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DGMK Tagung Thermochemische Konversion – Schlüsselbaustein für zukünftige Energie- und Rohstoffsysteme, 23.-24. Mai 2019, Dresden

Vorschlag einer katalytischen Methanisierung für die kleinskalige dezentrale SNG Erzeugung

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I - Motivation

II - Simulation based evaluation of SNG production

III - Experimental methanation of syngas

IV - Heat pipe cooled reactor concept

V - Conclusion and outlook

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Motivation for SNG production

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Heating systems in newly built domestic houses

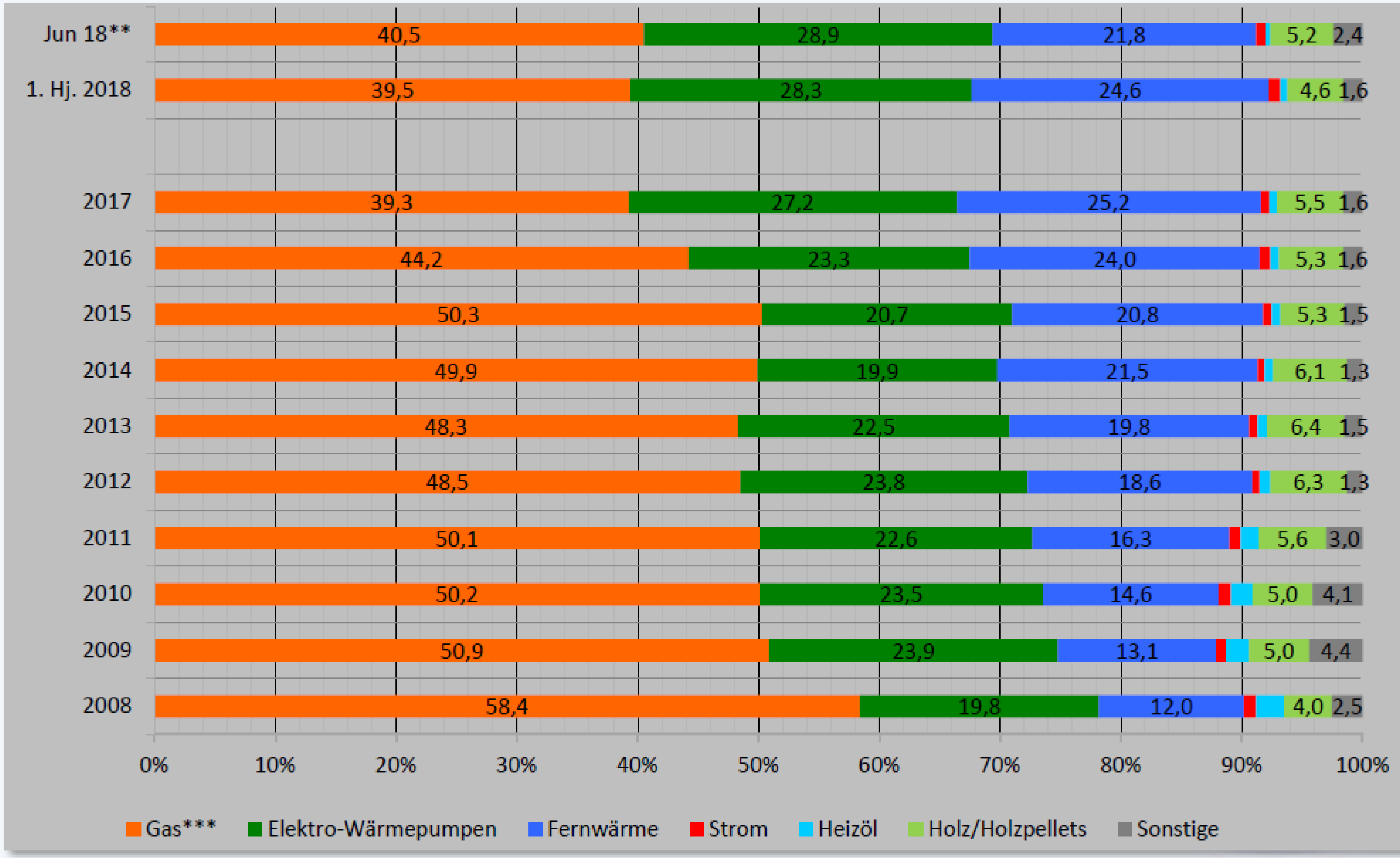
- ~ 45 % less emissions from building sector until 2030

- ~ 40 % of newly installed heating systems in 2018 base on natural gas
- Domestic natural gas demand (~ 1/3)

  2010: 254 bil. kWh

  2018: 281 bil. kWh

AG Energiebilanzen, 1.-3. Quartal 2018



Subsitute Natural Gas (SNG) has to be considered in energy transition

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SNG production

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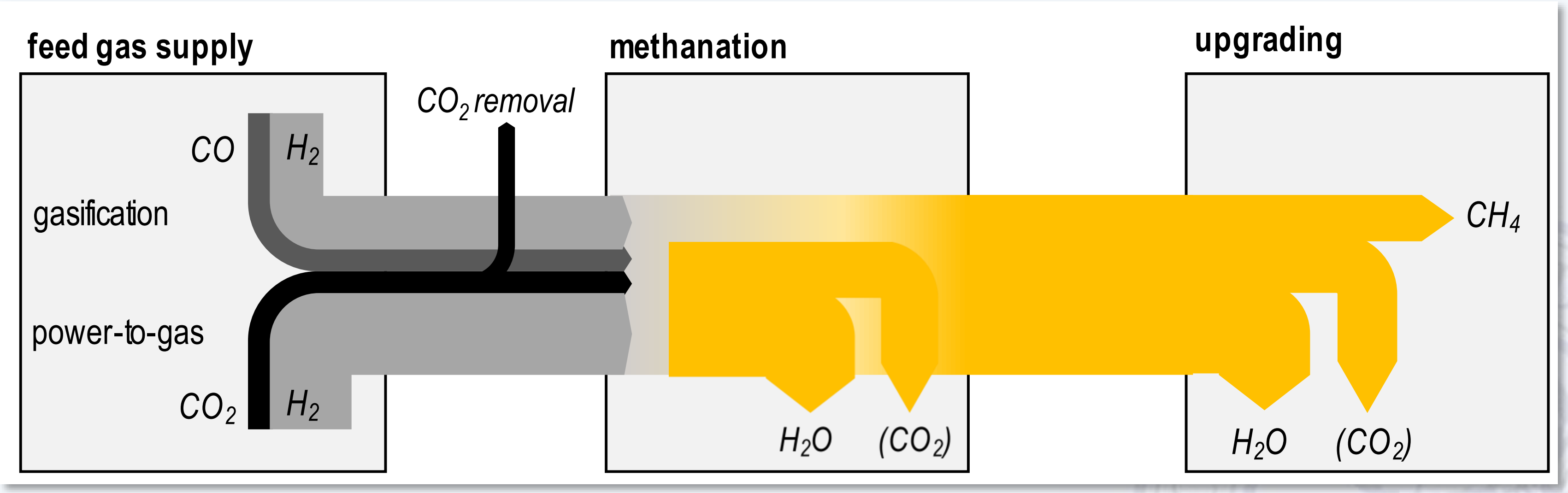

- Two main feedstocks
  - Syngas from gasification
  - Power-to-gas
  - **Carbon is mandatorily required**
- High methane formation
  - Catalyst's limits
  - Equilibrium
- Water removal
- (CO_2 removal)
- Gross calorific value increase

Design flexibility of a simple process without product gas recycle: CO_2 removal, H_2O injection/sequestration, product gas purification

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Thermodynamics of methanation

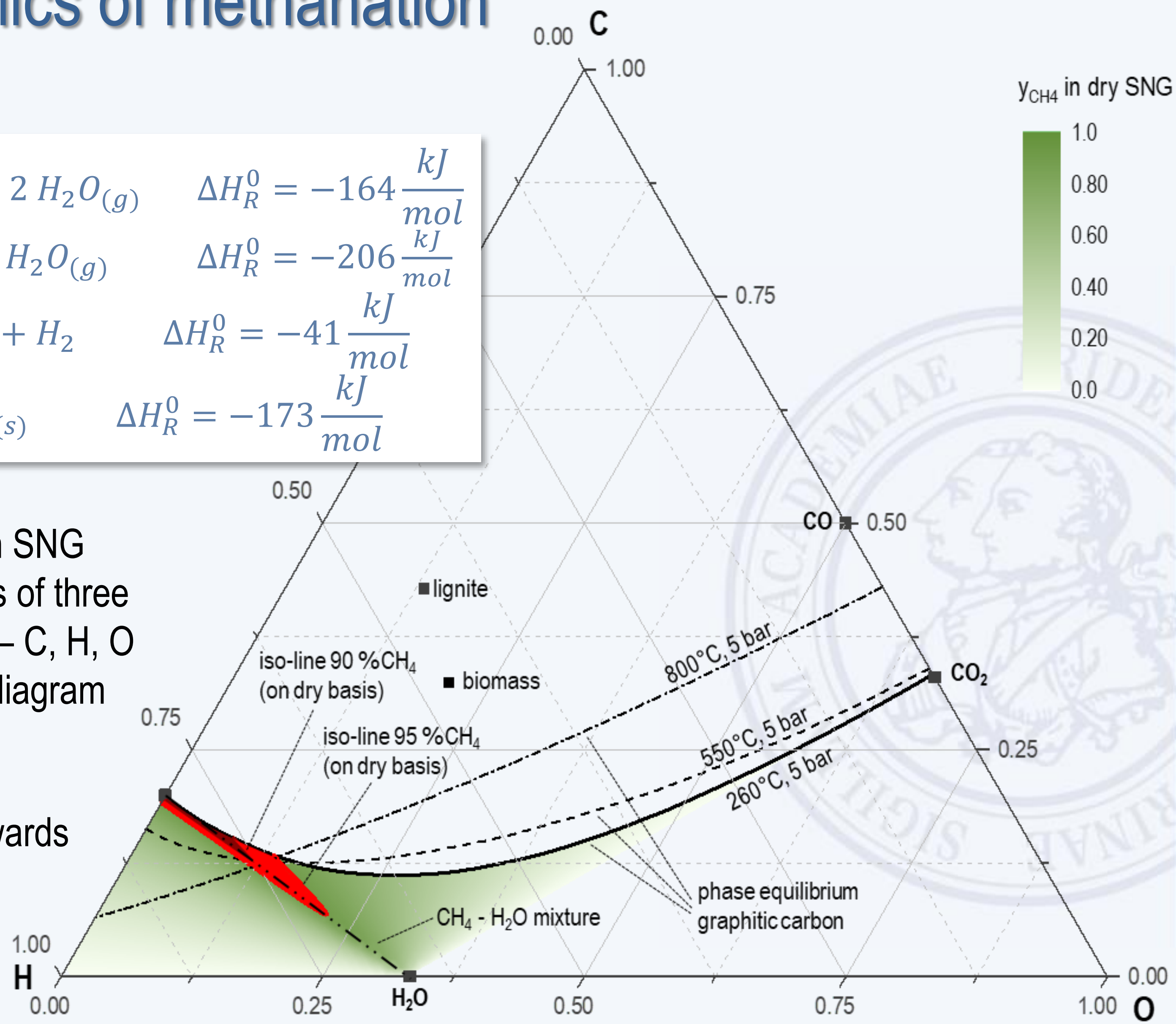
$$CO_2 + 4\,H_2 \leftrightarrow CH_4 + 2\,H_2O_{(g)} \qquad \Delta H_R^0 = -164\,\frac{kJ}{mol}$$

$$CO + 3\,H_2 \leftrightarrow CH_4 + H_2O_{(g)} \qquad \Delta H_R^0 = -206\,\frac{kJ}{mol}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_R^0 = -41\,\frac{kJ}{mol}$$

$$2CO \leftrightarrow CO_2 + C_{(s)} \qquad \Delta H_R^0 = -173\,\frac{kJ}{mol}$$

- Reaction system in SNG production consists of three different elements – C, H, O
  →ternary diagram
- High sensitivity towards T, p, C/H/O ratio



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Pathways for SNG production

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Equilibrium limits methanation

→ ideal C/H/O ratio is on CH_4-H_2O line

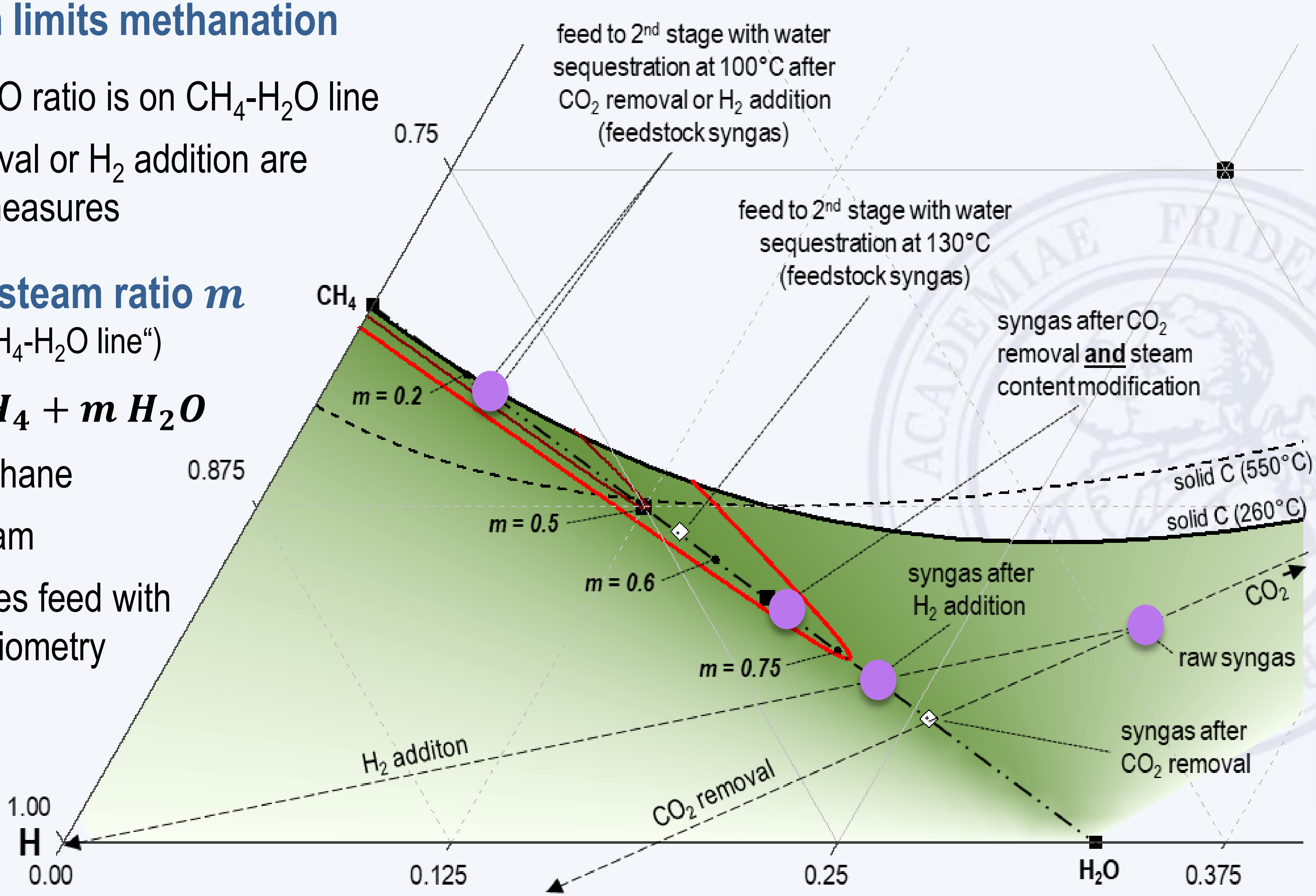
→ CO_2 removal or H_2 addition are suitable measures

Equivalent steam ratio *m*

(„position on CH_4-H_2O line“)

$$(1-m)\ CH_4 + m\ H_2O$$

- 0: pure methane
- 1: pure steam
- characterizes feed with ideal stoichiometry



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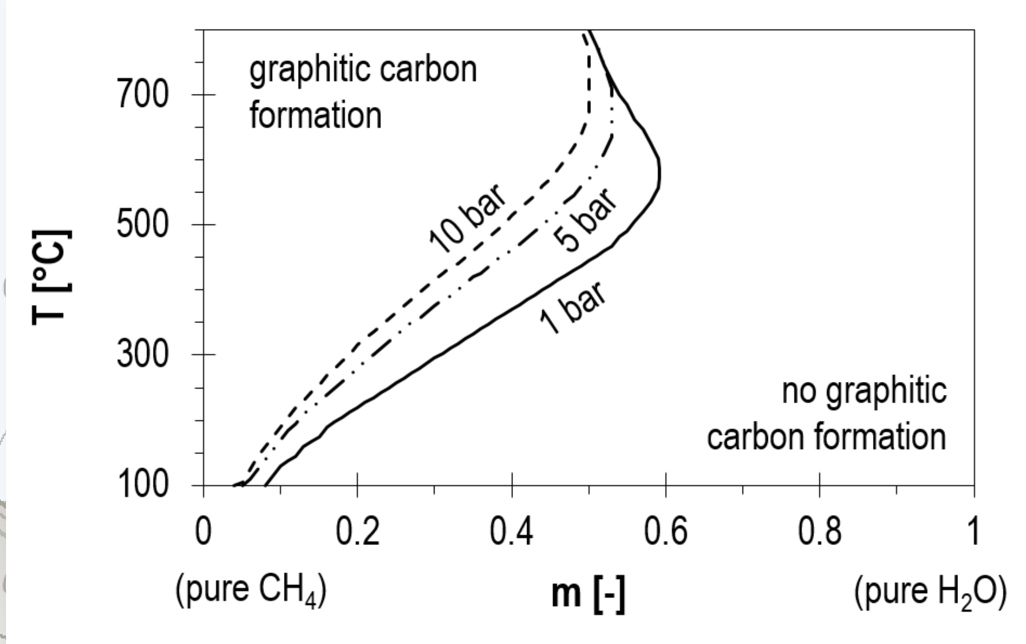
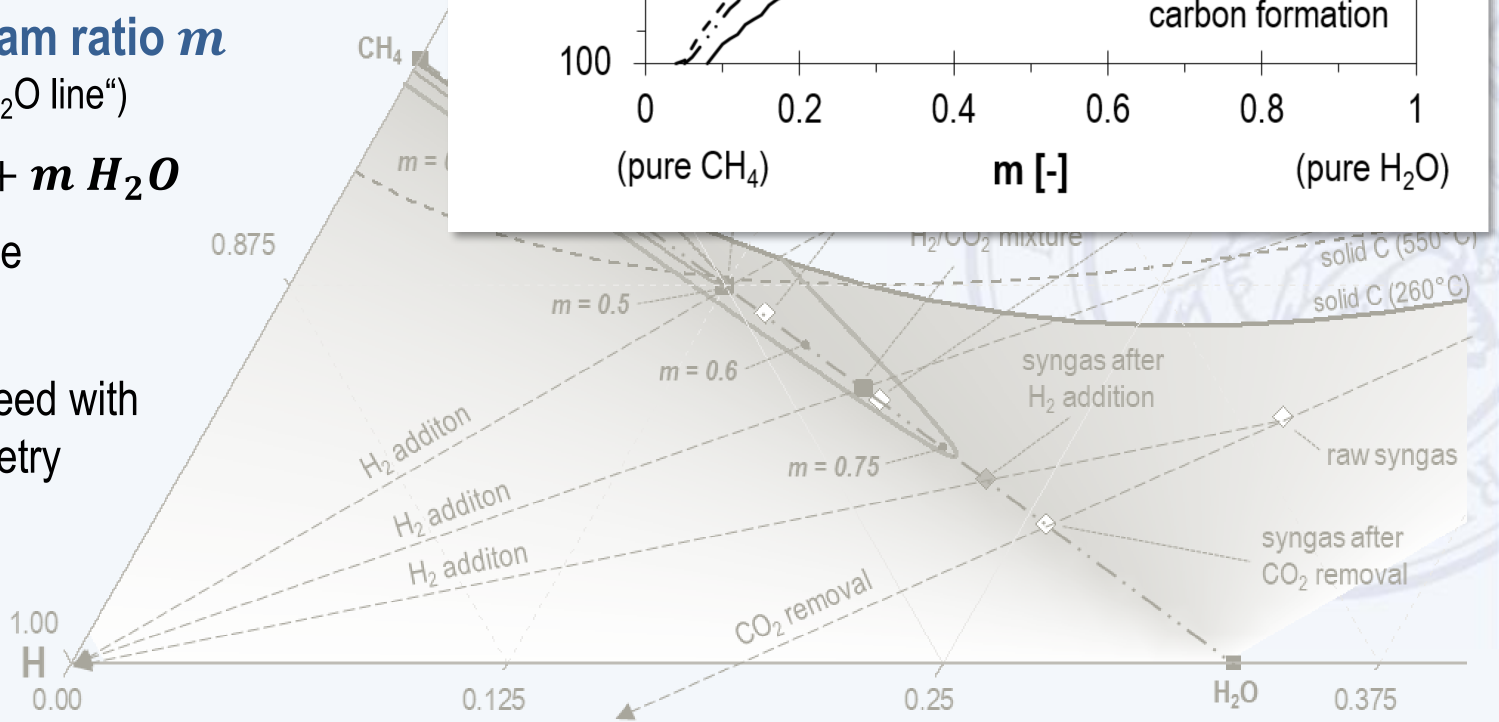
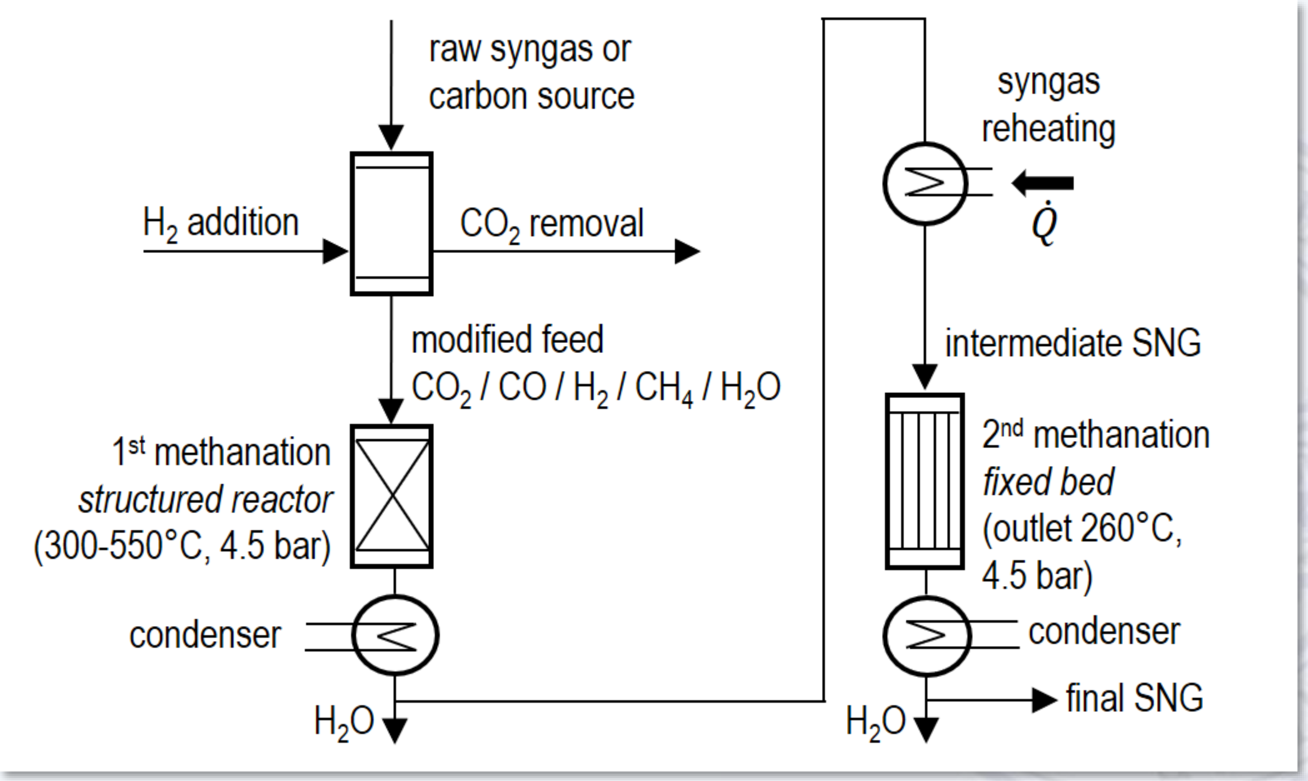




Two-stage methanation with H_2O sequestration

- \+ No product gas recycle compressor
- \+ Suitable for wide range of gas qualities due to upstream gas conditioning
- − Severe conditions in 1st stage
- − Cooled reactor in 1st stage necessary



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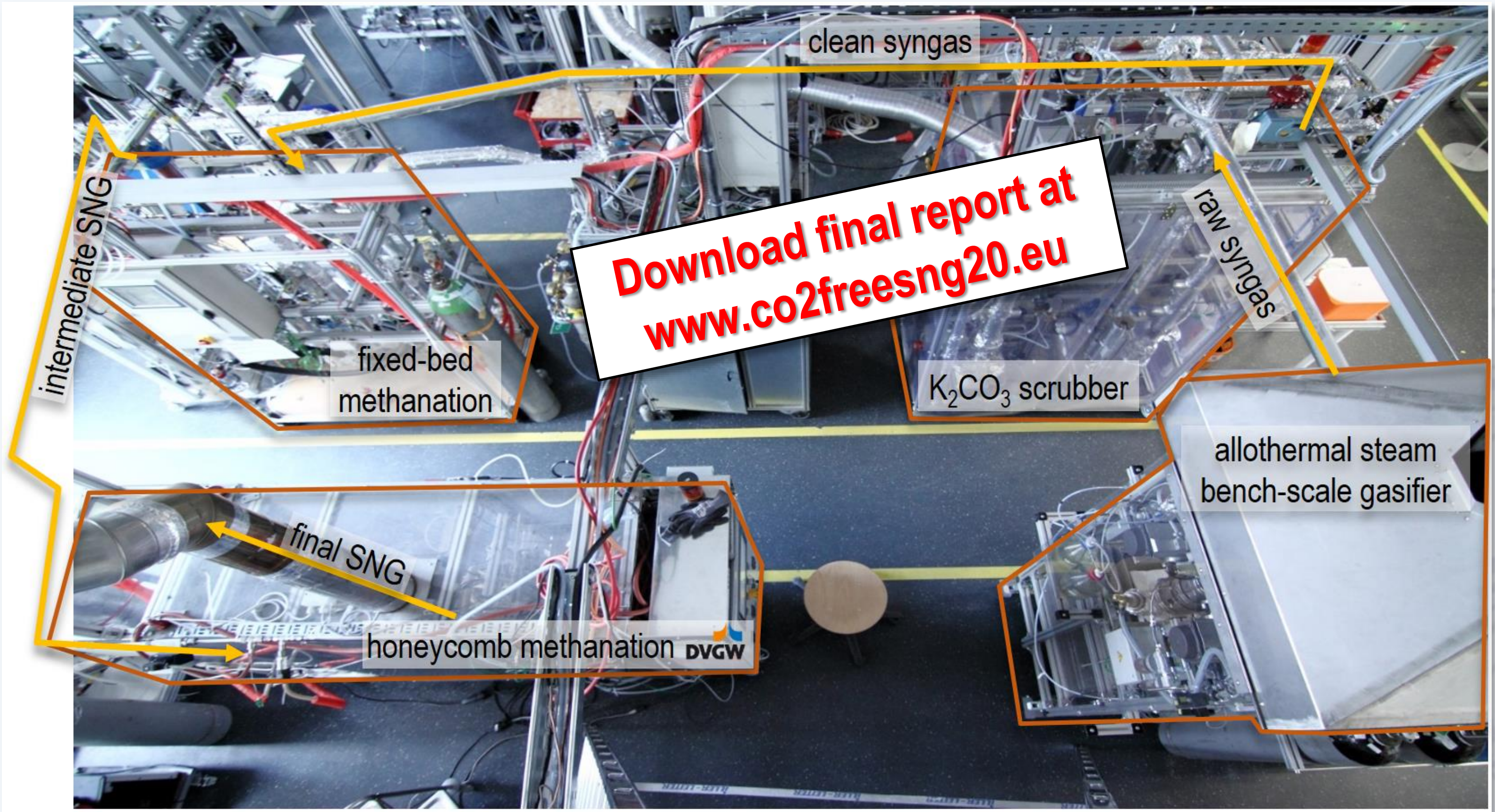
Bench-scale coal-to-SNG process chain



pressurized coal-to-SNG in bench-scale at FAU laboratories

- Designed for maximum fuel input to allothermal steam gasifier P_{th} = 5 kW
- Fixed-bed methanation (D = 42 mm) with air cooling; semi-commercial Ni-catalyst (T_{max} = 550°C)

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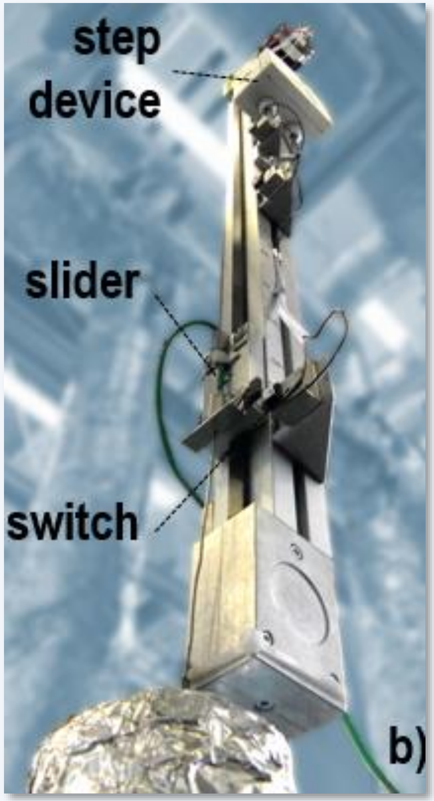
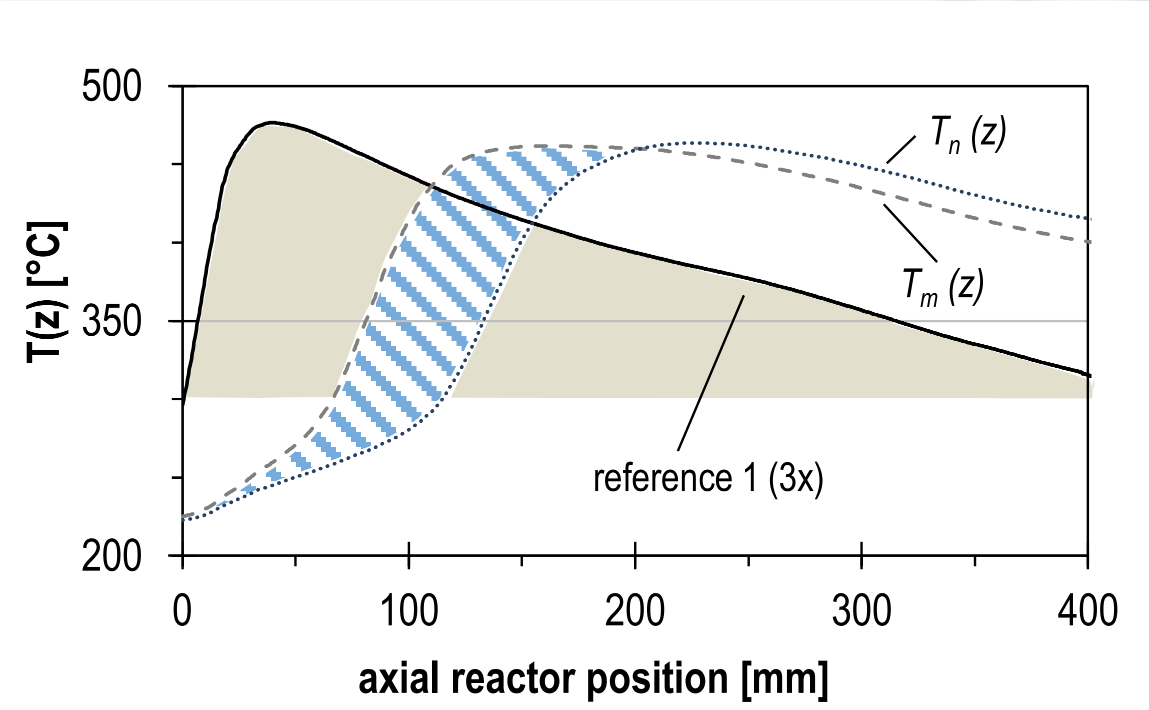
Bench-scale coal-to-SNG process chain

Catalyst deactivation in fixed-bed methanation

- Shift of **axial T-profile under reference conditions** is measure for catalyst deactivation
- Automated device to measure axial temperature profile in methanation reactor



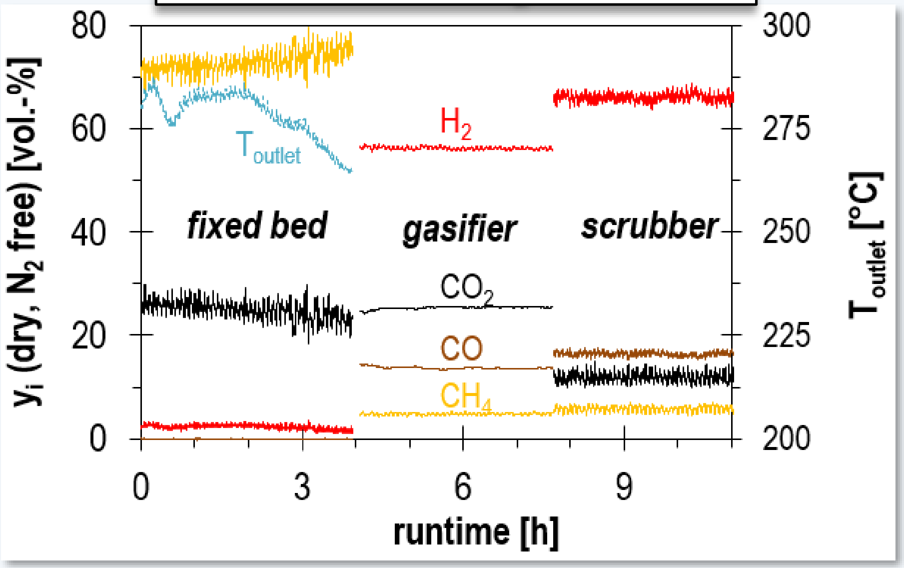


M. Neubert et al. – Influence of hydrocarbons and thiophene on catalytic fixed-bed methanation, Fuel 207 (2017), 253-261

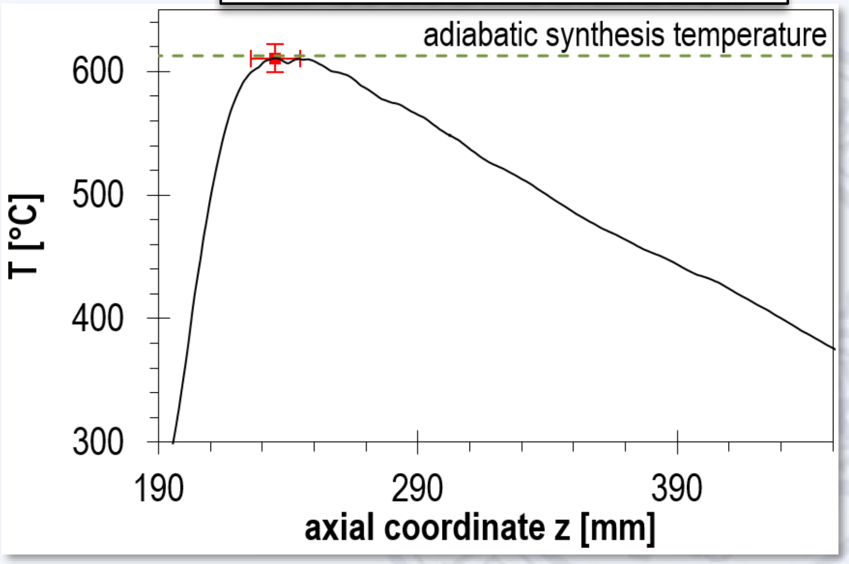
Experiments with lignite-derived syngas

CO_2 removal with Benfield unit at 5 kW bench-scale process chain

insufficient CO_2 removal



adiabatic behaviour of air-cooled methanation



additional 15% nitrogen in feed to methanation

- Insufficient CO_2 removal – only 60 % in experiment, but 85 % would be ideal
  → unfavorable C/H/O ratio
- Hot spot temperature of air-cooled fixed-bed methanation reactor matches the adiabatic one

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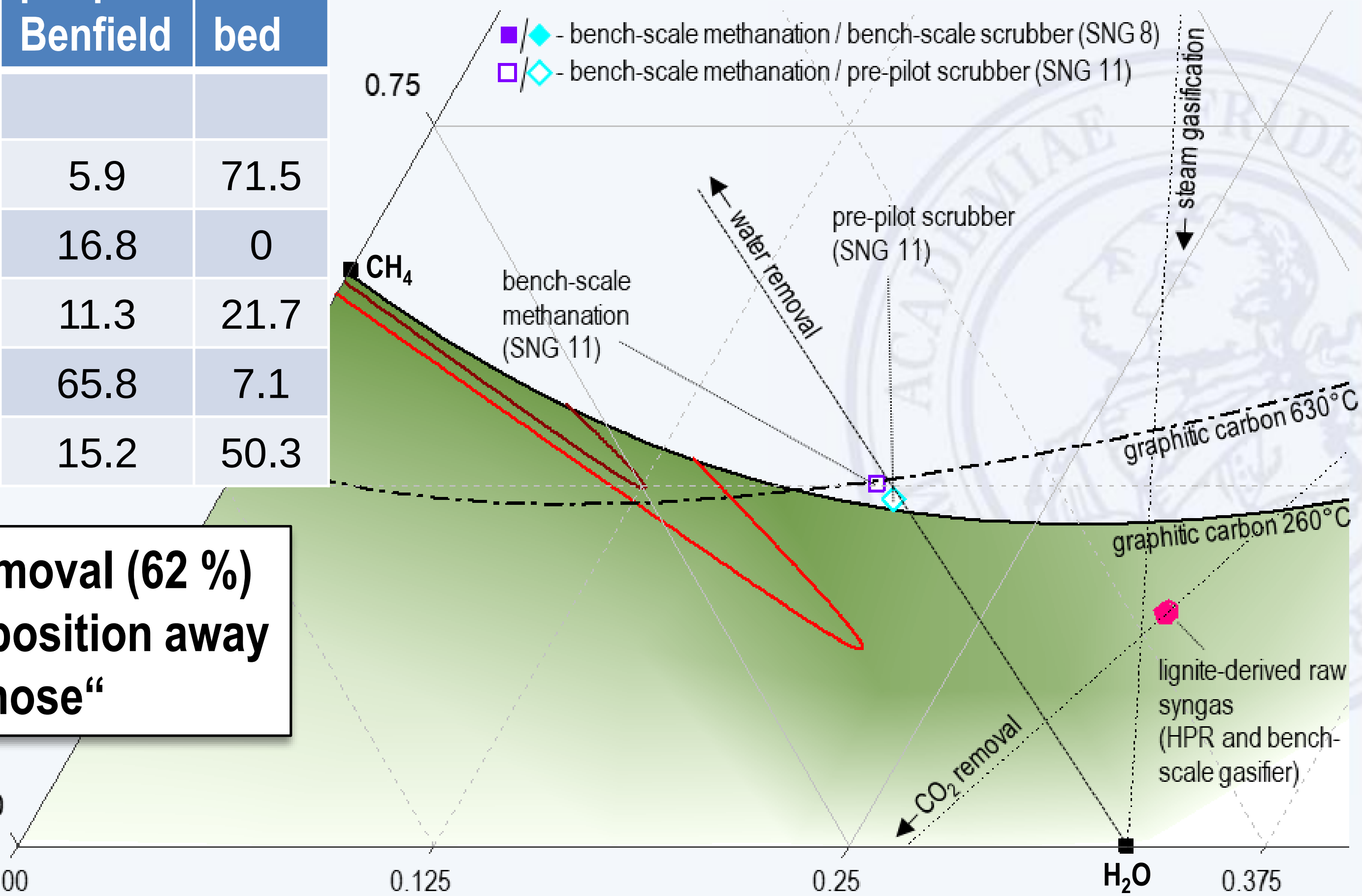
Experiments with lignite-derived syngas

Heatpipe Reformer – pre-pilot Benfield scrubber – slipstream methanation

conc.	Heatpipe Reformer	pre-pilot Benfield	fixed bed
dry			
- CH_4	4.7	5.9	71.5
- CO	14.0	16.8	0
- CO_2	25.3	11.3	21.7
- H_2	55.9	65.8	7.1
H_2O	50	15.2	50.3

insufficient CO_2 removal (62 %) pulls final gas composition away from „CH_4 nose“



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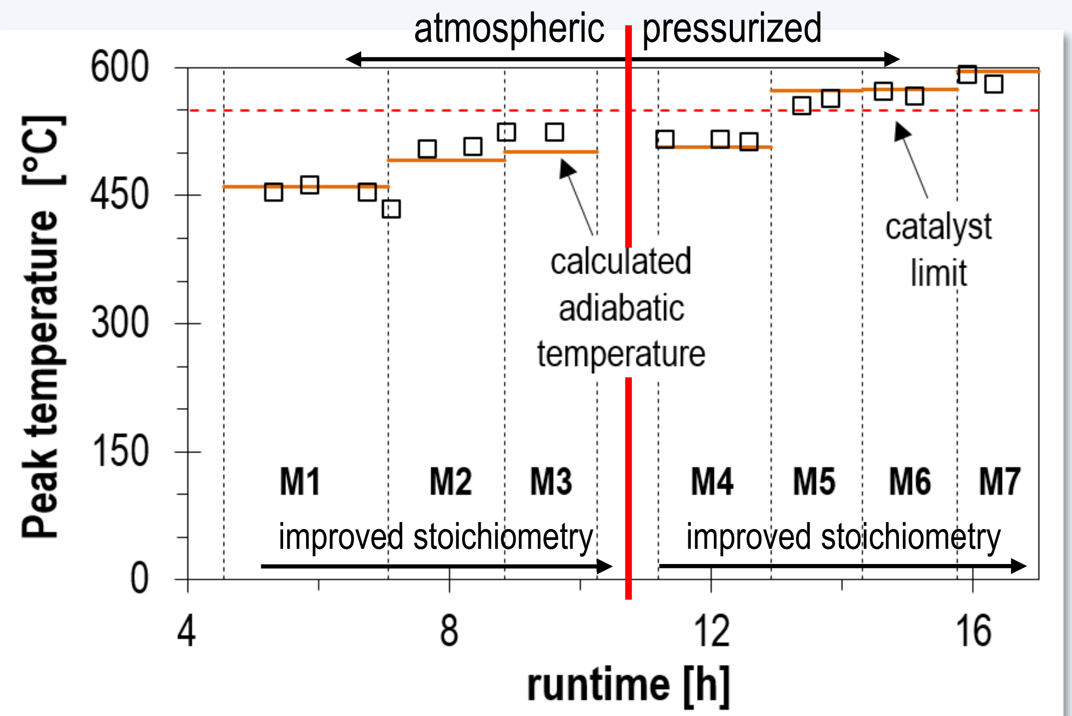
Experiments with biomass-derived syngas

Heatpipe Reformer – addition of bottled hydrogen – slipstream methanation



J. M. Leimert, M. Neubert, P. Treiber, M. Dillig, J. Karl - Combining the Heatpipe Reformer technology with hydrogen-intensified methanation for production of synthetic natural gas, Applied Energy 217 (2018), pp. 37-46

- Stable operation with biomass-derived syngas and additional hydrogen possible
  - Adsorptive gas cleaning upstream of methanation
  - No higher hydrocarbons at outlet of methanation
- Increasing synthesis temperature with improving stoichiometry

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Experiments with syngas

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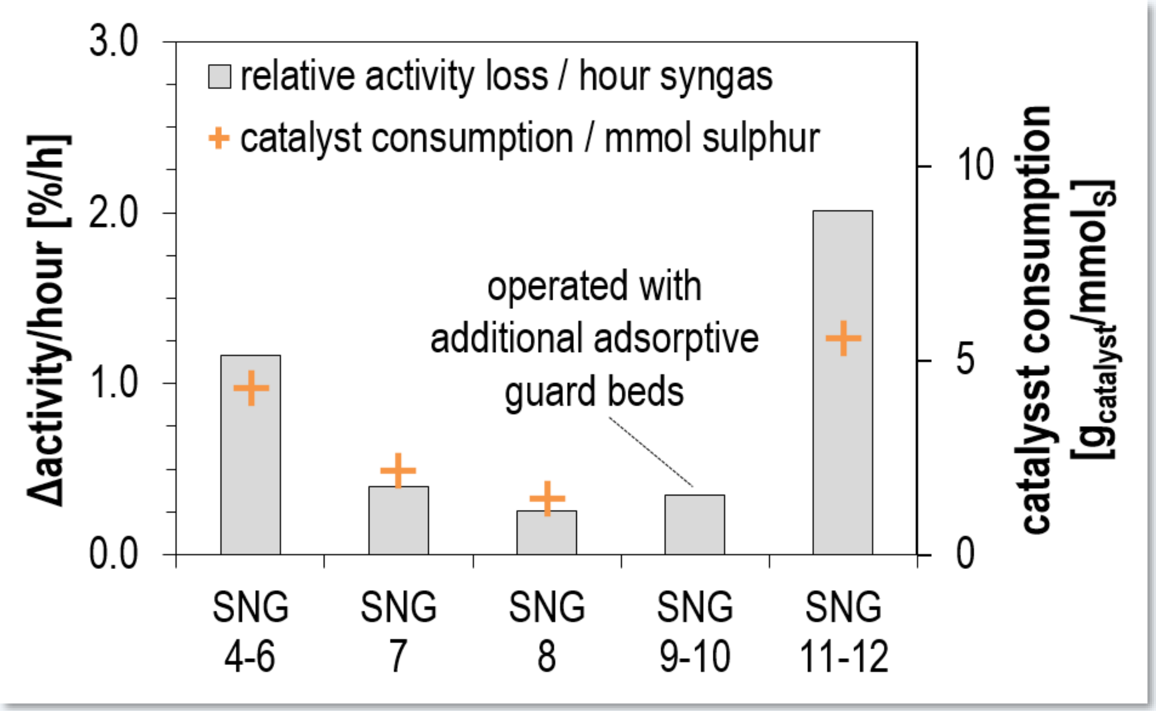
Deactivation of catalytic fixed-bed



- Deactivation of fixed-bed determined by axial shift of temperature profile
- Deactivation remains at similar level even with additional sulfur removal

  → Sintering predominates

Simple „once-through“ SNG process needs reactor with high in-situ cooling capability

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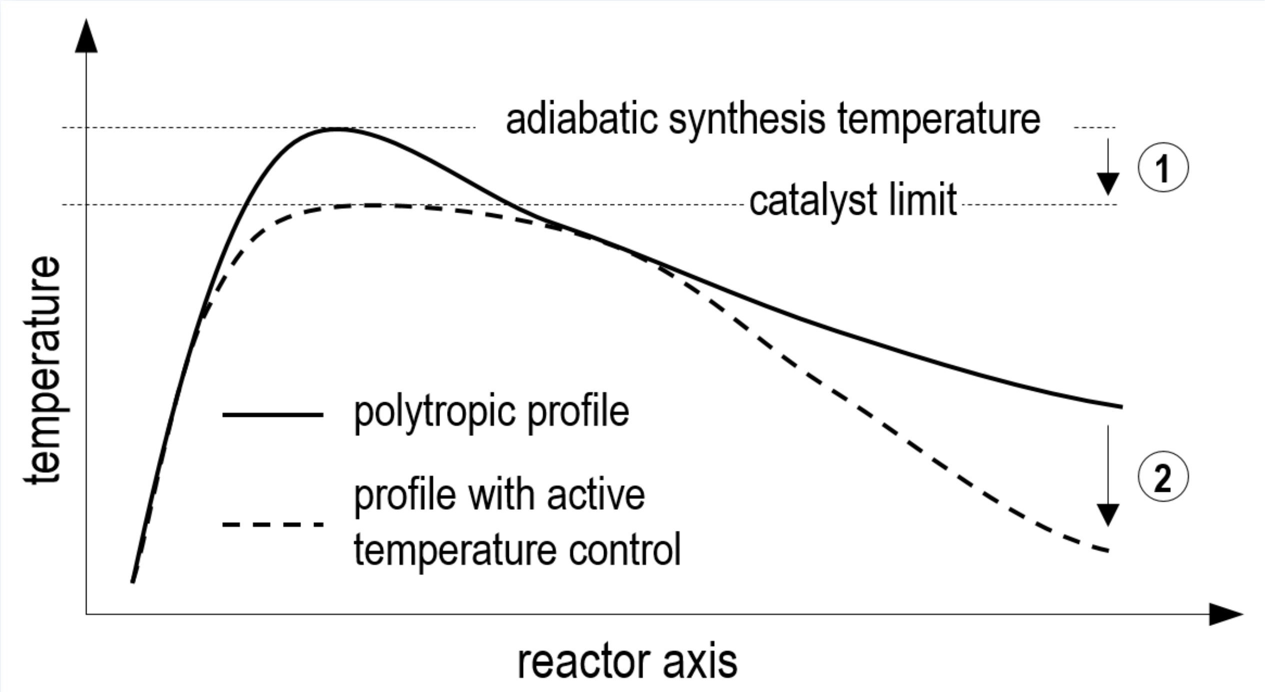
Objectives of heat pipe cooled reactor



- Objective 1 of cooled reactors: Avoiding catalyst sintering
  → with stoichiometric feed, the adiabatic synthesis temperature **(~ 680°C)** must not be reached
- Objective 2 of cooled reactors: High methane concentration (= low outlet temperature)
- Main obstacle in fixed-bed reactors: Poor effective radial heat conductivity

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Structured reactor

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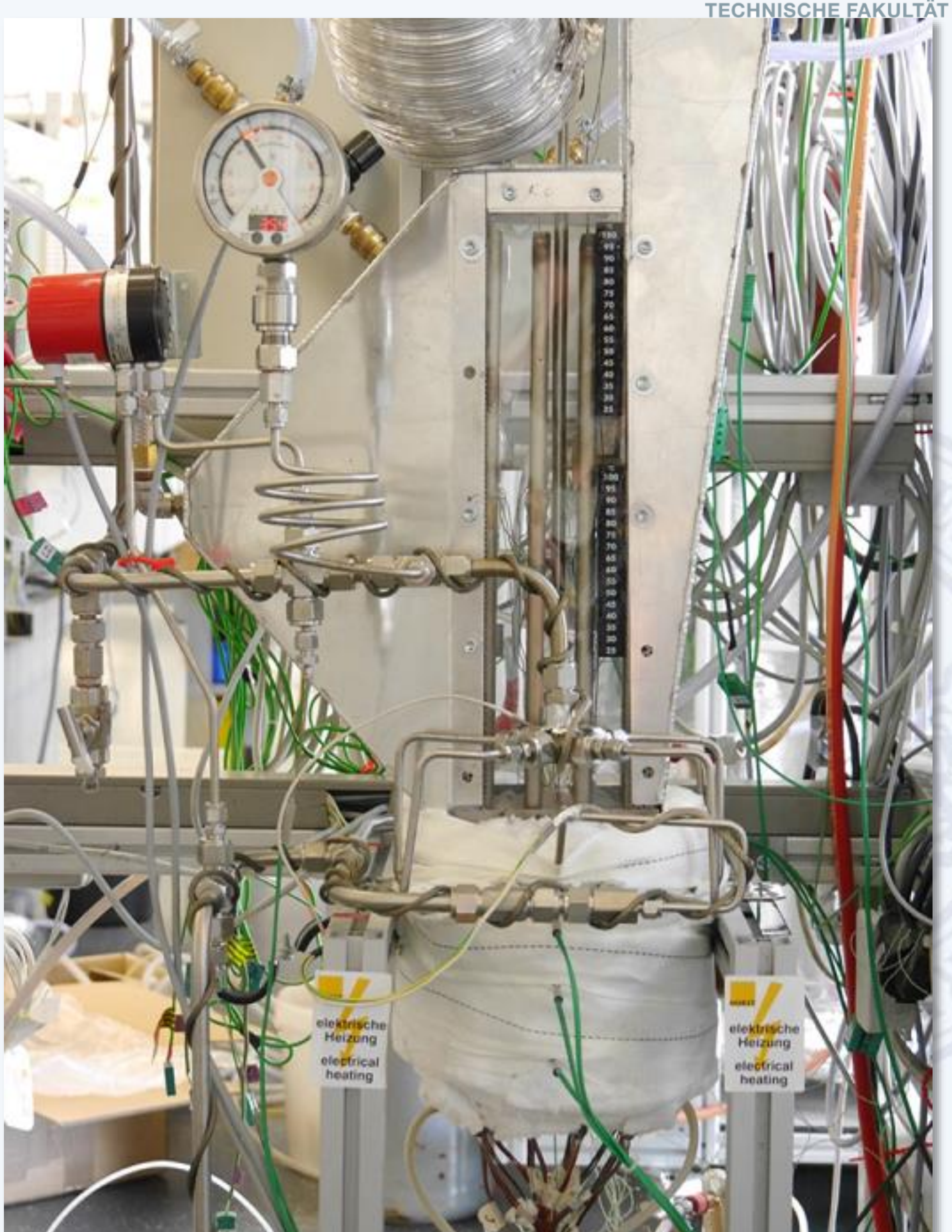
Design criteria

- Structured reactor
- Utilization of a commercial catalyst
- Defined flow of fluid in reaction channel
- Internal educt gas preheating
- Scalable



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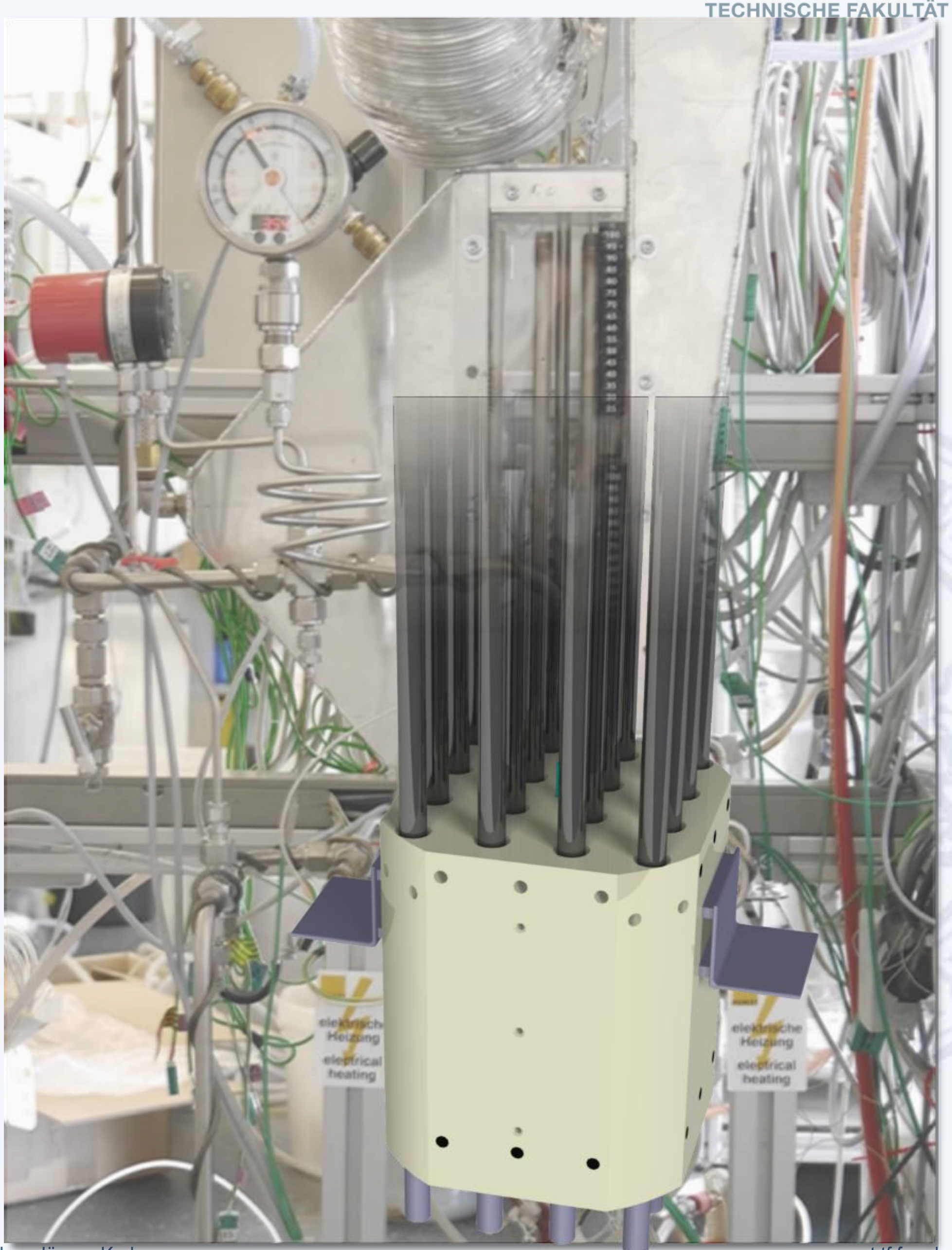
Realization as 5 kW lab-scale reactor

- Reactor body made of stainless steel with channels
- 16 heatpipes for cooling of block ($12x2$ mm, mesh, H_2O as Fluid)
- 9 reaction channels (**8 mm diameter**) 12 preheating channels (6 mm)



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Heatpipes for heat removal

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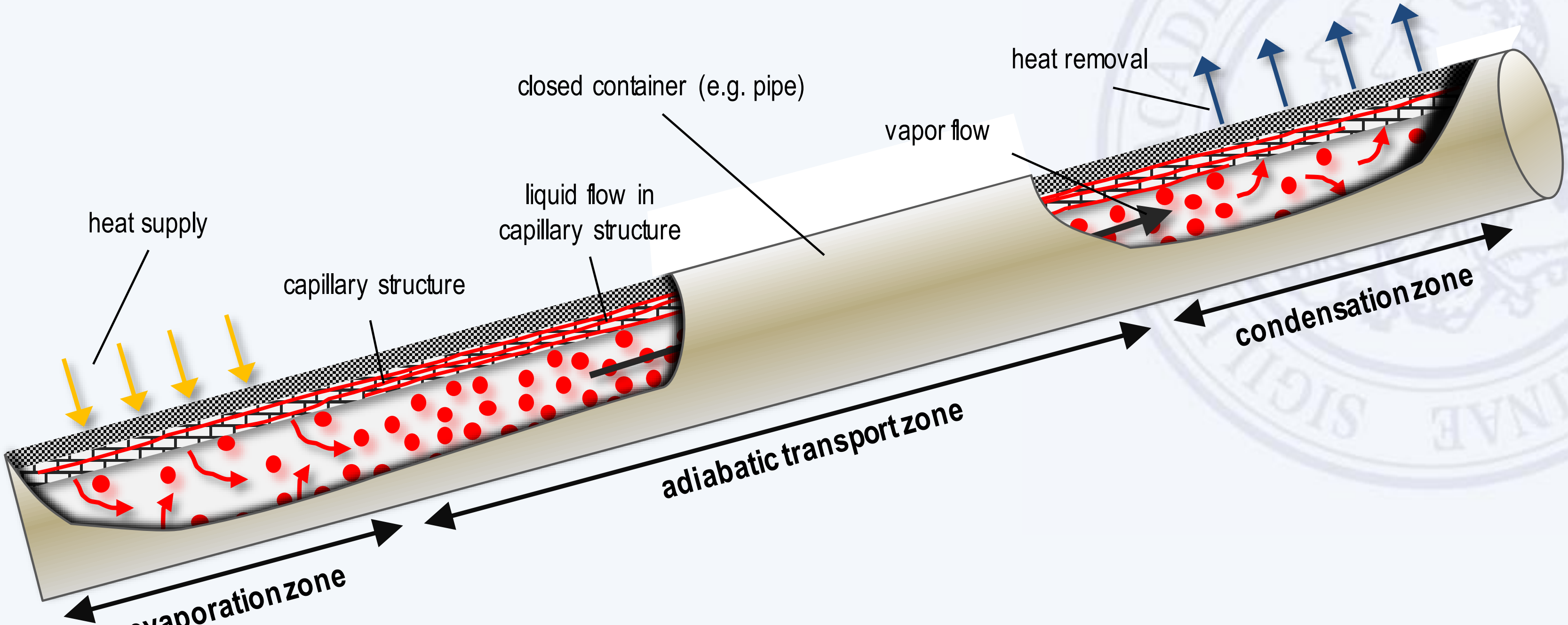
- Passive element for heat transport
- Transport of evaporation enthalpy from heat source to heat sink in a closed two-phase system

\+ **(Almost) isothermal heat transport with high heat flux density in main reaction zone**

\+ **Water evaporation at ~250-300°C without auxiliary high-pressure system**



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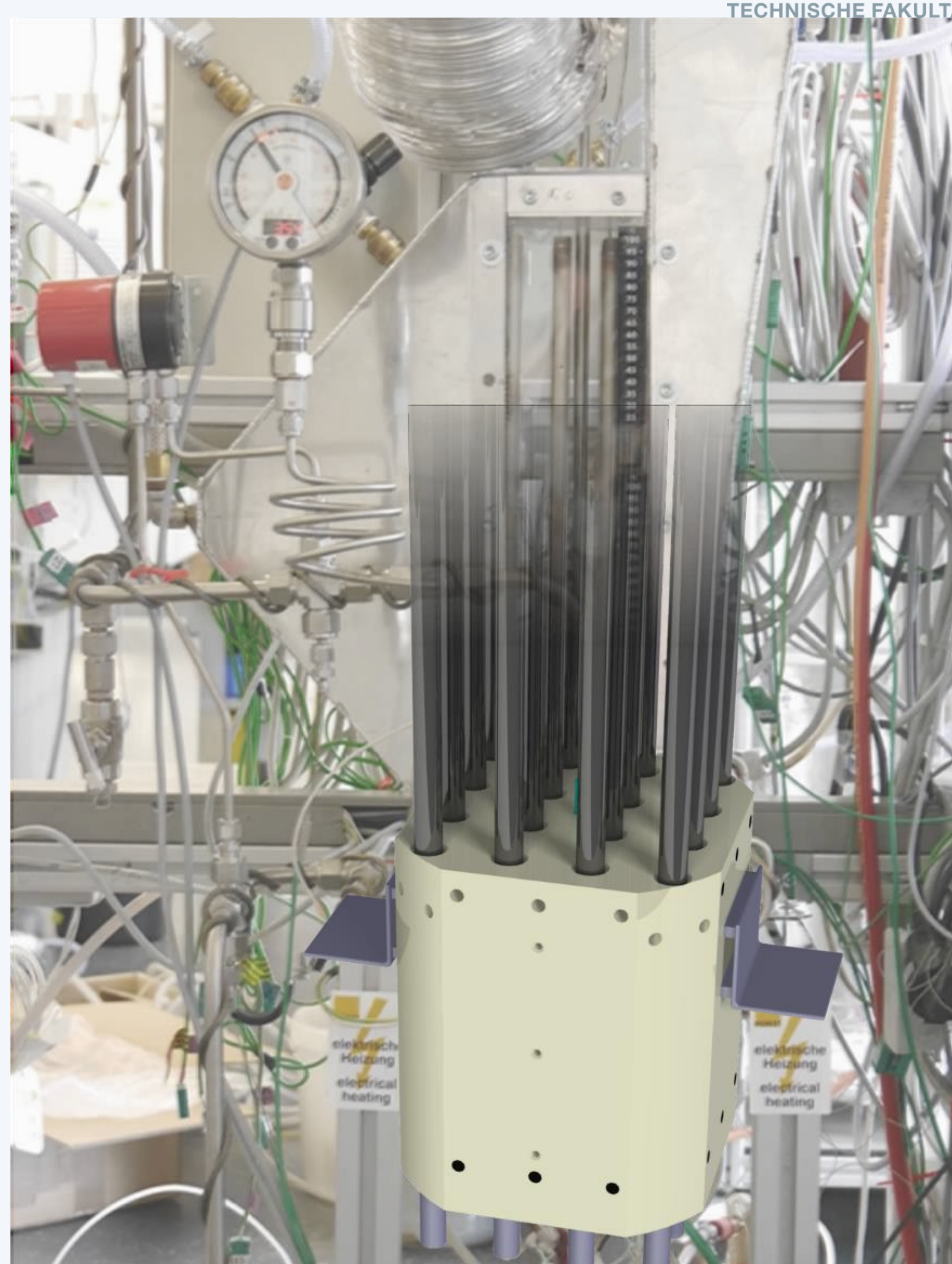

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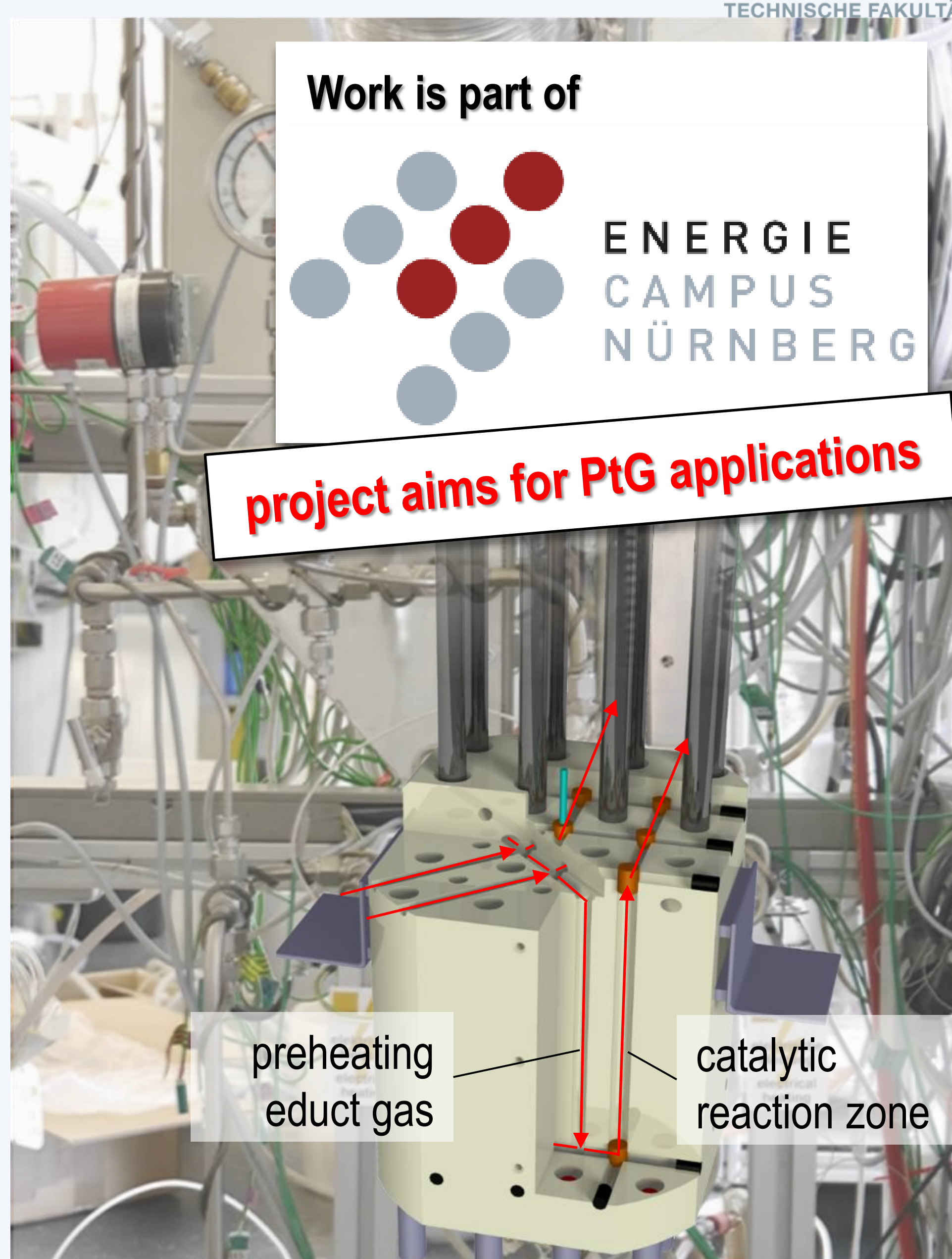

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Two-stage methanation with H_2O sequestration

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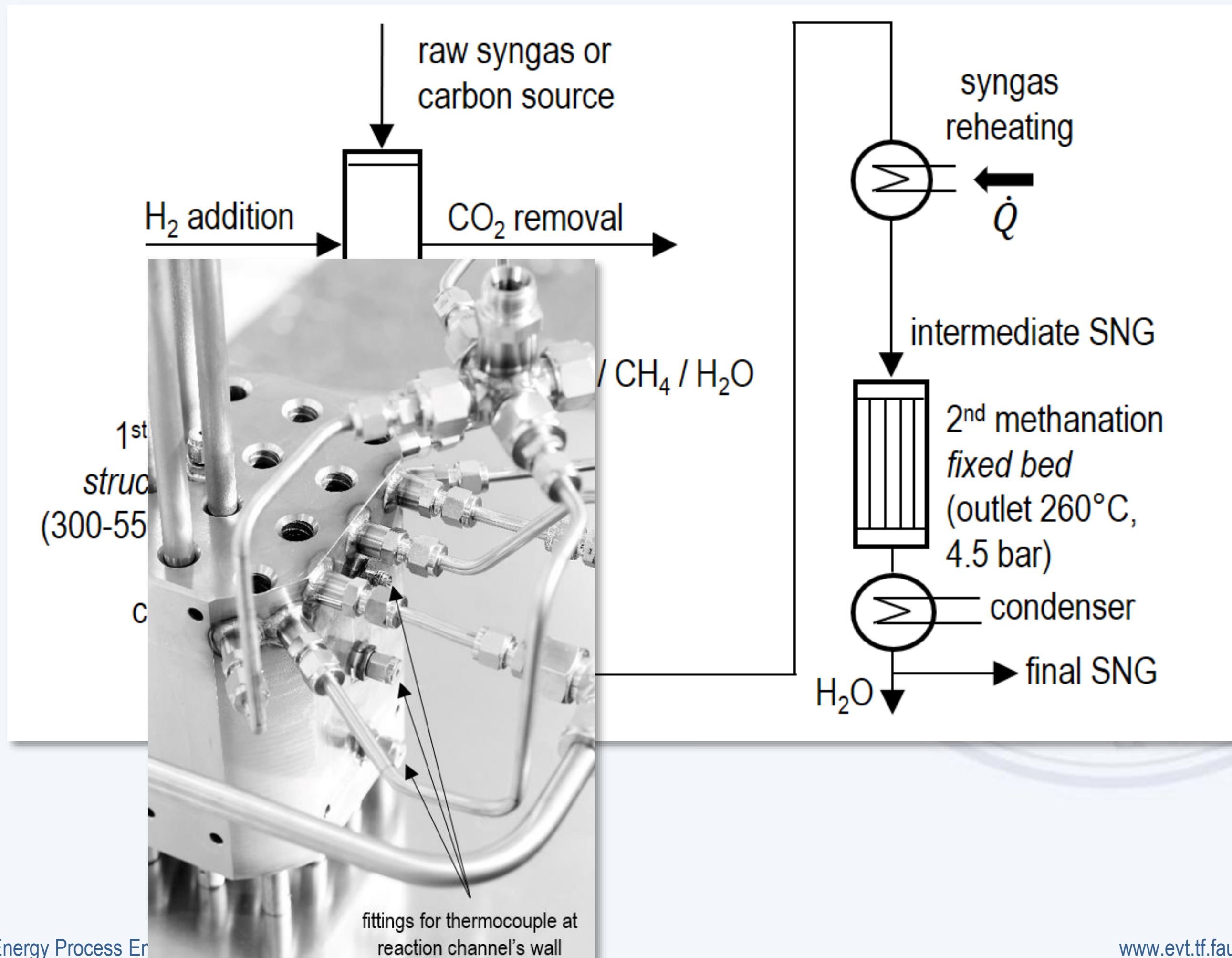
- Suitable for wide range of gas qualities due to upstream gas conditioning
- Severe conditions in 1st stage
- Cooled reactor in 1st stage necessary



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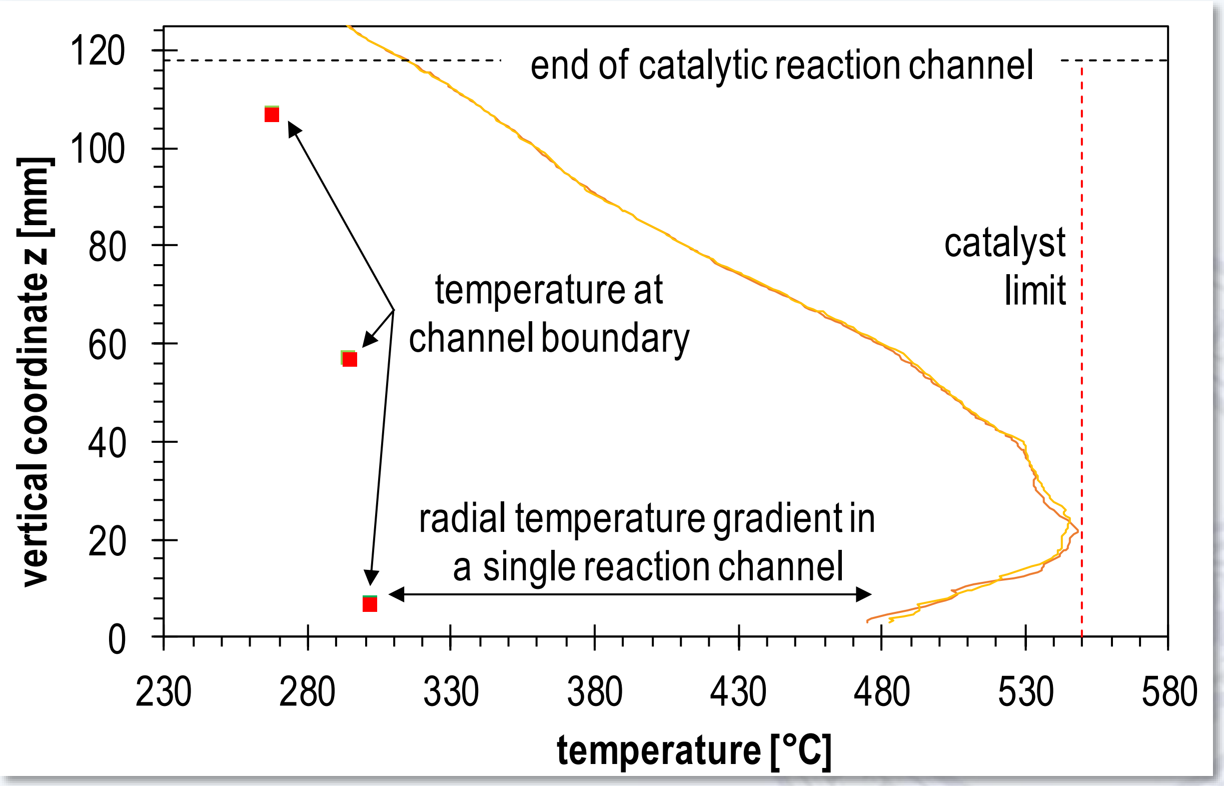
Maximum temperature in heat pipe cooled reactor

- Full load
  - 5 kW
  - CO_2 (7 Nl/min) + H_2 (28 Nl/min) + steam (1.4 Nl/min)
- Maximum temperature below 550°C
- Educt conversion ~ 85 %
- Radial temperature gradient more than 200 K
- Heatpipe operating temperature ~ 273°C



Axiale temperature profile in a single reaction channel; CO_2 (7 Nl/min) + H_2 (28 Nl/min) ***+ 3.9 vol.-% steam****; ($T_{in,channel}$ ~ 300°C, $T_{in,reactor}$ ~ 190°C, p = 4.5 bar, GHSV 40900 h^{-1})*

⇨ **Maximum temperature in experiment is significantly lower than adiabatic one (~ 680°C)**

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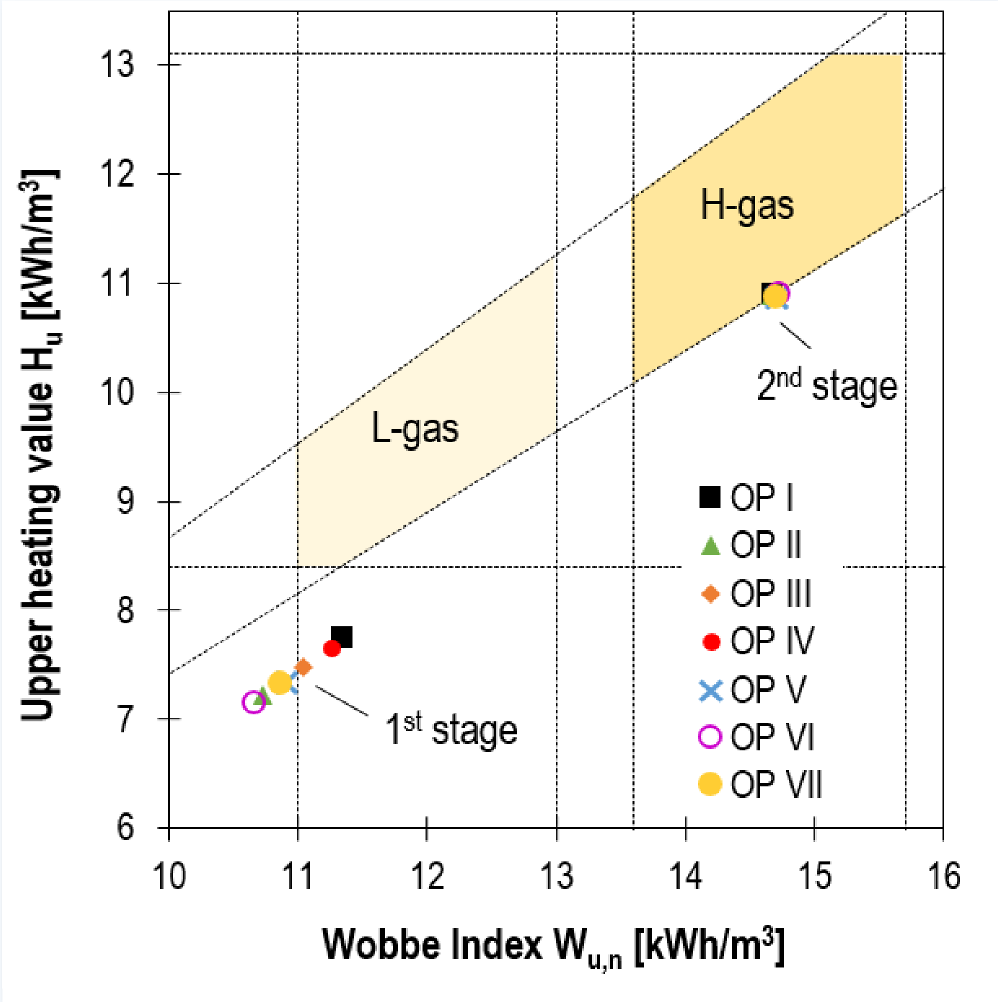
Gas quality of two-stage methanation system

- Operating conditions varied
  - thermal power input
  - cooling flux
  - steam content in feed
  - pressure

- System shows high resilience

Buffering behaviour of two-stage system allows full conversion



Gas qualities according to German G260 standard; stoichiometric H_2/CO_2 feed (N_2 free)

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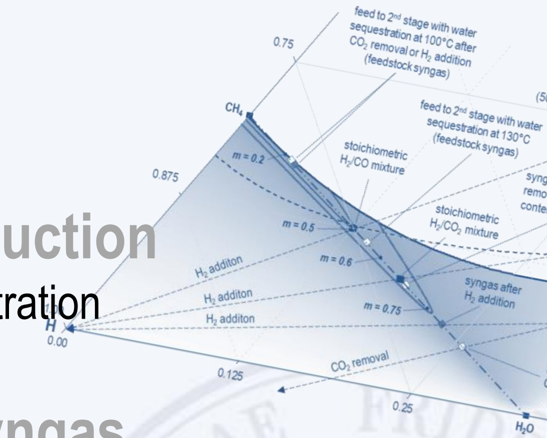
I - Motivation

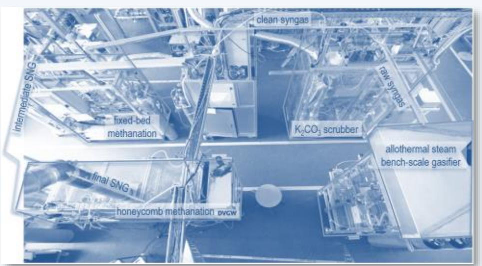
- Renewable SNG will be necessary



II - Simulation based evaluation of SNG production

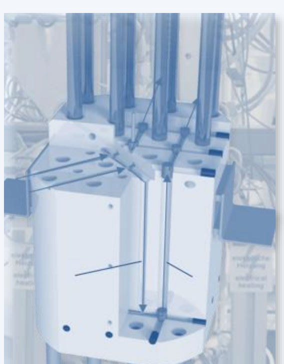
- Two-stage methanation with intermediate water sequestration

III - Experimental methanation of syngas



- Sintering predominates catalyst deactivation
- Hydrogen addition for full carbon utilization

IV - Heat pipe cooled reactor concept



- Cooling with heat pipes allows non-adiabatic operation
- Evaporation at 250-280°C without high pressure equipment

Conclusion and outlook

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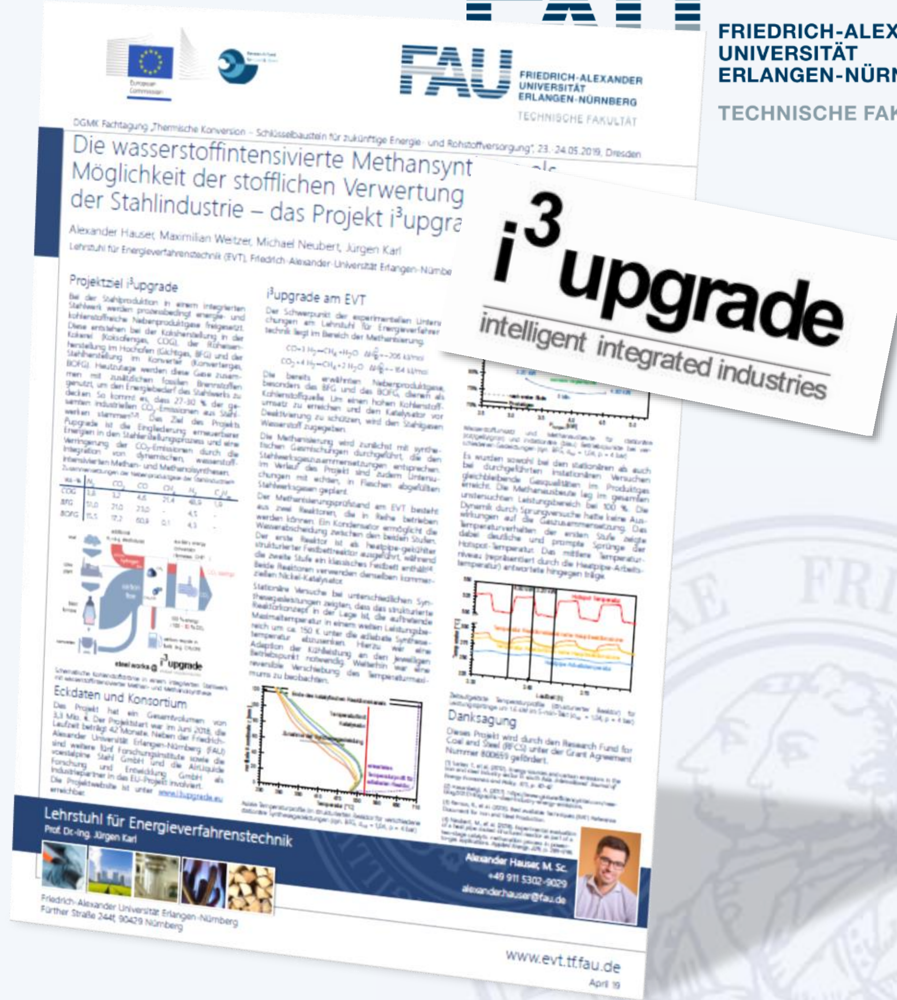
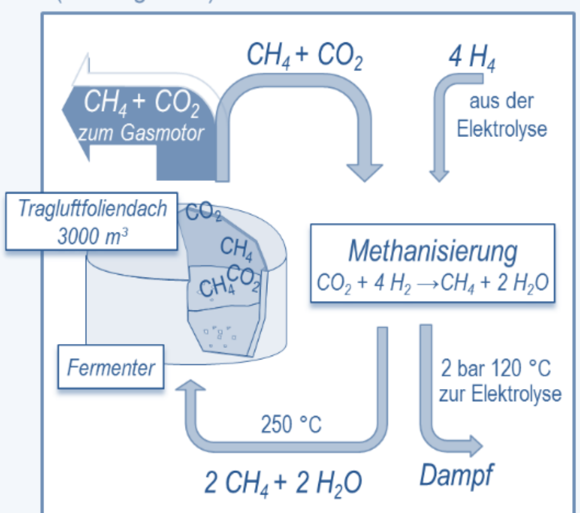
Outlook

i³upgrade - www.i3upgrade.eu

- Hydrogen intensified synthesis (CH_4, methanol) of by-product gases from integrated steel works
- Focus on intelligend dispatcher tool to control synthesis units
- European RFCS project



Einspeicherung von Methan
(z.B. tagsüber)



Hydrogen enriched methanation of biogas

- Local power storage
- Heat utilization favorable and necessary due to high temperature level of heat pipes