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)

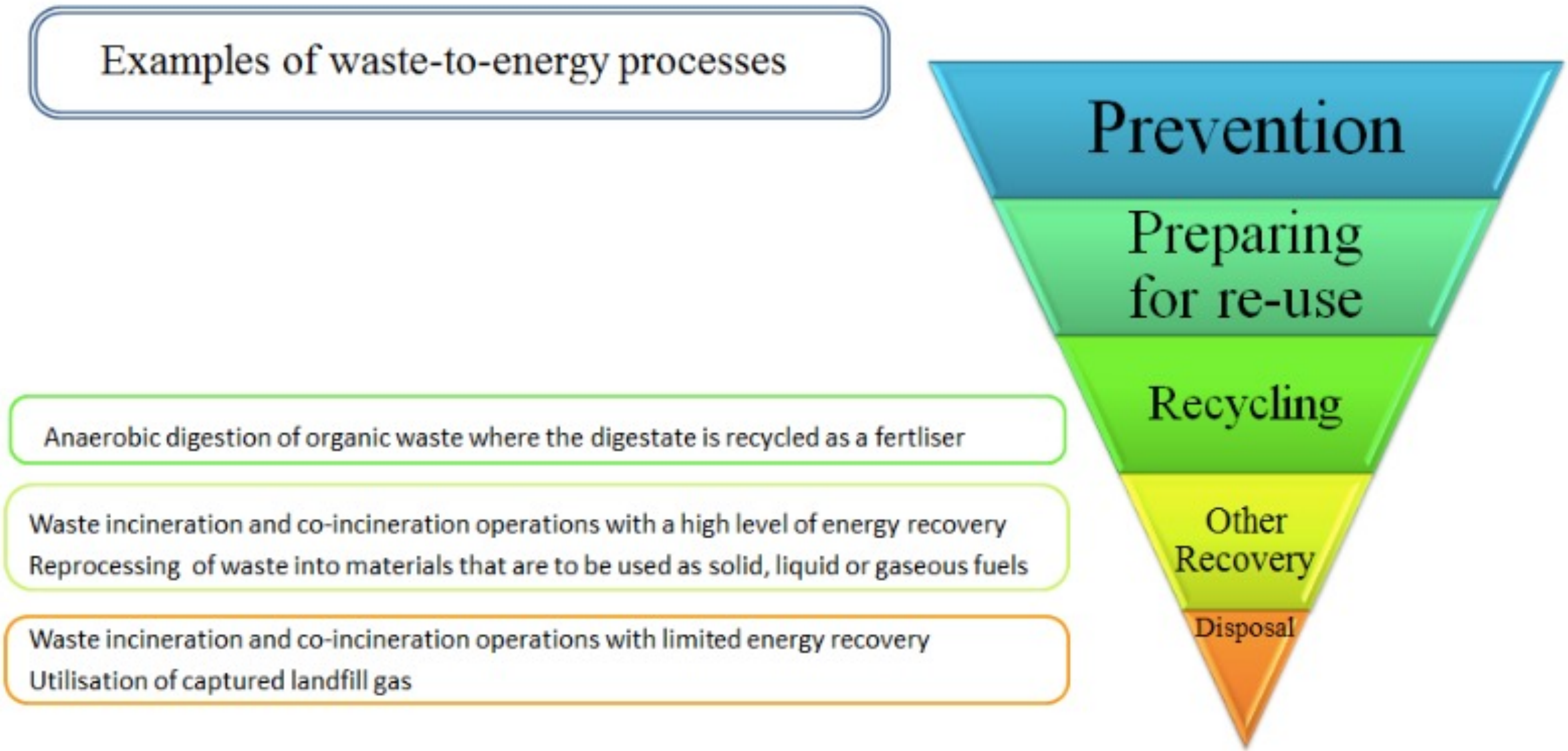
When to *digest* waste?

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

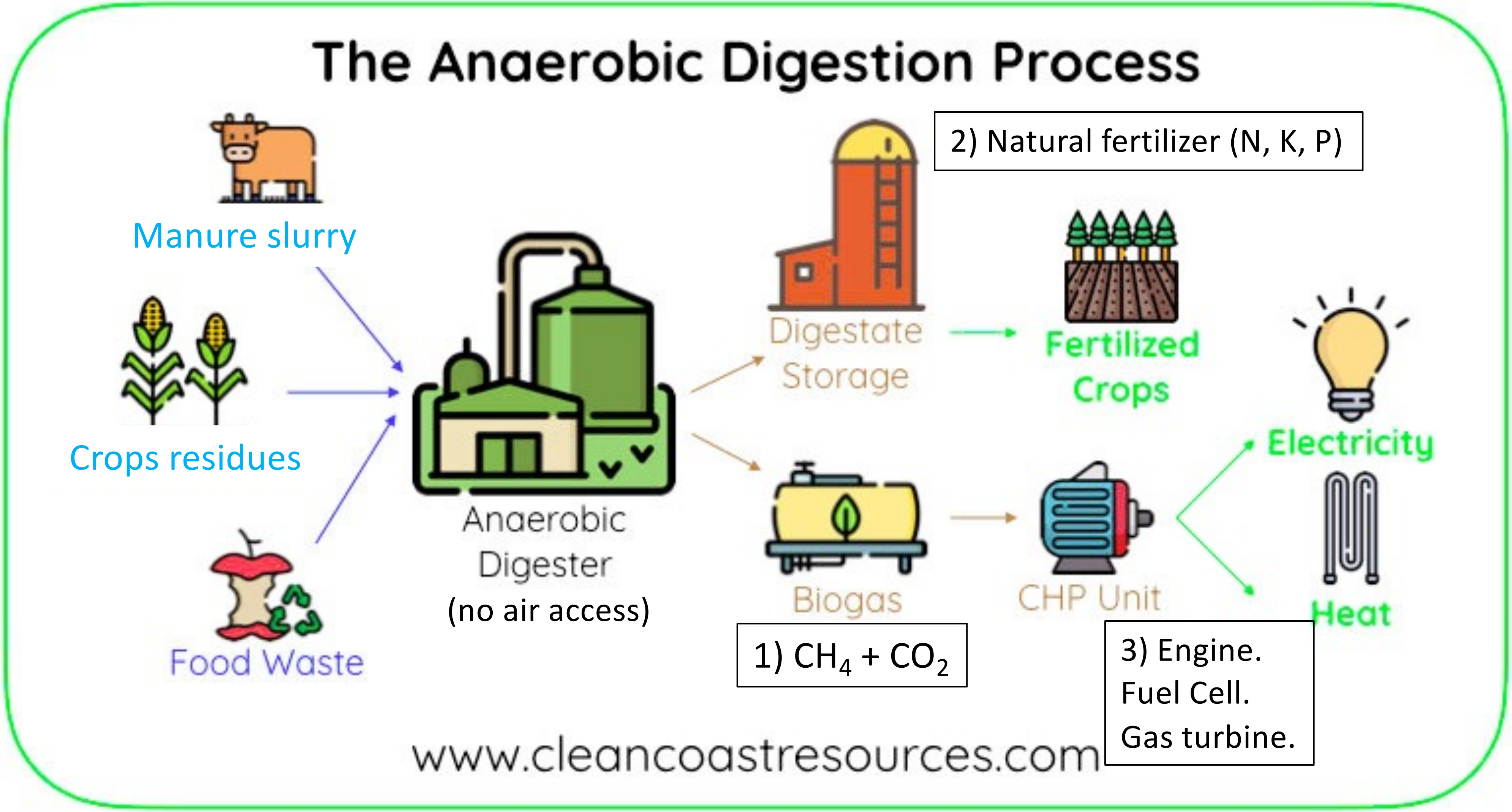
Anaerobic digestion - AD (1)

- =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:

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

4. ‘**Methanogenesis**’:

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

   b. $\underline{CO_2 + 4\ H_2} \rightarrow \mathbf{CH_4} + 2\ H_2O$ (**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), and reduces CO_2 emissions overall since it replaces fossil fuels.
3. Digesting the biowastes in a sealed tank, especially manure, instead of letting them freely rot (compost) in open air, will reduce uncontrolled CH_4 GHG emissions and instead recover the CH_4 as fuel in a controlled way.
   - agriculture in Switzerland contributes to 14% of overall GHG emissions of which 61% as CH_4 (partly from the animals directly (enteric), partly from their manure).
4. Biodigestate is a natural fertilizer of superior quality than synthetic fertilizer (made from fossil fuels through e.g. industrial ammonia-synthesis): the soil absorbs it better and therefore releases less N_2O back to the atmosphere, therefore reducing N_2O GHG
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:

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

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

$$C_4H_8O_2 + [4 - 2 - 1]H_2O \rightarrow \left(2 + 1 - \tfrac{1}{2}\right)CH_4 + \left(2 - 1 + \tfrac{1}{2}\right)CO_2 = \tfrac{5}{8}CH_4 + \tfrac{3}{8}CO_2$$

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

$$C_aH_bO_cN_dS_e + \frac{1}{4}[4a - b - 2c + 3d + 2e]H_2O$$

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

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

$$+ dNH_3 + eH_2S$$

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):
  $$\theta = \frac{V_{reactor}\left[m^3\right]}{\dot{V}_{org}\left[m^3/d\right]}$$
  - saturation after 20 days
- daily specific load (kg/m^3.d)
  $$M_{day} = \dot{V}_{org} \cdot \frac{M}{V} = \frac{M}{\theta}$$
  - M can designate fresh or dry organic matter
- biogas production can be expressed as:
  $$m^3_{biogas} / m^3_{reactor}$$
  $$m^3_{biogas} / kg_{org.matter}$$

Example:

Farm with 60 animals. Manure waste: 3 m^3/day. (≈3000 kg)

Organic dry matter = 50 kg/m^3 (=150 kg/day=5% organics)

Mean residence time θ = 20 days. Biogas production = 65 m^3/day. (≈433 L / kg d.m.)

- Reactor volume :

$$V_{reactor}\left[m^3\right] = \theta.\dot{V}_{org} = 20 * 3 = 60 m^3$$

- Daily specific load:

$$M_{day} = \frac{M_{org}}{\theta} = \frac{50 kg/m^3}{20 days} = 2.5 kg/m^3.day$$

- Specific biogas production:
  - per reactor volume:

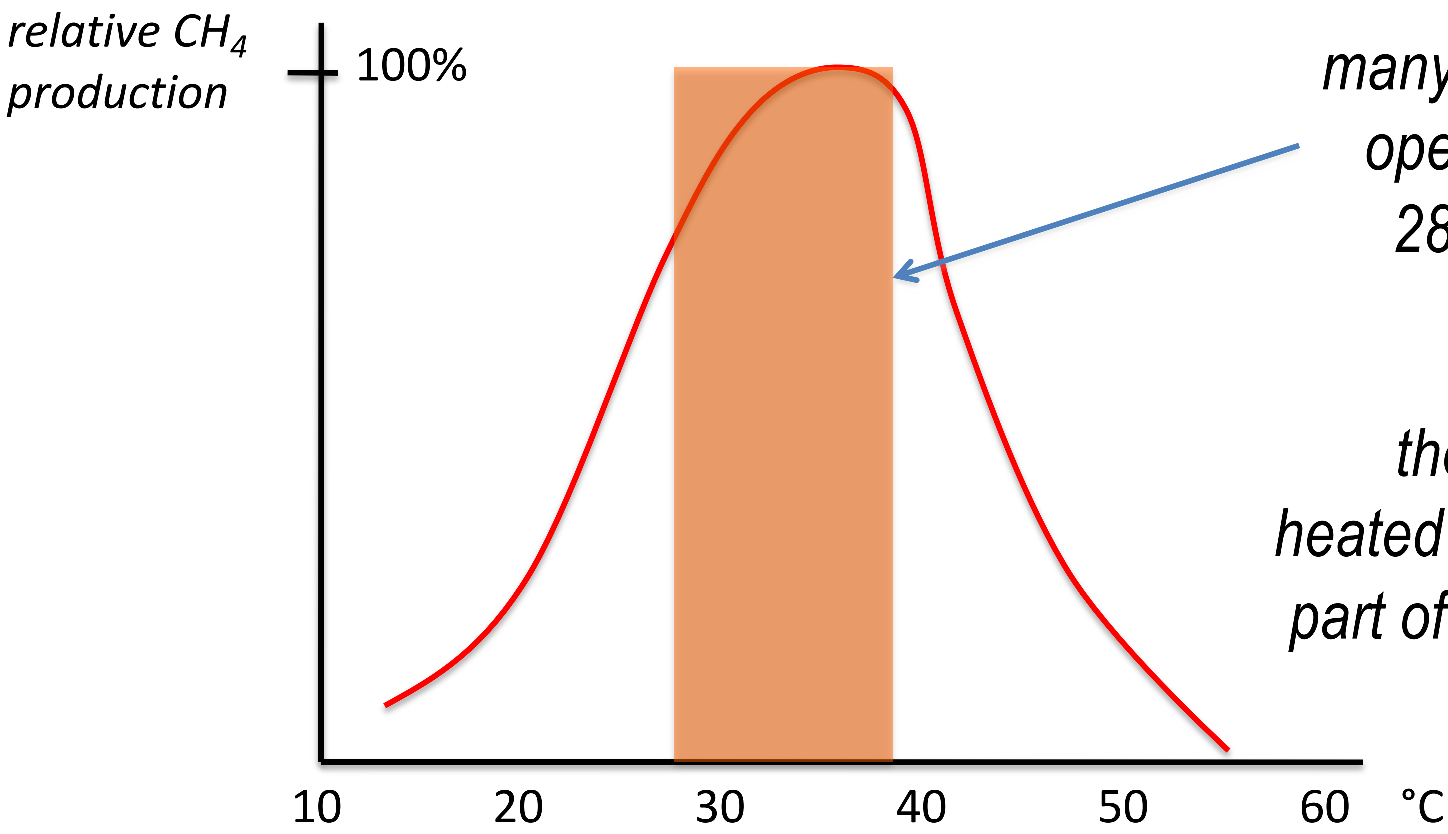
$$P = \frac{65 m^3/d}{60 m^3} = 1.08 \frac{m^3/d}{m^3}$$

  - per organic matter:

$$P = \frac{65 m^3/day}{M_{org}\left[\frac{kg}{m^3}\right].V_{reactor}\left[m^3\right] / \theta\left[days\right]} = \frac{65}{50.\frac{60}{20}} = 0.43 \frac{m^3}{kg_{org.matter}}$$

Digestor reactor temperature

Enzyme	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 has to be imported, which is made from natural gas in huge plants and has a very large impact: 1% of global GHG emissions and 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 use and potential (EU)

Source	Use (PJ)	kW_e/site	Potential
	2007	gas engines	ultimate
Effluents	7	200 kW	140 PJ
Sewage	37	50-200	215
Manure	30	10-100	750
Solid agro	45		1370
MSW,ISW	15	0.1-1 MW	330
Landfill	120	1 MW	-
TOTAL	**254 PJ** (6 Mtoe)	*huge margin* →	**2805 PJ** (67 Mtoe)

30% efficiency

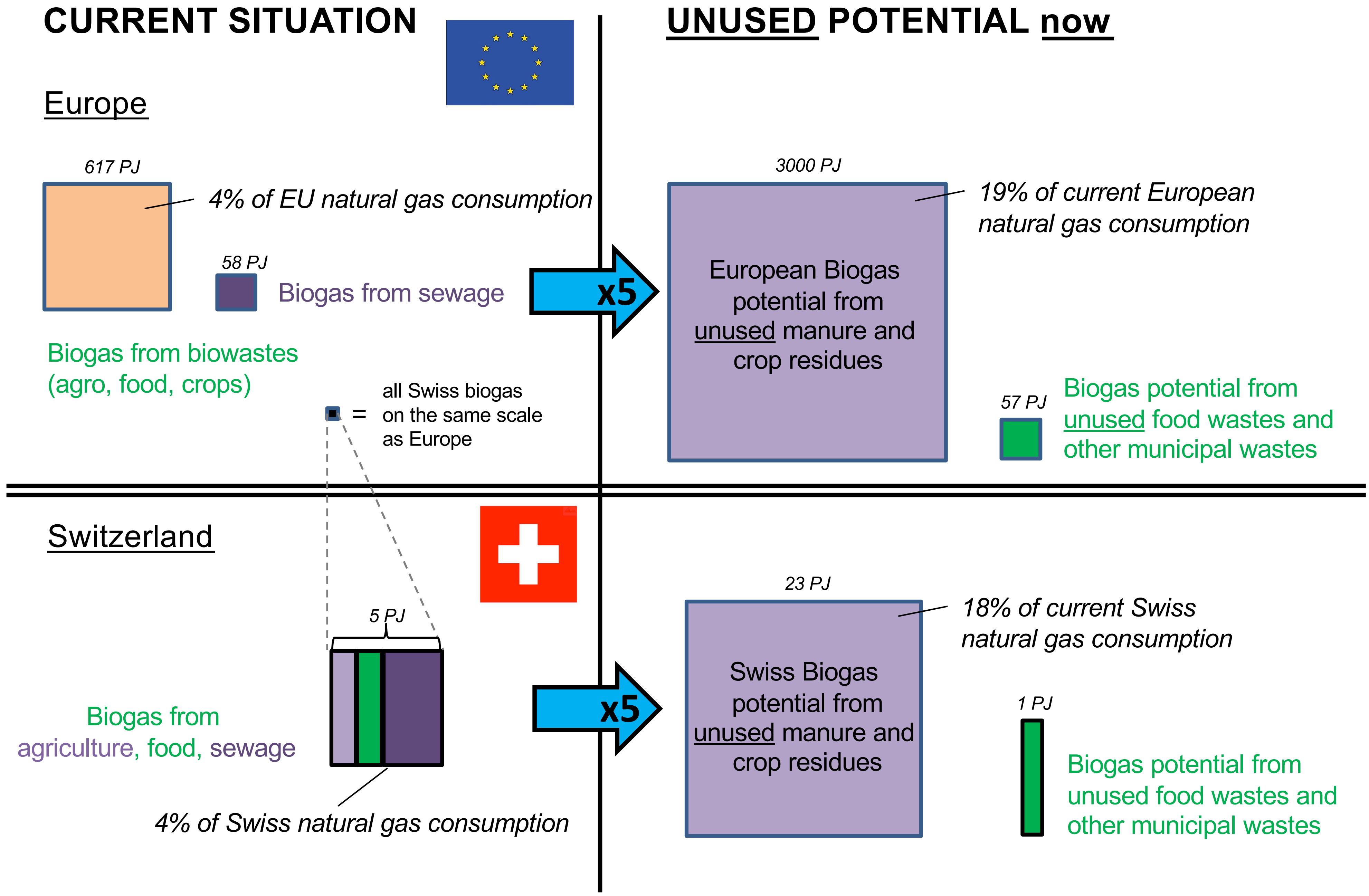
20 TWh_{el} (0.6% of total)

=25% of NG import in EU

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%**

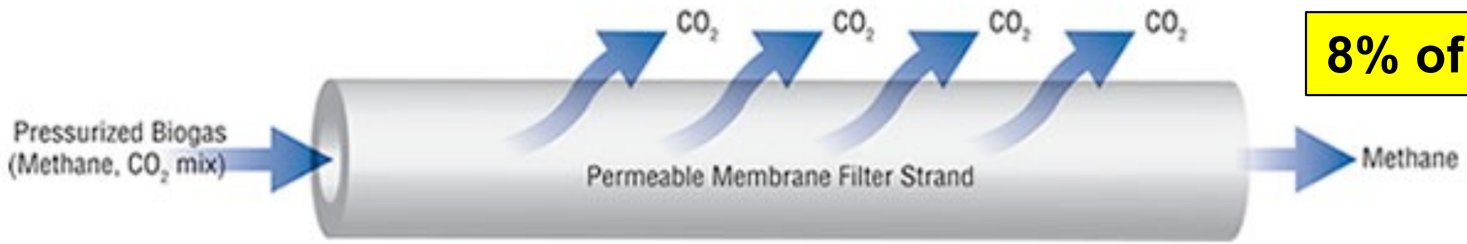
=> *small power sites (gas engines); low (electrical) efficiency*


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.



8% of use

gas grid

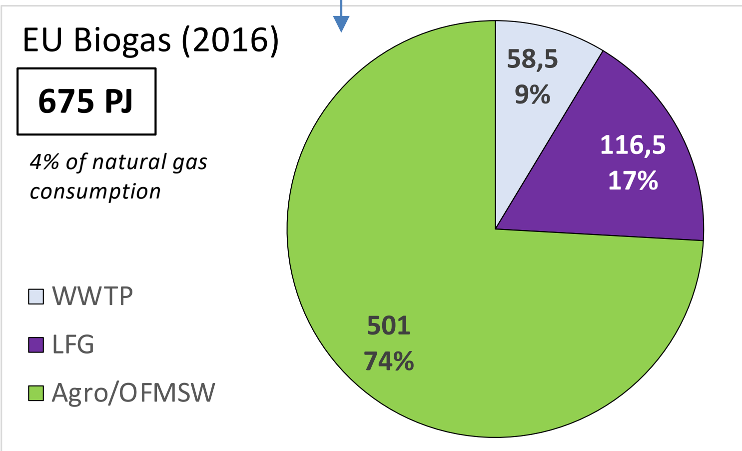
2) Burn the biogas into a large engine to generate electricity and heat.

500 kW_{el}
biogas engine

92% of use

Part is used in burners only

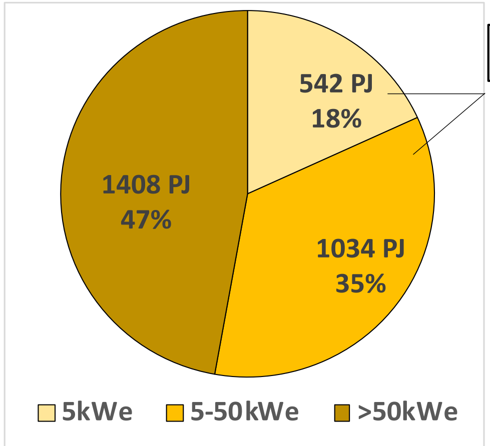
Status and potential in Europe



Unused potential in agriculture:

3000 PJ

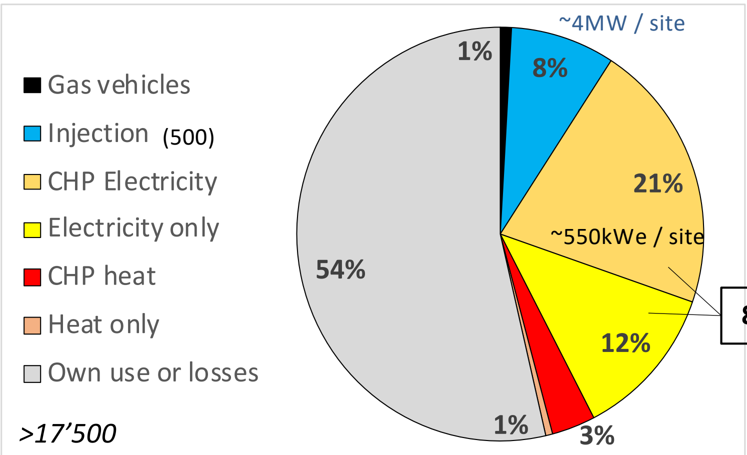
18% of natural gas consumption



25 GWe

500'000 installations of 50 kWe

use:



8.7 GWe

>17'500 installations

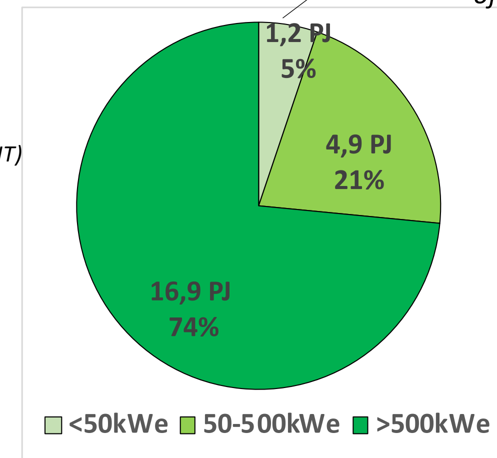
Unused potential in OFMSW:

(only for CH/D/F/IT)

23 PJ

19 MWe

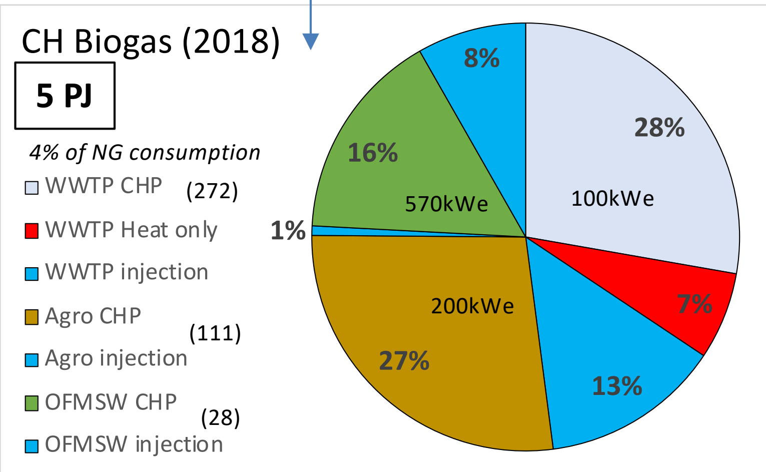
400 installations of 50 kWe



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

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

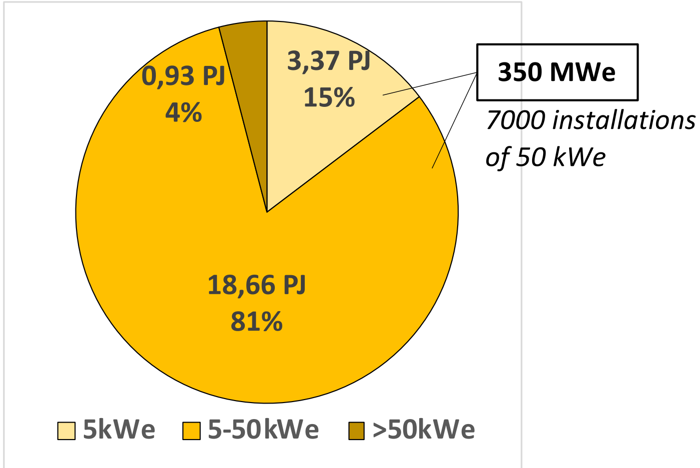
Status and potential in Switzerland



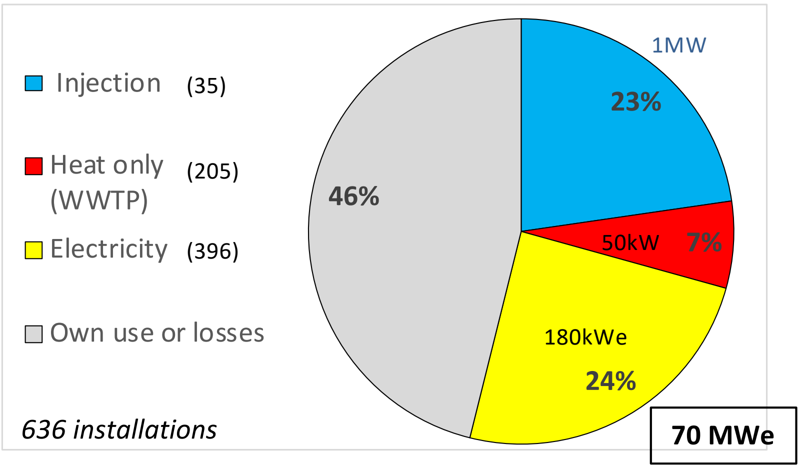
Unused potential in agriculture:

23 PJ

18% of natural gas consumption

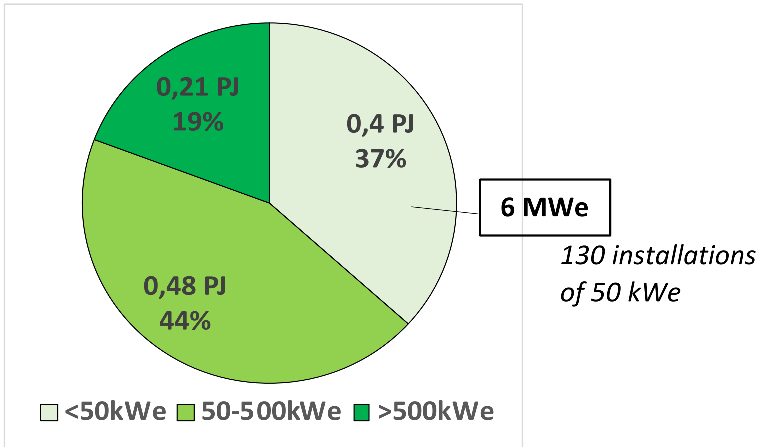


use:



Unused potential in OFMSW:

1.1 PJ



Biogas figures for Switzerland (2018)

	Application:	Energy resource		Biological cleaning		TOTAL or *average*
		Agriculture	OFMISW	**WWTP**	Industry effluents	
(1)	Biogas total (PJ)	1.44	1.243	2.28	0.2	5.16 PJ
(2a)	- gas grid **injection** (PJ)	-0.037	-0.425	-0.636	-0.073	-1.17 PJ
(2b)	- **heat** only (PJ) (WWTP only)			-0.34		-0.34 PJ
(3)	= Biogas for **CHP** (PJ) (1)-(2)	= 1.4	= 0.82	= 1.3	= 0.126	= 3.65 PJ
(4)	of which **electricity** (PJ)	0.50	0.306	0.43	0.03	1.266 PJ
(4b)	= electricity in TWhe	0.14	0.085	0.121	0.008	0.35
(5)	=> elec. efficiency (%) (4) / (3)	35.7%	37.4%	33.5%	25%	*avg 34.7%*
(6)	Installations CHP (or injection)	111	28	272	20	431
	Installations for heat only (WWTP)			205		205
(7)	Energy / site (TJ) (1) / (6)	13	44.4	4.8 (CHP) 1.7 (heat)	10	*avg 8.5 TJ*
(8)	Power / site (kW_{CH4}) = (7) / (8760hx3600s)	411 kW_{CH4}	1408 kW_{CH4}	151 (CHP) 53 (heat)	315 kW_{CH4}	*avg 269kW$_{CH4}$*
(9)	Installed power total **(MWe)**	22.6	16.0	29.7	1.86	70.2 MWe
(10)	Elec. power / site (kWe) (9) / (6)	204 kWe	570 kWe	109 kWe	93 kWe	*avg 163 kWe*
	Load (h / %) (4b) / (9)	6125h 70%	5312h 60.6%	4060h 46%	4346h 50%	4986h 57%

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 (0.6-6MW_{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 <50kWe, a biogas engine does not reach 30% electrical efficiency

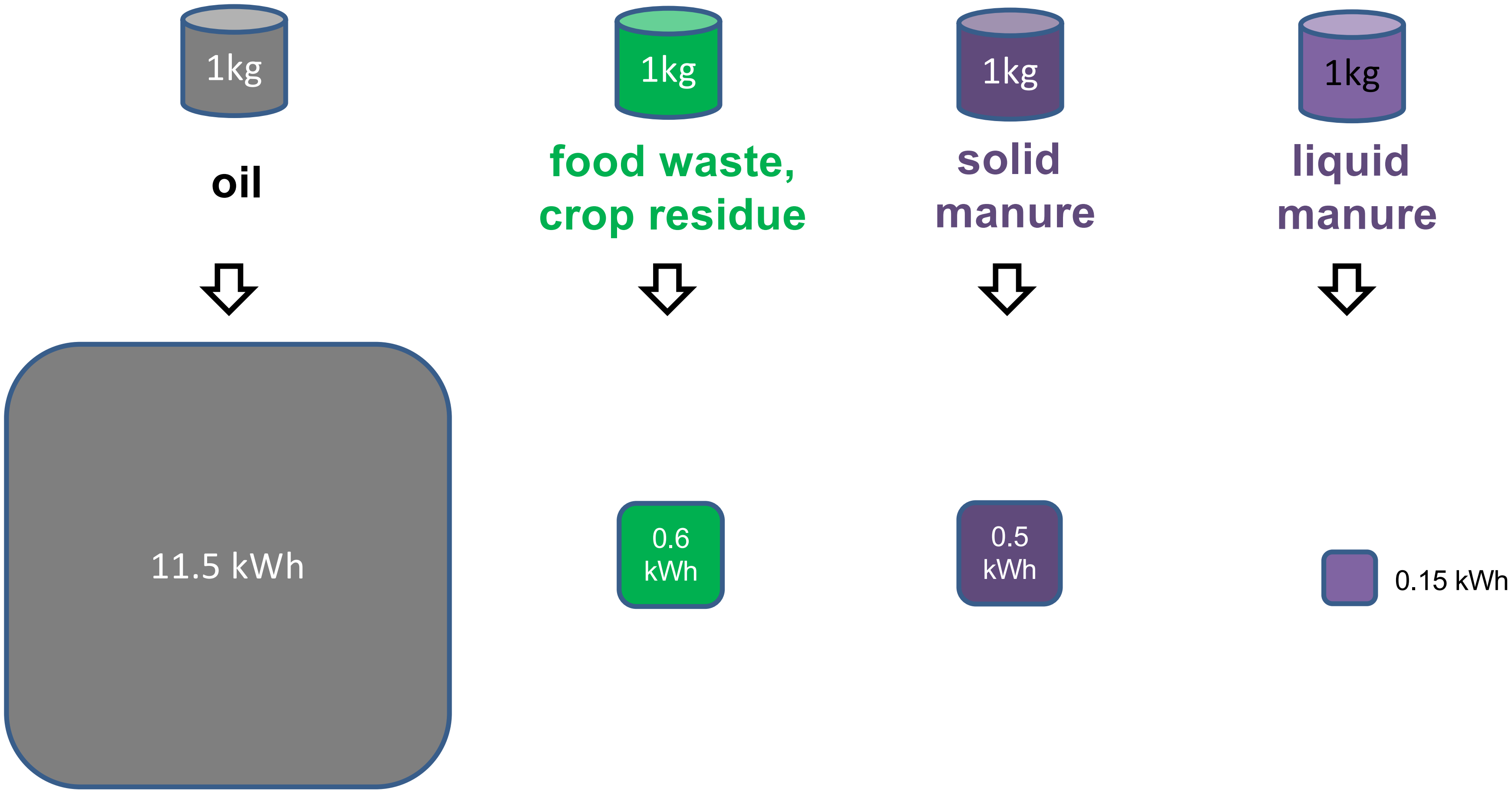
=> as a consequence, small-scale biogas generation remains unused, whereas this represents the majority of the resource

- 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

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

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

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

Footnote

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

Transporting biowaste fuel

- A tractor consumes 50L 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.

Summarised:

- Biowaste better be used locally, over a few km^2
- The available energy is then a few $100kW_{CH4}$, 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~~)

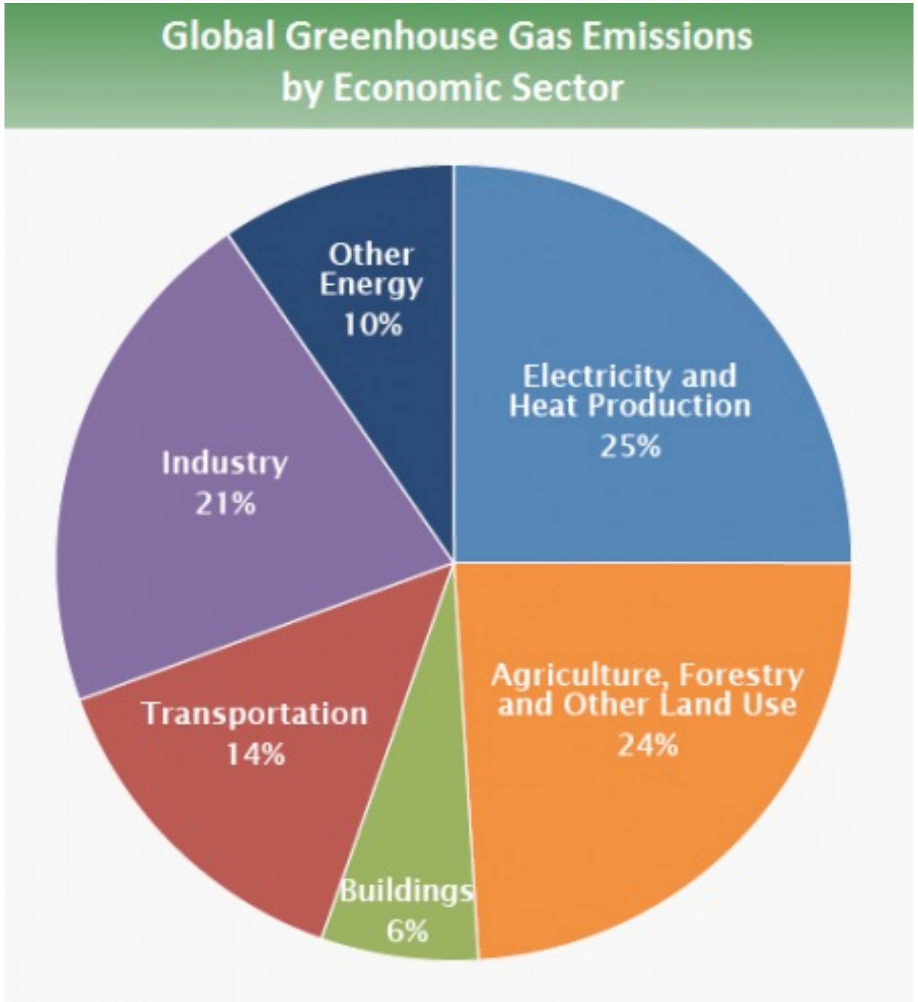
*1.6 m^3/h biogas (60%CH_4-40%CO_2) = 1 m^3/h CH_4 = 10 kWh_CH_4 = 3 kWe in a 30% efficient engine

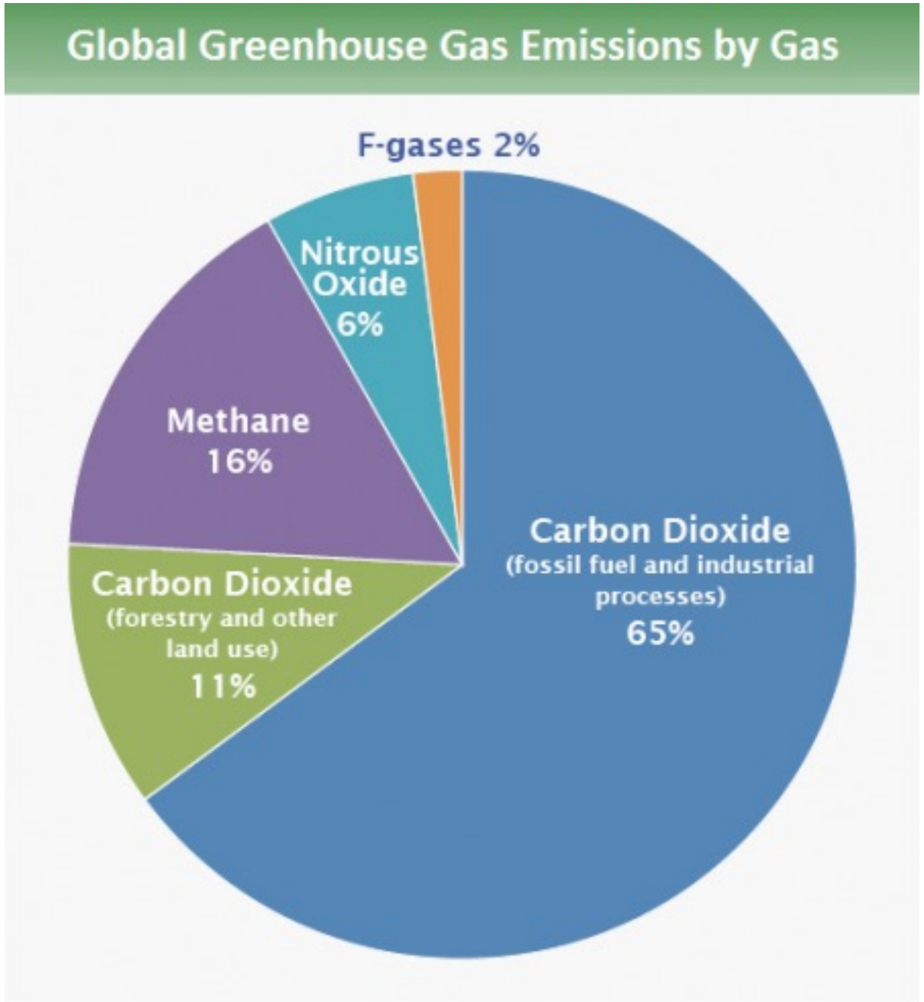
Special case of landfill gas (LFG)

- (multi)MW_{el}-size sites (with gas engines, gas turbines)
- an important fraction of world biogas (20 Mtoe)
- 3 Mtoe in EU-27
- important anthropogenic GHG emitter! (as CH_4)
- 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 !

Global GHG

Source : https://www.epa.gov/ghgemissions/global-greenhouse-gas-emissions-data
(International Panel for Climate Change 2014)





Impact of agriculture, animal breeding and deforestation on climate change tends to be underestimated