IEA Bioenergy
Technology Collaboration Programme

Workshop: Strategies for emission control on biogas upgrading plants

Technologies for the treatment of gases with low methane content

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- Applications with gases with low methane content to be treated
- Basics for the treatment of the gases
- Technologies for the treatment of gases
- Biogas Upgrading as particular case

Methane

Methane properties	
Elemental formular	CH_4
average residence time of in the atmosphere	12.4 years
global warming potential in relation to carbon dioxide	Over 20 years, 84 times; over 100 years, 28 times the potential (IPCC AR 5)
State of aggregation at 1013 mbar and 293.15 K	gaseous
Colour	colourless
Odour	odourless
Density at 1013 mbar and 273.15 K	0.7175 kg/m^3
Ignition temperature	595 °C
Lower and upper explosion limit	4.4 Vol% - 16.5 Vol.%
Solubility in water at 293.15 K and 1013 hPa	24.4 mg/l
Flame temperature	1970 °C

Applications with gases with low methane content to be treated

Biogas technology

- Exhaust gases of Combined Heat and Power (CHP) units
- Exhaust gases from biogas upgrading
- Open and non gas-tight digestate storage

Agriculture

- Livestock farming, in particular manure management or manure storage
- Cultivation of rice

Waste Management

- Landfills
- Biological waste treatment as e.g. composting, drawing off air from waste handling areas

Basics for the treatment of the gases

Application	Methane concentration in the gas to be treated	Volume flow methane	Oxygen content	Pollutant content
	Vol. %	m^3/h	Vol %	
Biogas upgrading exhaust treatment	0.1-2	Depending throughput and technology of plant Example: 200 m^3/h offgas with 1,2 % Vol. CH4: 2,4 m^3/h	Depending on technology: 0-18	Depending on upstream treatment, possibly H_2S, siloxanes
CHP exhaust gas treatment (Example: 800 kW_{el}; lambda 1.5)	around 0.2; in some cases significant higher-	Exhaust gas: 1800 ppm CH_4 3,5 $m^3 CH_4$ /h Overall gas: 1940 m^3_n /h	at λ 1: 0 at λ 1.5: 6.2	Sulphur oxides, hydrogen sulphide, formaldehyde, NOx,

Basics for the treatment of the gases

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Enthalpy of reaction is - 890.95 kJ/mol (ΔG_0 = 780 kJ/mol, Scheutz 2009)

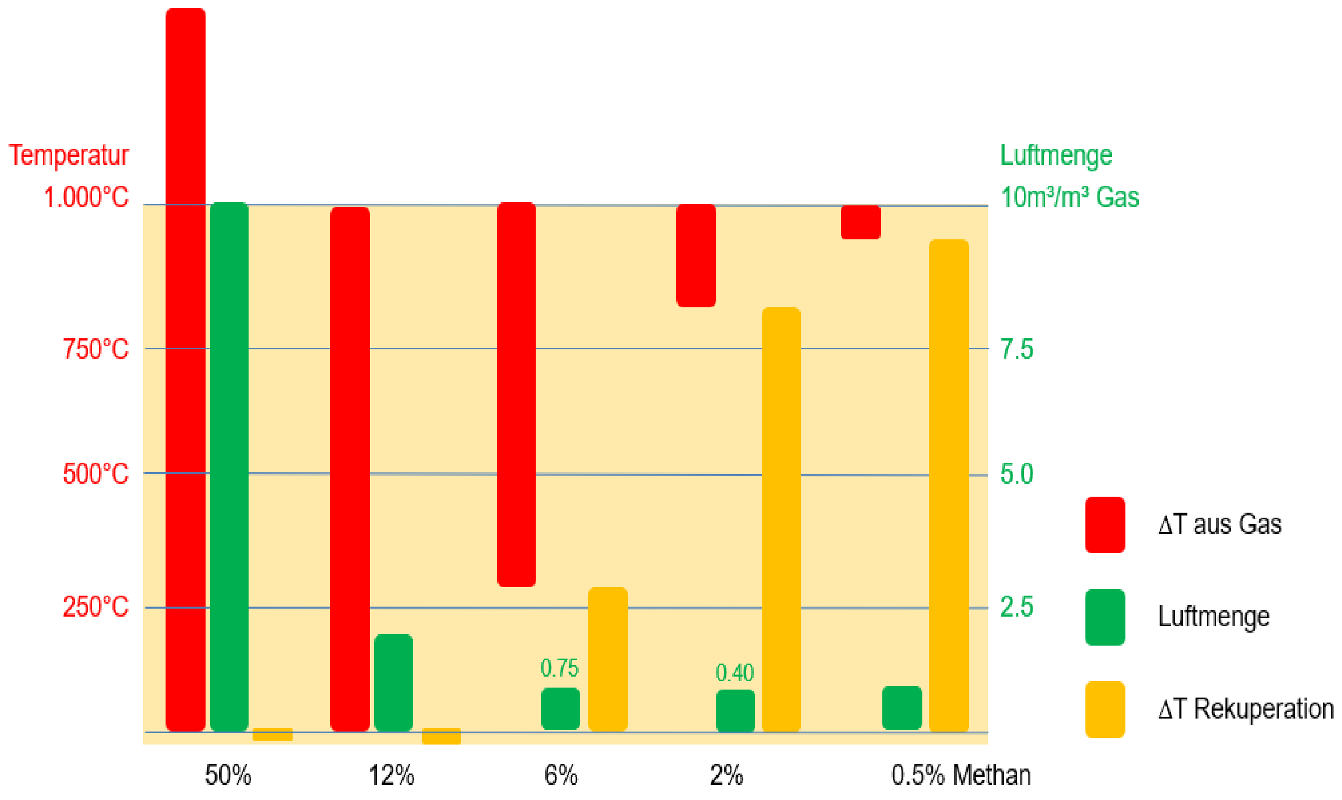
Parameter influencing oxidation process and technology

- methane concentration in fuel gas and fuel gas/air mixture,
- oxygen concentration,
- content of pollutants and/or
- concentrations and composition of other gases (e.g. water vapour, hydrogen sulphide)

Basics for the treatment of the gases - Oxidation process

- Retention time,
- Combustion temperature,
- Temperature distribution,
- Turbulence and
- (Excess) Oxygen

Basics for the treatment of the gases



Source: Ramthun 2022

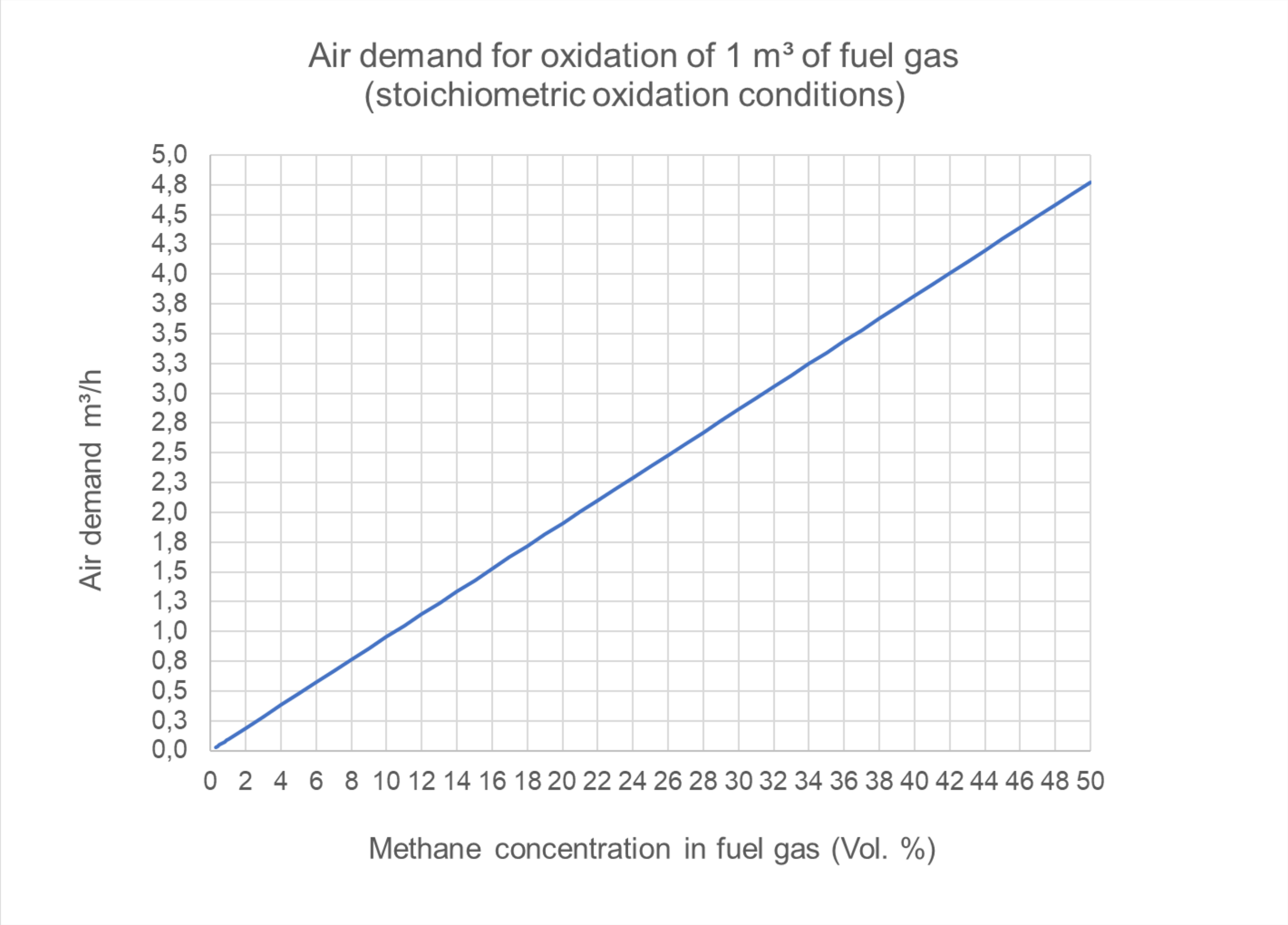
Air is added for oxidation and temperature control (Lambda)

At high methane concentrations air is needed to cool oxidation process

The lower the methane content the lower the temperature increase caused by the oxidation in the gas mixture

The lower the methane content, losses need to be minimized and heat needs to be recuperated to achieve required temperature levels

Basics for the treatment of the gases



Oxidation with a flame
- Flare
- CHP

Flameless oxidation
- Flare like applications
- E Flox
- RTO
- Catalytic oxidation

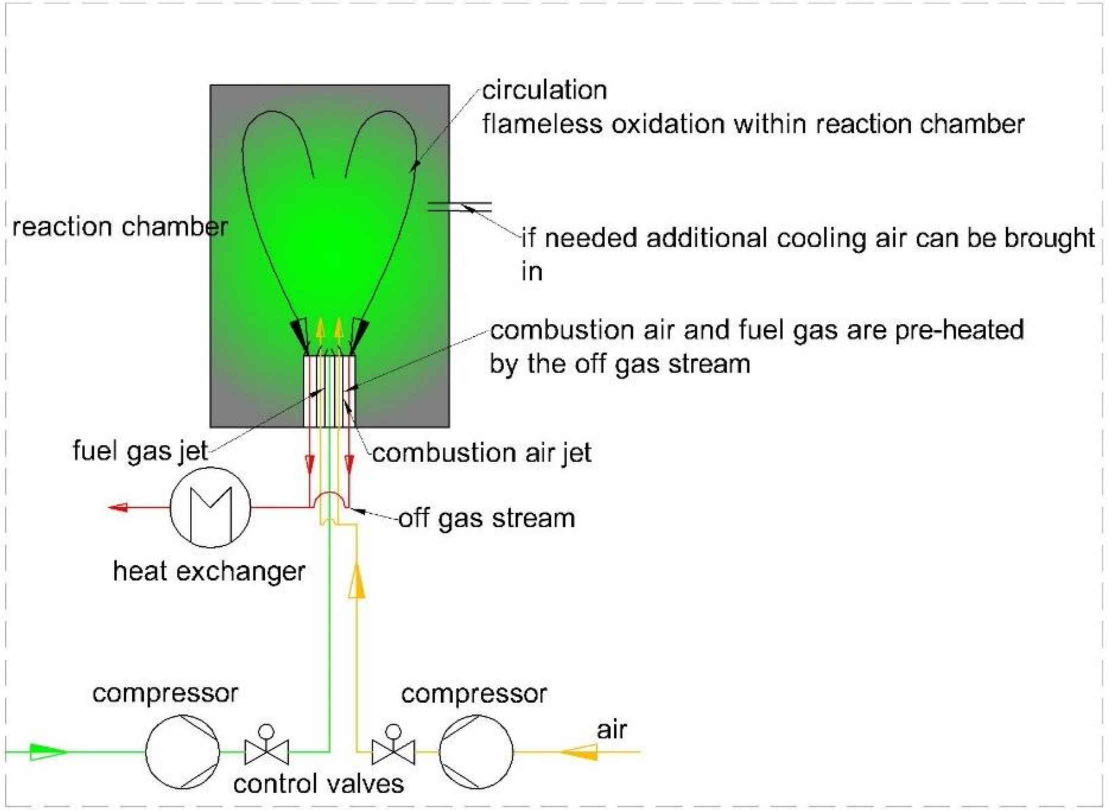
Biological oxidation
- Methane oxidation filter

Co-inceration

Basics for the treatment of the gases

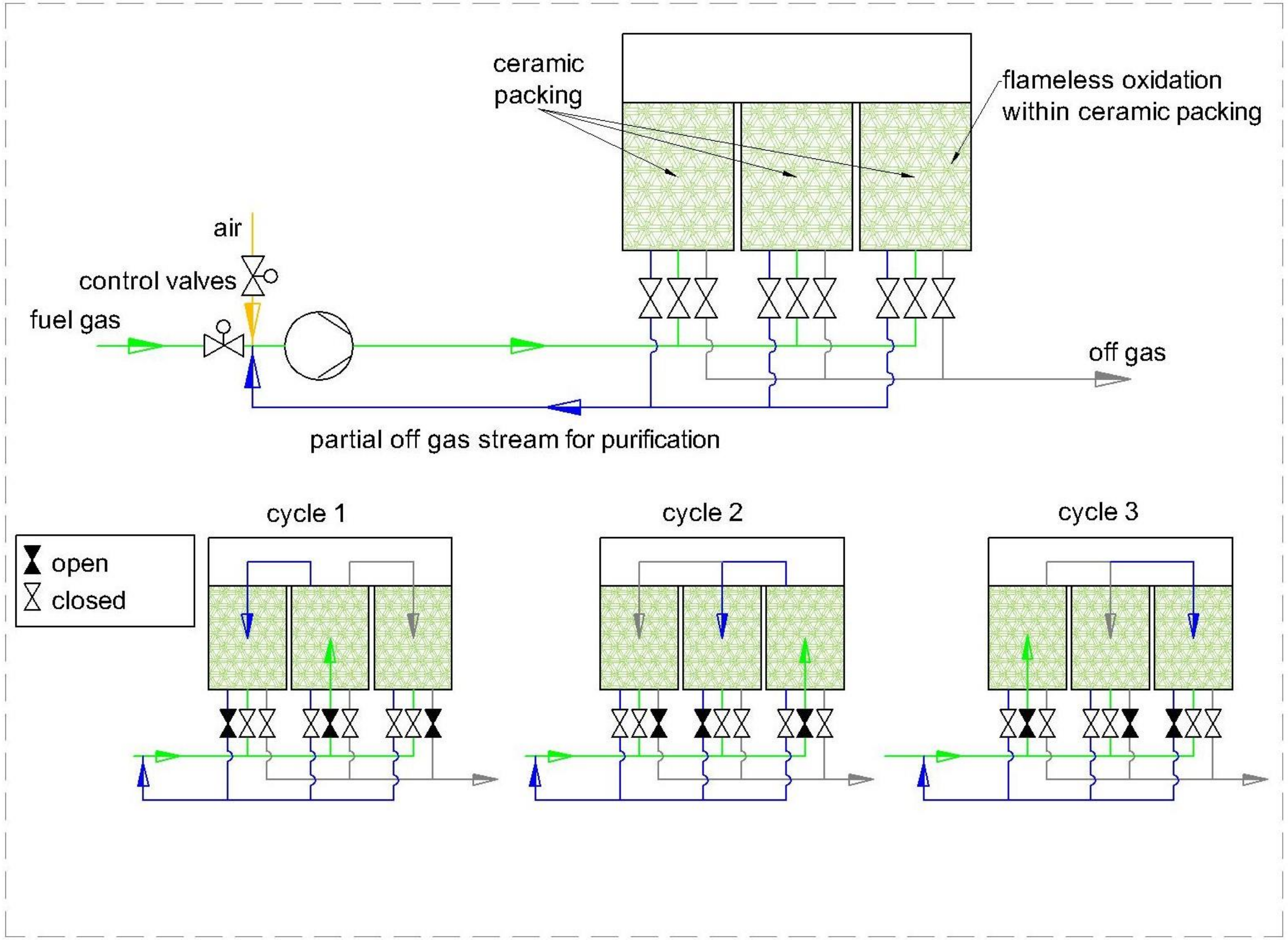
Technology	Concentration of methane in fuel gas (oxygene free)	Remark
Combined heat and power unit (CHP) CHP with lean gas fuel mixer	20-100 Vol%	Low methane concentrations make the startup procedure difficult, lean gas mixers can add more fuel gas than the conventional mixers for natural gas or biogas
Flare	25-100 Vol%	Oxygen (air) supply and cooling by air is achieved by natural ventilation
Flare with controlled air supply	12-100 Vol%	Oxygen (air) supply and cooling air is added by means of a controller; operation of flare can be adjusted to changing conditions if needed (only relevant applications with changing gas composition (e.g. landfills)
Oxidation system with heat recuperation to air supply	6-100 Vol%	Heat recuperation and air supply can be adjusted to changing conditions if needed (only relevant applications with changing gas composition (e.g. landfills)
Oxidation system with heat recuperation to air and fuel gas supply	(2) 3-100 Vol%	Heat recuperation and air supply can be adjusted to changing conditions if needed (only relevant applications with changing gas composition (e.g., landfills)
Regenerative thermal oxidation	0,37 – 100 Vol%	High methane concentrations are causing high costs for air addition

E Flox Process



- Flameless oxidation
- Efficient oxidation – also for natural gas
- Heat Recuperation through burner design and mixing of exhaust and incoming gases in chamber
- Different Burner designs allow different process parameter

Regerative thermal oxidation



- Heat exchange on ceramic packing material
- Discontinuous, changing flow directions
- Reduction of heat losses
- Low off gas temperature
- High heat regeneration capacity
- Autothermic from about 0,37 Vol. CH_4
- 2 chamber and 3 chamber systems
- Simple process
- Energy intensive start up process

Biogas upgrading

- Upgrading removes CO_2 from Biogas to reach standard gas composition (most often natural gas)
- Different technologies are applied to achieve that
- Methane slip is different for the technologies
- According to regulations and plant specific permission the slip is emitted directly or treated
- The regulations refer usually to legislation for clean air as well as regulations for eligibility for support mechanism within the renewable gas utilization
- Monitoring is varying

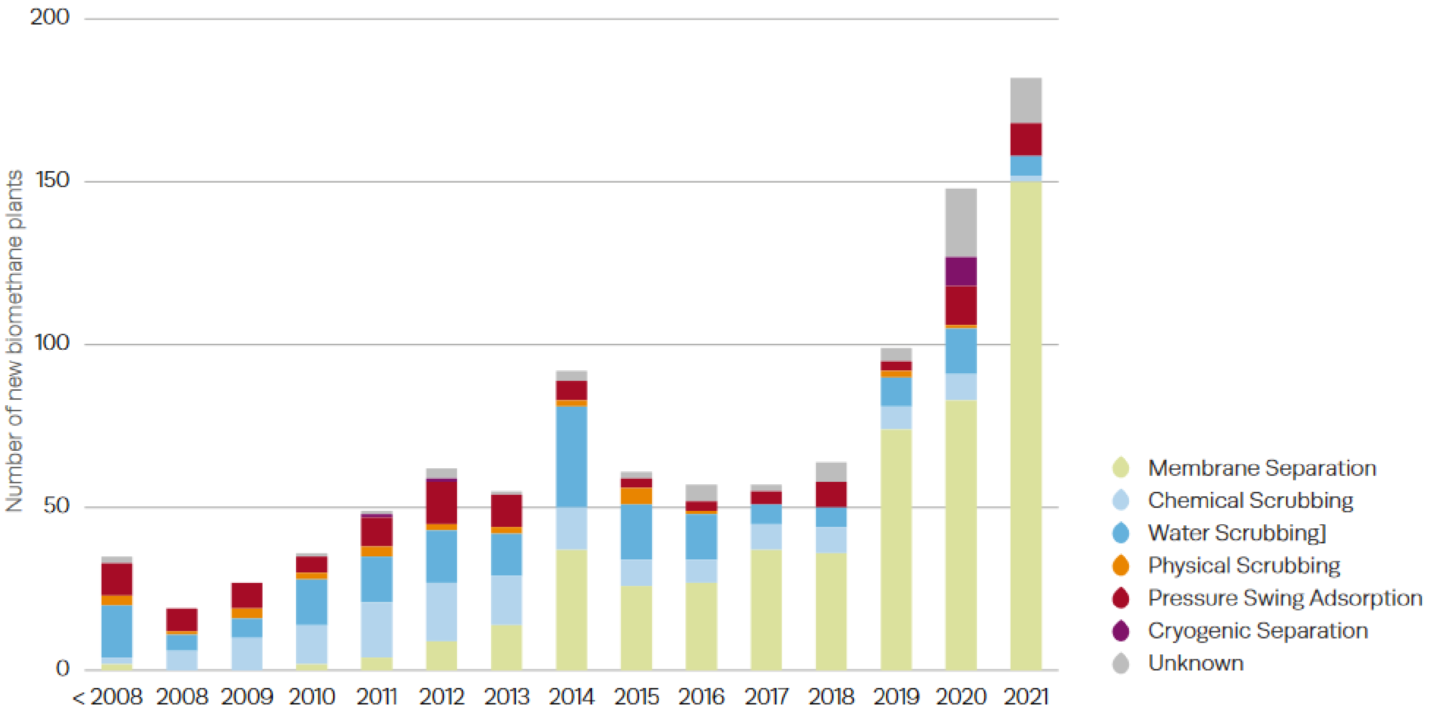


Figure 2.15 – Number of new biomethane plants in Europe per upgrading technology, 2008 – 2021

Source EBA 2022

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Biogas upgrading - options to reduce emissions

1. Optimization of upgrading technology to reduce methane slip
2. Combination of upgrading and subsequent methane oxidation in post treatment
3. Combination of biomethane upgrading and CO_2 liquefication – if the liquefication exhaust is recycled back to the upgrading or utilized, the emissions are reduced
4. Parallel upgrading (e.g. for a local fueling station) and CHP operation – the upgrading exhaust can be recycled into the raw gas and used in the CHP, works only for a fraction of the biogas to the upgrading - until the methane concentration is too low for efficient upgrading and CHP operation.
5. (Co-Incineration of off gases)

Biogas upgrading – methane slip from upgrading

Biogas upgrading technology	Methane slip (Vol% from upgraded methane)	Sources
Pressure swing adsorption (PSA)	< 2 1.8-2	Angelidaki et al. 2018 Bauer et al. 2012
Water scrubber	1.1-2 < 2 1	Kvist and Aryal 2019 Angelidaki et al. 2018 Bauer et al. 2012
Chemical adsorption (Amin)	0.04-0.07 < 0.1 0.1	Kvist and Aryal 2019 Angelidaki et al. 2018 Bauer et al. 2012
Physikalische Adsorption (PGK)	2-4	Angelidaki et al. 2018
Membrane technology	0.5-0.6 < 0.6 0.7-1 0.5	Kvist and Aryal 2019 Angelidaki et al. 2018 Ardolino et al. 2017 Bauer et al. 2012
Cryogenic separation	2	Angelidaki et al. 2018

Biogas upgrading - methane slip from upgrading

- PSA and Water scrubber tend to be above 1 %,
- Membrane technologies between 0,5 – 1 %
- Chemical scrubbing processes (amine wash) below 0,1 %

Biogas upgrading - methane slip from upgrading

Membrane technology can control the methane slip by means of

- membrane used,
- dimensions of the membrane and
- the operation

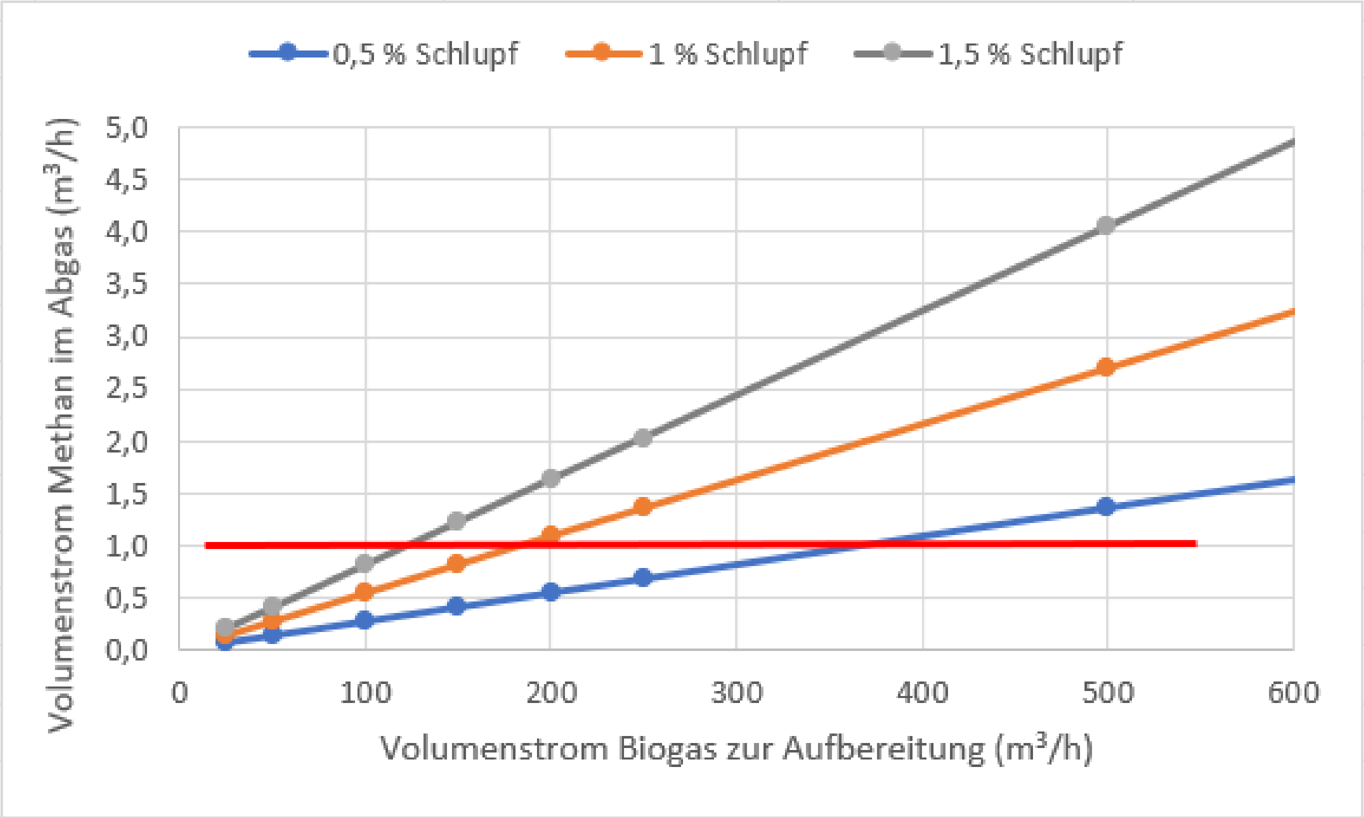
Effect is limited, costs are increasing due to higher throughput through compressor and more membrane area needed

Different manufacturer give 0,2 %; 0,5 and 1 % (for small plants) as limits to be achievable

Post treatment

Technical limits for Regenerative Thermal Oxidation

- < 10 kW or 1m³CH_4/h
  (app. Manufacturer given limit – no standard application in this size! So difficult to judge costs)
- 0.37 Vol. % methane in the fuel gas for autothermic conditions



Limits of treatment via regenerative thermal oxidation (RTO)

	Plant capacity					
	m³/h					
Biogas	92	185	370	740	1481	2963
Methane	50	100	200	400	800	1600
Carbon dioxide	41	83	167	333	666	1333
Methane slip	Volume flow of methane in the exhaust gas					
0,2%	0,1	0,2	0,4	0,8	1,6	3,2
0,5%	0,2	0,5	1,0	2,0	4,0	8,0
1%	0,5	1,0	2,0	4,0	8,0	16,0

Emission reduction on upgrading facilities

- Upgrading processes have different slip characteristics
- Amine wash has very low slip
- Membrane tend to have slip between 0,5 and 1 %, indifferent feedback from manufacturer
- Posttreatment with RTO has technical limits and high specific costs at small units

- Regulation for small plants (e.g. below 100 m^3CH_4/h) should reflect on that, or plants will have high specific costs

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