

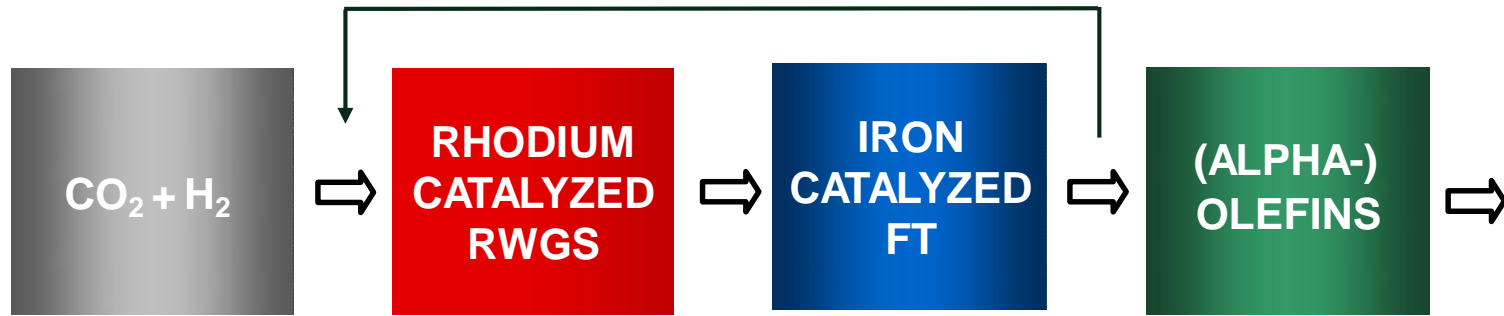


# CO<sub>2</sub> conversion to light olefins

Aki Braunschweiler

26/08/2022 VTT – beyond the obvious

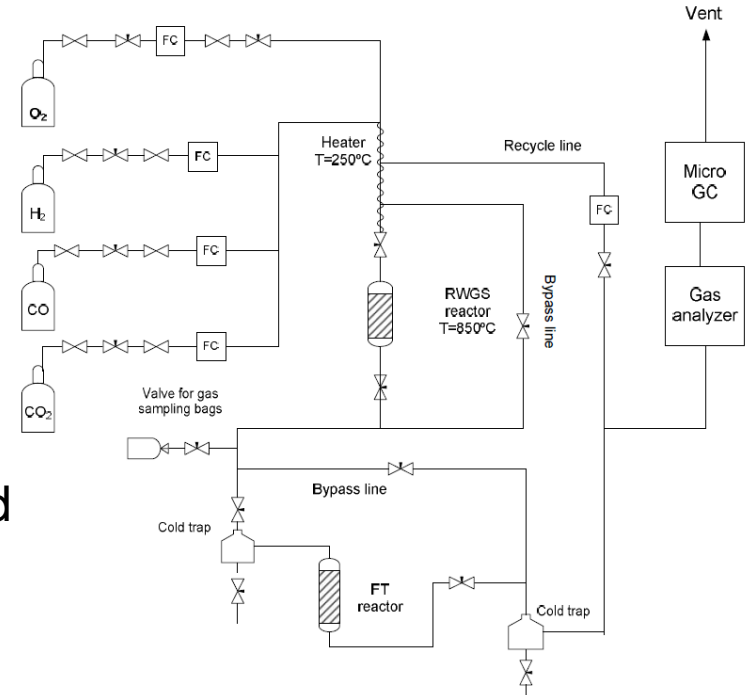
# Two step process from CO<sub>2</sub> to light olefins



- Step 1: Reverse Water Gas Shift (RWGS)  
 $\text{CO}_2 + \text{H}_2 \rightarrow \text{Synthesis gas (CO + H}_2\text{) and water}$
- Step 2: Fischer Tropsch synthesis (FT)  
 $\text{CO} + 2\text{H}_2 \rightarrow \text{Hydrocarbons}$
- FT process conditions determine the quality of the hydrocarbons
  - High temperature and low pressure to yield lighter products

# Experimental setup & Research plan

- RWGS and FT reactors in series
  - Rh/Al<sub>2</sub>O<sub>3</sub> washcoated catalyst in RWGS
  - Packed-bed FT reactor in fluidized sand bath
- Objective of the research to test different process conditions and FT catalysts to find the optimal conditions for light olefin production from CO<sub>2</sub>



# FTO catalysts prepared and tested

1. Fe-Mn-Cu/SiO<sub>2</sub>
  2. Fe-Pb/SiO<sub>2</sub>
  3. Fe-Na-S/AC
  4. Co-Ru/TiO<sub>2</sub>
  5. Fe-Na-S/Al<sub>2</sub>O<sub>3</sub>
  6. Fe-Mn/Al<sub>2</sub>O<sub>3</sub>
- Desired properties
    - High selectivity to lower olefins
    - Low selectivity to methane
    - High CO conversion
    - Stability



# Experiments with the catalysts

- Experiments with different process conditions and with gas recycling
  - $H_2/CO_2$  feed ratio
  - volumetric flow rate (Q)
  - FT reaction temperature
  - amount of recycled gas
- Cobalt-based catalyst in temperatures of 210-240°C

## Without gas recycling

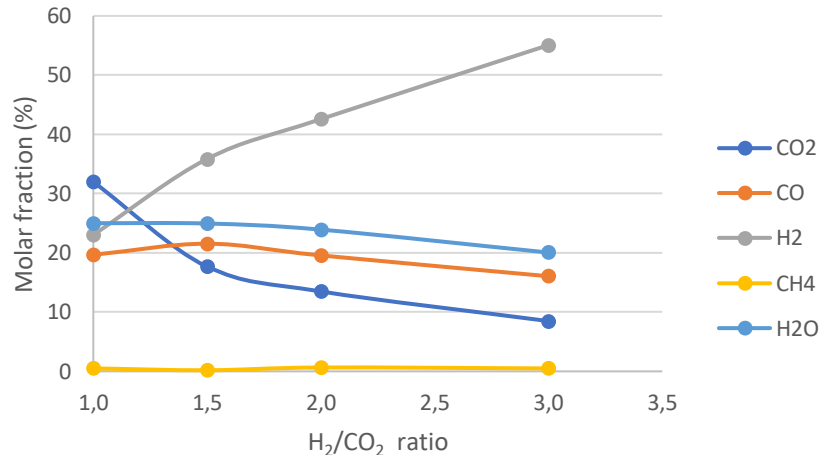
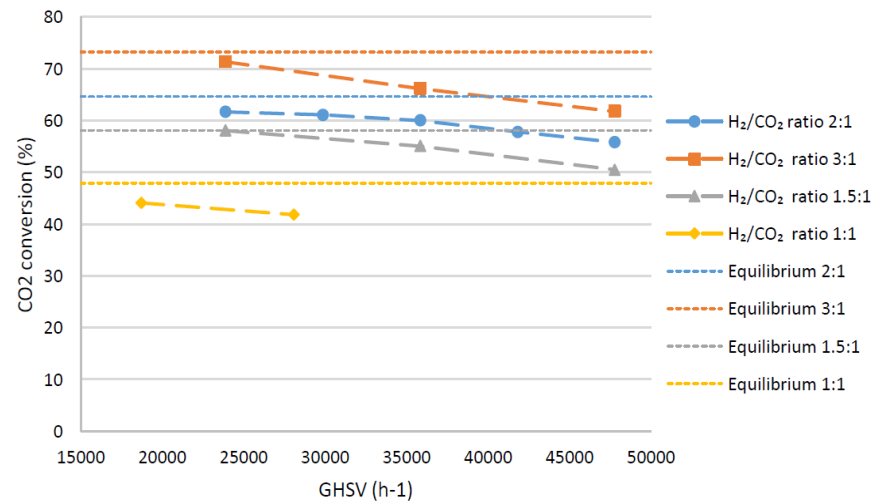
RWGS			FT
Temperature (°C)	H <sub>2</sub> /CO <sub>2</sub> feed ratio	Q (l/min)	Temperature (°C)
850	2,0	0,75-1,25	<b>320-350</b>
850	1,0	0,5-1,25	<b>320-350</b>

## With gas recycling

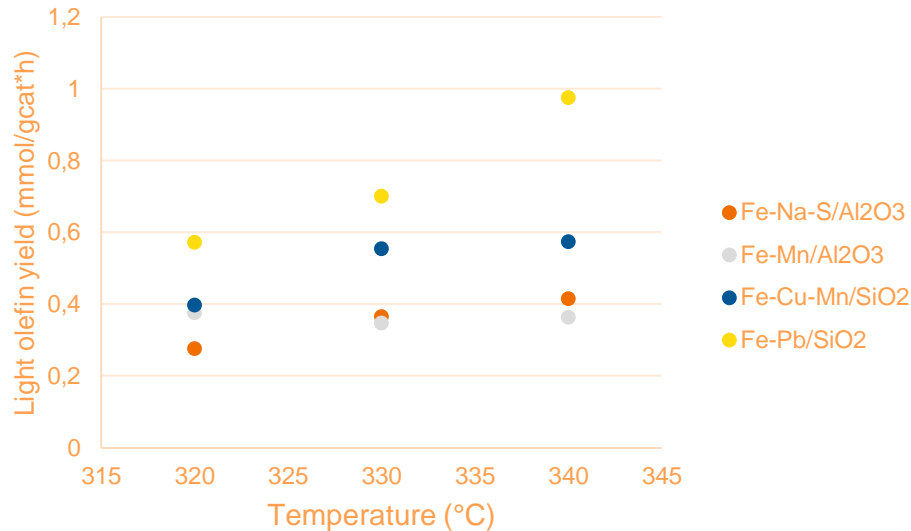
RWGS			FT	
Temperature (°C)	H <sub>2</sub> /CO <sub>2</sub> feed ratio	Q (l/min)	Temperature (°C)	Gas recycling Q (l/min)
850	2,0	0,5-1,25	340	<b>0,15-0,45</b>
850	1,0	0,5-1,25	340	<b>0,15-0,45</b>

# RWGS results

- Conversions close to equilibrium
- Good quality syngas
- Methane selectivity 2-10 %
  - Dependent on  $H_2/CO_2$  ratio
- No catalyst deactivation
- No carbon deposition



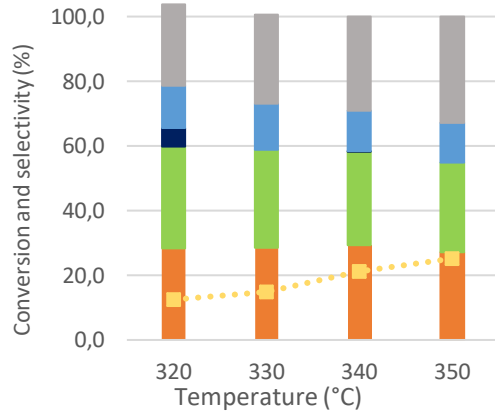
# Comparison between different iron catalysts



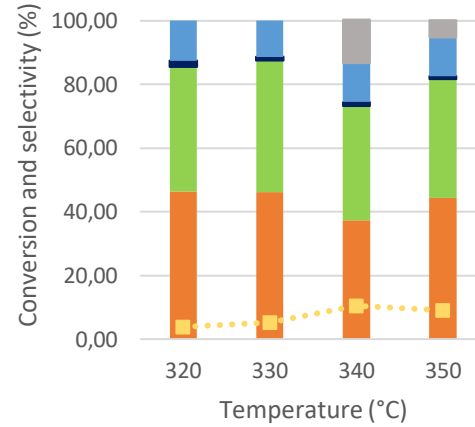
- GHSV 2200 h<sup>-1</sup>
- H<sub>2</sub>/CO ratio 2
- No gas recycling

# Effect of GHSV and H<sub>2</sub>/CO<sub>2</sub> ratio, Fe-Pb/SiO<sub>2</sub> catalyst

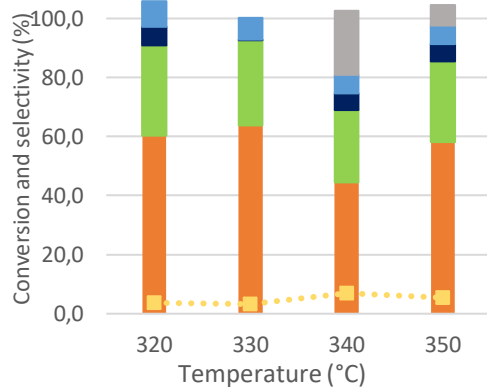
A



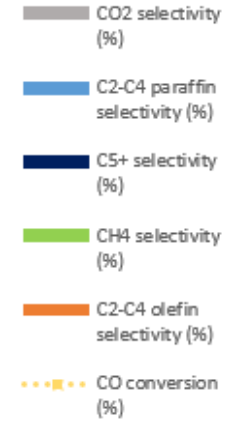
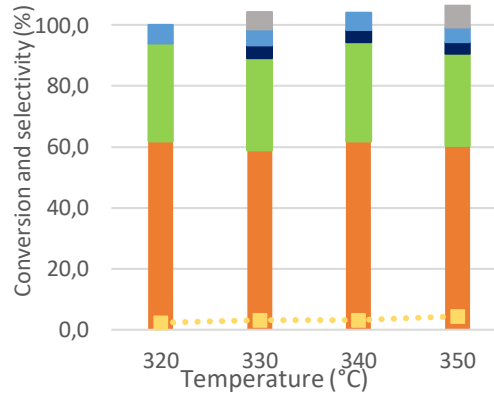
B



C



D

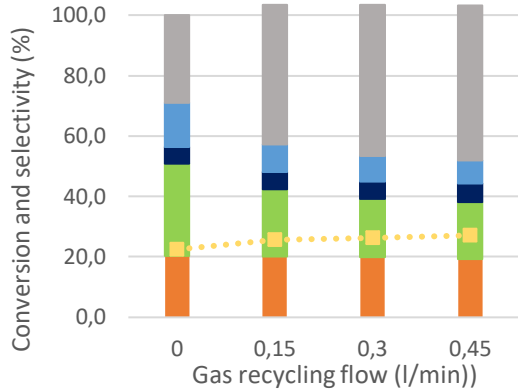


- A. 2:1 GHSV of 1830 h<sup>-1</sup>
- B. 2:1 GHSV of 2460 h<sup>-1</sup>
- C. 1:1 GHSV of 1830 h<sup>-1</sup>
- D. 1:1 GHSV of 2440 h<sup>-1</sup>

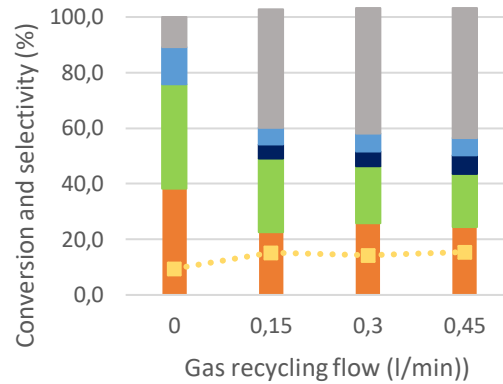


# Effect of gas recycling, Fe-Pb/SiO<sub>2</sub> catalyst

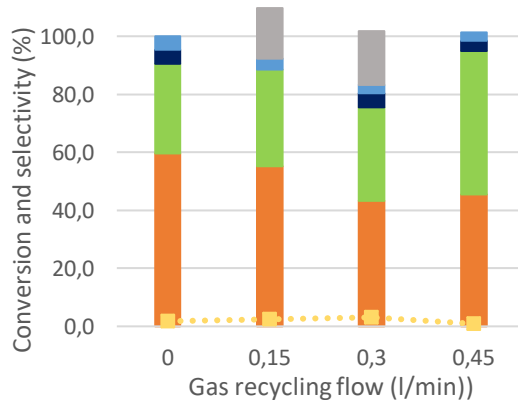
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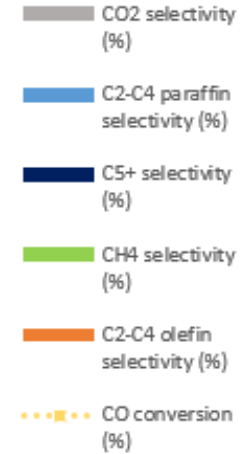
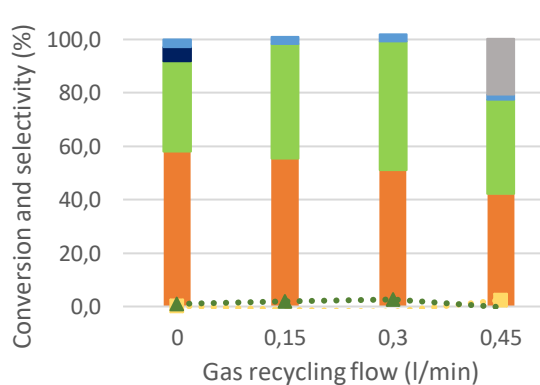
B



C

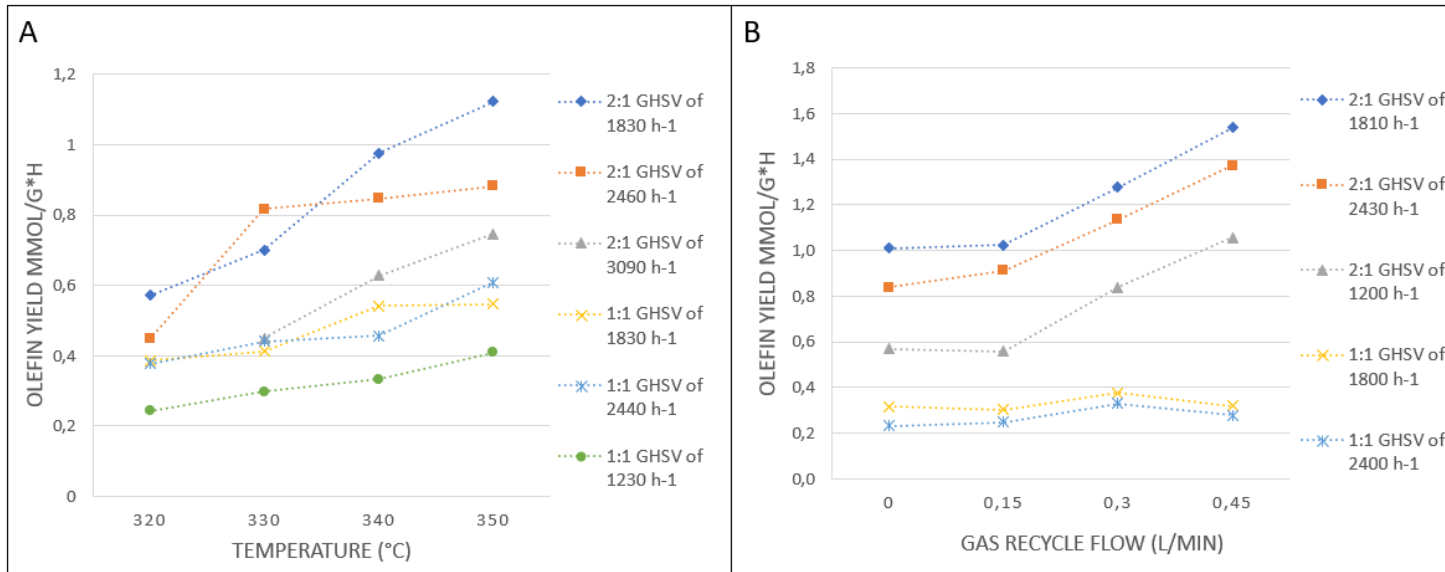


D



- A. 2:1 GHSV of 1810 h<sup>-1</sup>
- B. 2:1 GHSV of 2430 h<sup>-1</sup>
- C. 1:1 GHSV of 1800 h<sup>-1</sup>
- D. 1:1 GHSV of 2400 h<sup>-1</sup>

# Light olefin yields at different process conditions, Fe-Pb/SiO<sub>2</sub> catalyst



# Conclusion

## Project objectives were successfully achieved

- Integration of RWGS and FT reactors with working gas recycling system to produce light olefins from CO<sub>2</sub>
- Fischer-Tropsch to olefins production developed by thorough catalyst testing
  - A lot of results – over 250 different set points tested
  - Six different catalysts, Fe-Pb/SiO<sub>2</sub> had the highest light olefin yield
  - Targeted light olefin selectivity of >45% achieved
- Good catalyst found but reactor design needs to be improved to diminish mass and heat transfer limitations when moving to larger scale.
- To take things further, the CO<sub>2</sub> to olefins process should be tested in a larger scale, downstream of electrolyzer and CO<sub>2</sub> capture

# bey<sup>0</sup>nd

## the obvious

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