Biogas + SOFC: some considerations

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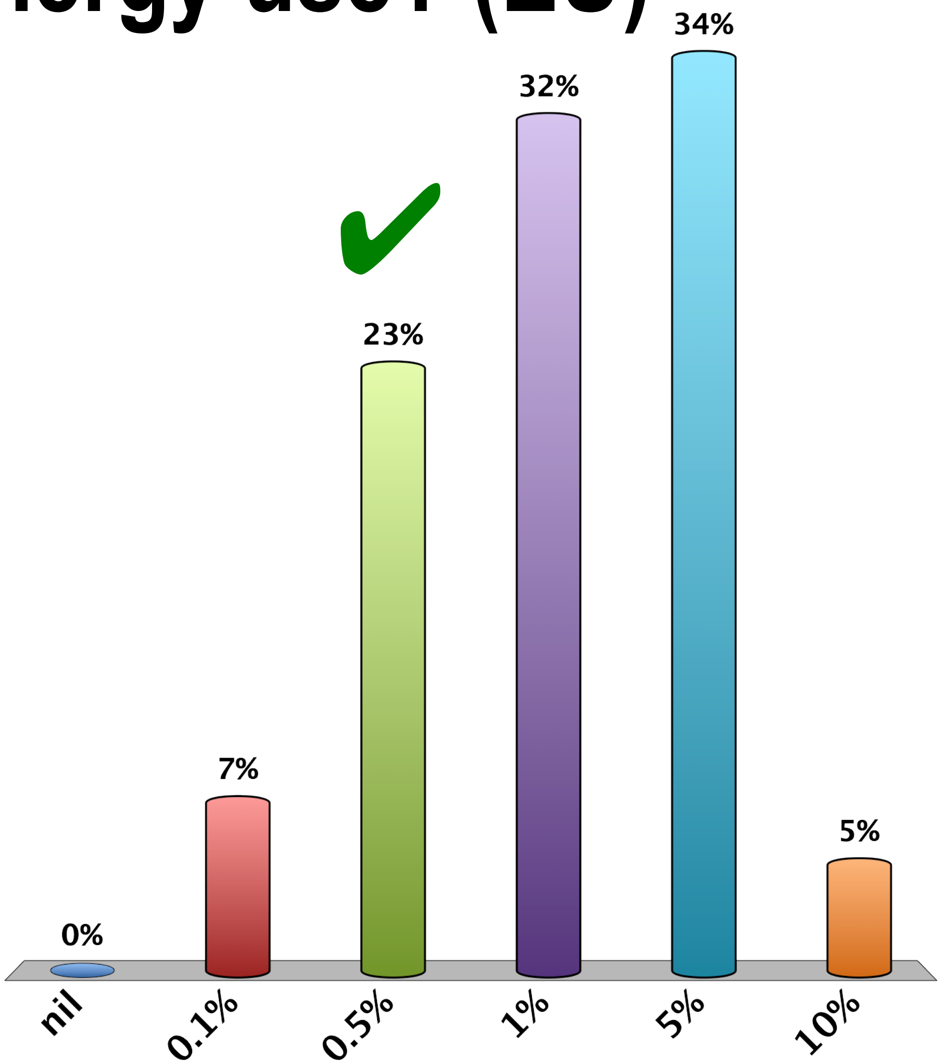
Torino
DEMOSOFC kick-off
2015-Sep-24

What is the *present* share of biogas energy in the total energy use? (EU)

A. nil
B. 0.1%
C. 0.5%
D. 1%
E. 5%
F. 10%



What is the *potential* share of biogas energy in the total energy use? (EU)

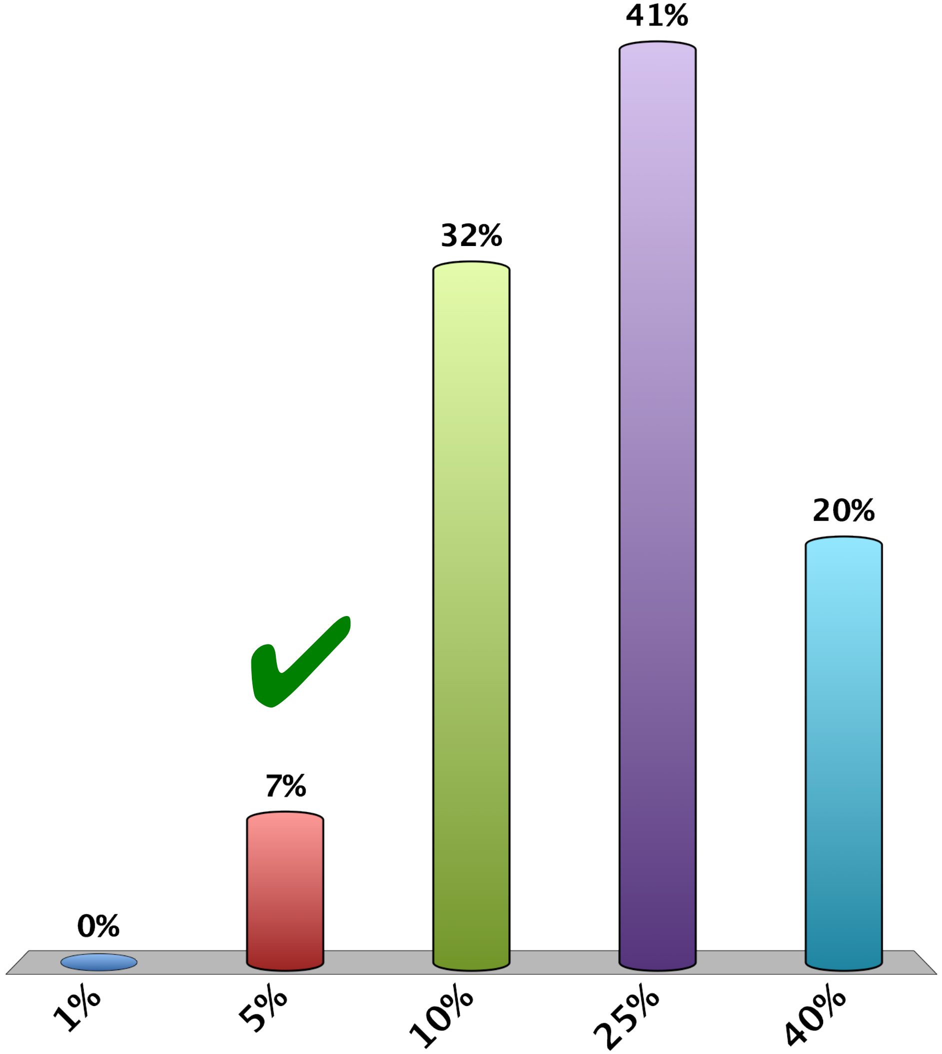
A. 1%

B. 5%

C. 10%

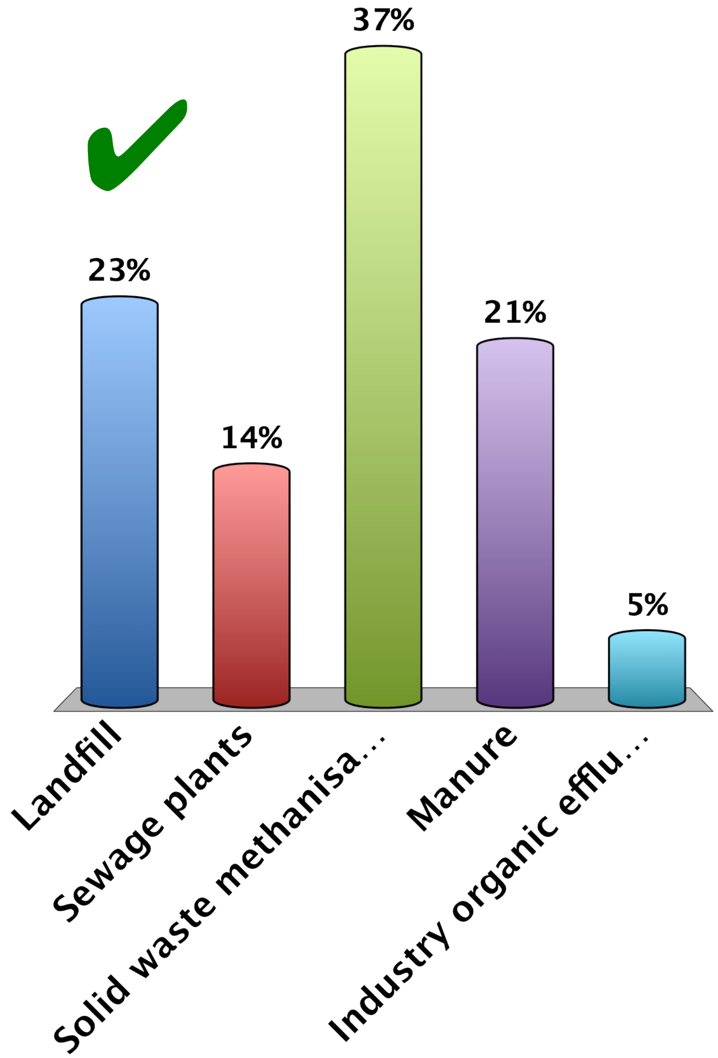
D. 25%

E. 40%



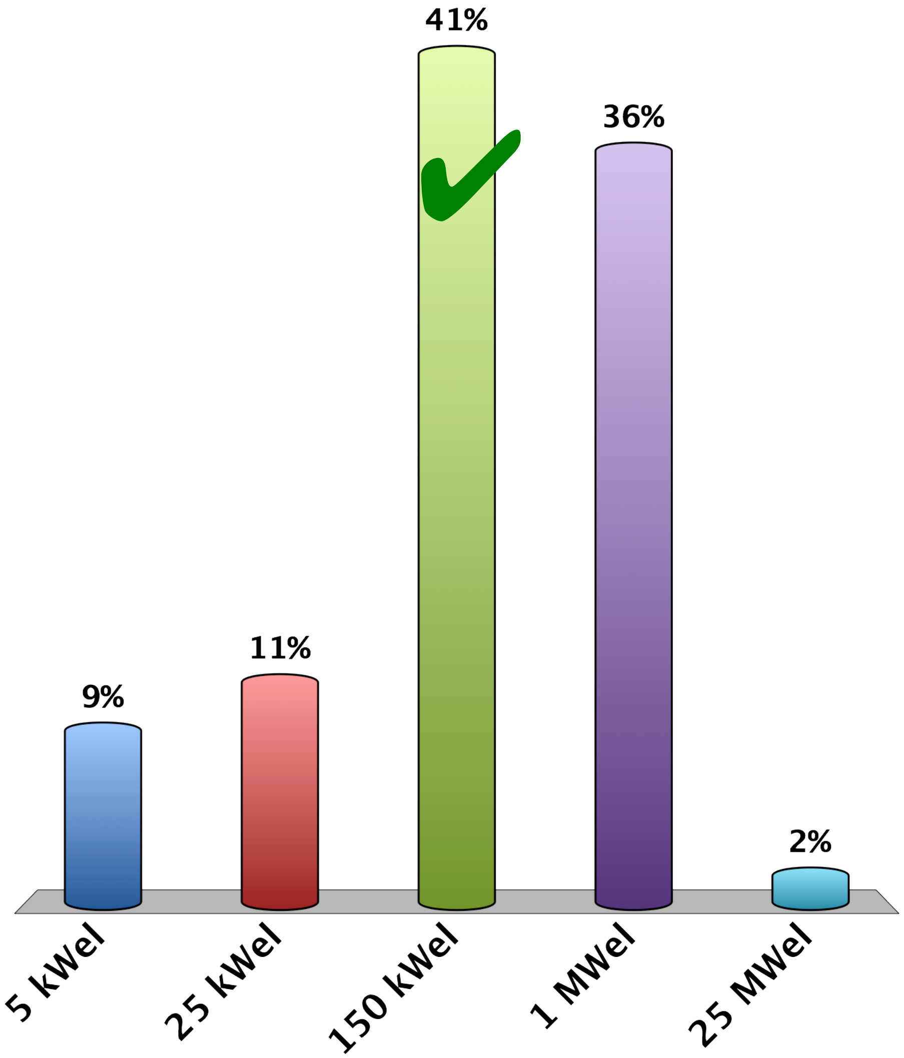
Which source is the biggest biogas producer? (worldwide, and in Europe)

A. Landfill
B. Sewage plants
C. Solid waste methanisation
D. Manure
E. Industry organic effluents



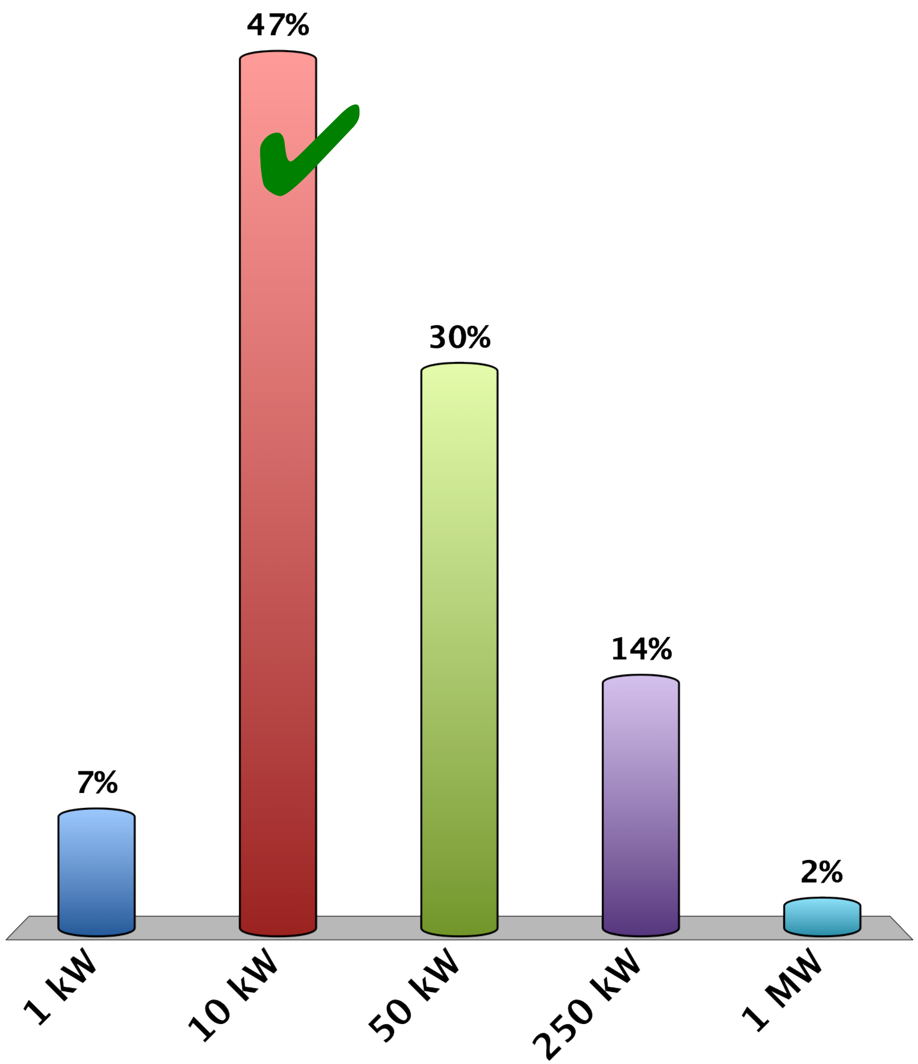
What electrical power size is typical for an existing biogas production site?

A. 5 kW_{el}
B. 25 kW_{el}
C. 150 kW_{el}
D. 1 MW_{el}
E. 25 MW_{el}



Considering an average farm, how much energy from biogas could you recover?

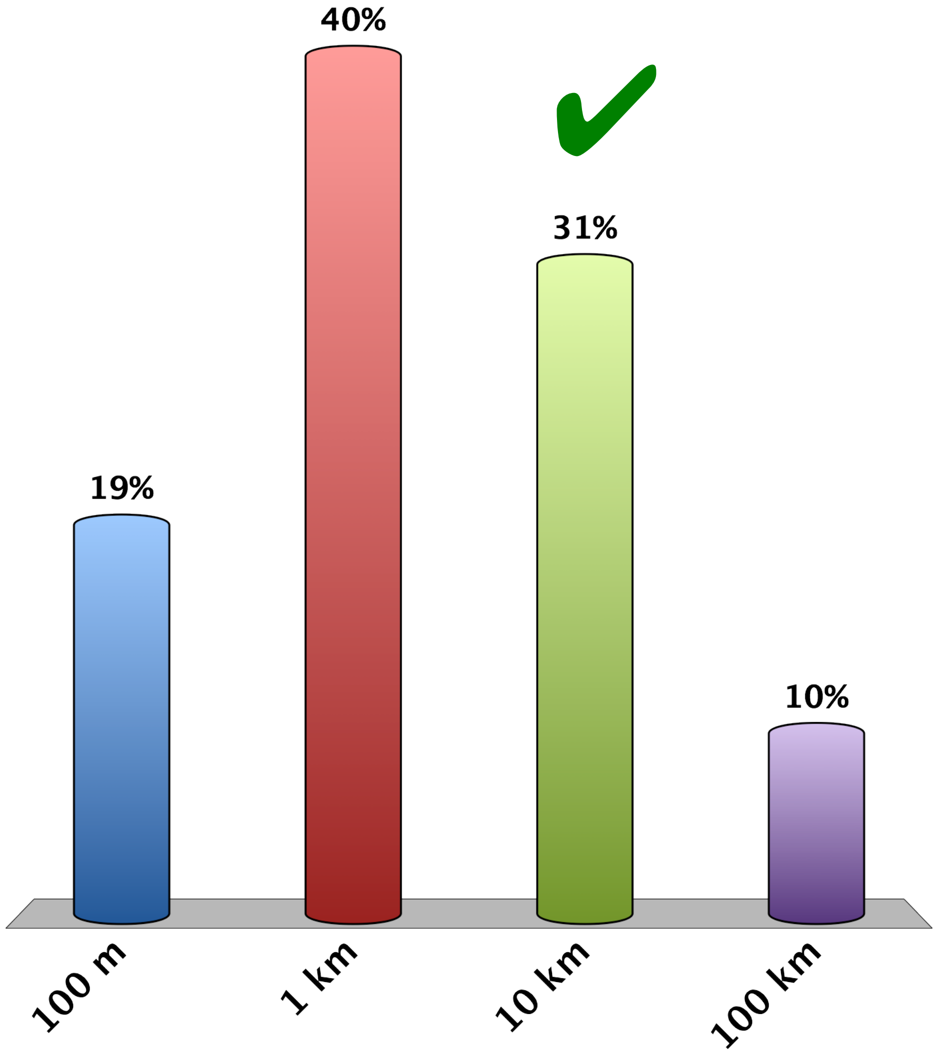
A. 1 kW
B. 10 kW
C. 50 kW
D. 250 kW
E. 1 MW



Jari's special: how far can you drive a car on one day's worth of bullshit…? (*sorry*)

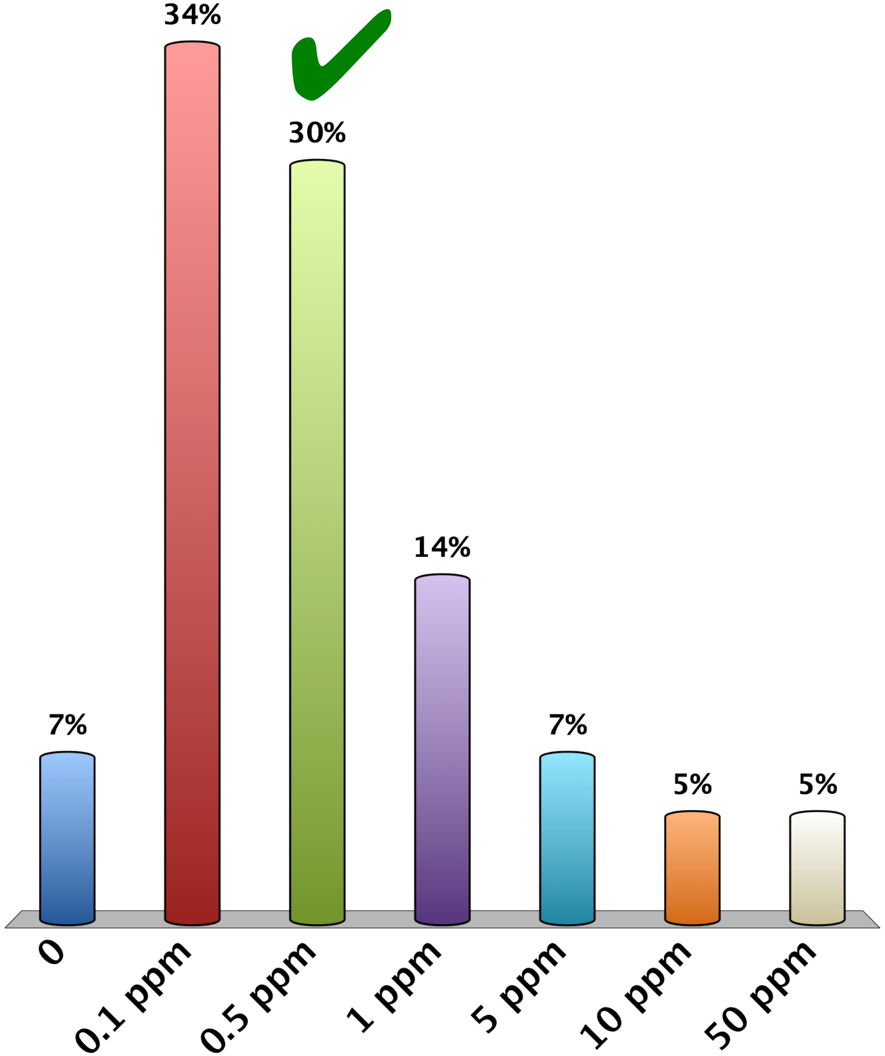
(…converted into biogas)

A. 100 m
B. 1 km
C. 10 km
D. 100 km



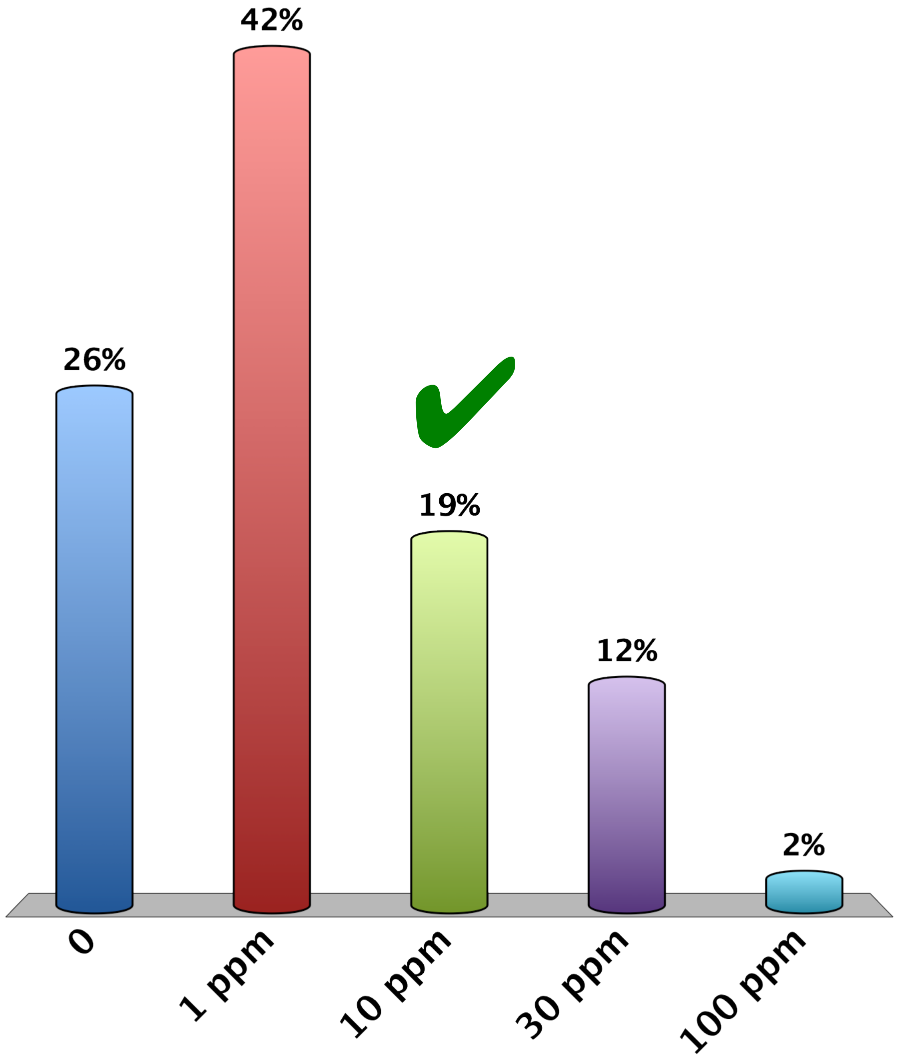
SOFCOM project results: what is the required H_2S contaminant tolerance for a Solid Oxide Fuel Cell system?

A. 0
B. 0.1 ppm
C. 0.5 ppm
D. 1 ppm
E. 5 ppm
F. 10 ppm
G. 50 ppm



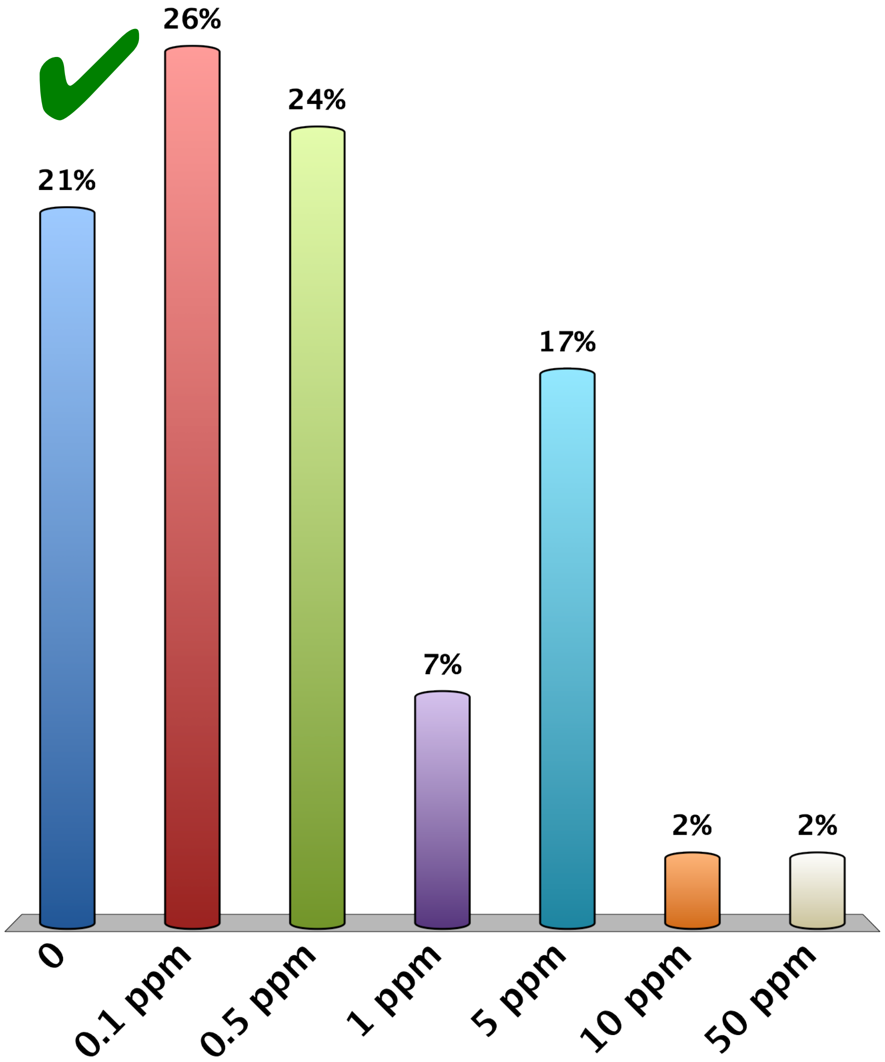
And the HCl tolerance?

A. 0
B. 1 ppm
C. 10 ppm
D. 30 ppm
E. 100 ppm



And siloxane contaminant tolerance?

A. 0
B. 0.1 ppm
C. 0.5 ppm
D. 1 ppm
E. 5 ppm
F. 10 ppm
G. 50 ppm



Anaerobic digestion

- transformation of organic (waste) streams that are too wet to burn
- the 1st objective is **depollution** from the organic charge => exploitation schemes are in place because it is 'mandatory' (for sewage, (food) industry effluents)

  => biogas = **by-product**
- farm waste (manure, crop residues) and MSW/ISW, by contrast, are largely untapped (underexploited)

  => biogas = **energy vector** (especially for electricity)
- inherent process drawback: digestion = slow

Digestion process (4 steps)

overall ≈ $C_6H_{12}O_6$ -> $3\ CH_4 + 3\ CO_2$

1. **Hydrolysis** : ***slowest,*** rate-determining
   cellulose, starch → cellobiose, maltose, glucose
2. **Digestion :** formation of organic **acids**
   acetic, propionic, butyric, lactic acid, ethanol, v. little H_2 and CO_2
3. **Acidogenesis :** all acids decomposed to => **acetic acid, H_2, CO_2**
   ≈ $C_6H_{12}O_6 + 2\ H_2O \rightarrow \underline{2\ CH_3COOH} + \underline{2\ CO_2 + 4\ H_2}$
4. **Methanogenesis :** 2 parallel pathways
   $\underline{2\ CH_3COOH} \rightarrow 2\ \mathbf{CH_4} + 2\ CO_2$ (**70-80%** of CH_4 product)
   $\underline{CO_2 + 4\ H_2} \rightarrow \mathbf{CH_4} + 2\ H_2O$ (**20-30%** of CH_4 product)
   These 2 parallel reactions explain why biogas compositions typically are (60±5)% CH_4 and (40±5%) CO_2

Biogas generation: energy balance

Buswell-Boyle formula:

$$C_aH_bO_cN_dS_e + \frac{1}{4}\left[4a - b - 2c + 3d + 2e\right]H_2O$$
$$\rightarrow \frac{1}{8}\left(4a + b - 2c - 3d - 2e\right)CH_4$$
$$+ \frac{1}{8}\left(4a - b + 2c + 3d + 2e\right)CO_2$$
$$+ \; dNH_3 \; + \; eH_2S$$

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

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

1 kg dry = 18 MJ → **86%** → **0.82 m^3 biogas = 15.5 MJ**

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

Swiss biogas situation as example

	Today	Potential
Use (total)	3 PJ	30 PJ
Sites	435	>50'000
Installed power	82 MW_{el}	1 GW_{el}
Efficiency	35% (engines)	50% (SOFC)
Elec. production	0.3 TWh_{el}	4 TWh_{el} (-1.5 Mt CO_2)
Share of total (elec.)	0.5%	6%

x 10

EU-27: biogas use and potential

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

30% efficiency → **20 TWh_{el} (0.6% of total)**

=25% of NG import in EU (Import: 310 billion m^3 / yr)

Special case of landfill gas (LF)

- MW_{el} sized sites (gas engines, gas turbines)
- by far the **largest** fraction of world biogas (60%)
  (20 Mtoe, 23 billion m^3 CH_4)
- nearly 50% share even in EU-27
- **=> not yet accessible by SOFC; maybe by MCFC**
- 3rd most important anthropogenic GHG emitter (as CH_4)
- contaminated (F, Cl, NH_3, H_2S, Si,…)
- low calorific value
  – engines stop running <45-50% CH_4
  – fuel-assisted flaring or venting !

‘Economy of scale’ is tiptoed with (agro)biogas installations

The existing exploitation paradigm:

to be able to install efficient engines (**>100 kW_{el}, >35%**), digesters are built big, hence waste must be collected in sufficient quantity => this excludes ‘small’ sites and ‘enforces’ larger waste concentration sites

Taking this chain by its tail:

Waste is mostly available locally in ‘small’ quantities (**10 kW**) => a technology is needed to convert this efficiently on this scale

=> SOFCs (**50%**)

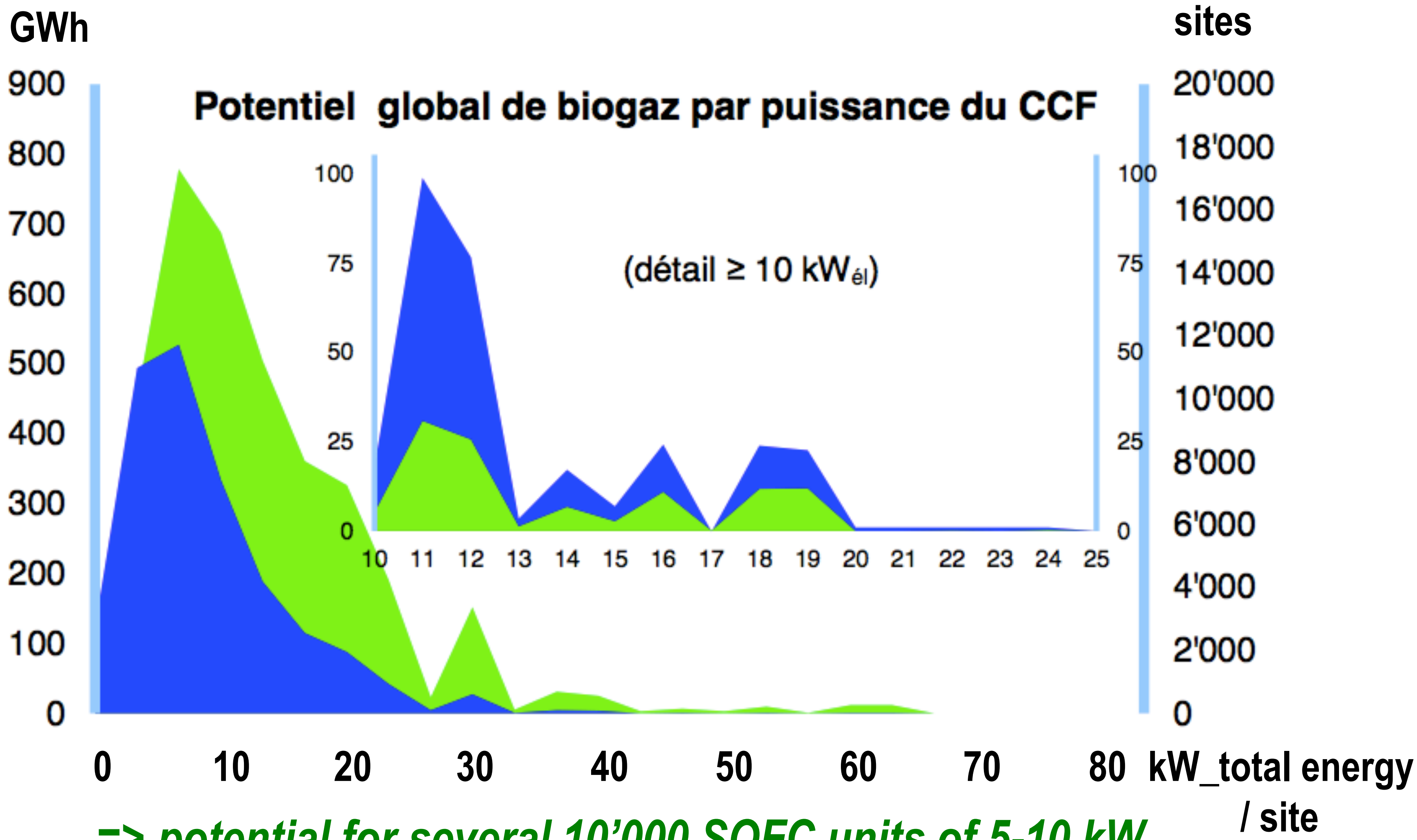
Energy from (animal) farms

1 cow (= 1 large cattle equivalent LCE)
= 2.5 kg dry organics / day
= 1.5 m^3 biogas /day
= 0.9 m^3 CH_4 / day
= 30 MJ / day
= 8 kWh / day (300 W per LCE)
= 2 m^2 of solar thermal collectors
= 10 km / day by (gas) car

There are ca. half as many LCE as human beings on the planet…
$\Rightarrow$ 3 billion m^3 CH_4 / day
$\Rightarrow$ **1100 billion m^3 CH_4 / year**
Compare with worldwide **natural gas** consumption of **3300 billion m^3 / yr**

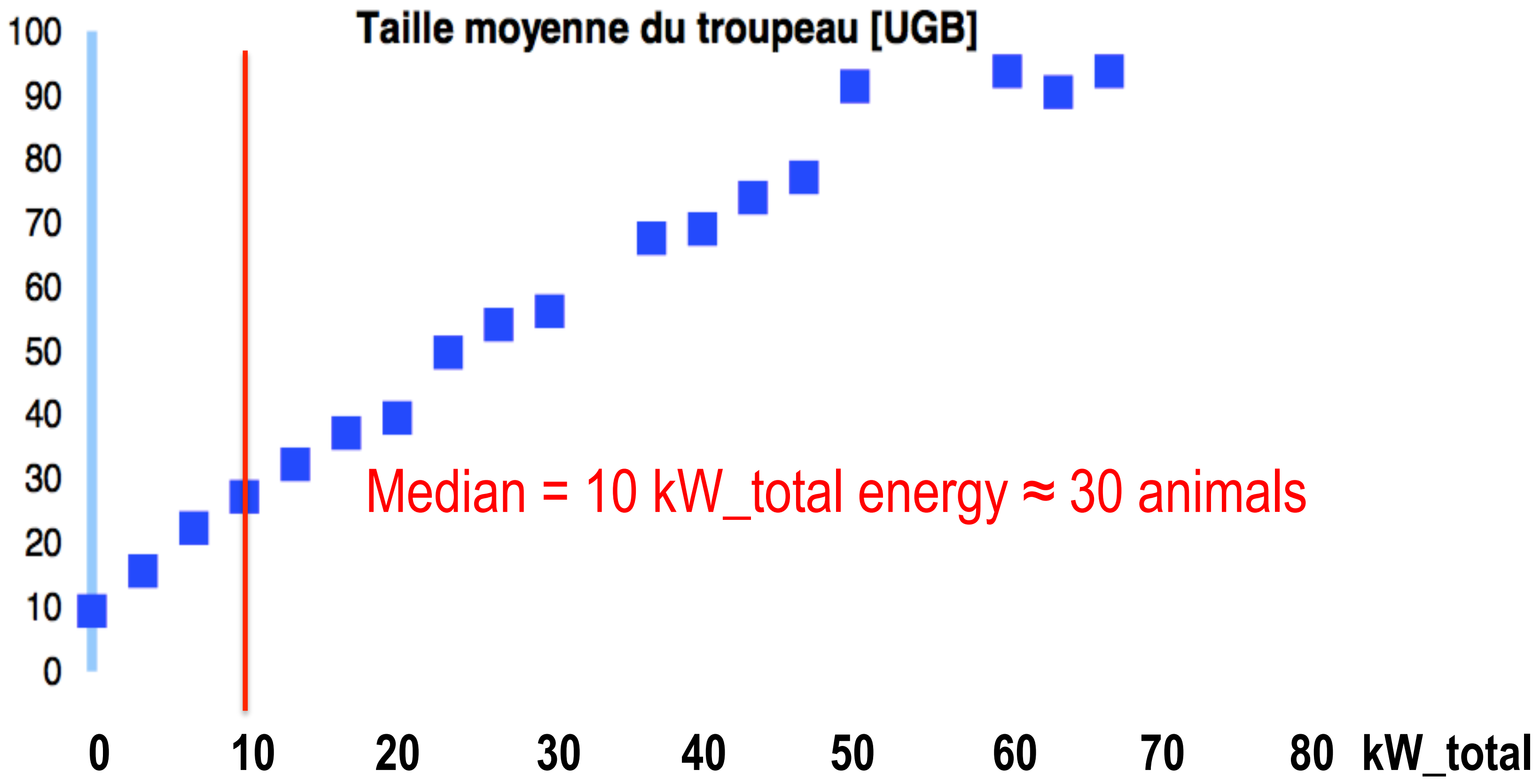
Swiss 'Mini-Biogas' study

Funded by the Swiss Federal Energy Office, published Feb 2014, available on web

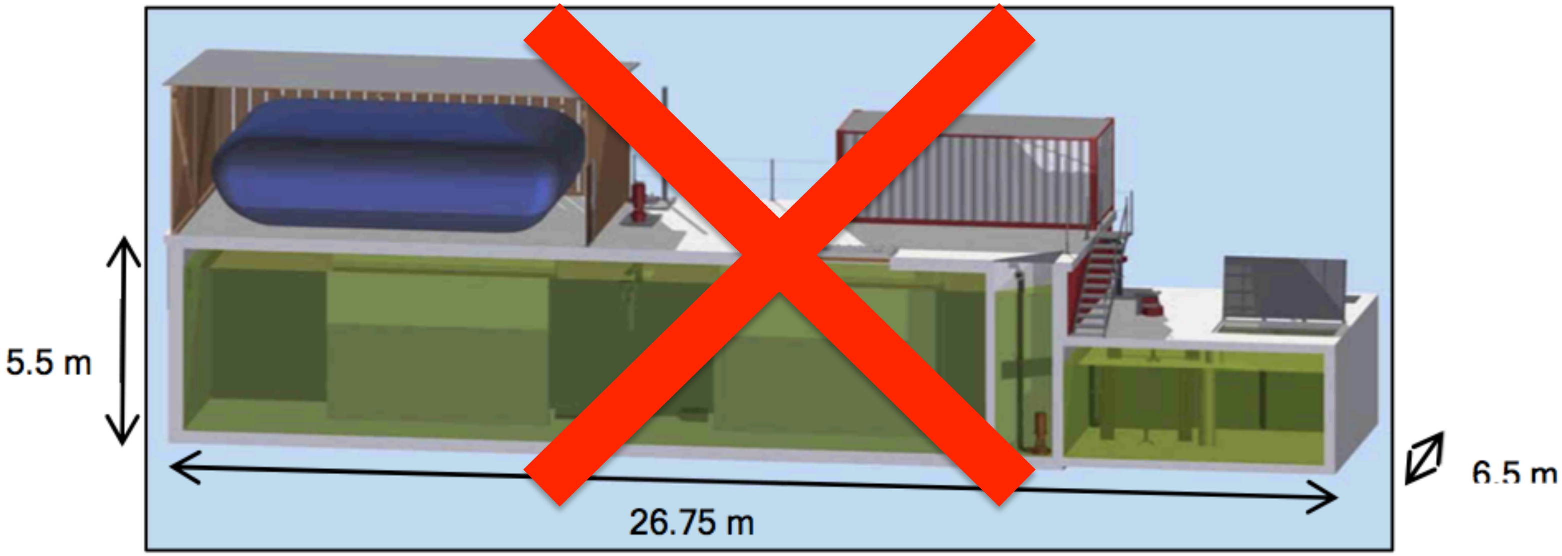


=> *potential for several 10'000 SOFC units of 5-10 kW_{el}*

Mean cattle number per farm site



On farms, keep things simple!

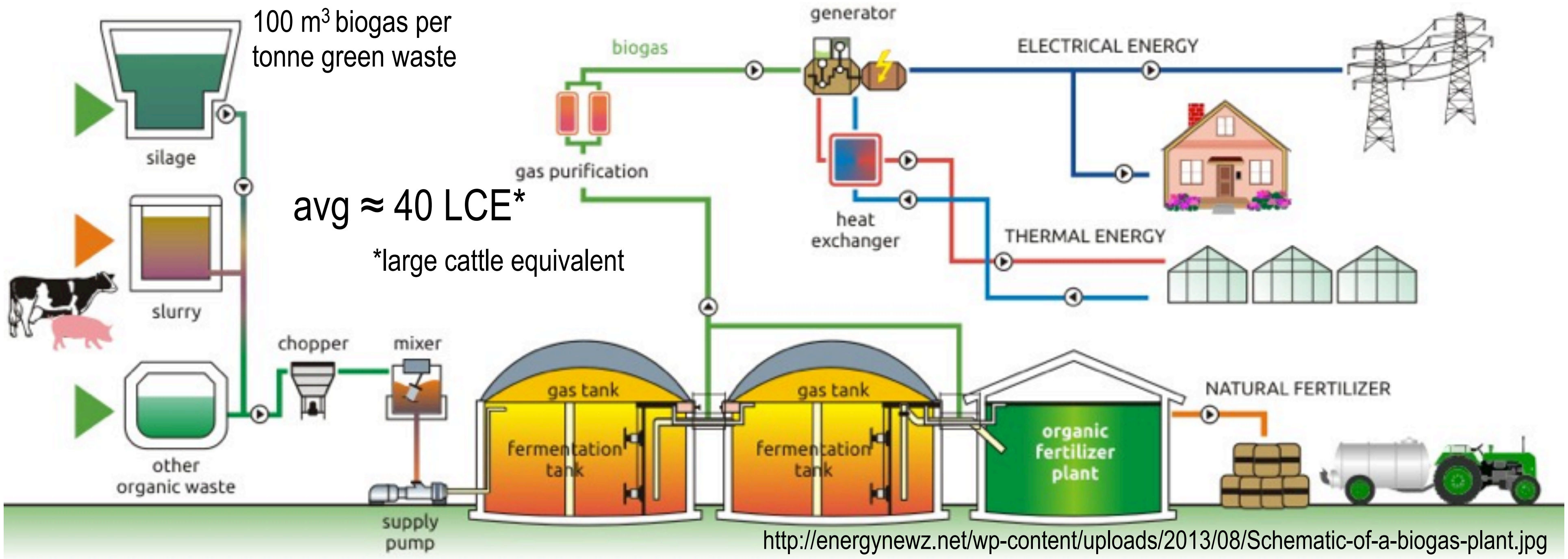


An average farm

71 m^3 biogas/day
=> 544 GJ/yr
=> 17 kW- total energy equivalent

Typical annual load (CH): 41% (3600h/yr)
⇒ with 50% elec efficiency + 10% used heat
⇒ **SOFC size of 21 kW_{el}**

Switzerland: 55'000 farm sites on 10500 km^2 => 19 hectare/site
EU: **12.2 million** farm sites; on average: 14.4 hectare/site



100 m^3 biogas per tonne green waste

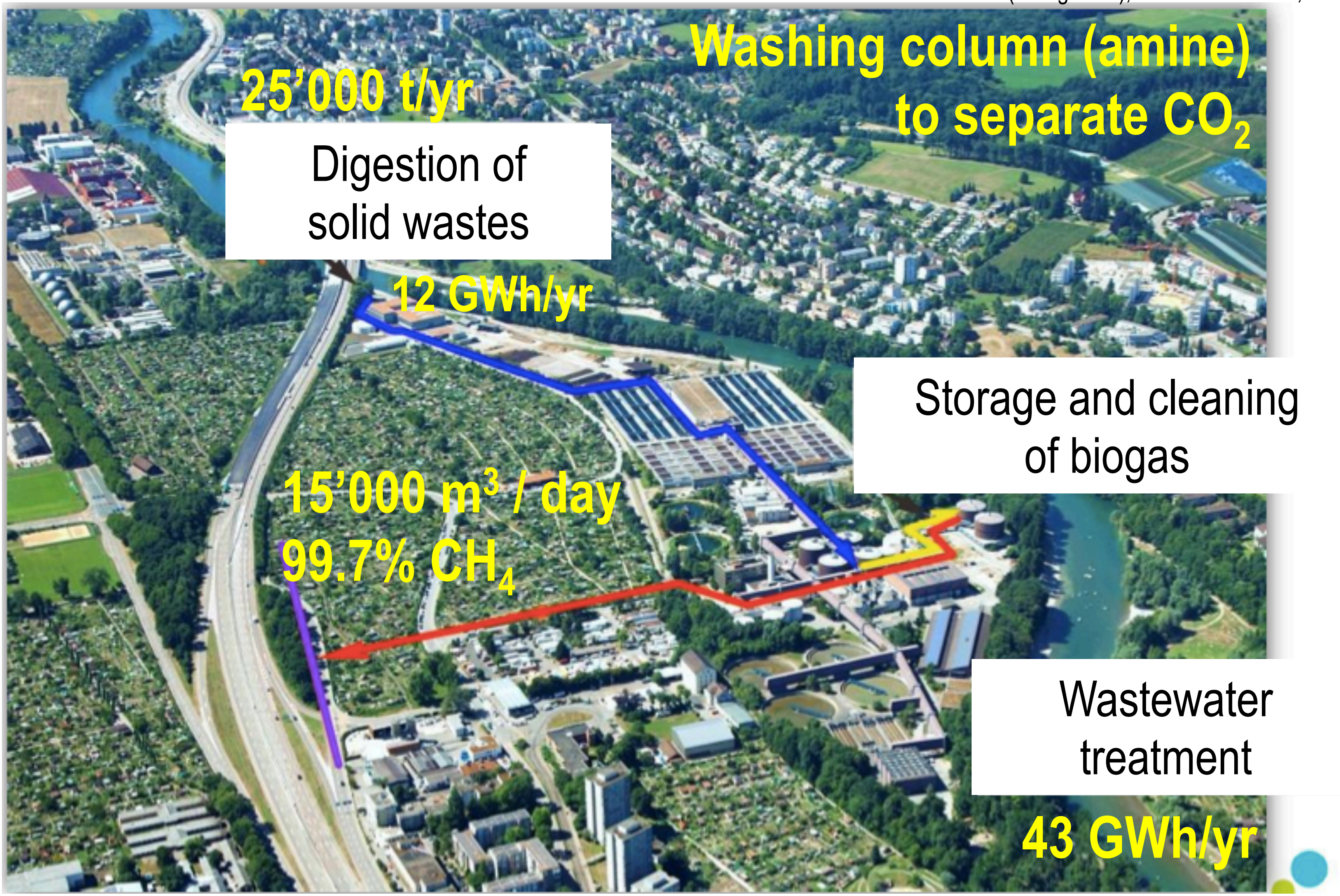
avg ≈ 40 LCE*

*large cattle equivalent

http://energynewz.net/wp-content/uploads/2013/08/Schematic-of-a-biogas-plant.jpg

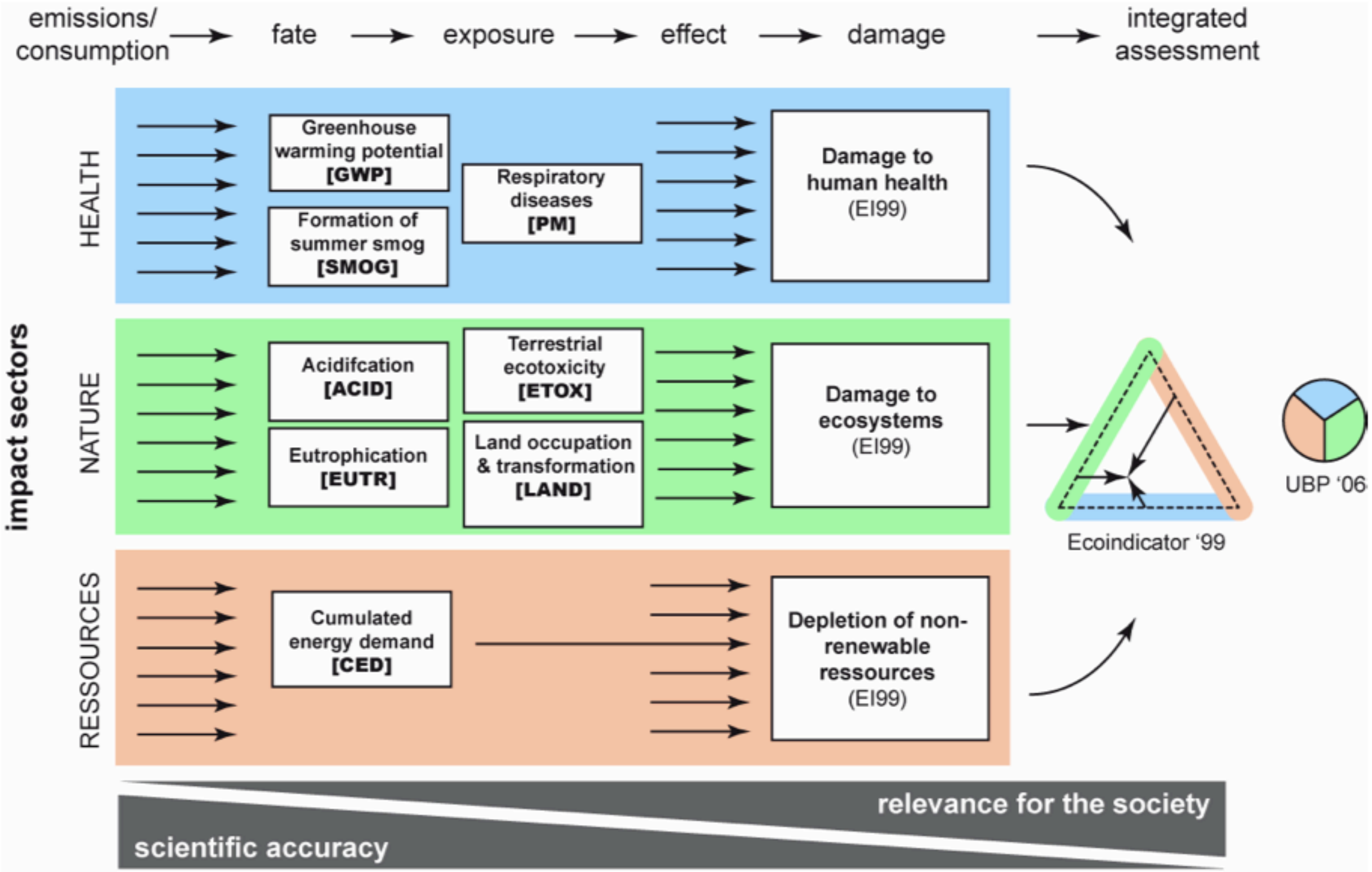
Larger production: injection of biomethane in the gas grid (Zürich wastewater treatment plant)

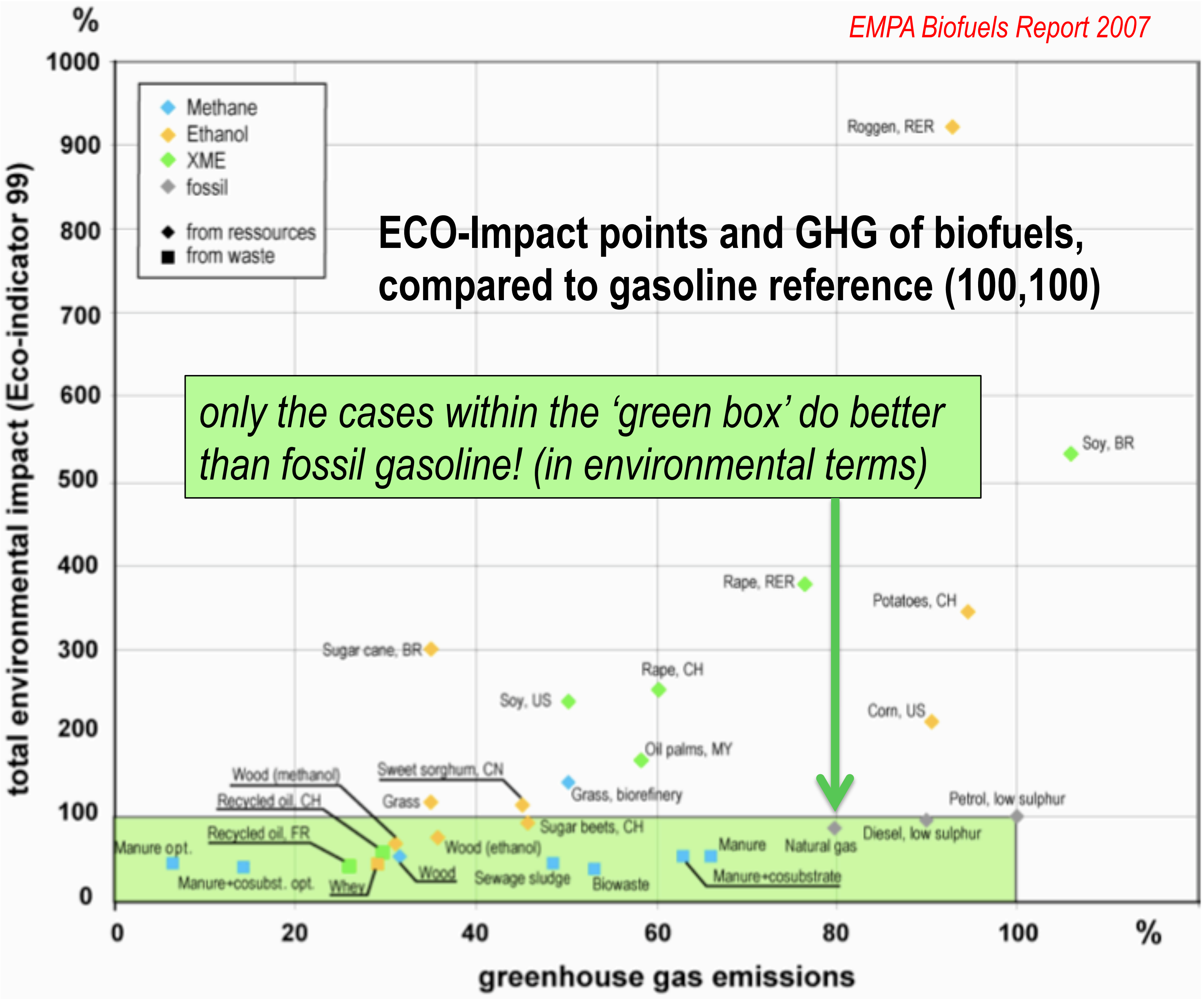
Source: P. Dietiker (Energie360), Seminar Biomass, Dec 2014



‘Best use of biofuels in general: Swiss report (Empa, 2007, revised 2013)

LCA study (Life Cycle Analysis)





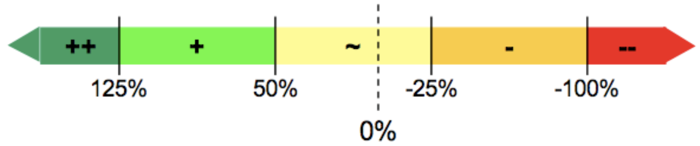
EMPA Biofuels Report 2007
ECO-Impact points and GHG of biofuels, compared to gasoline reference (100,100)
only the cases within the 'green box' do better than fossil gasoline! (in environmental terms)
%
total environmental impact (Eco-indicator 99)
greenhouse gas emissions
Methane
Ethanol
XME
fossil
from ressources
from waste
Roggen, RER
Soy, BR
Rape, RER
Potatoes, CH
Sugar cane, BR
Rape, CH
Soy, US
Corn, US
Oil palms, MY
Grass, biorefinery
Wood (methanol)
Sweet sorghum, CN
Recycled oil, CH
Grass
Petrol, low sulphur
Sugar beets, CH
Recycled oil, FR
Diesel, low sulphur
Manure opt.
Wood (ethanol)
Manure
Natural gas
Wood
Sewage sludge
Manure+cosubstrate
Manure+cosubst. opt.
Whey
Biowaste

GHG-impact

energy carrier / use path	Wood min	Wood max	Grass min	Grass max	Manure min	Manure max	Waste wood min	Waste wood max	Whey min	Whey max	Biowaste min	Biowaste max	Sewage sludge min	Sewage sludge max
Heating	++	++												
Cogeneration (CHP)	++	++	+	++	++	++			++	++	~	+	++	++
Car (methane)	++	++	+	+	++	++	++	++	+	+	~	~	+	+
Car (ethanol)	++	++	++	++					+	+				
Municipal solid waste incineration "average technology"							++	++			~	~	--	--
Municipal solid waste incineration "latest technology"											++	++		
Cement kiln							++	++					~	~

‘Best use’ practice of the biofuels

SCALE:



ECO99’-impact

energy carrier / use path	Wood min	Wood max	Grass min	Grass max	Manure min	Manure max	Waste wood min	Waste wood max	Whey min	Whey max	Biowaste min	Biowaste max	Sewage sludge min	Sewage sludge max
Heating	~	++												
Cogeneration (CHP)	~	++	~	~	+	++			+	++	-	-	+	++
Car (methane)	+	+	~	~	++	++	+	+	+	+	~	~	++	++
Car (ethanol)	~	~	+	+					++	++				
Municipal solid waste incineration "average technology"							~	+			-	-	--	--
Municipal solid waste incineration "latest technology"											+	++		
Cement kiln							+	+					-	-

EMPA Biofuels Report 2007

Influence of biogas contaminants on SOFC anodes and fuel processing catalysts; biogas cleaning

Jan Van herle, Hossein Madi (EPFL)
Andrea Lanzini (POLITO), Massimo Santarelli (POLITO),
Matteo Lualdi (TOFC),
Vitaliano Chiodo (CNR),
Markus Rautanen (VTT), Jari Kiviaho (VTT),
Gerardo Scibilia (SMAT)
….and many others

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

SOFCOM project Workpackage Objectives

- Effect of impurities on anode and fuel processing catalysts
  - threshold concentrations?
  - understanding poisoning mechanisms

→Testing on (1) reforming catalyst, on (2) cells, on (3) stacks

→ Cleaning requirements guidelines
  - efficiency of cleaning (sorbents)

sofcom
FCH-JU project

New Energy World JU
fuel cells & hydrogen for sustainability

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

→ Selected biogas contaminants for SOFC testing

Type	Contaminants	range in digester biogas [ppm]
Sulfurous	H_2S	50-100 (average ~70)
Siloxanes	D4	< 1
	D5	~1
Halogenated	(inorg.) HCl	~1
	(org.) C_2Cl_4	< 1
Hydrocarbons	C_2H_4, C_7H_8	< 0.1

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FCH-JU project

New Energy World JU
fuel cells & hydrogen for sustainability

Findings on biogas reforming catalyst (CNR)

- ✓ Steam reforming (T=1073K; H_2O/CH_4=2), for a fluctuating biogas composition (60/40 vol% < CH_4/CO_2< 50/50 vol%)

- ✓ A commercial Ni/Al_2O_3-CaO catalyst ensures good performance in clean biogas and durability tests of 500 hours (GHSV=15,000 h^{-1})

- ✓ Catalytic activity suffers in the presence of **H_2S ≥0.4 ppm**, while the presence of hydrocarbon compounds (≤200 ppm) and very low D5 siloxane (<0.5 ppm) resulted as less harmful.

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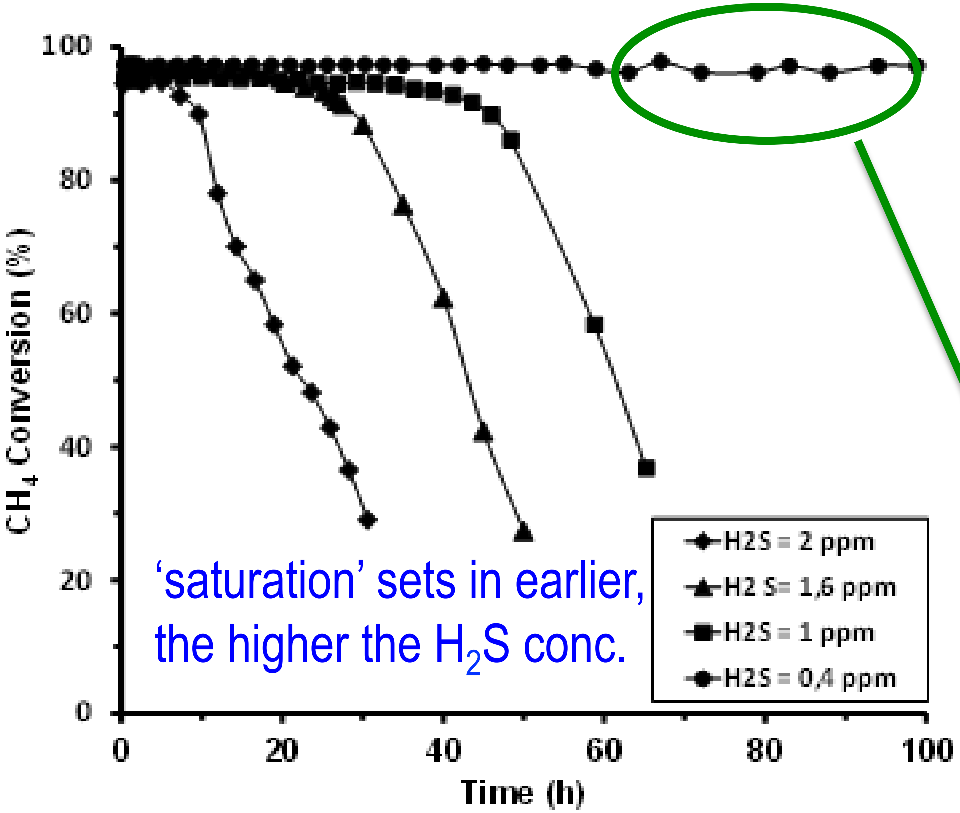
Biogas steam reforming with H_2S (CNR)

GHSV=15,000 h^{-1}; T = 1073K; CO_2/CH_4 = 45 / 55%; H_2O/CH_4 = 2



$xH_2S + yNi_{(surface)} \rightarrow Ni_yS_{x(surface)} + xH_2$

the sulfur is chemisorbed on Ni-metal until equilibrium is reached

for H_2S = 0.4 ppm, the catalytic performance is preserved

Effect of H_2S on Ni-anode

H_2S dissociative chemisorption on Ni.
Sulfur-coverage (Θ_S) of Ni is a function of temperature and pH_2S/pH_2.
Anode performance drop varies linearly with sulfur-coverage (Θ_S), only above a certain treshold coverage (≈60-80%).*

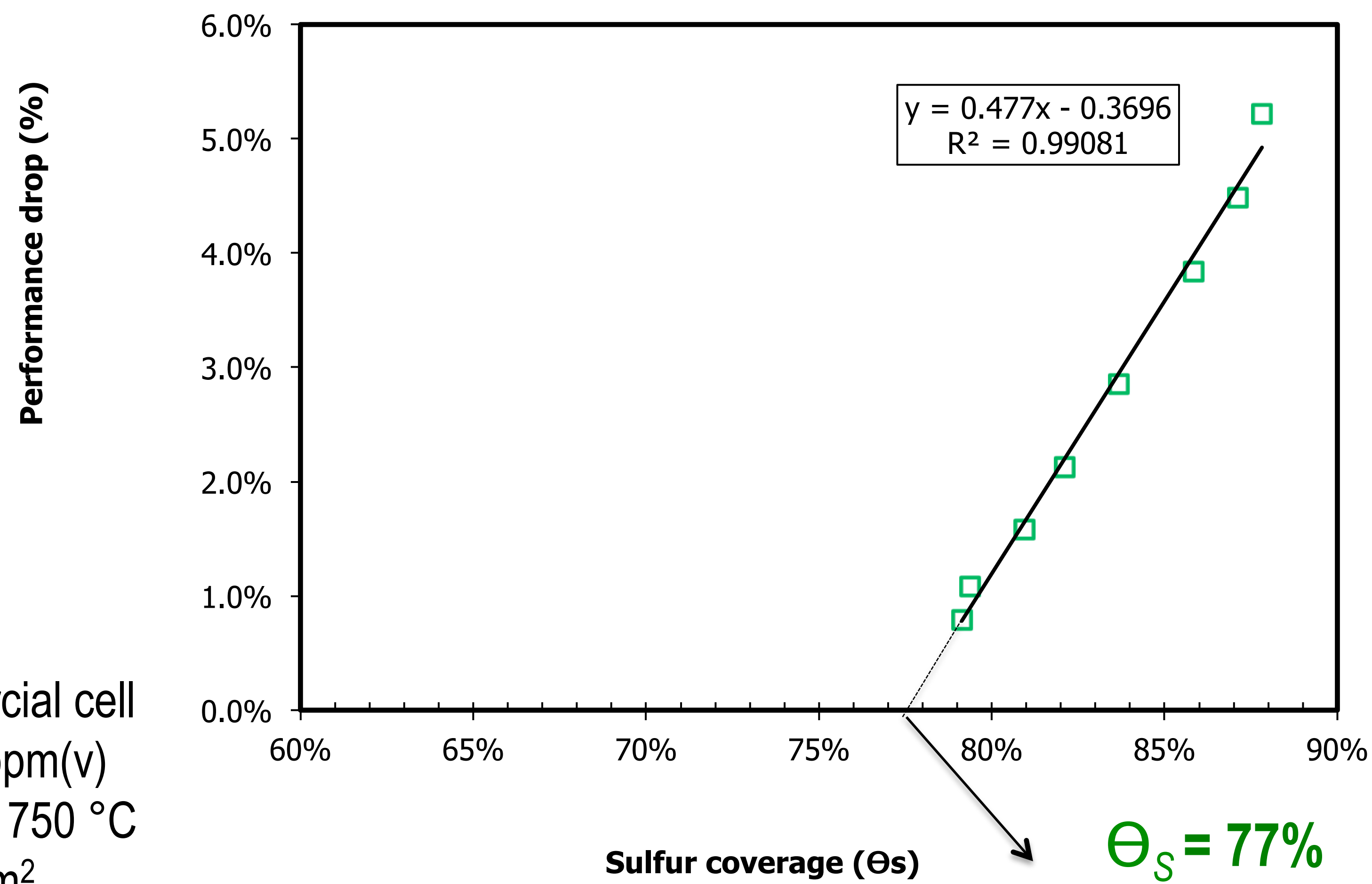
$$\frac{p(H_2S)}{p(H_2)} = \exp\left(\Delta H^0 \times \frac{1-\alpha\theta_s}{RT} - \frac{\Delta S^0}{R}\right)$$

Temkin isotherm

$$\theta_s = 1.45 - 9.53 \times 10^{-5}T + 4.17 \times 10^{-5}T ln\left[\frac{p(H_2S)}{p(H_2)}\right]$$

*J.B. Hansen, *Correlating Sulfur Poisoning of SOFC Nickel Anodes by a Temkin Isotherm,* Electrochemical and Solid-State Letters, 11 10 B178-B180 (2008).

S-chemisorption on Ni (<100 ppm H_2S)



ASC commercial cell
$0 < H_2S < 7$ ppm(v)
FU 30%   T = 750 °C
i = 300 mA/cm²

Θ_S = 77%
=> $p(H_2S)$ = 0.4 ppm

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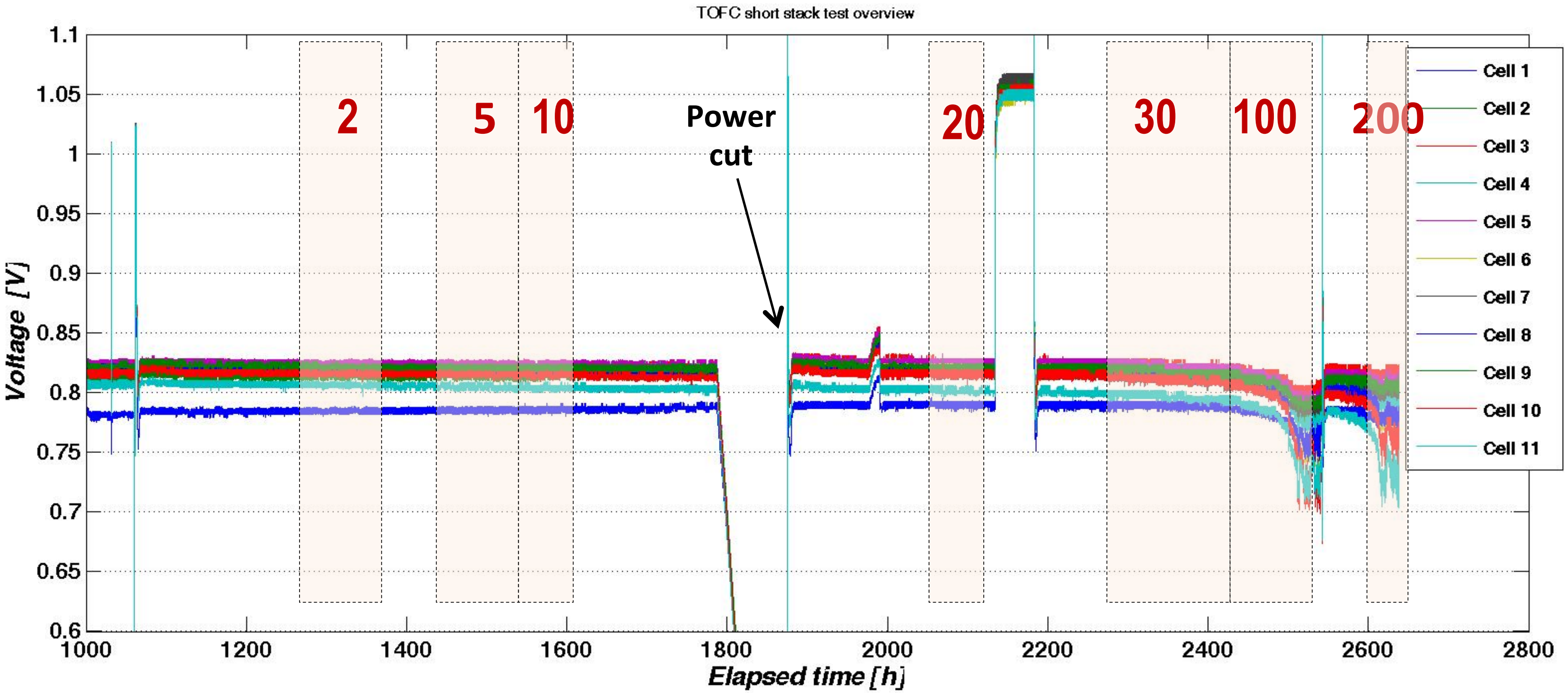
SOFC stack under HCl poisoning (0-200 ppm)



no apparent problem until 20 ppm HCl

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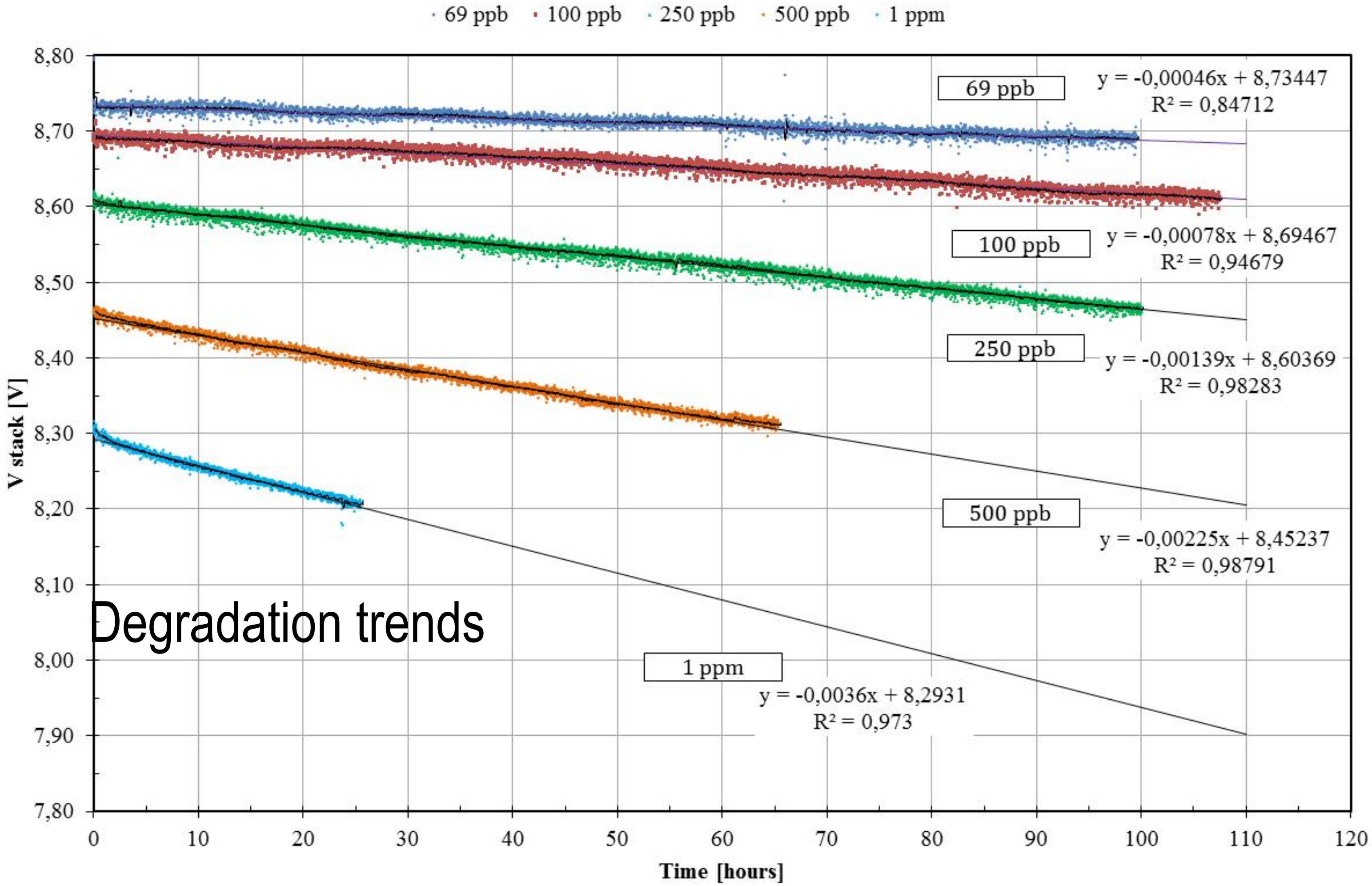
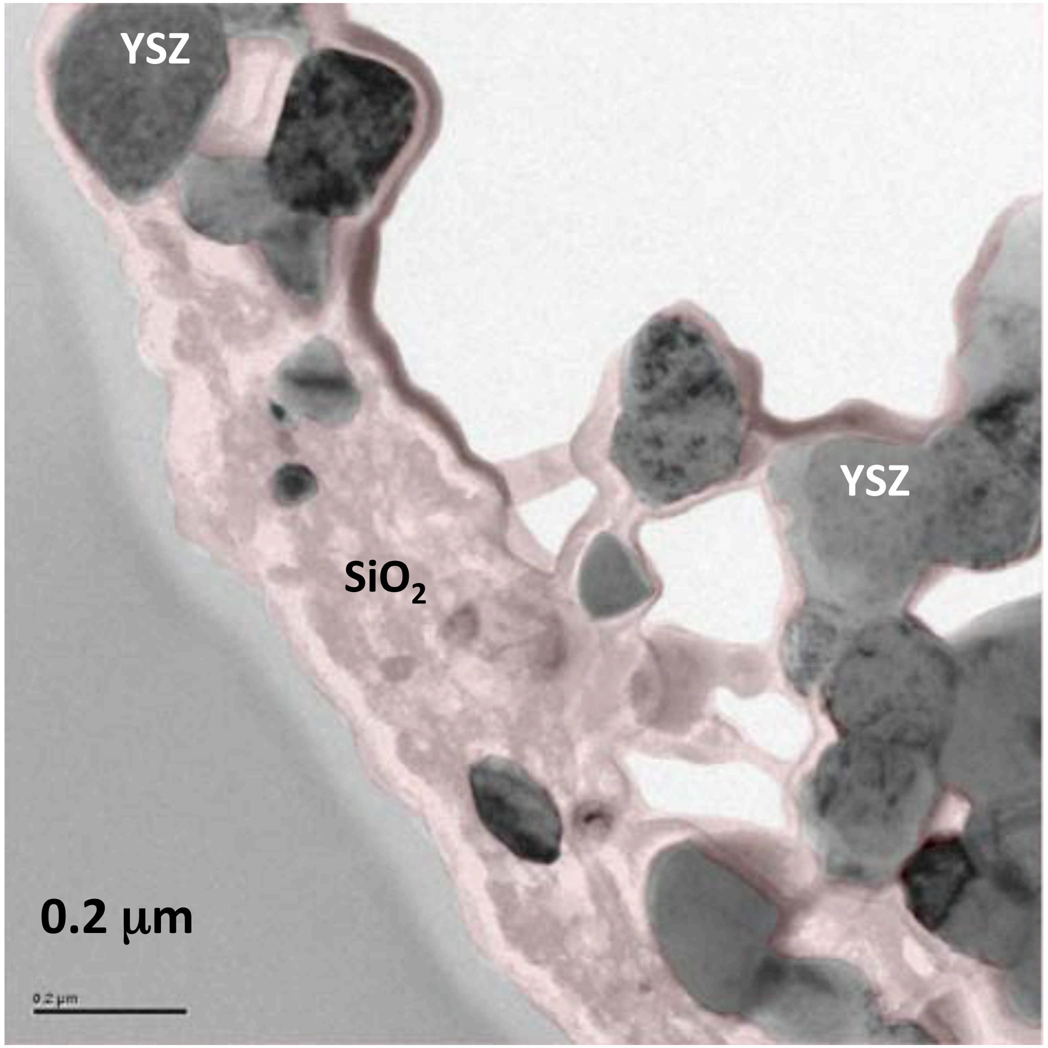
SOFC stack with D4-siloxane poisoning (POLITO)



=> *no way to escape degradation, even with 69 ppb D4-siloxane*

TEM evidence

SiO_2 deposits on YSZ



Findings on biogas cleaning options (VTT, Finland)

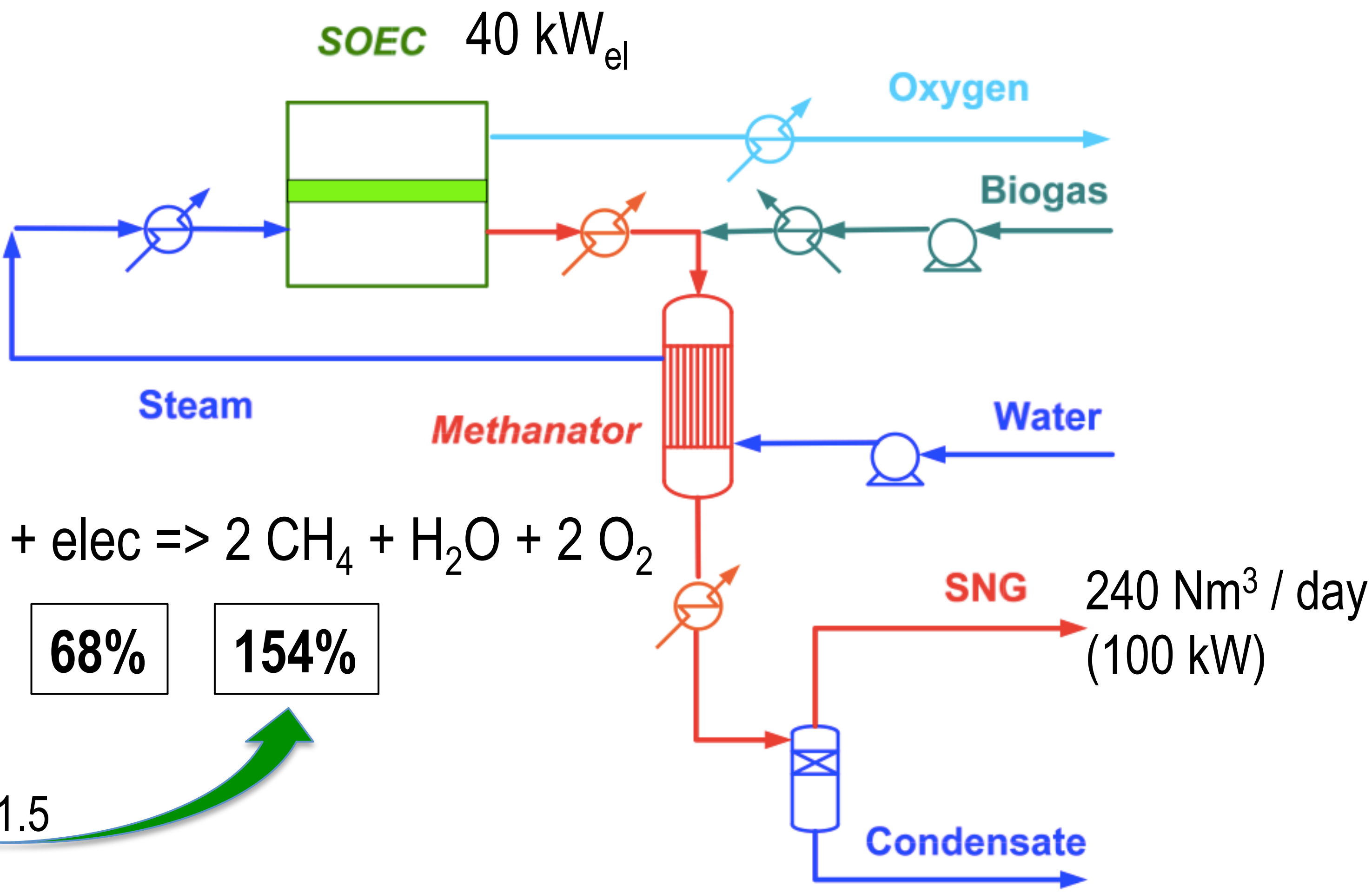
- no efficient & economic method for simultaneous removal of H_2S + siloxanes
- H_2S and siloxanes are removed separately
- adsorption = the most efficient removal method for siloxanes
- for H_2S : depends on the capacity required

Final SOFCOM recommendations for contaminants tolerance

- H_2S : < 0.5 ppm
- HCl : no cleaning required
- Siloxanes : total removal

Biogas upgrade with SOEC (co)electrolysis

Source: J. Bogild Hansen, Power-to-Gas, Düsseldorf, March 2015



$$CH_4 + CO_2 + 3H_2O + elec \Rightarrow 2\ CH_4 + H_2O + 2\ O_2$$

100% **68%** **154%**

X 1.5

Danmark (100% renewable target): need for 4-8 Gw$_{el}$ electrolysis capacity

Summary

- **biogases** are (very) under-used for power generation, esp. from manure, agro-residues and MSW/ISW, and are a valuable natural gas complement
- currently converted in **engines** (0.1-1 MW_{el}) with **30-40%** electrical efficiency, their potential could be substantially increased with SOFC (**50%** elec. efficiency) especially in the 1 kW-100 kWe range
- issues = **cost** and mass production of SOFC, as well as their compatibility & **robustness** in the harsh exploitation reality of biogas sites