

Hydrogen sulfide and siloxane removal from biogas for its usage in fuel cells



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Contents

- Biogas from anaerobic digestion
- Biogas for fuel cells
- Hydrogen sulfide removal
- Siloxane removal



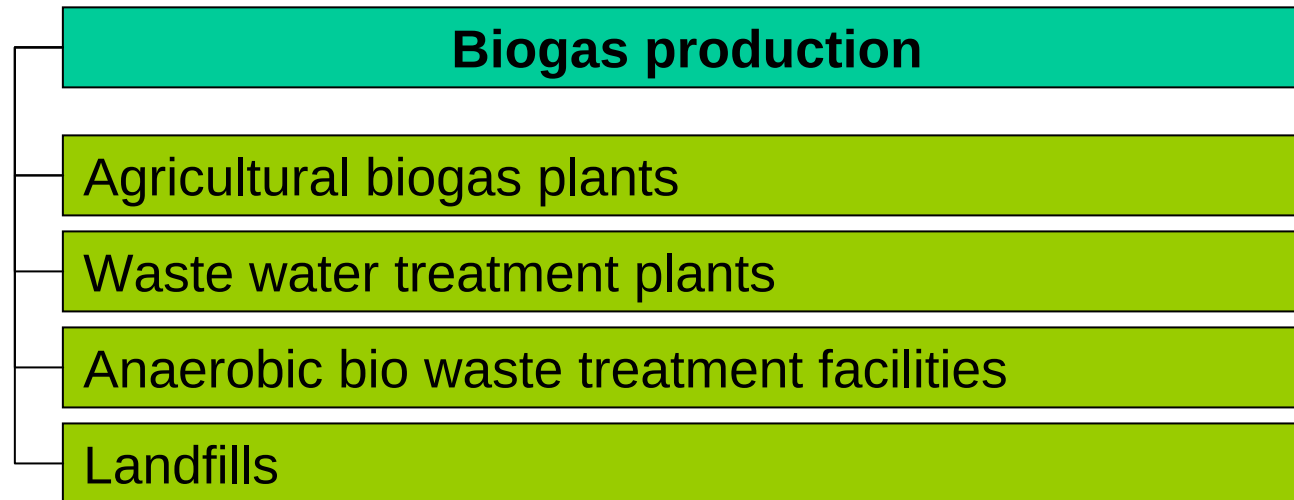
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Biogas from anaerobic digestion

Sources



Possible materials:

- Manure, energy crops
- organic waste from agriculture and food industry
- Municipal bio waste
- Sewage, landfill disposal
- ...

Biogas from anaerobic digestion

Biogas composition and contaminants

Main compounds (%)	{	CH ₄	40 - 70 %
		CO ₂	30 - 50 %
		N ₂	0 - 20 %
		O ₂	0 - 5 %
main contaminations (ppm)	{	H ₂ S	0 - 2000 ppm
		Mercaptanes	0 - 100 ppm
Traces contaminations (mg/m ³)	{	Siloxanes	0 - 100 mg/m ³
		Halogenated HC	0 - 100 mg/m ³

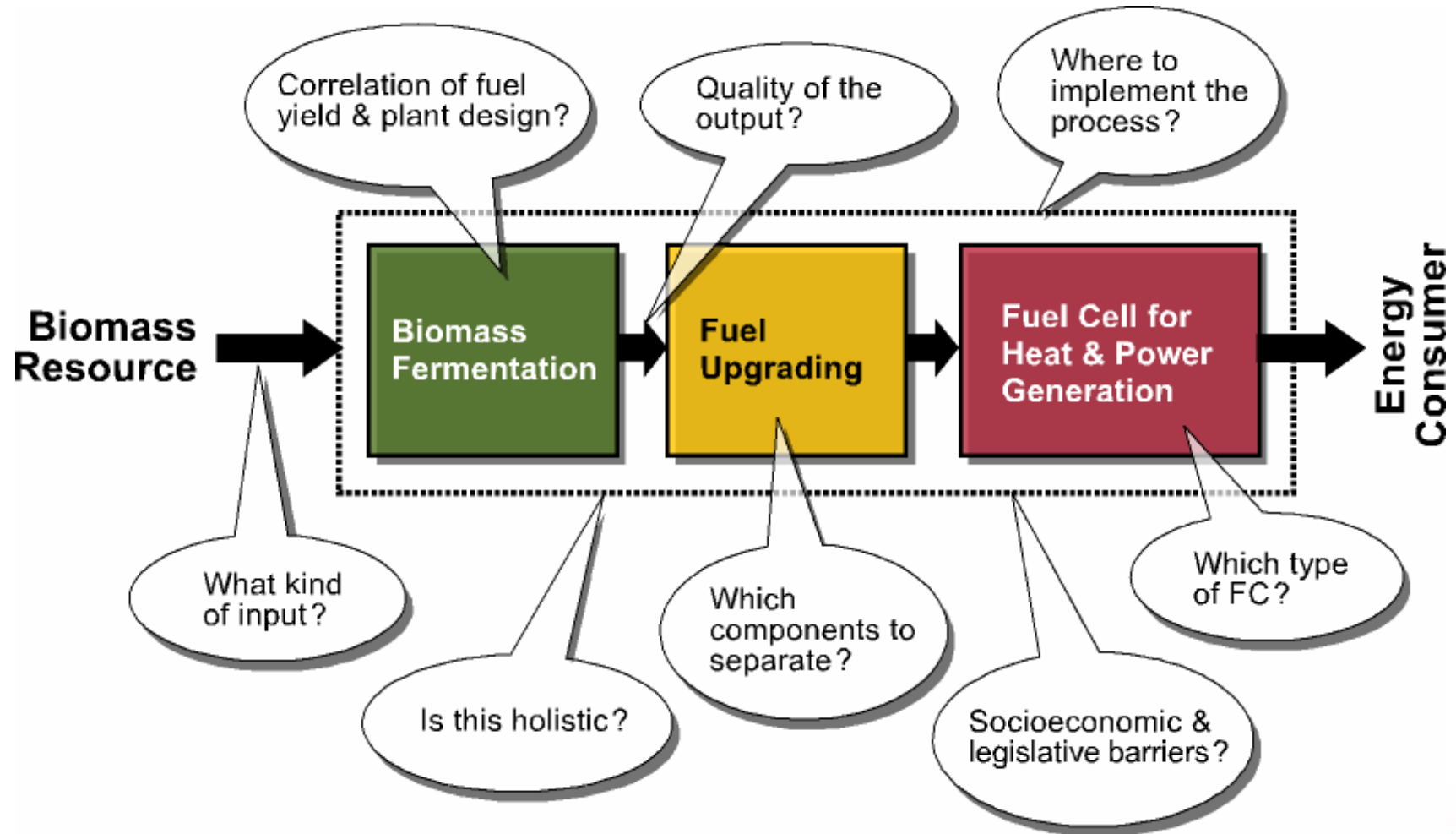
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Biogas for fuel cells

A holistic approach



Biogas for fuel cells

A holistic approach

		Low Temperature FC			High temperature FC		
FC-Typ		PEFC	AFC	PAFC	MCFC	ITSOFC	SOFC
Gas comp.	Temp.°C	80	100	200	650	800	1000
H ₂		F	F	F	F	F	F
CH ₄ , C _n H _m		IG	poison	IG	IG/F	F	F
CO ₂		IG	poison	IG	React.	IG	IG
CO		poison (<50ppm)	poison	poison (<500ppm)	F	F	F
H ₂ S, COS		nd	poison	poison (<50ppm)	poison (<0.5ppm)	poison	poison (<1.0ppm)
NH ₃		poison	F	poison	F	F	F

F.....Fuel, IG.... Inert gas, React. Takes part in electrode reaction

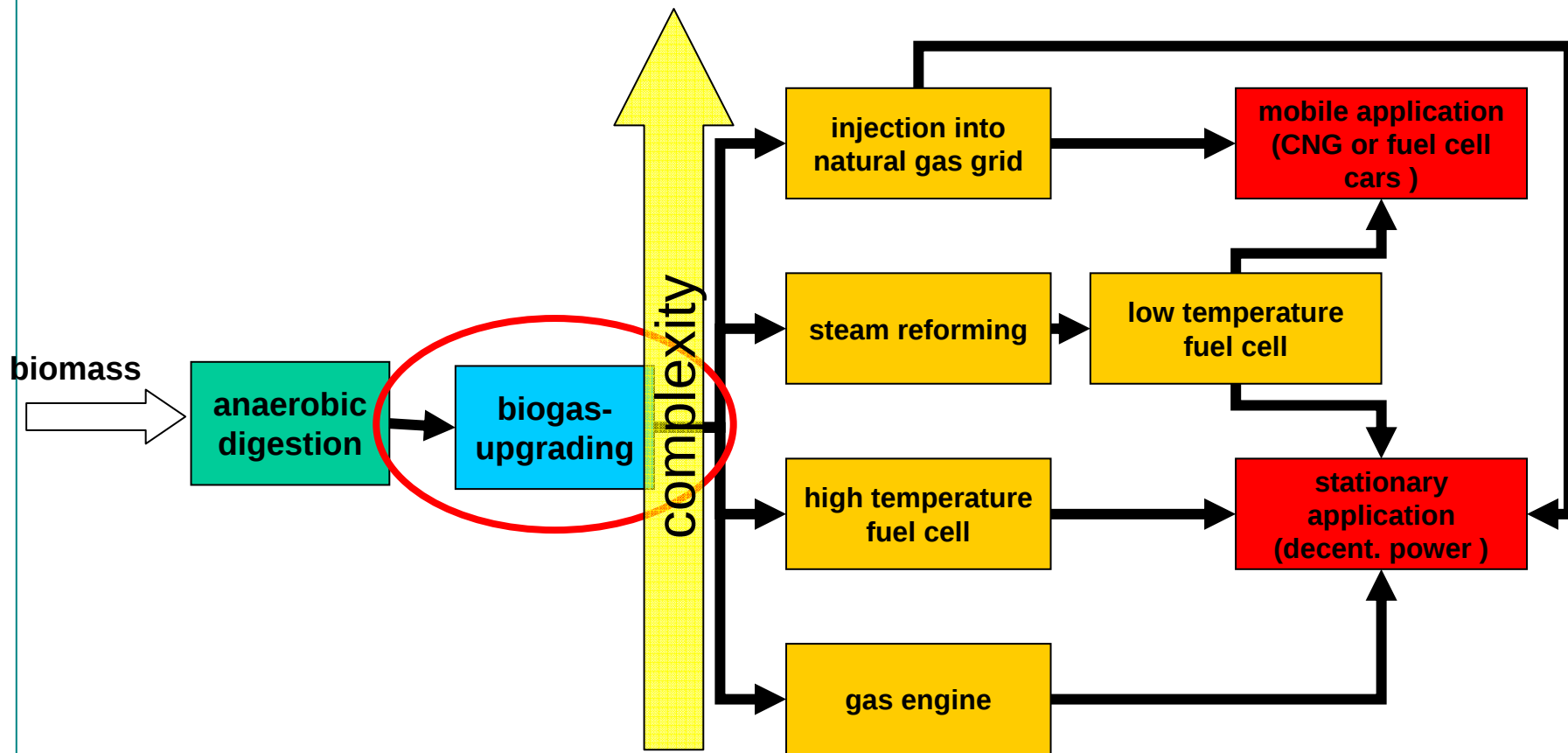
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Upgrading of biogas – general overview

Biogas as fuel for fuel cells (stationary / mobile)



Principles of biogas upgrading

Removal of hydrogen sulphide

➤ Physical – Chemical Methods

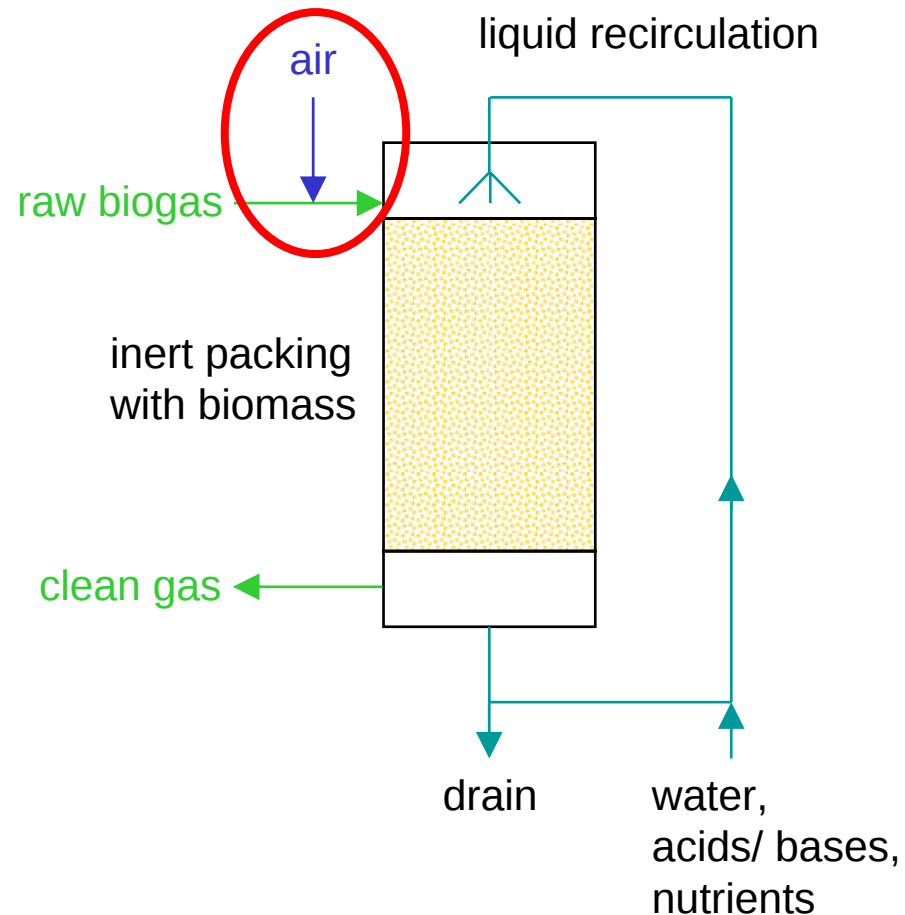
➤ Biotechnological Methods

- High efficiency
- Lower investment costs
- Lead to savings on energy
- Avoid catalysts
- Avoid formation of secondary contaminants

Biofilter
Bioscrubber
Biotrickling filter

Biotrickling filter concept

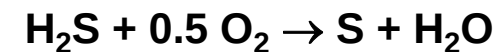
Removal of hydrogen sulphide



➤ Microorganisms to degrade H_2S :

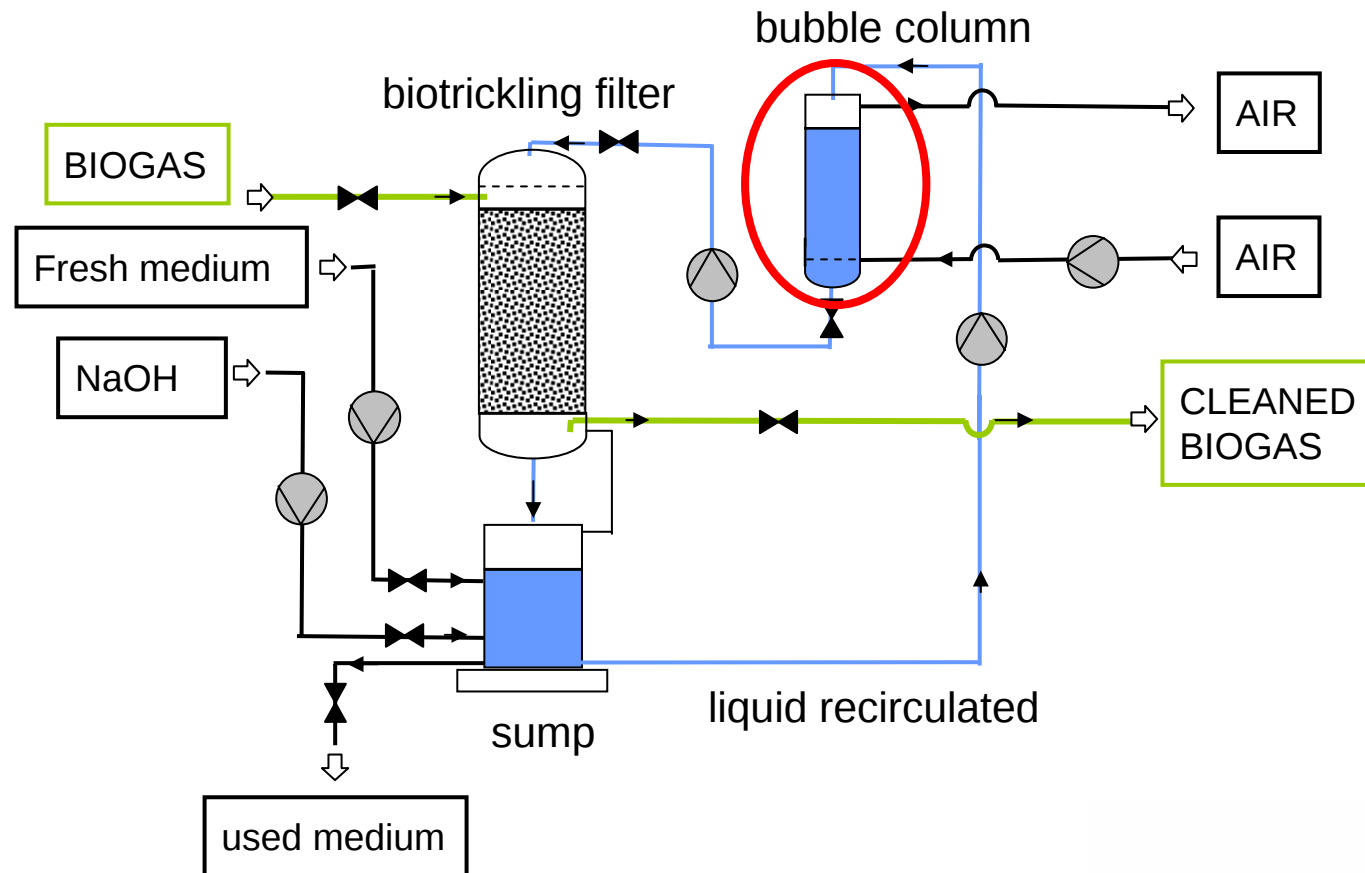
bacteria genus Thiobacillus

- ✓ Common bacteria.
- ✓ They do not oxidise CH_4 .
- ✓ Their carbon source is CO_2 .
- ✓ They obtain energy for growth from oxidising inorganic sulphur substrates.



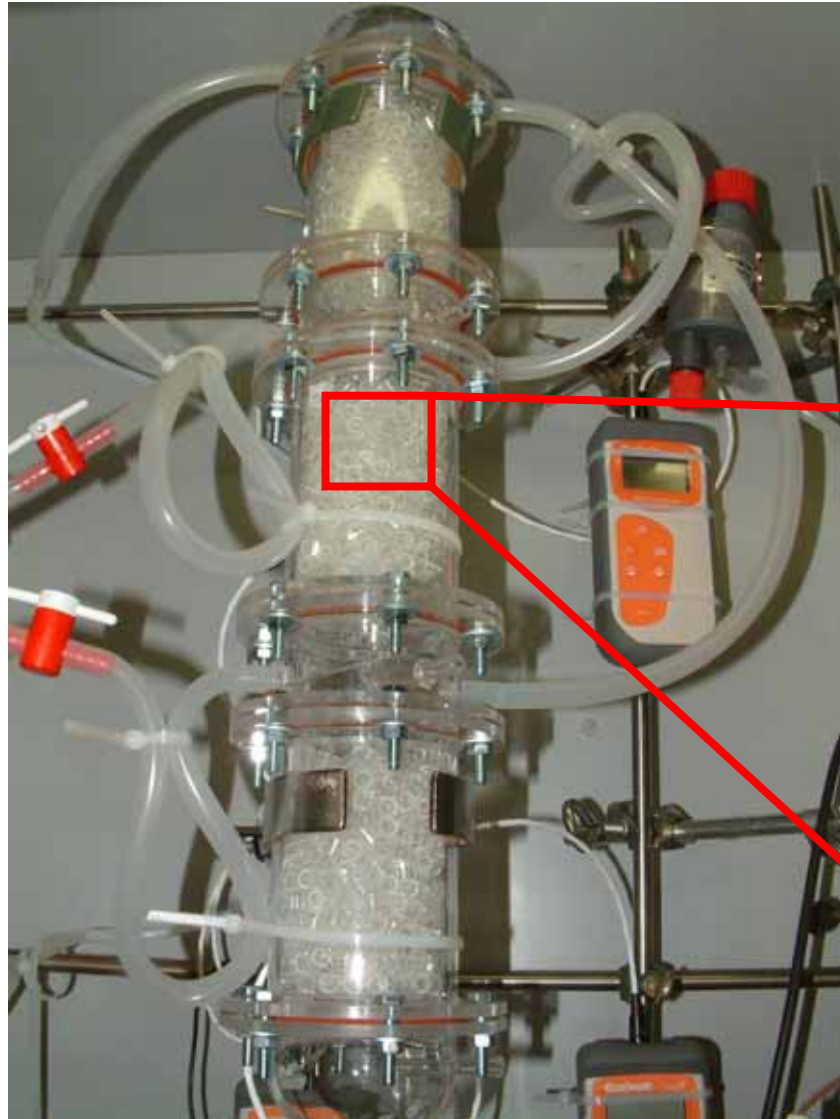
Biotrickling filter concept

The EFFECTIVE way



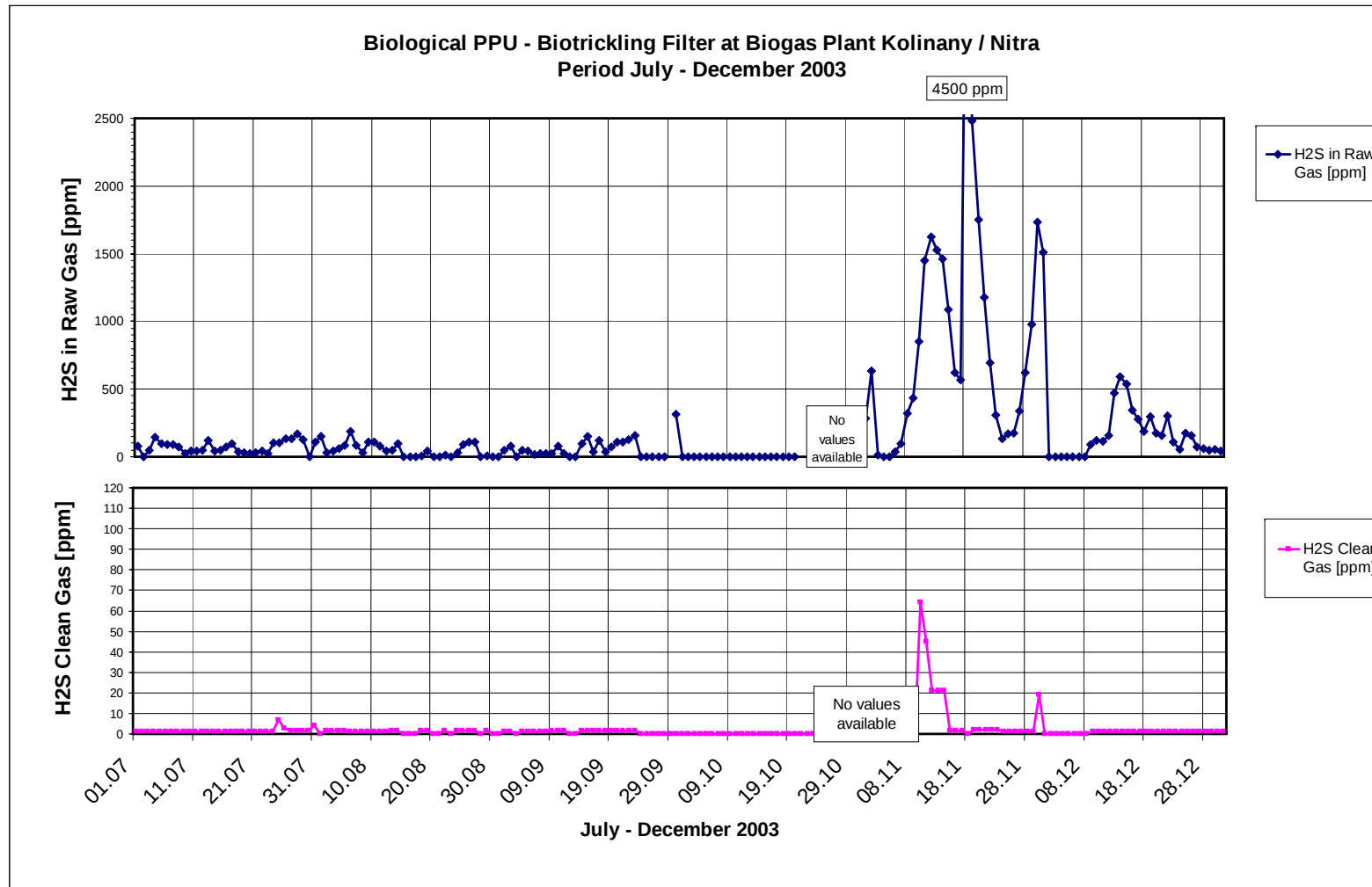
Biotrickling filter concept

The 2nd generation



Biotrickling filter concept

Filter performance



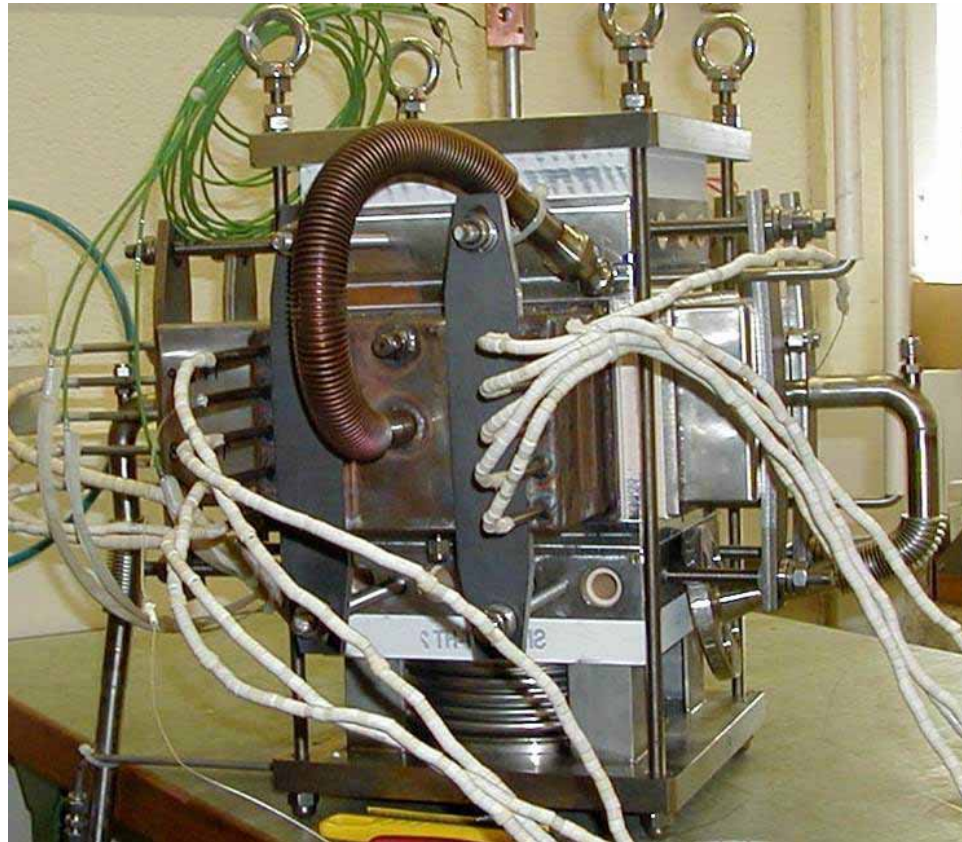
Application of biogas in MCFC

The EFFECTIVE project



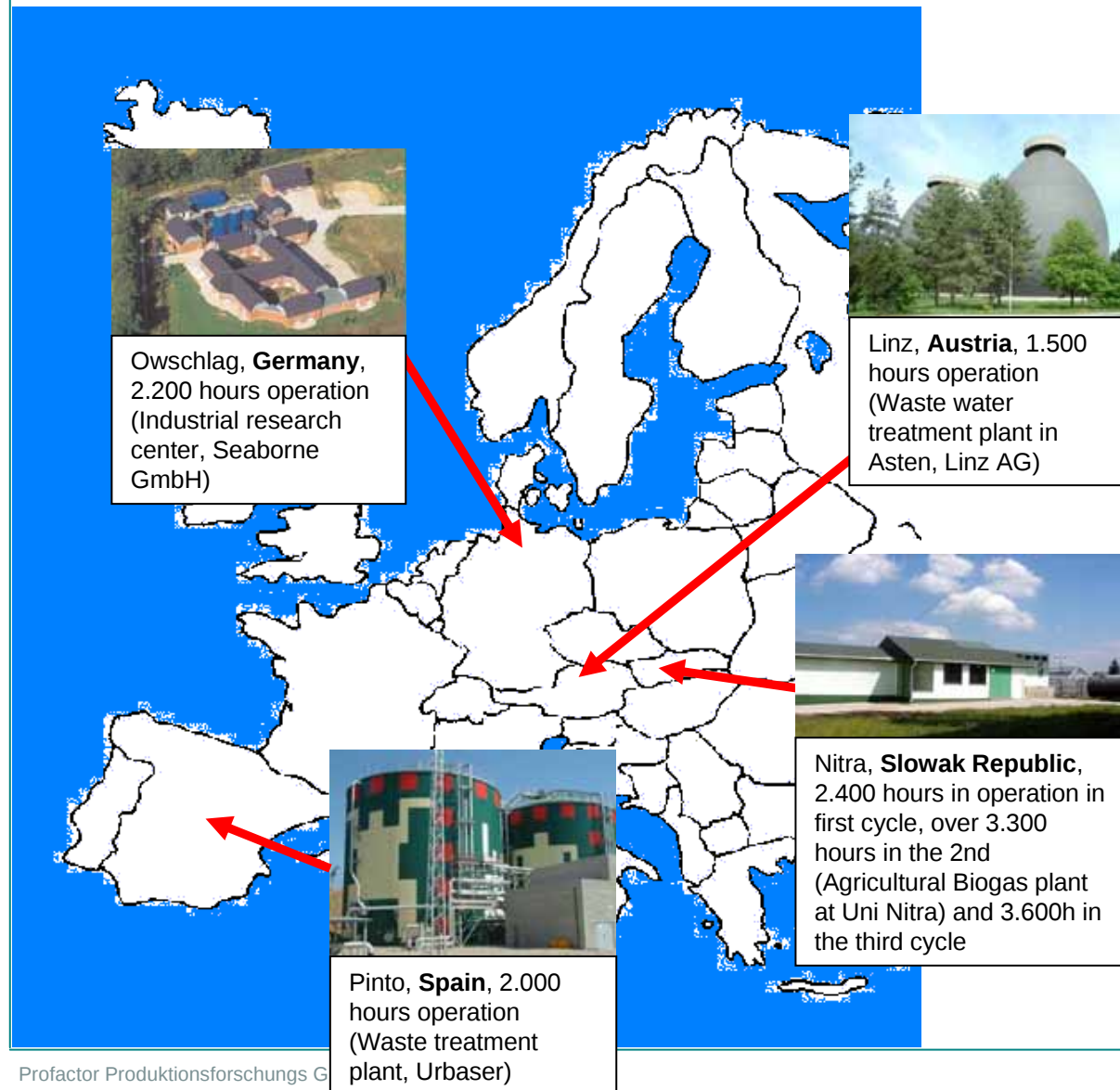
Application of biogas in MCFC

The EFFECTIVE project



Application of biogas in MCFC

Locations for Biogas – MCFC test cycles in EFFECTIVE



Tested Fuels

- Germany: industrial waste biogas
- Austria: waste water treatment biogas
- Spain: Landfill gas
- Slovakia: agricultural biogas

Application of biogas in MCFC

Results from EFFECTIVE

- Biogas operation of MCFC without any problems (more than 9.000€ operating experience)
- Challenging operation with MCFC testbed, which is delicate to changes in the surroundings
- Thermal cycling has a negative effect on the stack
- “Post mortem” analyzes indicates no severe interaction between biogas and fuel cell system components
- MCFC electr. efficiency of over 50% achieved (Seaborne)
- Gas upgrading systems fulfilled the expectations
- NH_3 reduction by catalytic decomposition (lab scale single cell experiments)

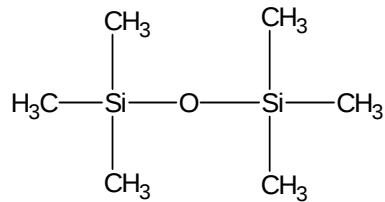
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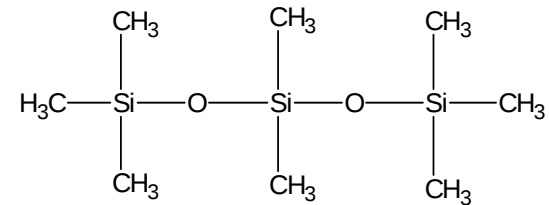


Silicon contaminations

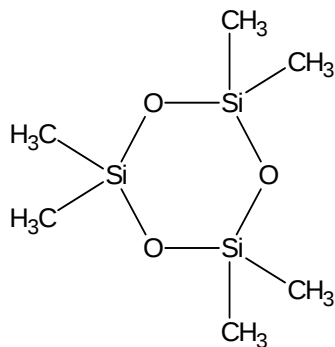
Linear and cyclic siloxanes



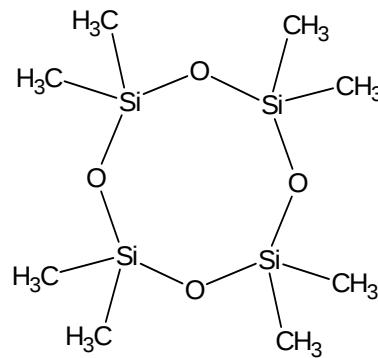
hexamethyldisiloxane (L2)



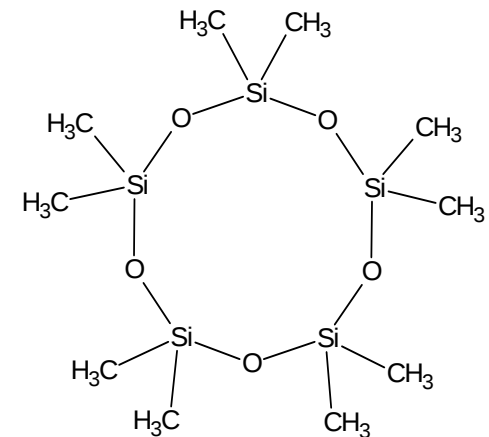
octamethyltrisiloxane (L3)



hexamethylcyclotrisiloxane (D3)



octamethylcyclotetrasiloxane (D4)



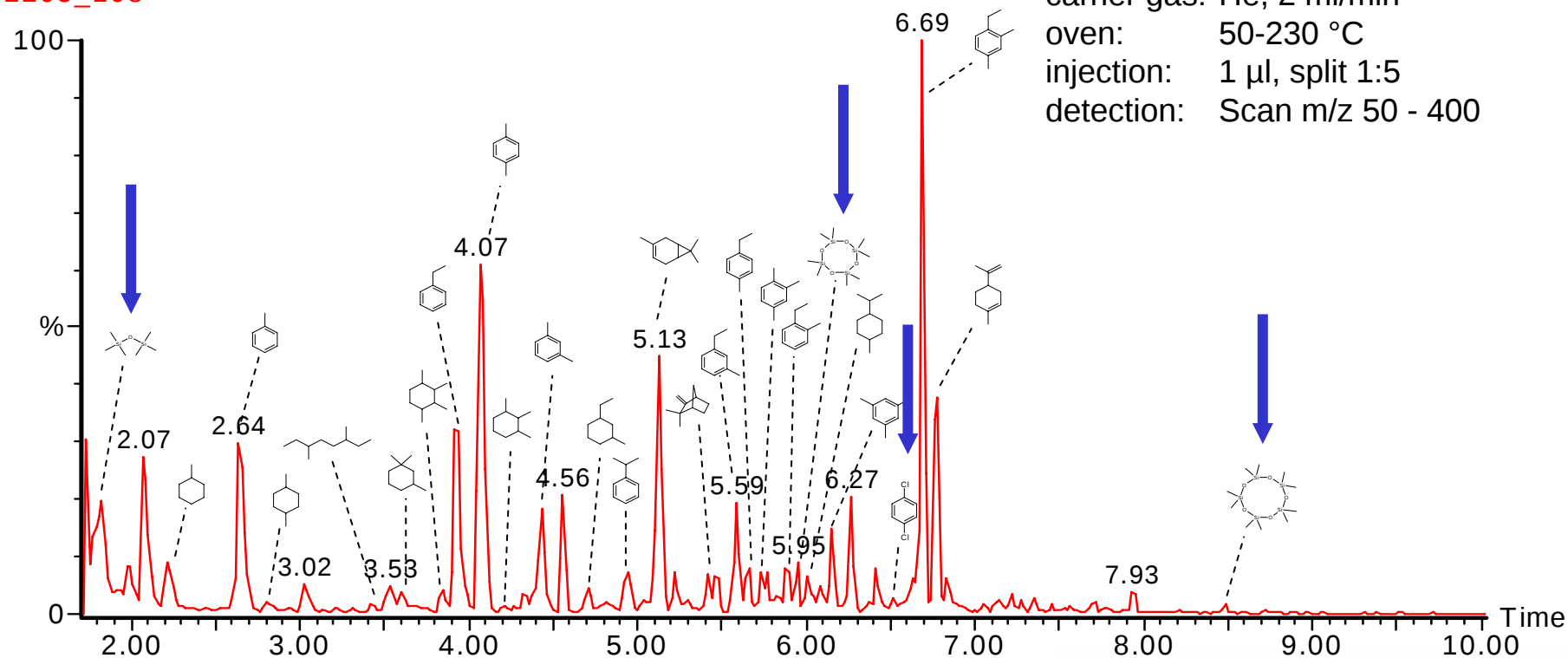
decamethylcyclopentasiloxane (D5)

Analytics of siloxanes

GC-MS analytics

Deponie Asten XAD2

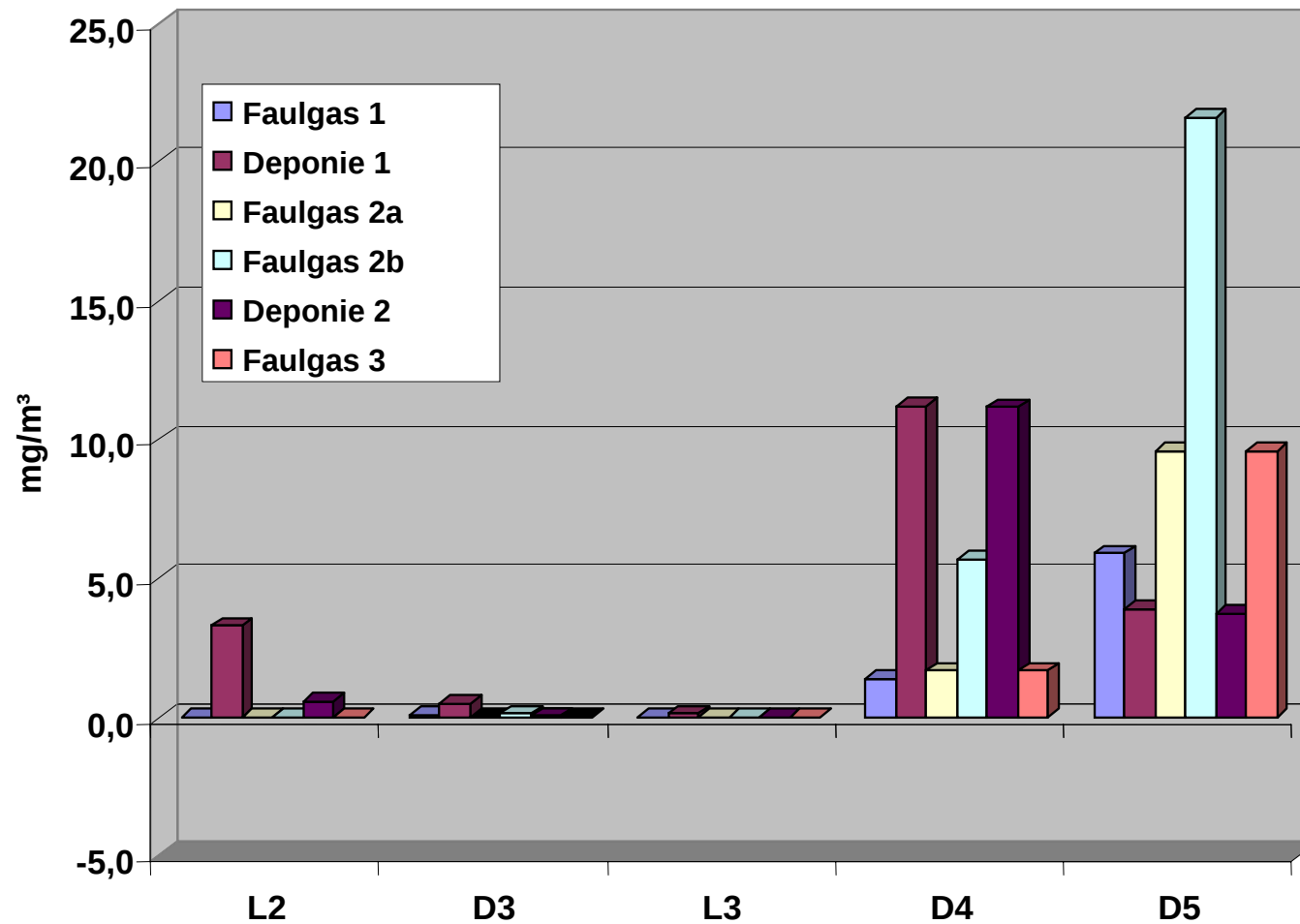
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instrument: PE Turbomass GC/MS
capillary: PE 5 MS, 30 m, 320 μ m
carrier gas: He, 2 ml/min
oven: 50-230 $^{\circ}$ C
injection: 1 μ l, split 1:5
detection: Scan m/z 50 - 400

Analytics of siloxanes

Siloxane contents in sewage and landfill gas



Removal of siloxanes

Available technologies

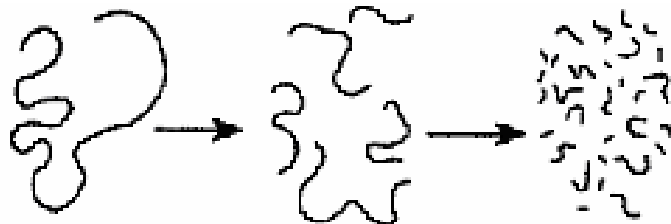
- Adsorption on activated carbons + cooling to -30°C (down to 1 mg/m^3)
- Adsorption on polymorphous graphite (down to $0,3 \text{ mg/m}^3$);
- Absorption in solvents (polyethylene glycol);

High costs for regeneration and material disposal

Removal of siloxanes

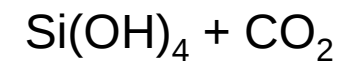
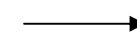
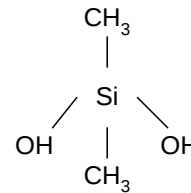
Biological principals

- Degradation of PDMS in soil (Carpenter *et al.*, 1995, Sabourin *et al.*, 1996):



Decrease in Molecular Weight

Chemical !



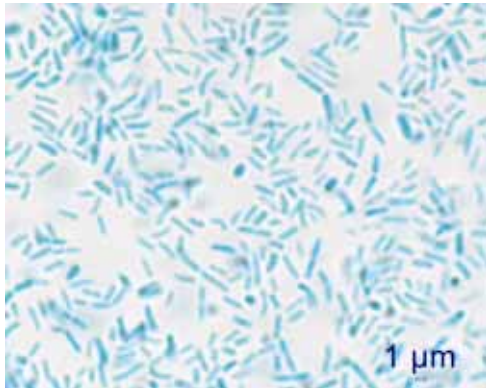
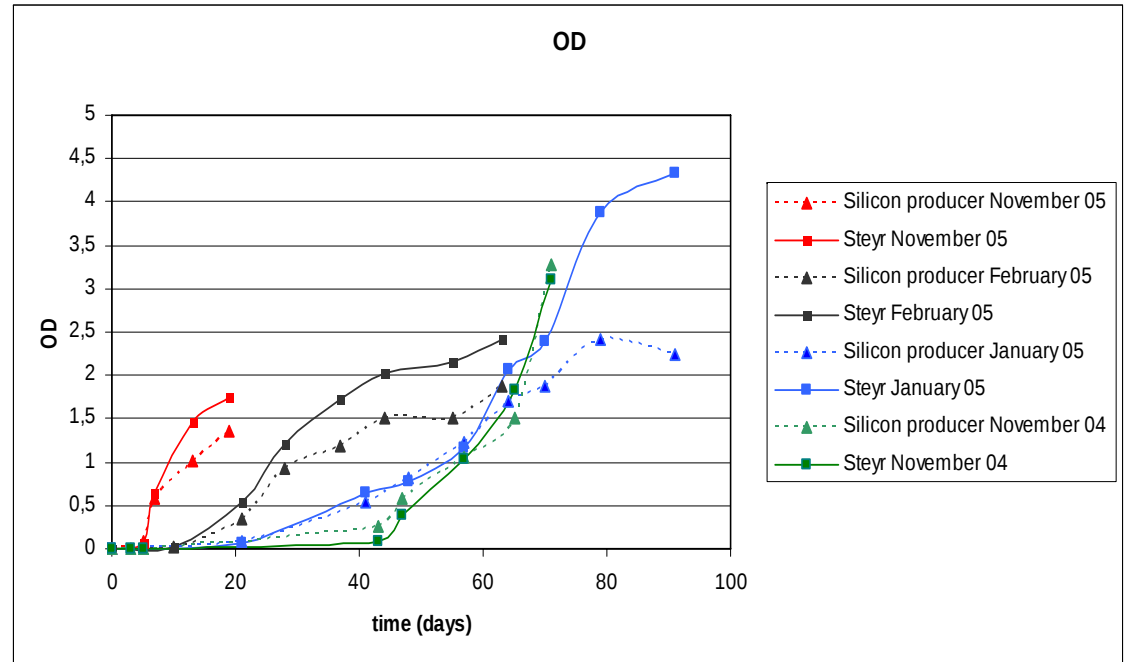
Biological !

- *Fusarium Oxysporum*: 0,9 % per month, initial concentration 100 ppM;
2,4 % when adding 2-propanol
 - *Arthrobacter*: 4 % per month when adding dimethylsulfone
- Biodegradation of PDMS by *Pseudomonas* (Wasserbauer *et al.*, 1990)

Removal of siloxane

Isolation & adaptation of bacteria

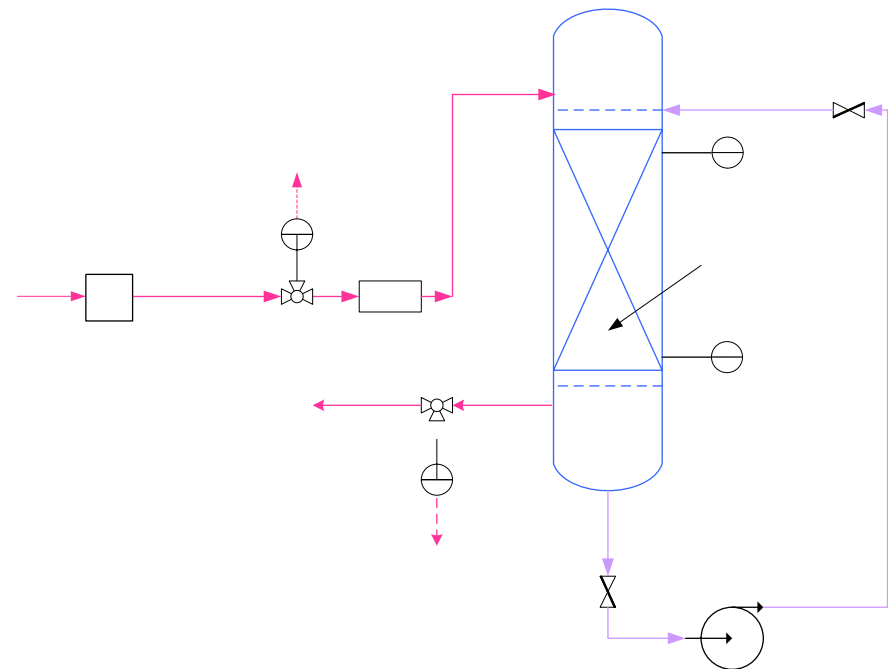
- Sludge from silicon producer-waste water treatment plant ;
- Sludge from Steyr waste water treatment plant;



First identification with 16S rDNA sequencing:
Predominance of bacteria from genus Pseudomonas:
P. citronellosis
P. putida

Removal of siloxane

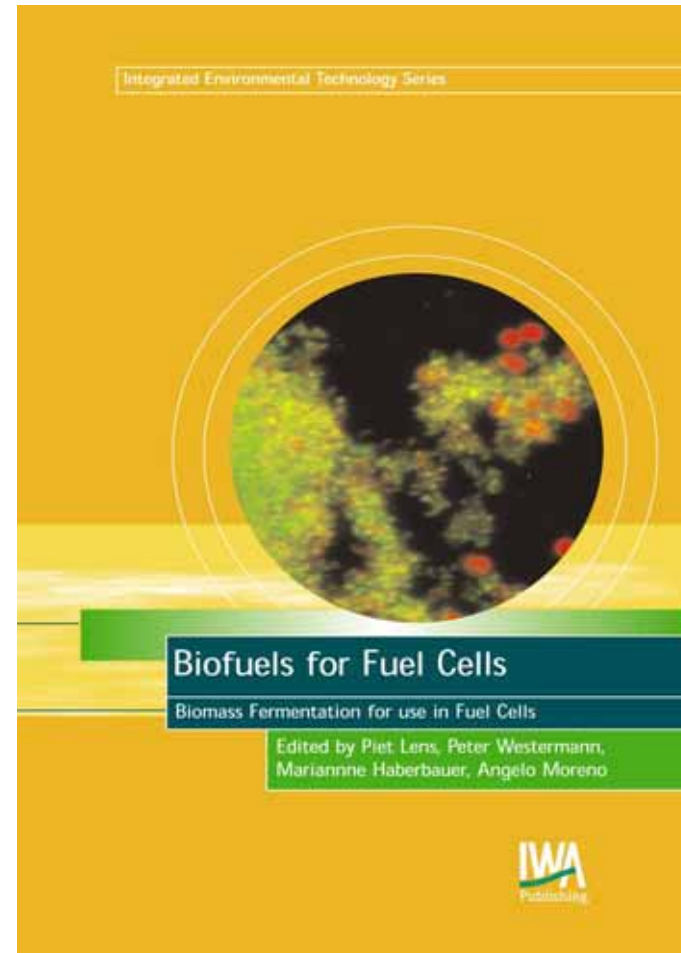
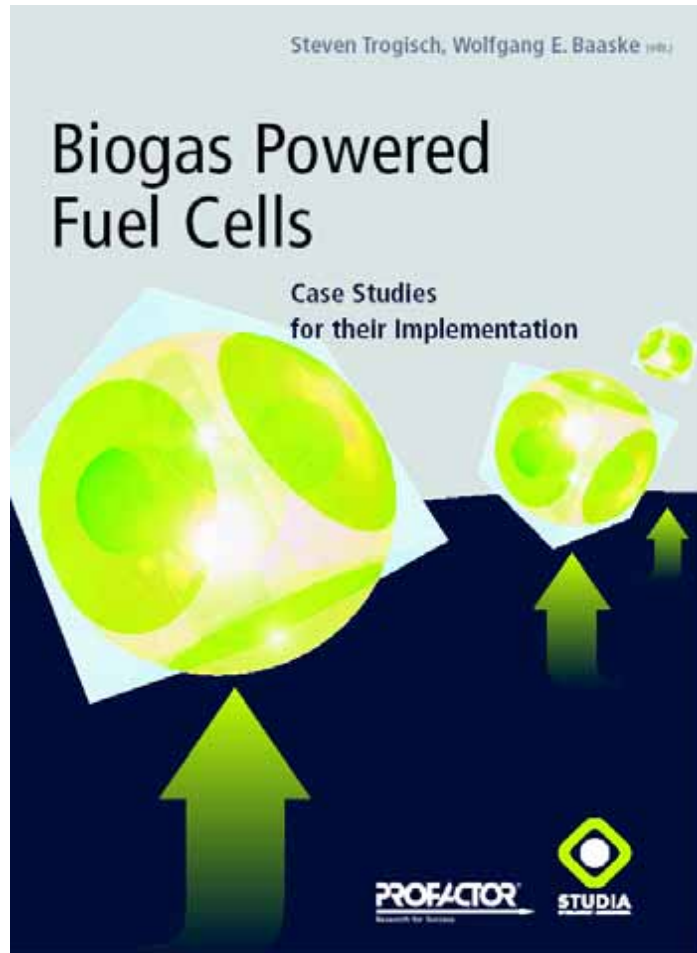
Biotrickling filter



Conclusions

- The operation of HT-fuel cells proved to be feasible with a good electrical efficiency
- Hydrogen sulfide and siloxanes are detrimental to the fuel cell performance
- Removal of these contaminations using biological means is a promising approach
- The area of application of the biogas upgrading technologies are useful beyond application with fuel cells (injection of biogas into the natural gas grid)

Biogas for fuel cells – further reading



Thank you for your attention !



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