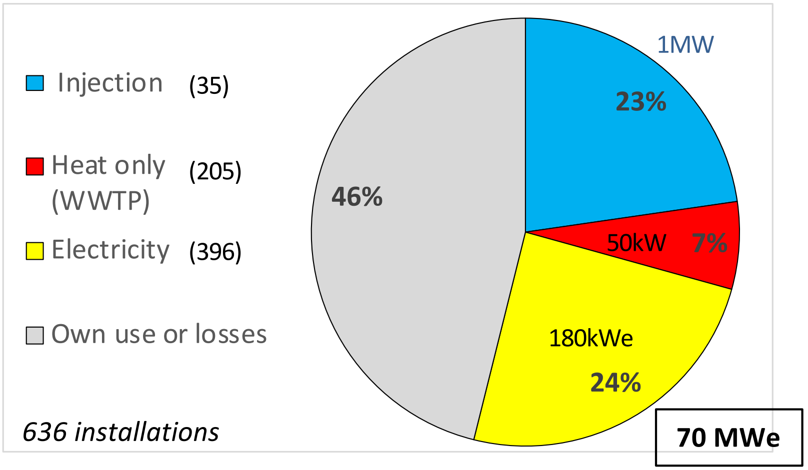
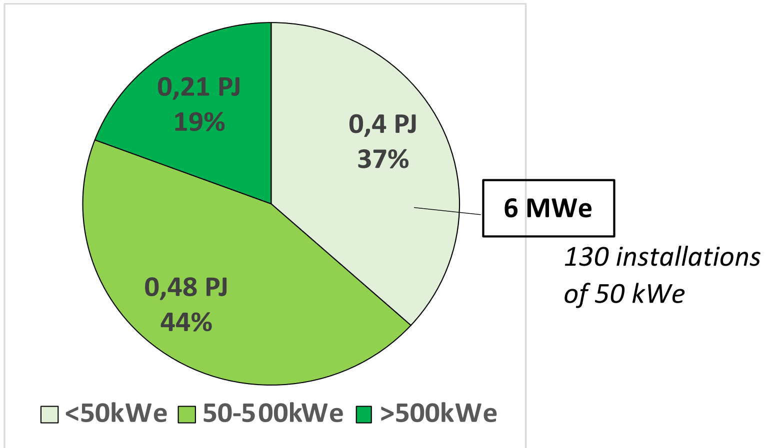


Unused potential in OFMSW:

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

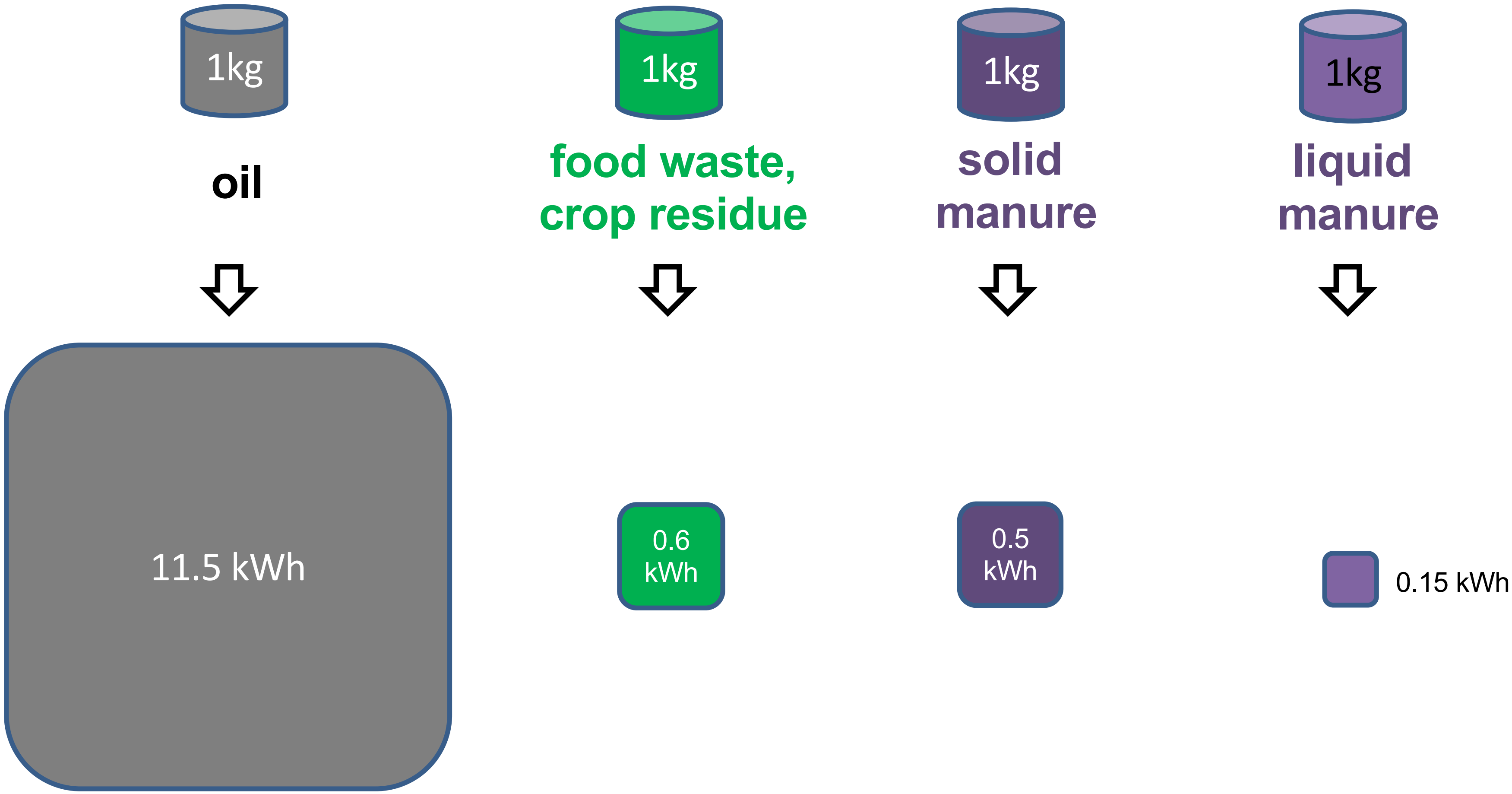
=> as a consequence, small-scale biogas generation remains unused, whereas this represents the majority of the resource

- 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 locally, 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

W2W Waste2Watts

EPFL

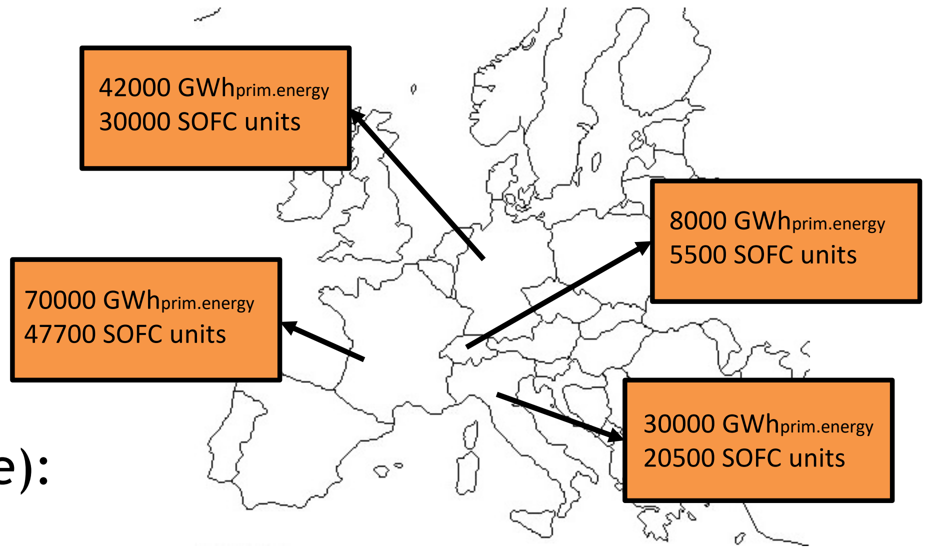
Initial result
52% elec efficiency.
Test to continue 2 years.
New sorbents to clean the biogas from sulfur.

=> semester or master projects

Biogas potential

For 🇩🇪 + 🇫🇷 + 🇮🇹 + 🇨🇭 :

>100’000 sites of 50 kWe equiv.
from agrowaste presently not-used, assuming only 50% of potential sites would be equipped

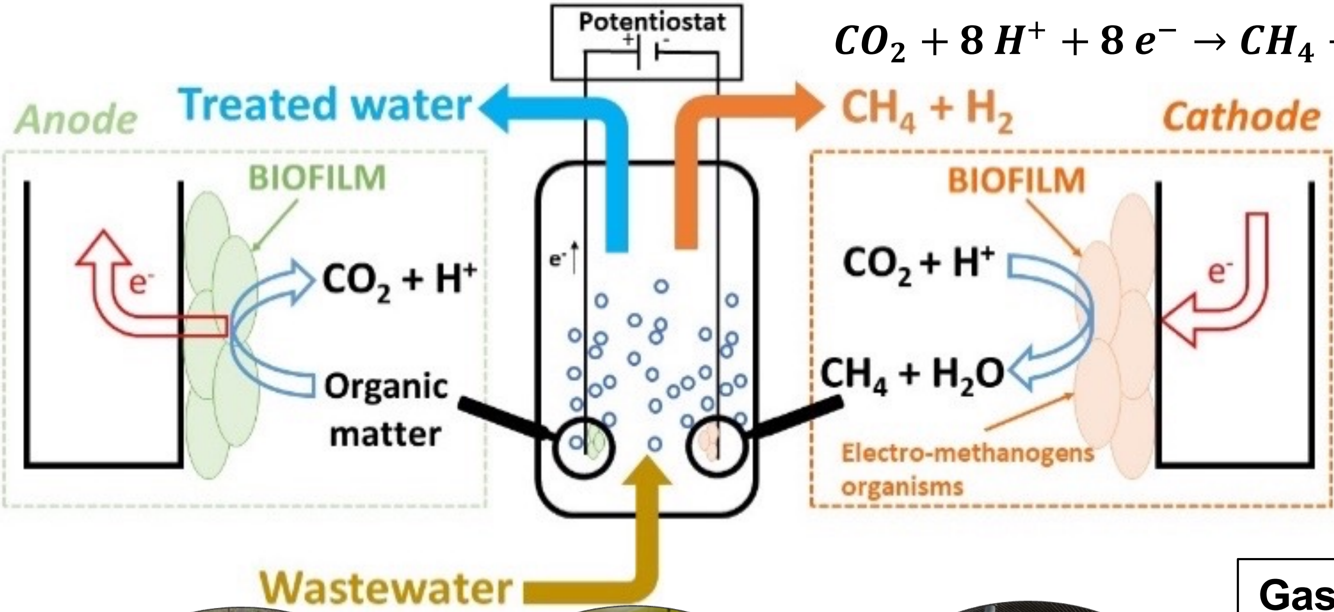


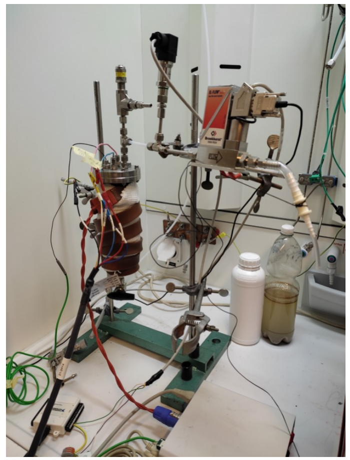
- For Switzerland (5500 units of 50 kWe):
- 275 MWe * 8000 h => 2.2 TWhe
- = **4% of CH electricity**
- = as much as the solid waste incineration plants (2.2 TWhe from 13 TWh solid wastes, electrical efficiency <20%)

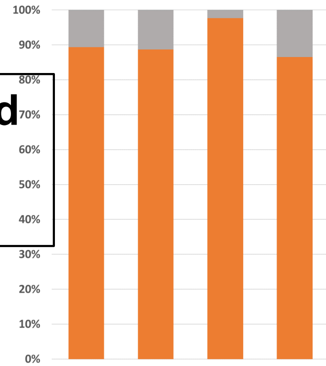
Bio-electrical systems (BES)

- 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.

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





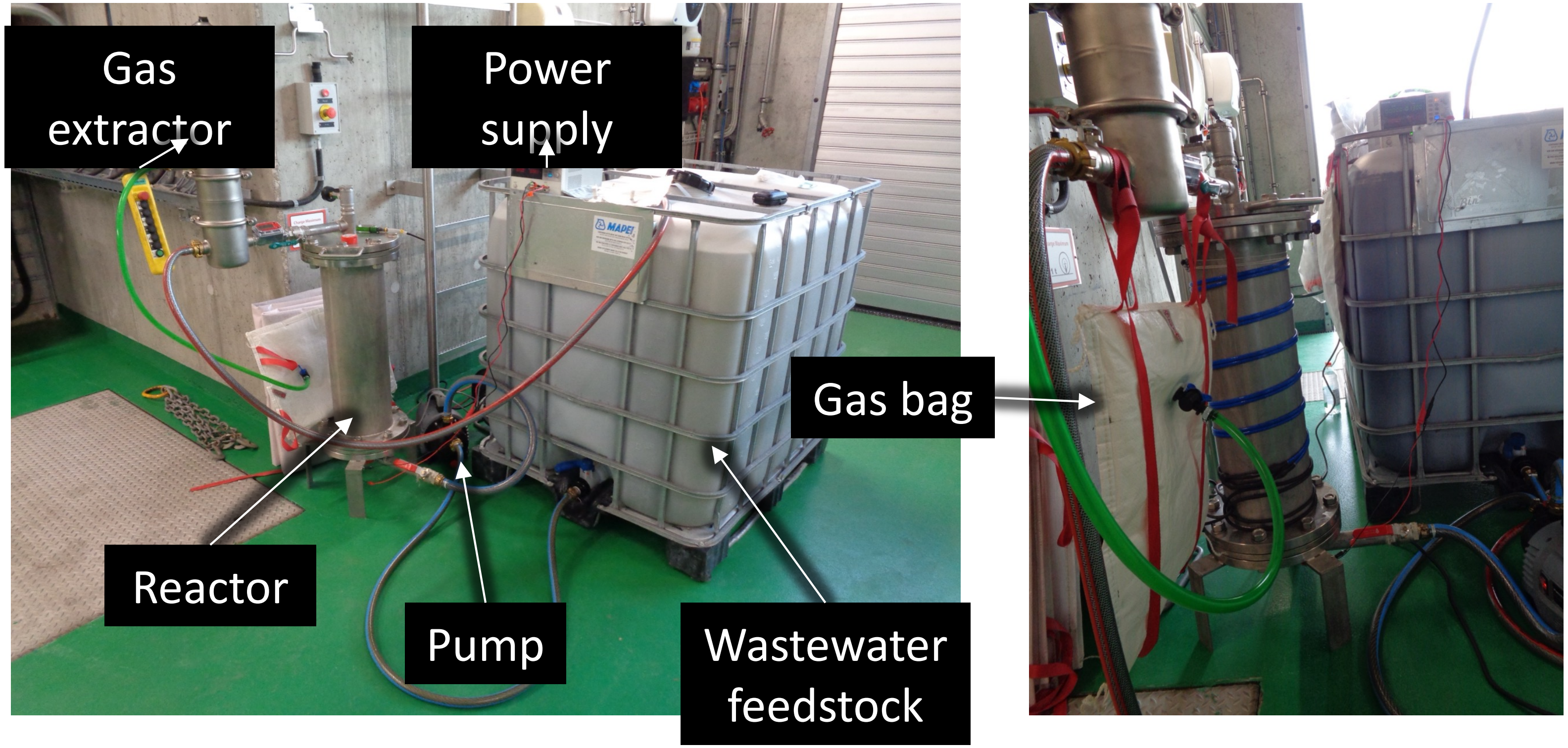


Gas produced in 1 step: 99% CH_4

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% CH_4 gas
2. The process can also convert NH_4^+ to N_2, to meet new strict regulations

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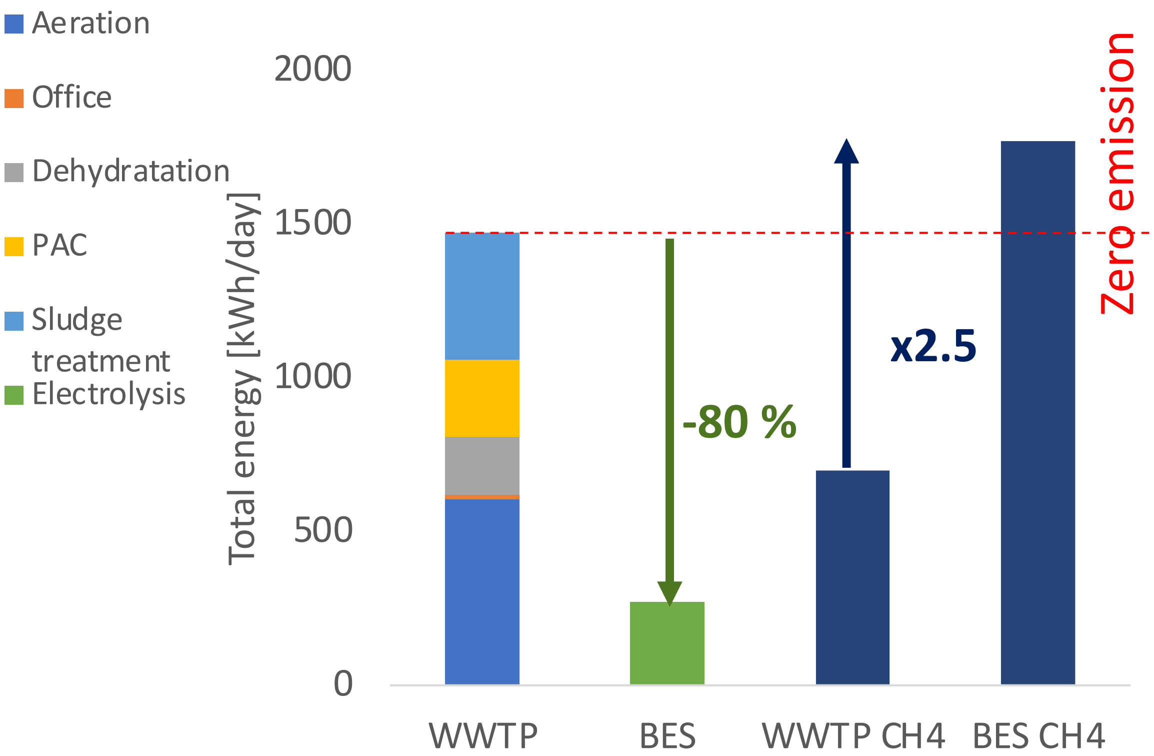
Waste water treatment with BES

- 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

Bioelectrocatalysis can produce other chemicals

- Other than CH_4, also acetate or methanol can be prodced
- New stacked plate electrodes design prepared => **semester / master projects**