"Energy Storage Technologies: Focus on Power-to-Gas Technology"

Introduction / main features of methanation

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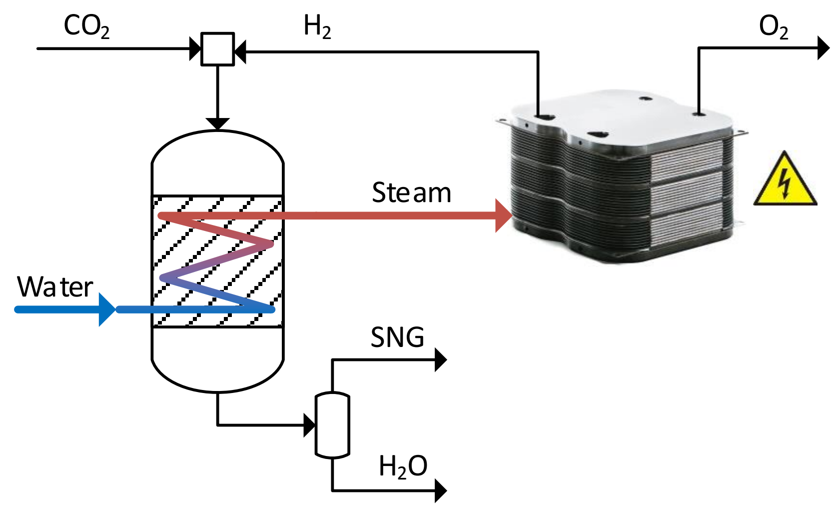
HELMETH methanation module targets

- Produced SNG corresponding to (future) NG grid standards
  - H_2: < 5 vol.-%
  - CO_2: < 2.5 vol.-%
  - CH_4: > 92.5 vol.-%
  - → Multistep reactor concept
  - → Elevated pressure

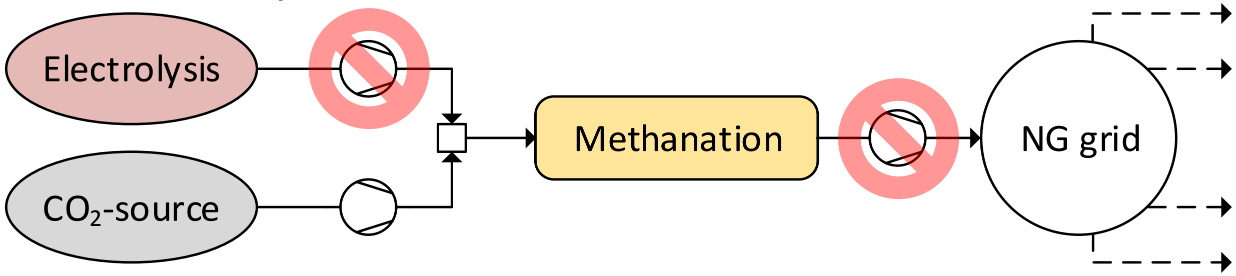


- Continuous steam generation
- Modulation from 20 to 100 % load & stand-by operation
- Thermal integration

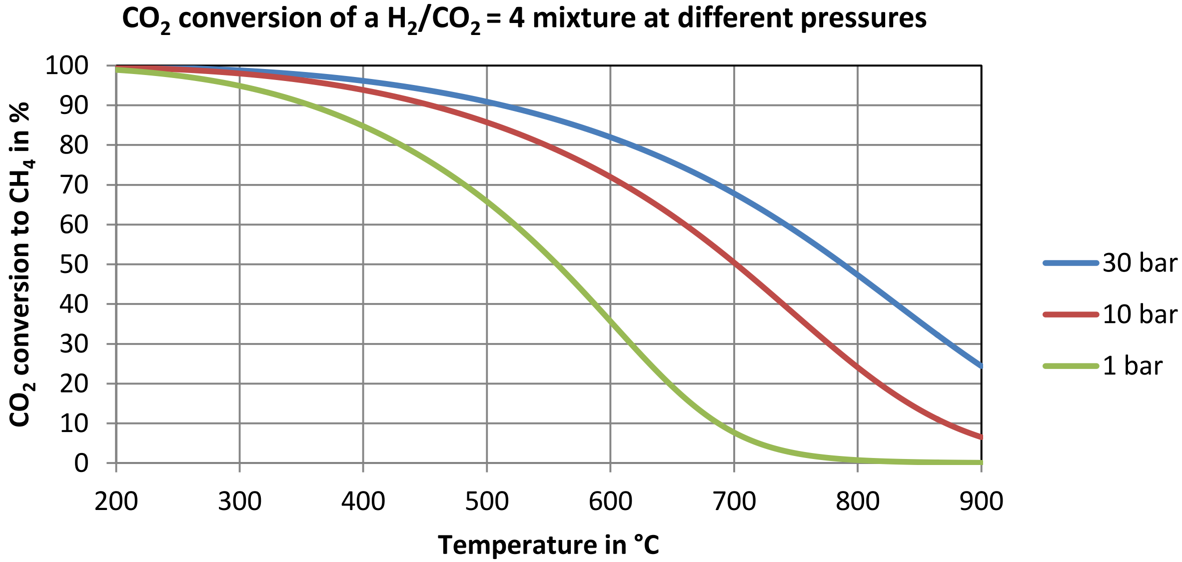
Advantages of pressurized operation

Operation of the PtG system at up to 30 bar:

- Reduces compression effort

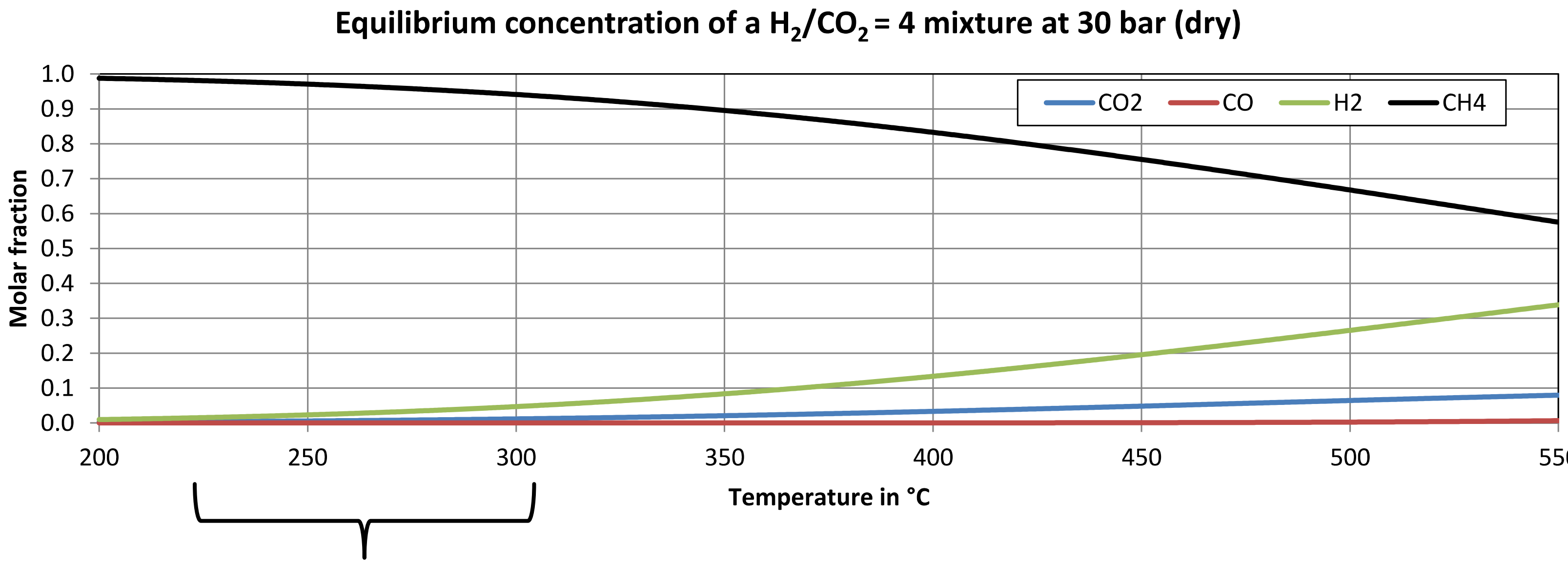


- Shifts chemical equilibrium towards methane $CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$



SNG quality requirements

Methanation module design for low hydrogen content in SNG



- 2 vol.-% H_2 at 240°C (current regulations, e.g. DIN51624)
- 5 vol.-% H_2 at 305°C (forecast for future European standards)

HELMETH targets: H_2 < 5; CO_2 < 2.5; CH_4 > 92.5 vol.-%

CATALYSTS SCREENING

Catalyst screening: test conditions

Methanation tests under atmospheric pressure and stable T

(catalysts screening and activation/deactivation phenomena)

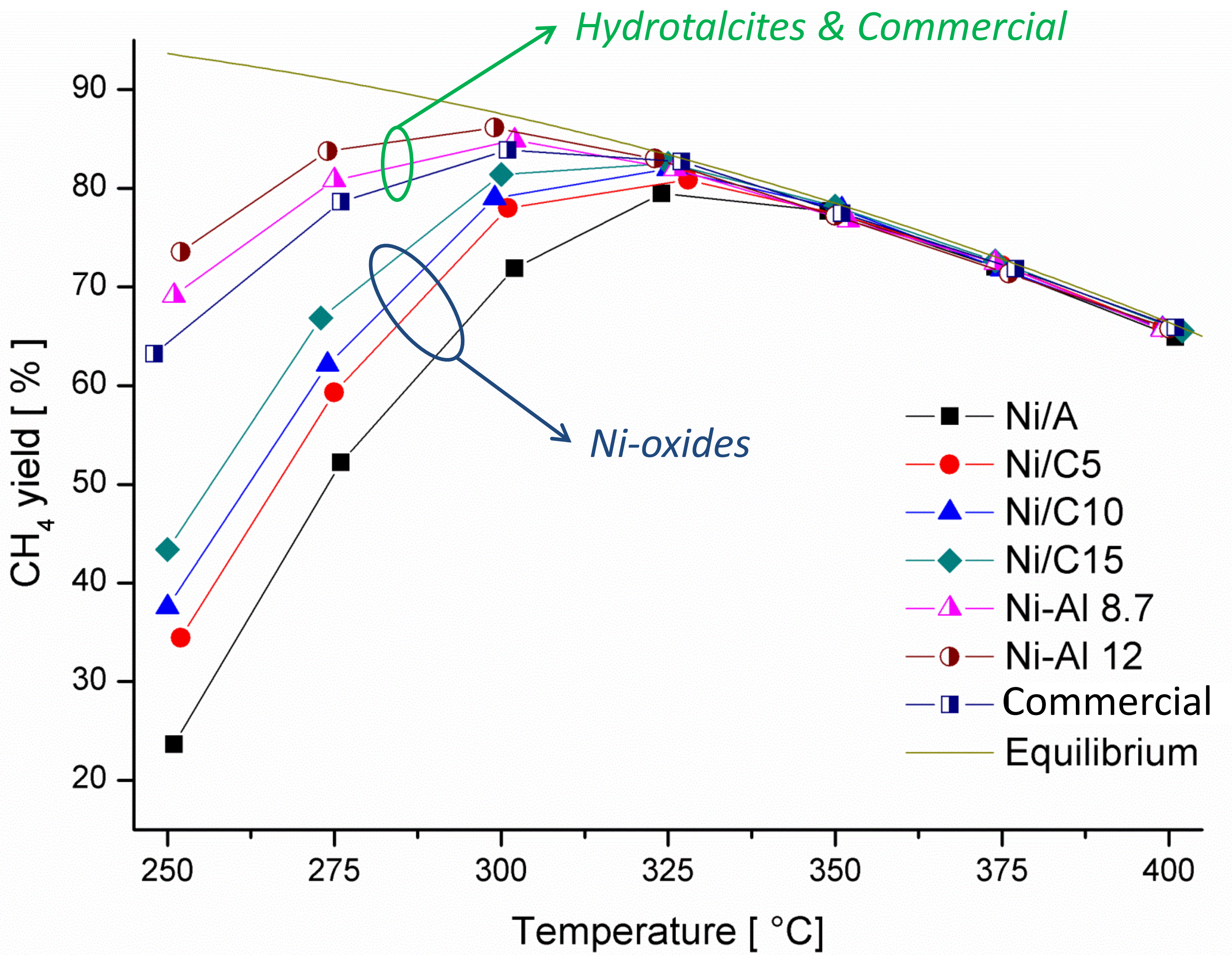
- Oven Temperature: 250 – 400 °C (steps of 25 °C)
- Atmospheric pressure
- Stoichiometric feed (H_2/CO_2=4) diluted with N_2
- Catalysts:
  - *Supported Nickel on different oxides (Al_2O_3; ZrO_2; CeO_2; TiO_2)*
  - *Ni-Al Hydrotalcites*
  - *Commercial Ni-based catalyst*
- Reaction Volume: ≈ 600 mm^3
- Reactant mixture flow rate: 200 Nml/min (GHSV ≈ 20000 h^{-1})
- Evaluation of CH_4 yield

Catalysts

- Oxides-supported Nickel catalysts
  - ***Ni/A*** → 20%Ni / 100% γ-Al_2O_3
  - ***Ni/C5*** → 20%Ni / 85% γ-Al_2O_3; 5% ZrO_2; 5% CeO_2; 5% TiO_2
  - ***Ni/C10*** → 20%Ni / 70% γ-Al_2O_3; 10% ZrO_2; 10% CeO_2; 10% TiO_2
  - ***Ni/C15*** → 20%Ni / 55% γ-Al_2O_3; 15% ZrO_2; 15% CeO_2; 15% TiO_2
- Ni-Al Hydrotalcites (Ni-content: ≈ 75%)
  - ***Ni-Al 8.7*** → prepared at a ph of 8.7
  - ***Ni-Al 12*** → prepared at a ph of 12
- Commercial catalyst
  - 75%Ni / γ-Al_2O_3

Activation procedure:
pre-treatment of catalysts with Hydrogen (10%vol) at 500 °C for 3 h

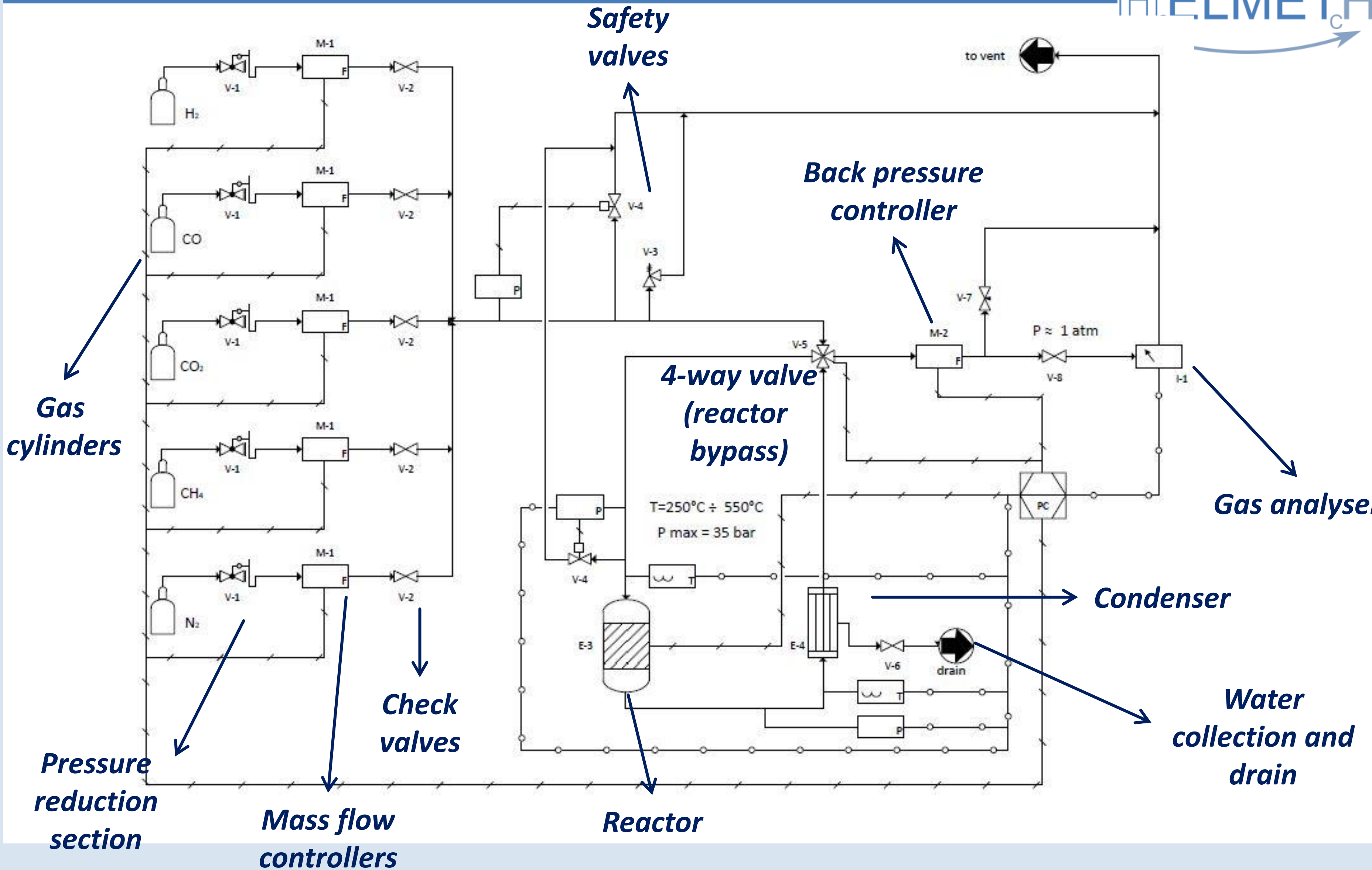
Overview of tested catalysts



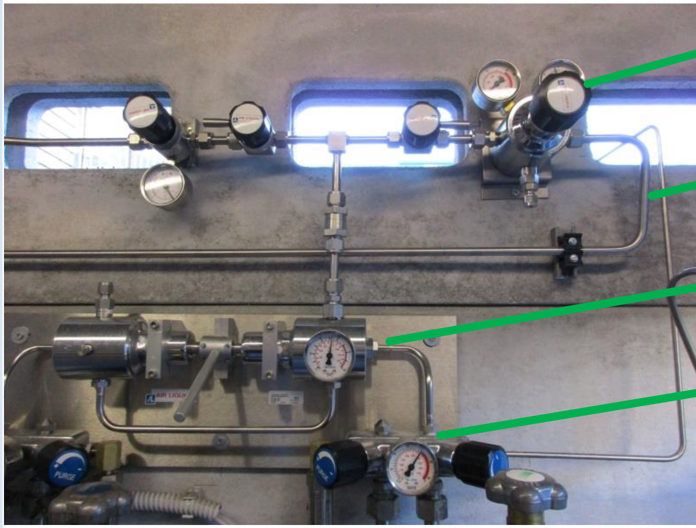
Hydrotalcites and commercial catalyst present superior performance than oxides-supported nickel catralysts

DESIGN OF THE PRESSURIZED TEST UNIT

System P&ID


Safety valves
Back pressure controller
4-way valve (reactor bypass)
Gas cylinders
Gas analyser
Condenser
Water collection and drain
Pressure reduction section
Mass flow controllers
Check valves
Reactor
M-1
V-1
V-2
H₂
CO
CO₂
CH₄
N₂
to vent
V-4
V-3
V-7
M-2
P ≈ 1 atm
V-5
V-8
I-1
PC
T=250°C ÷ 550°C
P max = 35 bar
E-3
E-4
V-6
drain

Pressure reduction section



2^{nd} stage pressure reduction

Feeding line (to the test unit)

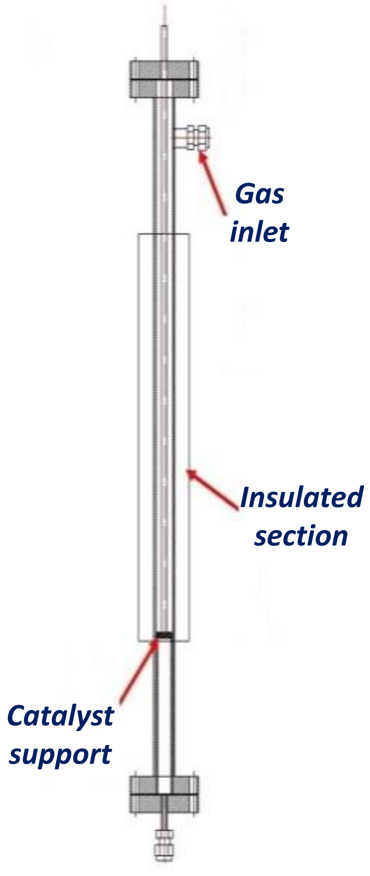
1^{st} stage pressure reduction

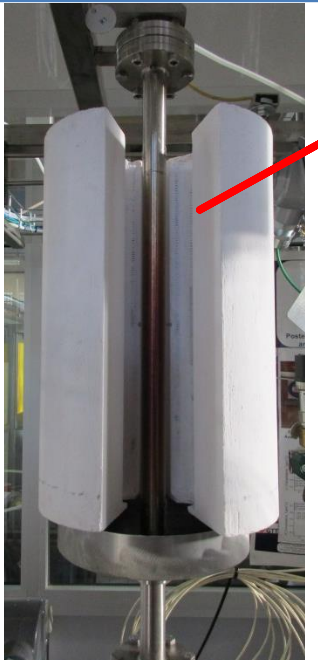
Cylinder pressure indicator + manual valve

Both 1^{st} and 2^{nd} stage are placed in a box outside the lab

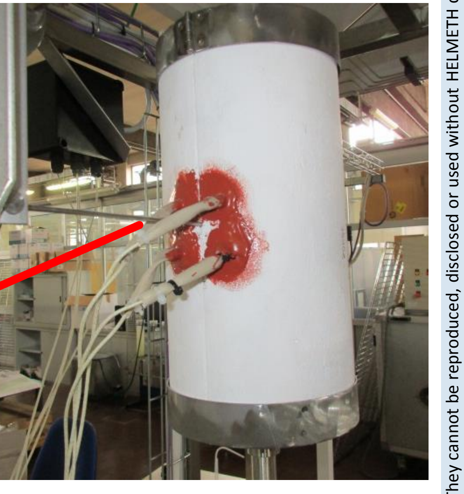
3^{rd} stage pressure reduction inside the lab (before mass flow controllers)

Reactor

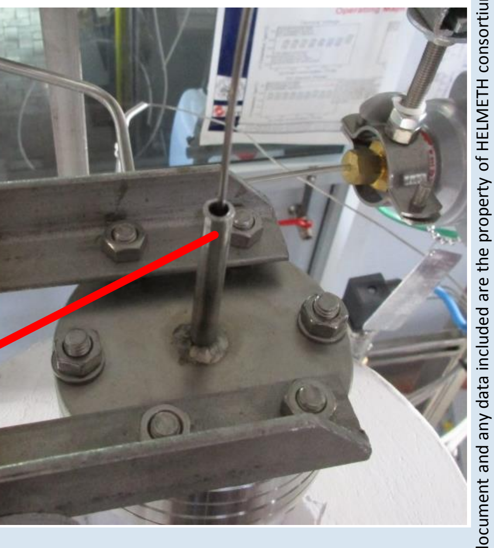




Thermal insulation and temperature control



Electric heating controlled by a thermocouple (in the middle of the reactor)



Atmospheric well for the reading thermocouple (temperature measured within the catalyst support)

Pressurized test unit

Insulated and controlled reactor

Safety valves

Condenser

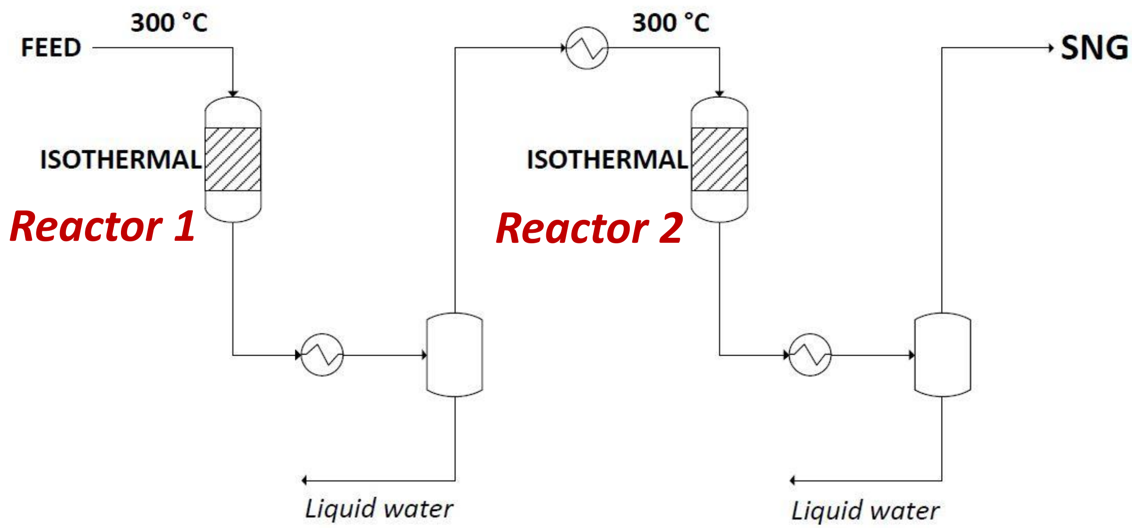
Pneumatic valves for by-pass

Back pressure controller

Tank for liquid water collection and drain

EXPERIMENTAL ACTIVITY AT HIGH PRESSURE

Methanation concept



Chosen methanation concept → ***2 isothermal reactors operating at 300 °C***

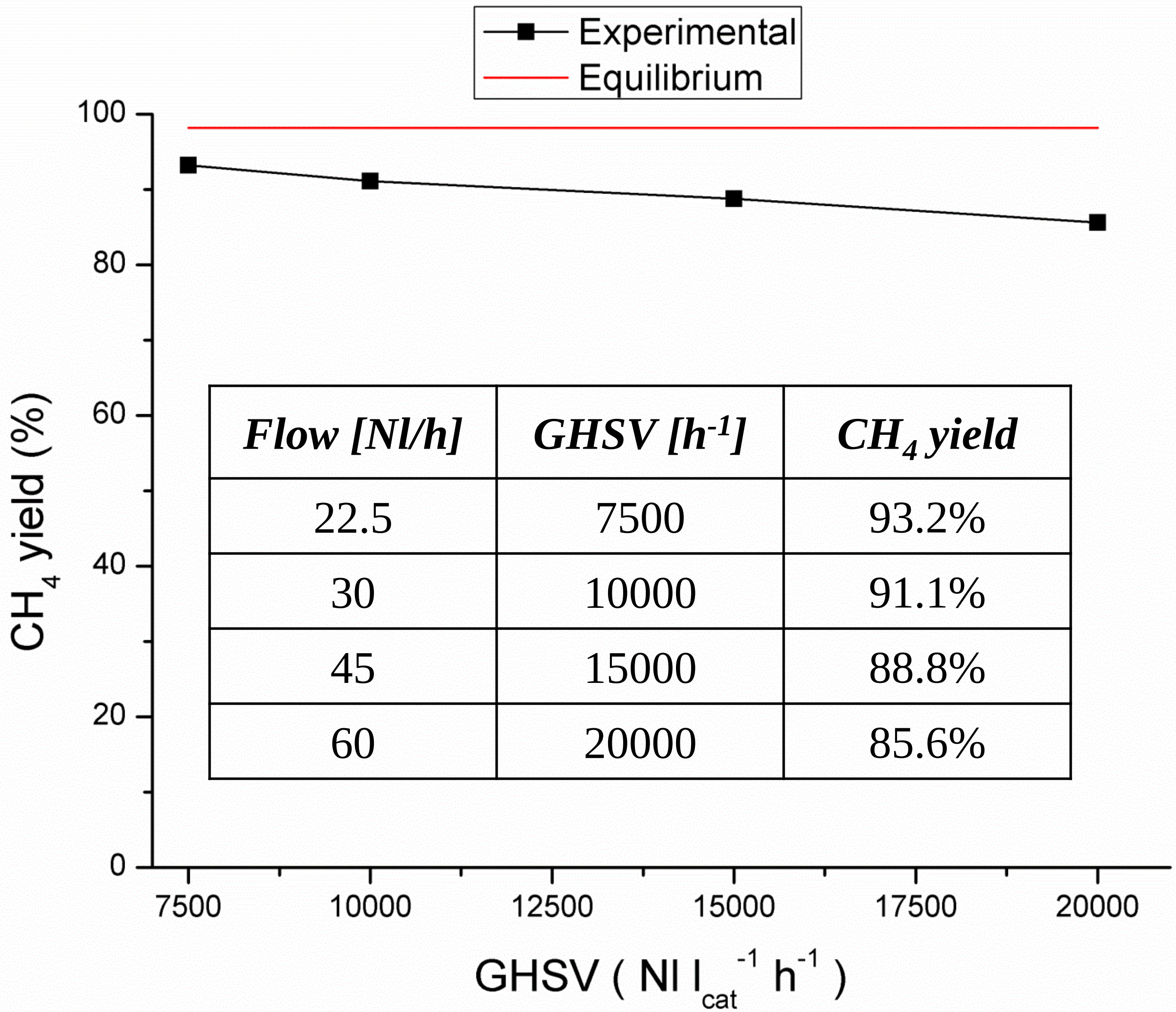
Experimental analysis on pellet size catalyst focused on this configuration

Commercial catalyst: pellet size

Methanation tests under pressurized conditions

- **Commercial Ni-based catalyst :**
  - Particles size: ≈3mm
  - Catalyst amount: ≈3.7 g
  - Reaction volume ≈ 3 cm^3
- **Operating pressure → 15 bar**
- **Operating temperature → 300 °C**
- **Stoichiometric feed (H_2/CO_2=4) with low Nitrogen dilution (10%)**
- **Two inlet mixture compositions:**
  - *Reactor 1* → [H_2]=72% - [CO_2]=18% - [N_2]=10%;
  - *Reactor 2* → [CH_4]=60% - [H_2]=24% - [CO_2]=6% - [N_2]=10%;

Commercial catalyst: Reactor 1

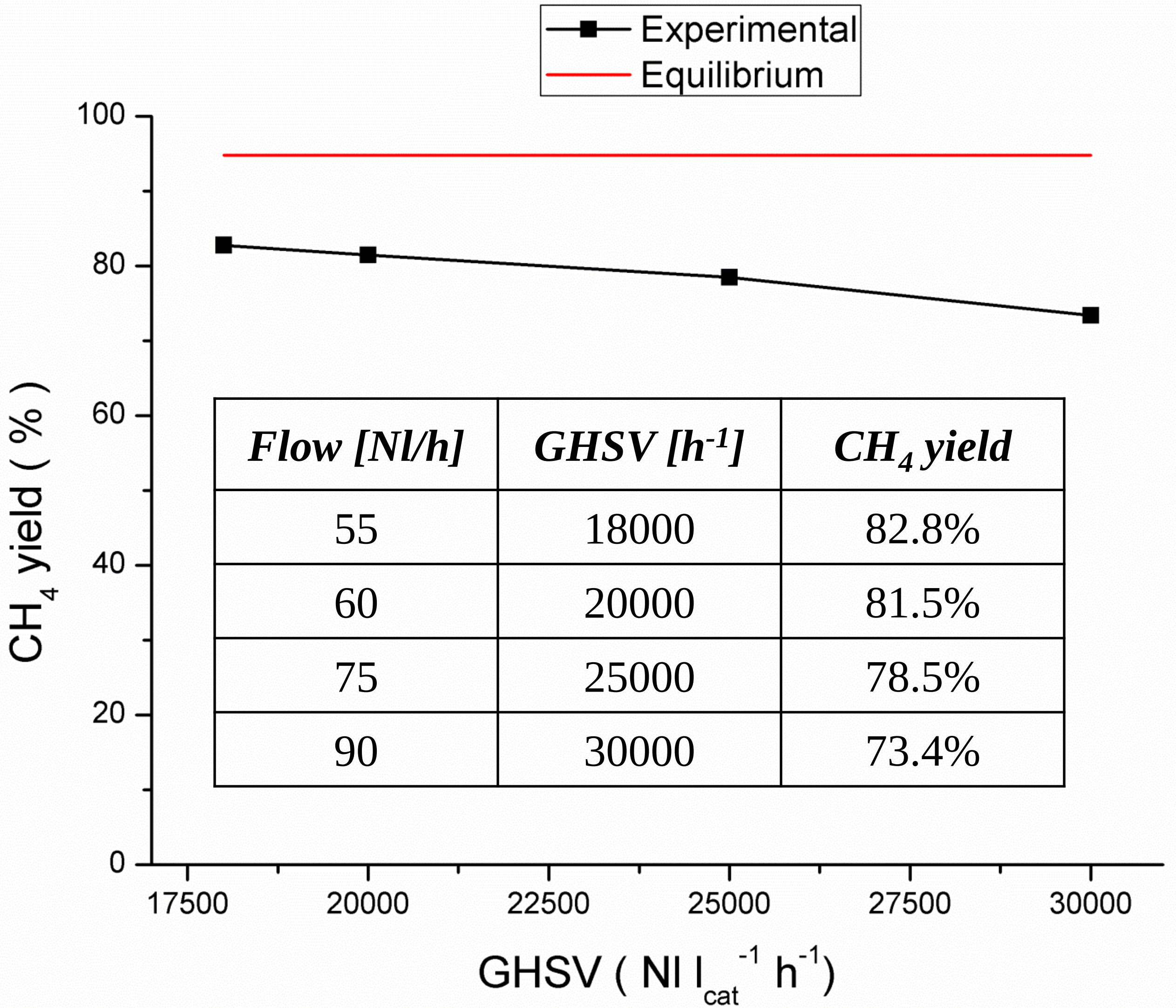


Flow [Nl/h]	*GHSV [h^{-1}]*	*CH_4 yield*
22.5	7500	93.2%
30	10000	91.1%
45	15000	88.8%
60	20000	85.6%

INLET MIXTURE COMPOSITION

[H_2]	*[CO_2]*	*[N_2]*
72%	18%	10%

Commercial catalyst : Reactor 2

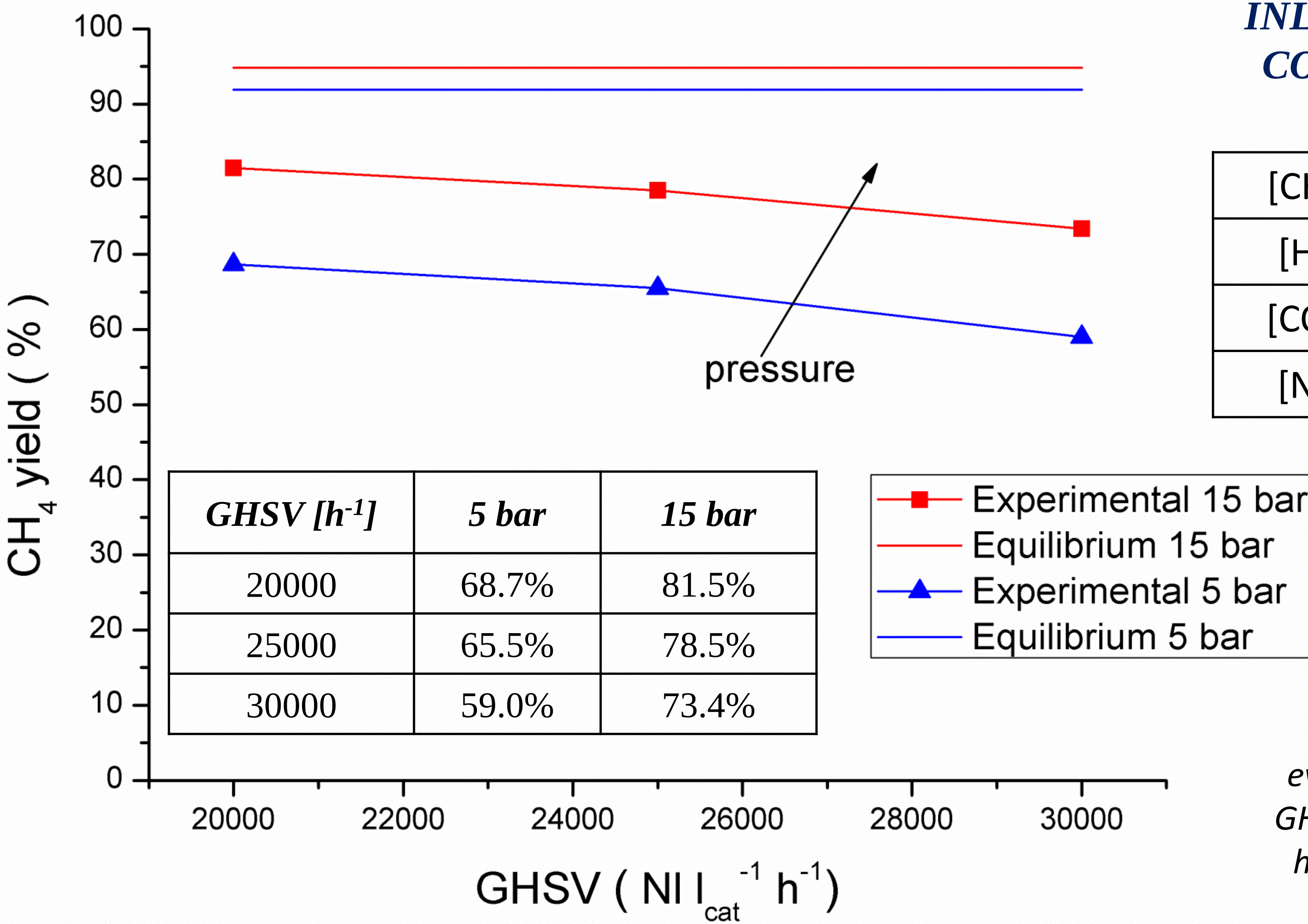


Flow [Nl/h]	*GHSV [h^{-1}]*	*CH_4 yield*
55	18000	82.8%
60	20000	81.5%
75	25000	78.5%
90	30000	73.4%

INLET MIXTURE COMPOSITION

[CH_4]	60%
[H_2]	24%
[CO_2]	6%
[N_2]	10%

Commercial catalyst - Reactor 2: pressure effect



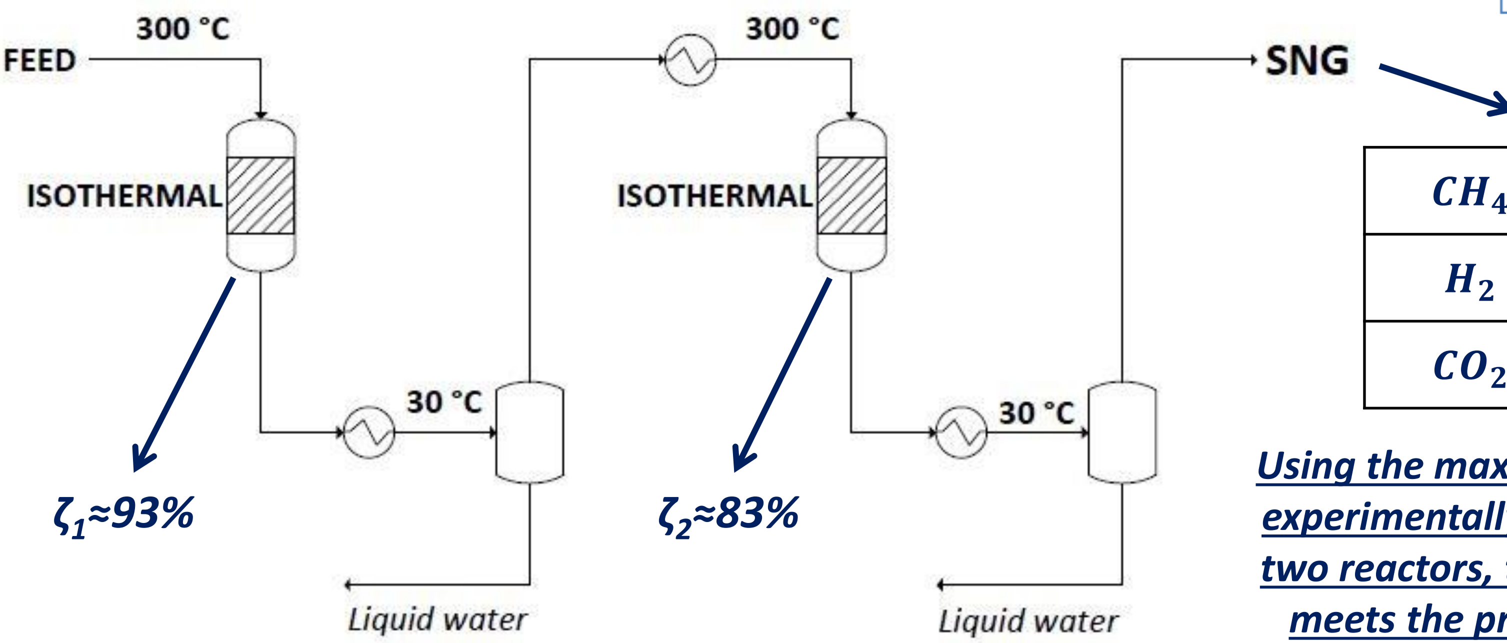
GHSV [h^{-1}]	*5 bar*	*15 bar*
20000	68.7%	81.5%
25000	65.5%	78.5%
30000	59.0%	73.4%

INLET MIXTURE COMPOSITION

[CH_4]	60%
[H_2]	24%
[CO_2]	6%
[N_2]	10%

even though the GHSV is the same, higher pressure means higher residence time

Commercial catalyst - Reactor 1 + Reactor 2



CH_4	94.1%
H_2	4.5%
CO_2	1.1%

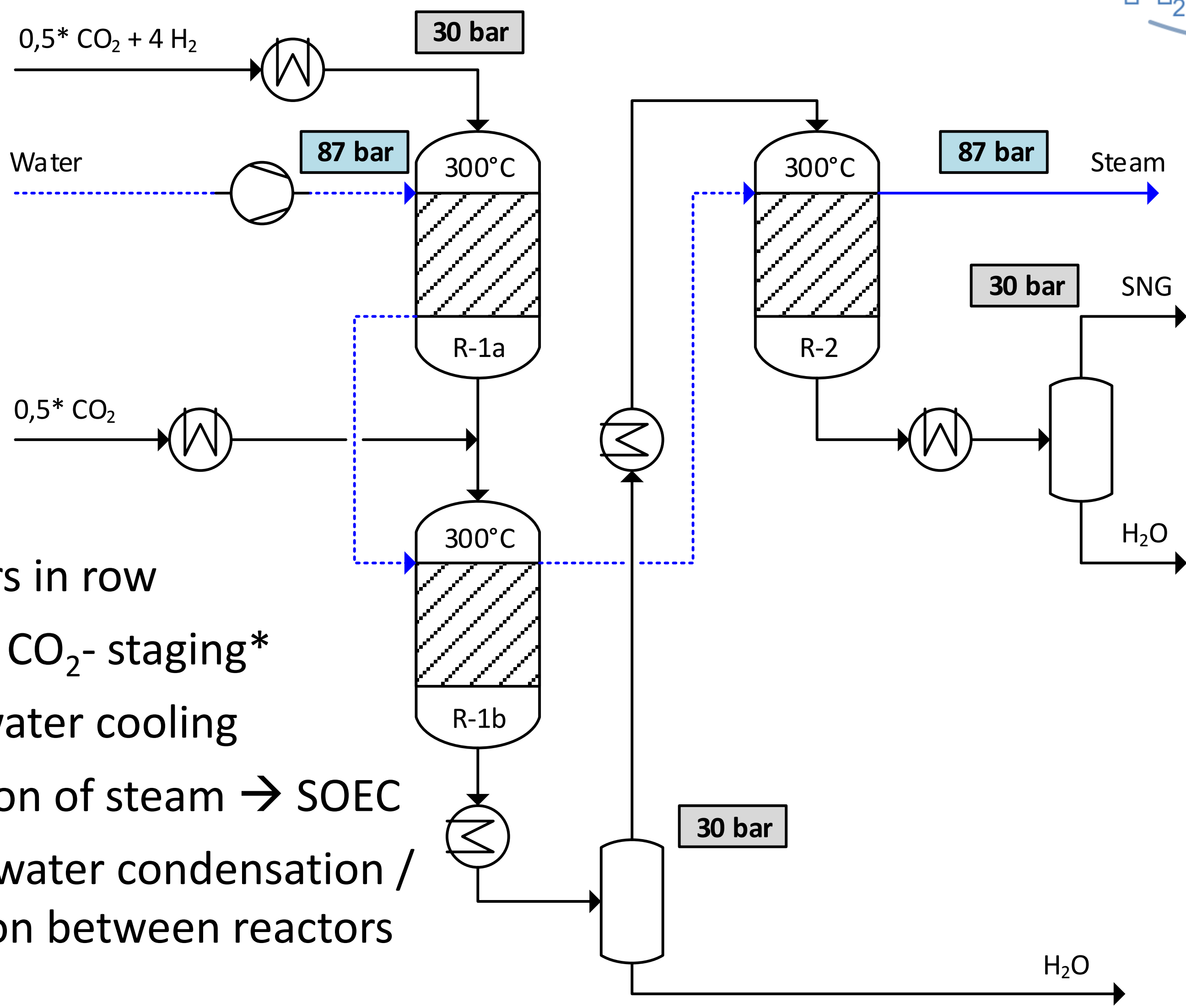
Using the maximum conversions experimentally obtained for the two reactors, the produced SNG meets the project target and could be injected into the NG grid.

ζ_2≈83% has been used, even though with ζ_1≈93% the 2nd reactor inlet mixture is slightly different (higher methane content) than 'Reactor 2' mixture considered during the experimental campaign.

HHV [MJ/Sm³]	36.1 ✔
Wobbe Index [MJ/Sm³]	48.9 ✔
[H_2]	< 5% ✔
[CH_4]	> 92.5% ✔

Selected HELMETH methanation concept

Selected methanation concept for prototype



- 2 reactors in row
- Optional CO_2- staging*
- Boiling water cooling
- Production of steam → SOEC
- Product water condensation / separation between reactors

Conclusion

- Catalysts have been tested and optimized. Suitable self developed and commercial catalysts were identified
- Kinetic modelling at elevated pressure performed and ongoing
- Lab tests of the HELMETH reactor concept confirm that SNG quality criteria can be met
- Methanation module is under construction

Outlook:

- Operation of complete PtG prototype in early 2017

Questions ?

www.helmeth.eu

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