Supercritical Water Gasification and Downstream Gas-Upgrading

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CERESiS

ContaminatEd land Remediation through Energy crops for Soil improvement to liquid biofuel Strategies

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FAPEG Fundação de Amparo à Pesquisa do Estado de Goiás

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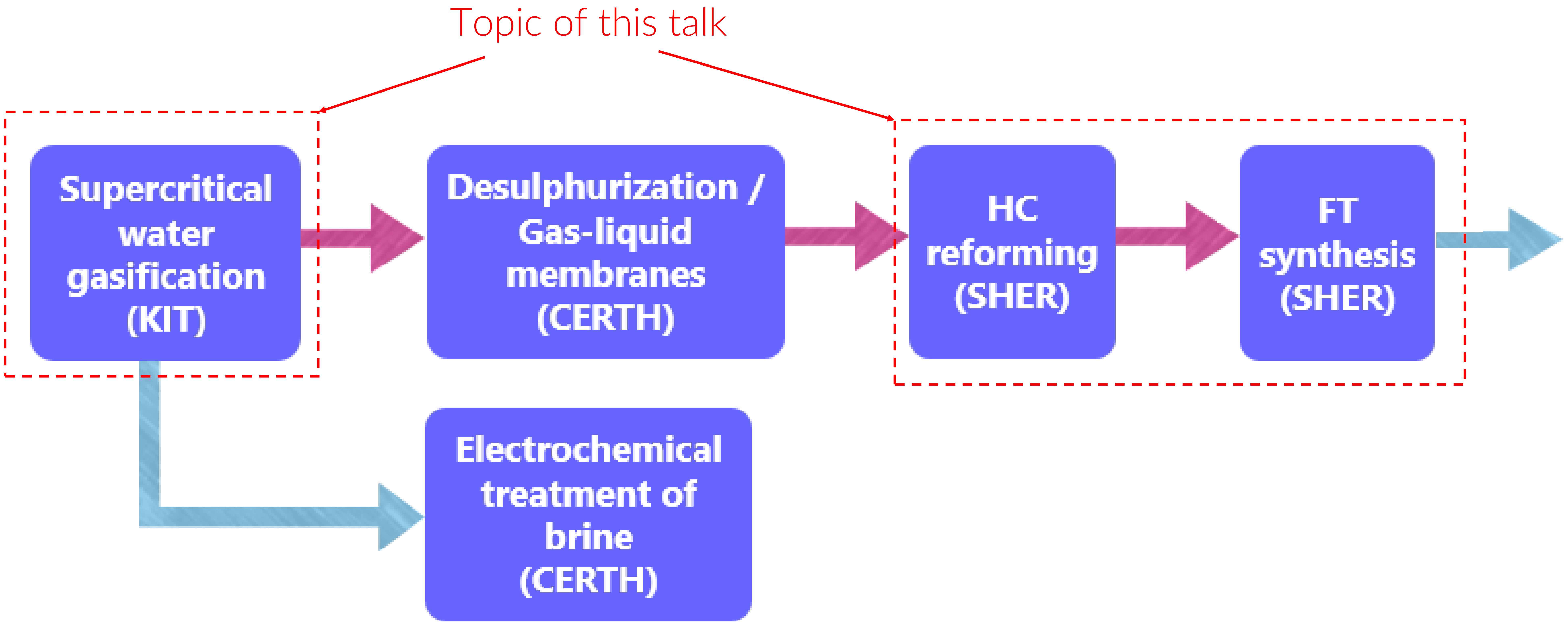
SCWG Process Chain



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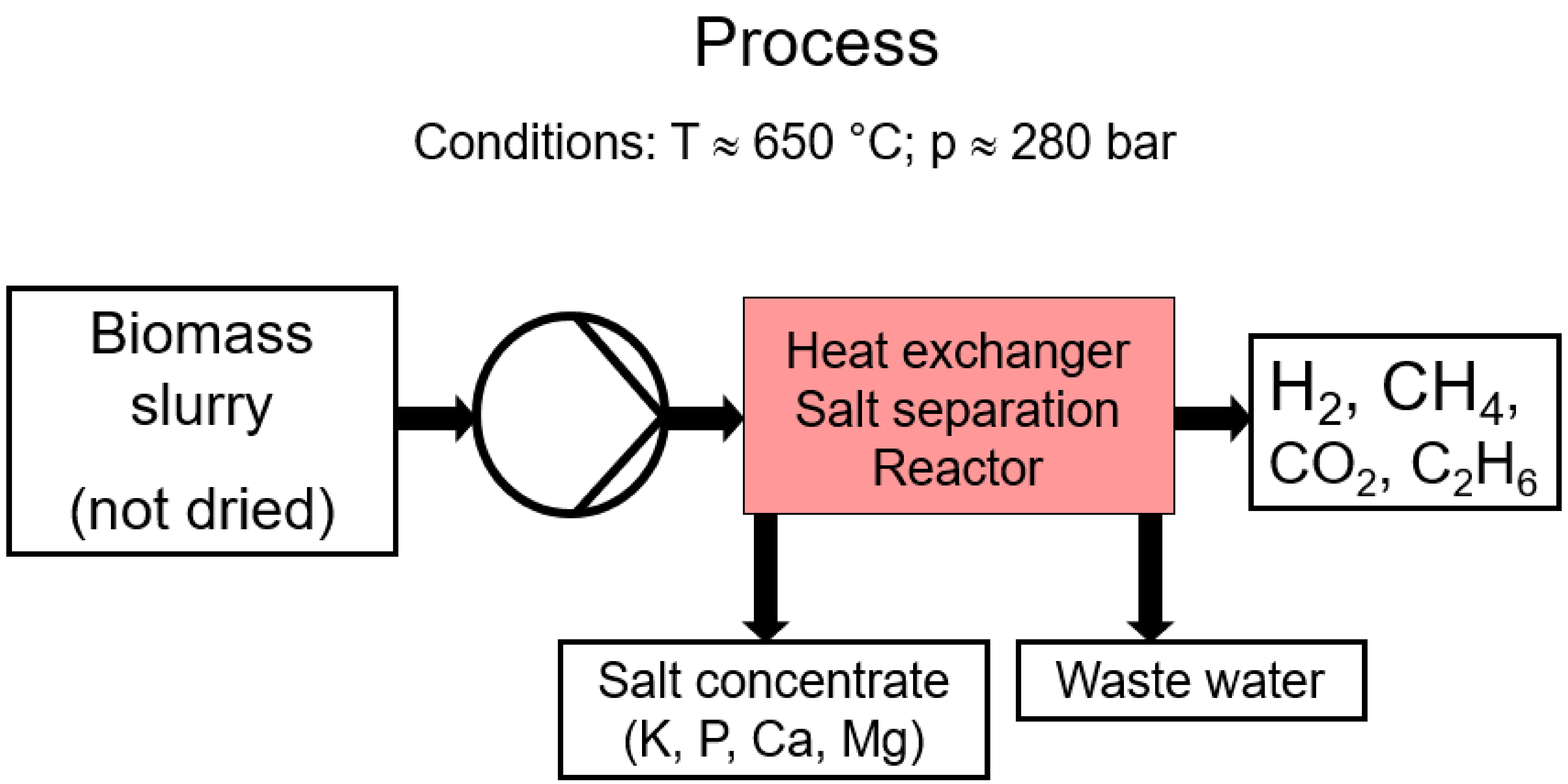
Supercritical Water Gasification



General process flow of SCWG plants.

SCWG laboratory plant at KIT, 1 kg/h

Part of the SCWG pilot plant at KIT , 100kg/h

Supercritical Water Gasification

Benefits of the technology

- Decentralized applications feasible
- Various biomasses (wet and dry biomasses) usable as a feedstock
- Product gas is rich in H_2 and CH_4
- Separation of inorganic contaminants within the process (salt brine)
- Decomposition of organic contaminants

Size reduction of biomass for creation of biomass slurry

Drawbacks of the first experiments

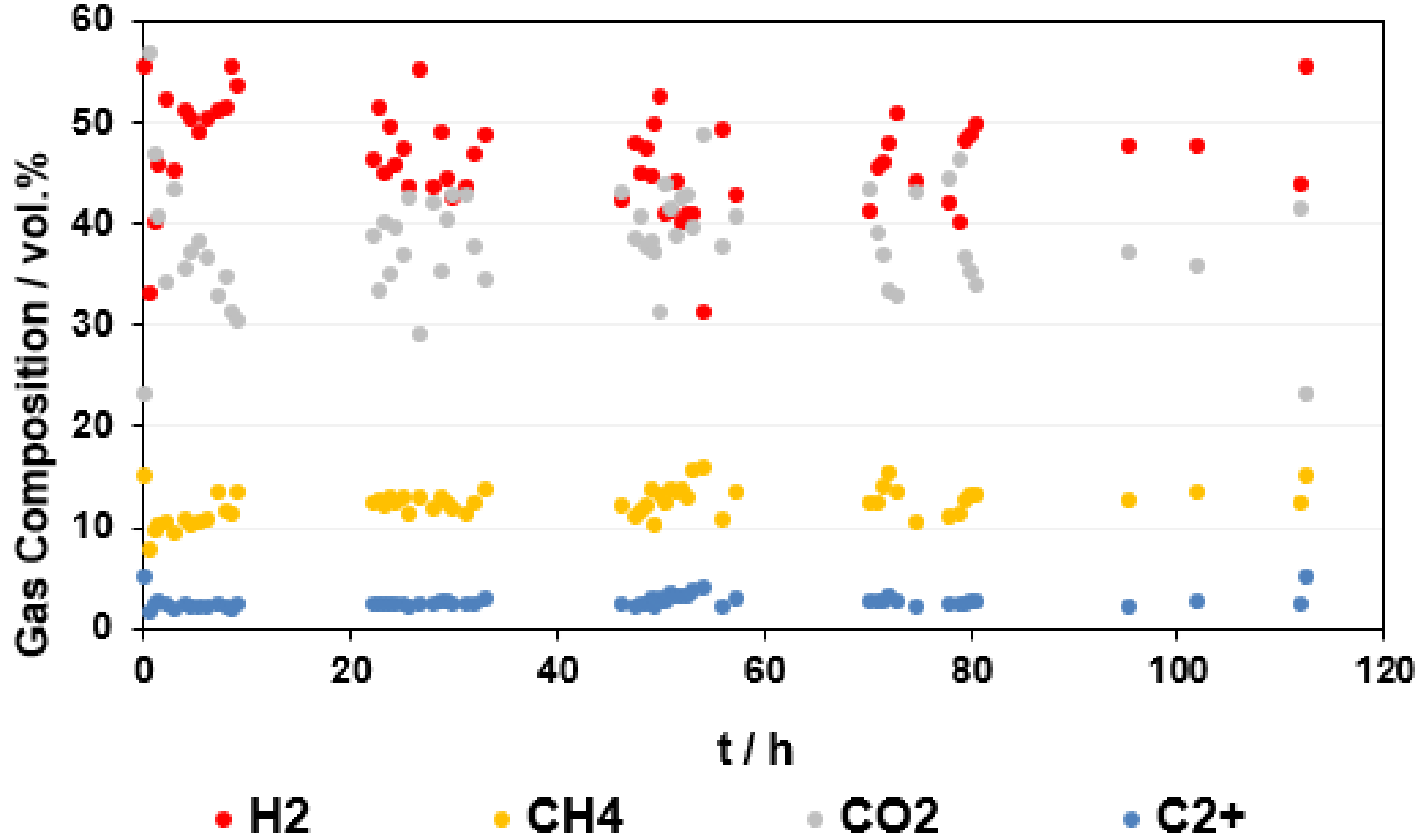
- Relatively low gasification efficiencies (CE < 75 %) due to the size of the lab-plant (low residence times, slow flow rates)
- Some carbon still contained in the effluent
- Salt separation needs to be improved since salts can precipitate and cause blockage of the flow [1]
- Some formation of coke in reactors

[1] Dutzi, J.; Boukis, N.; Sauer, J. Processes 2023. https://doi.org/10.3390/pr11030797

Supercritical Water Gasification

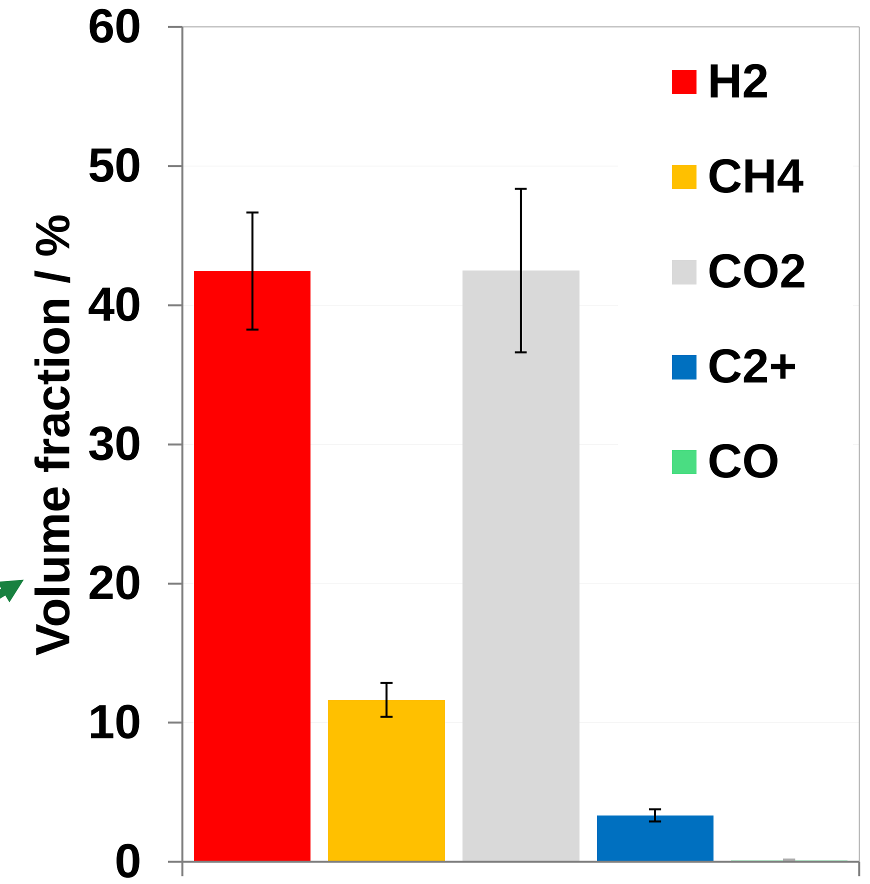
Progress in the CERESiS project

- Over 100 experiments performed
- Development of a suitable process configuration, leading to
  - **>100 h of continuous operation**
  - **Gasification efficiencies CE of about 90% (→ clean effluent)**
  - **Minimization of solid deposits**



Product gas over time during gasification of Reed Canary Grass (1.2 wt.%) at T = 650 °C, p = 280 bar

Feed slurry



Product Gas Composition

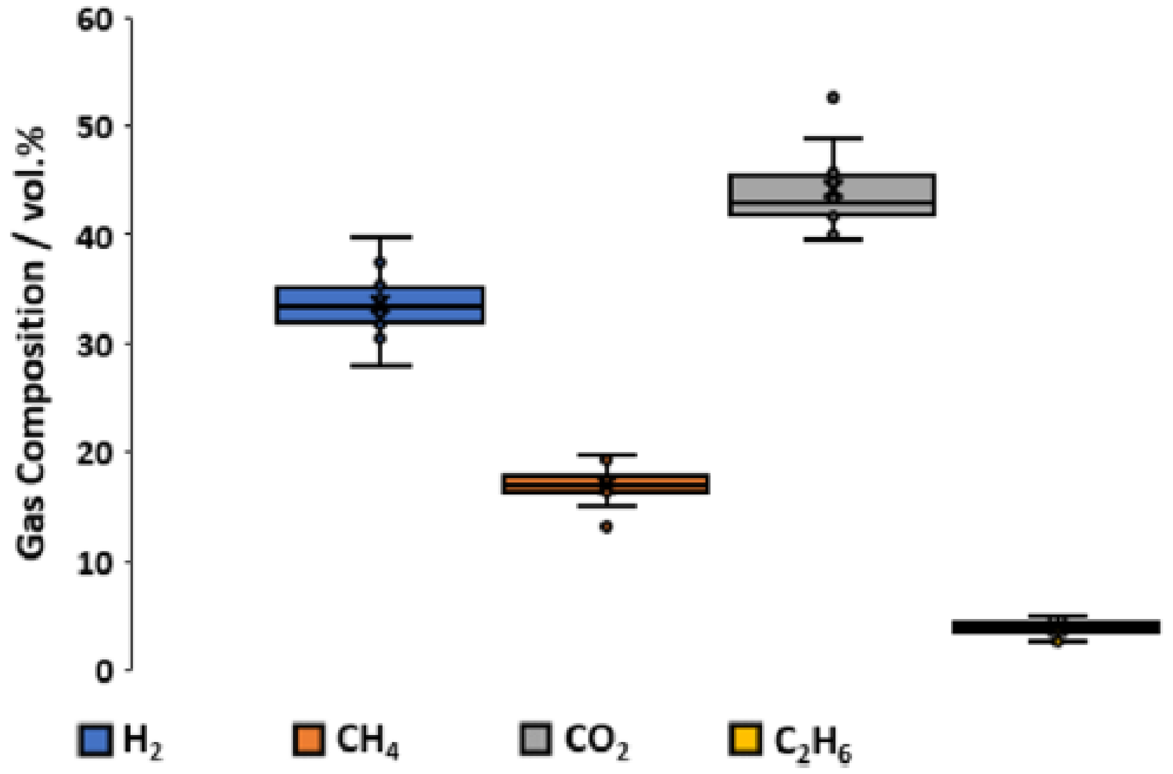
Reactor effluent samples over the course of one experiment

Supercritical Water Gasification

Important knowledge gained

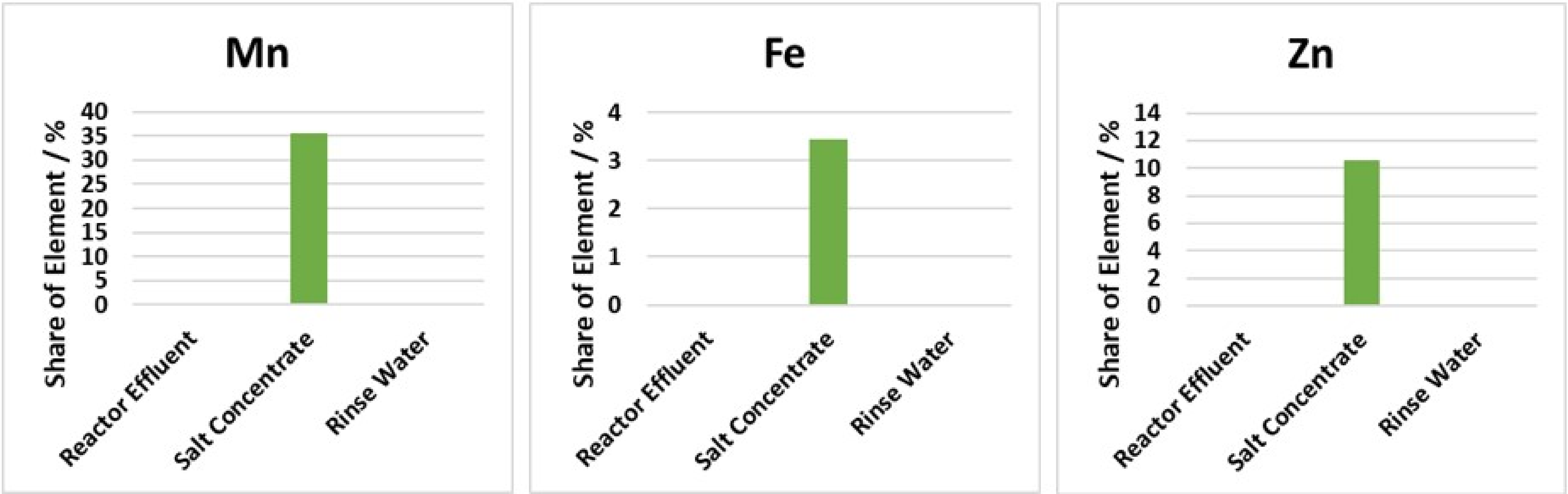
- Process effluent can be recycled to minimize fresh water usage [1]

- No significant difference in the gasification of different CERESiS biomasses regarding CE or gas composition [3]



Product gas of SCWG experiments with 10 different CERESiS biomasses.

- Process effluent is heavy metal free [2]



Distribution of heavy metals in the effluents during gasification of grapevines

- Important process parameters identified that lead to solid deposition [4]

[1] Dutzi, J.; Boukis, N.; Sauer, J. Processes 2023. https://doi.org/10.3390/pr11030797
[2] Dutzi, J.; Boukis, N.; Sauer, J. Biomass & Bioenergy 2024. https://doi.org/10.1016/j.biombioe.2024.107059
[3] Dutzi, J.; Stoll, I.K.; Boukis, N.; Sauer, J. Sustainable Chemistry for the Environment 2024. https://doi.org/10.1016/j.scenv.2024.100062
[4] Dutzi, J.; Boukis, N.; Sauer, J. ***not submitted yet***

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Reforming the product gas (SCWG) and adjusting it to perform FT synthesis using available commercial catalysts

- Reforming via **dry reforming**

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$$

- **Investigated reactor materials:** Ni-base alloy 625, stainless steel

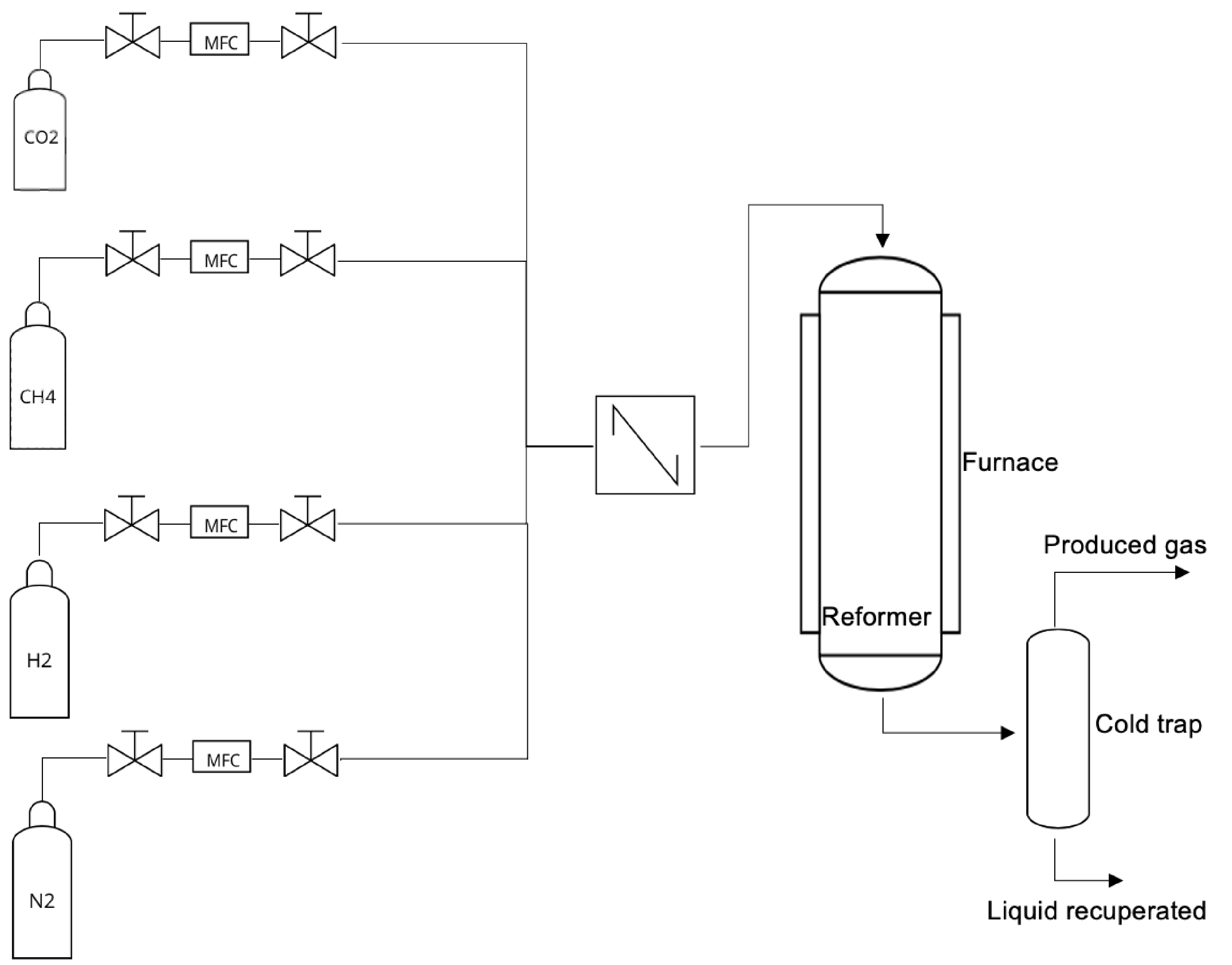
- **Investigated gas mixture**

Detailed gas composition of SCWG product gas (from Panicum virgatum)

Gas	Vol-%
H_2	33.05
CO	0.79
CH_4	19.72
CO_2	40.44
C_2H_4	0.31
C_2H_6	4.61
C_3H_6	0.30
C_3H_8	0.79

Gas composition for reforming tests

Gas	Vol-%
H_2	33.05
CH_4	25.73
CO_2	41.23

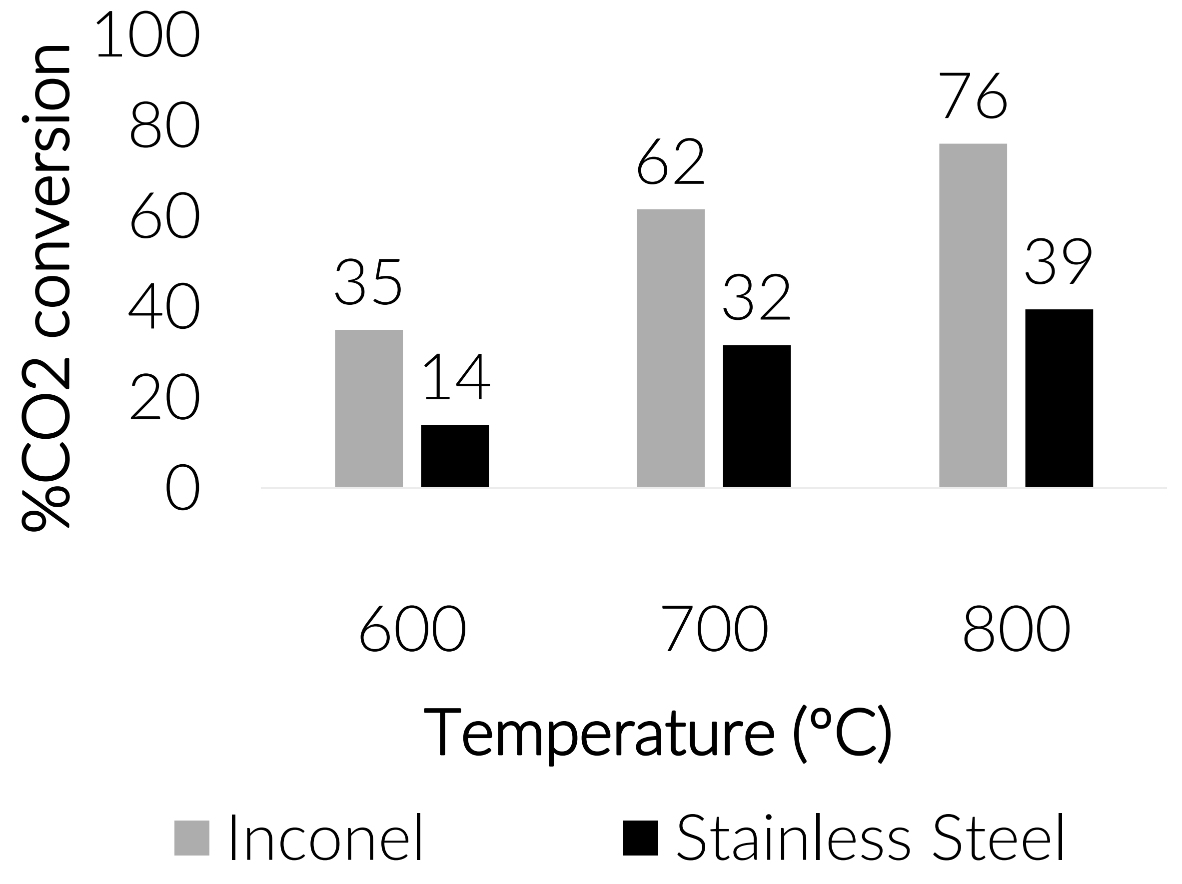


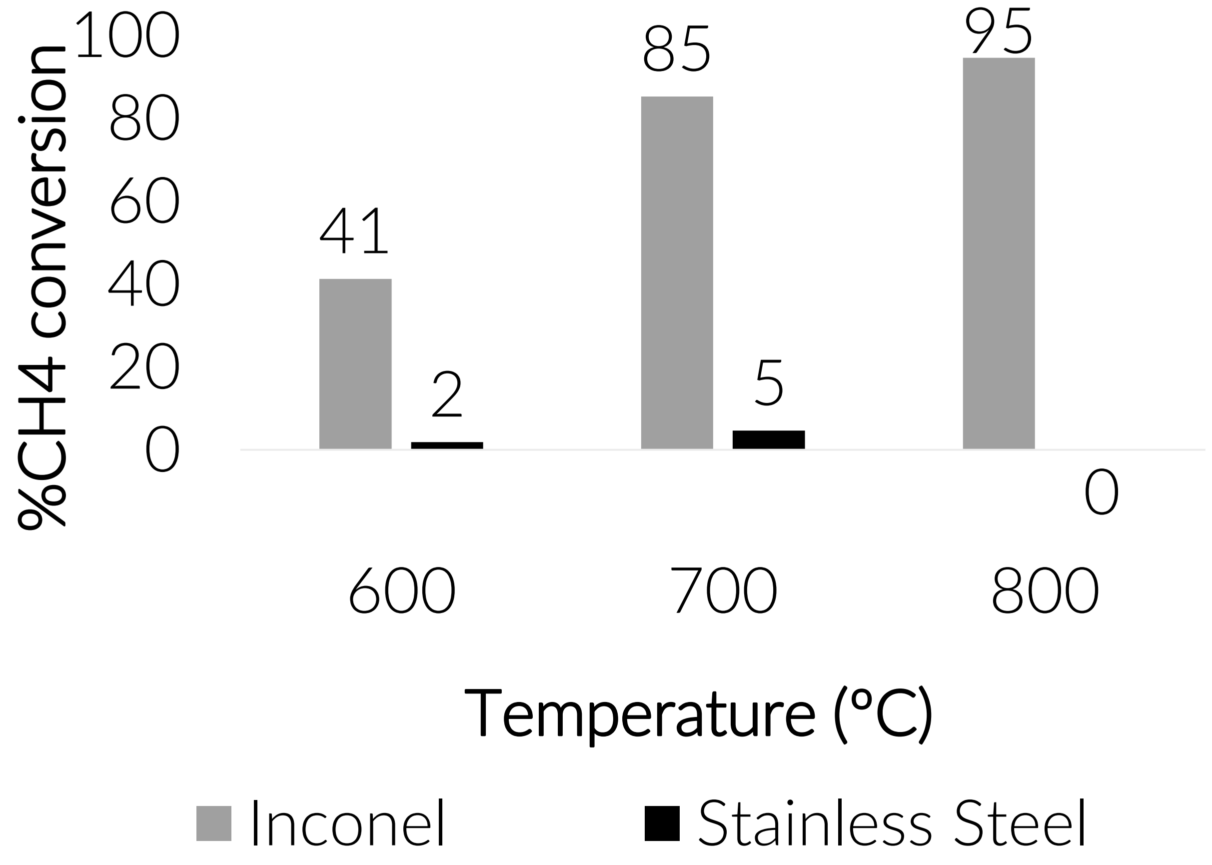
Simplified flow diagram for reforming experiments

Reforming the product gas (SCWG) and adjusting it to perform FT synthesis using available commercial catalysts

Main knowledge gained

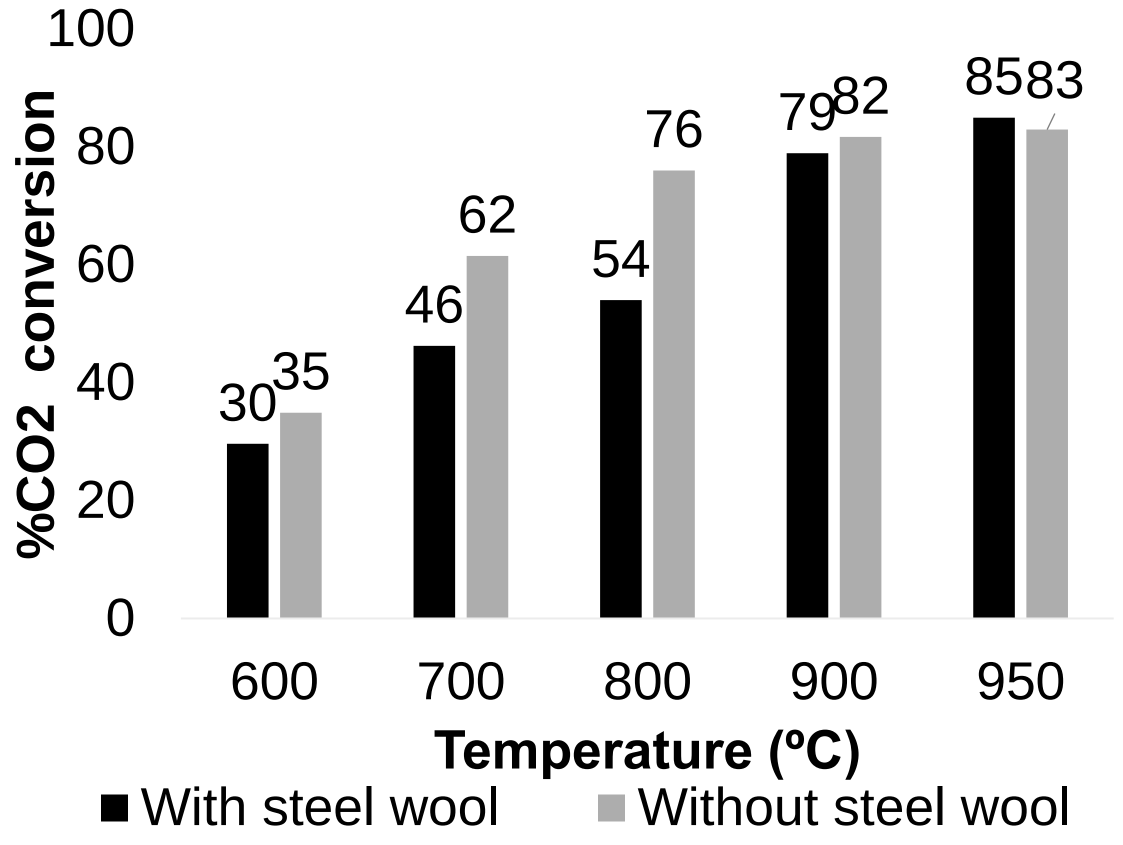
- Comparison of two reactor materials (without catalyst):
  Inconel 625 vs. Stainless Steel

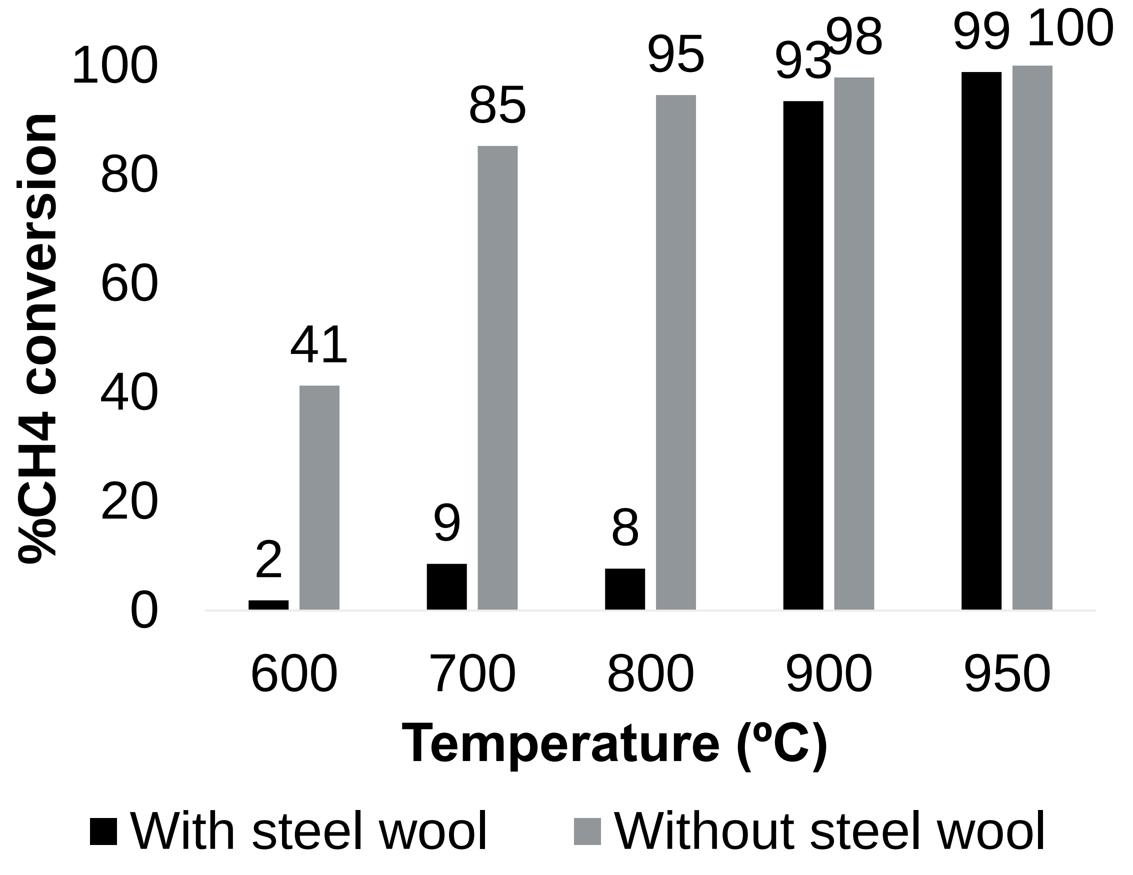




Performance of **Inconel reactor superior** at all temperatures tested.

- Influence of catalyst (steel wool) investigated in Inconel reactor





Higher conversions were achieved **without a catalyst** (maximum of 100% and 83% for CH_4 and CO_2, respectively, at 950 ºC).

Higher temperatures are beneficial for the reforming.

Inconel reactor material was catalyzing the reaction.

Fischer Tropsch Synthesis

- Production of hydrocarbons via the following polymerization reaction

$$CO + 2H_2 \rightarrow -(CH_2)_n + H_2O$$

→ **Main products**: Olefins and paraffins

Product spectrum obtained from FT experiments.

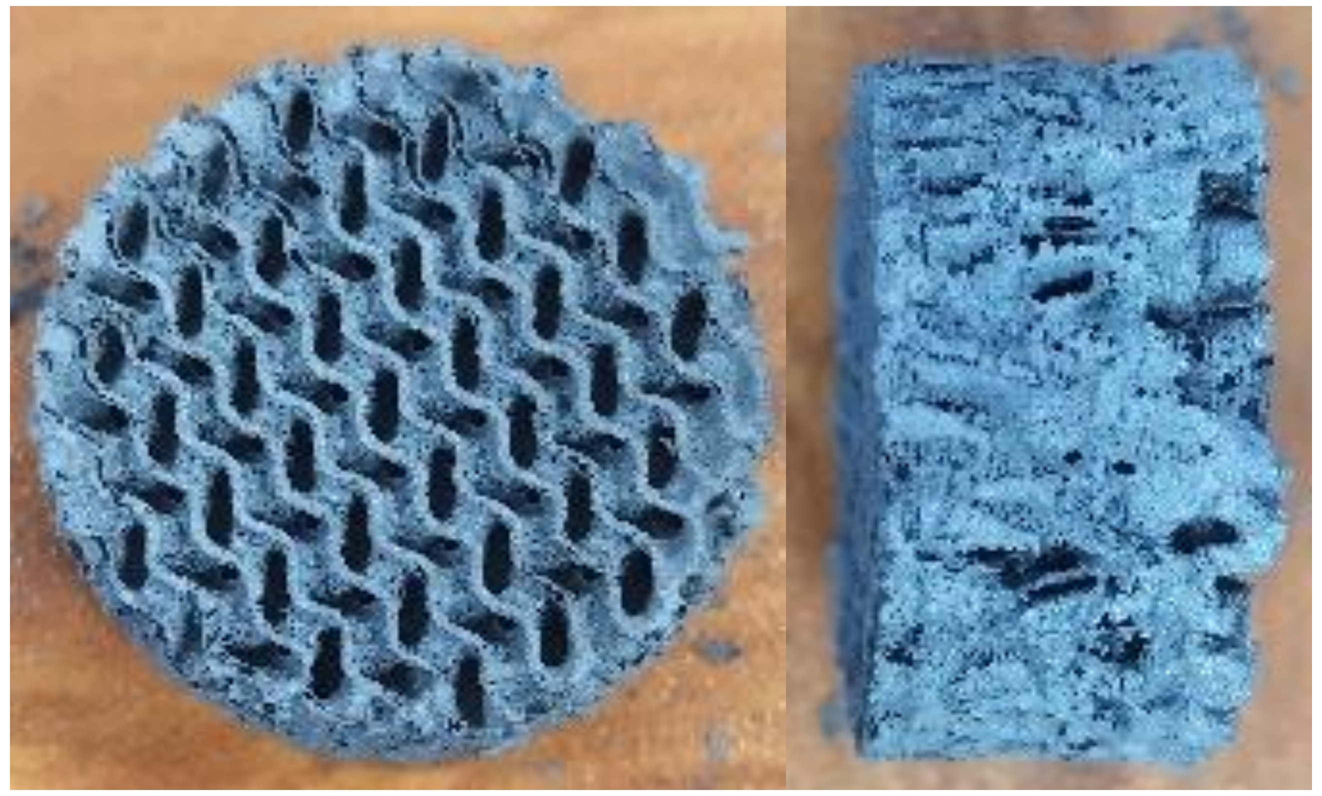
- Typical process conditions:
  - T = 200 – 350 °C
  - p = 5 – 60 bar
  - Catalyst: Co and Fe (and Ni and Ru)

Fischer Tropsch reactor at BTL-Université de Sherbrooke.

Fischer Tropsch Synthesis

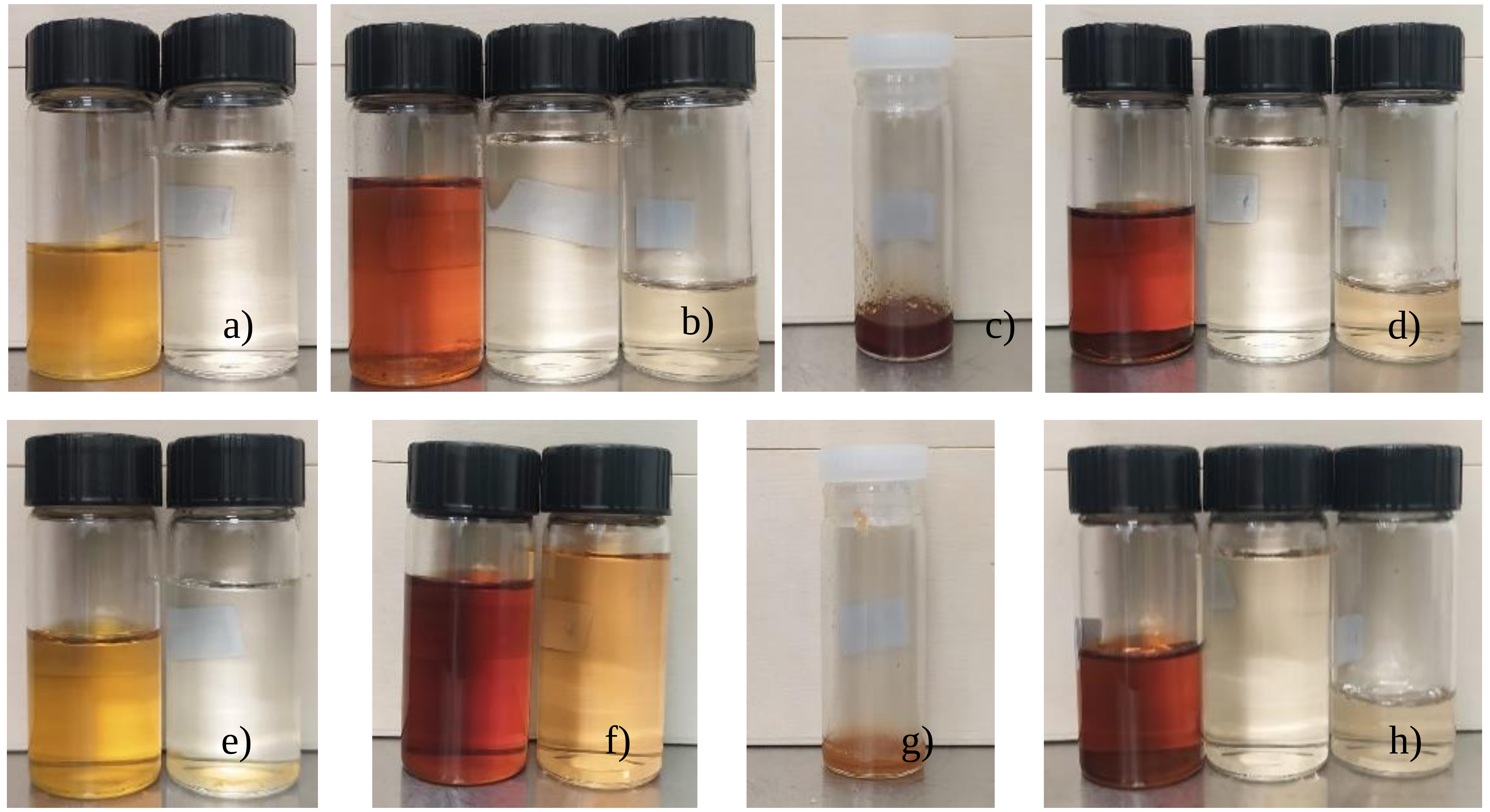
Production of structured catalysts

3D printing Fe-catalysts



→ Variation in void fraction possible

→ Additions of promoters (like K or Cu) possible



Liquid products of FTS using structure iron catalyst. Panel a) 0.72 Fe, b) 0.72 FeCu, c) 0.72 FeK; d) 0.72 FeKCu; e) 0.77 Fe; f) 0.77 FeCu; g) 0.77 FeK; h) 0.77 FeKCu. Vails with black cap 20 ml and white cap 10 ml.

Void Fraction

Promotors

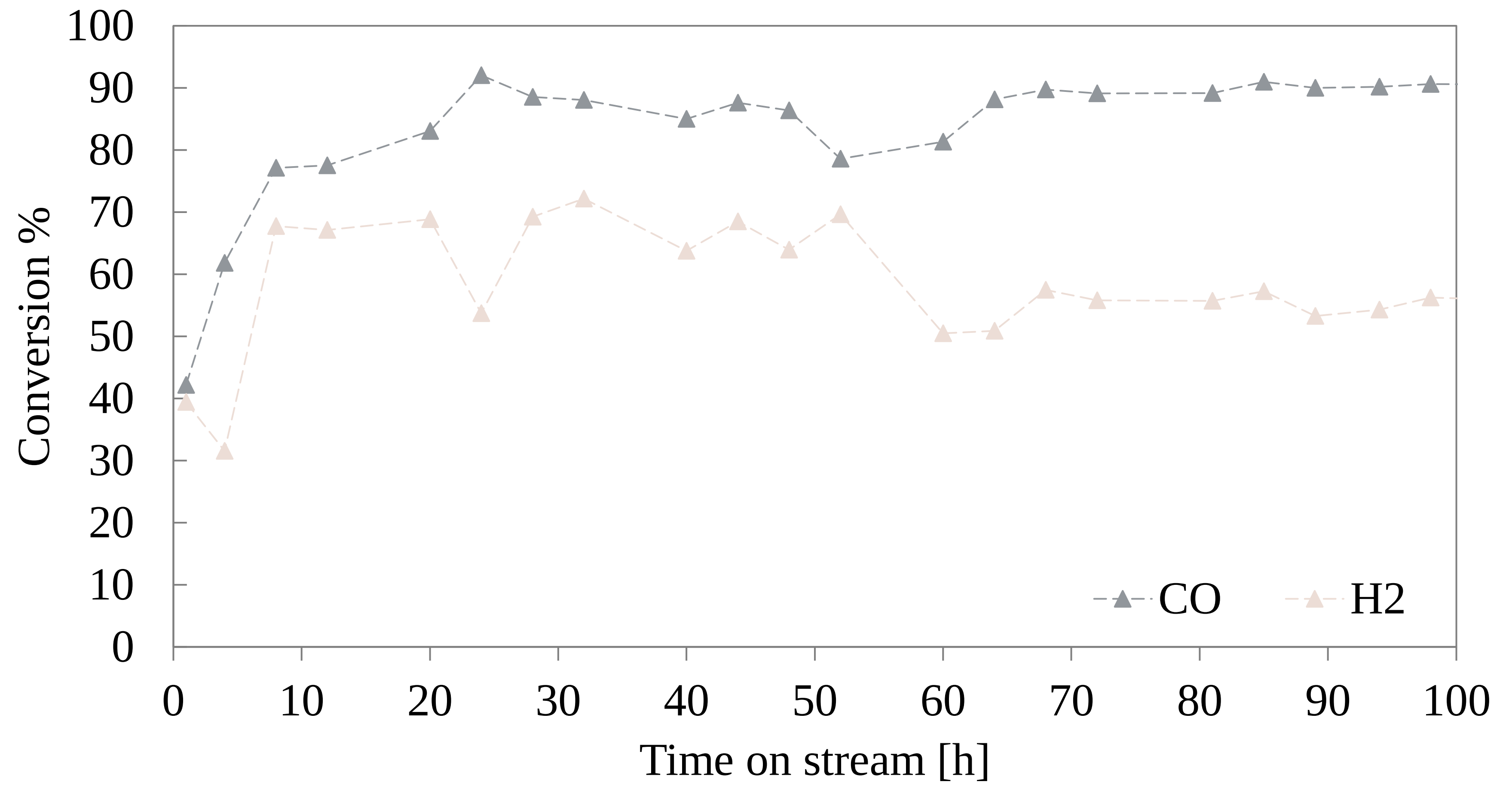
Notable influence of promoters – higher catalyst activity when K and Cu are present.

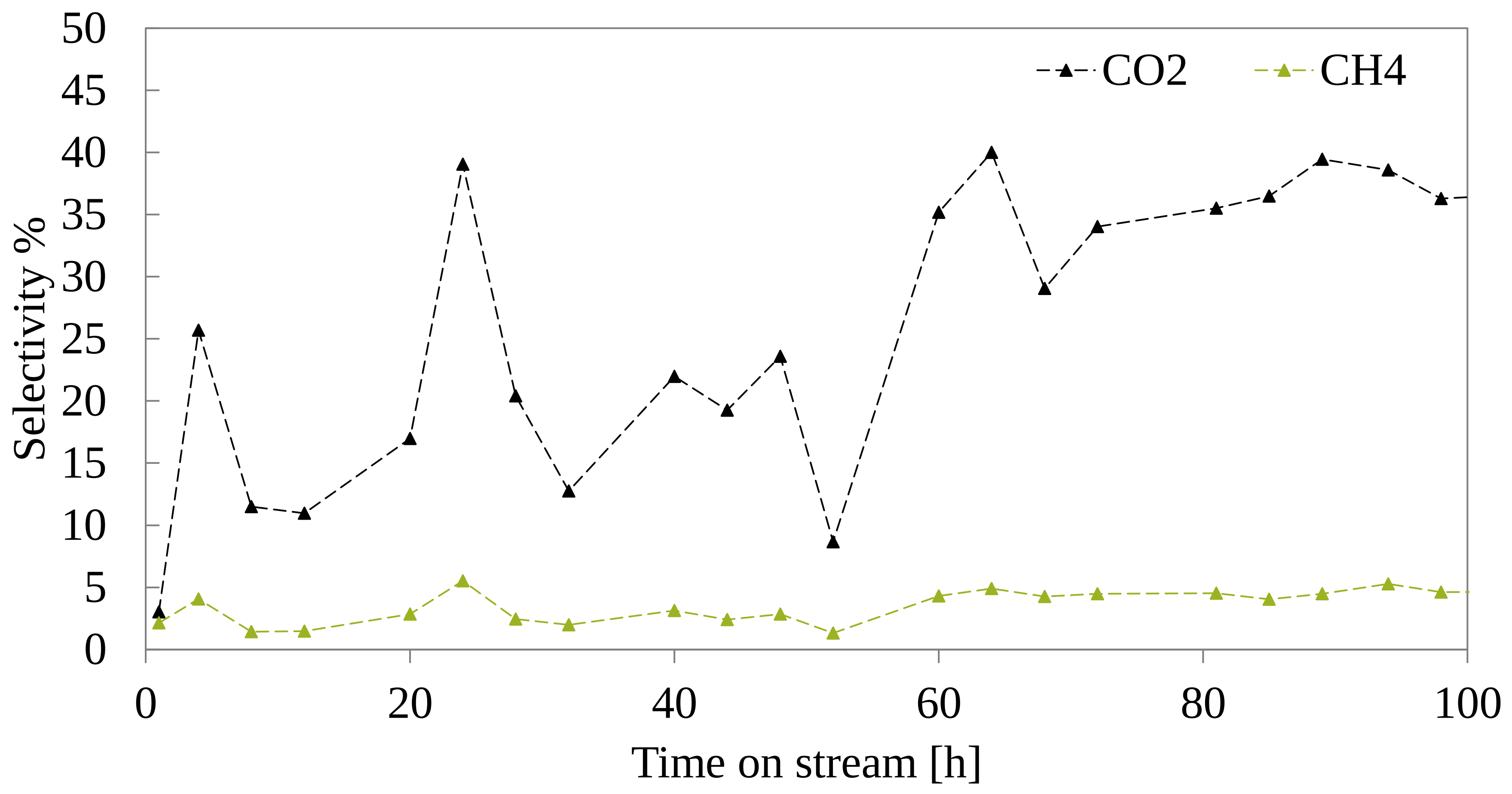
Positive effect of **increased void fraction** regarding CH_4 and CO selectivity.

Fischer Tropsch Synthesis

- **Optimal process conditions identified:** T = 250 °C, p = 20 bar, WHSV = 600 $l \cdot (g_{Fe} \cdot h)^{-1}$

- **Long-time experiments carried out**
  - 100 h stable operation
  - Very high CO conversion over complete TOS (~90%)
  - Low CH_4 selectivity achieved



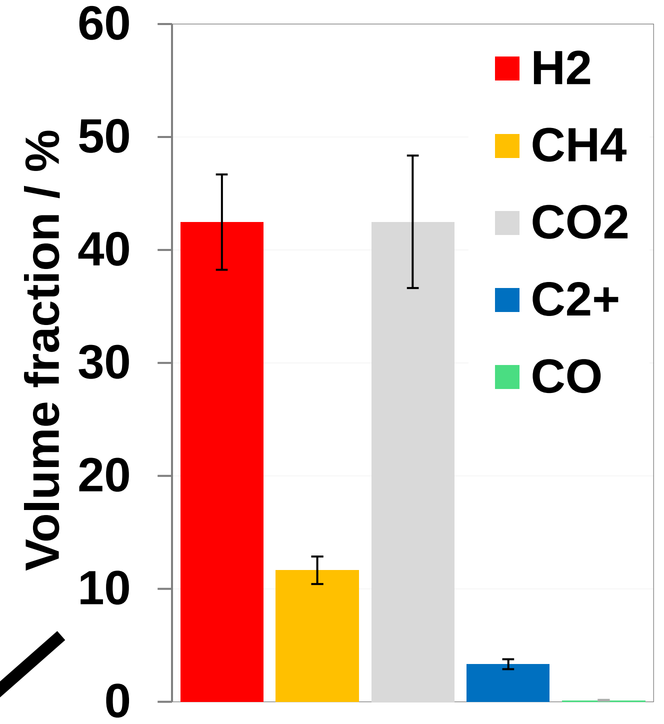


Conversion and selectivity as function of time on stream for the structure catalyst 72FeKCu in the FTS. Operation conditions: T=250 °C, P=20 bar, H_2:CO = 1.2, WHSV = 600 $l \cdot (g_{Fe} \cdot h)^{-1}$.

Conclusion

- **Each technology was developed separately, so that**
  - it is suitable for the CERESiS use-cases
  - long-time operation is possible
  - high conversions were achieved

- **No physical integration of the systems was performed**, but it should be possible in the future



Valuable process chain developed to gain useful fuels from contaminated biomass.

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