FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT

International Conference on Polygeneration Strategies, 18th/19th November 2019, Vienna

Dynamic methanation of by-product gases from the steel industry in the scope of the project i³upgrade


Quelle: voestalpine

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Outline

- Motivation
- The project i³upgrade
  - Aim of the project
  - Consortium
- Fundamentals
  - Methanation
  - By-product gases from the steel industry
- Experimental setup and results
  - Reactor concept and methanation test rig
  - Experimental results from the methanation of steel work's by-product gases
- Conclusion

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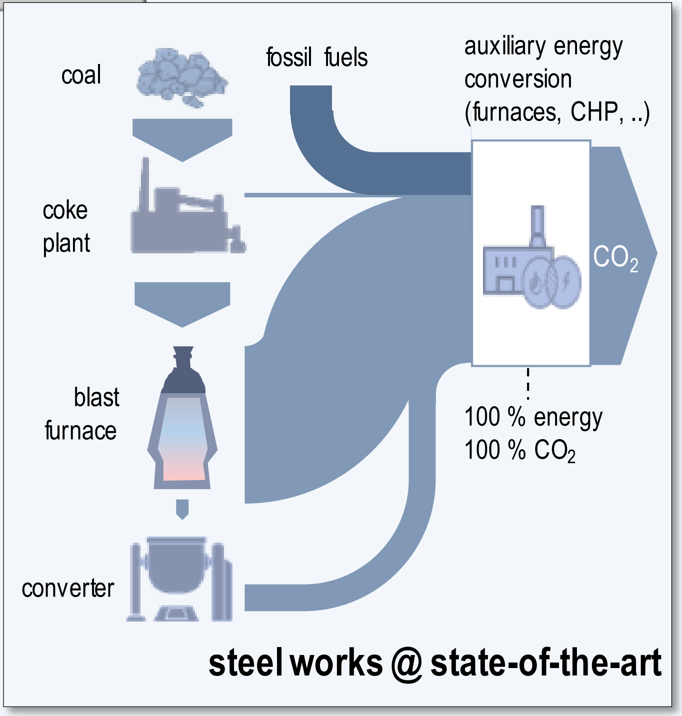
CO_2 emissions from integrated steelworks

- Energy and carbon rich by-product gases emerge process-related
  - Thermodynamic optimum for the consumption of reducing agent is already reached (~498 $kg_C/t_{hot\ metal}$; theoretical minimum: 414 $kg_C/t_{hot\ metal}$)[1]
  - Nowadays used thermally internally
  - Do not cover the entire energy demand → additional fossil fuels necessary



- 27 – 30 % of the total industrial CO_2 emissions originate from steel works[2,3]
- This equals 5 – 6 % of the total anthropogenic CO_2 emissions[2,3]
- Focus of i³upgrade:

  Reduction of the CO_2 impact of the integrated steel works through hydrogen-intensified syntheses

1) www.eurofer.org
2) A review of thermochemical processes and technologies to use steelworks off-gases, W. Uribe-Soto et al., Renewable and Sustainable Energy Reviews 74 (2017), pp. 809-823
3) A. Hasanbeigi, 2017, https://www.globalefficiencyintel.com/new-blog/2017/nfographic-steel-industry-energy-emissions

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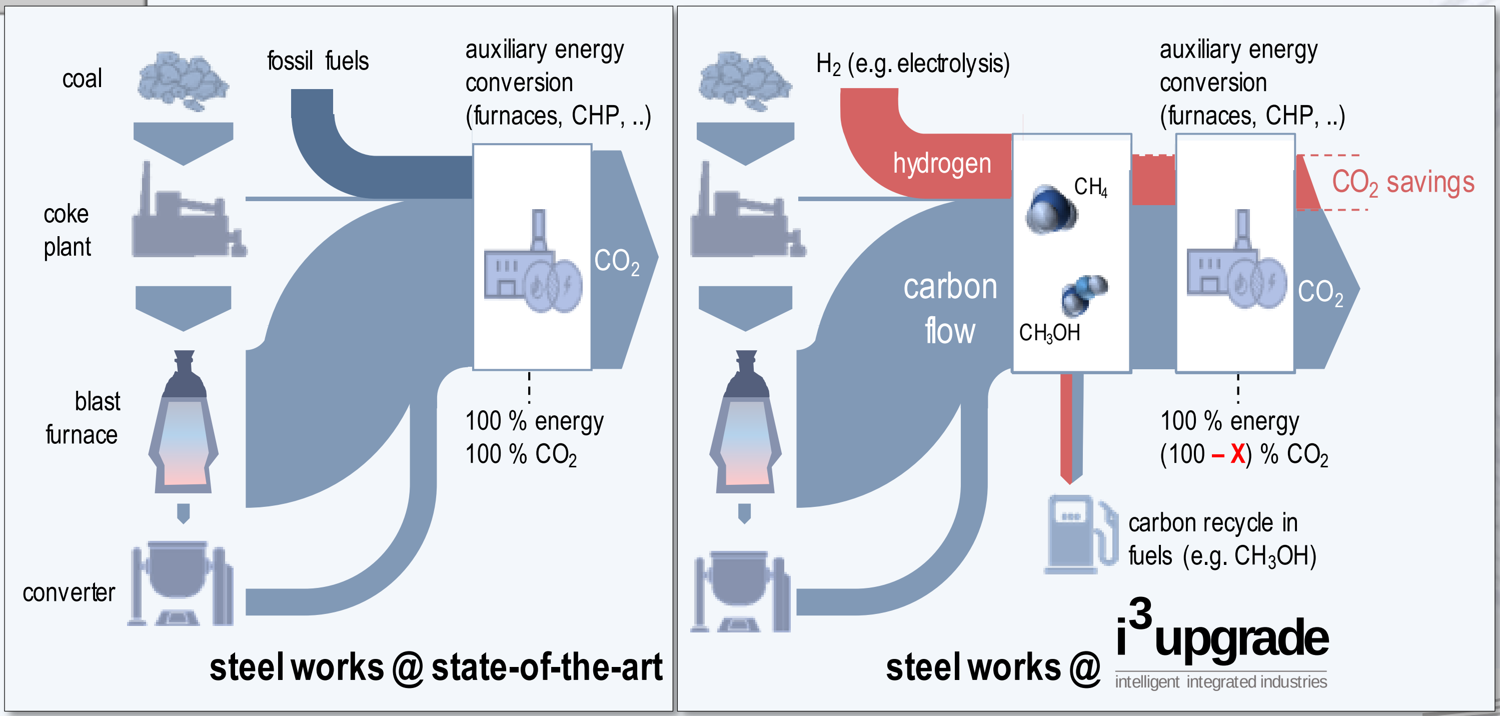
Project objective i³upgrade (1)

- Aim: Integration of renewable energies into the steelmaking process and thereby reduction of the CO_2 impact of integrated steel works
- No major changes to the steelmaking process itself
- Integration of dynamic syntheses (methane, methanol) into an integrated steel works in combination with (renewable) hydrogen



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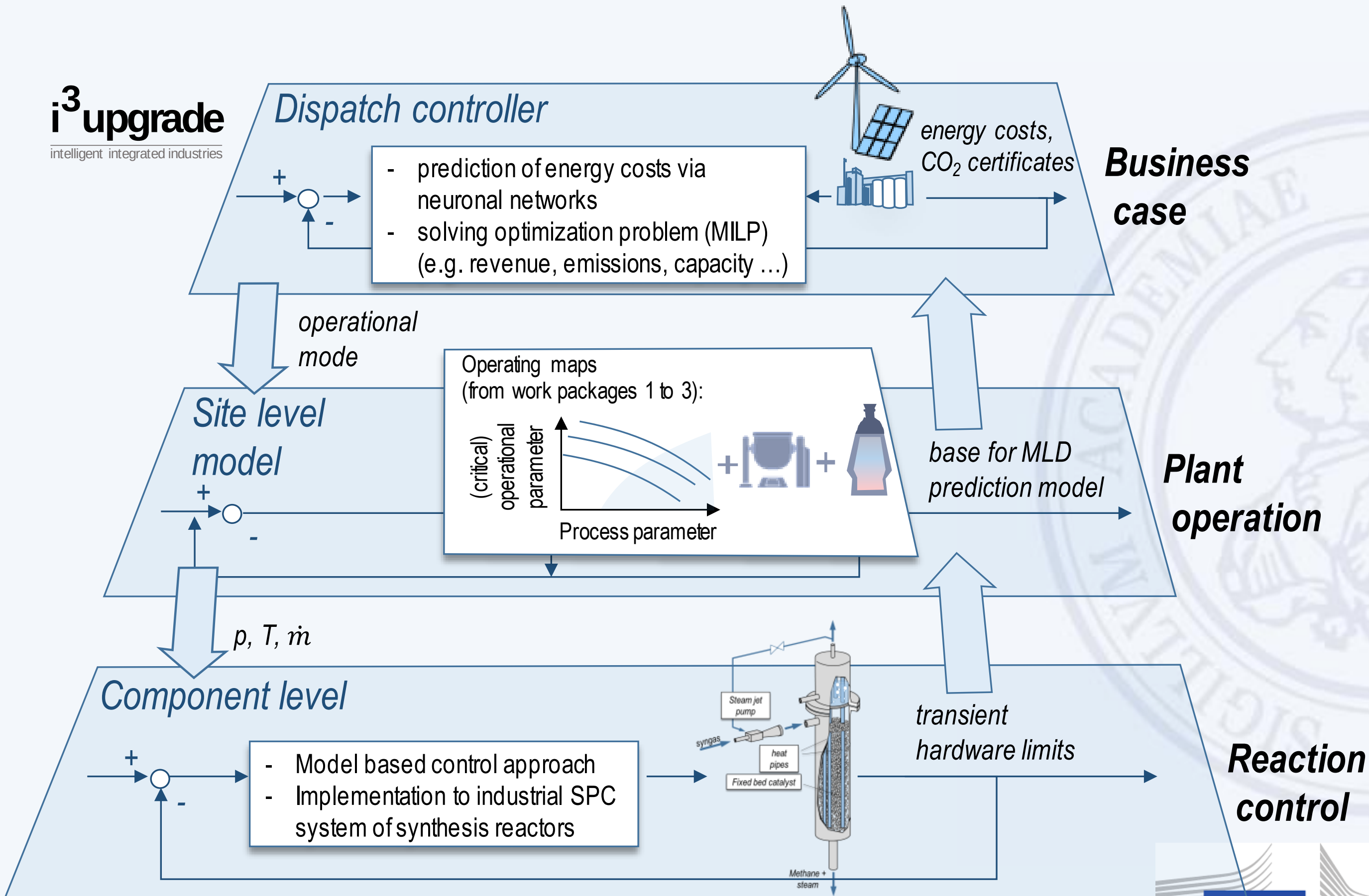
Project objective i³upgrade (2)

- Intelligent process control strategy for dynamic operation with integrated dispatcher tool
- Approach with three control levels, from technical to economic level



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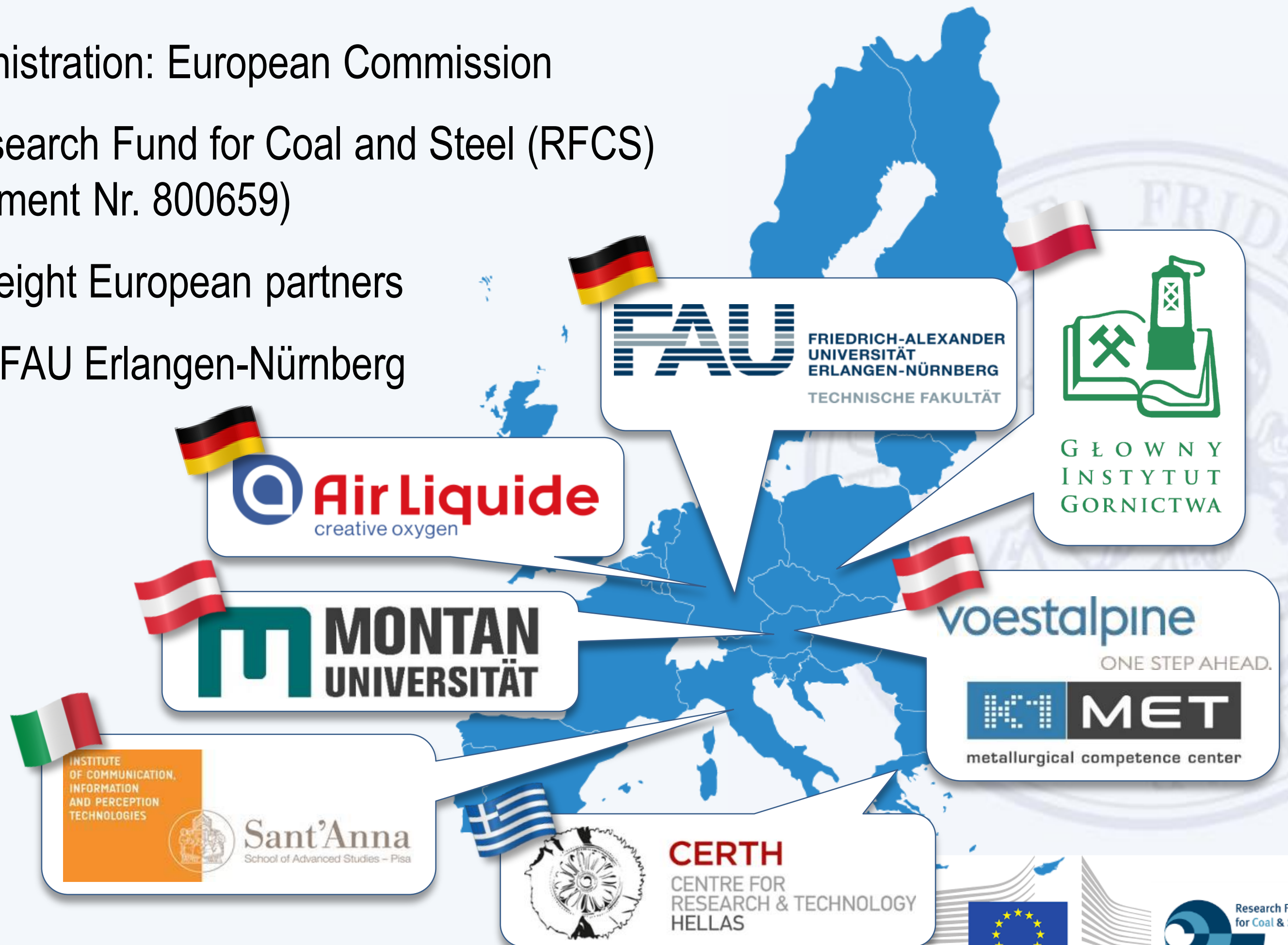
Consortium of i³upgrade

- Term: 1st June 2018 to 30th November 2021; 42 months
- Total budget: 3.3 MM €
- Project administration: European Commission
- Funding: Research Fund for Coal and Steel (RFCS) (Grant Agreement Nr. 800659)
- Consortium: eight European partners
- Coordinator: FAU Erlangen-Nürnberg



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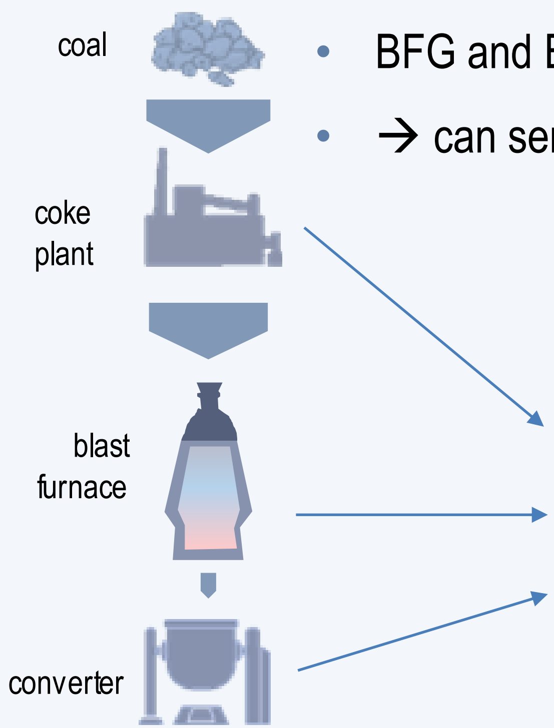
By-product gases from the steel industry

- 3 process steps with energy and carbon rich by-product gases
  - Production of coke in coking plant → coke oven gas (COG); max. 65 000 m_N^3/h
  - Production of pig iron in blast furnace → blast furnace gas (BFG); max. 800 000 m_N^3/h
  - Production of steel in converter → converter gas (BOFG / CG); max. 75 000 m_N^3/h



- BFG and BOFG contain high shares of carbonaceous species
- → can serve as carbon sources for hydrogen-intensified syntheses

[vol.-%](4)	N_2	CO_2	CO	CH_4	H_2	C_nH_m
COG	3.8	3.2	4.6	21.4	48.9	1.9
BFG	51.0	21.0	23.0	-	4.5	-
BOFG / CG	15.5	17.2	60.9	0.1	4.3	-

(4) Unweighted mean values: R. Remus et al., Best Available Techniques (BAT) Reference Document for Iron and Steel Production, 2013.

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Methanation – Reaction system and main challenge

- Reaction system containing CO and CO_2 methanation and water-gas-shift reaction
- Formation of solid carbon possible (Boudouard equation)

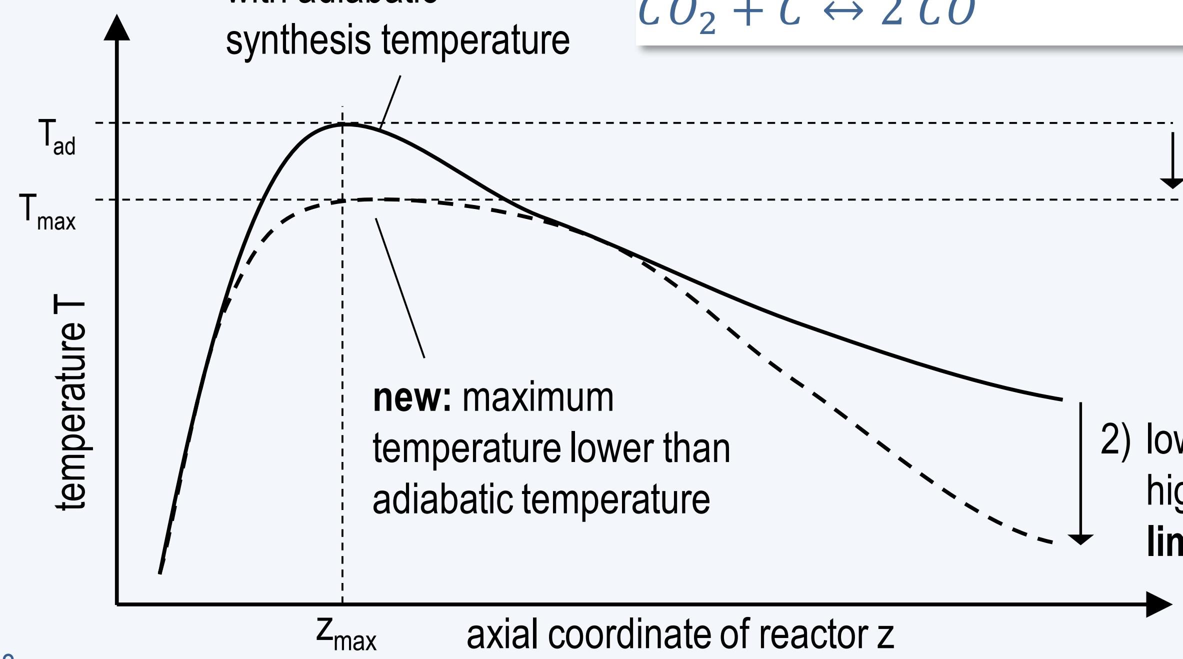
$$CO + 3\,H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H_R^0 = -206\ \mathrm{kJ/mol}$$

$$CO_2 + 4\,H_2 \leftrightarrow CH_4 + 2\,H_2O \qquad \Delta H_R^0 = -164\ \mathrm{kJ/mol}$$

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

$$CO_2 + C \leftrightarrow 2\,CO \qquad \Delta H_R^0 = +173\ \mathrm{kJ/mol}$$

to date: polytropic temperature profile with adiabatic synthesis temperature



1) Maximum temperature must be lower than the maximum temperature of the catalyst, **limited by heat flow density**

2) low temperature at the reactor outlet for high methane content, **limited by heat exchanger surface**

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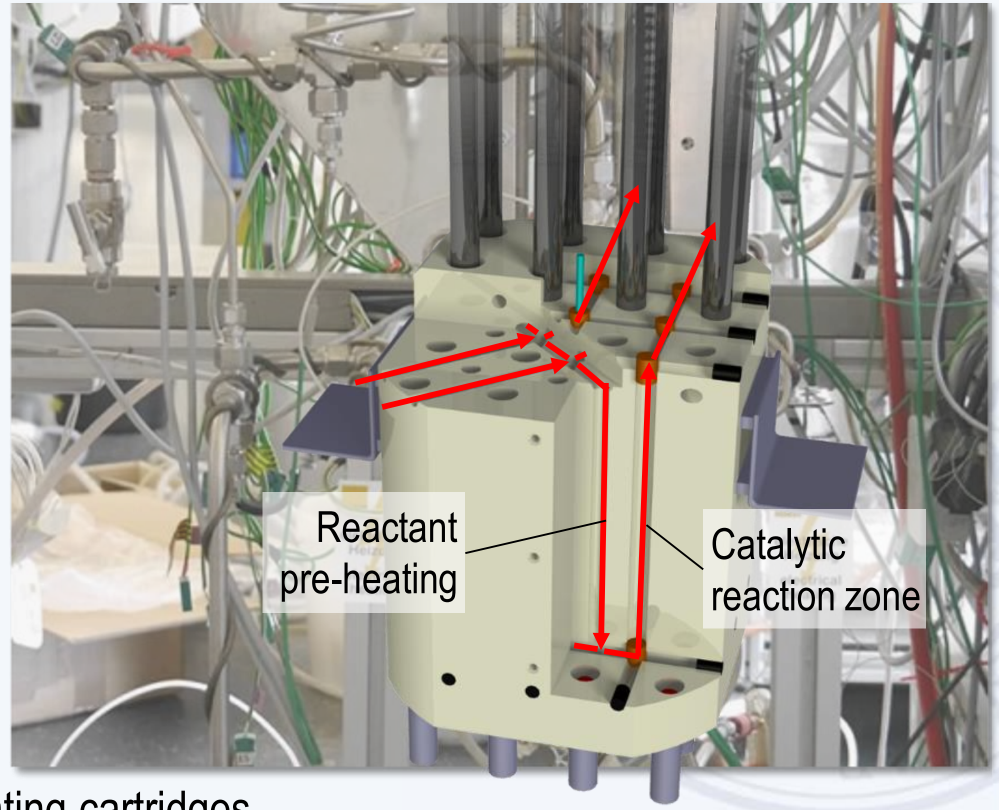
Experimental setup – Structured fixed-bed reactor

- Minimizing the radial heat conductance length in fixed-bed (limiting factor causing hot-spots)
- Alternating reaction zones and heat sinks
- Heat pipes for reactor cooling



- Block of stainless steel with drillings for
  - 9 reaction channels filled with commercial catalyst
  - 16 drillings for water heat pipes for heat dissipation
  - 12 pre-heating channels
  - Gas inlet, outlet and redirection
- Electrical heating especially for start-up by heating cartridges
- Cooling of heat pipe condenser zones by compressed air

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Heat dissipation with heat pipes

- Passive component for heat dissipation
- Transport of high power densities over long distances with low temperature difference
- Principle: Transmission of the enthalpy of vaporization between the heat source and the heat sink in a closed two-phase system
- Liquid backflow usually driven by capillary forces

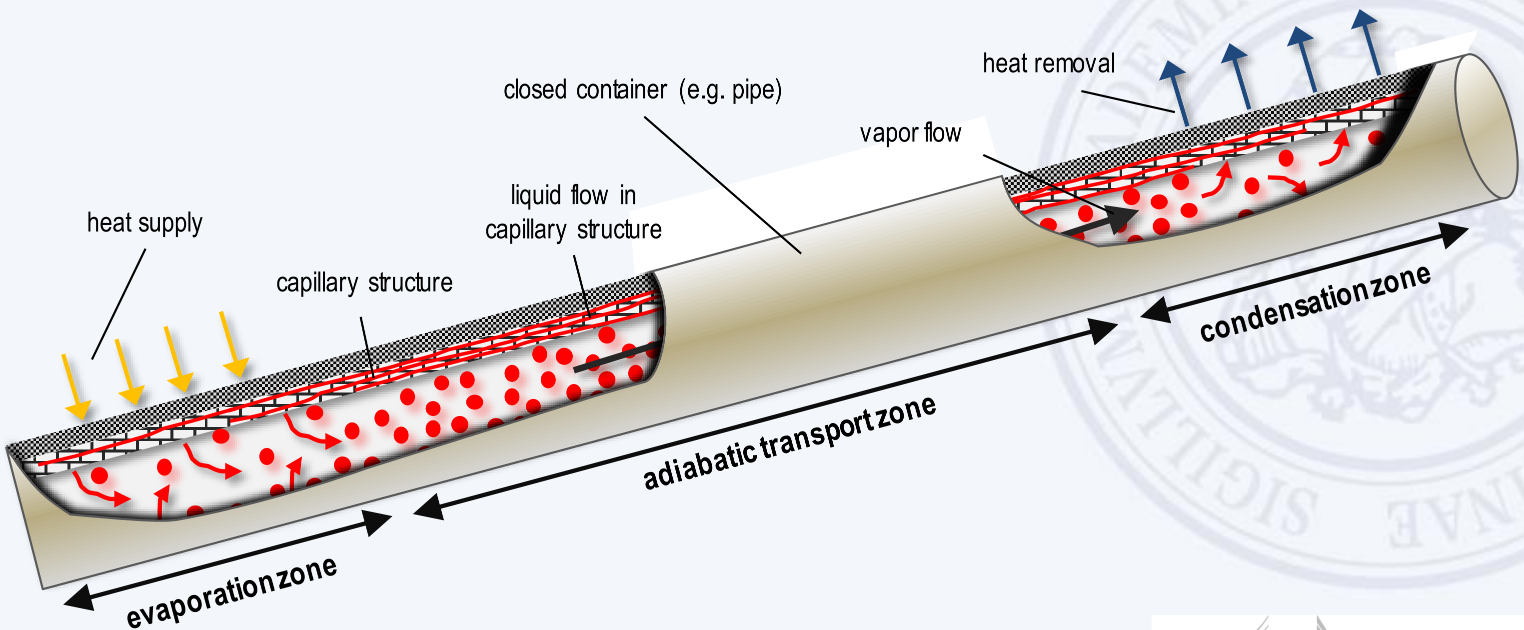
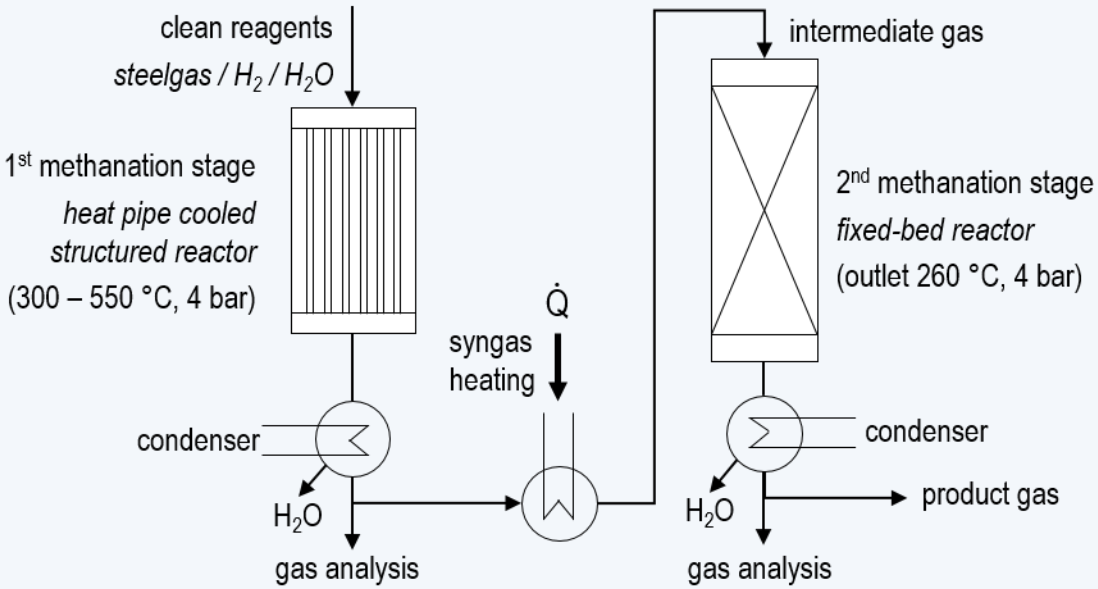


Figure source: Neubert, M., Hauser, A., Pourhossein, B., Dillig, M., & Karl, J. (2018). Experimental evaluation of a heat pipe cooled structured reactor as part of a two-stage catalytic methanation process in power-to-gas applications. *Applied energy*, 229, 289-298.

Test rig and performed experiments



Test rig

- Two stage methanation concept
- Intermediate water sequestration
- Pressures up to 5 bar
- Commercial Ni/Al_2O_3 catalyst with high Ni loading (~ 50 wt.-%)
- Gas analyser for permanent gases

Performed experiments

Steady-state methanation of BFG and BOFG with different

- Syngas powers / volume flow rates
- Stoichiometric ratios

Dynamic methanation of BFG and BOFG by step attempts

- Up to ± 20 % in syngas power / volume flow rate
- Over- to sub-stoichiometric regime

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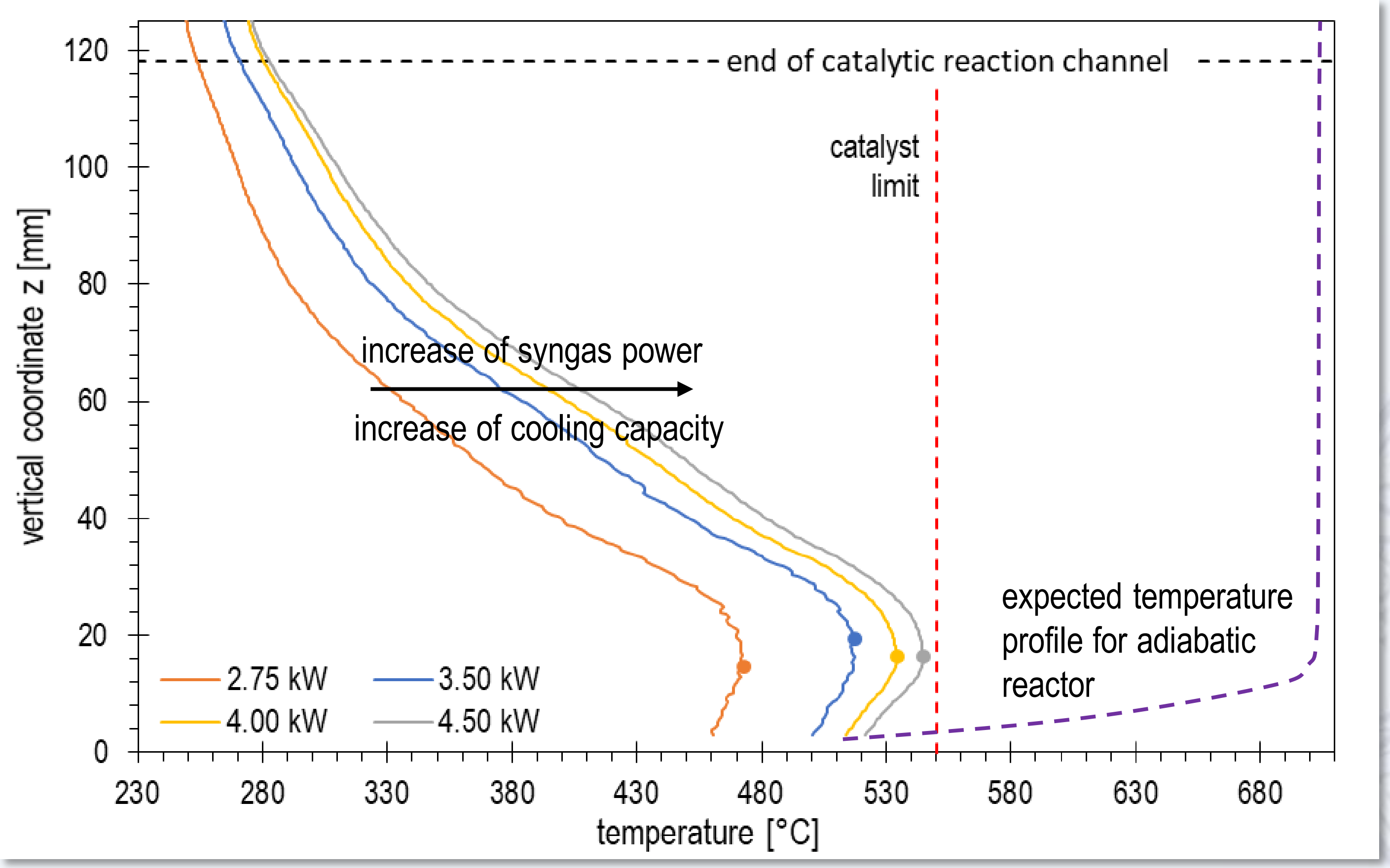
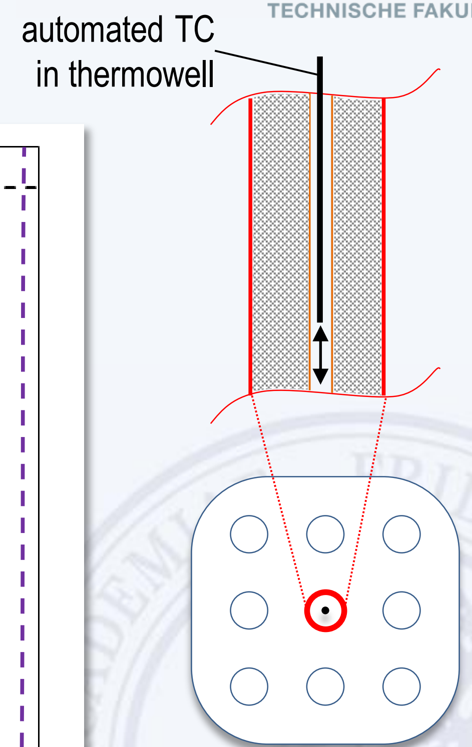
Temperature control with heat pipes





positioning of measurement

Axial temperature profiles of the structured reactor for different steady-state syngas powers (synthetic BOFG, σ_{H2} = 1.04, p = 4 bar)

- Maximum temperature can be limited below the catalyst limit
- T_{max} ~150 K lower than expectable adiabatic synthesis temperature
- Dynamic adaption of cooling power to the different operating points necessary

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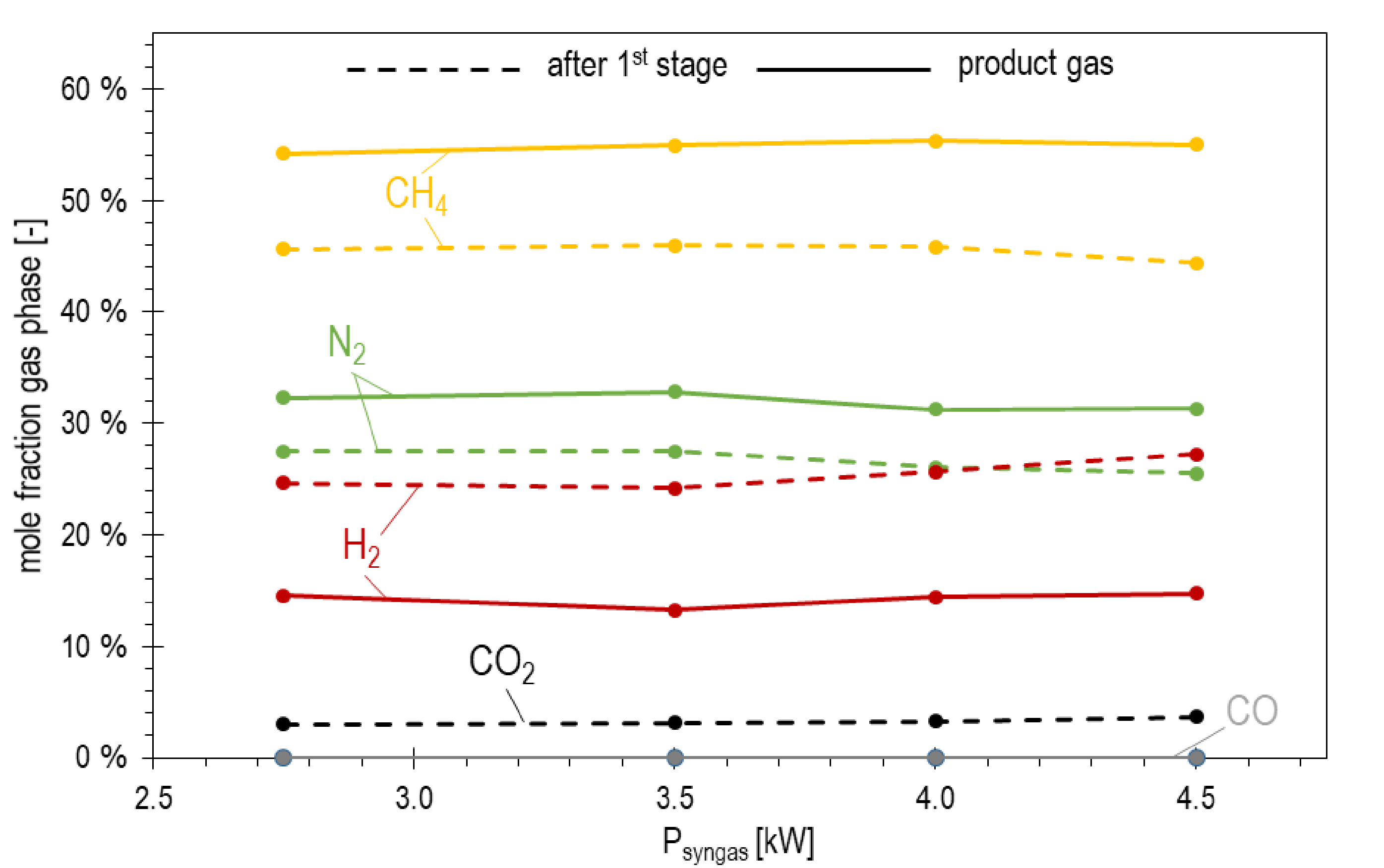
Product gas composition of BOFG methanation



Gas compositions after the 1st and 2nd methanation stage for different steady-state syngas powers (synthetic BOFG, σ_{H2} = 1.04, p = 4 bar)

- Full CO_x conversion after two-stage process with intermediate H2O sequestration
- Constant product gas quality after two-stage process over a wide syngas power range
- Significant amount of N_2 (~31 vol.-%) in the product gas

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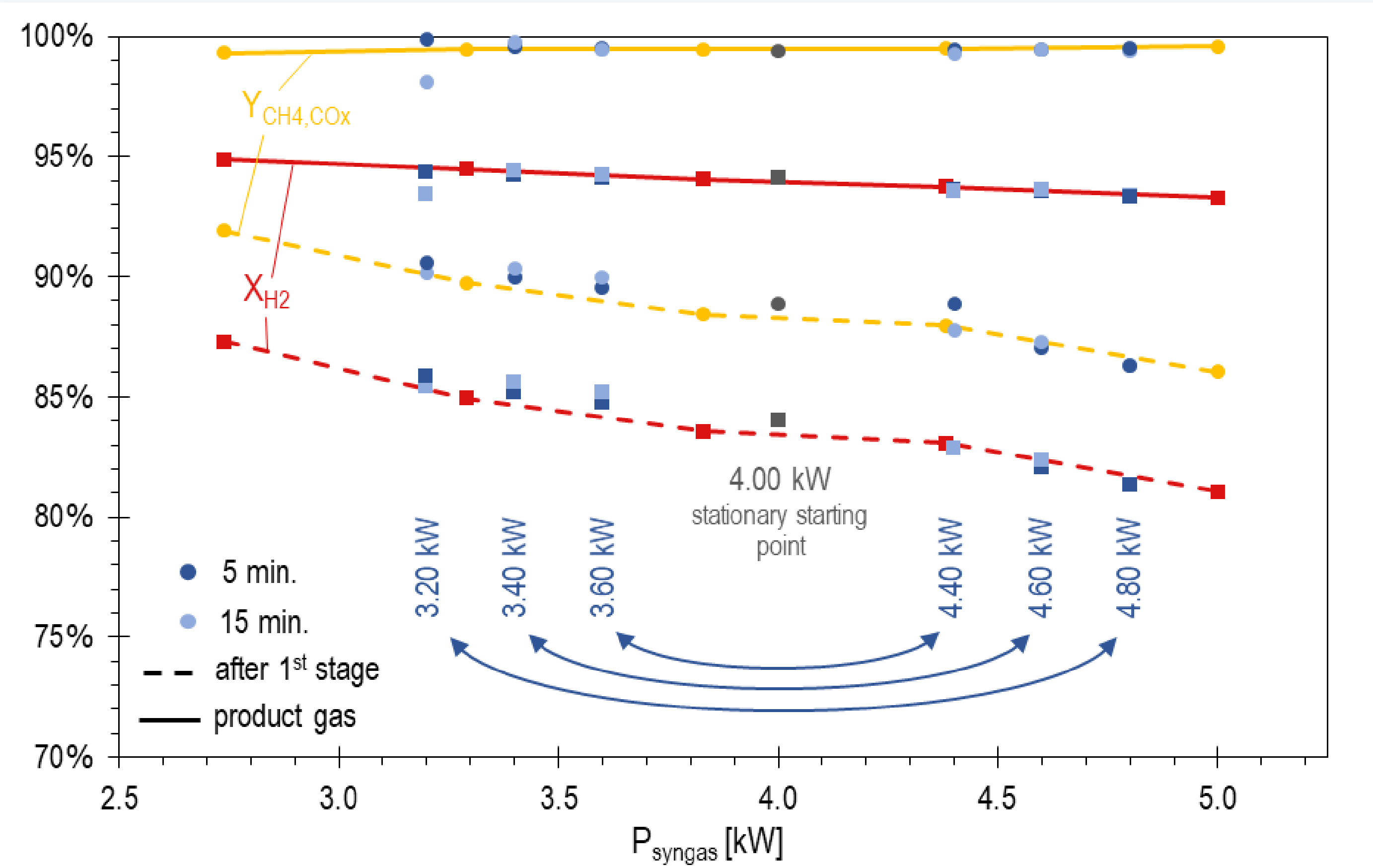
Yield and conversion of dynamic BFG methanation



$$X_{H_2} = \frac{\dot{n}_{H_2,0} - \dot{n}_{H_2}}{\dot{n}_{H_2,0}}$$

hydrogen conversion

$$Y_{CH_4,CO_x} = \frac{\dot{n}_{CH_4} - \dot{n}_{CH_4,0}}{\dot{n}_{CO_2,0} + \dot{n}_{CO,0}}$$

methane yield

Hydrogen conversion and methane yield after the 1st and 2nd methanation stage for different steady-state syngas powers (ye/rd/bk) and dynamic experiments (bu) (synthetic BFG, σ_{H2} = 1.04, p = 4 bar)

- Full methane yield after two-stage methanation, $X_{H2} \approx 95$ % (over-stoichiometric methanation)
- Slight shift of conversion from 1st to 2nd stage; kinetic limitation assumed
- Dynamic experiments: no influence of step width and cycle time on $Y_{CH4,COx}$ and X_{H2}

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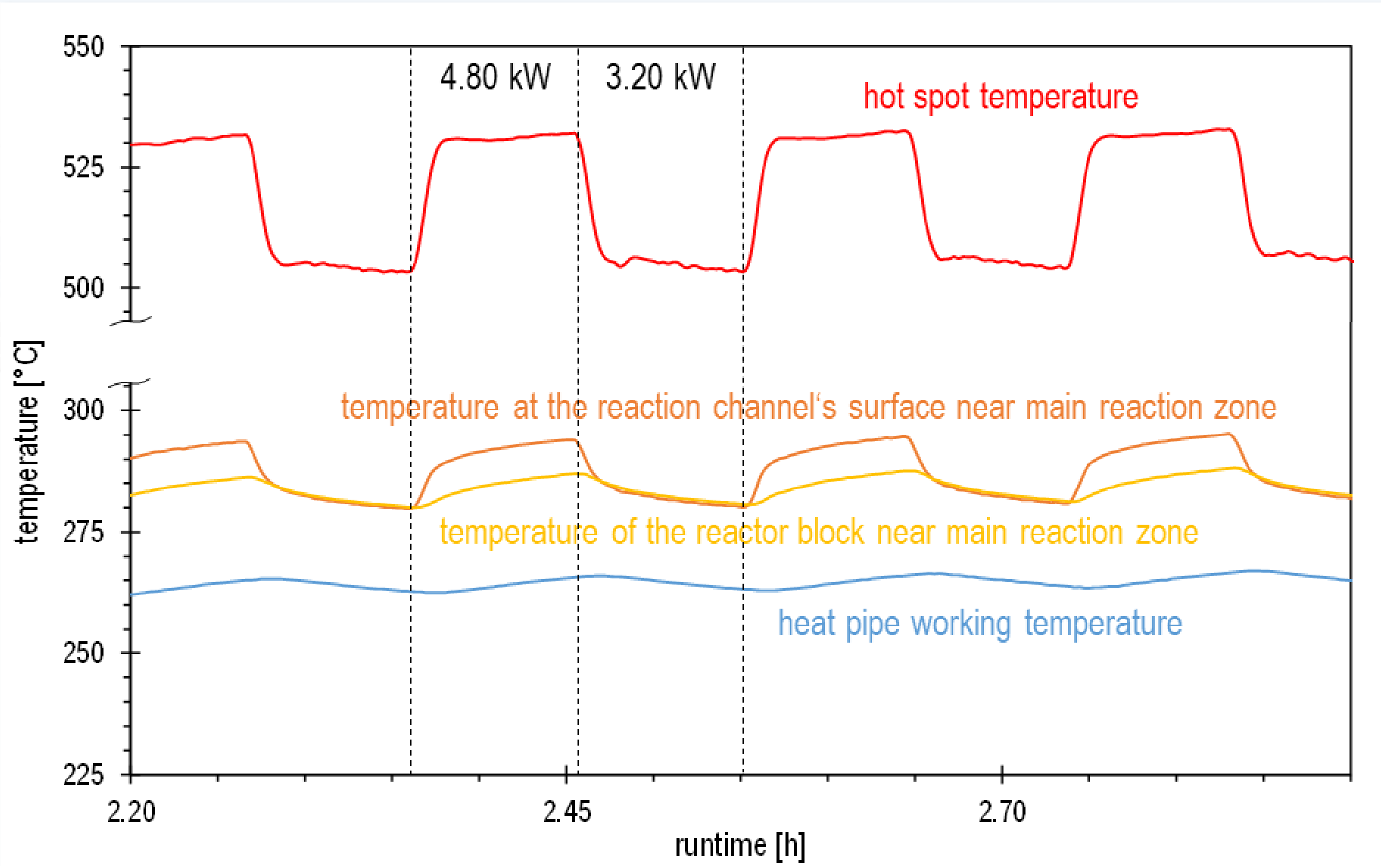
Temperature response during dynamic BFG methanation



Timely resolved temperature profiles (structured reactor) for jumps in syngas power by 1.6 kW in 5 min cycles (σ_{H2} = 1.04, p = 4 bar, $\dot{V}_{cool}$ = 85 Nl/min)

- Prompt and significant jumps of the hot spot temperature (~30 K) for jumps in syngas power by 1.6 kW
- Mean temperature level (represented by heat pipe working temperature) shows sluggish response

→ Short-term fluctuations in syngas power require no adaption of cooling capacity

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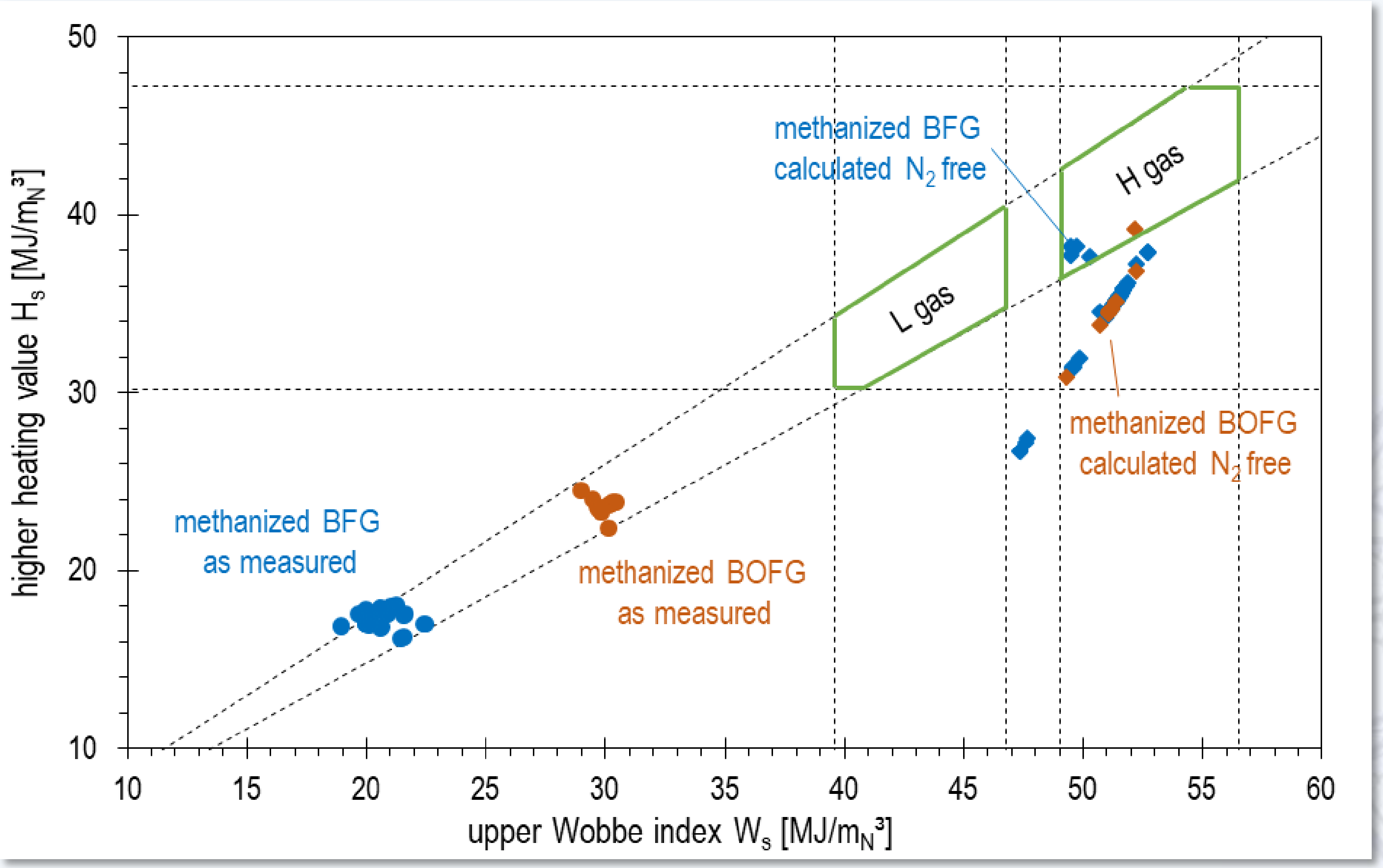
Gas quality of product gases from BFG and BOFG methanation



Classification of product gas quality from BFG / BOFG methanation as measured and calculated N2 free (limits according to DVGW G260)

Measured gas compositions

- Good match of W_s/H_s ratio
- Not injectable to gas grid, high share of N_2

Calculated N_2 free gas compositions

- Some operating points would reach H gas quality
- Influence of H_2 dilution increases

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Conclusion

- Aim i³upgrade: Integration of renewable energies into the steelmaking process and thereby reduction of the CO_2 impact of integrated steel works
- Dynamic H_2 intensified methanation with steelworks' by-product gases as carbon source
- Results from steady-state and dynamic experiments
  - Heat pipe cooled structured reactor is suitable for advanced temperature control
  - Constant product gas quality over a wide syngas power range (after two-stage process with intermediate H_2O sequestration)
  - Dynamic experiments:
    - No influence of step width and cycle time on $Y_{CH4,COx}$ and X_{H2}
    - Prompt temperature response at hot spot
    - Sluggish response of mean temperature, dampening character of the reactor
  - Gas quality not sufficient for grid injection because of high shares of N_2

Thank you for your attention!

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