GAFT
Gasification and FT-Synthesis
of Lignocellulosic Feedstocks

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FT-Catalysts for Aviation Fuel from Biomass

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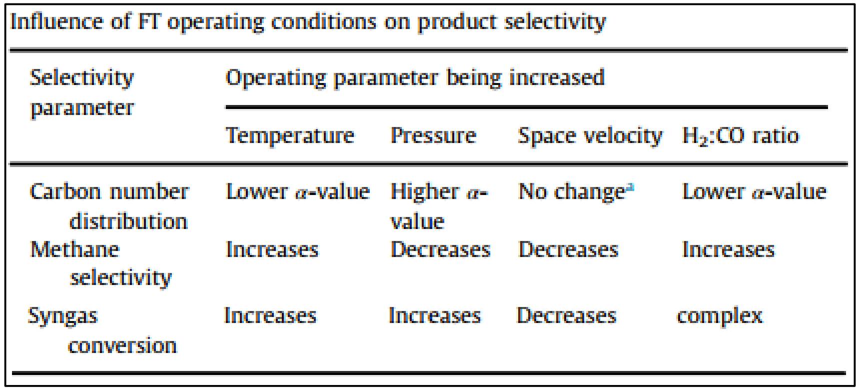
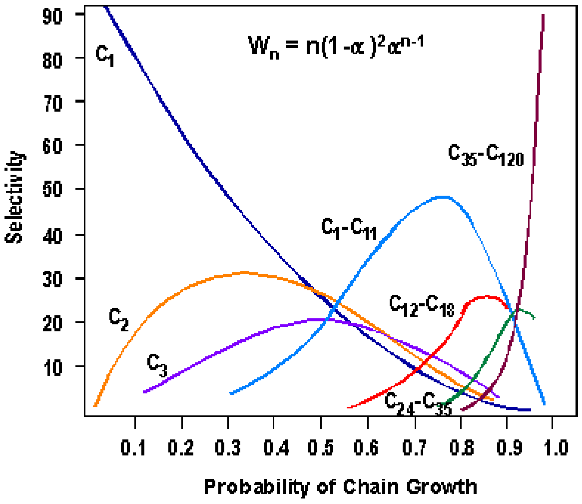
Fischer-Tropsch Synthesis

- Polymerisation reaction
  - Product distribution determined by chain growth probability, α
  - α depends of catalyst and reaction conditions

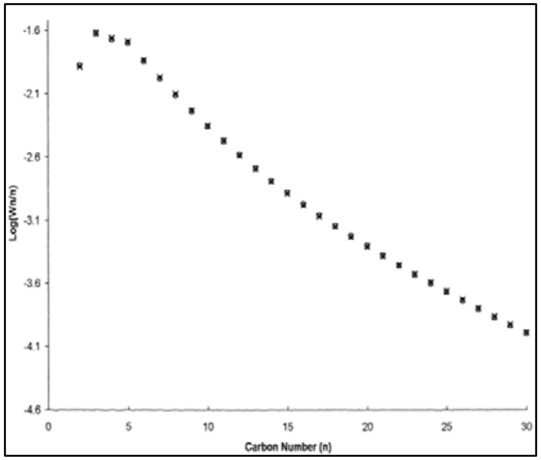


Influence of FT operating conditions on product selectivity

Selectivity parameter	Operating parameter being increased			
	Temperature	Pressure	Space velocity	H_2:CO ratio
Carbon number distribution	Lower α-value	Higher α-value	No change[a]	Lower α-value
Methane selectivity	Increases	Decreases	Decreases	Increases
Syngas conversion	Increases	Increases	Decreases	complex



- In practice, deviation from "ideal" weight distribution as α changes with carbon number
  - Related to secondary reactions of olefins (chain length dependant)
  - α deviations depends on catalyst and reaction conditions



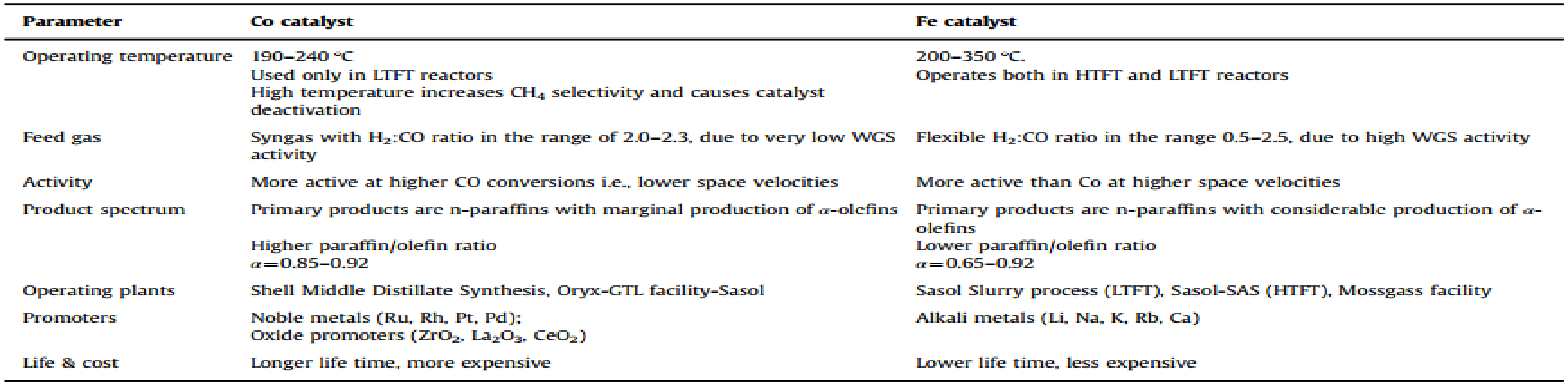
Fischer-Tropsch Catalysts

- Co- or Fe-based catalyst
- Supported (i.e. Al_2O_3, TiO_2, SiO_2) or unsupported
- Promoters affecting activity, selectivity and stability

Common promoters

- Co-catalysts
  - Re, Mn
- Fe-catalyst
  - Cu, K, Zn

Increased catalyst activity and supressed methane formation



Parameter	Co catalyst	Fe catalyst
Operating temperature	190–240 °C Used only in LTFT reactors High temperature increases CH_4 selectivity and causes catalyst deactivation	200–350 °C. Operates both in HTFT and LTFT reactors
Feed gas	Syngas with H_2:CO ratio in the range of 2.0–2.3, due to very low WGS activity	Flexible H_2:CO ratio in the range 0.5–2.5, due to high WGS activity
Activity	More active at higher CO conversions i.e., lower space velocities	More active than Co at higher space velocities
Product spectrum	Primary products are n-paraffins with marginal production of α-olefins Higher paraffin/olefin ratio α=0.85–0.92	Primary products are n-paraffins with considerable production of α-olefins Lower paraffin/olefin ratio α=0.65–0.92
Operating plants	Shell Middle Distillate Synthesis, Oryx-GTL facility-Sasol	Sasol Slurry process (LTFT), Sasol-SAS (HTFT), Mossgass facility
Promoters	Noble metals (Ru, Rh, Pt, Pd); Oxide promoters (ZrO_2, La_2O_3, CeO_2)	Alkali metals (Li, Na, K, Rb, Ca)
Life & cost	Longer life time, more expensive	Lower life time, less expensive

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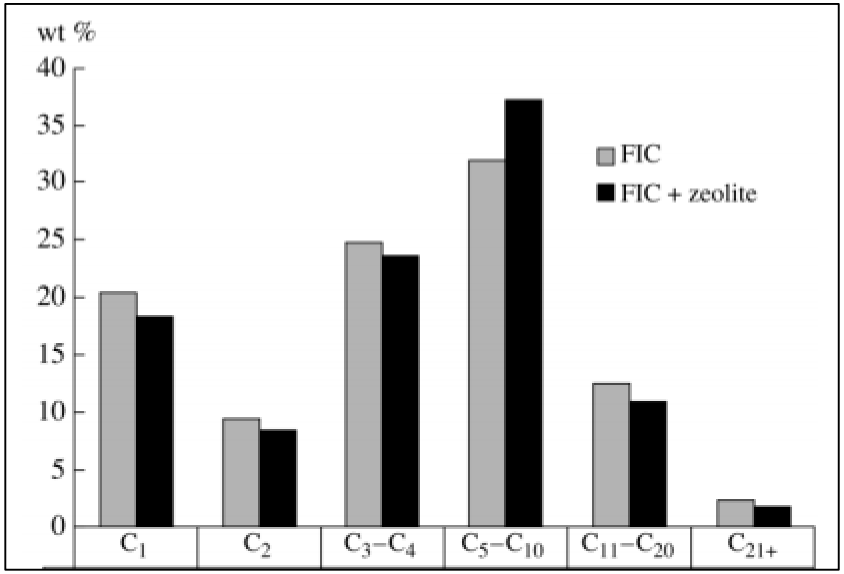
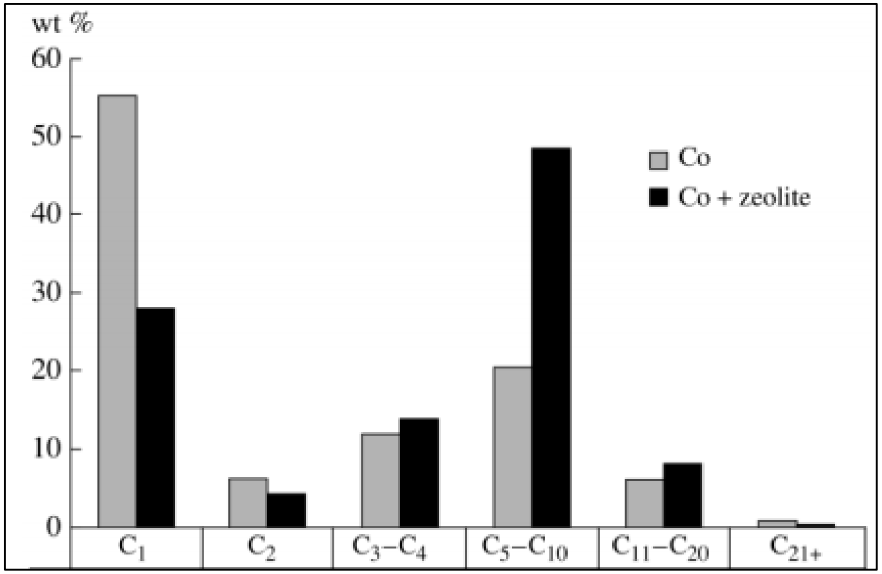
In situ hydrocracking

- Upgrading of FT-wax commonly performed *ex situ* by hydrocracking
- Extensive studies in literature on *in situ* hydrocracking. Combinations of Co- and Fe-catalyst with zeolites as mixed or bi-functual catalysts are investigated

\+ Selectivity control possible

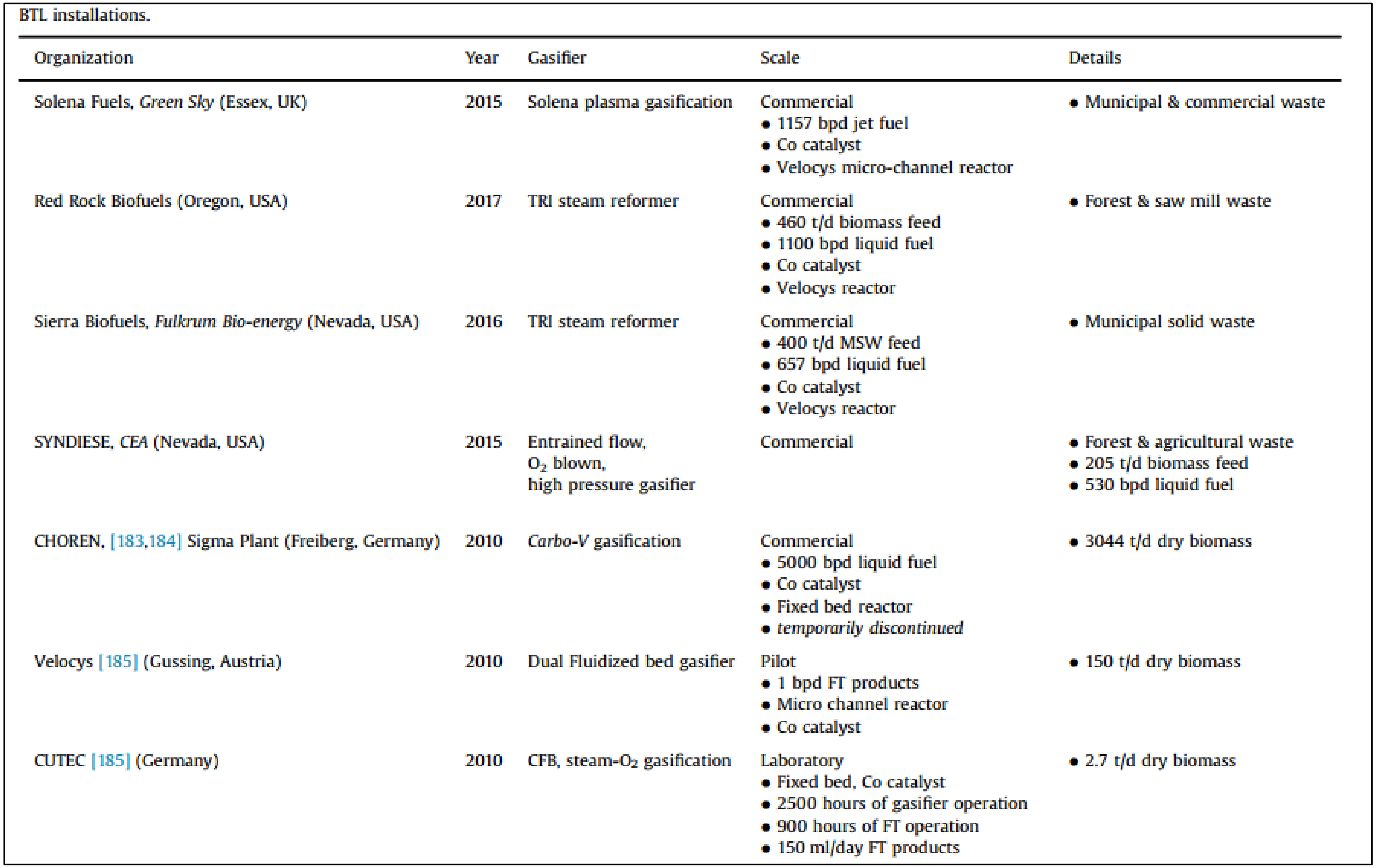
– Zeolites deactivates much faster than FTS-catalyst





Pet. Chem., vol. 46, no. 2, pp. 103–109, Mar. 2006

Current BTL installations



BTL installations.

Organization	Year	Gasifier	Scale	Details
Solena Fuels, *Green Sky* (Essex, UK)	2015	Solena plasma gasification	Commercial • 1157 bpd jet fuel • Co catalyst • Velocys micro-channel reactor	• Municipal & commercial waste
Red Rock Biofuels (Oregon, USA)	2017	TRI steam reformer	Commercial • 460 t/d biomass feed • 1100 bpd liquid fuel • Co catalyst • Velocys reactor	• Forest & saw mill waste
Sierra Biofuels, *Fulkrum Bio-energy* (Nevada, USA)	2016	TRI steam reformer	Commercial • 400 t/d MSW feed • 657 bpd liquid fuel • Co catalyst • Velocys reactor	• Municipal solid waste
SYNDIESE, *CEA* (Nevada, USA)	2015	Entrained flow, O_2 blown, high pressure gasifier	Commercial	• Forest & agricultural waste • 205 t/d biomass feed • 530 bpd liquid fuel
CHOREN, [183,184] Sigma Plant (Freiberg, Germany)	2010	*Carbo-V* gasification	Commercial • 5000 bpd liquid fuel • Co catalyst • Fixed bed reactor • *temporarily discontinued*	• 3044 t/d dry biomass
Velocys [185] (Gussing, Austria)	2010	Dual Fluidized bed gasifier	Pilot • 1 bpd FT products • Micro channel reactor • Co catalyst	• 150 t/d dry biomass
CUTEC [185] (Germany)	2010	CFB, steam-O_2 gasification	Laboratory • Fixed bed, Co catalyst • 2500 hours of gasifier operation • 900 hours of FT operation • 150 ml/day FT products	• 2.7 t/d dry biomass

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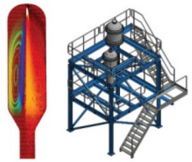
GAFT: SP3 Fischer-Tropsch Synthesis



The major objective of SP3 is to demonstrate an iron based medium to high temperature FT technology for the production of liquid biofuels

Background

- EF of biomass yields synthetic gas with $H_2:CO \leq 1$
- For FTS ideally $H_2:CO \approx 2$, achieved by WGS step after EF ($CO + H_2O \leftrightarrow CO_2 + H_2$)
  - For $H_2:CO = 2$, Cobalt based catalysts normally preferred, maximising wax yield before cracking into diesel fraction
  - Co based FT catalysts, low tolerance for impurities (catalyst poisons) in synthetic gas
- $H_2:CO$ adjustment avoided by use of Fe-based catalysts (intrinsic WGS activity)
  - Eliminate a process step
  - Fe based FT catalysts, higher tolerance for impurities in feed gas
- Fe-based FTS, typical > 300 °C, yielding light hydrocarbons and chemicals

GAFT: Fe based medium to high temperature FTS (240 – 270 °C)

- **Aims to tune product into diesel range**
- **Simplified product upgrading (eliminate cracking step?)**
- **Promoted Co-based catalyst included in screening phase (after discussions with JM)**

GAFT SP3 Fischer-Tropsch Synthesis

Experimental

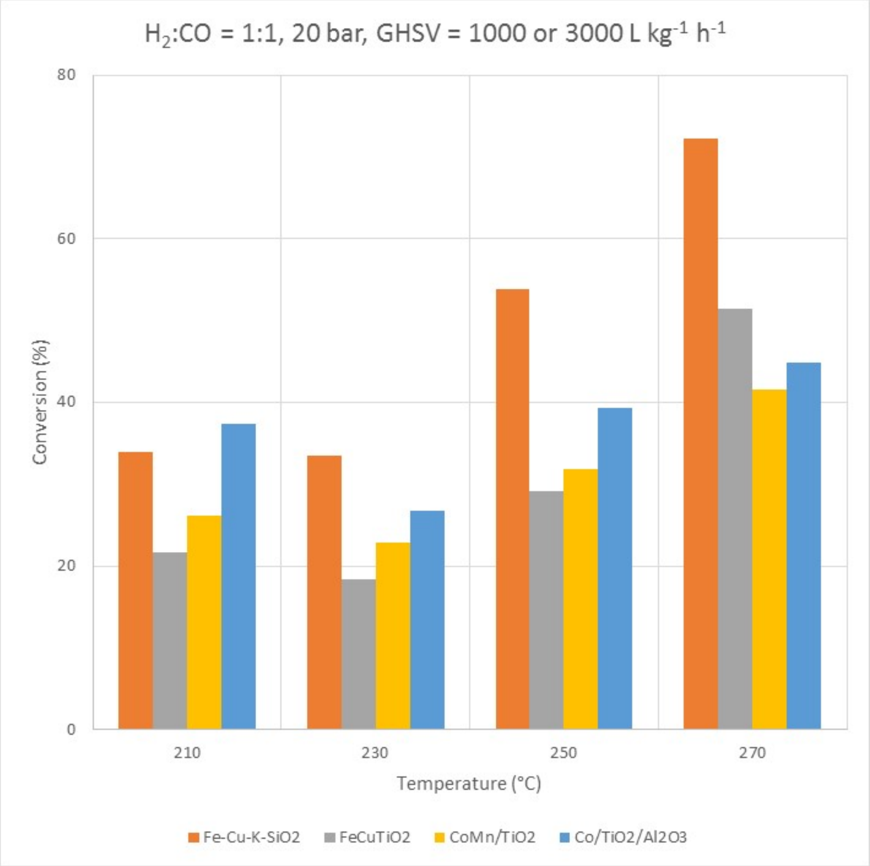
- 4 parallel Fixed-bed reactors, ½" o.d, ca. 30 cm long
- Currently, on-line GC for light gases. GC for wax analyses are in progress.

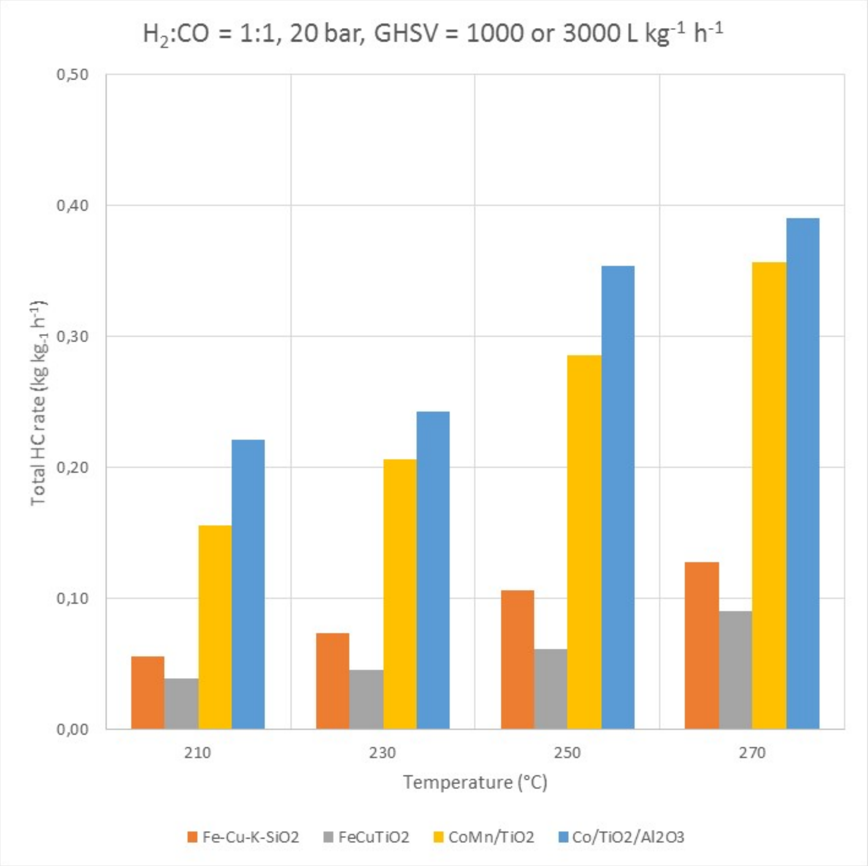
- **Preliminary results from 4 catalysts**
  - Fe-Cu/TiO_2
  - Fe-Cu-K/SiO_2
  - Co/TiO_2/Al_2O_3
  - CoMn/TiO_2

Diluted with SiC

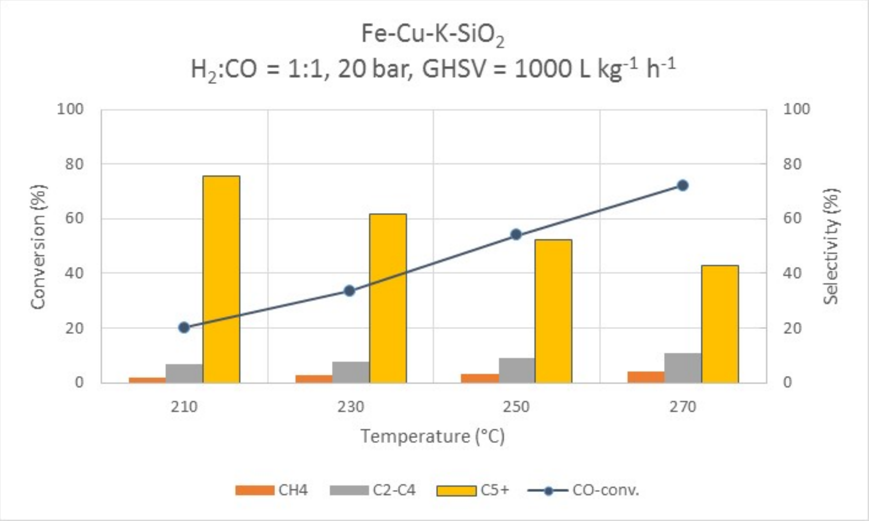
  - H_2:CO = 1.0, H_2:(CO+CO_2) = 1.7 (with 0 and 5 % CO_2) and H_2:CO = 2.1
  - 20 bar, 210-270 °C

Effect of Temperature on CO-conv. and Total Hydrocarbon-rate, H_2:CO=1

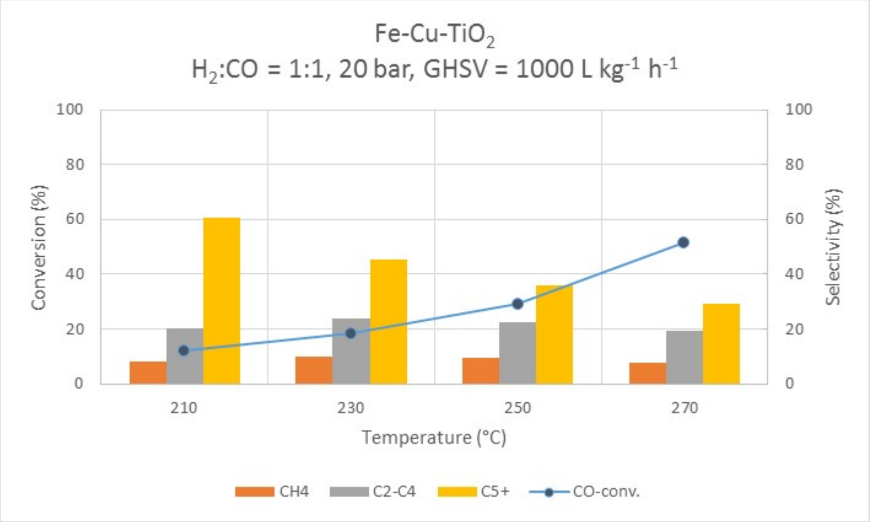




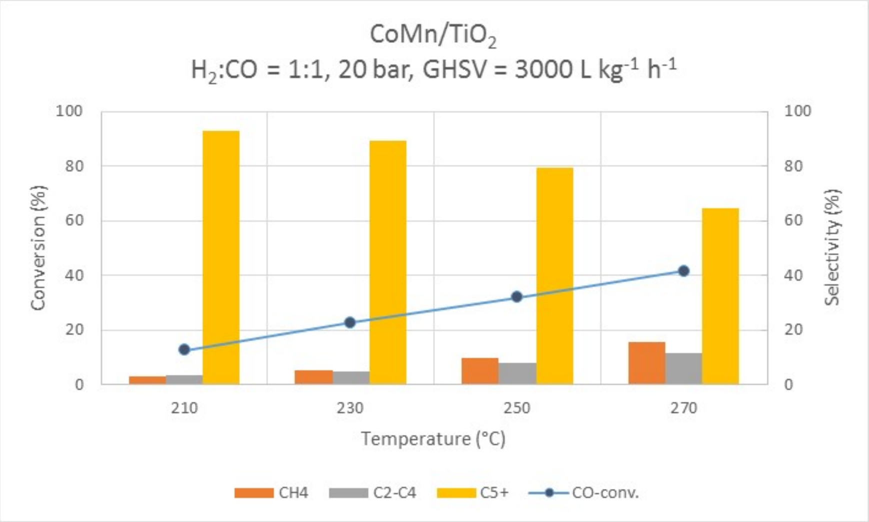
Effect of Temperature on CO-conv. and selectivity, H_2:CO=1


Fe-Cu-K-SiO_2

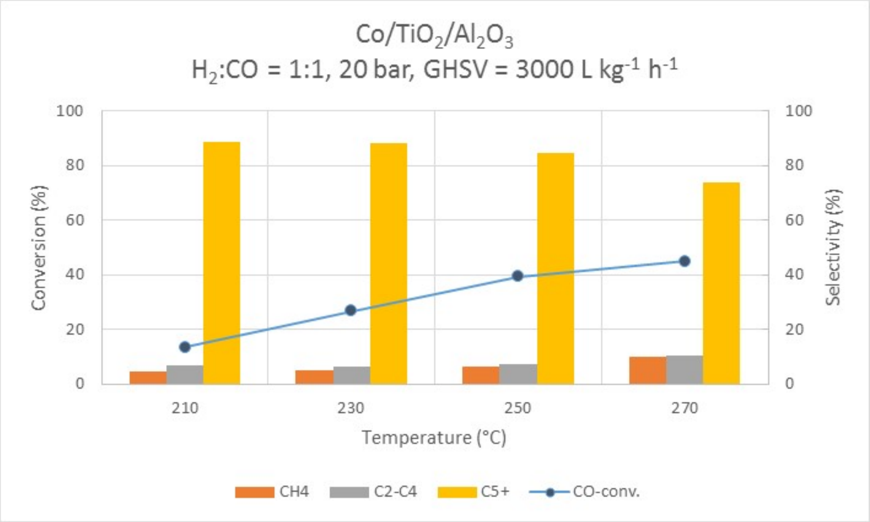
H_2:CO = 1:1, 20 bar, GHSV = 1000 L kg^{-1} h^{-1}


Fe-Cu-TiO_2

H_2:CO = 1:1, 20 bar, GHSV = 1000 L kg^{-1} h^{-1}

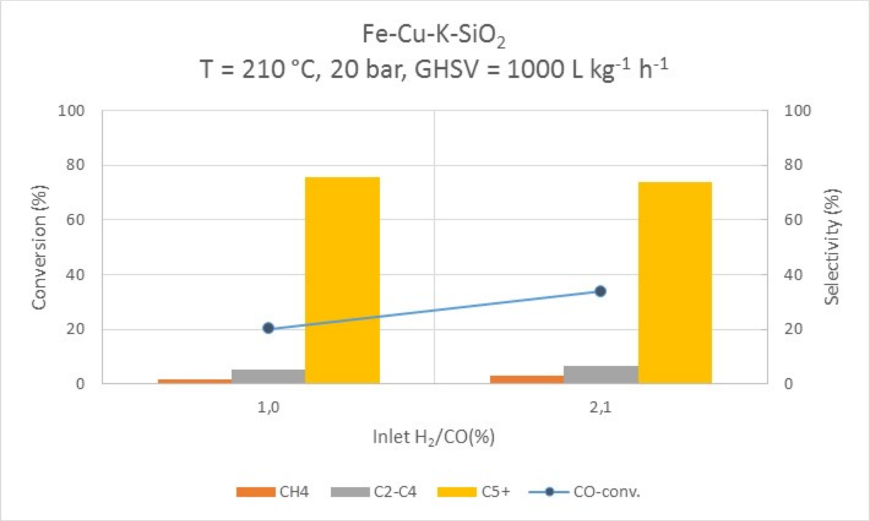

CoMn/TiO_2

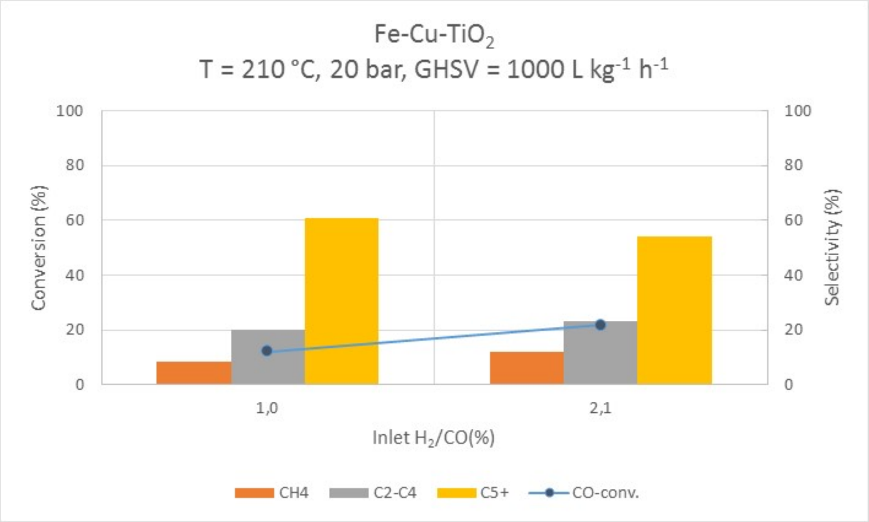
H_2:CO = 1:1, 20 bar, GHSV = 3000 L kg^{-1} h^{-1}

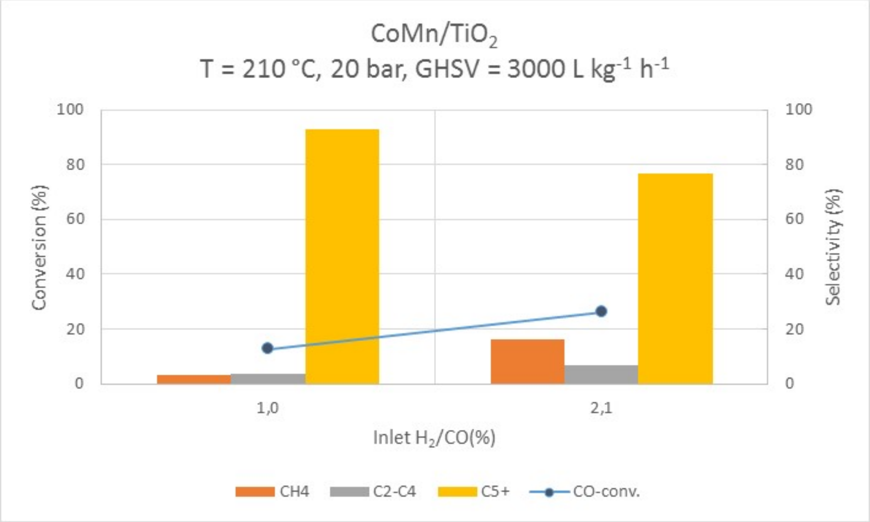

Co/TiO_2/Al_2O_3

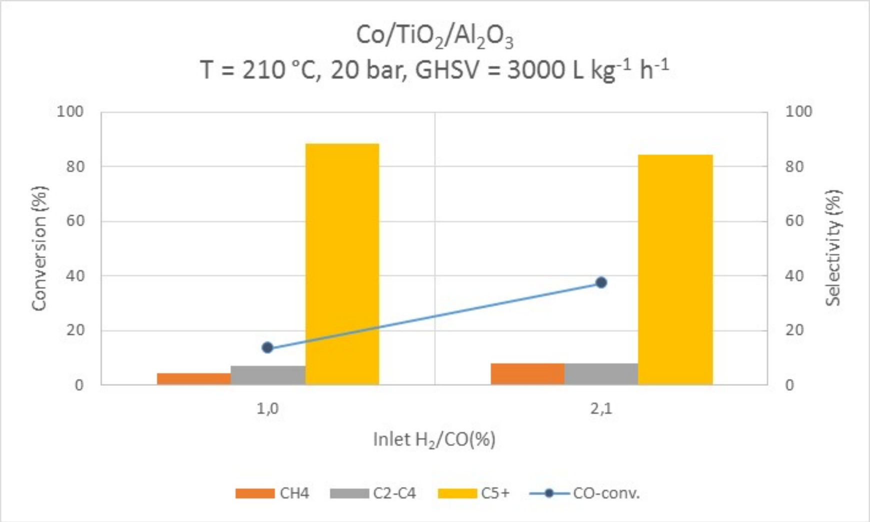
H_2:CO = 1:1, 20 bar, GHSV = 3000 L kg^{-1} h^{-1}

Effect of inlet H_2/CO on CO-conv. and selectivity, 210 °C

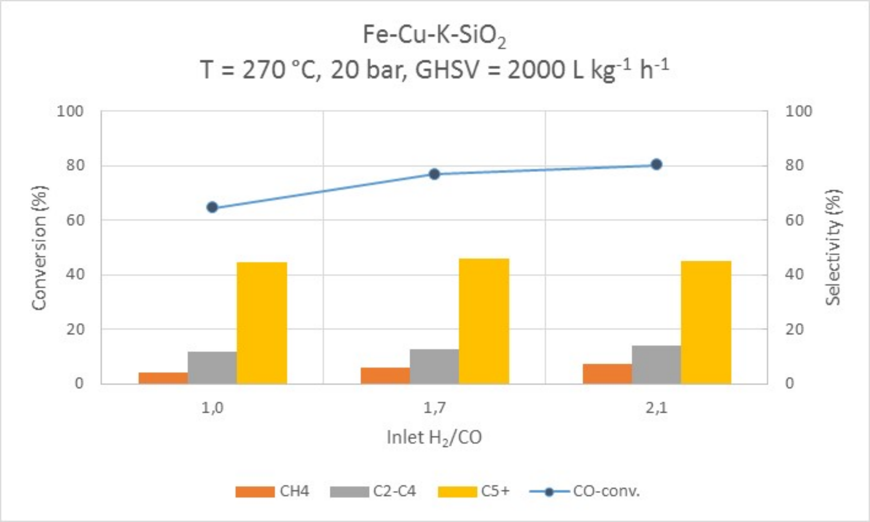


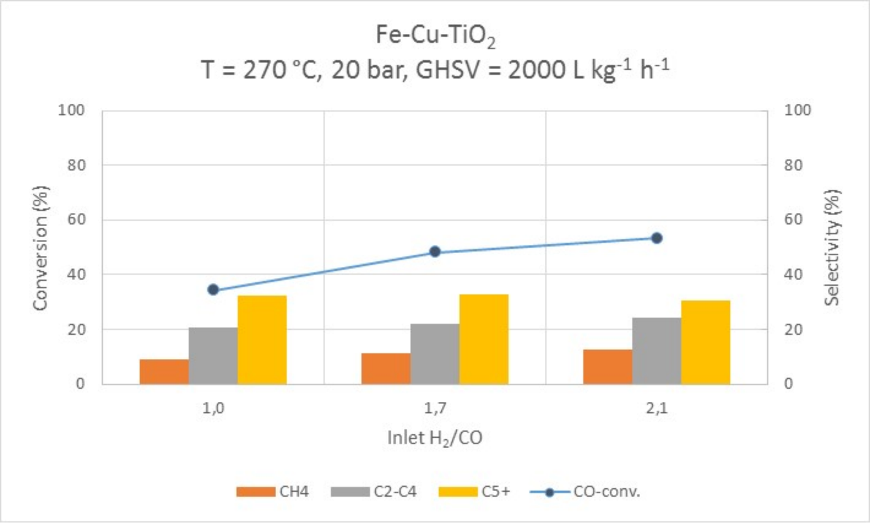


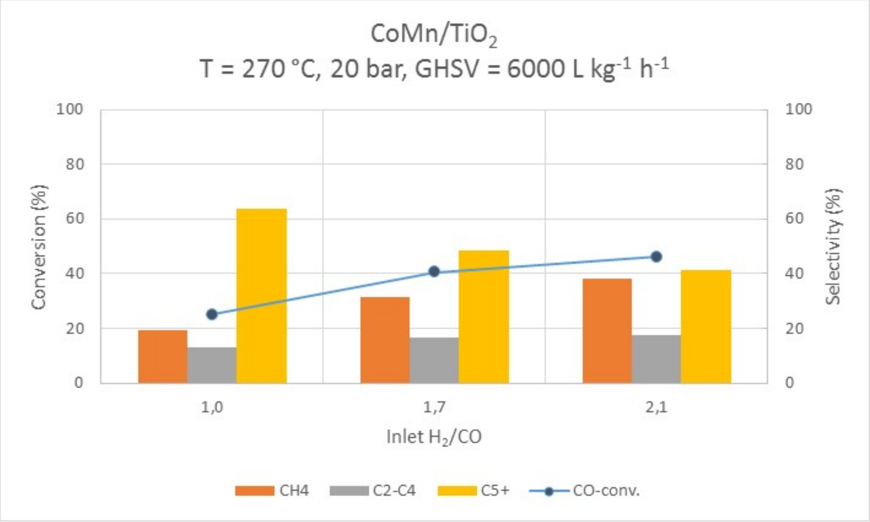


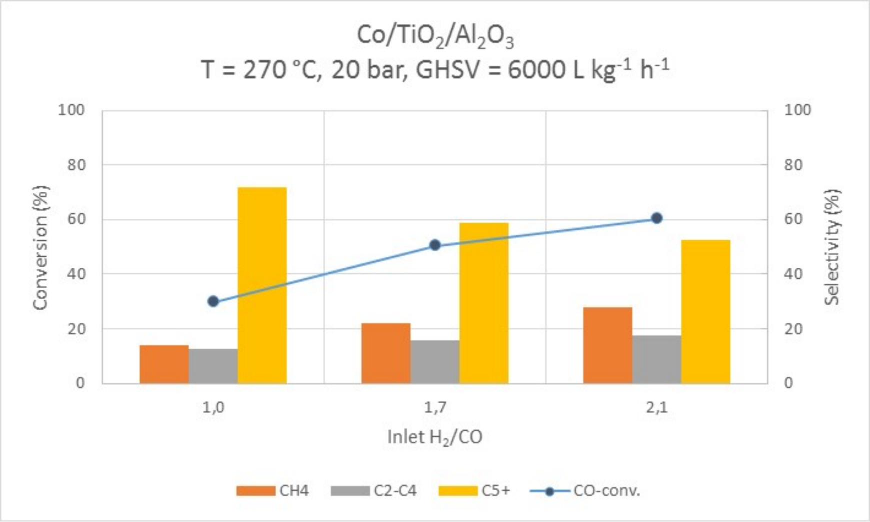


Effect of inlet H_2/CO on CO-conv. and selectivity, 270 °C

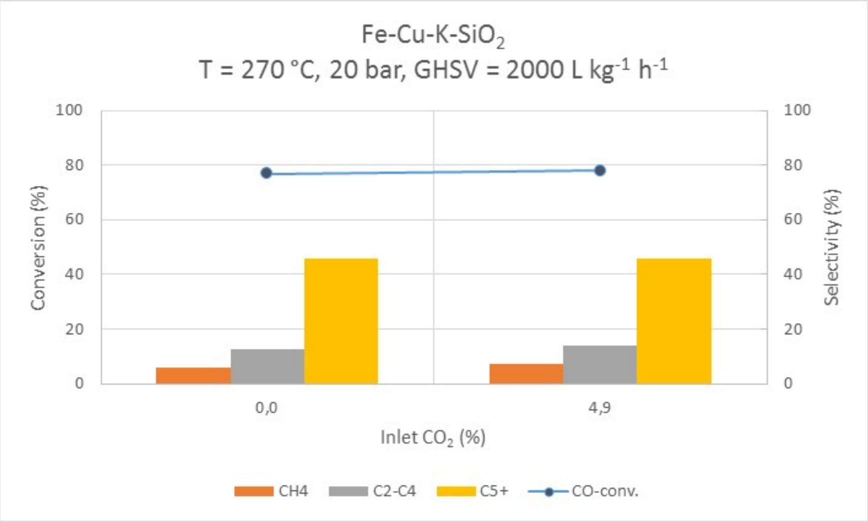

Fe-Cu-K-SiO_2
T = 270 °C, 20 bar, GHSV = 2000 L kg^{-1} h^{-1}


Fe-Cu-TiO_2
T = 270 °C, 20 bar, GHSV = 2000 L kg^{-1} h^{-1}

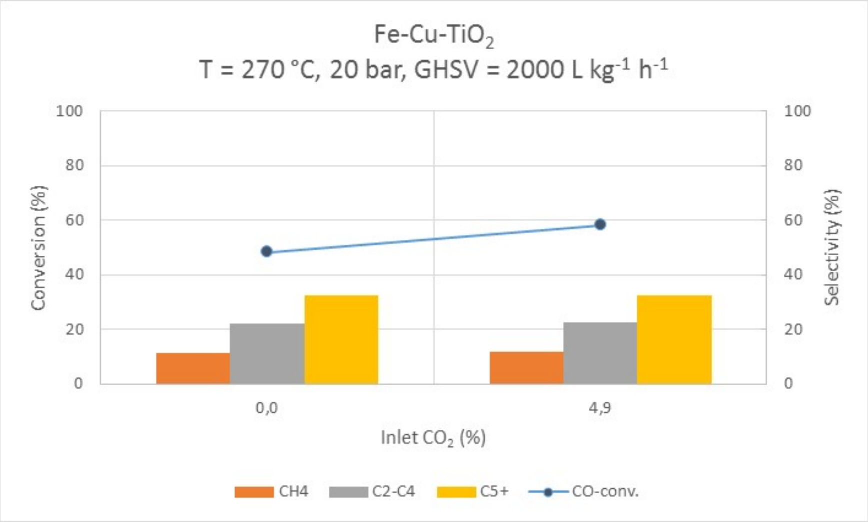

CoMn/TiO_2
T = 270 °C, 20 bar, GHSV = 6000 L kg^{-1} h^{-1}


Co/TiO_2/Al_2O_3
T = 270 °C, 20 bar, GHSV = 6000 L kg^{-1} h^{-1}

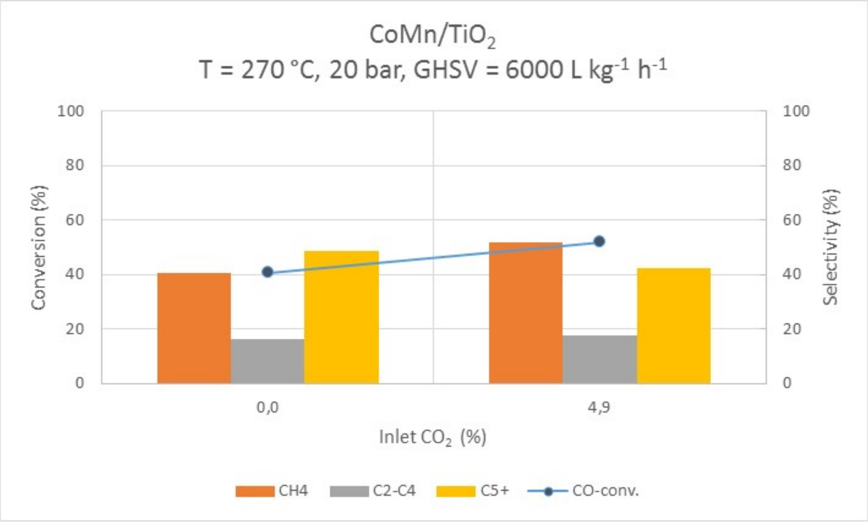
Effect of inlet 5% CO_2 on CO-conv. and selectivity, 270 °C


Fe-Cu-K-SiO_2

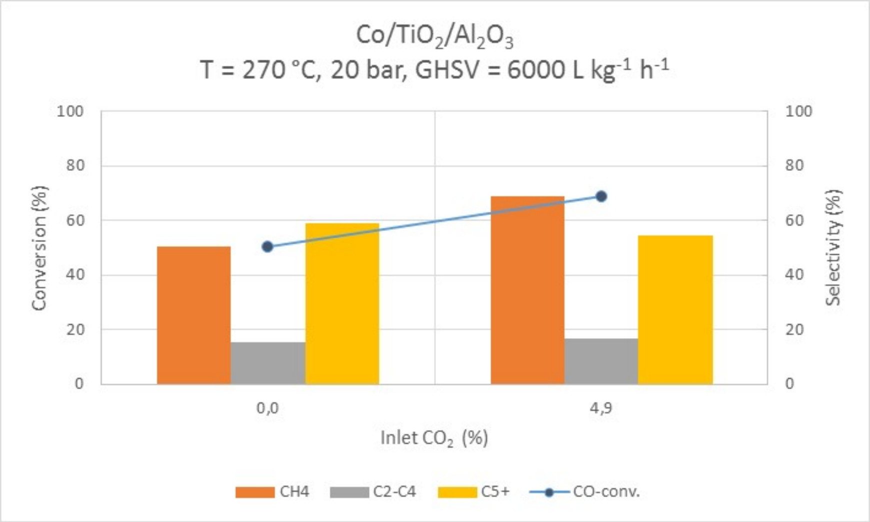
T = 270 °C, 20 bar, GHSV = 2000 L kg^{-1} h^{-1}


Fe-Cu-TiO_2

T = 270 °C, 20 bar, GHSV = 2000 L kg^{-1} h^{-1}


CoMn/TiO_2

T = 270 °C, 20 bar, GHSV = 6000 L kg^{-1} h^{-1}


Co/TiO_2/Al_2O_3

T = 270 °C, 20 bar, GHSV = 6000 L kg^{-1} h^{-1}

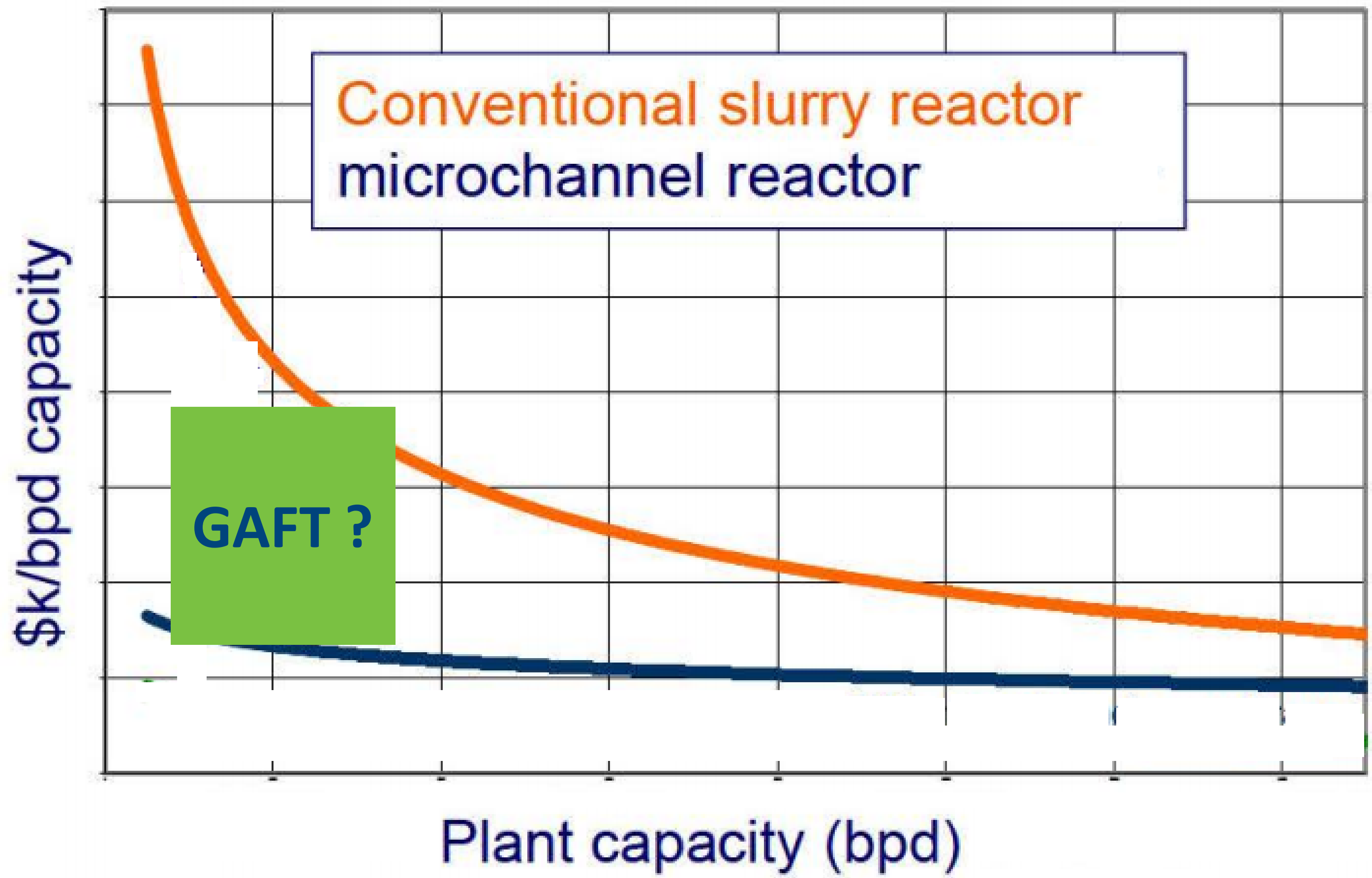
Summary and further work

- ☐ From the Fe catalysts, Fe-Cu-K-SiO_2 most promising
- ☐ Both Co-catalysts interesting performance and apparently better selectivity picture than the Fe catalysts.

- ➢ Considering to include some supported Fe-catalysts
- ➢ Modified versions of the Co-catalysts are upcoming
- ➢ Tests with higher (up to 20%) CO_2-content and low H_2:CO to be performed on selected Fe and Co catalysts
- ➢ Analyses of wax fractions is prerequisite to conclude upon catalyst choice
- ➢ Further process conditions to be included on selected catalyst(s)

THANK YOU!

Estimated microchannel benefits at low plant capacity



Microstructured reactors in GAFT

- Catalyst screening and effect of process conditions will be performed in fixed-bed reactors (due to capacity and ease of operation)
- Microstructured reactor successfully tested in lab with Co-based catalysts
- Microstructured reactor might be tested with 1-2 catalysts towards end of WP 3.1.
- Data from WP 3.2 could give input to microstructured reactor performance