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Power-to-gas Technologies

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STORE&GO Workshop

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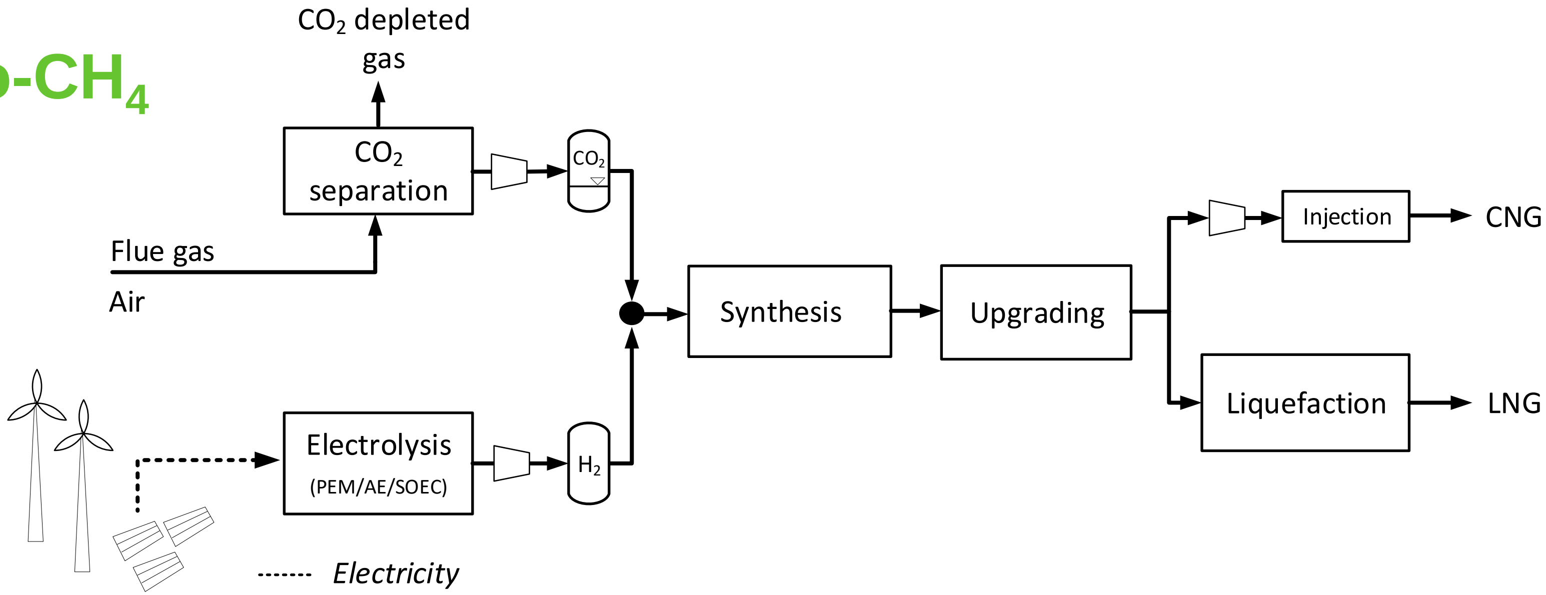
Power-to-CH_4

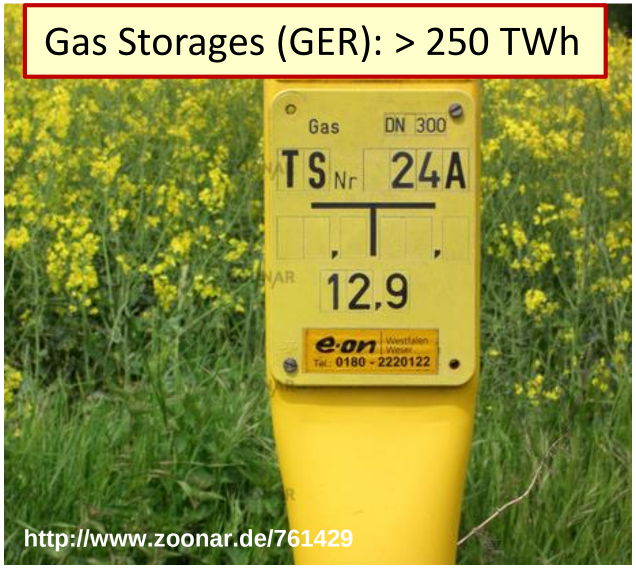


Session AGENDA: Technical Background

- **Electrolysis**
- **CO_2 separation and supply**
- **Methanation concepts**
- **Process integration**
- **Outlook for technological improvement**

Background…

The Gas Grid as Power Grid?



Long-distance gas pipeline

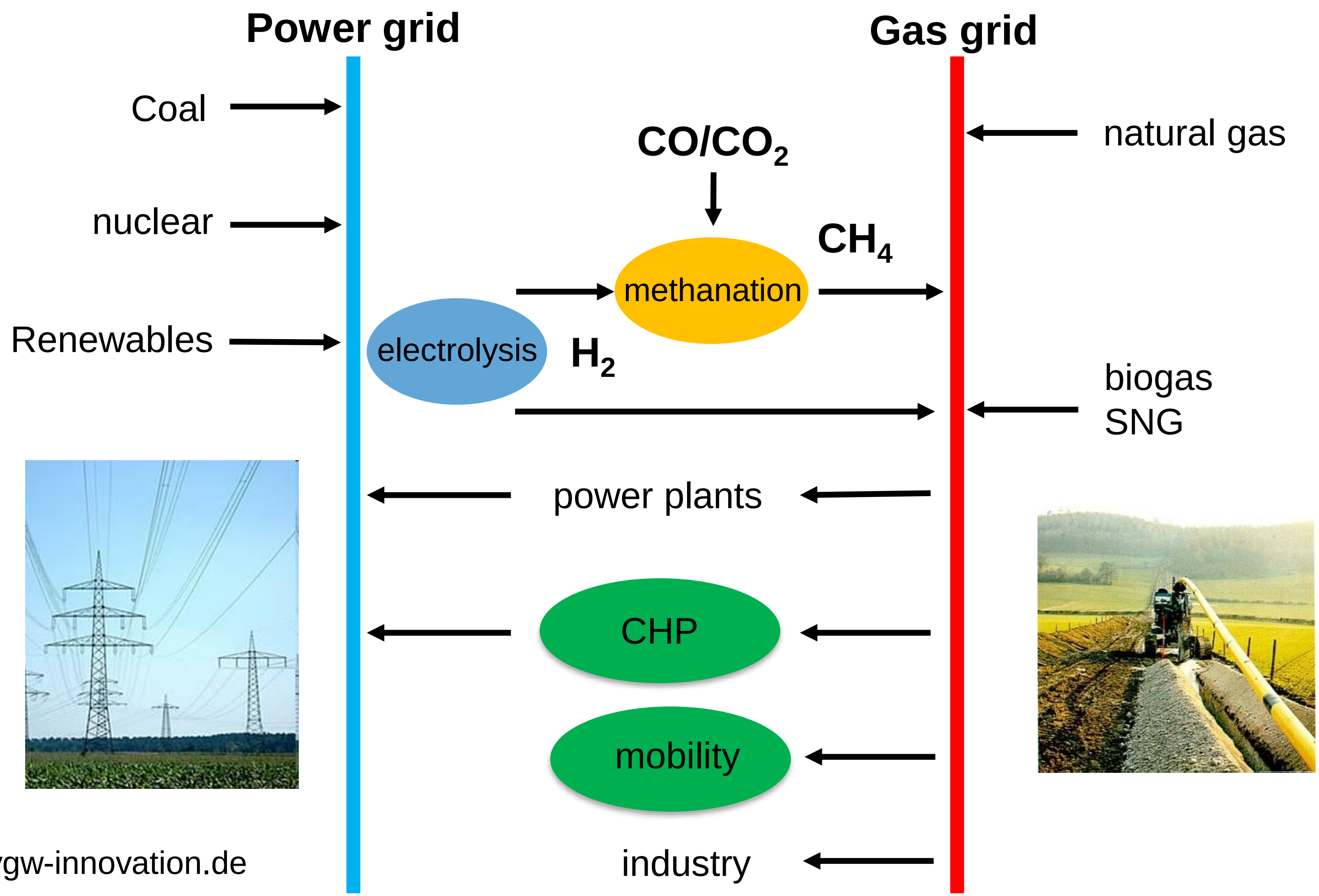
- 80 bar
- 1200 mm
- 50 GW
- 0.5 % loss on 500 km

High voltage aerial line

- 380 kV
- AC
- 2 · 1.8 GW
- 5 % loss on 500 km

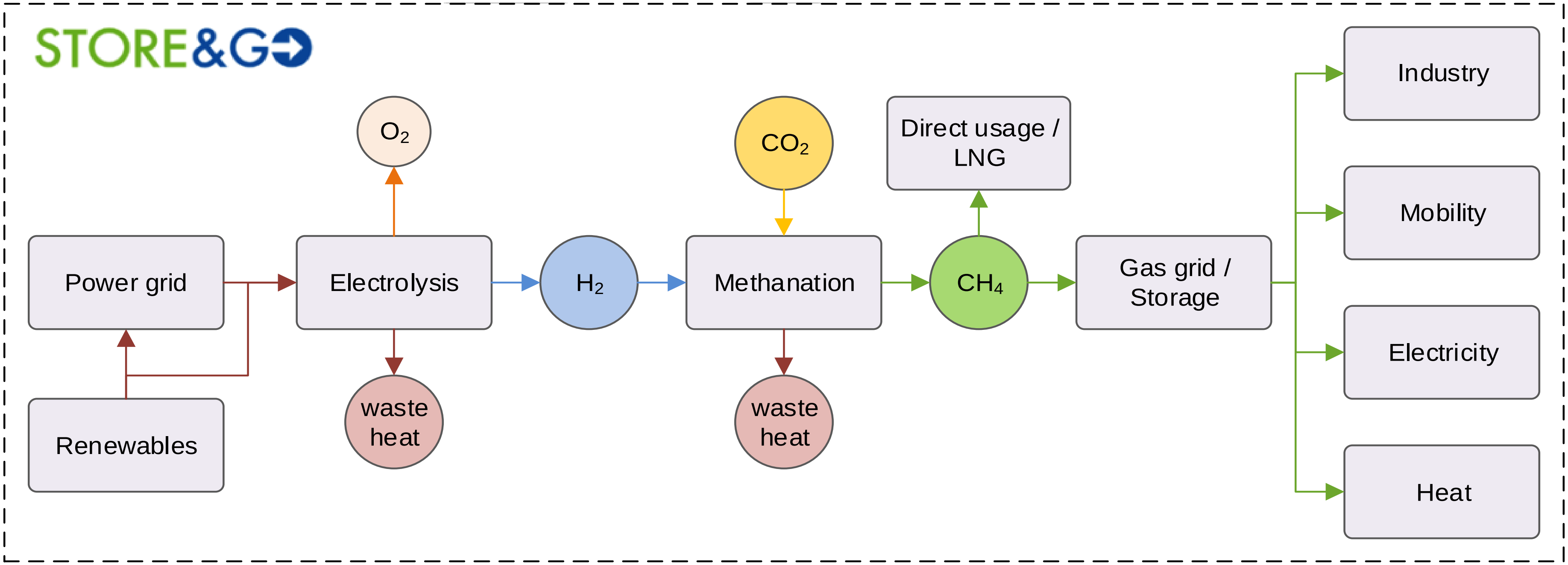
The „missing link“ between gas and power grid

=> new stimulus for methanation!



www.dvgw-innovation.de

Process chain of PtG within the project STORE&GO



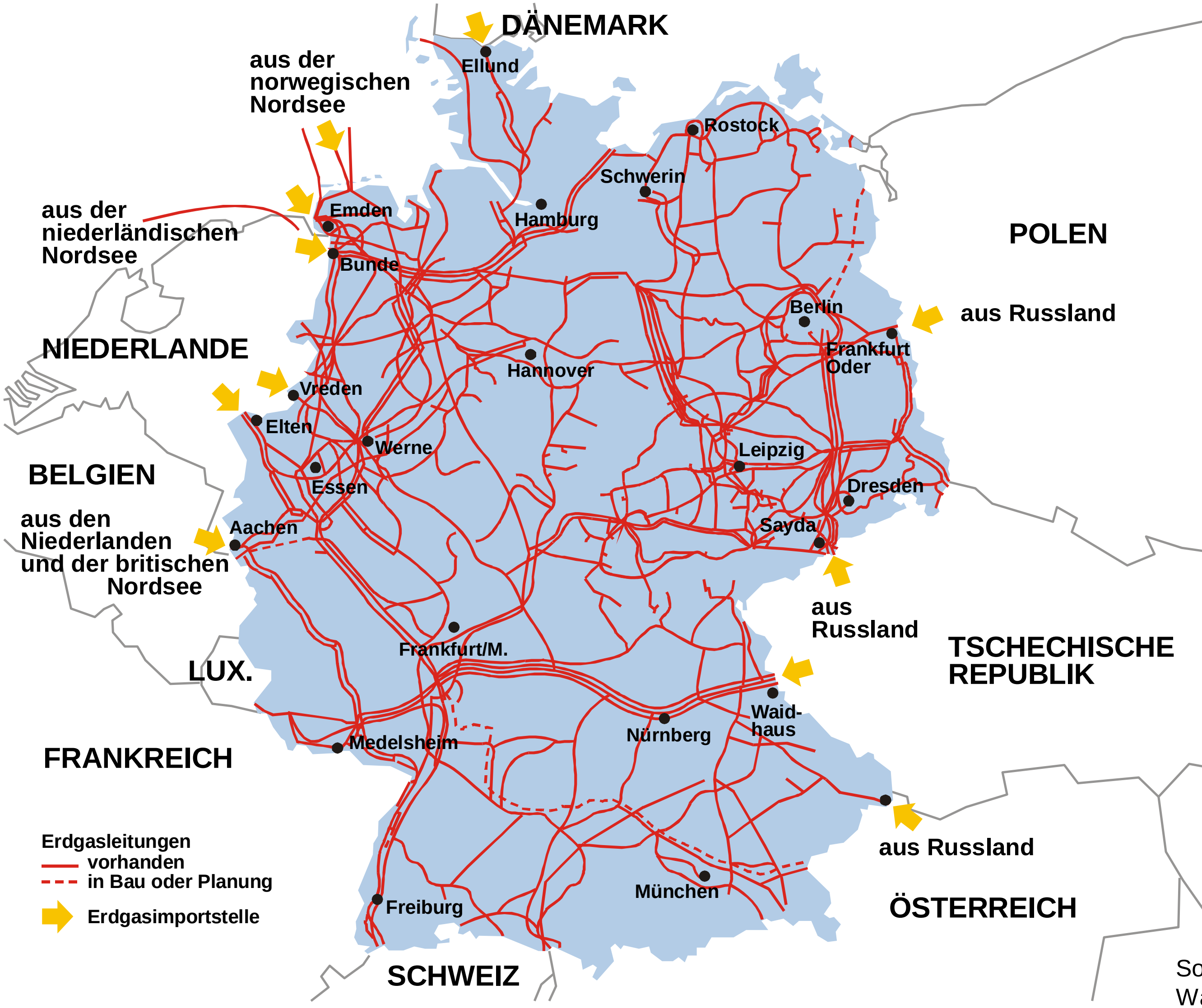
Focus on methanation; in accordance with funding call no H_2 investigated

Green molecules can be transported via existing gas infrastructure

- Europe has a well developed and highly integrated gas supply system
  - 2.2 Mio km of gas pipelines
  - 100 billion m³ of gas storage
- Highly efficient gas infrastructure
- The system can be used for efficient transport of energy (hydrogen & methane)

Source: Gas Innfrastructure Europe, Sytem Develoment Map

The natural gas grid in Germany – omnipresent!



Grid Connections:
19 Mio. households
= 50 %

Total NG demand
(2016 Germany)
= $84 \cdot 10^9$ m^3 (STP)
≈ $900 \cdot 10^9$ kWh

Source: Bundesverband der Energie- und Wasserwirtschaft e.V. (BDWE)

Limits for (direct) H_2 injection: Technical limits

- Underground gas storage (porous rock):
  - H_2 consumption from bacteria and transformation into H_2S

    => (real) H_2 limit not yet identified (ongoing investigations)

- Steel tanks in natural gas vehicles (CNG technology):
  - H_2 diffusion into steel tanks => danger of serious tank ruptures!

    => H_2 limit is 2 vol.-% (DIN EN 51624)

    Bottleneck!

- Gas turbines:
  - H_2 addition in natural gas changes combustion properties

    => H_2 limit is max. 5 vol.-%

Limits for (direct) H_2 injection: Legal limits

Comparison of H_2 injection limits in Europe/Canada

Countries	Volumetric H_2 limit in %
Austria	4
Belgium	0.1
Canada	**5**
France	6
Germany	**2**
Italy	0.5
Sweden	0.6
Switzerland	4
UK	0.1

- No binding gas quality in Europe
- EU-wide regulations for natural gas and biogas are under development (prEN 16726, prEN 16723-1)
- Current regulations do not consider gases from PtX (e. g. no CO limit)

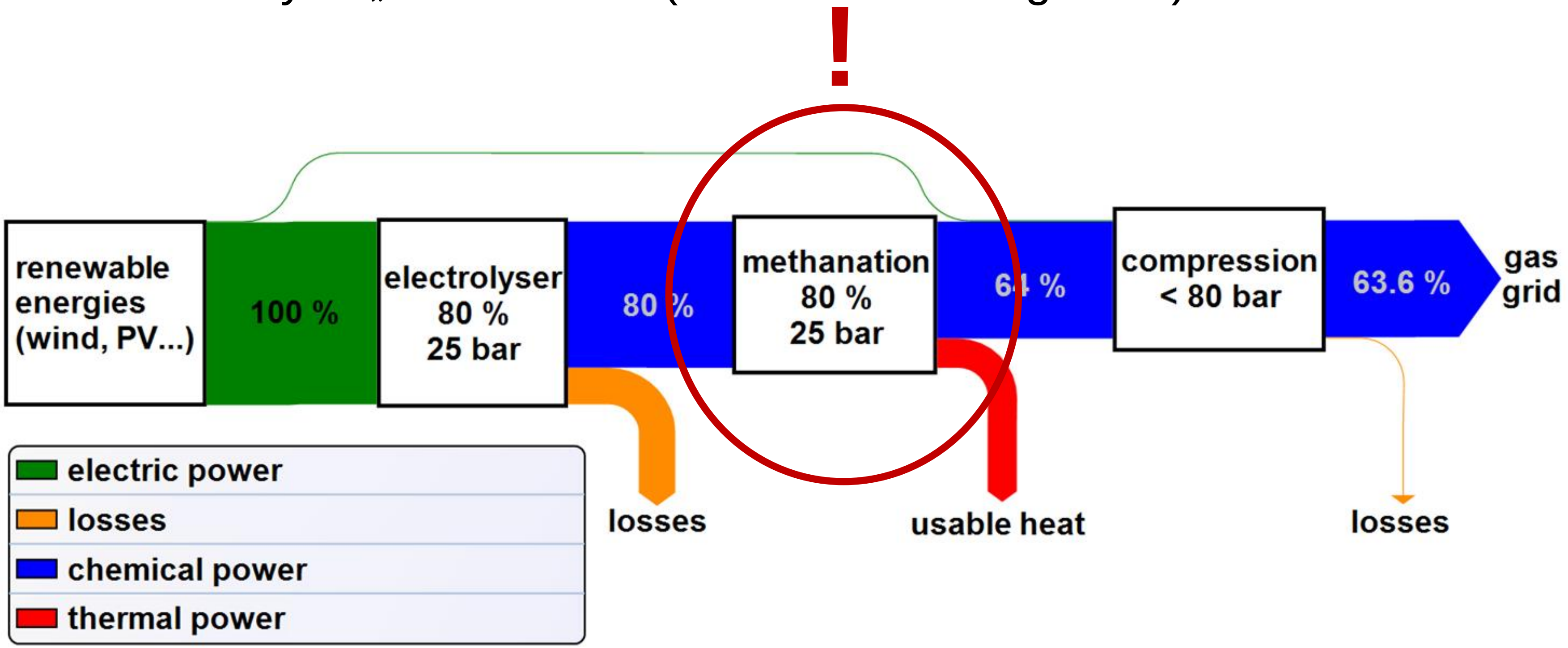
Source: EE Consultant, *Etude portant sur l´hydrogène et la méthanation comme procédé de valorisation de l'électricité excédentaire*, ADEME, 2014.

Walker et al., *Economic analysis with respect to Power-to-Gas energy storage with consideration of various market mechanisms*, International Journal of Hydrogen Energy, 41, 19, 7754-7765, 2014

Comparing CH_4 with H_2 production

Pro CH_4:
CH_4 is fully compatible with natural gas (grid, storage, applications)

Contra CH_4:
total efficiency of „PtM“ < 65 % (without heat integration)



Background: Conclusions

1. PtG links gas grid with power grid bi-directional
2. Chemical energy carriers are ideal energy storages
3. Hydrogen vs. Methane?

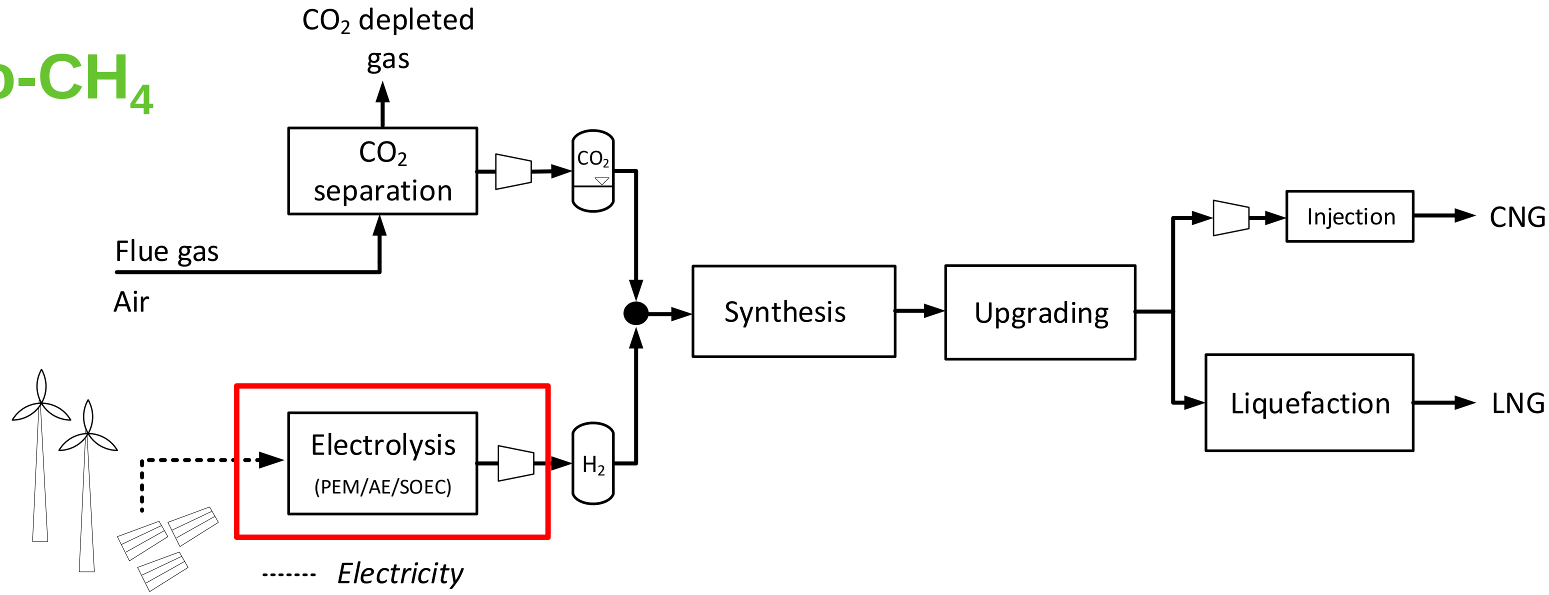
   - efficiency

   - constrains by established applications

   - (national/European) differences in regulations

Electrolysis

Power-to-CH_4



Session AGENDA: Technical Background

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- CO_2 separation and supply
- Methanation concepts
- Process integration
- Outlook for technological improvement

Electrolysis: Fundamentals

(Water-)**Electrolysis** => **Hydrogen** as main product

$$\mathbf{H_2O \rightarrow \tfrac{1}{2}\, O_2 + H_2} \qquad \Delta_R H = 286\ \text{kJ/mol}$$

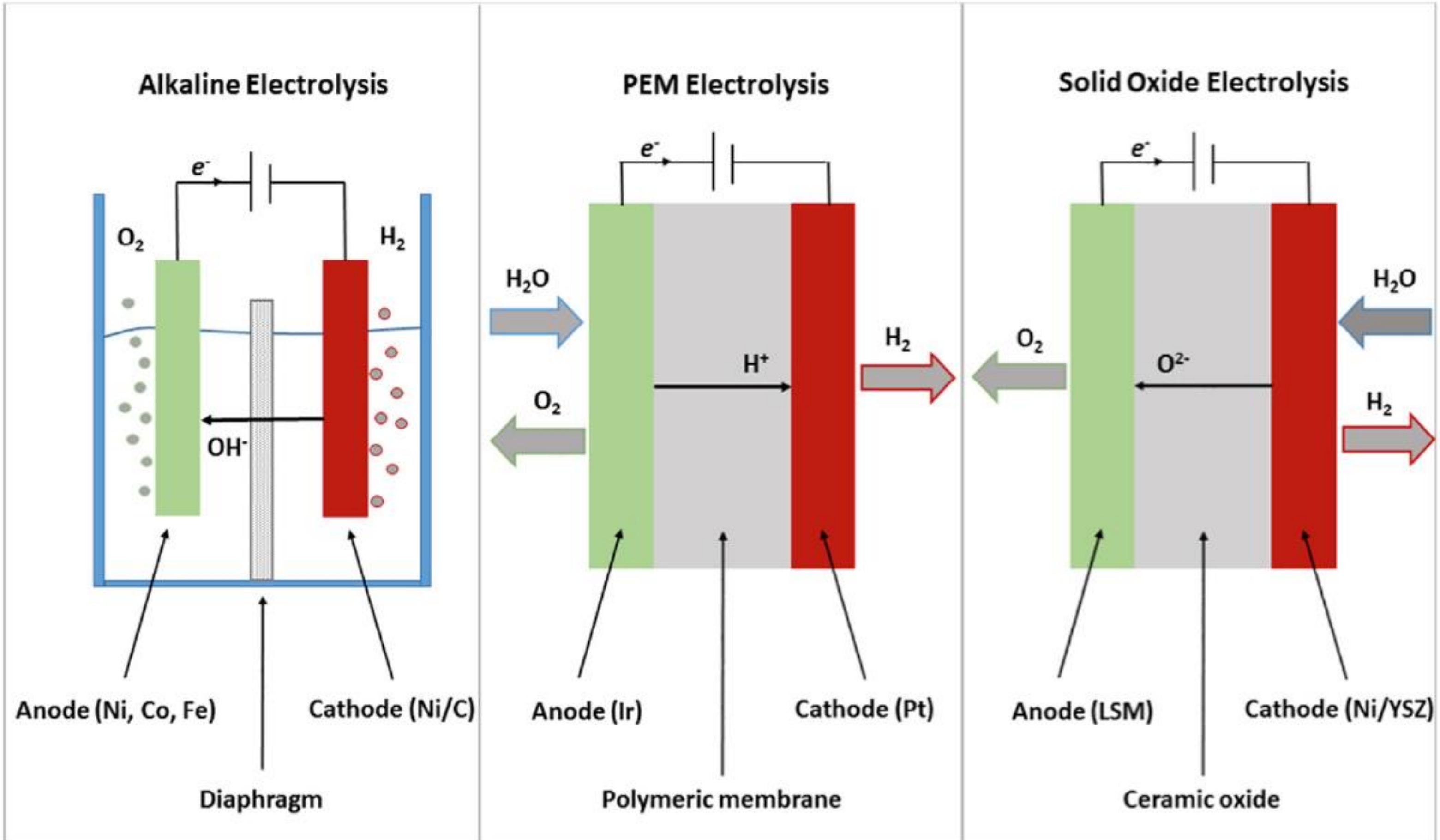
- Temperatures: 50 – 1000 °C [1, 2]
- Efficiency: 43 – 83 % [2]
- no „C" in educt → no „C" or CO_2 as by product
- oxygen (O_2) as by product value?!?

- keep an eye on the carbon footprint of the power source!

[1] T. Smolinka, M. Günther, J. Garche: Stand und Entwicklungspotenzial der Wasserelektrolyse zur Herstellung von Wasserstoff aus regenerativen Energien, Fraunhofer Institut für Solare Energiesysteme, 2010
[2] R. Bhandari, C.A. Trudewind, P. Zapp: Life cycle assessment of hydrogen production via electrolysis – a review, 2015

Electrolysis: Fundamentals

$$H_2O_{(l)} \rightarrow H_2 + \frac{1}{2}O_2 \qquad \Delta_R H^0_{298} = 286\ \frac{kJ}{mol}$$



	Alkaline Electrolysis	PEM Electrolysis	Solid Oxide Electrolysis
Anode	$4OH^- \rightarrow 2H_2O + 4e^- + \mathbf{O_2}$	$2H_2O \rightarrow 4H^+ + 4e^- + \mathbf{O_2}$	$O^{2-} \rightarrow ½\ \mathbf{O_2} + 2e^-$
Cathode	$4H_2O + 4e^- \rightarrow 4OH^- + 2\mathbf{H_2}$	$4H^+ + 4e^- \rightarrow 2\mathbf{H_2}$	$H_2O + 2e^- \rightarrow \mathbf{H_2} + O^{2-}$

F.M. Sapountzi et al. / Progress in Energy and Combustion Science 58 (2017) 1–35

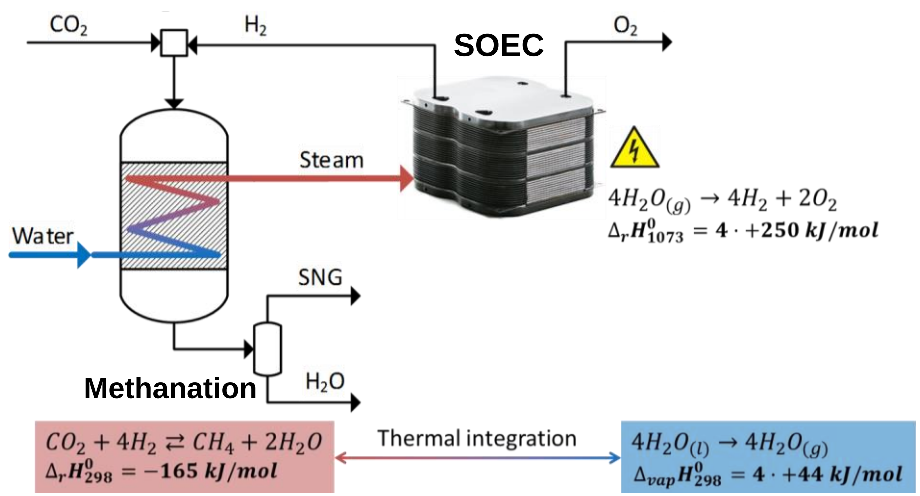
Electrolysis: SOEC

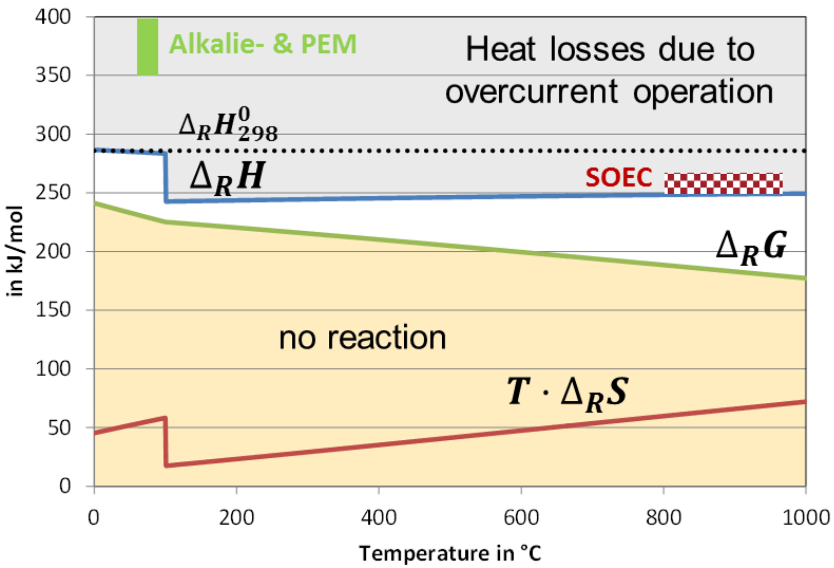
Only 87 % of 286 kJ/mol

$$H_2O_{(g)} \rightarrow H_2 + \frac{1}{2}O_2 \qquad \Delta_R H^0_{1073} = 250\,\frac{kJ}{mol}$$

HELMETH

Integrated **High**-Temperature **EL**ectrolysis and **METH**anation for Effective Power to Gas Conversion





$$\Delta_R H = \Delta_R G + T \cdot \Delta_R S$$

- Off-heat of methanation can be utilized for vaporization of water
- Heat can be incorporated instead of electricity at T ↑
- Overall efficiencies of near 100 % are possible with SOEC

➔ Further development of SOEC is important for PtX processes

Electrolysis: Conclusions

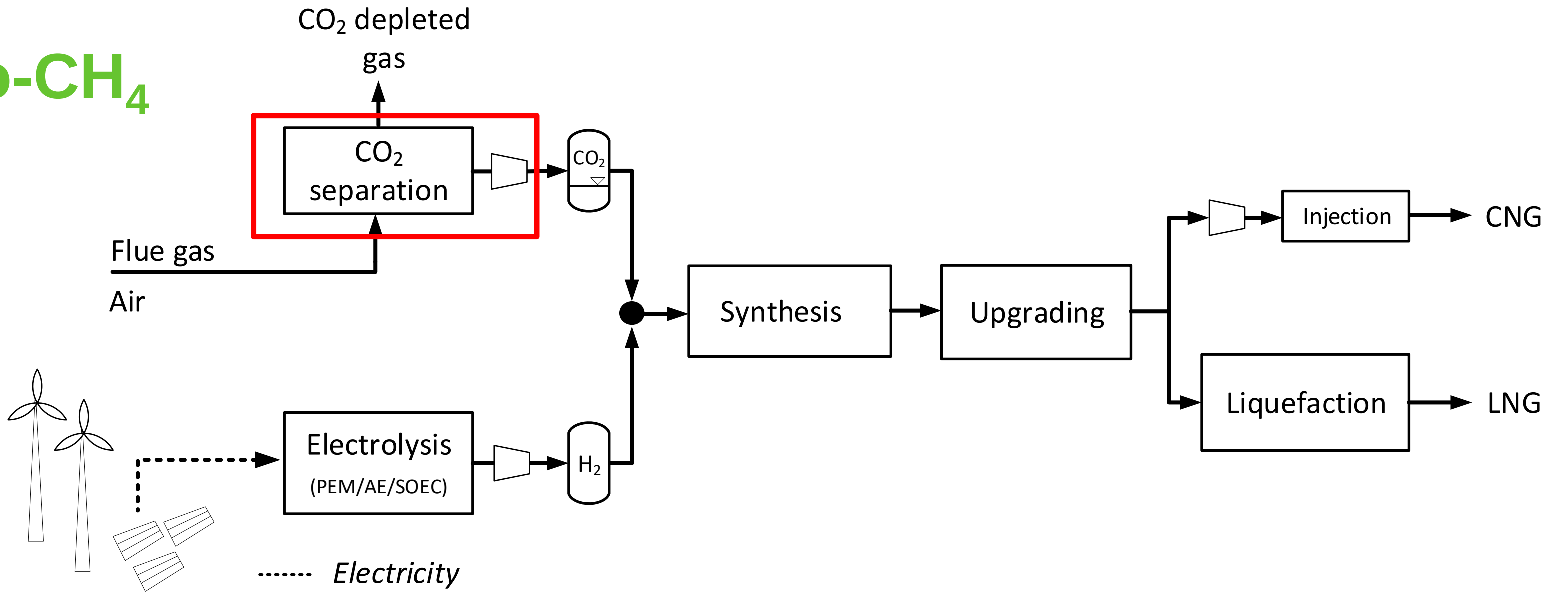
	Alkaline electrolysis	PEM electrolysis	SOEC
Operating temperature	50 - 120 °C	50 - 120 °C	700 - 1000 °C
Operating pressure	< 30 bar (100 bar)	< 30 bar (100 bar)	atm. (< 20 bar)
Electrical energy demand	4,3 - 5 kWh/m³	4.3 - 9 kWh/m³	2,6 - 4,5 kWh/m³
Flexible operation	above 20 % of nominal power very good	Very good	k. A.
Efficiency	62 - 82 %	67 - 85 %	60 – „100" %
Power density	0,2 - 0,4 A/cm²	0,6 - 2,0 A/cm²	< 1 A/cm²
Cell voltage	1,8 - 2,4 V	1,8 - 2,2 V	1,4 V
H_2 production per module	< 750 m³/h	< 200 m³/h	< 30 m³/h

Elecrolysis: Conclusions

1. (H_2O-) Electrolysis is an established technology
2. Efficiencies > 80 % are possible, especially if synergies with exothermic reactions (e.g. methanation) are used
3. Pressure, synergies, load flexibility are important criteria for choosing the “right” electrolyser

„C“ sources

Power-to-CH_4



Session AGENDA: Technical Background

- Electrolysis
- CO_2 separation and supply (and other carbon sources)
- Methanation concepts
- Process integration
- Outlook for technological improvement

$CO_2 + 4\ H_2 \rightleftharpoons CH_4 + 2\ H_2O$

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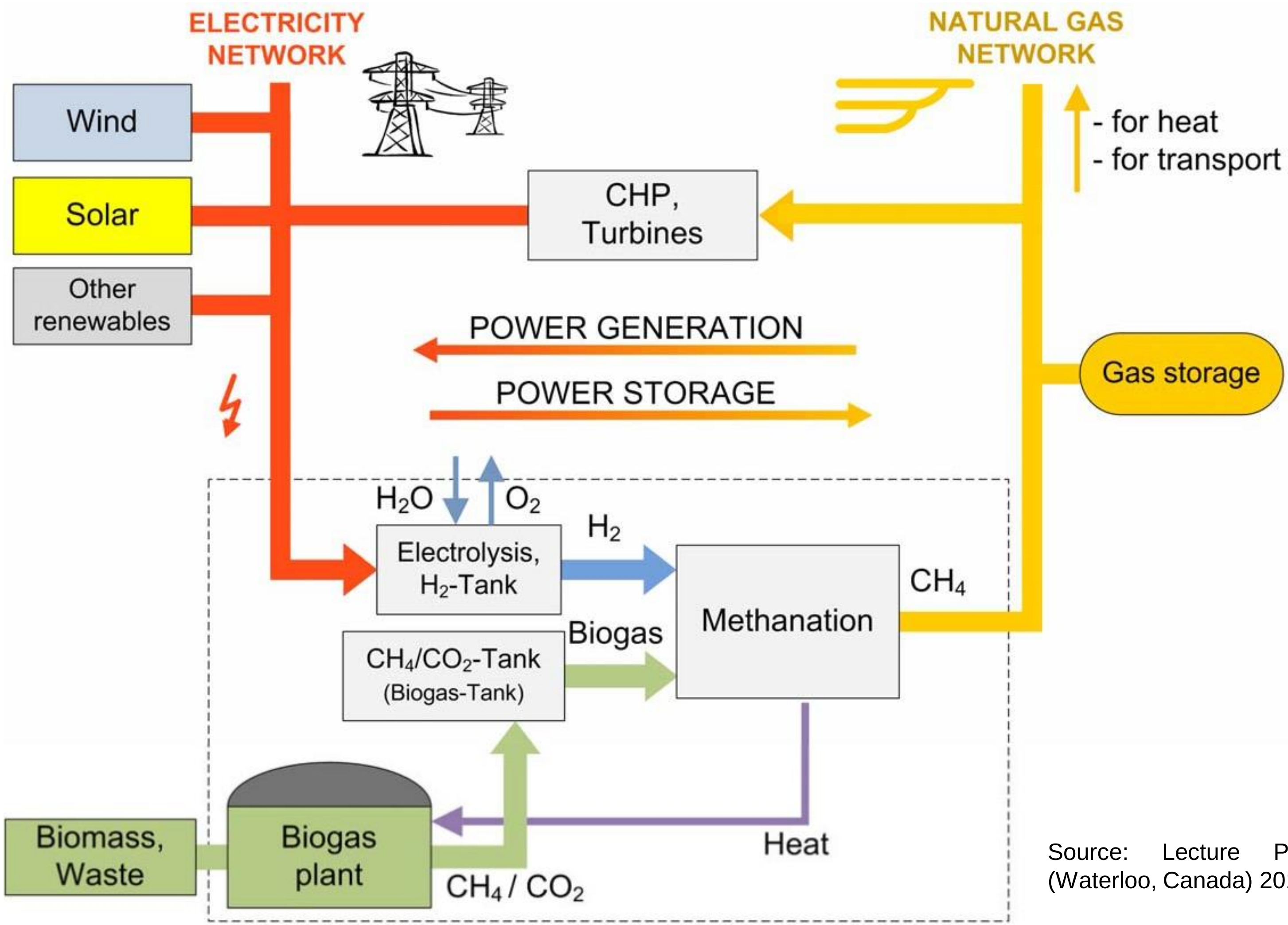
Methanation needs more than hydrogen



Source: Lecture Prof. Fowler (Waterloo, Canada) 2016-06-14

Possible carbon sources at different scales

Small: Biogas Plants

- ≈ 500 m³/h CO_2

→ ≈ 2 000 m³/h H_2 necessary

- „bio methane“ 500 m³/h

- product gas (bio CH_4 + SNG):

  1 000 m³/h CH_4

  ≈ 11 MW (chem.)

www.bbfm.de

Medium: BM-Gasification

- ≈ 2 100 m³/h CO_2
- ≈ 1 400 m³/h CO

→ ≈ 12 600 m³/h H_2 (8 100 m³/h from electrolysis)

- product gas:

  3 500 (4 500) **m³/h CH_4**

  ≈ **40** (50) MW (chem.)

(…) = incl. 1 000 m³/h CH_4 in the raw gas

http://www.repotec.at

Big: e. g. NH_3-Plants

- ≈ 30 000 m³/h CO_2

→ ≈ 120 000 m³/h H_2 necessary

- NH_3-plant: CO_2 is byproduct

- product gas:

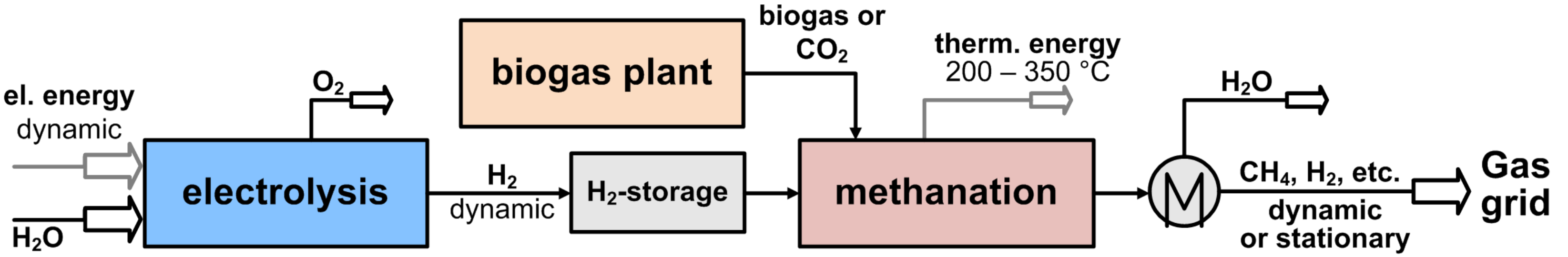
  30 000 m³/h CH_4

  ≈ 332 MW (chem.)

www.skwp.de/deutsch/main-nav/unternehmen/fotos.htm

Different PtM process chains…

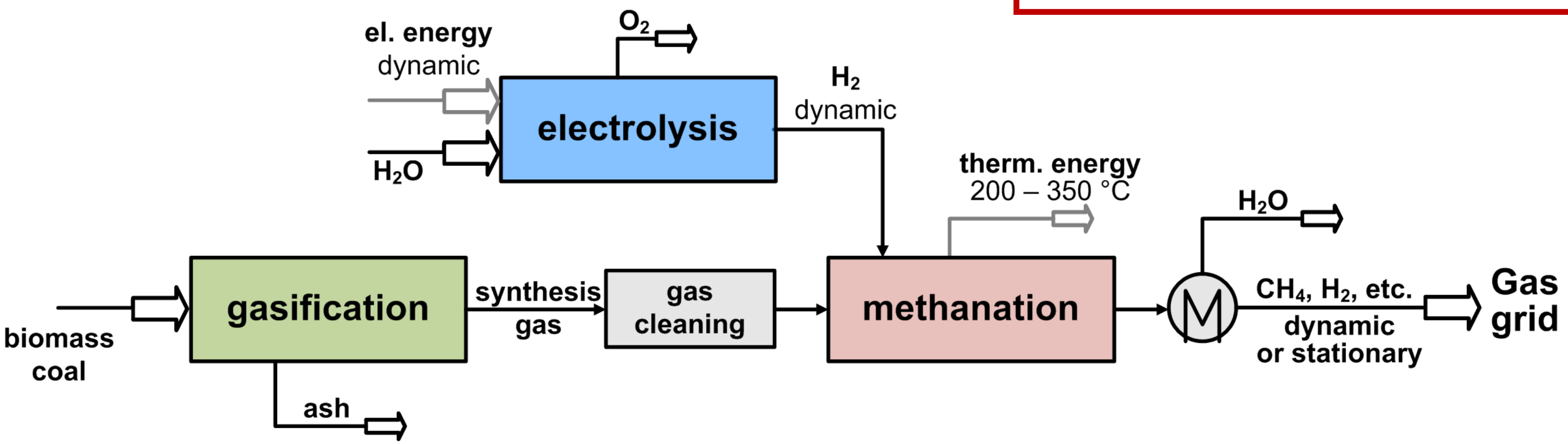
Power to Gas + Biogas



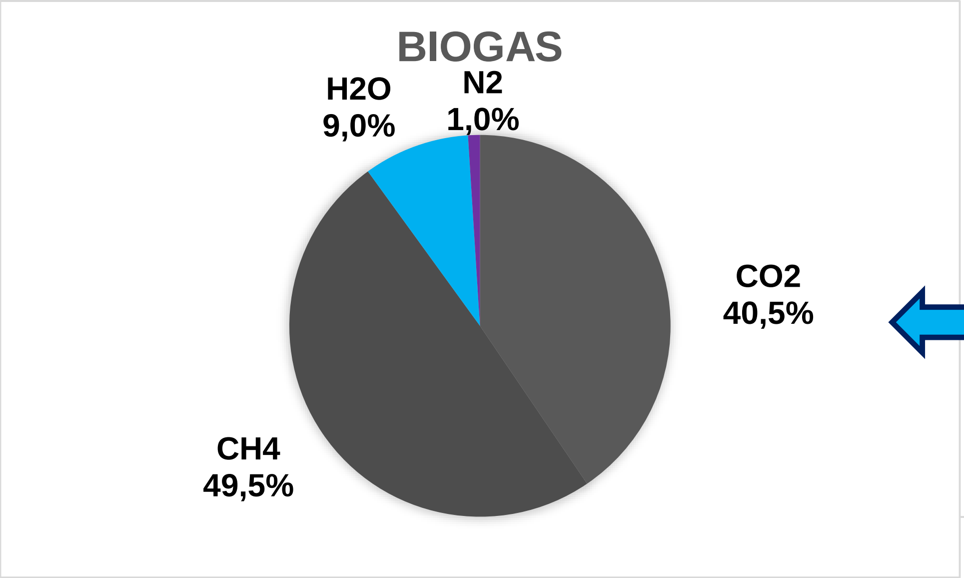
$$CO_2 + 4\ H_2 \rightleftharpoons CH_4 + 2\ H_2O$$

$$CO + 3\ H_2 \rightleftharpoons CH_4 + H_2O$$

Gasification (with optional PtG)



…with different raw gas compositions…

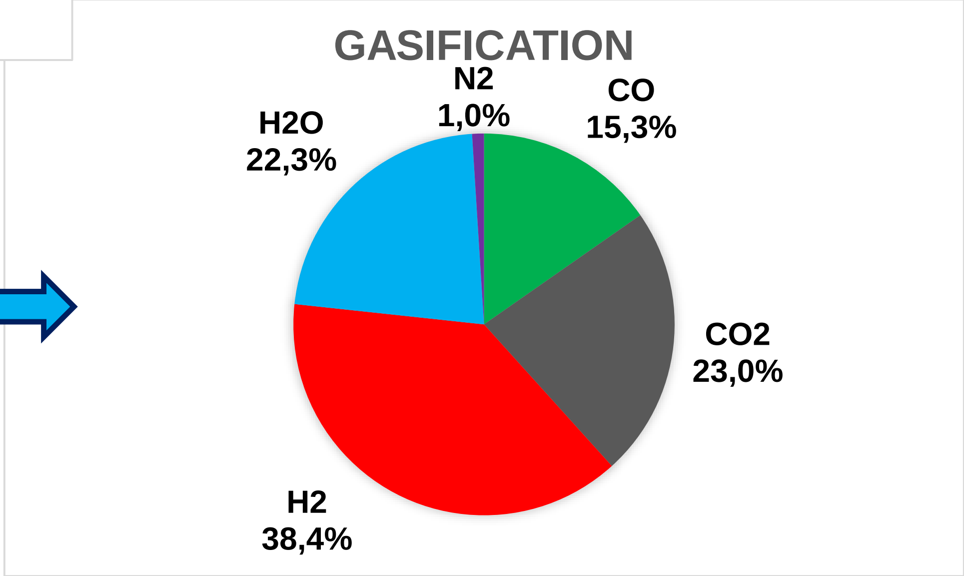


Biogas (from fermentation):

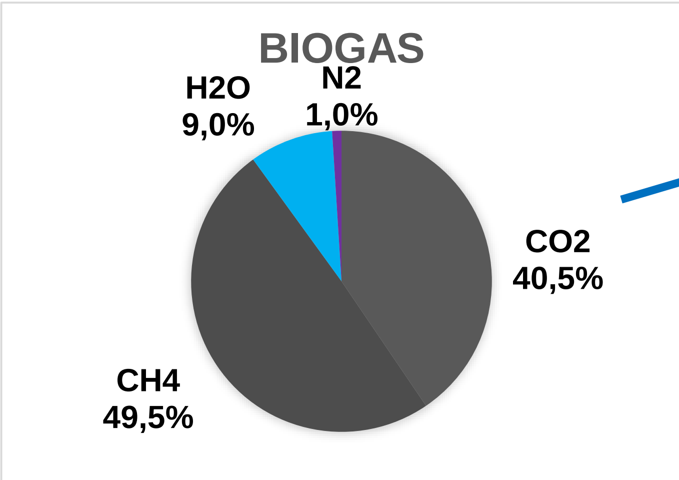
- H_2S and NH_3
- Si-species
- O_2 from upgrading process steps

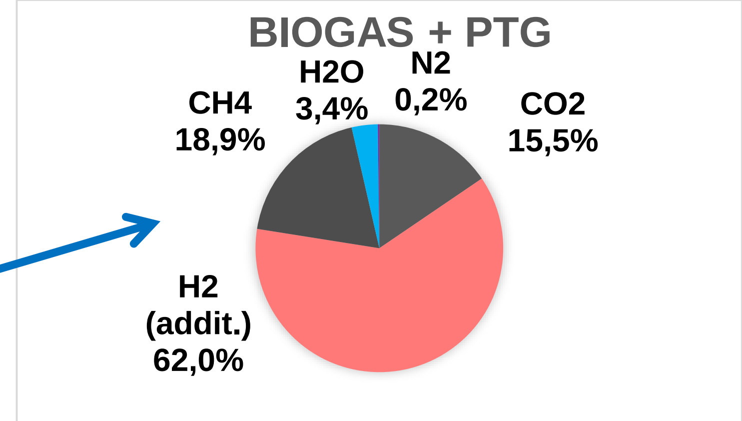
Gasification (wood, allothermal):

- S- and tar-species
- Ash
- volatile metals

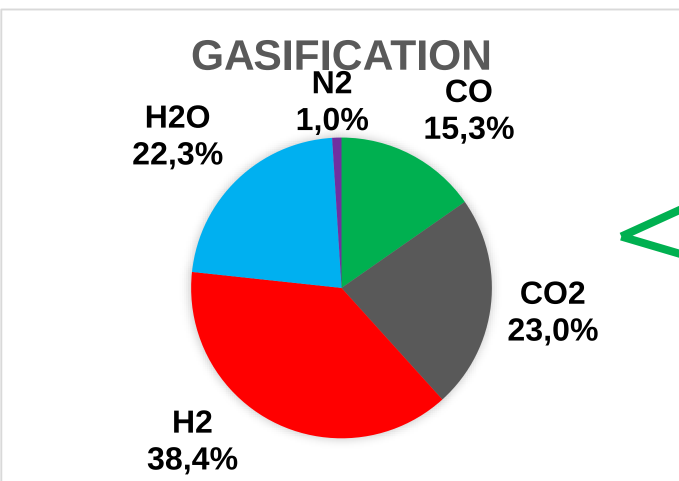


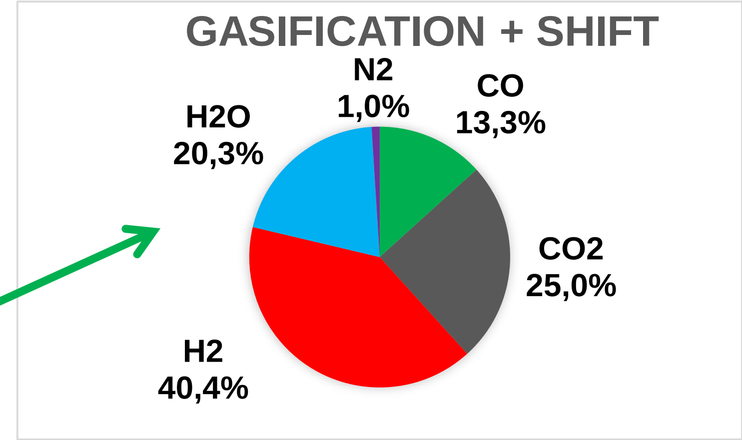
… require different feed gases!

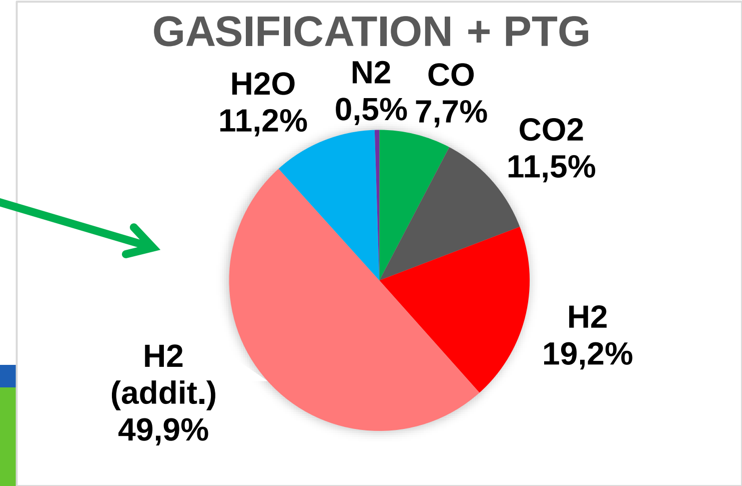




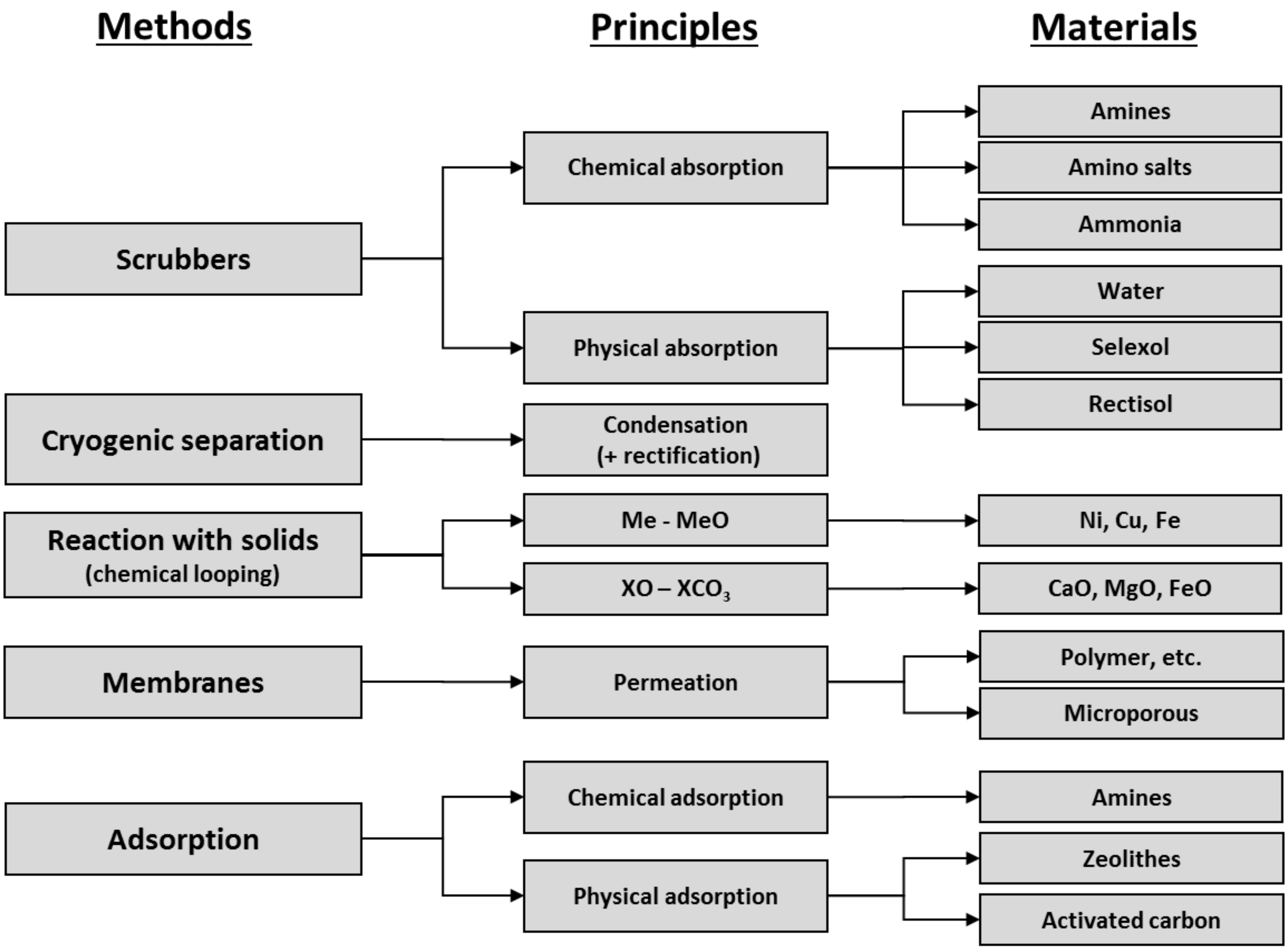
$CO + H_2O \rightleftharpoons CO_2 + H_2$







CO_2 Separation: Overview



CO_2 Separation: Technologies

Adsorption	Membranes	Scrubbing (absorption)

Technology Development:

Adsorption	Membranes	Scrubbing (absorption)
• High TRL • 300 – 1000 m³/h (Biogas); industrial e.g. for H_2 prod. • High purity possible	• Biogas: TRL high • Flue gases: TRL 5 • 200 - 200.000 m³/h • Purity < 98 %	• High TRL • 200 - 6 Mio. m³/h (e.g. in NH_3 synthesis) • Very high purity (> 99,5 %)

Specific energy demand and costs (per m^3 CO_2):

Adsorption	Membranes	Scrubbing (absorption)
• Electric: 0,25 - 1,25 kWh/m³ • Thermal: - • CAPEX: 1,2 - 3 ct/m³ • OPEX: 6 - 8 ct/m³	• Electric: 0,3 - 0,5 kWh/m³ • Thermal: - • CAPEX: 1 - 10 ct/m³ • OPEX: 1 - 15 ct/m³	• Electric: 0,1 - 0,6 kWh/m³ • Thermal: 0,2 - 1,2 kWh/m³ • CAPEX: 0,4 - 3 ct/m³ • OPEX: 1,4 - 16 ct/m³

Adsorption	Membranes	Scrubbing (absorption)
Mature technology in biogas upgrading and H_2 prod.	High Potential for further improvements	Well established method for large-scale applications

CO_2 Separation: Technologies

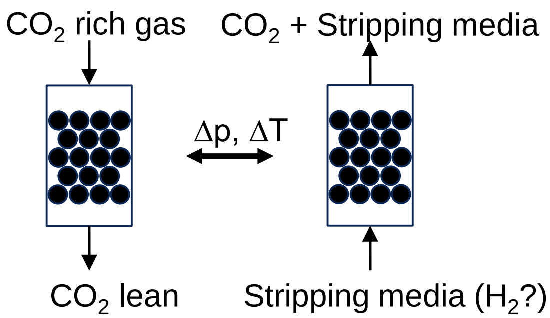
Adsorption	Membranes	Scrubbing (absorption)

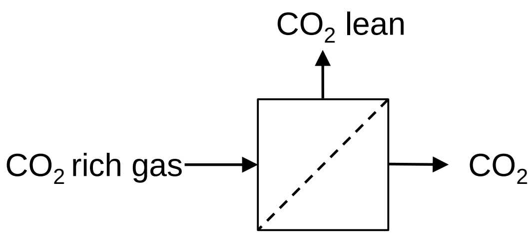
Principles:

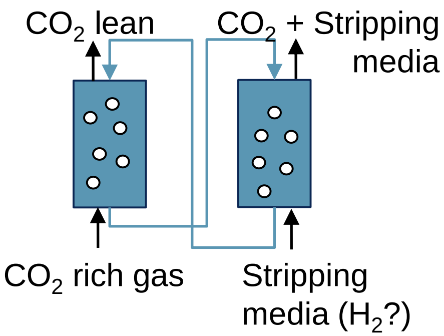
Adsorption	Membranes	Scrubbing (absorption)
Physical/chemical bonds with the surface of a solid material	Selective permeation (adsorption+diffusion) through a membrane	Physical/chemical bonds with the scrubbing media inside of a liquid phase

Important parameters:

Adsorption	Membranes	Scrubbing (absorption)
• p, T • CO_2 concentration • Phase equilibrium • Material	• p, T • CO_2 concentration • Permeability • Material	• p, T • CO_2 concentration • Solubility • Heat of reaction • Scrubbing media

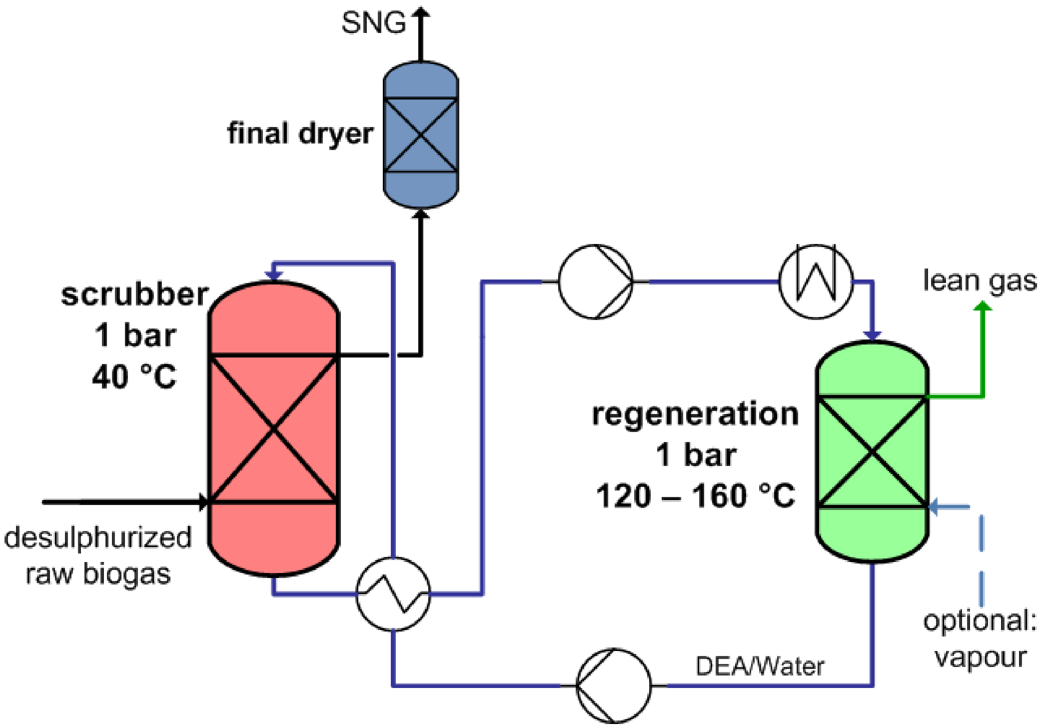






CO_2 Separation: Technologies

Upgrading by **chemical scrubbing**



Chemical reaction of CO_2 with solvent (30 ma.-% DEA in water)

No elevated pressure in scrubber necessary

Advantages

Almost complete CO_2-removal

Very low methane slip

Disadvantages

High thermal energy demand

Alkanolamines: Degradation in the presence of oxygen

Gas composition

gas	unit	raw gas	SNG
CH_4	vol.-%	54.3	99.7
CO_2	vol.-%	45.7	0.3

→

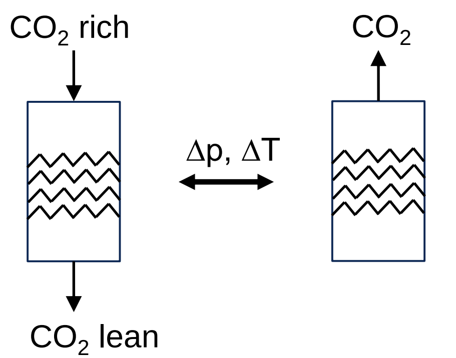
pressure	bar	1
methane slip	%	< 0.2
specific solvent flow	l/m³	15
electricity demand	kWh/m³	0.07
heat demand	kWh/m³	0.6

CO_2 Separation: DAC Technologies

CO_2 from air (*Direct Air Capture*, DAC)

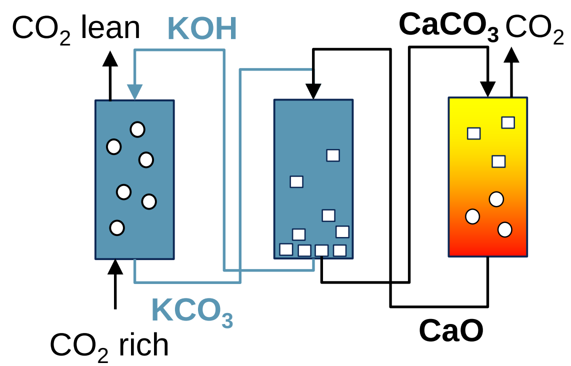
Problem: Very low CO_2 concentration (ca. 0.04 vol.-%)

Adsorption
with amine-coated „filters“



- Energy demand: 11-14 MJ/m^3 CO_2
- Costs: 60 - 250 €/t CO_2

Absorption
in aqueous KOH



- Energy demand: 18 MJ/m^3 CO_2
- Costs: 75 - 200 €/t CO_2

➔ DAC of CO_2 from air is technically feasible

➔ Large spread of possible costs → Technologies are under development

Quellen: www.climeworks.com; Keith et al., *Joule* 2018, 2, 1-22.

Carbon Sources: Conclusions

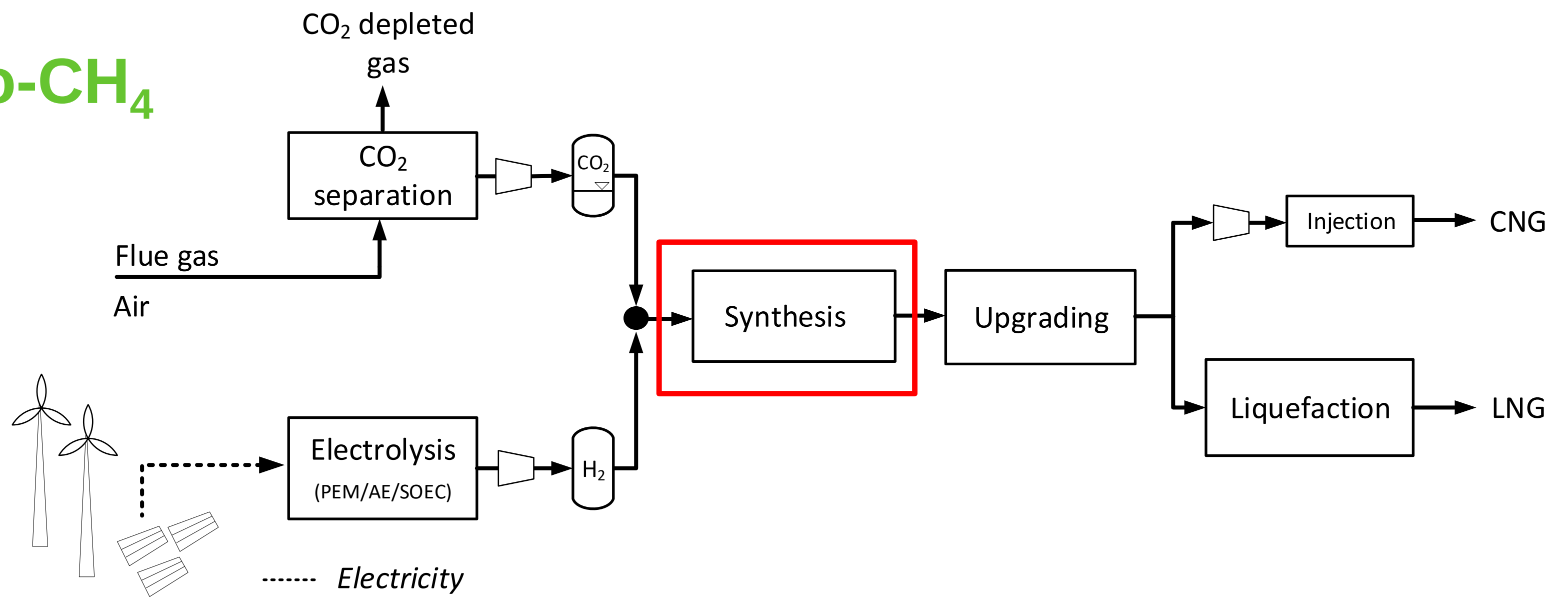
1. CO and/or CO_2 are suitable C-sources; (Focus for PtM mostly on CO_2)

2. Scales from 1 MW up to >1 GW are available

3. Gas cleaning/pretreatment depends on scale and process chain

Methanation

Power-to-CH_4



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- Electrolysis
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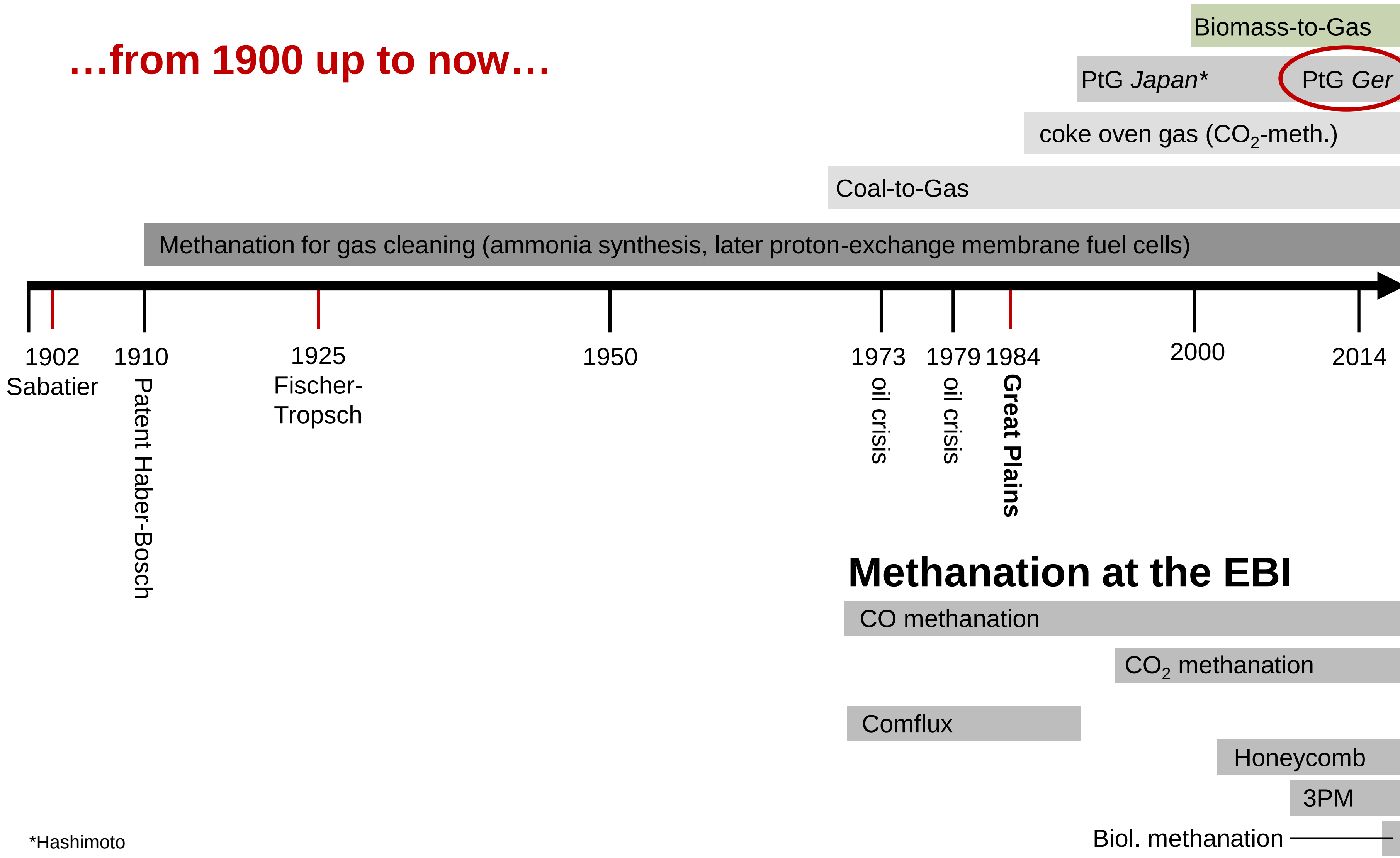
- **Methanation (concepts)**
- Process integration
- Outlook for technological improvement

History of Methanation

…from 1900 up to now…



*Hashimoto

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Basic reactions and stoichiometry

CO and CO_2 methanation

$$CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O_{(g)} \qquad \Delta_R h^0 = -206 \text{ kJ/mol}$$

$$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O_{(g)} \qquad \Delta_R h^0 = -165 \text{ kJ/mol}$$

Carbon Sources

(costly) **Hydrogen**

(most wanted) product **Methane**

by product **Water**

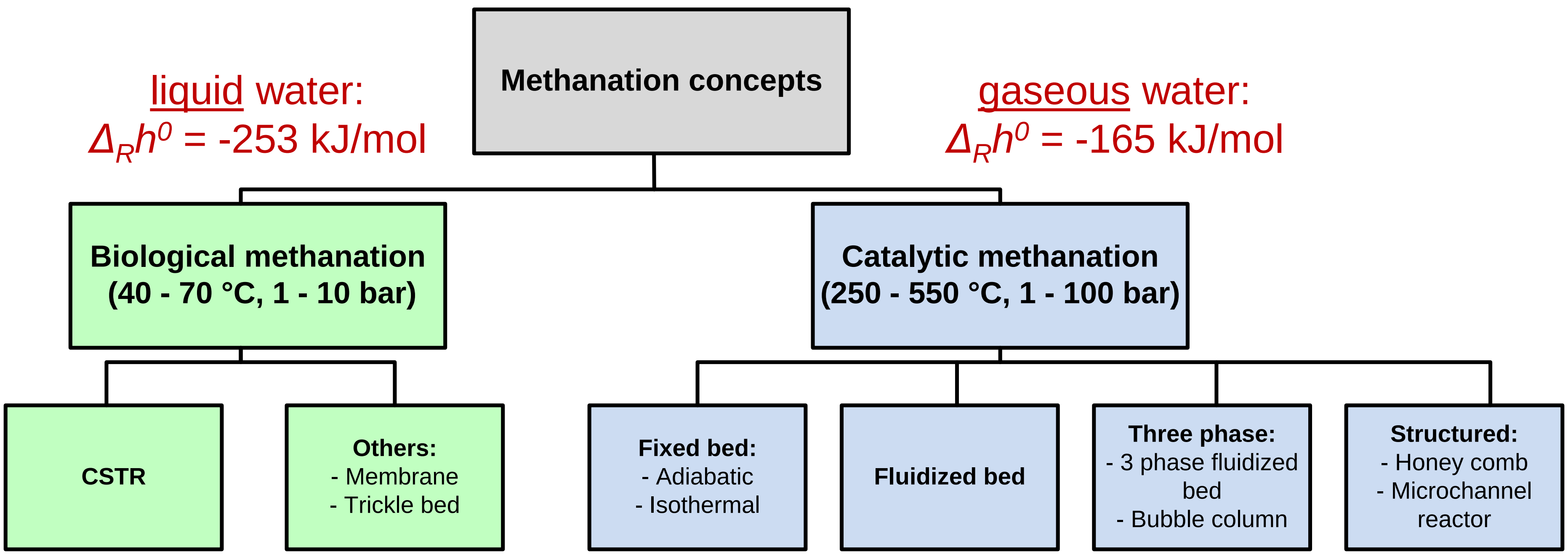
Fundamentals of Methanation (I)

Reaction Equation (example CO_2 as carbon source):

$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O$

- Methanation is a highly exothermal reaction

⇨ Removal / use of reaction heat is significant issue



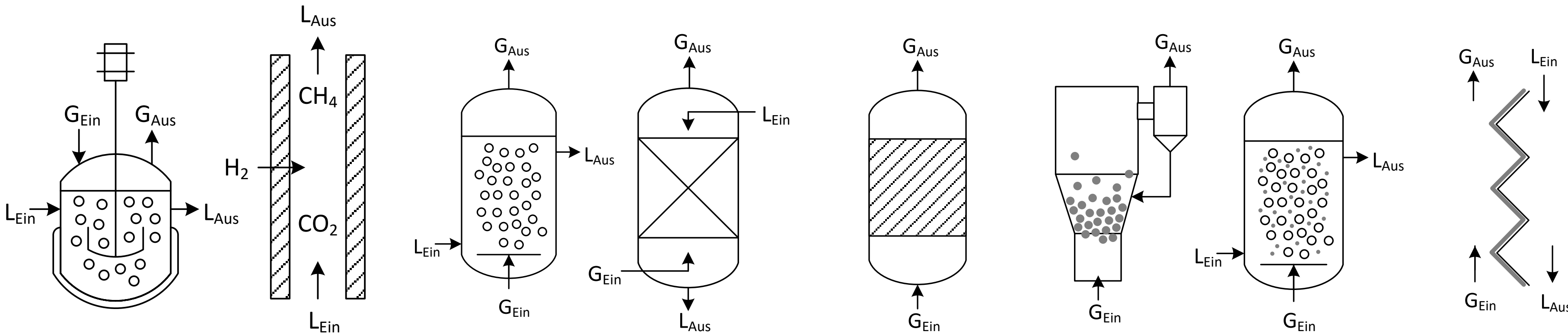
Fundamentals of Methanation (II)

Biological Methanation (BM)

- Stirred tank / CSTR
- Membrane-reactor
- Bubble column
- Trickle bed reactor

Catalytic Methanation (CM)

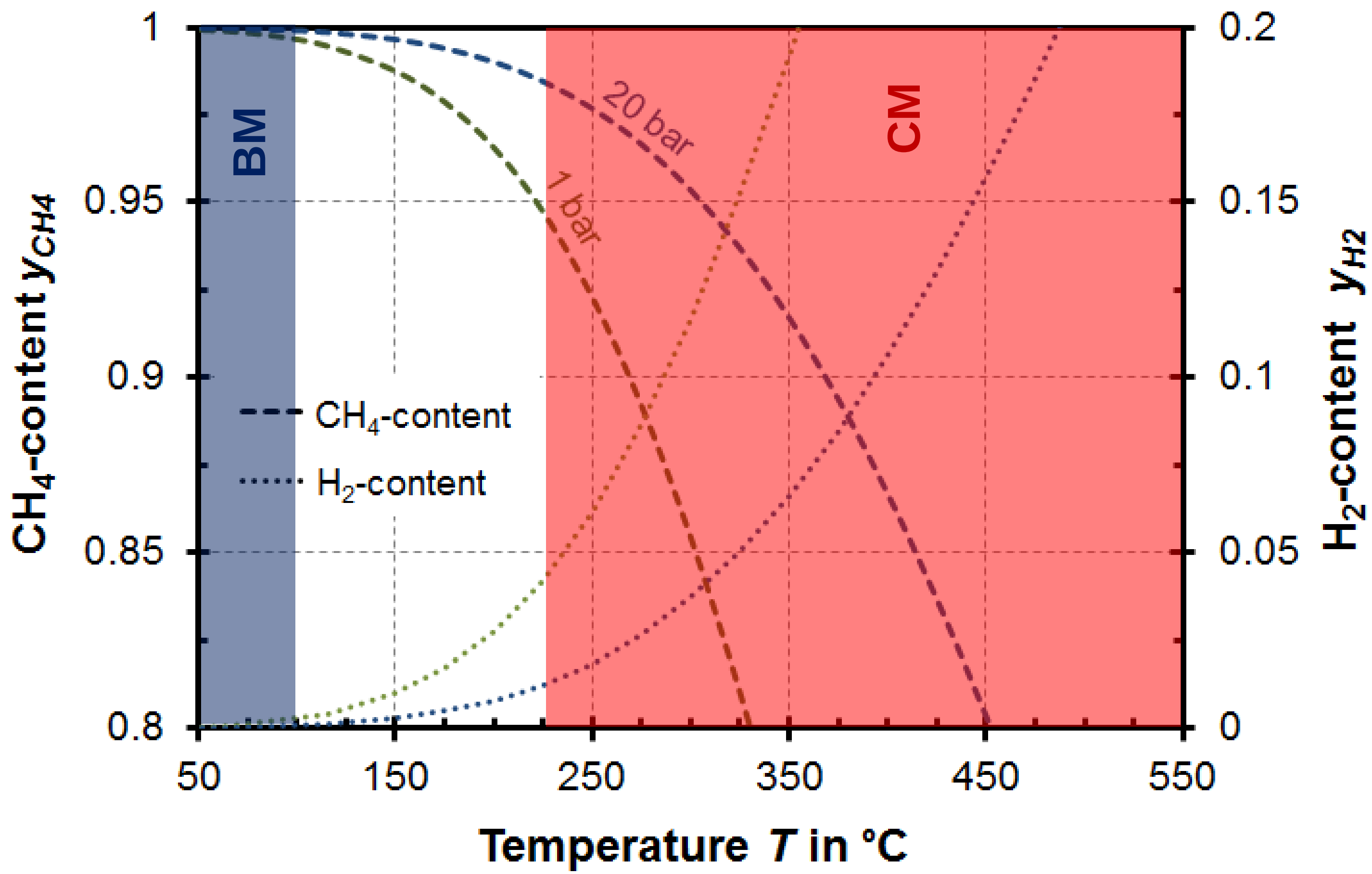
- Fixed bed
- Fluidized bed
- Bubble column
- Structured reactor



Objectives: - Technical simplification
- Reduction of costs

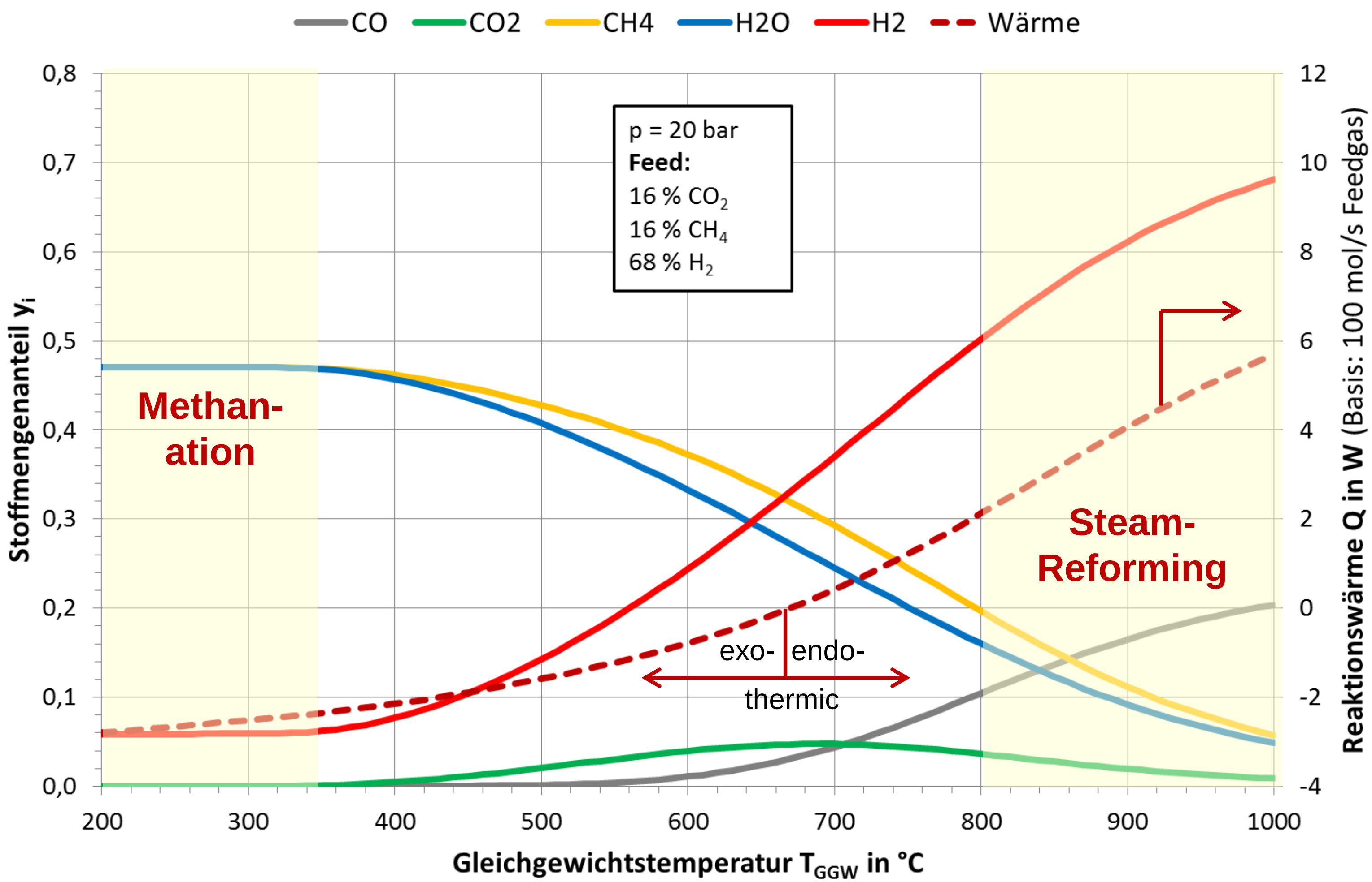
} Increase applicability in small scale plants (5 – 100 MW)

Equilibrium Conversion (feed: $H_2/CO_2/CH_4$ = 4/1/1)



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

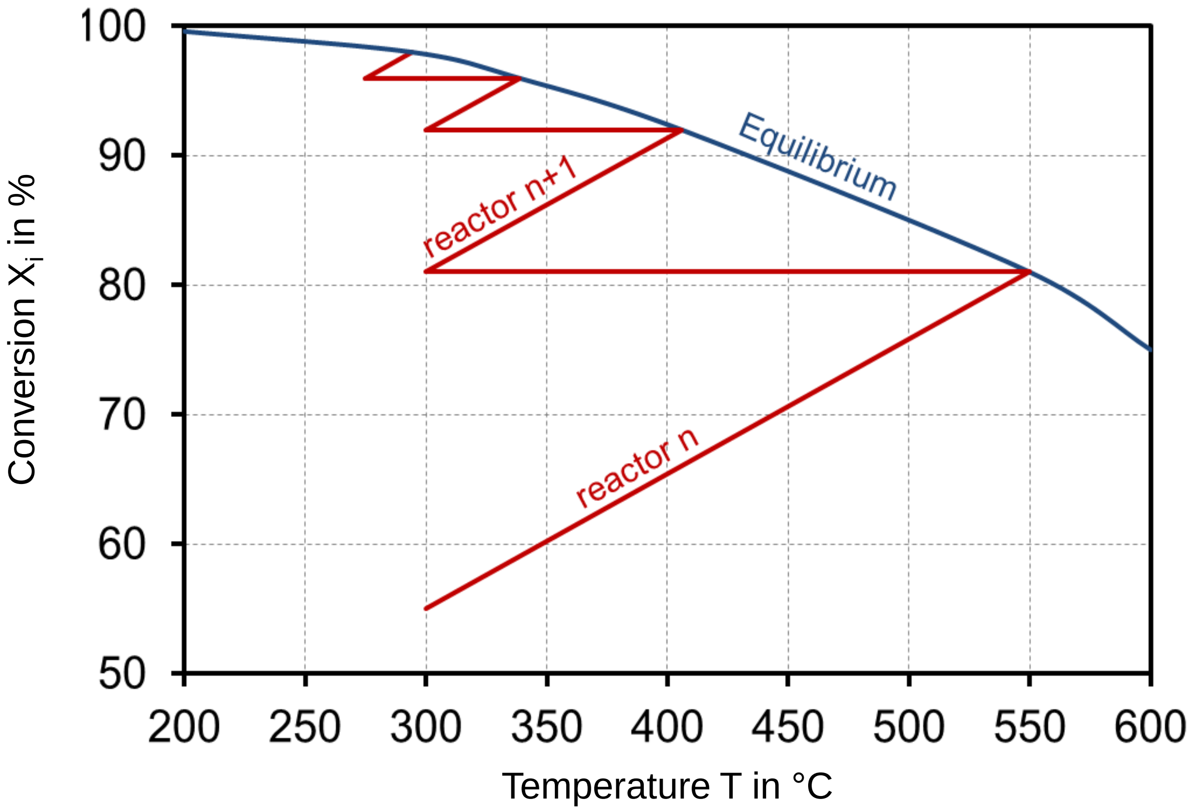
Equilibrium Conversion



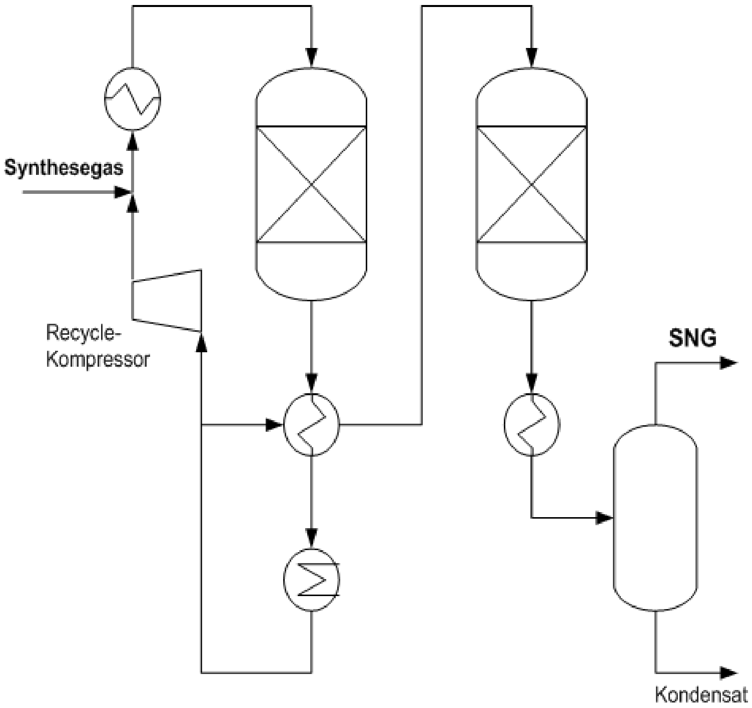
Methanation: How to deal with the reaction heat?

- **Adiabatic fixed-bed reactors** in series (with intermediate cooling and water condensation)
- Used in **commercial coal gasification** plants (e.g. Great Plains, USA; Quinghua, China [1,8 GW SNG]; Huineng, China [500 MW SNG]; Gobigas, Sweden [20 MW SNG from biomass])

„Reactor Cascade“



State of the Art SNG plant „Great Plains“



more Info: www.dakotagas.com/Products/pipeline_liquefied_gases/synthetic-natural-gas/

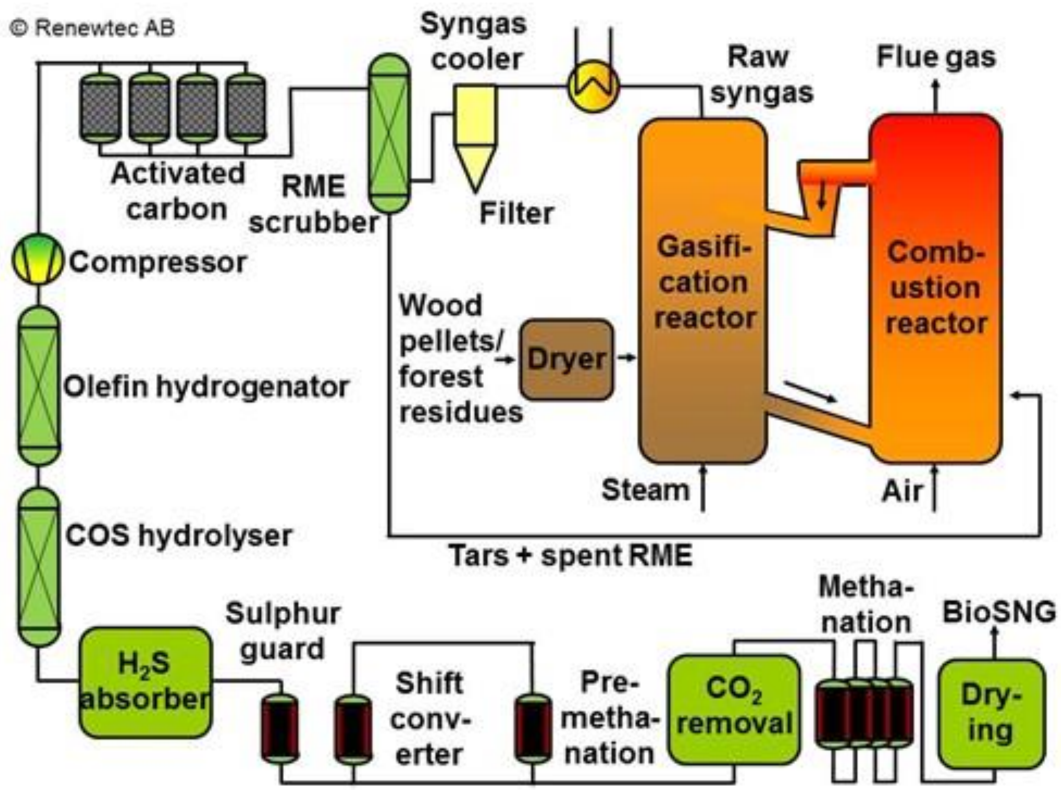
Ref.: Moeller, 1974; Lukes, 2005

Lignite

- 2 consecutive adiabatic fixed bed reactors
- 1st reactor with (partial) recycle; T_{in} ≈ 300 °C; T_{out} ≈ 450 °C
- 2nd reactor T_{in} ≈ 260 °C ;T_{out} = 315 °C
- Commercial scale (Great Plains (USA); production of **4.8 · 10^6 m³/d SNG** from lignite)

GiBiGas project (Göteborg, Sweden)

- 20 MW methanation plant (cost up to now: ca. 200 M€)
- Biomass = wood
- Indirect (steam) gasification
- Syngas cleaning
- Syngas methanation (only CO and no PtM!)
- Status: operative since 2015, mothballed in 2018



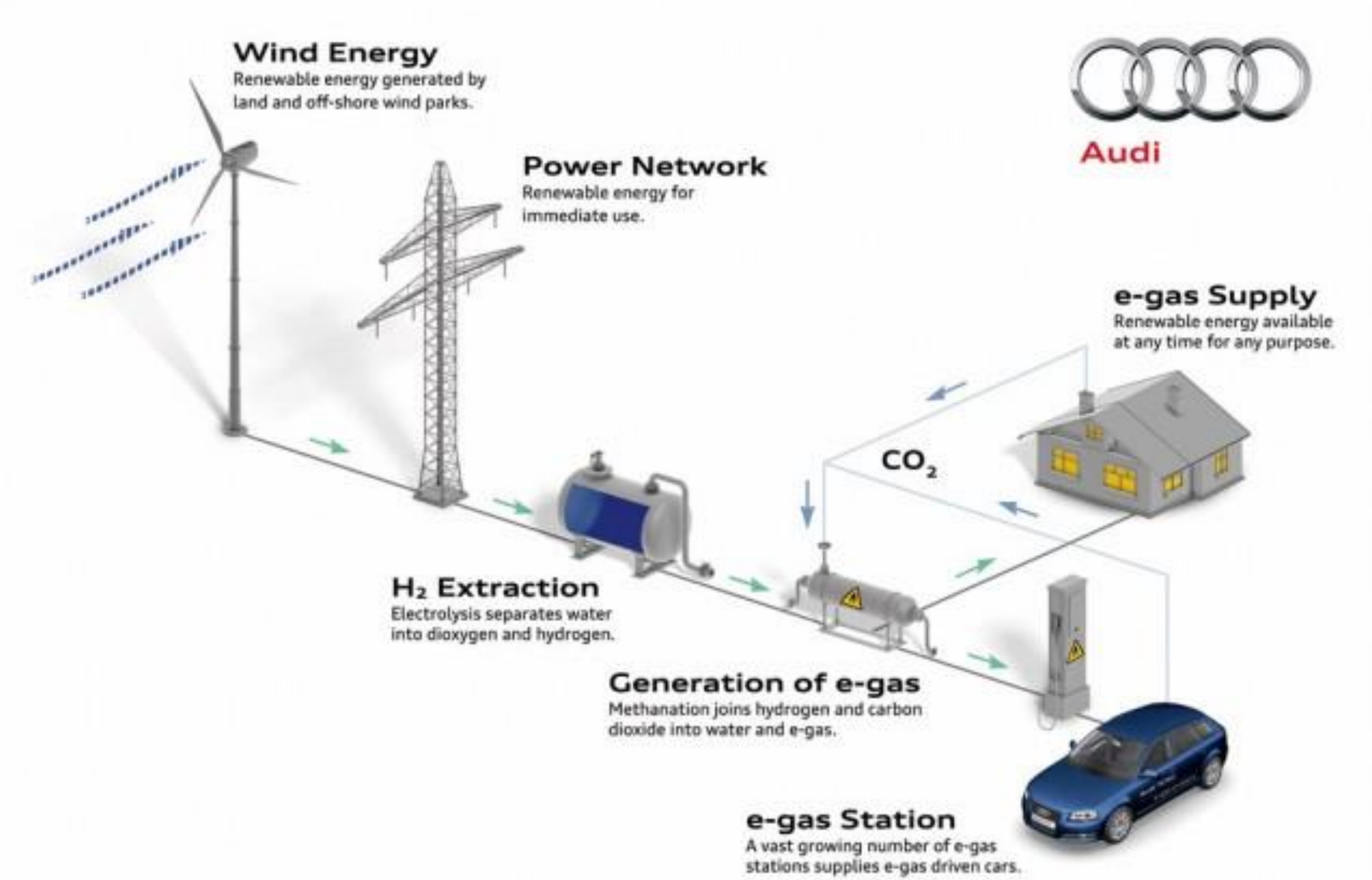
Biomass

PtG-Methanation: Pilot projects

Project/ Location	Company	Status	Power Input (kW)	CO_2-Source	SNG output (m^3/h)	Further information
Chemical						
Audi e-gas Werlte (D)	Solarfuel (Today:Etogas)	Opened in 2013	6300	Biogas	300	
EXYTRON Rostock (D)	Exytron	2015	21	Flue gas of CHP	1	Micro energy system; closed carbon cycle
Biological						
Schwandorf (D)	MicrobEnergy/ Viessmann	2012	100	Biogas	5,3	In-situ methanation
BioPower2Gas Allendorf (D)	Viessmann	2015	1,000	Biogas	15 - 55	Ex-situ methanation
Bad Hersfeld (D)	IWES	2012	25	Biogas	4	In-situ methanation
Stuttgart (D)	ZSW	2012	250	tbd	12,5	
GICON Cottbus (D)	Gicon	2015	-	-	1	Trickle-bed
Avedøre (DK)	Electrochaea	2016	1,000	Biogas	50	

http://www.powertogas.info/power-to-gas/pilotprojekte-im-ueberblick/exytron-demonstrationsanlage/

Audi e-gas project (6.3 MW) in Werlte, Germany

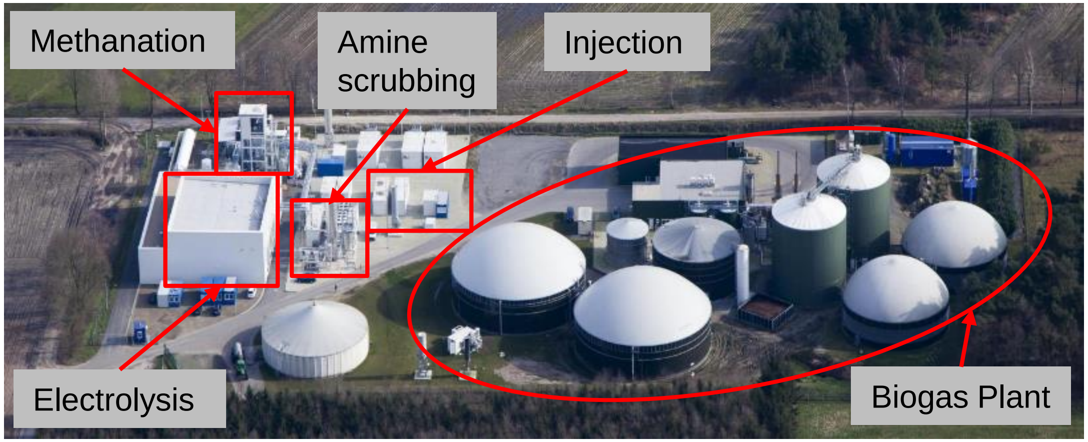


Source: http://www.motorauthority.com/news/1085024_audis-new-e-gas-plant-comes-online

e-gas project (Werlte): Catalytic Methanation

Audi e-gas

- Location: Werlte, Niedersachsen, Germany
- Start of Operation: 2013
- Methanation: Chemical, Fixed bed, Tube reactor
  300 m³/h SNG
- Electrical power input: 6.3 MW
- CO_2 source: Neighbouring biogas plant
- Efficiency (AC/VN → CH_4): 54 % +/- 3 % [1]
- Heat integration:
  - Heat production:
    Electrolyte solution (65 °C),
    E-gas cooling (95 °C),
    Reactor cooling (170 °C)
  - Heat sink:
    Hygienisation,
    amine scrubbing,
    fermenter heating



[2]

[1] http://forschung-energiespeicher.info/projektschau/gesamtliste/projekt-einzelansicht/95/Weltweit_erste_industrielle_Power_to_Gas_Anlage/
[2] https://www.vde-suedbayern.de/resource/blob/842012/061b1950ff17ae21c68774bd0d798379/download20160317-data.pdf

Audi e-gas project (6.3 MW) in Werlte, Germany

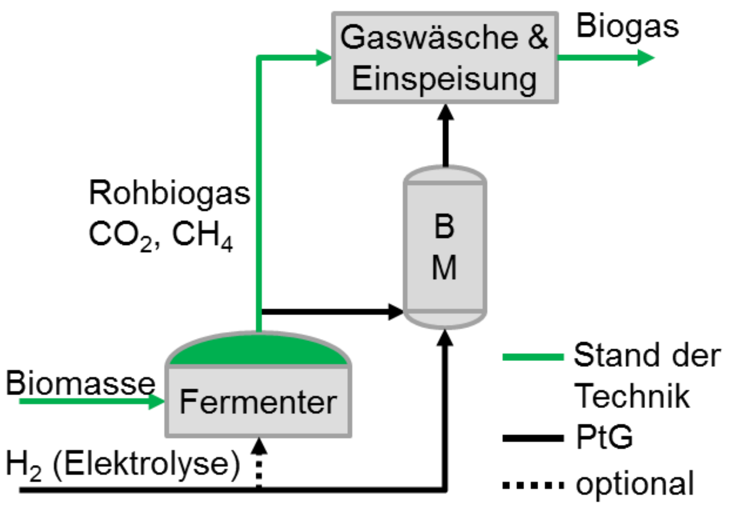
Electrolyzer hall

One of three 2MW$_{el}$ electrolyzers

Methanation reactor

Source: ETOGAS, AUDI

Alternative to Cat. Methanation: Biological Methanation (BM)



In-situ BM

- No additional reactor necessary
- Process conditions fixed by biogas process
- Increase of c_{CH4} possible
- Retrofit of existing biogas plants is demanding (safety aspects of H_2!)

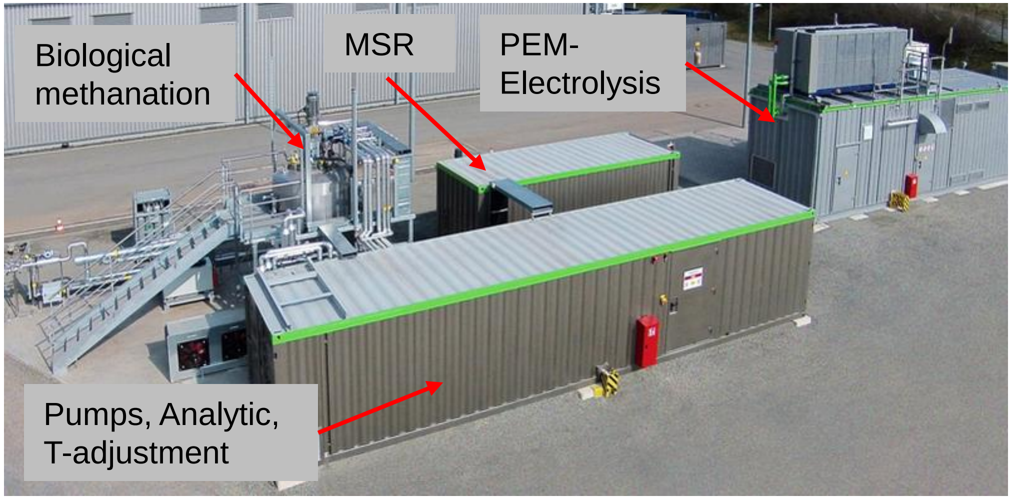
Ex-situ BM

- Additional reactor = additional cost
- Process conditions BM can be optimised independently of biogas process
- High H_2 conversion (> 99 %) theoretically possible

BioPower2Gas (Allendorf): Biological Methanation

- Location: Allendorf (Eder), Hesse, Germany
- Operation: Opened in 2015 (project period 2013 - 2016)
- Electrical power input: 1,200 kW[1]

- Methanation:
  - Configuration: Ex-situ
  - $\dot{V}_{SNG}$: 15 - 55 m³/h
  - Gas quality: ~ 98 % CH_4 [1]
  - Space-time yield: 2,1 $m^3_{CH4}/(m^3_{Reactor}\ h)$[1]



[2]

[1] Heidrich, T., et. al: BioPower2Gas – Vergleichende Simulation, Demonstration und Evaluation von optimal leistungsregelbaren Biogastechnologien, Bonn, 2017.
[2] https://www.house-of-energy.org/powertogasallendorf

Catalytic vs. Biological Methanation

	Biological Methanation (BM)	Catalytic Methanation (CM)
Catalyst	Enzymes and Microorgansims	e. g. Nickel
Temperature	40 - 70 °C	200 - 550 °C
Pressure	> 5 bar	> 10 bar
TRL	Pilot-/Demoplants	commercially available
GHSV	< 100 h^{-1}	500 - 10.000 h^{-1}
Limitations	Gas liquid mass transfer	Thermodynamics
Tolerance on feed gas purity	high	low
Load change rate	flexibel (highly dependent on applied reaction system)	moderate (highly dependent on applied reaction system)
Electric energy demand in kWh/m^3 SNG (16 bar)	0,4 - 1,8	< 0,4

Methanation: Conclusions

1. Methanation is an established technology (Sabatier 1902!);

   "Benchmark" PtM is the Werlte plant (P_{el} = 6.3 MW)

2. Biological vs. catalytic methanation?

3. PtM is a new technology with new challenges

   - downscaling, fluctuations, national/international standards
   - limitations by thermodynamic (equilibrium)
   - limitations by chemistry (reaction kinetic, catalyst,…)
   - imitations physics (solubility)

Thank you

for your attention

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