# 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 | |
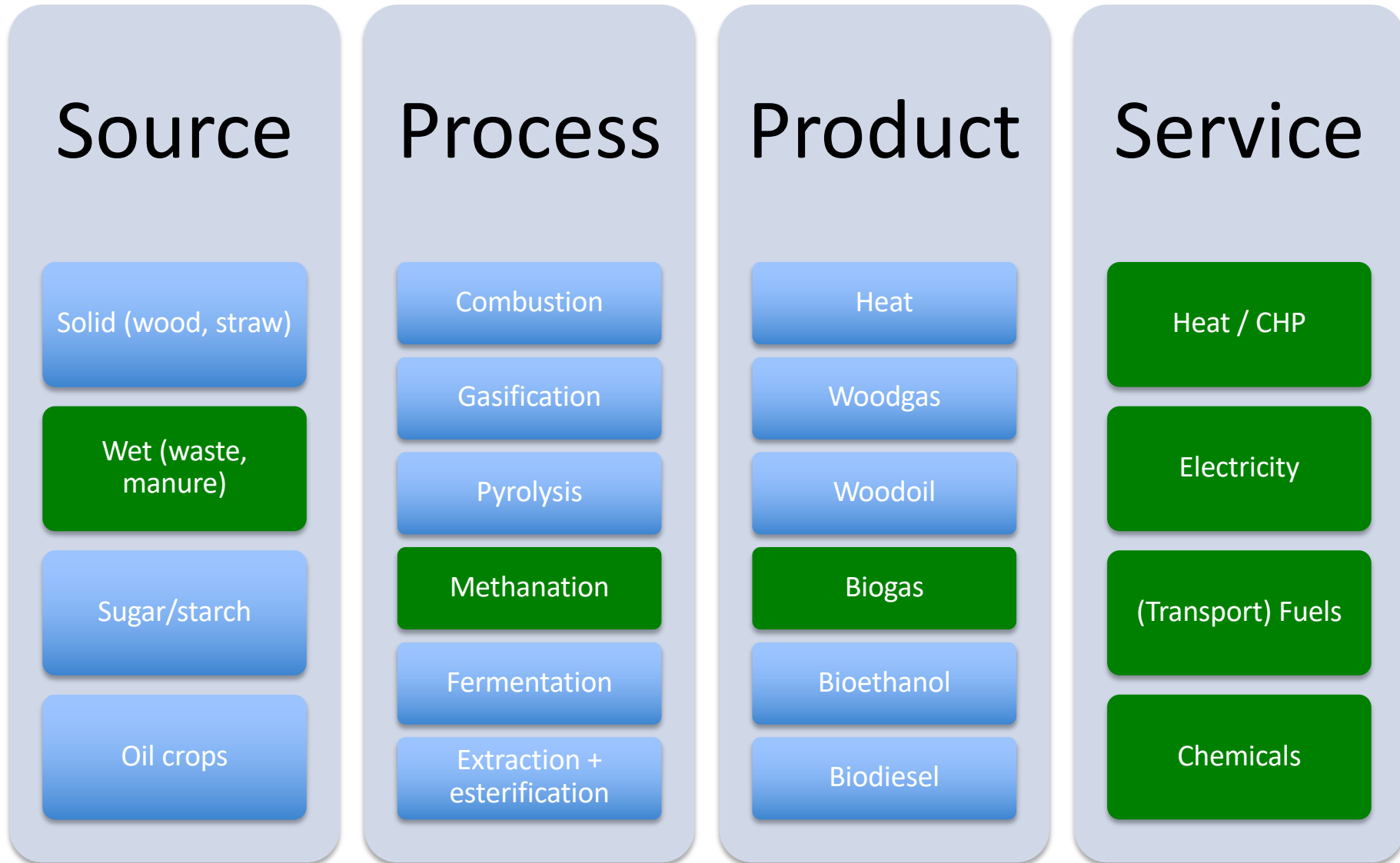
# Sources for biogas generation

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

- organic industrial effluents       <5% organic dry matter
- sewage       5%
- farming residues       10%
- solid wastes (digesters, landfill)       >20%
  - municipalities ($\approx$20 m$^3$/yr.person)       MSW
  - industry       ISW
  - >100 m$^3$ biogas produced per tonne 'solid' waste ($\approx$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 <u>organic</u> wastes

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

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

Examples of waste-to-energy processes

Anaerobic digestion of organic waste where the digestate is recycled as a fertliser

Waste incineration and co-incineration operations with a high level of energy recovery
Reprocessing of waste into materials that are to be used as solid, liquid or gaseous fuels

Waste incineration and co-incineration operations with limited energy recovery
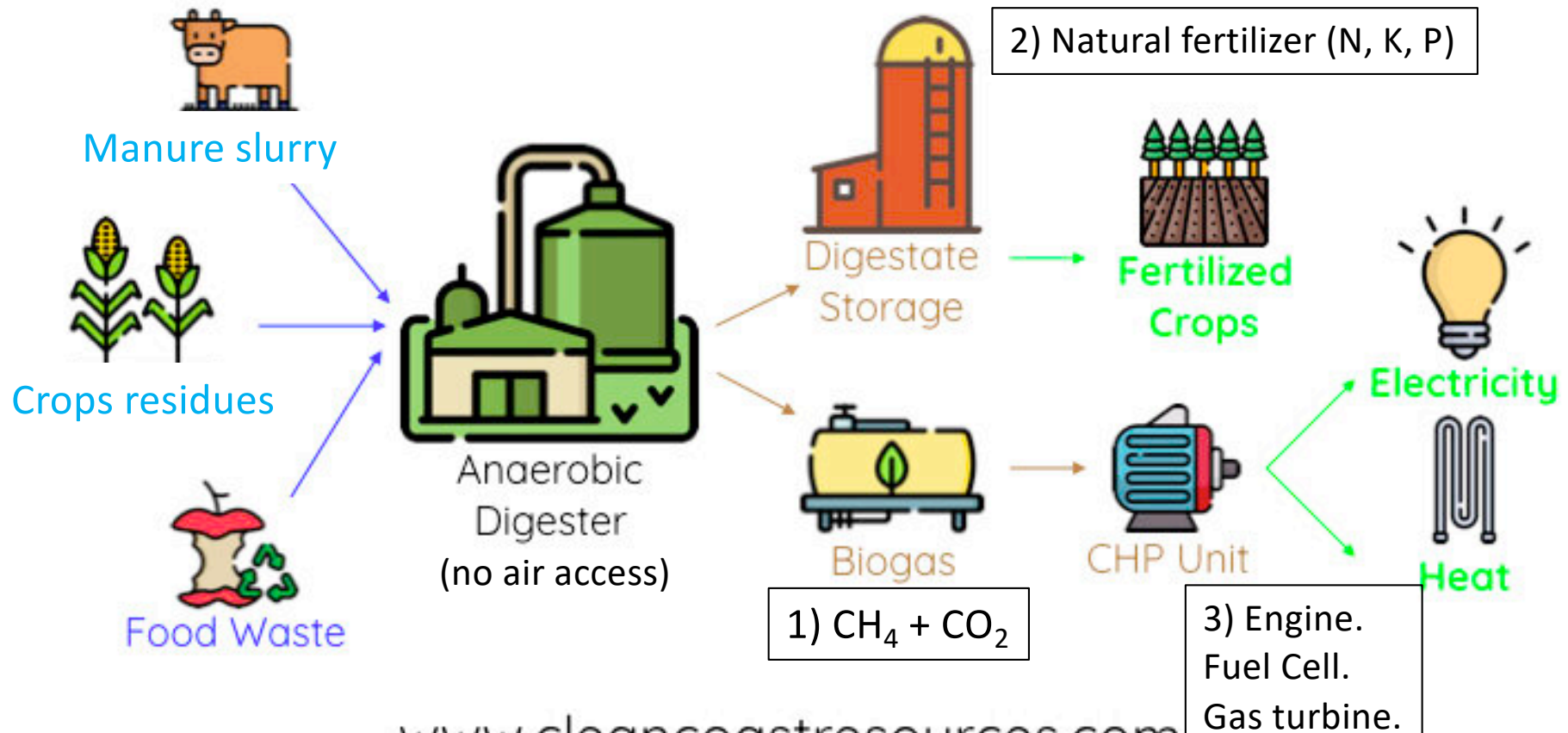Utilisation of captured landfill gas

Prevention

Preparing for re-use

Recycling

Other Recovery

Disposal

''**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

## The Anaerobic Digestion Process

Manure slurry

Crops residues

Food Waste

Anaerobic Digester (no air access)

Digestate Storage

2) Natural fertilizer (N, K, P)

Fertilized Crops

Biogas

1) $CH_4 + CO_2$

CHP Unit

3) Engine. Fuel Cell. Gas turbine.

Electricity

Heat

www.cleancoastresources.com

# 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

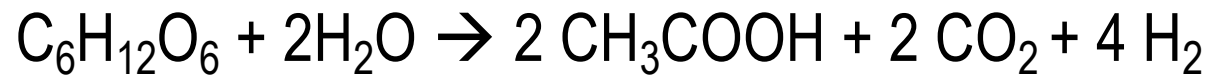    starch   → maltose   + glucose

2.  **Digestion**

    = formation of organic **acids**

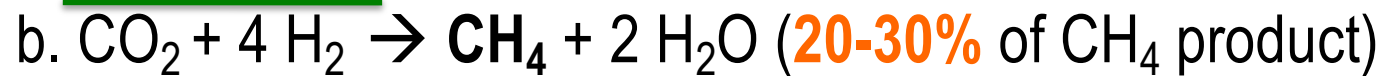    acetic / propionic / butyric acid (=$C_2$/$C_3$/$C_4$-OOH), lactic acid, ethanol, and little $H_2$ and $CO_2$

# 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. $2CH_3COOH \rightarrow 2\ \textbf{CH}_4 + 2\ CO_2$ (**70-80%** of $CH_4$ product)
   b. $CO_2 + 4\ H_2 \rightarrow \textbf{CH}_4 + 2\ H_2O$ (**20-30%** of $CH_4$ product)
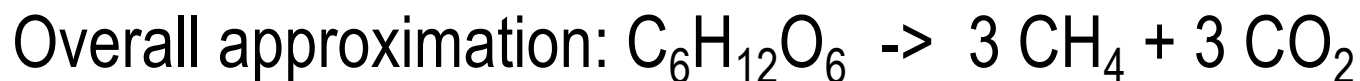
   Reactions a & b take place upon different bacterial actions.

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

Overall approximation: $C_6H_{12}O_6 \rightarrow 3\ CH_4 + 3\ CO_2$
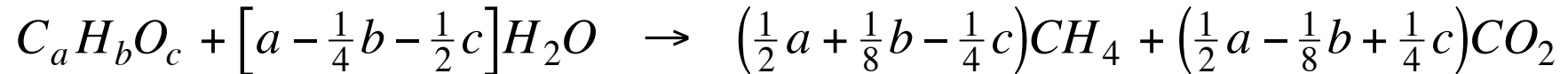
# **Anaerobic** digestion - AD (4)

- The main objective for <u>sewage and similar effluents</u> (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 <u>farm waste</u> (manure, crop residues) and <u>MSW/ISW</u>, 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

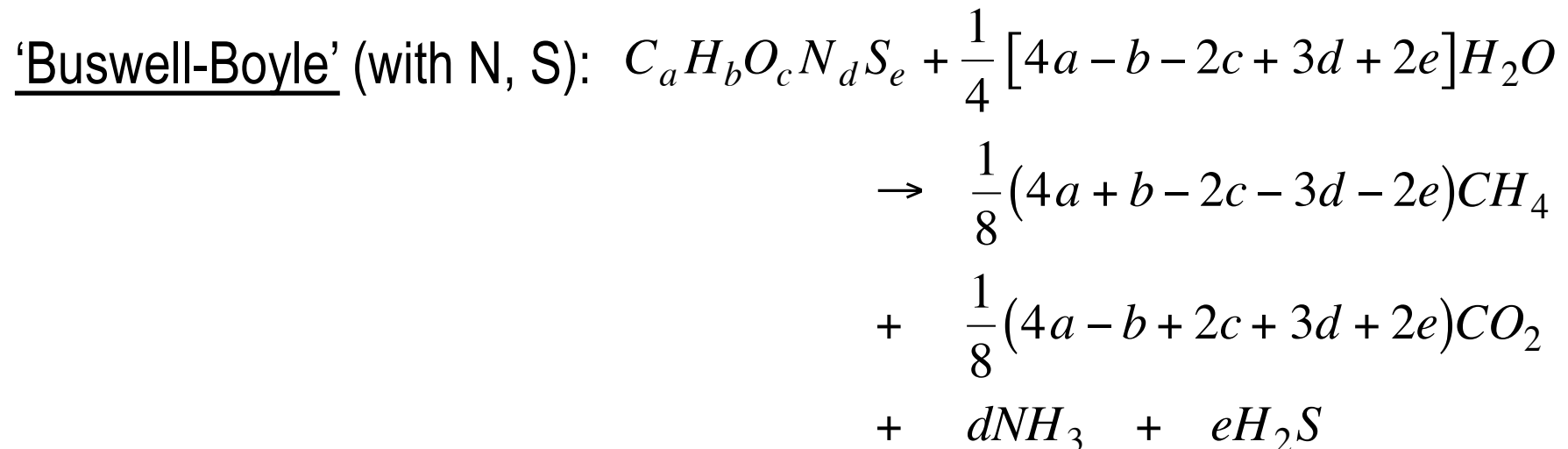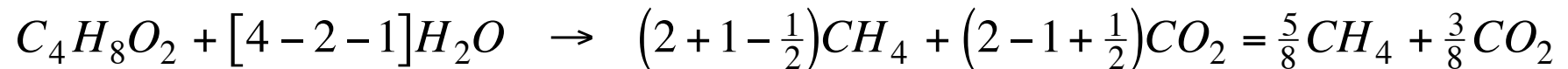1. Biowastes become an energy source (=> biogas), not a burden.

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:

$$C_a H_b O_c + \left[ a - \tfrac{1}{4}b - \tfrac{1}{2}c \right] H_2 O \quad \rightarrow \quad \left( \tfrac{1}{2}a + \tfrac{1}{8}b - \tfrac{1}{4}c \right) CH_4 + \left( \tfrac{1}{2}a - \tfrac{1}{8}b + \tfrac{1}{4}c \right) CO_2$$

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

$$C_4 H_8 O_2 + \left[ 4 - 2 - 1 \right] H_2 O \quad \rightarrow \quad \left( 2 + 1 - \tfrac{1}{2} \right) CH_4 + \left( 2 - 1 + \tfrac{1}{2} \right) CO_2 = \tfrac{5}{8} CH_4 + \tfrac{3}{8} CO_2$$

'Buswell-Boyle' (with N, S):  $C_a H_b O_c N_d S_e + \dfrac{1}{4} \left[ 4a - b - 2c + 3d + 2e \right] H_2 O$

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

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

$$+ \quad dNH_3 \quad + \quad eH_2 S$$

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 **<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):
  $$\theta = \frac{V_{reactor}\left[m^3\right]}{\dot{V}_{org}\left[m^3/d\right]}$$
  – 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:
  $$m^3{}_{biogas}\Big/m^3{}_{reactor}$$
  $$m^3{}_{biogas}\Big/kg_{org.matter}$$

# Example:

Farm with 60 animals. Manure waste: 3 m³/day. (≈3000 kg)

Organic dry matter = 50 kg/m³ (=150 kg/day=5% organics)

Mean residence time θ = 20 days. Biogas production = 65 m³/day. (≈433 L / kg d.m.)

- Reactor volume :

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

- Daily specific load:

$$M_{day} = \frac{M_{org}}{\theta} = \frac{50kg/m^3}{20days} = 2.5kg/m^3.day$$
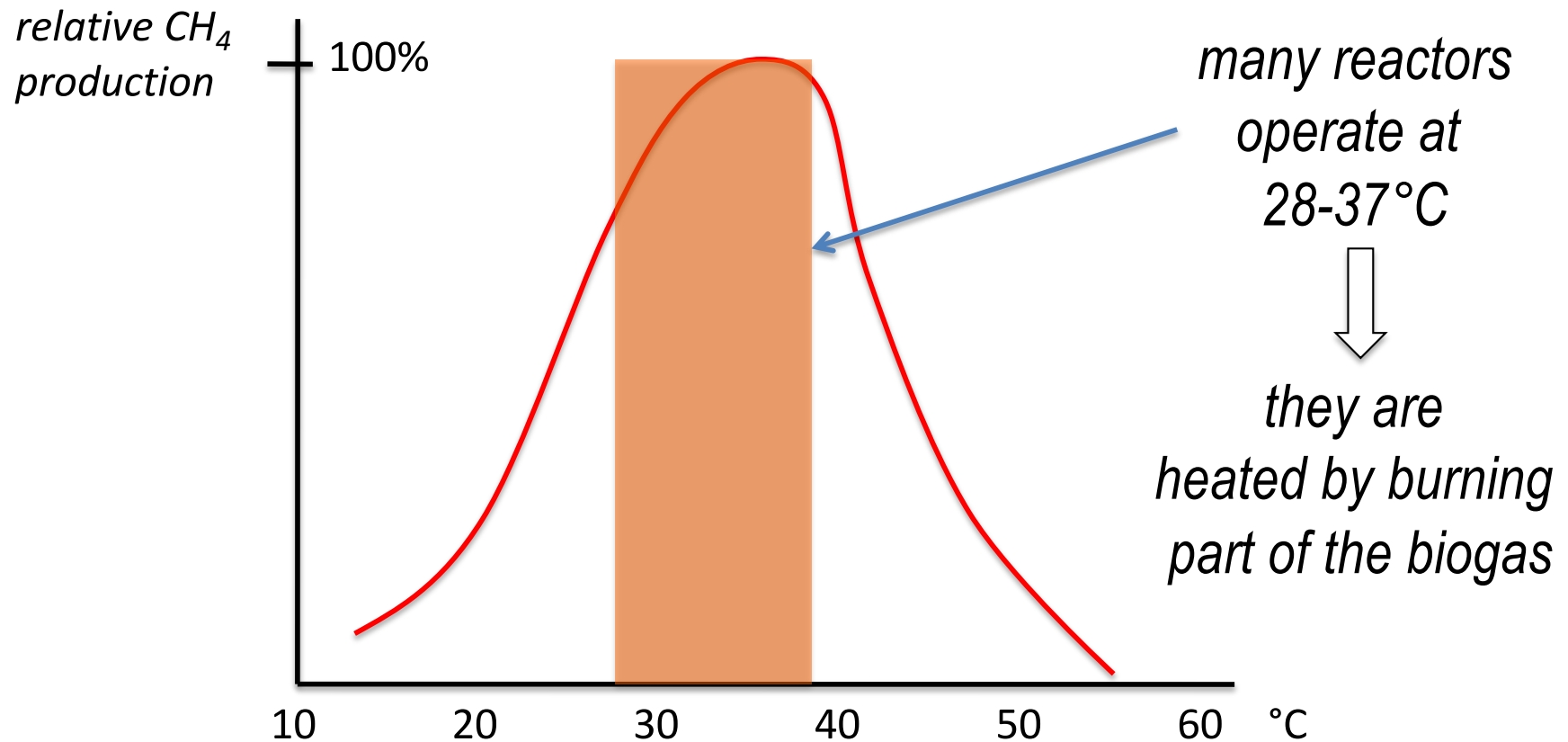
- Specific biogas production:
  - per reactor volume:

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

  - per organic matter:

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

# Digestor reactor temperature

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

*relative CH$_4$ production*

100%

*many reactors operate at 28-37°C*

⇩

*they are heated by burning part of the biogas*

10    20    30    40    50    60    °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 m³/day @ 20 MJ/m³ = 30 MJ/day ≈ 8 kWh/day

= equivalent to 2 m² 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)
- 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 | 2007 Use (PJ) | gas engines kW$_e$/site | ultimate Potential |
|--------|--------|---------------|-----------|
| 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
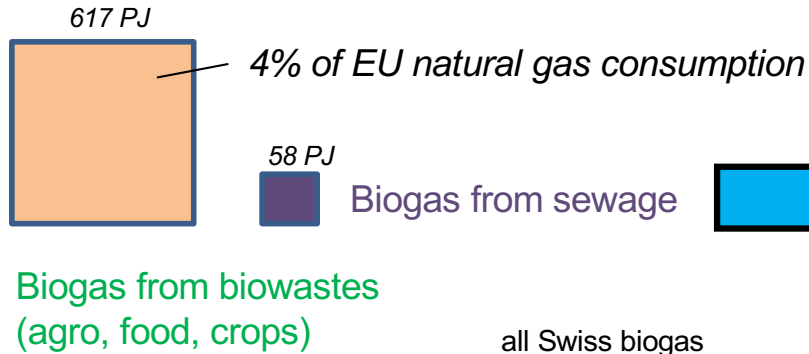
# Biogas application examples (CH)

| 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

**x5**

*3000 PJ*

European Biogas potential from <u>unused</u> manure and crop residues

*19% of current European natural gas consumption*

Biogas from biowastes (agro, food, crops)

■ = all Swiss biogas on the same scale as Europe

*57 PJ*

Biogas potential from <u>unused</u> 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 <u>unused</u> manure and crop residues

*18% of current Swiss natural gas consumption*

*1 PJ*

Biogas potential from unused food wastes and other municipal wastes

21
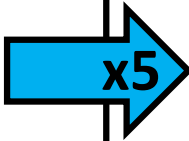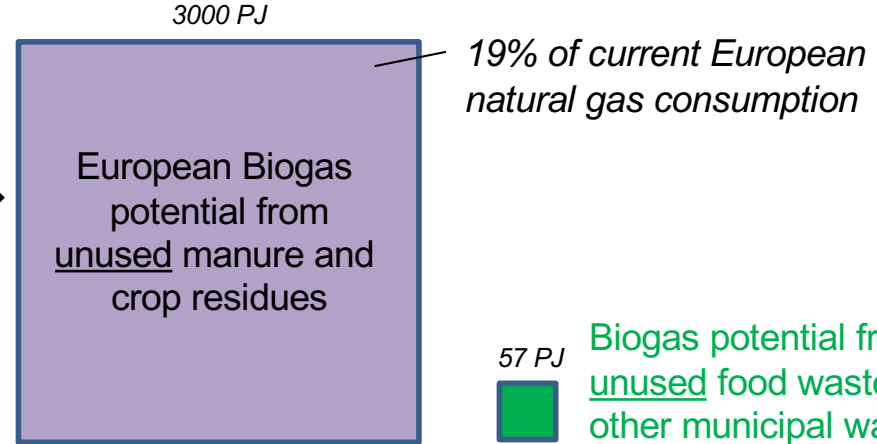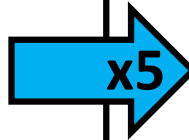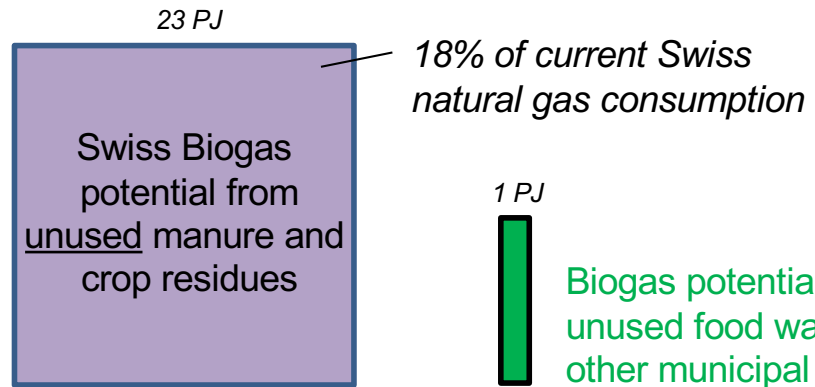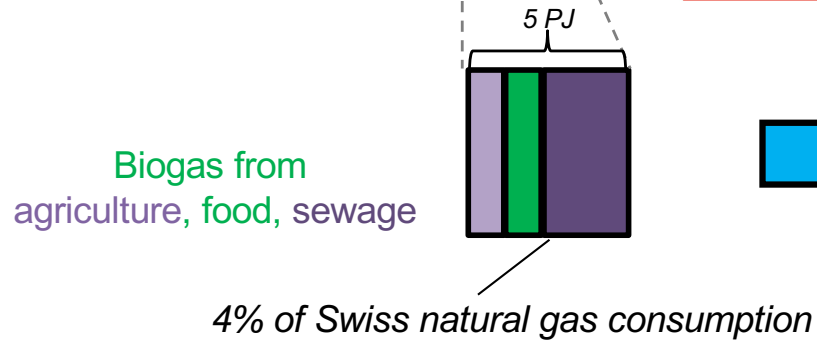
# Current uses of biogas

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.



CO₂  CO₂  CO₂  CO₂

**8% of use**

Pressurized Biogas
(Methane, CO₂ mix)

Permeable Membrane Filter Strand

Methane  ⇨ gas grid
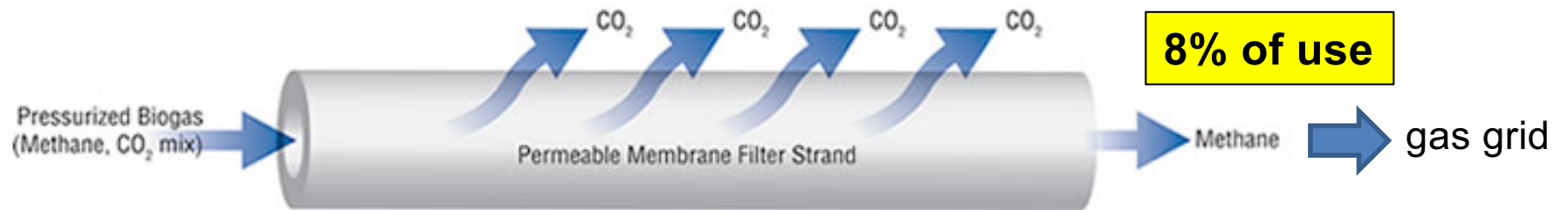
2) Burn the biogas into a large engine to generate electricity and heat.



500 kW$_{el}$
biogas engine

**92% of use**

*Part is used in burners only*

# Status and potential in Europe

**EU Biogas (2016)**

**675 PJ**

*4% of natural gas consumption*

- ☐ WWTP
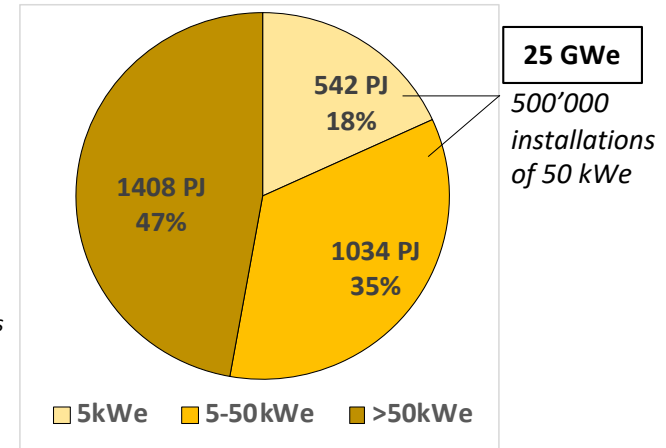- ■ LFG
- ■ Agro/OFMSW

Pie chart:
- 58,5 / 9% (WWTP)
- 116,5 / 17% (LFG)
- 501 / 74% (Agro/OFMSW)

**use:**

- ■ Gas vehicles
- ■ Injection (500)
- ☐ CHP Electricity
- ☐ Electricity only
- ■ CHP heat
- ■ Heat only
- ☐ Own use or losses

Pie chart:
- 1%
- ~4MW / site — 8%
- 21% ~550kWe / site — **8.7 GWe**
- 12%
- 3%
- 1%
- 54%

*>17'500 installations*

Use : mainly large installations >200m³/h (>1 MW$_{CH4}$)
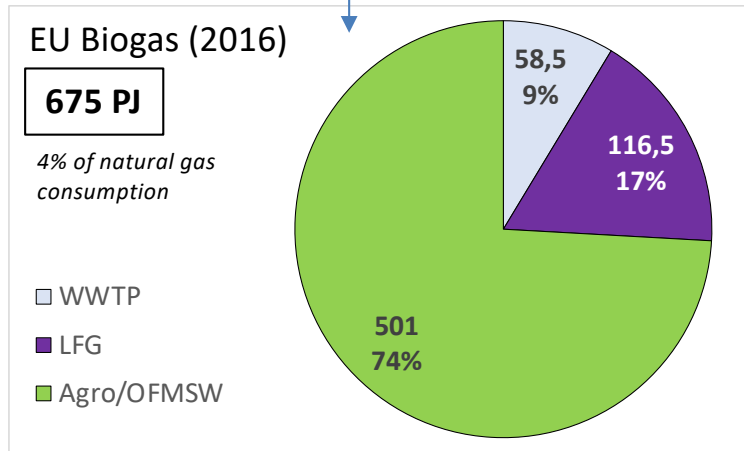
**Unused potential in agriculture:**

**3000 PJ**

*18% of natural gas consumption*

Pie chart:
- 542 PJ / 18% — **25 GWe** *500'000 installations of 50 kWe*
- 1034 PJ / 35%
- 1408 PJ / 47%

- ☐ 5kWe
- ☐ 5-50kWe
- ■ >50kWe
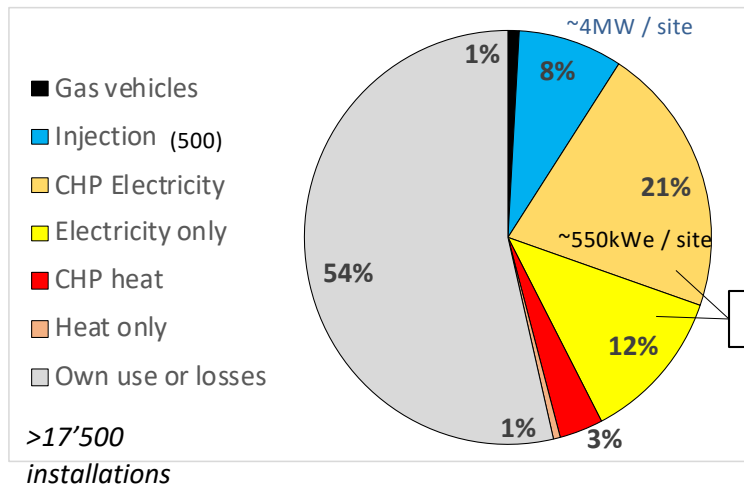
**Unused potential in OFMSW:**
*(only for CH/D/F/IT)*

**23 PJ**

Pie chart:
- 1,2 PJ / 5% — **19 MWe** *400 installations of 50 kWe*
- 4,9 PJ / 21%
- 16,9 PJ / 74%

- ☐ <50kWe
- ☐ 50-500kWe
- ■ >500kWe

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

# Status and potential in Switzerland



**CH Biogas (2018)**

**5 PJ**

*4% of NG consumption*

- ☐ WWTP CHP (272)
- ■ WWTP Heat only
- ■ WWTP injection
- ■ Agro CHP (111)
- ■ Agro injection
- ■ OFMSW CHP (28)
- ■ OFMSW injection

28% — 100kWe
8%
16% — 570kWe
1%
7%
13%
27% — 200kWe

use: ⬇

- ■ Injection (35)
- ■ Heat only (WWTP) (205)
- ☐ Electricity (396)
- ☐ Own use or losses

23% — 1MW
7% — 50kW
24% — 180kWe
46%

*636 installations*

**70 MWe**
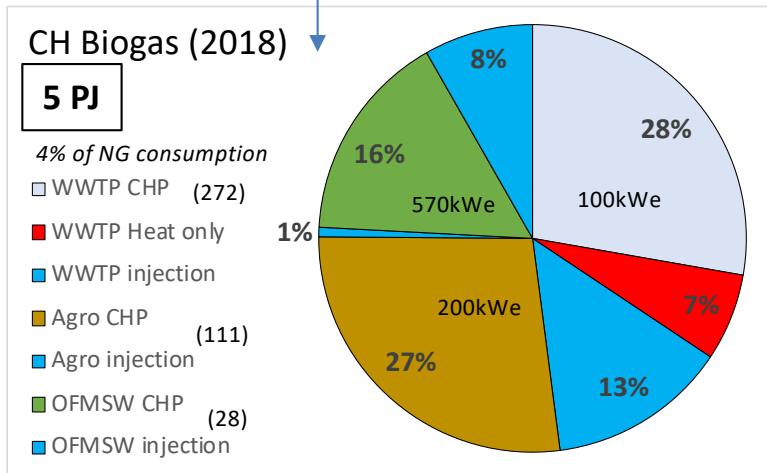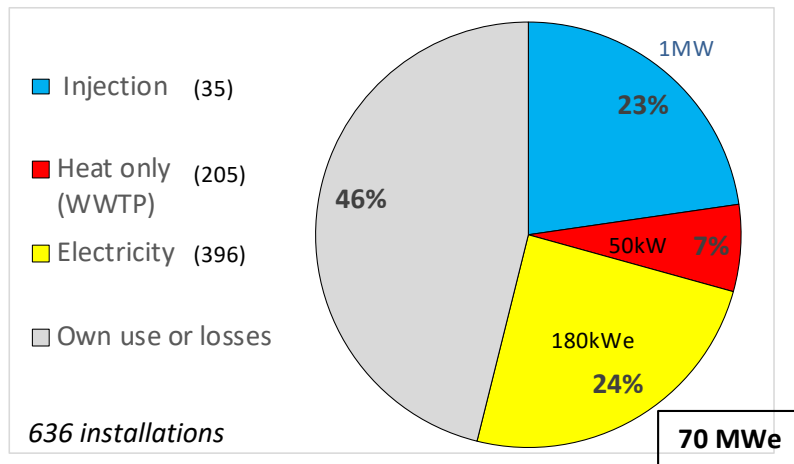
Unused potential in agriculture:

**23 PJ**

*18% of natural gas consumption*

3,37 PJ 15%
0,93 PJ 4%
18,66 PJ 81%

**350 MWe**

*7000 installations of 50 kWe*

- ☐ 5kWe
- ■ 5-50kWe
- ■ >50kWe

Unused potential in OFMSW:

**1.1 PJ**

0,21 PJ 19%
0,4 PJ 37%
0,48 PJ 44%

**6 MWe**

*130 installations of 50 kWe*

- ☐ <50kWe
- ■ 50-500kWe
- ■ >500kWe
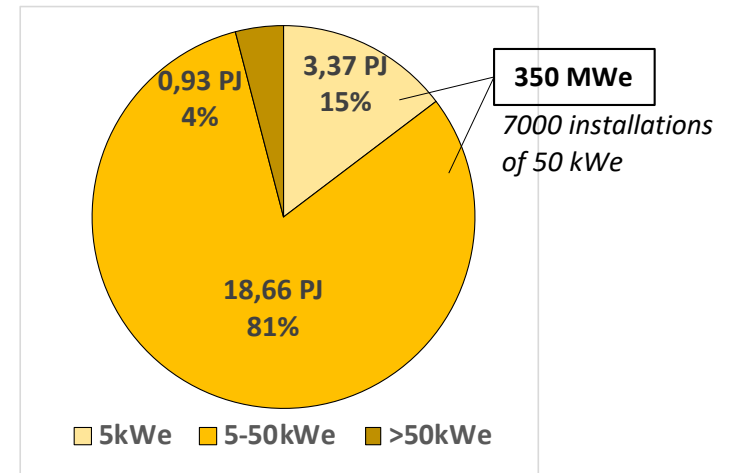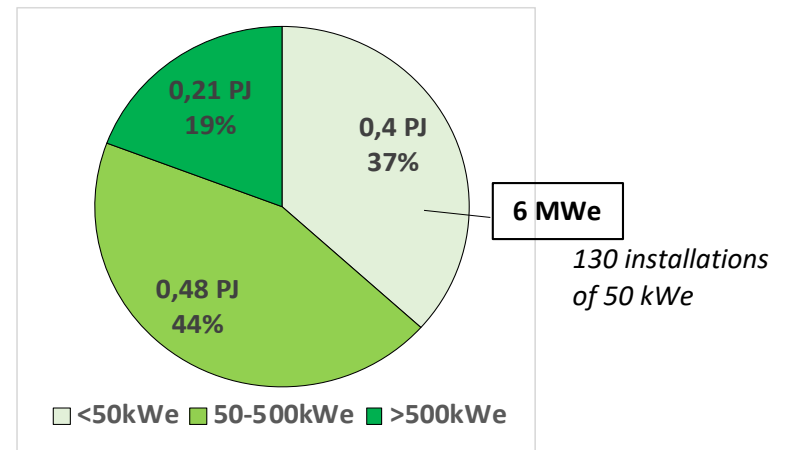
# Biogas figures for Switzerland (2018)

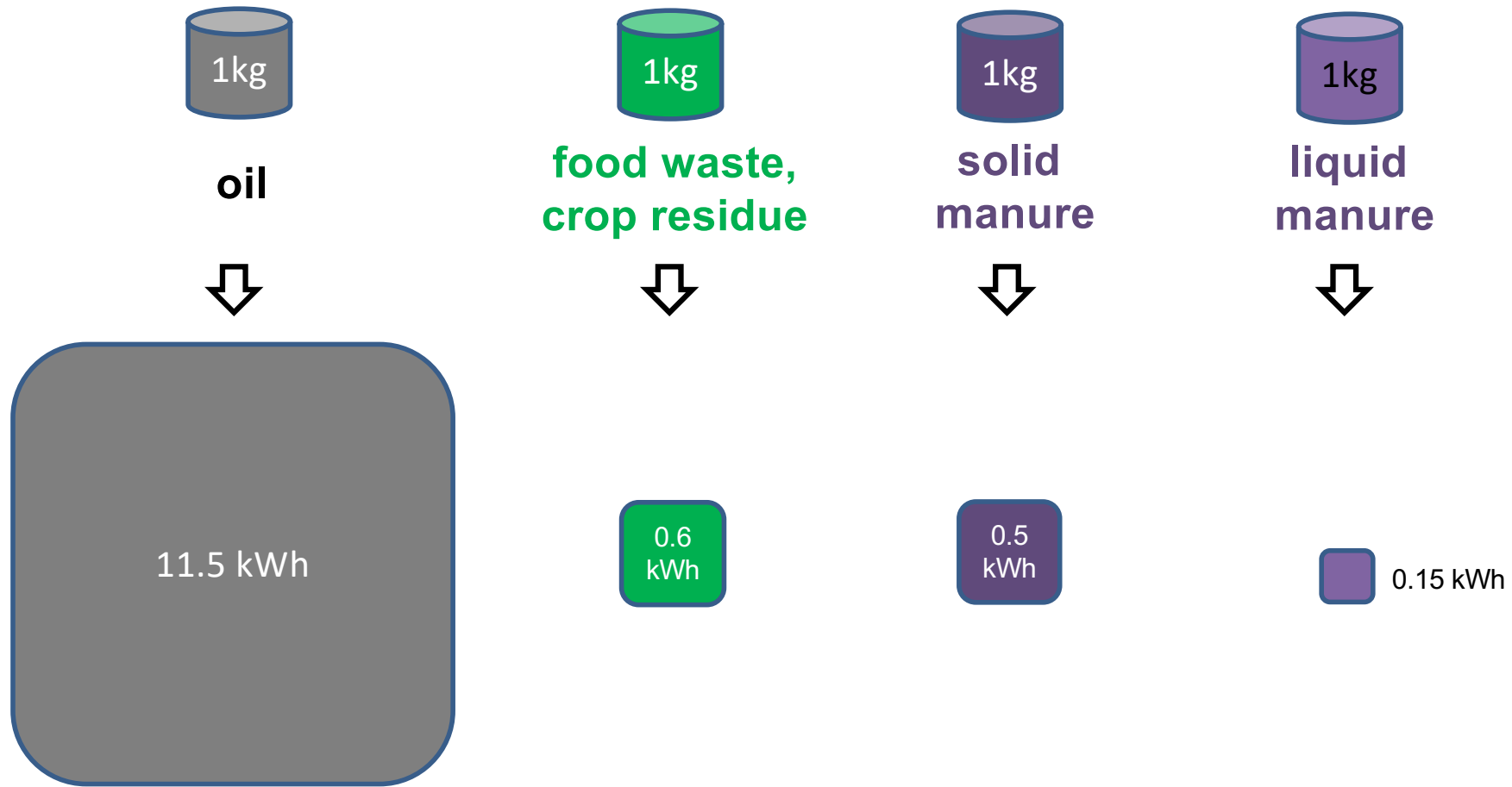| | Application: | **Energy** resource | | **Biological** cleaning | | **TOTAL** or *average* |
|---|---|---|---|---|---|---|
| | | **Agriculture** | OFMISW | **WWTP** | Industry effluents | |
| (1) | Biogas total (PJ) | 1.44 | 1.243 | 2.28 | 0.2 | 5.16 PJ |
| (2a) | - gas grid **injection** (PJ) | -0.037 | -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) / (8760h x 3600s) | 411 $kW_{CH4}$ | 1408 $kW_{CH4}$ | 151 (CHP) 53 (heat) | 315 $kW_{CH4}$ | *avg 269$kW_{CH4}$* |
| (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 <u>large digesters</u> to generate biogas <u>flows of 100-1000 m$^3$/h</u> (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.
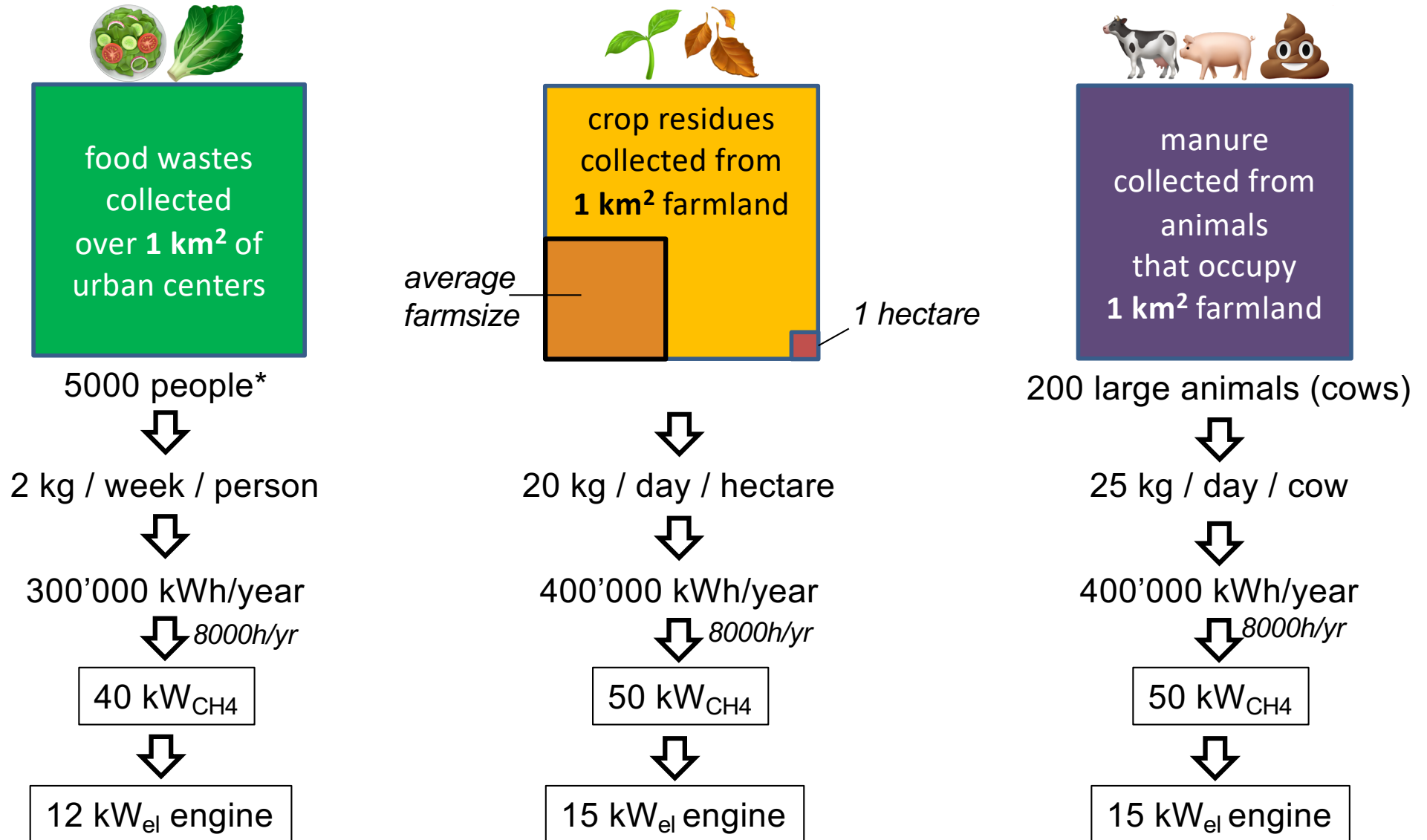
*presently, average biogas engine efficiency is 38% in Europe and 34% in Switzerland*

# The issue of scale (1)

Biowastes are a <u>dilute</u> energy source

| | | | |
|---|---|---|---|
| **1kg** | **1kg** | **1kg** | **1kg** |
| **oil** | **food waste, crop residue** | **solid manure** | **liquid manure** |
| ⬇ | ⬇ | ⬇ | ⬇ |
| 11.5 kWh | 0.6 kWh | 0.5 kWh | 0.15 kWh |

# The issue of scale (2)



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

crop residues collected from **1 km²** farmland

*average farmsize*

*1 hectare*

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

| | | |
|---|---|---|
| 5000 people* | 200 large animals (cows) | |
| ⬇ | ⬇ | ⬇ |
| 2 kg / week / person | 20 kg / day / hectare | 25 kg / day / cow |
| ⬇ | ⬇ | ⬇ |
| 300'000 kWh/year | 400'000 kWh/year | 400'000 kWh/year |
| ⬇ *8000h/yr* | ⬇ *8000h/yr* | ⬇ *8000h/yr* |
| 40 kW$_{CH4}$ | 50 kW$_{CH4}$ | 50 kW$_{CH4}$ |
| ⬇ | ⬇ | ⬇ |
| 12 kW$_{el}$ engine | 15 kW$_{el}$ engine | 15 kW$_{el}$ engine |

*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 <u>locally</u>, 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 <span style="color:blue">more efficient and cleaner</span> than engines, on small-scale

$\Rightarrow$ **Solid Oxide Fuel Cells** : **>50% electrical efficiency**
**no pollution (N~~O~~, ~~C~~O, ~~S~~O$_2$)**

*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 <span style="color:red">GHG emitter</span>! (as CH$_4$)

- often heavily contaminated (with F, Cl, NH$_3$, H$_2$S, Si,…)
- often of low calorific value (diluted with N$_2$/O$_2$)
  - engines stop running <45% CH$_4$
  - <span style="color:red">fuel-assisted flaring or venting !</span>