WP3 Synthesis
Final seminar

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Objectives WP3

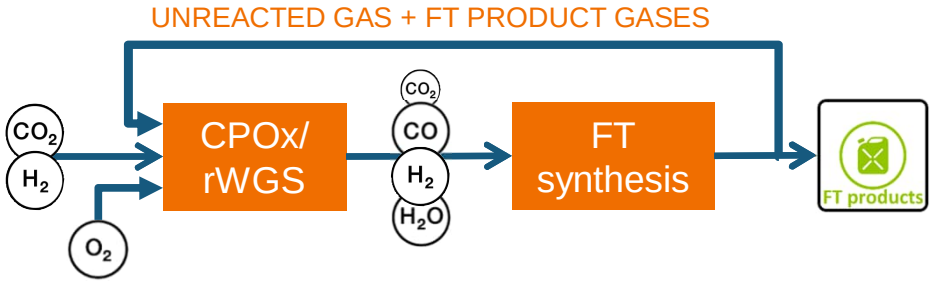
- **T3.1 RWGS/CPOX**

- A) CPOX/rWGS technology long term piloting, TRL5, **Christian Frilund**
  - ensure correct reactor design and dimensioning of the equipment for large scale process design
  - determine feasible circulation ratio of the off-gases to ensure operation conditions that allow long term coking free runs
- B) e-reactor concept development for rWGS, TRL3, **Pekka Simell**
  - PoC at lab scale

- **T3.2 Fischer-Tropsch synthesis (FT), Niko Heikkinen**

  - find out the role of water concentration on catalyst activity and selectivity
  - to make sure that adequate catalyst stability can be achieved

T3.1 MOBSU CPOx/rWGS Process

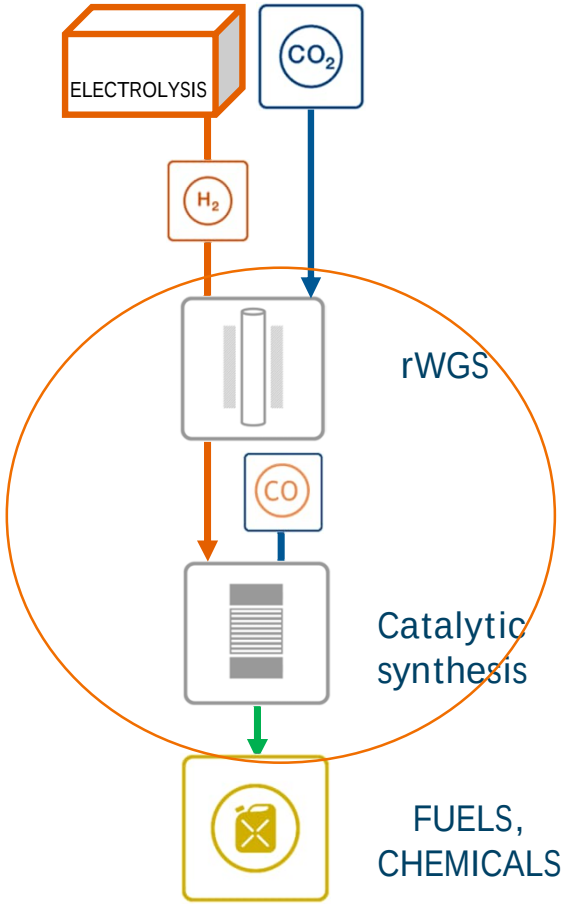


- Converts CO_2+H_2 gas feeds to syngas (H_2,CO,CO_2,CH_4, H_2O)
  - $rWGS$: $CO_2 + H_2 + Heat \rightarrow CO + H_2O$
  - *Methanation:* $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O + Heat$
  - *Catalytic partial oxidation (CPOx) or reforming of hydrocarbons*
  - *Combustion e.g.* $2H_2 + O_2 \rightarrow Heat + 2H_2O$

- CPOx mode allows for **improved recycling of FT gas streams** and provides in-situ heat generation

- **High-throughput** catalytic reactor
  - In-house developed concept and reactor design with catalyst
    - Patent granted WO2019/175476 A1

EFUEL concept

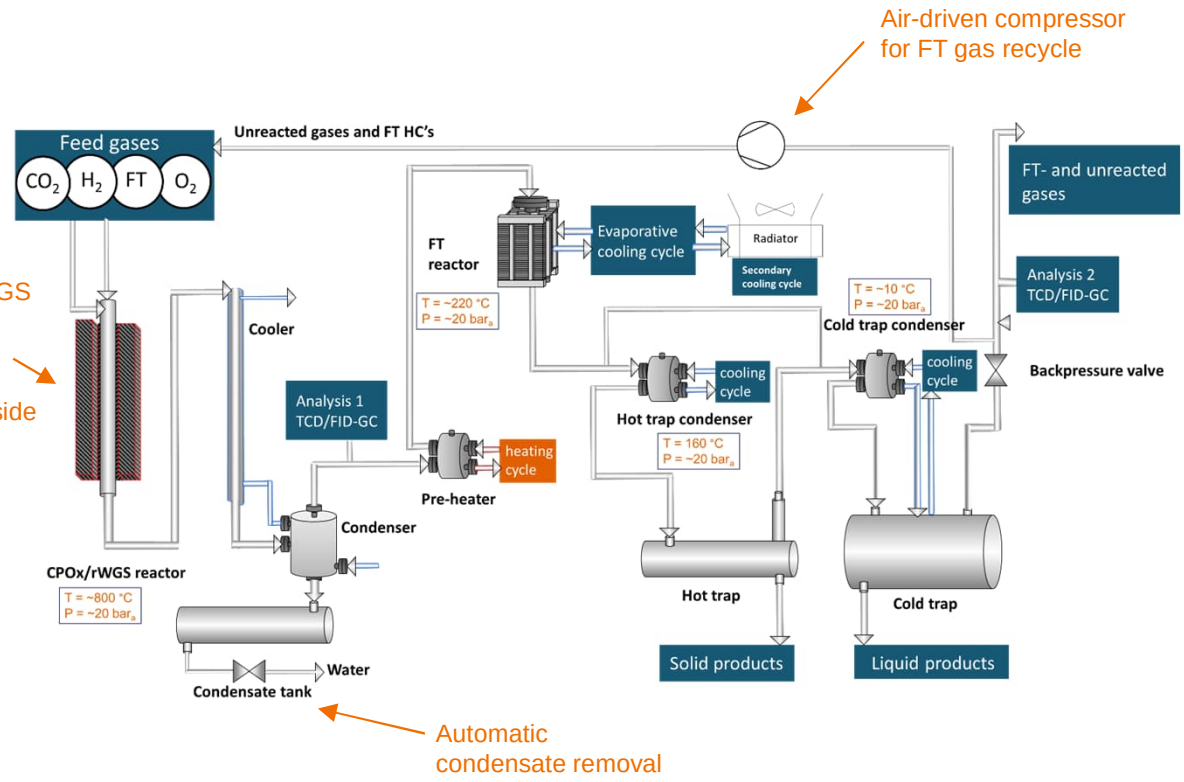


MOBSU bench-scale implementation

Gas preheaters

Tubular CPOx/rWGS in furnace.

3 temperature measurements inside reactor



EFUEL results for CPOx/rWGS

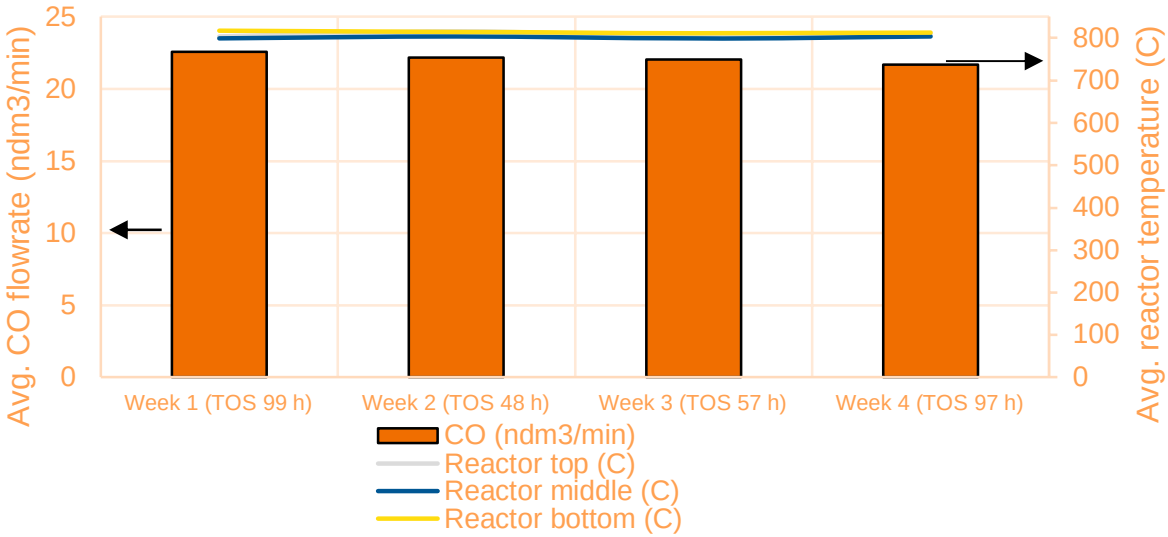
- The CPOx/rWGS process (version 2.0) was integrated in bench-scale inside the MOBSU container at TRL 4/5

- The main unknowns of the CPOx/rWGS process studied for further development:
  - Validation of the reactor design & dimensioning
  - The effect of FT recycle gases on solid carbon formation
  - Longer-term performance (stability) of the catalyst

- Improved bench-scale (MOBSU) system:
  - Operation with high FT-off gas recycle
  - Unmanned operation of CPOx/rWGS in preparation for EFUEL demo (WP4)

Extended duration CPOx/rWGS testing
With recycle

- **4 test weeks** at (semi)fixed conditions (300 h)
  - 38 ndm^3/min fresh CO_2 feed rate at H_2/CO_2 ratio of 2.3. Recycle ratio ca. 0.2. Slight variations in recycle gas composition depending on FT performance.
  - Ca. 800 C and 19 bar reaction conditions
  - No solid carbon removal (oxidation) performed
- Higher CO production rate at lower fresh gas feed rate than in tests without recycle
  - **Higher carbon-efficiency** achieved
- **Slight deactivation** detected (replicates)
  - Regeneration afterwards restores activity



Replicate setpoint (40 ndm^3/min CO_2 at H_2/CO_2 ratio 2.2, without recycle):
(Combined TOS ~320 h including 5 startups/shutdowns)

	Before	After
Process conditions		
CPOx/rWGS Tavg (C)	809	809
P (bar)	19.9	19.4
Results (gas GC)		
Specific CO activity (mmol CO /cm$^3_{cat}$*h)	320	303
Carbon balance (IN/OUT)	1.00	0.985

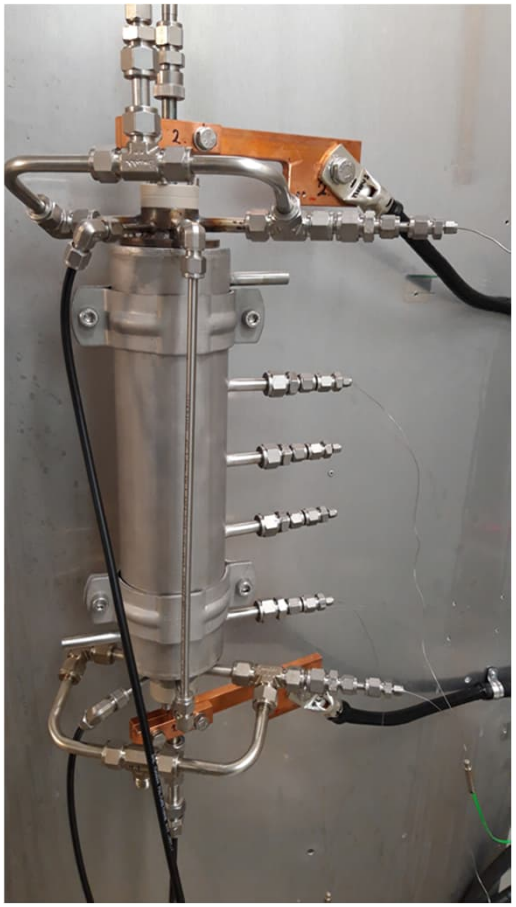
T.3.1 e-rwgs reactor

- **Porous Kanthal tube that is heated resistively**
  - Ni-catalyst coating
  - Gases flow through porous layer
    = radial flow type reactor
  - Porous tube inserted in a quartz tube to N2-flush gases out of reactor
- Total gas flow ca. 27 l/min
  - 9 l/min CO2, 18 l/min H2
  - Flush 5 l/min N2
- Temperature range 800-850C, atmospheric pressure

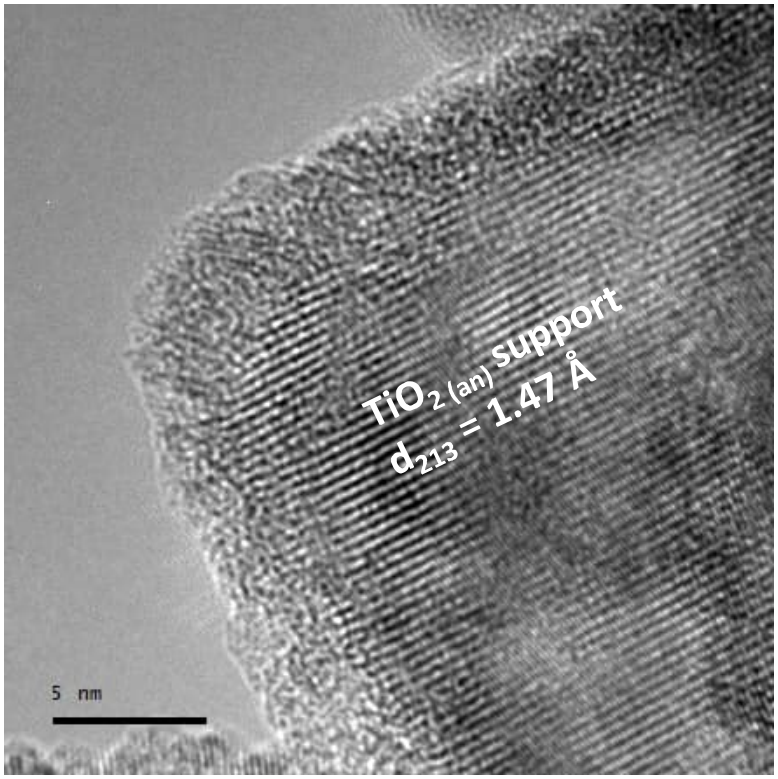
750
80.0
Spot 731* °C
FLIR

Bench scale e-reactor testing

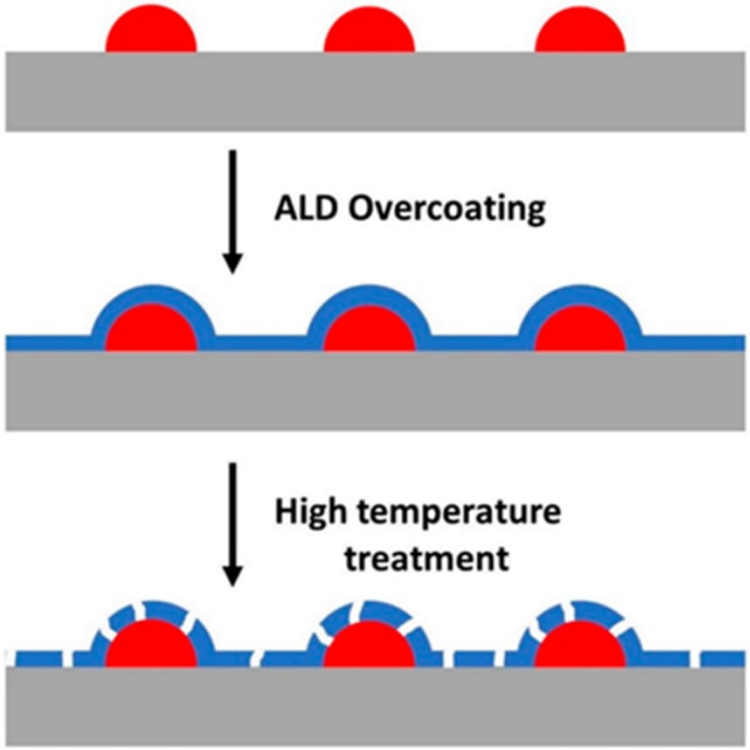
- First reaction tests carried out in MOBSU
  - 32 l/min flow rate, temperature at approximately 800-850 °C
- **CO2 conversion 61%, equilibrium 65%** at this temperature
- **No carbon deposition** on the porous reactor!
- However, the reactor is fragile and cannot handle the thermal expansion => new design
- Temperature control and measurement challenging
  - Indirect temperature measurement by gas composition (measured vs equilibrium)
- Work continued in a follow-up project



T.3.2 Overcoating deposition and reformation into a porous structure



30 deposition cycles, **no** thermal treatment

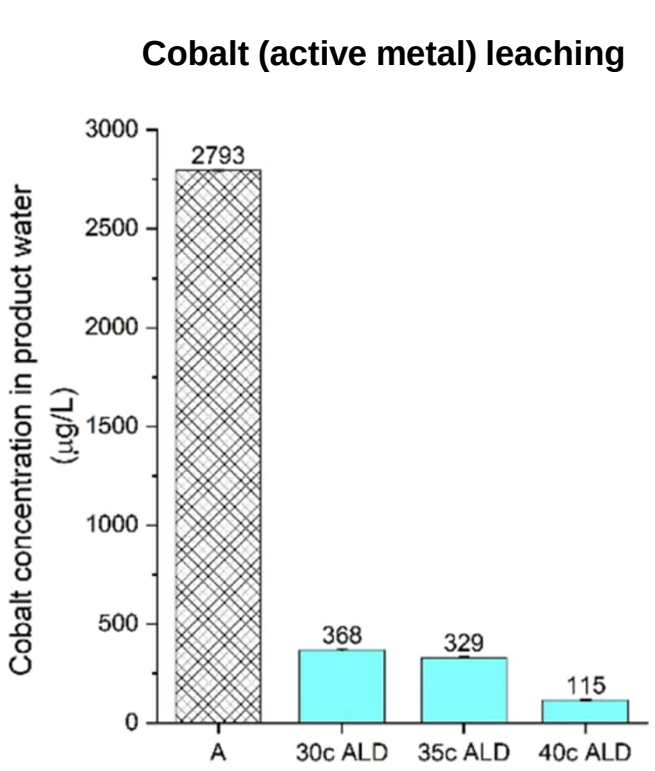


Overcoating after deposition

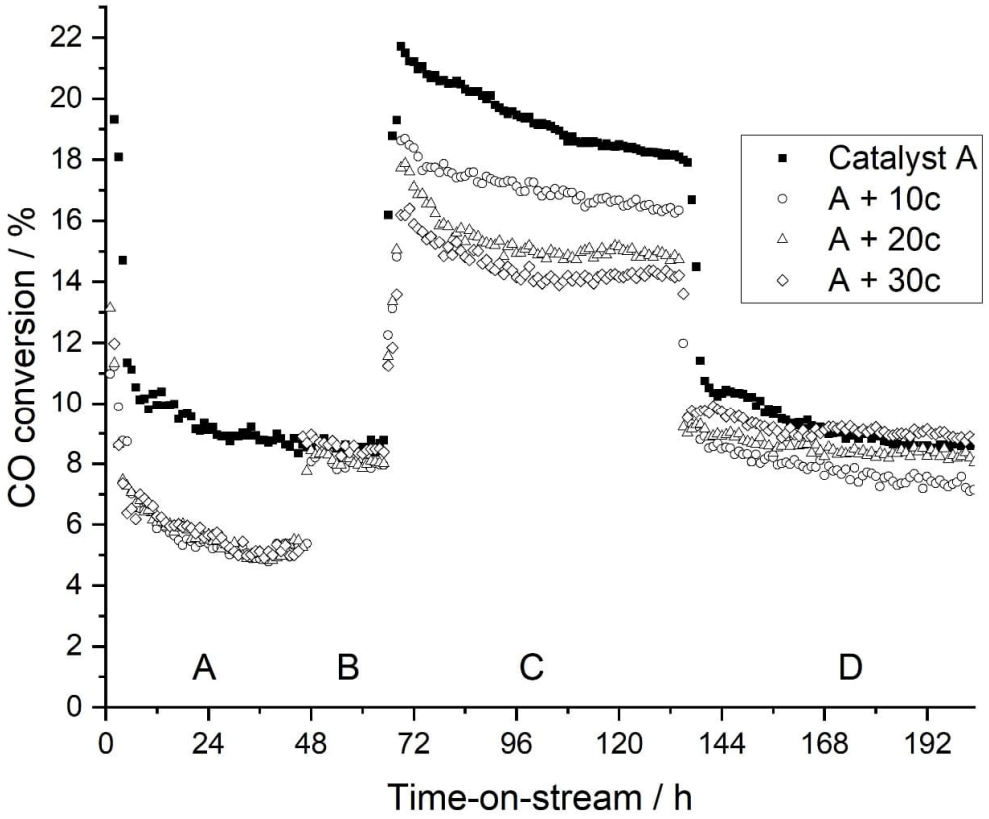
Porous overcoating

Sarnello et al., ACS Catal. 2021, 11, 2605−2619
https://dx.doi.org/10.1021/acscatal.0c05099

Catalyst reaction performance



ICP−MS analysis results from produced water samples



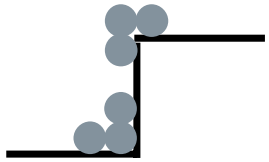
Fischer-Tropsch reaction overall activity as carbon monoxide conversion versus time-on-stream. Catalyst A non-overcoated sample and three samples with 10, 20, and 30 cycle ALD overcoating. Reaction steps A (initial activity), B (conversion adjusted to ~9%), C (added water conditions, simulated conversion level ~70%) and D (back to step B conditions, no added water to reactor inlet).

T3.2 Conclusions

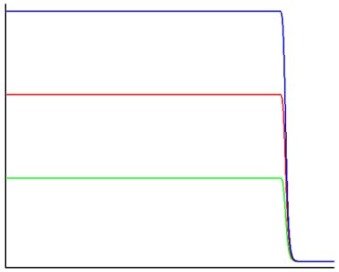
- Catalyst active sites are covered due to ALD overcoating
  - Thermal treatment is required to induce porosity into the overcoating

- The total amount of active sites decrease due to overcoating application
  - Some active sites are permanently covered
  - However, **re-opened active sites are protected against deactivation** ”anchored to the support”

- ALD overcoating (TMA/H_2O) process seems to prefer low coordination site for initial deposition cycles
  - Fischer-Tropsch activity and hydrocarbon chain growth is mainly dependent on defect sites, kinks and corners with low coordination number



- Diffusion-reaction model can be used to estimate penetration depth and to design ALD process on porous catalyst structures



VTT

beyond

the obvious