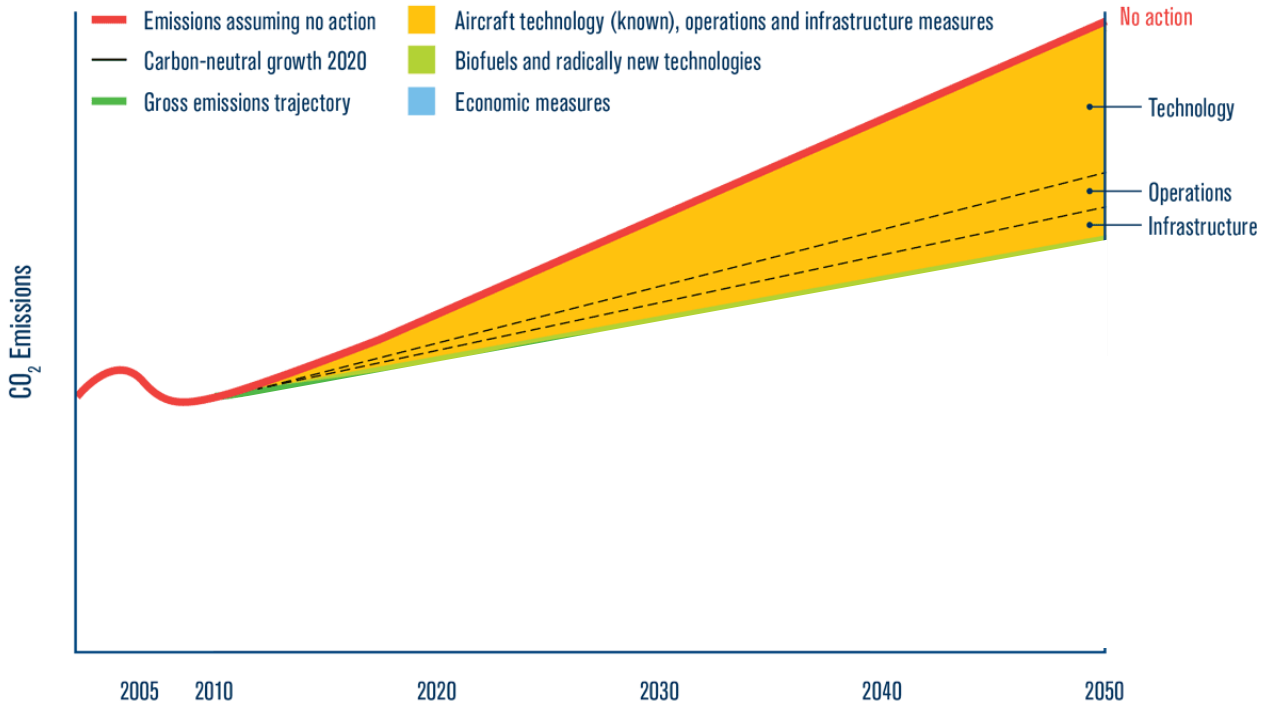
Experimental investigation of the reverse water-gas shift reaction at high temperature and elevated pressure

Sandra Adelung, Torsten Ascher, Fabian Klein, Ralph-Uwe Dietrich

DLR

Motivation: IATA Technology Roadmap

4. Edition, June 2013



Motivation: IATA Technology Roadmap

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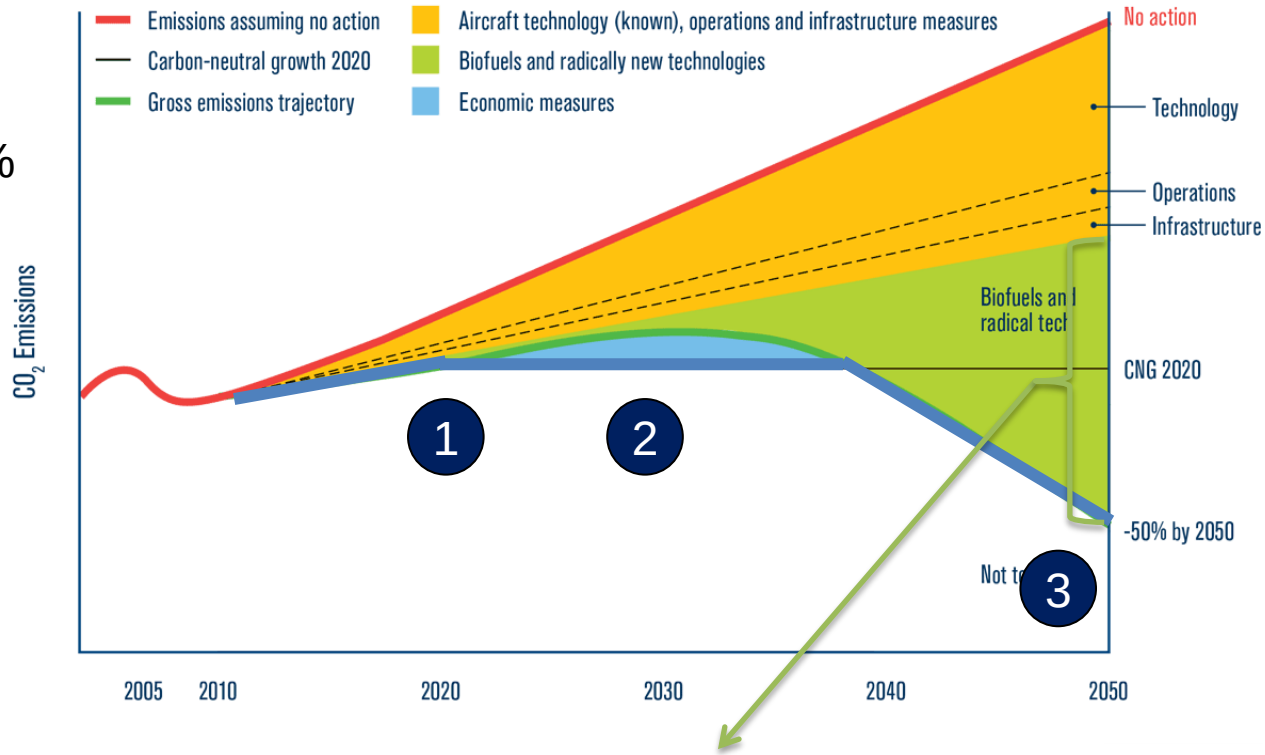
Main goals:

1. Improvement of fuel efficiency about 1.5 % p.a. until 2020
2. Carbon-neutral growth from 2020
3. 50 % reduction of CO_2 emissions by 2050



Closing the gap: ICAO vision (2017) → "Power-to-Liquids: Sustainable alternative fuels produced from renewable electricity"

Power-to-Liquid Process

Carbon source:
- Power/ Industrial Plant
- Air

CO_2, H_2, light hydrocarbons, CO, H_2O

CO_2 capture

CO_2

3 H_2

Production of Syngas

CO + 2 H_2

Fischer-Tropsch-Synthesis

Liquid Fuels

Electrolysis

$$RWGS: CO_2 + \boldsymbol{H_2} \rightleftharpoons CO + \boldsymbol{H_2O}$$
$$\Delta\ {}_R H^0{}_{298} = \boldsymbol{41\ kJ/mol}$$

- high volumetric energy density
- easy to handle
- existing infrastructure

Renewable electricity:
- Solar
- Wind

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Power-to-Liquid Process – RWGS operating conditions

Increasing temperature…

- Reaction kinetics
- Equ
  -
  -
- Material

→ Tem

Most investigations at elevated pressure use high temperature steel or stainless steel reactors

Decreasing pressure…

- Equilibrium composition
  - Less coke, CH_4
  - More CO
- Higher work-input for compression of recycle stream

→ Pressure range: 1-25 bar (FTS at 25 bar)

RWGS in Inconel 600 reactor

- Bustamente et al. (2004) found high CO_2 conversion in an Inconel reactor

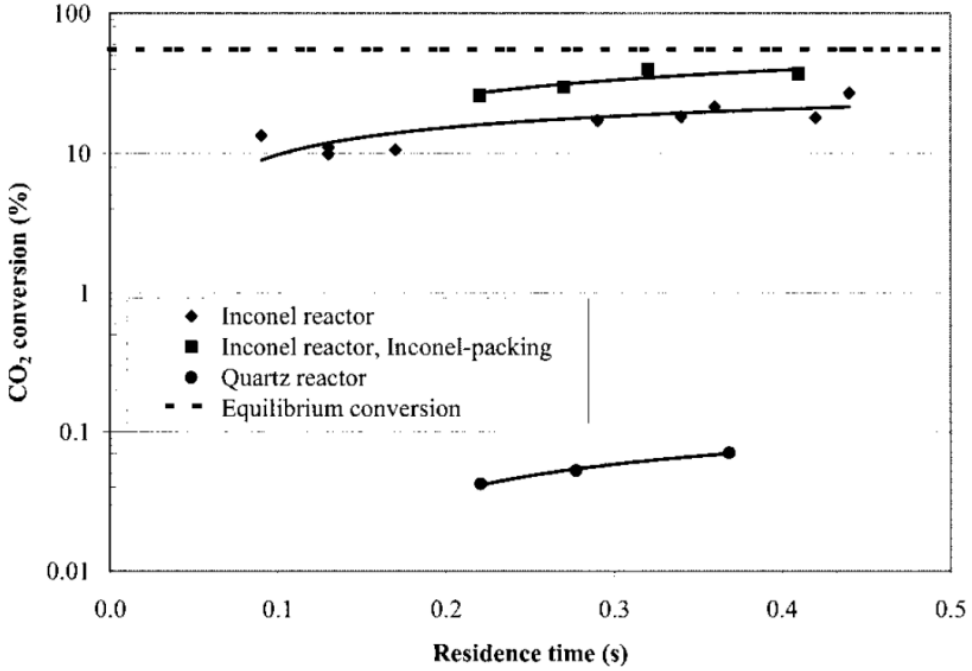
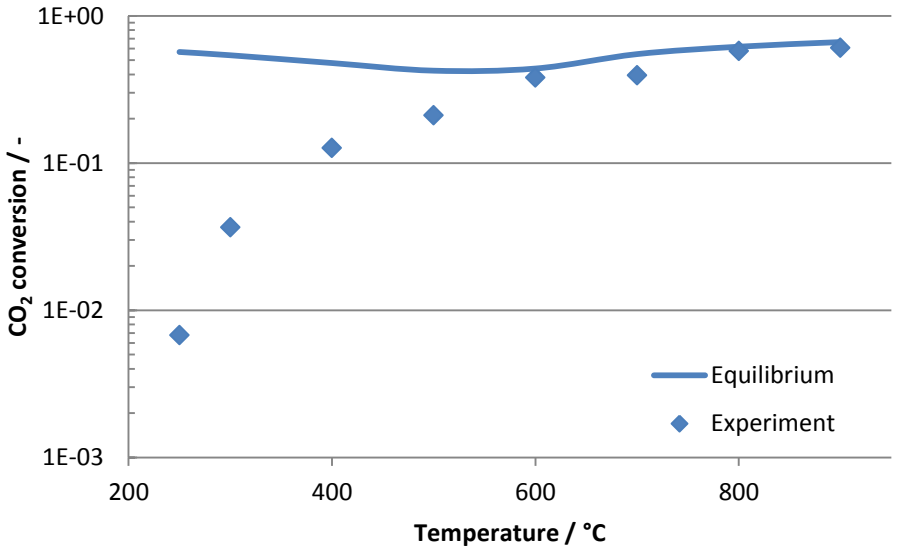


Figure 16. Reverse WGS reaction in an Inconel 600 reactor. 1173 K, 0.101 MPa, $[H_2]_0 = [CO_2]_0$.
Equilibrium conversion at these conditions is 55%.

- Conversion was found to be 2 orders of magnitude higher than in quartz glass reactor
- Inconel 600: approx. 72 % Ni-content, Nickel catalyzes reaction

RWGS in stainless steel reactor

Stainless steel (1.4571) with 10.5-13.5 % Nickel content



- H_2/CO_2 = 1.7
- Residence time $\tau \approx 5$ s
- Pressure p = 1.5 bar

- **Equilibrium** composition (Gibbs in Aspen Plus with CO, CH_4 and C as possible products) **reached for T > 600 °C**
- **To investigate performance of catalyst: High temperature zones must be inert (e.g. by using quartz glass)**

Novel reactor concept

Challenges:

- High temperature zone: inert
- Thermal expansion (Glass vs. Metal)
- High stress for reactor wall due to high temperature and elevated pressure

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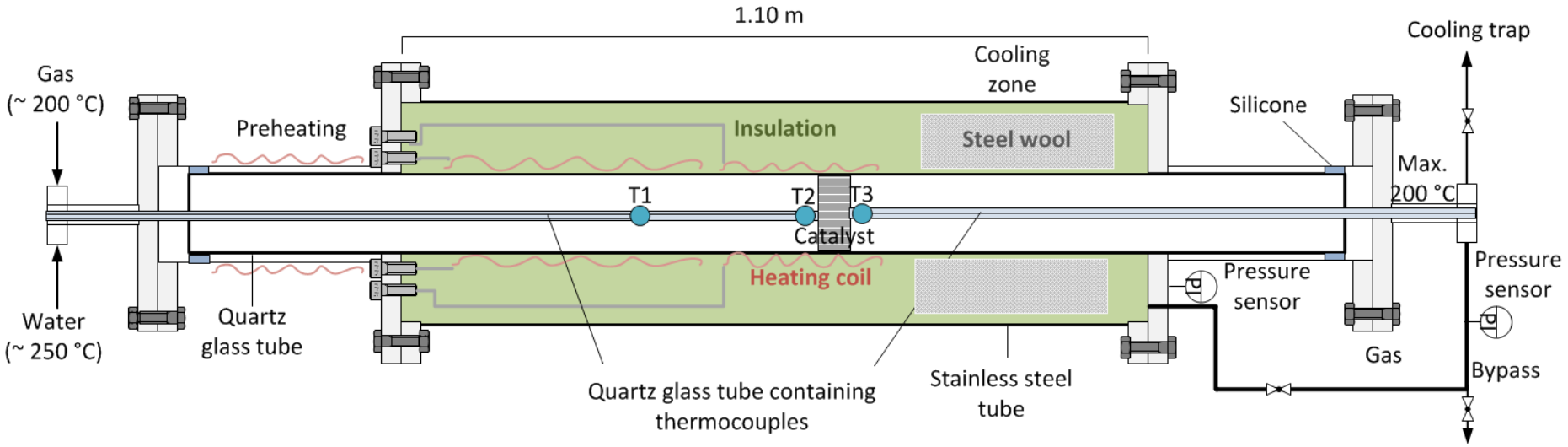

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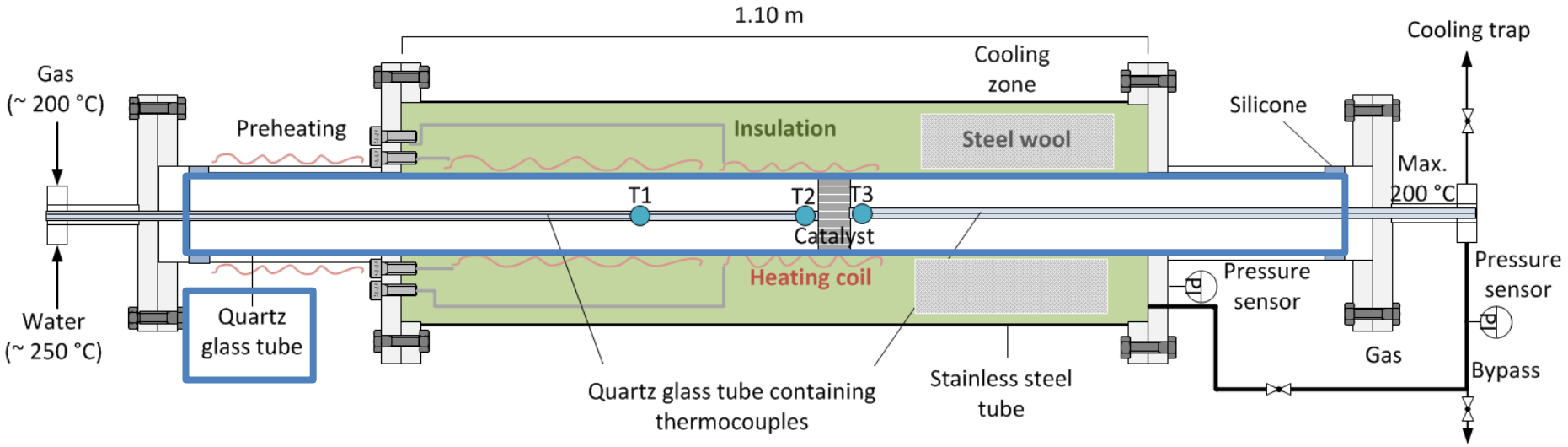

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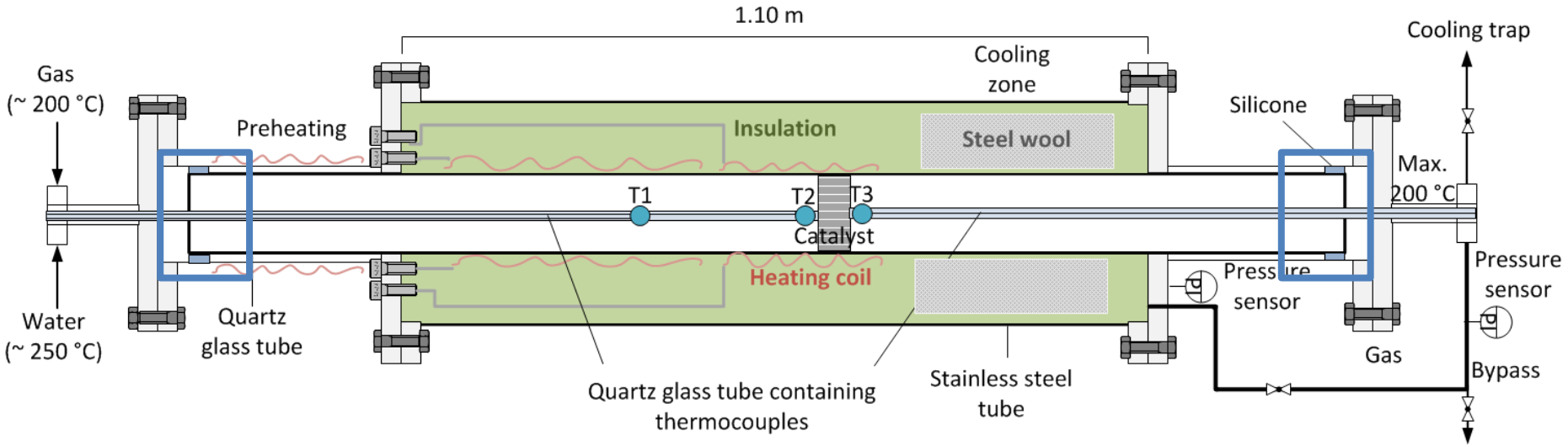

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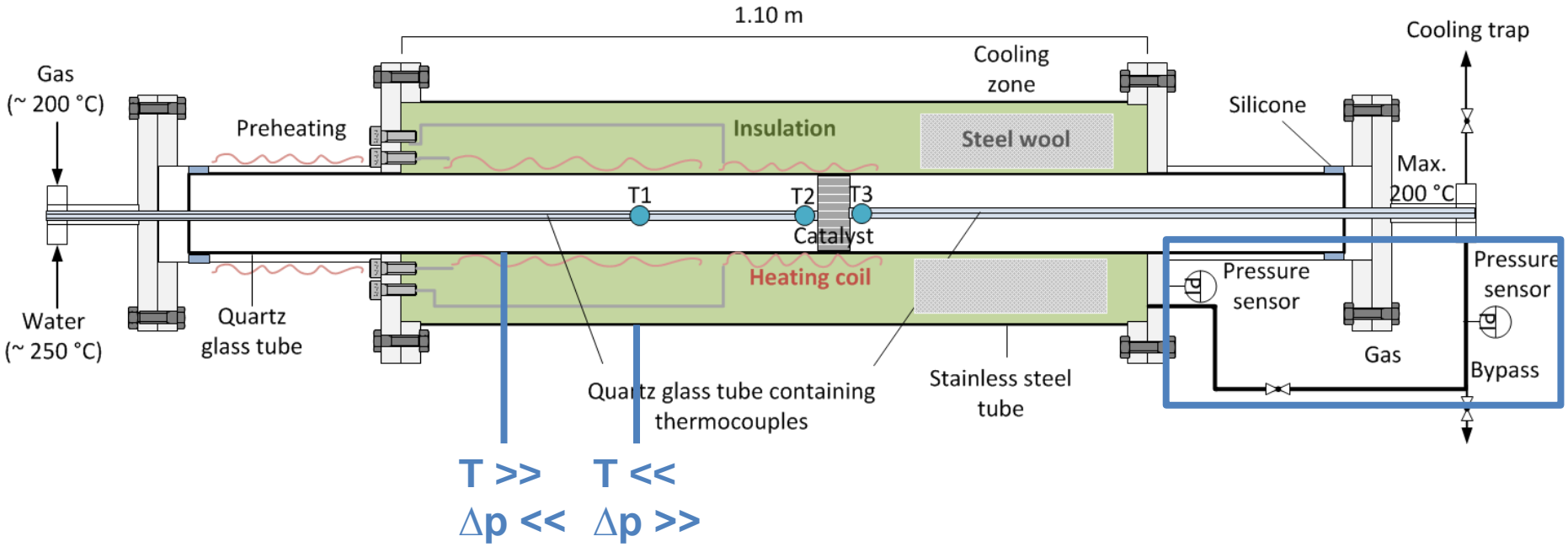
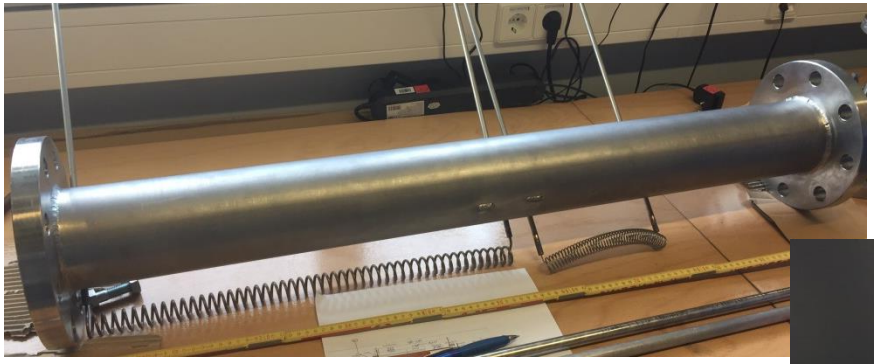
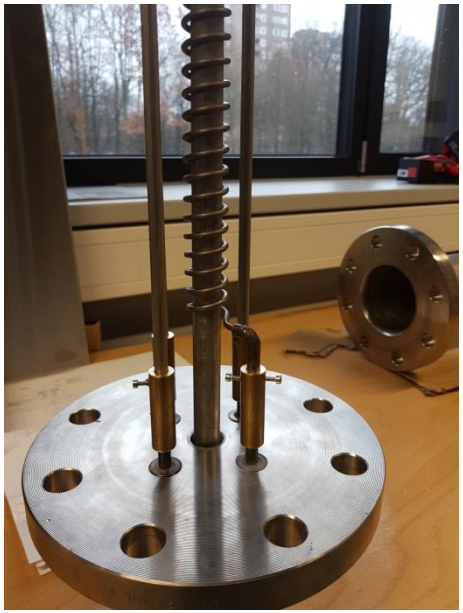
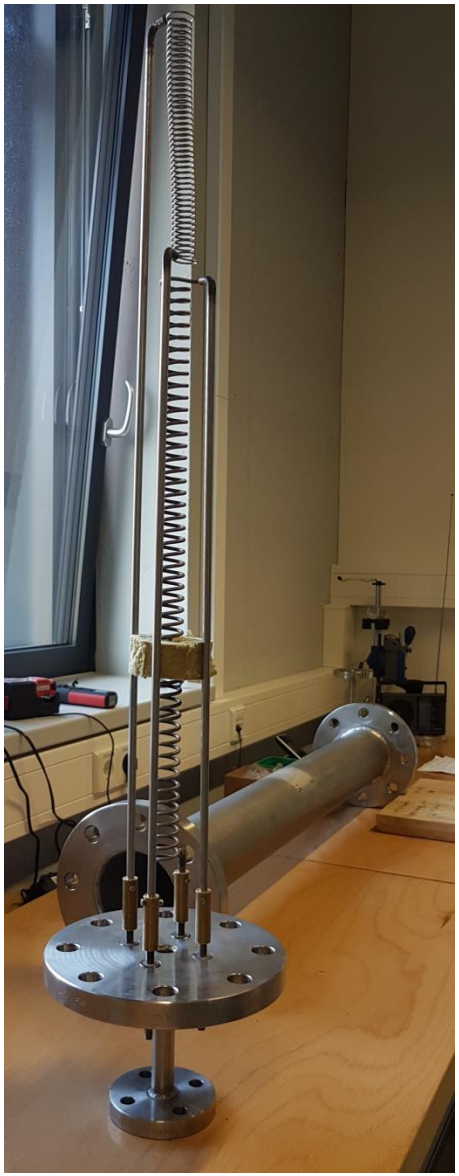


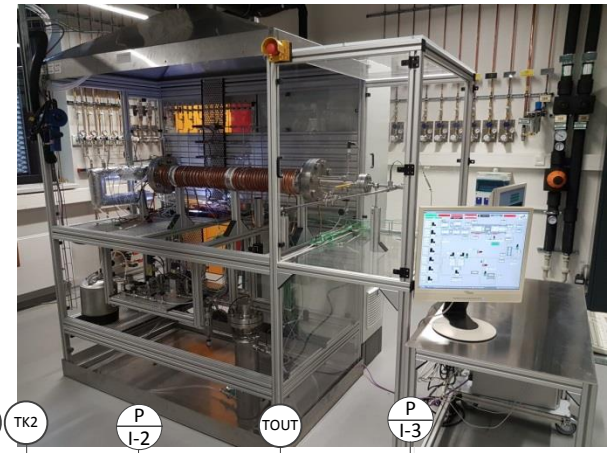
Reactor setup

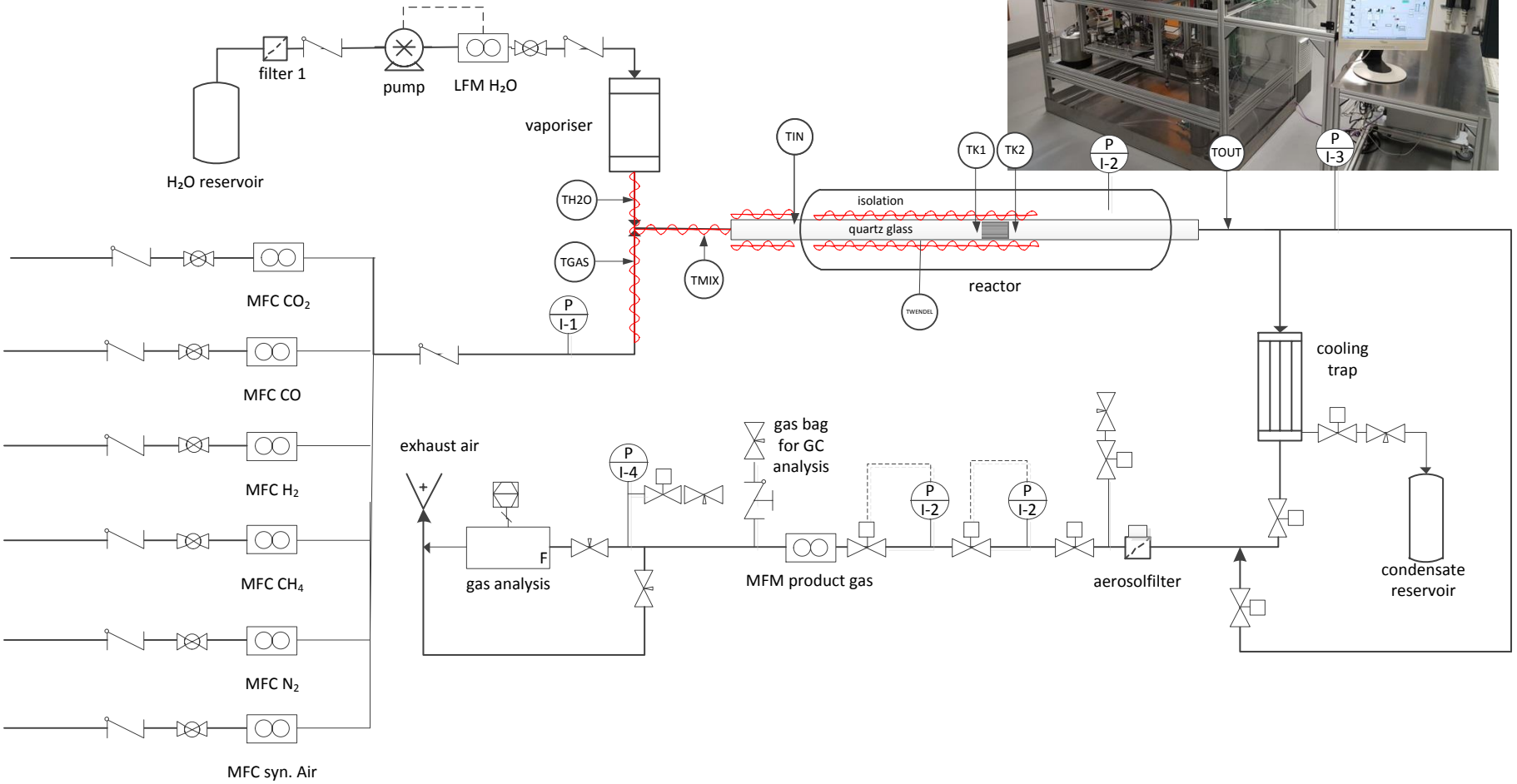






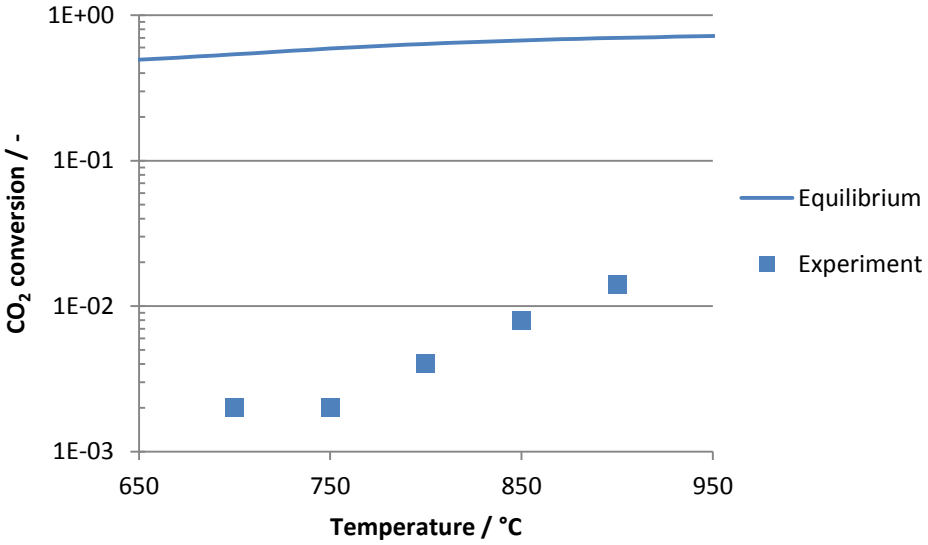
Process scheme





Experimental results in new reactor

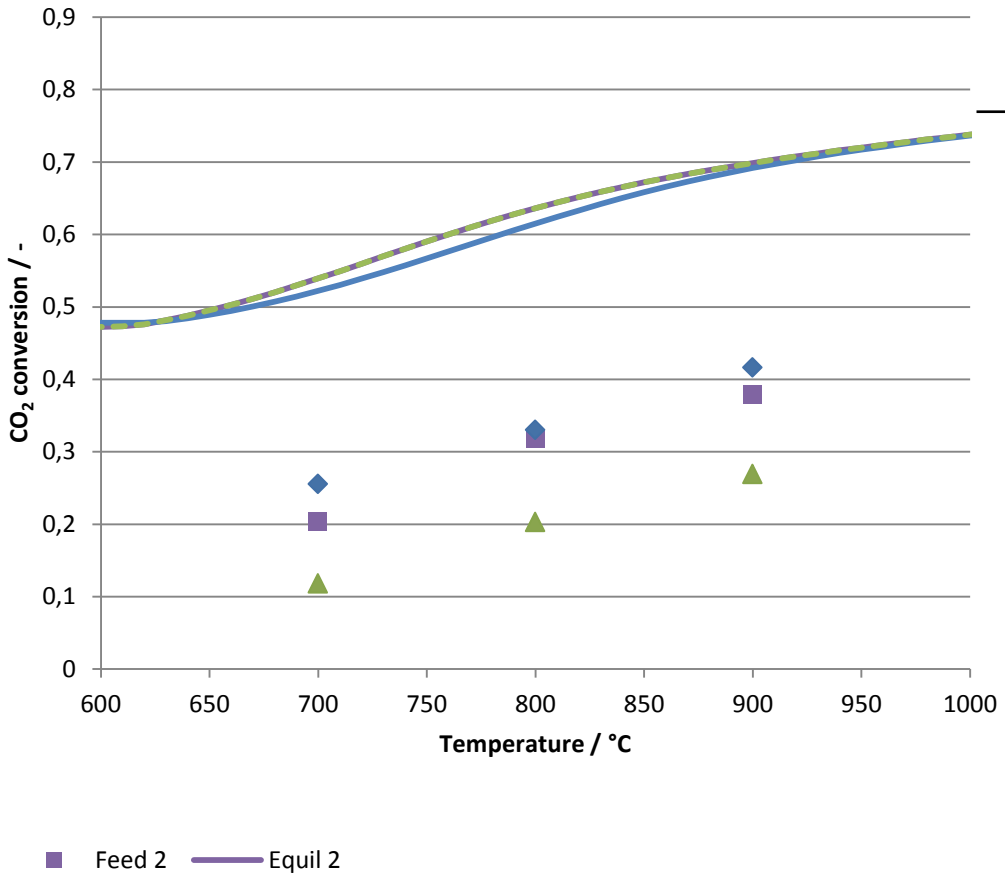
- Before: equilibrium composition reached above 600 °C
- With new setup:



- $H_2/CO_2 = 2$
- Residence time $\tau \approx 2$ s
- Pressure p = 25 bar

- CO_2 conversion in empty tube can be decreased significantly (below 2 %)
- **Catalyst's performance can be investigated with new reactor**

First results with noble catalyst (0.1 g catalyst)



Feed	p bar	V_{tot} L_N/min	H_2 L_N/min	CO_2 L_N/min
2	25	10	2	1

CO_2 conversion reaches 50-60 % of equilibrium conversion

Concentration doubled: slight increase in CO_2 conversion

Residence time halved: significant decrease in CO_2 conversion

Summary and Outlook

Summary

- Investigation of RWGS at elevated pressure relevant in PTL concept
- RWGS significantly catalyzed by stainless steel
- New reactor concept allows investigation of catalyst‘s performance at up to 900 °C and up to 25 bar

Outlook

- Kinetic performance of monolithic catalysts?
- Coke formation?

Thank you for your attention

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