DVGW research centre at the Engler-Bunte-Institut
of the Karlsruhe Institute of Technology (KIT)

State of the Art and Perspectives of CO_2 Methanation Process Concepts for Power-to-Gas Applications

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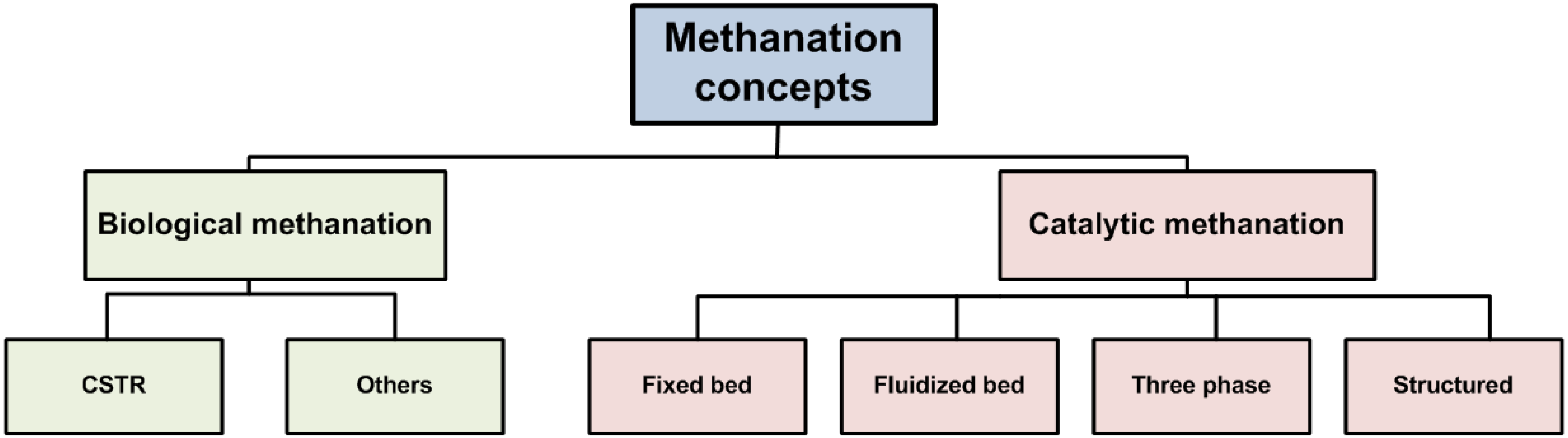


Overview

- Introduction
- Biological methanation concepts
- Catalytic methanation concepts
- Comparison
- Summary

Introduction

Fundamentals of methanation

Equations

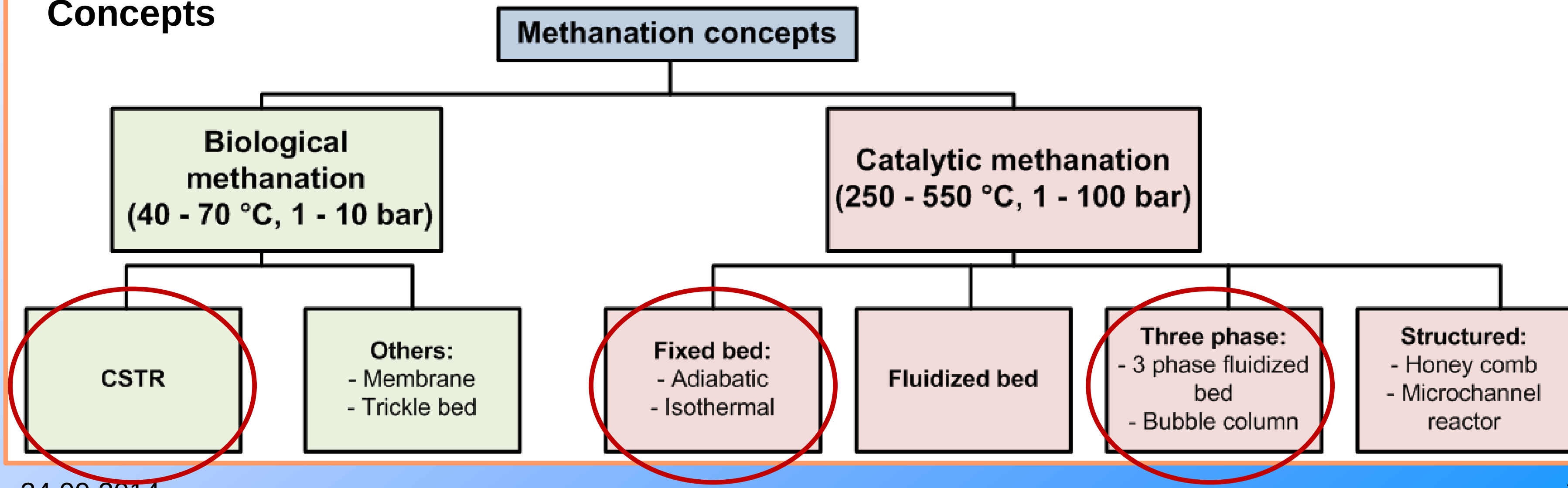
$CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O\,(g)$ $\quad \Delta_R h^0 = -206$ kJ/mol

$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O\,(g)$ $\quad \Delta_R h^0 = -165$ kJ/mol

$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O\,(l)$ $\quad \Delta_R h^0 = -253$ kJ/mol

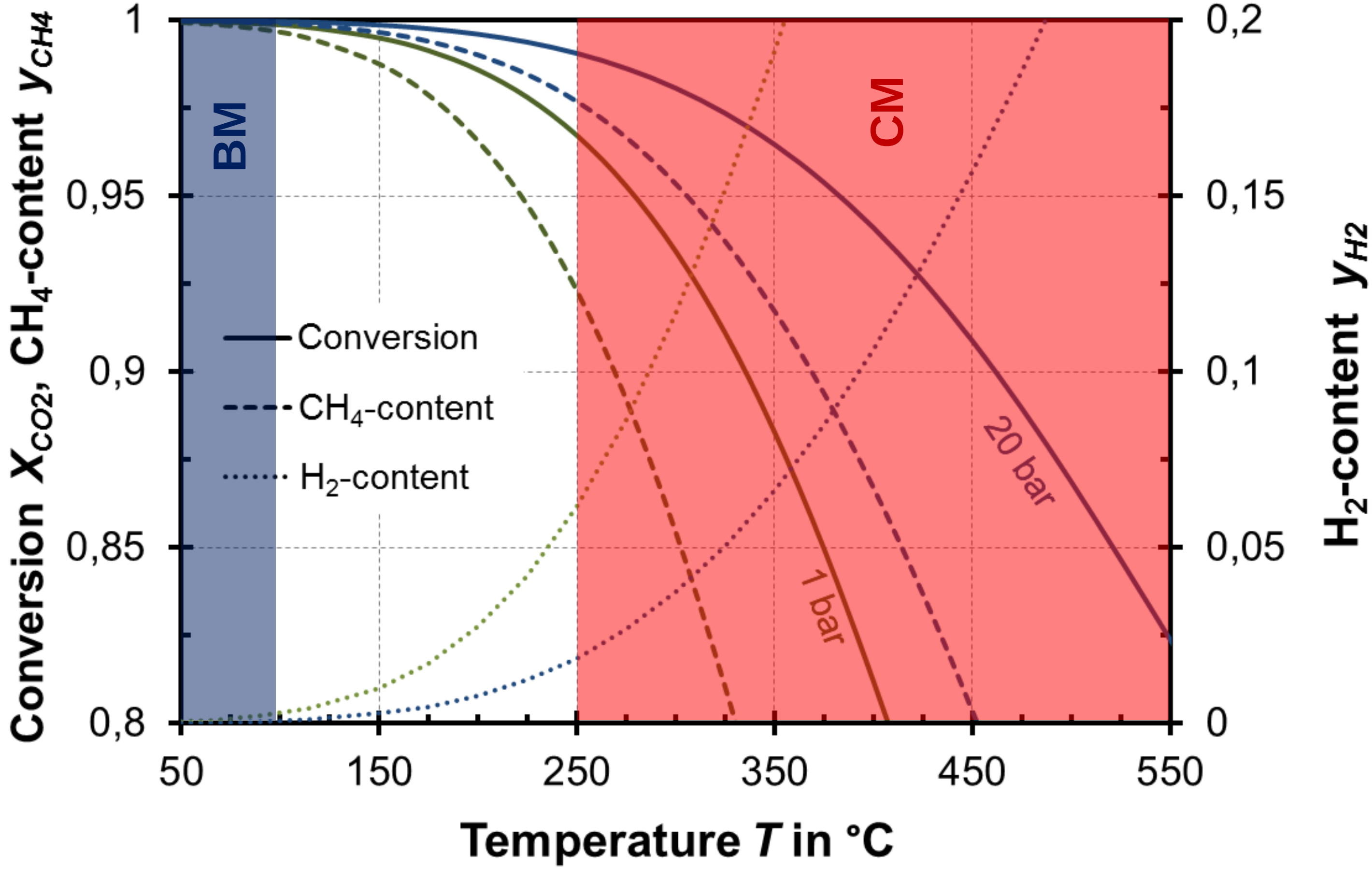
- Methanation is highly exothermic
- ⇨ Removal of reaction heat is a significant issue
- Usually, nickel-based catalysts are used for catalytic methanation

Concepts



Introduction

Equilibrium conversion ($H_2/CO_2/CH_4$ = 4/1/1)



- No thermodynamic limitation for biological methanation
- Catalytic methanation is limited by equilibrium, especially at 1 bar

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Biological methanation concepts

Overview and tasks

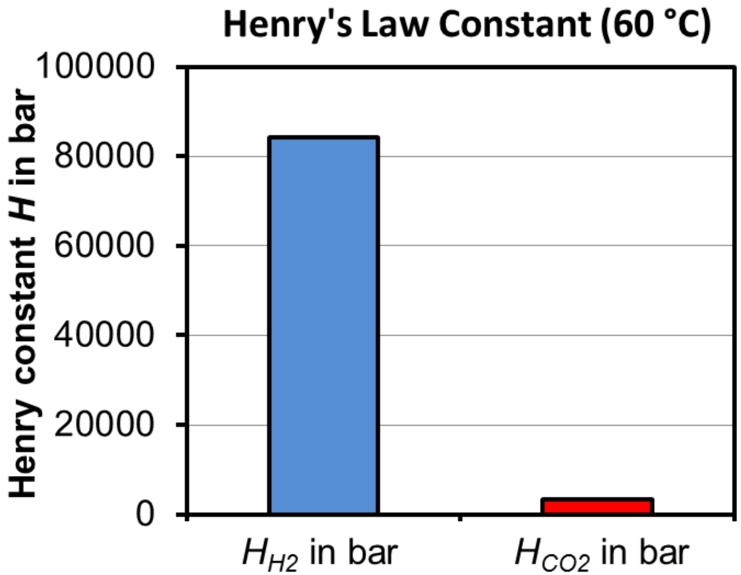
Process Overview

- Microorganisms serve as biocatalysts
- Proceeds at low temperatures (40 to 70 °C)
- Discovered in 1906
- So far no technical application for SNG production

Technical tasks

- Upscaling from lab scale reactors to industrial plants
- Supply of hydrogen to the microorganisms

⇨ Poor solubility of H_2 in fermentation liquid (CO_2 is 25 times more soluble than H_2)

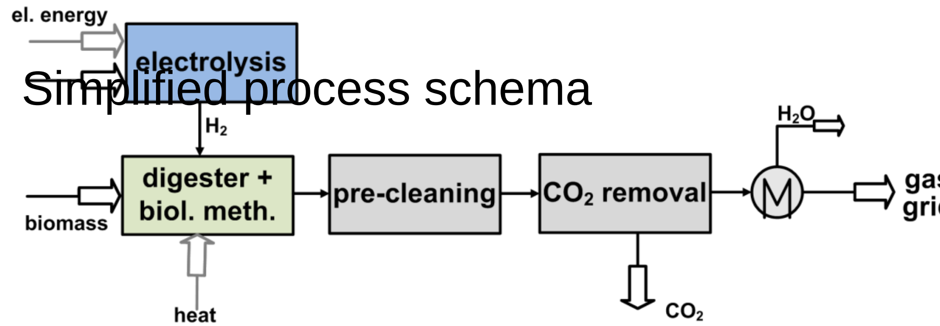


Biological methanation concepts

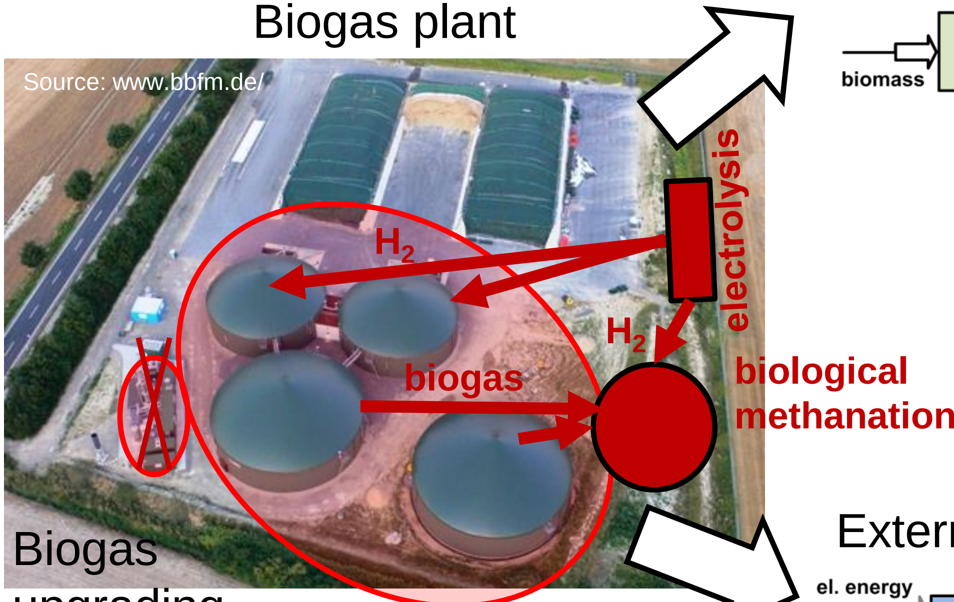
Concepts

H_2 addition to biogas digester

Simplified process schema



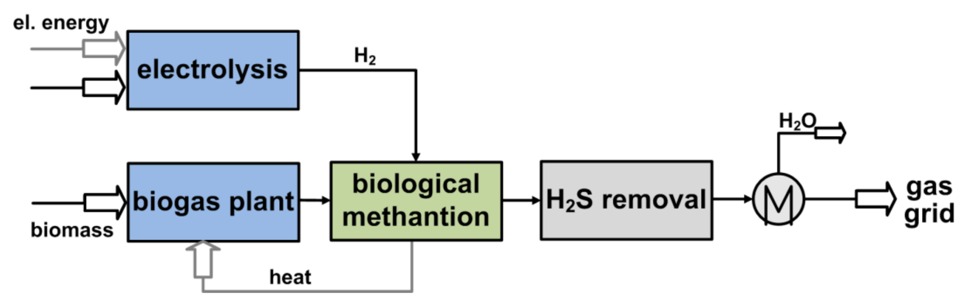
Biogas plant



Biogas upgrading

digesters

External reactor



Biological methanation concepts

In situ vs. external

Methanation in the biogas digester

- No further reactor necessary
- Limited to biogas as carbon source
- Process conditions determined by biogas process
- Increase in CH_4 content (e. g. 50 to 75 %)
- Safety aspects need to be considered

External biological methanation

- Further reactor necessary
- Pure cultures are used
- Process conditions and reactor design adjusted to biol. methanation
- High CO_2 conversion possible

	in situ	external
T in °C	40	65
p in bar	1	> 4
CO_2 Conversion > 95 %?	No	yes
Electrical Energy Demand in kWh/m³ SNG	1.8	0.4 - 1.3
Specific Investment Cost for a 5 MW SNG Plant in €/kWh SNG	≈ 400	≈ 600

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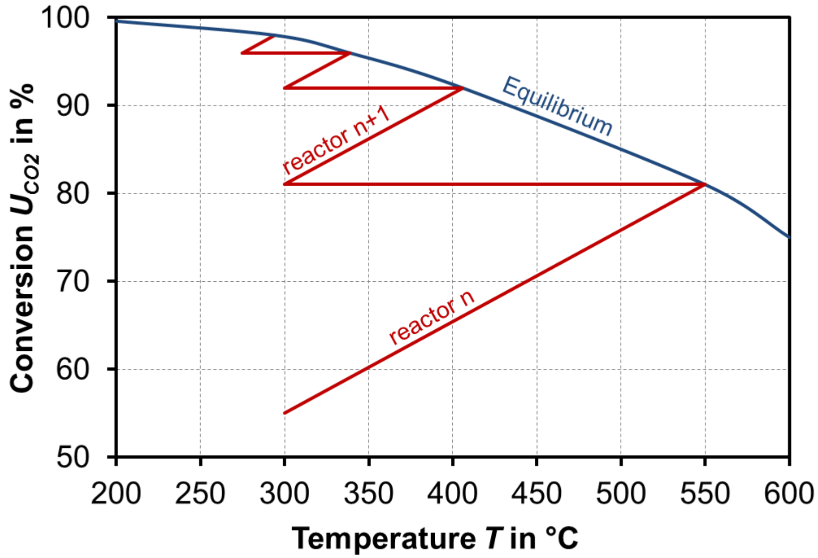
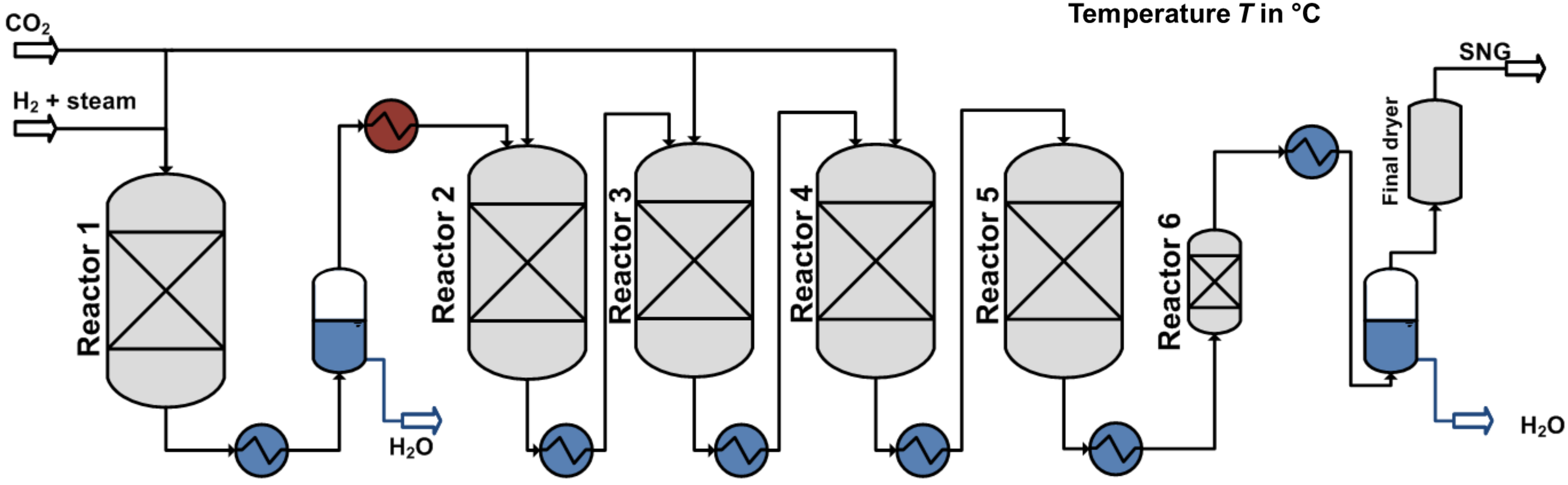
Catalytic methanation concepts

Adiabatic fixed-bed methanation (AFB)

- Reactor is packed with catalyst
- Several reactors in series with interstage cooling
- Some concepts use recycle streams
- State of the art
- Commercial SNG plants are based on this concept (e.g. Great plains, USA)

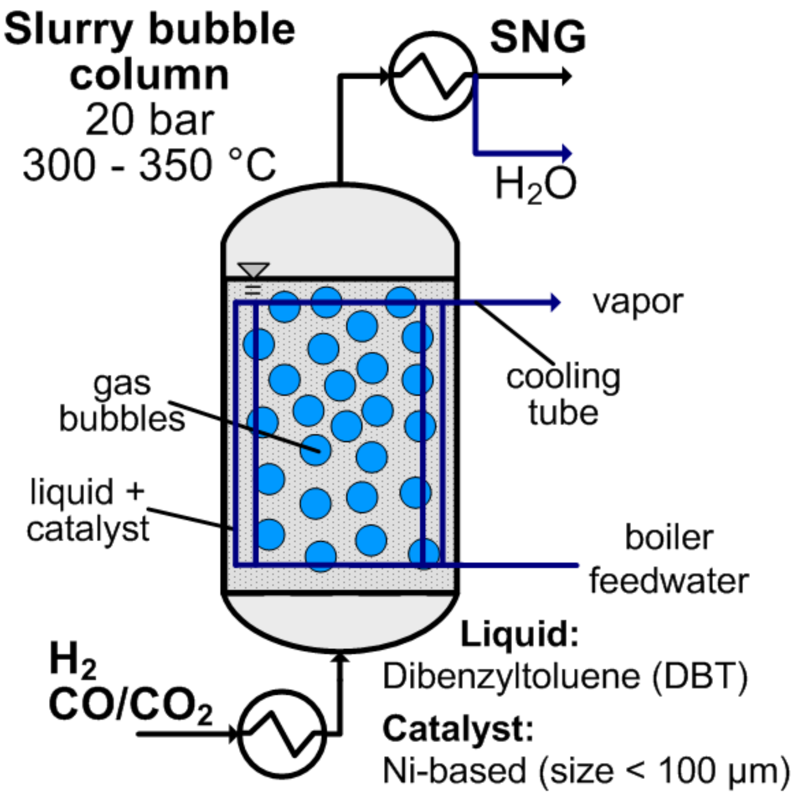




Catalytic methanation concepts

Three phase methanation (3PM)

- Catalyst (< 100 µm) is suspended in an inert liquid and (indirectly) fluidized by the feed gas
- p = 20 bar; $T \approx 300$ °C
- Developed at EBI, KIT



Advantages

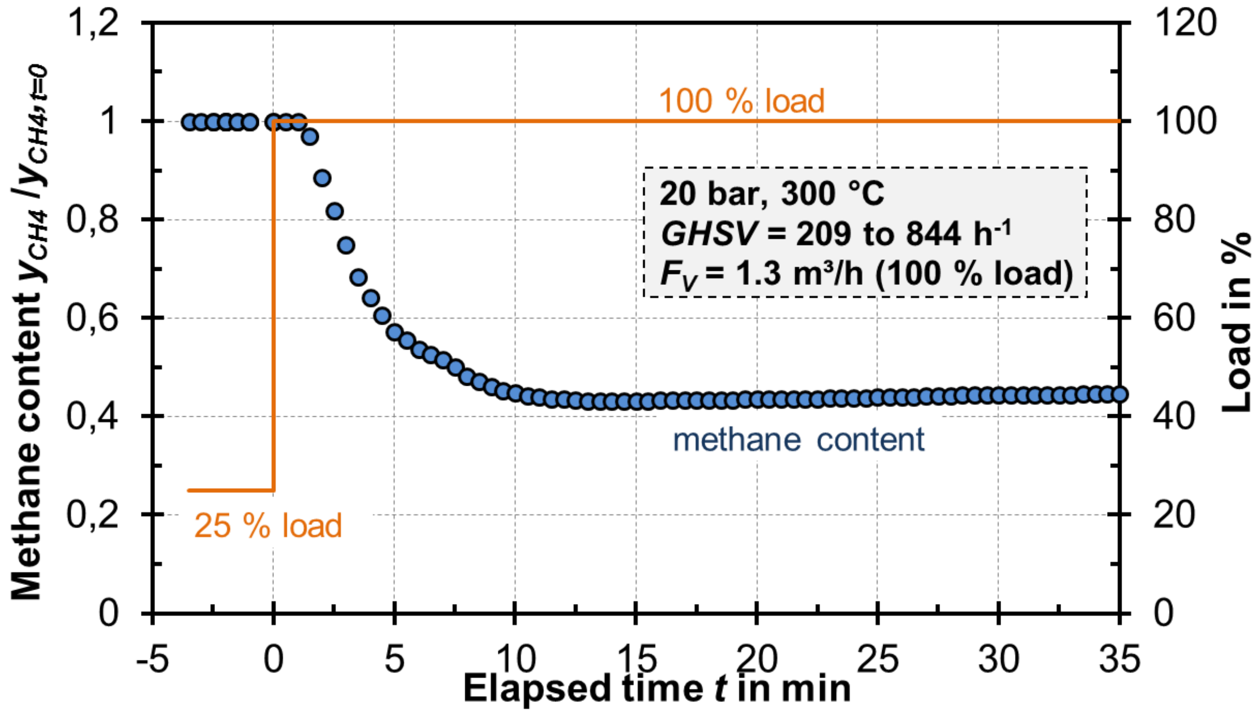
- High heat capacity of the liquid
- High thermal conduction
- ⇨ Simplified removal of reaction heat
- ⇨ Isothermal operation possible
- Simple process design
- Catalyst replacement during operation

Drawbacks

- Evaporation and decomposition of the suspension liquid
- Liquid-side mass transfer limitations

Catalytic methanation concepts

3PM: dynamic operation



- Less than 10 min to reach steady-state operation after load change
- Reactor reset time only depends on the gas velocity

⇨ Reactor hydrodynamics and reaction kinetics are not the limiting factors

- Fast load change possible

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Comparison

Technical parameters

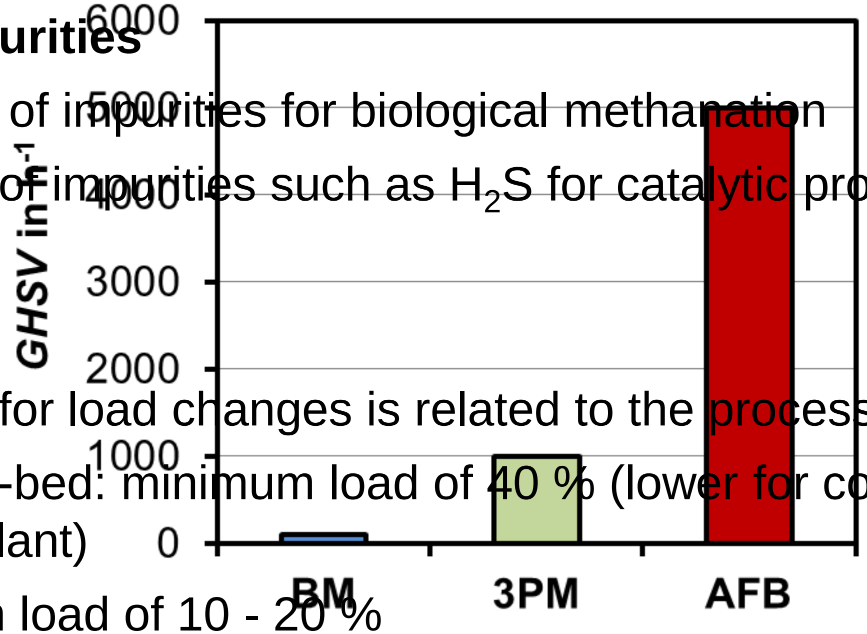
Gas Hourly Space Velocity *(GHSV)*

- Fixed-bed: highest operation temperature

⇨ Highest *GHSV* and therefore smallest reactor volume for a certain feed stream

Tolerance to impurities

- High tolerance of impurities for biological methanation
- Low tolerance of impurities such as H_2S for catalytic processes (3PM, AFB)



Flexibility

- Limiting factor for load changes is related to the process control system
- Adiabatic fixed-bed: minimum load of 40 % (lower for cooled fixed-bed such as in Welte PtG plant)
- 3PM: minimum load of 10 - 20 %
- Low minimum load for biological methanation

Comparison

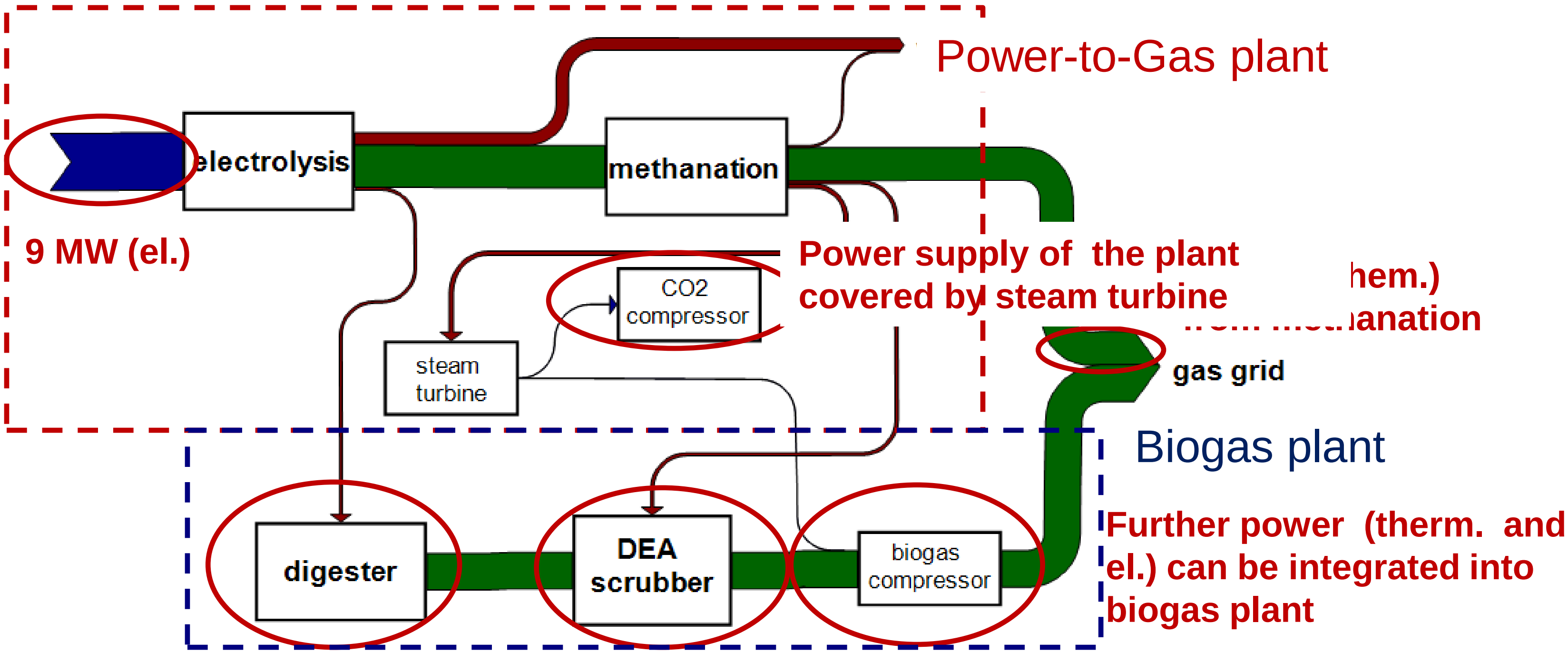
Efficiency

Biological methanation

- Additional power demand from the stirrer
- Opportunities for utilization of waste heat are sparse (low temperature level)

Catalytic methanation

- Heat can be used for steam/power production



Comparison

Efficiency

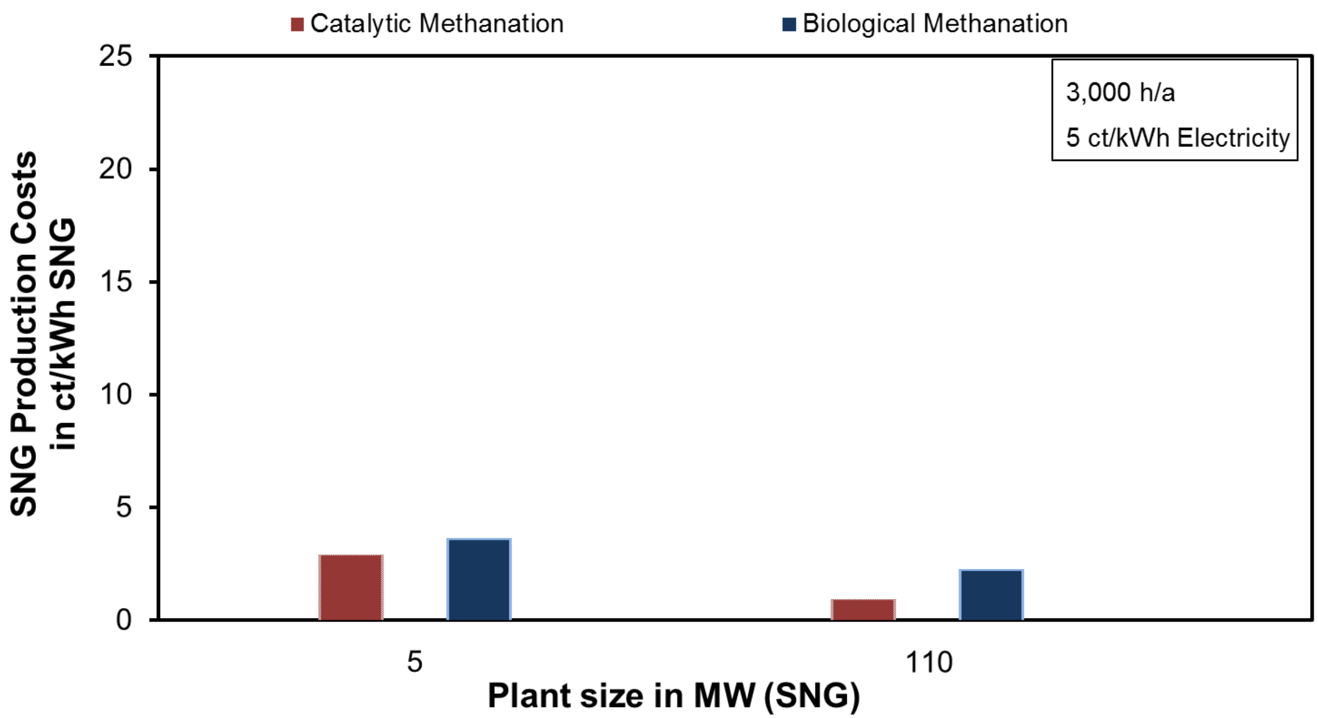
Comparison of methanation technologies

	Biological	Catalytic
Electrolysis	9000 kW	
Chemical output in product	5200 kW	
Power demand for PtG plant	150 – 560 kW	-
Further power/heat utilization	420 kW	1000 kW
Efficiency PtG in %	**59 – 61**	**69**

Higher efficiency for catalytic methanation

Comparison

Economics



- Small plant size: production costs for biological methanation are only slightly higher
- Large plant size: production costs for biological methanation are nearly 2.5 times that of catalytic methanation
- For all cases the costs for hydrogen production are the most significant contributor

Summary

Reactor Type	Biological methanation	Three phase methanation	Adiabatic fixed-bed
T in °C	40 - 70	300 - 350	250 - 550
p in bar	> 4	> 20	> 5 - 10
Stage of development	lab scale/pilot	lab scale	commercial
GHSV in h^{-1}	< 100	500 - 1,000	2,000 - 5,000
Tolerance of impurities	high	medium	low
Dynamic behaviour	good	good	medium
Efficiency PtG in %	60	69	69

- SNG costs depend on plant size, full load hours, methanation concept…
- ≈ 20 ct/kWh SNG

Take-home message

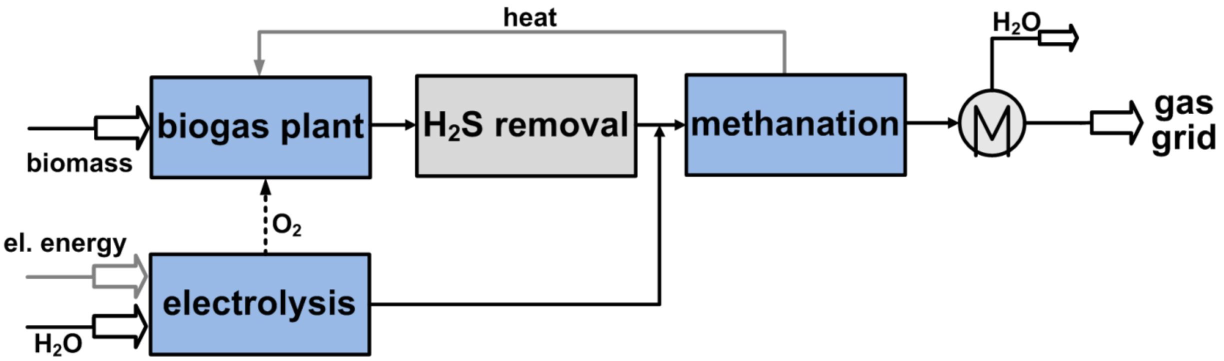
- Biological methanation is a robust process that is better suited for small plant sizes
- Catalytic methanation enables heat utilization and therefore higher efficiency
- Costs for hydrogen production dominate the SNG costs

Appendix

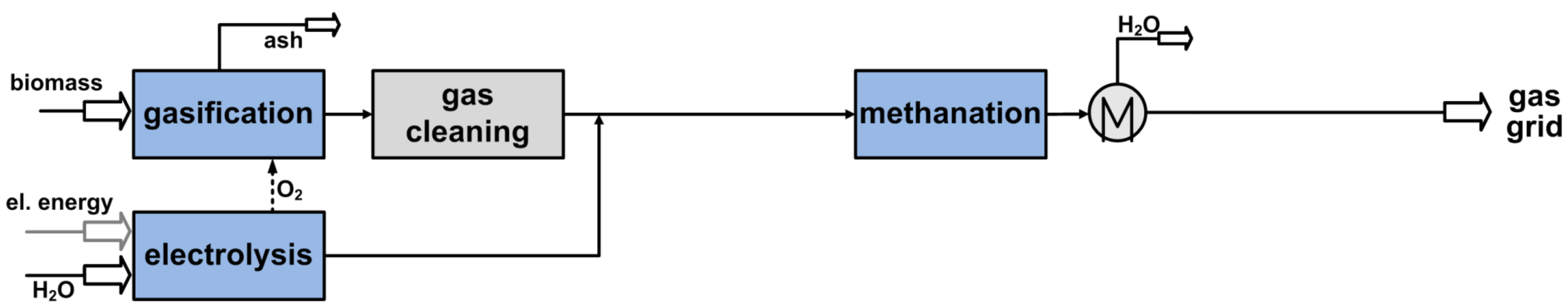
Introduction

Possible process chains

Power-to-Gas (PtG) + biogas



Power-to-Gas (PtG) + biomass gasification (BtG)



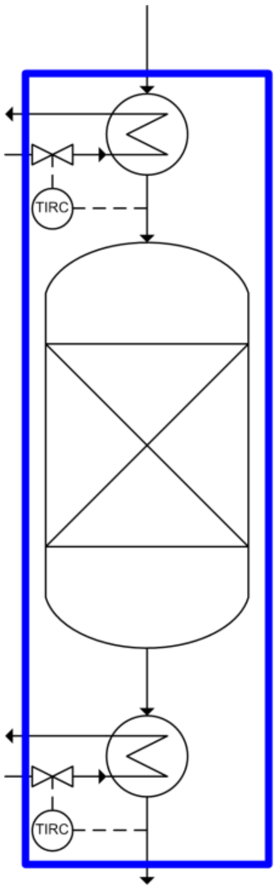
- Carbon exploitation can be increased by H_2 integration with biogas and BtG processes
- So far enough carbon sources are available

Catalytic methanation concepts

AFB: dynamic operation

Catalyst

- Temperature must always be in the range of 220 – 550 °C
- Effect of load change on catalyst lifetime?
- ⇨ Recent results indicate that load change does not significantly reduce the catalyst lifetime



Reactor reset time and minimum load

- Reaction responds immediately to load changes
- Reactor reset time is dominated by the process control, especially by the heat exchangers
- ⇨ The complex heat management for adiabatic fixed-bed methanation leads to a comparatively inflexible process
- Minimum load: 40 %

Improved dynamic behaviour if cooled fixed-bed reactors are used (such as in the Werlte PtG plant)