



Process Technology for Tunable Fischer Tropsch Synthesis Towards Middle Distillate Fuel Fractions

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14. ABSTRACT Develop Fischer Tropsch technologies that target the production of TP SBF through process, catalyst, and reactor improvements. Investigate Supercritical Fischer Tropsch Synthesis (SC-FTS) process performance as related to key reaction conditions. Develop Fe catalysts that operate over a wider range of process conditions in Supercritical Fischer Tropsch Synthesis (SC-FTS). Intergrate Iron-based SC-FTS into multiple bed reactor system that incorporates oligomerization and cracking/isomerization to improve desire product selectivity and quality.					
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Objectives

- Develop Fischer Tropsch technologies that target the production of FT SBF through process, catalyst, and reactor improvements.
- Investigate Supercritical Fischer Tropsch Synthesis (SC-FTS) process performance as related to key reaction conditions.
- Develop Fe catalysts that operate over a wider range of process conditions in Supercritical Fischer Tropsch Synthesis (SC-FTS)
- Integrate Iron-based SC-FTS into multiple bed reactor system that incorporates oligomerization and cracking/isomerization to improve desired product selectivity and quality



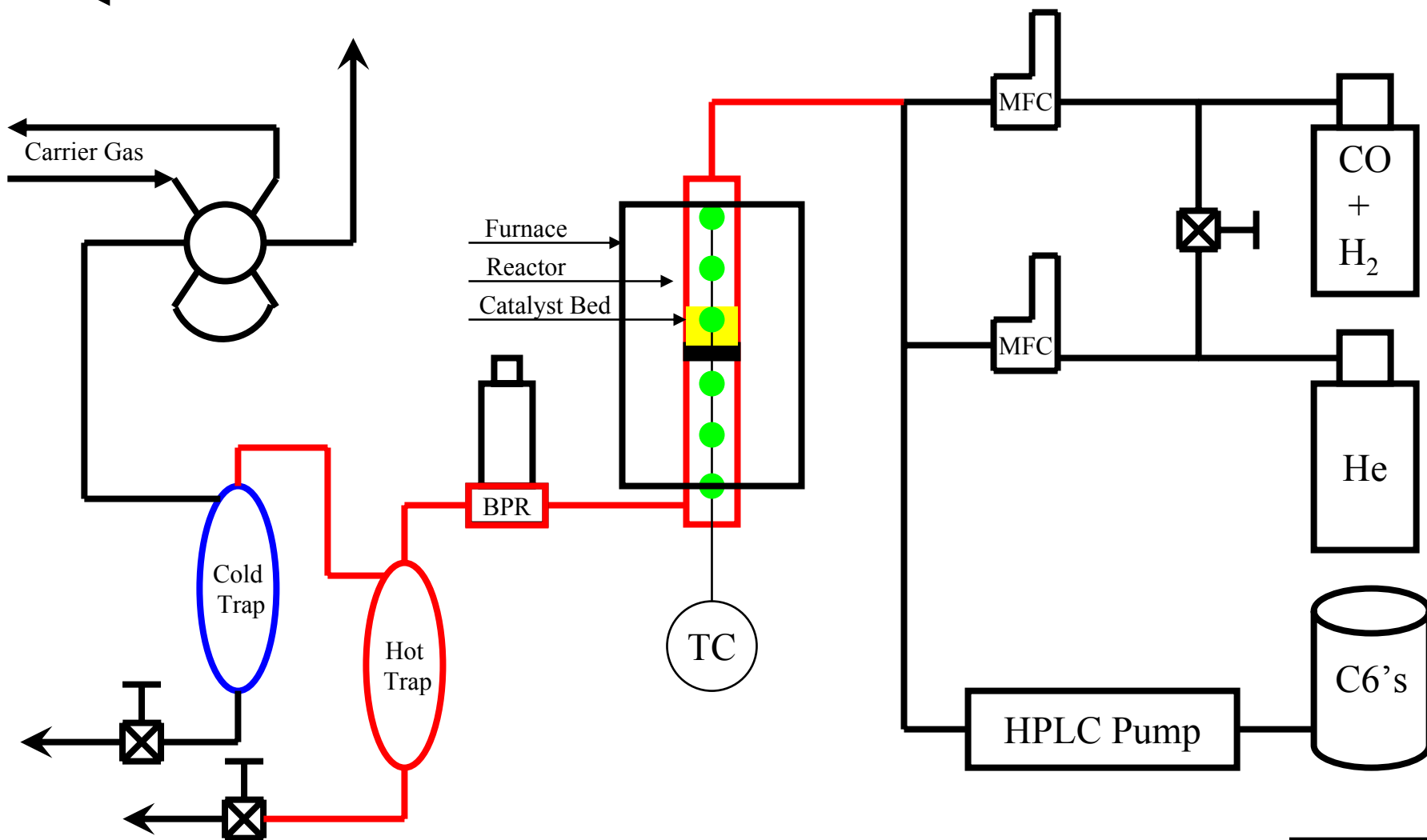
Iron – v – Cobalt

- Iron is less active and less expensive than cobalt
- Iron gives less methane, more olefins, and comparable maximum propagation probability
- Water Gas Shift (WGS) activity and the differing mechanism result in a lower $\text{H}_2:\text{CO}$ usage ratio, allowing for a lower $\text{H}_2:\text{CO}$ syngas ratio.

R. L. Espinoza, A. P. Steynberg, B. Jager, A. C. Vosloo: *Low temperature Fischer–Tropsch Synthesis from a Sasol Perspective*. [Applied Catalysis A: General](#) (1999): V 186, I 1-2, p13.



Reactor Re-Design





Reactor Re-Design





Cobalt Fischer Tropsch

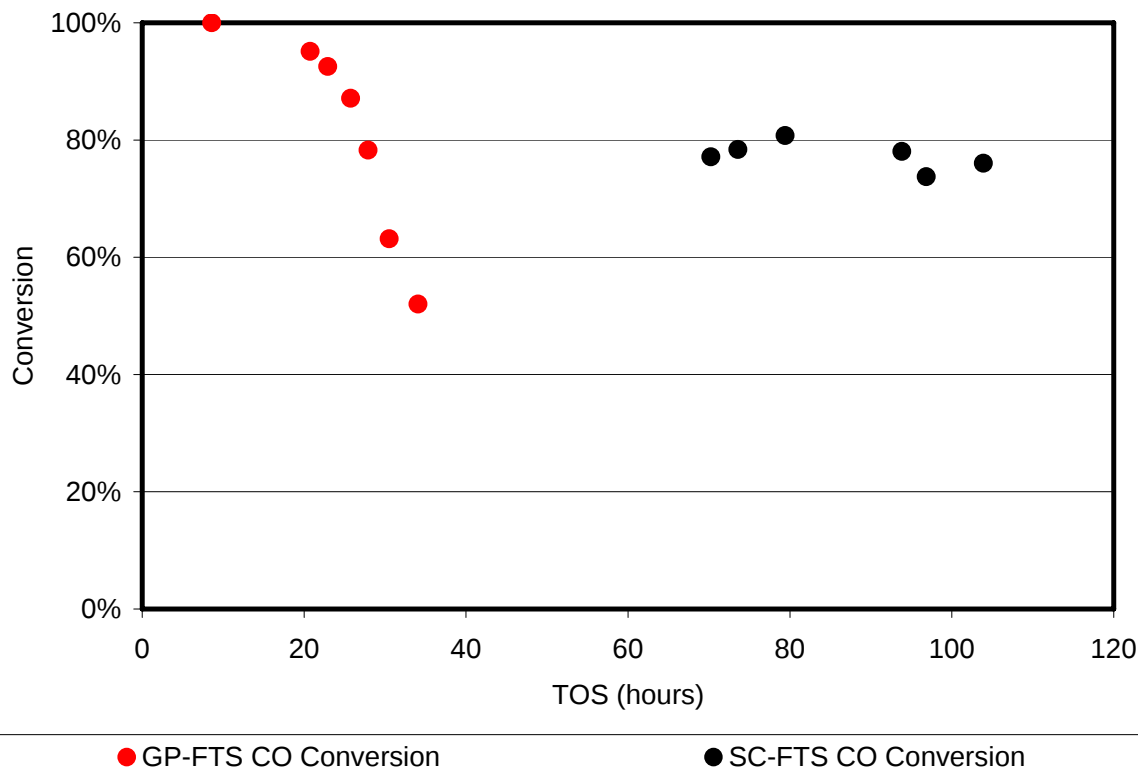
Gas Phase –v– Supercritical (SC) Phase FTS

- 1.5 g of 20% Co / Al₂O₃
- Catalyst reduced in situ for 4 hours in 50 SCCM hydrogen at T = 400°C and P ≈ 3 bar
- During gas phase FTS operation, pressure was maintained at 15 bar. During supercritical operation, the pressure was maintained at 65 bar (15 bar syngas partial pressure). Reaction temperature maintained at 240°C.
- Syngas: 2% N₂ (internal standard), 31% CO, 67% H₂ (Syngas Ratio = 2.15)



Cobalt Fischer Tropsch

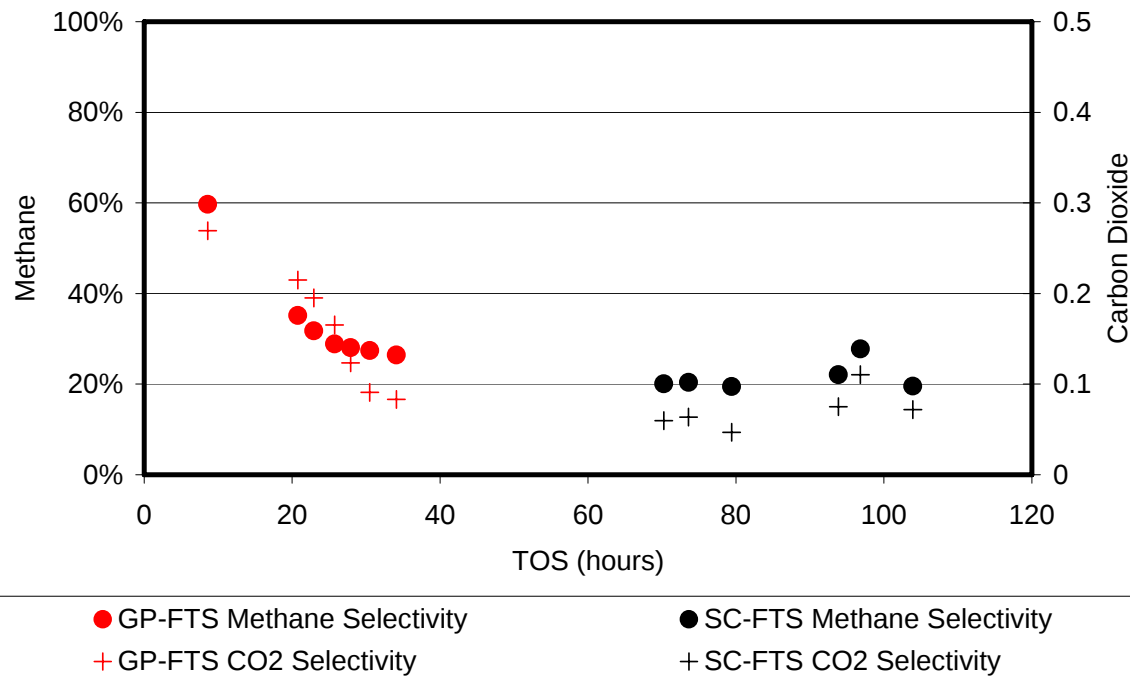
Gas Phase –v– SC Phase: Conversion





Cobalt Fischer Tropsch

Gas Phase –v– SC Phase: Gas Selectivities

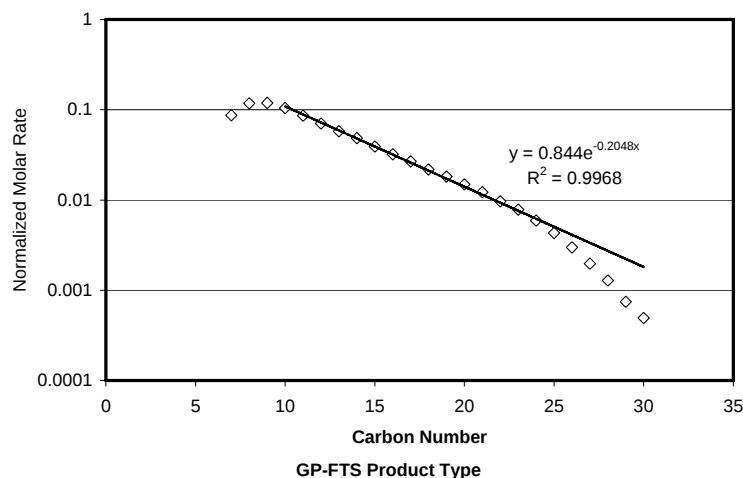




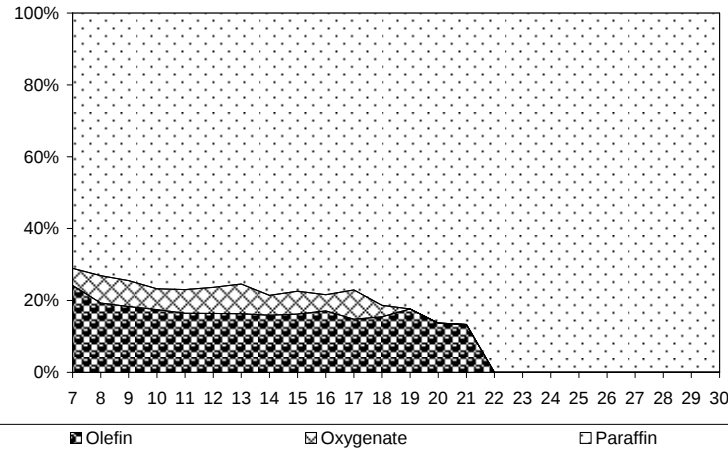
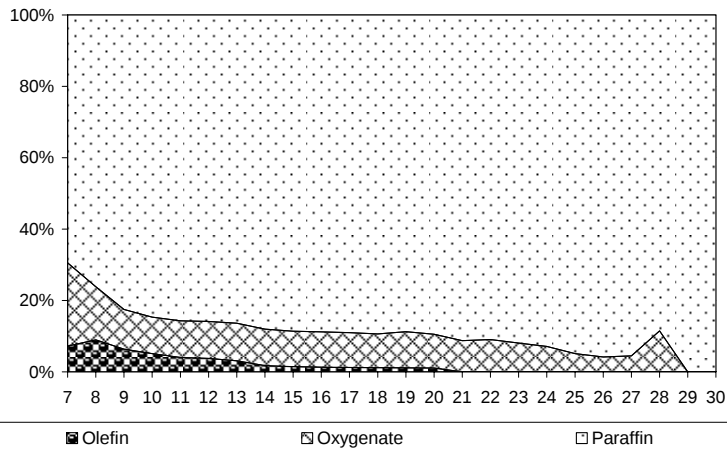
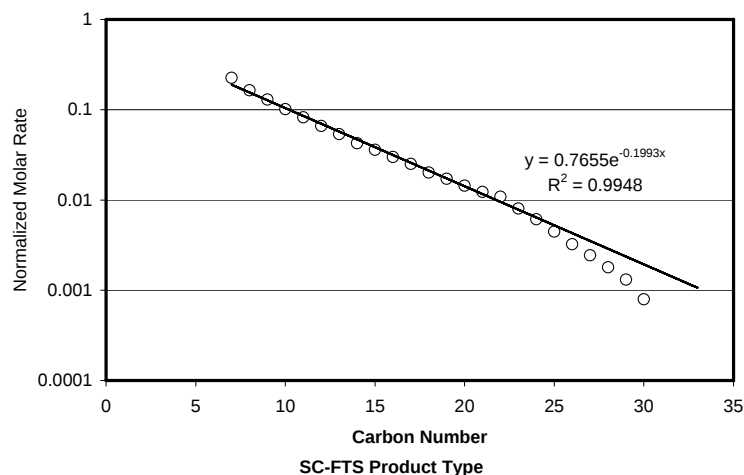
Cobalt Fischer Tropsch

Gas Phase –v– SC: Liquid Product Distribution

GP-FTS ASF Plot (Propagation Probability = 80%)



SC-FTS ASF Plot (Propagation Probability = 80%)





Summary from Cobalt Studies

- Redesigned reactor matches previous performance for both GP-FTS and SC-FTS.
 - Lower Methane and CO₂ selectivity in SC-FTS.
 - Improved olefin selectivity in mid range products in SC-FTS.
 - Comparable catalyst activity with GP-FTS and SC-FTS.



Iron Catalyst Preparation (I)

Iron Solution

- 1.0 M iron nitrate hydrate (Sigma Aldrich 216828),
- 0.11 M Zinc Nitrate Hydrate (SA 228737)

Reducing Solution

- Saturate Ammonium Carbonate (SA 207861)

Potassium Precursor

- Potassium Carbonate (SA 209619)

Copper Precursor

- Copper Nitrate Hydrate (SA 223395)

Senzi Li, Sundaram Krishnamoorthy, Anwu Li, George D. Meitzner, Enrique Iglesia: *Promoted Iron-Based Catalysts for the Fischer–Tropsch Synthesis: Design, Synthesis, Site Densities, and Catalytic Properties*. **Journal of Catalysis** (2002): V 206, I 2, p202.



Iron Catalyst Preparation (II)

- 2 mL / minute of Iron Solution added to 100 mL DIUF Water maintained at 80°C (Reducing Solution added manually to maintain pH at 7) until solution volume reaches 250 mL.
- Slurry Filtered. Solid redispersed in DIUF and filtered 3 times.
- Catalyst redispersed in drying liquid (DIUF water or ethanol) then filtered.
- Filter Cake dried overnight at 80°C then calcined for 1 hour at 350°C



Iron Catalyst Preparation (III)

- Incipient Wetness Used to impregnate Potassium Solution onto Iron (K / Fe atomic ratio = .02). Catalyst dried overnight at $T = 80^{\circ}\text{C}$ then calcined for 1 hour at $T = 350^{\circ}\text{C}$
- Incipient Wetness Used to impregnate Copper Solution onto Iron (Cu / Fe atomic ratio = .01). Catalyst dried overnight at $T = 80^{\circ}\text{C}$ then calcined for 1 hour at $T = 350^{\circ}\text{C}$
- Filter Cake dried overnight at 80°C then calcined for 1 hour at 350°C
- Catalyst reduced in situ with syngas at $T = 270^{\circ}\text{C}$, $P = 4.5$ bar.



Pore Volume of Pre-Promoted Iron Catalyst

- Saturated with DIUF water prior to drying
→ Pore Volume ≈ 0.2 mL / g
- Saturated with ethanol prior to drying
→ Pore Volume ≈ 1.0 mL / g



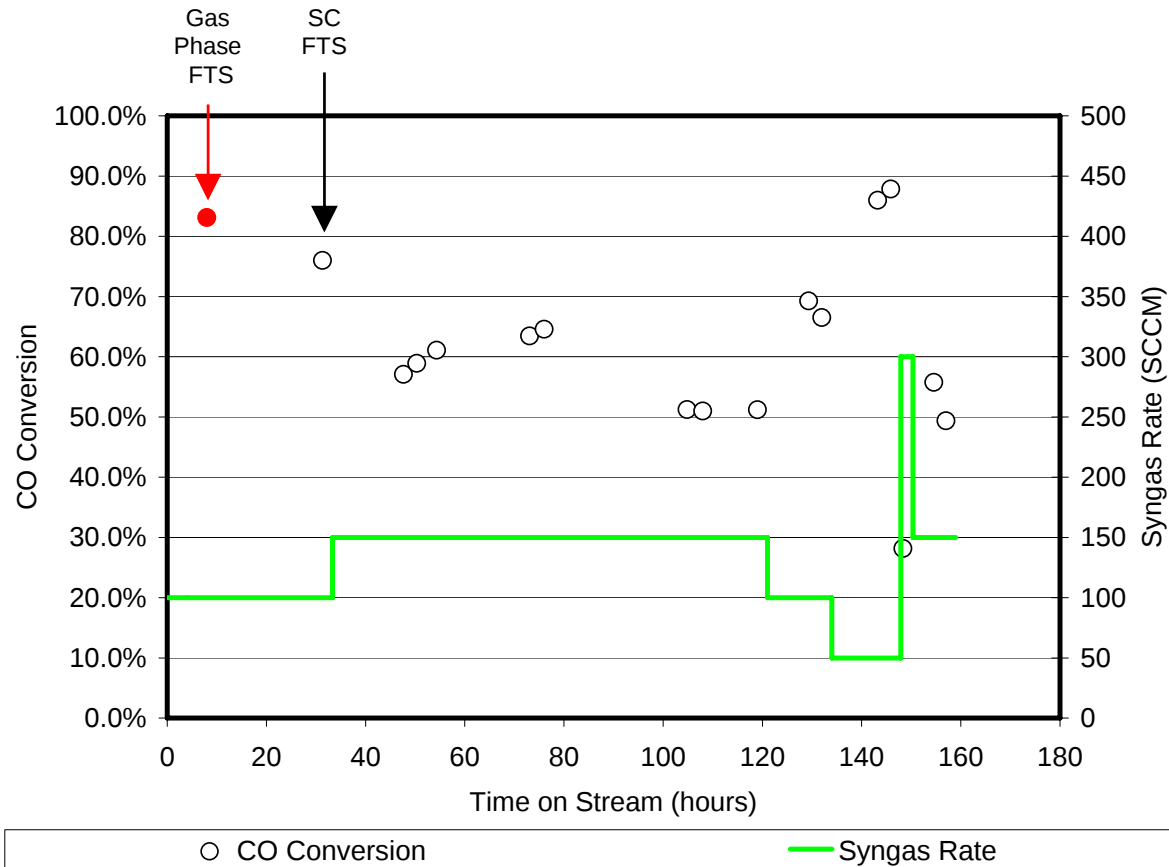
Fischer Tropsch Parameters

- 2 g of calcined promoted catalyst loaded into reactor
- Syngas is 1.5% N₂, 37.1% CO, 61.4% H₂
(Syngas Ratio = 1.65)
- During supercritical operation, the ratio of hexanes to syngas feed is 1 mL / 50 SmL
- 21 bar pressure during GP-FTS, 75 bar pressure during SC-FTS (17 bar syngas partial pressure).
- T = 240°C for most of study



Iron SC-FTS Performance

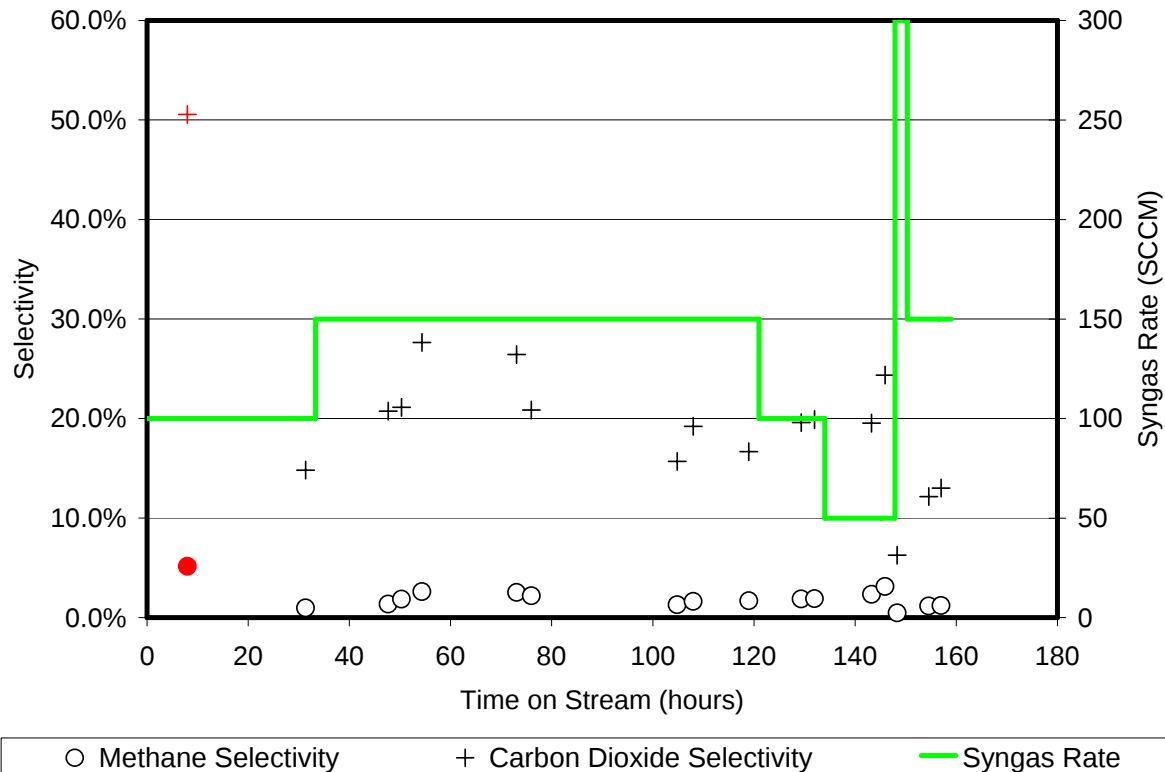
Conversion





Iron SC-FTS Performance

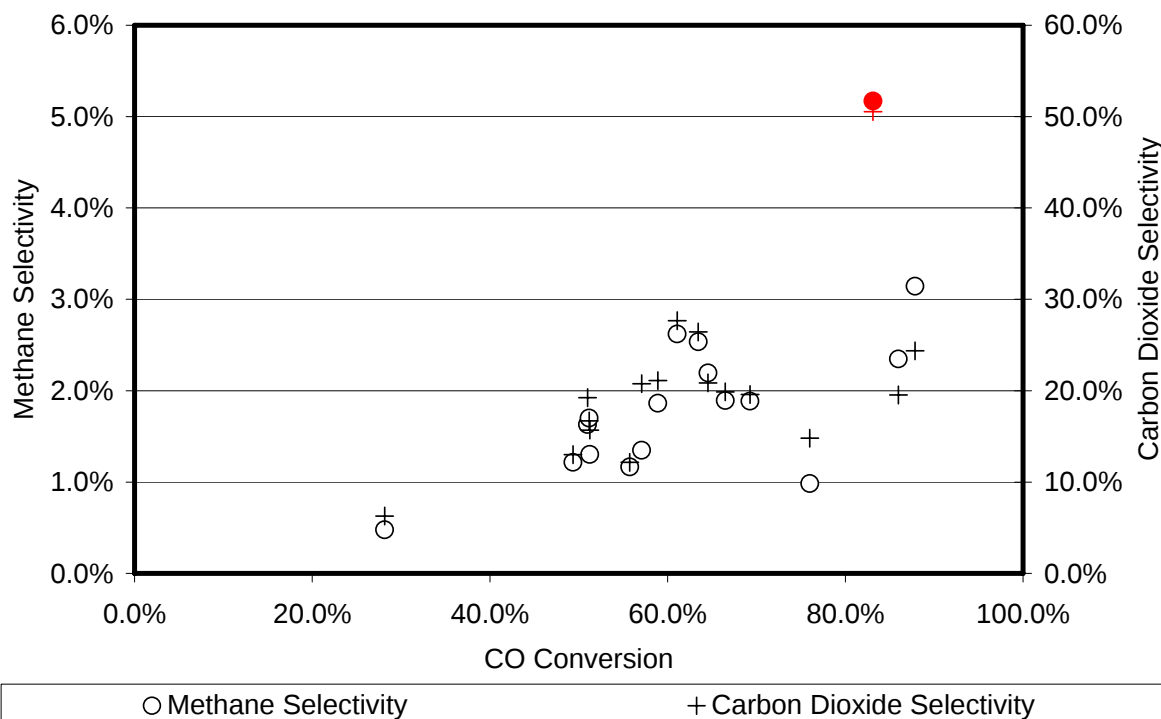
Methane and CO₂ Selectivity





Iron SC-FTS Performance

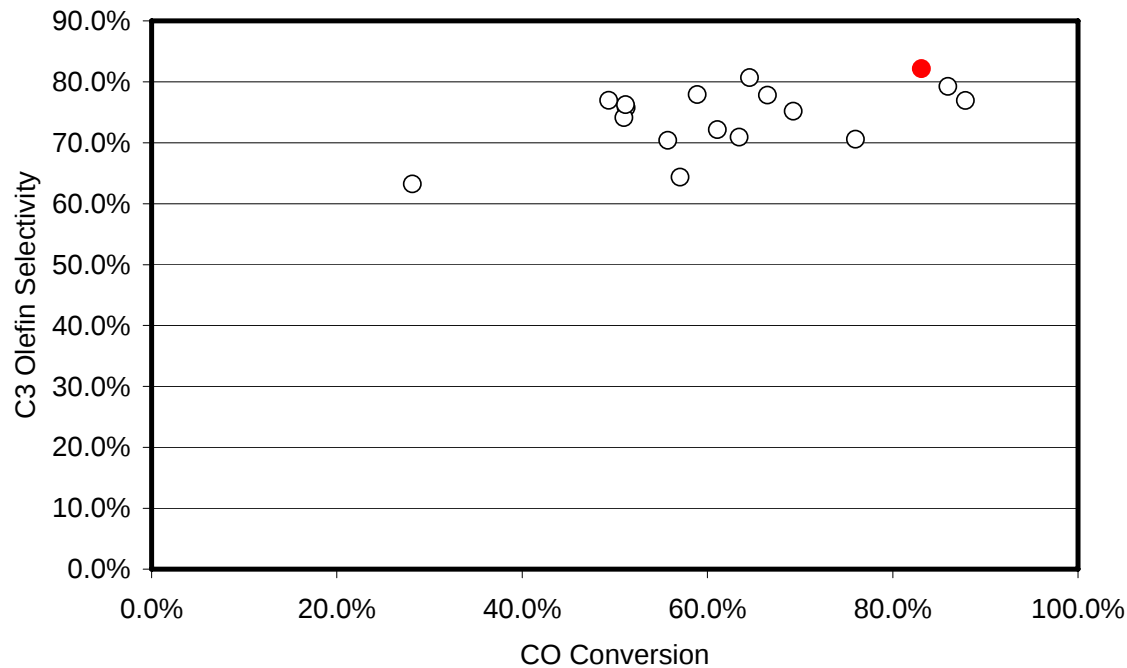
Selectivity Cross-Plot





Iron SC-FTS Performance

C3 Olefin Selectivity Cross-Plot

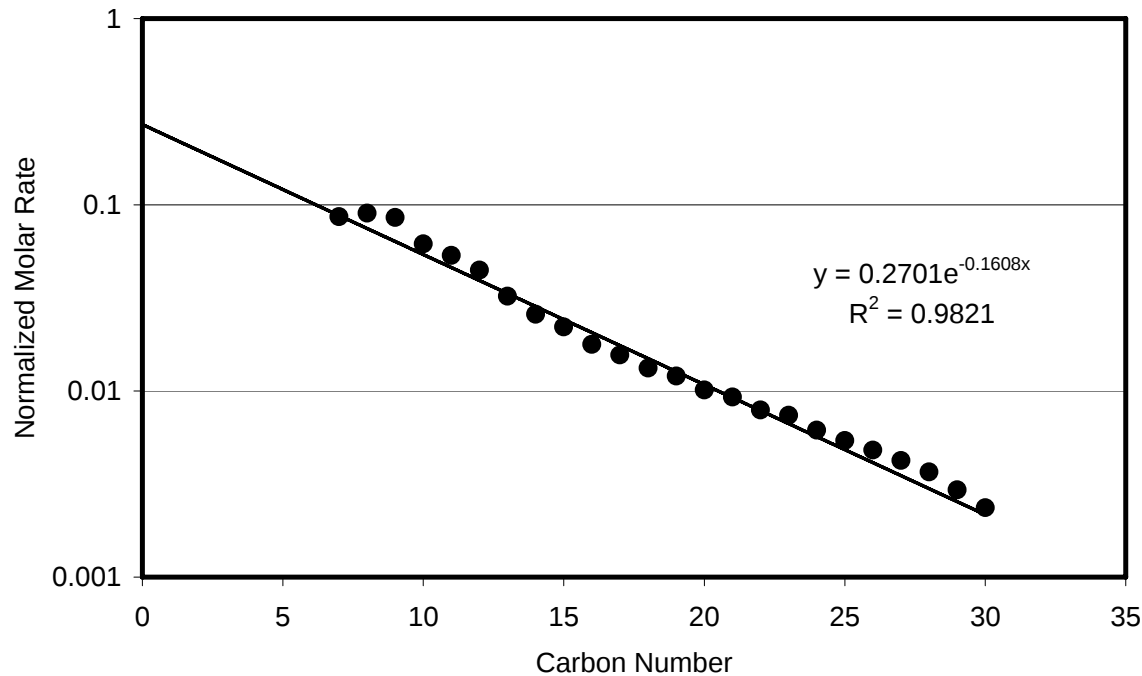




Iron GP-FTS Performance

Liquid Products: ASF Plot

GP-FTS ASF Plot (Propagation Probability = 84%)

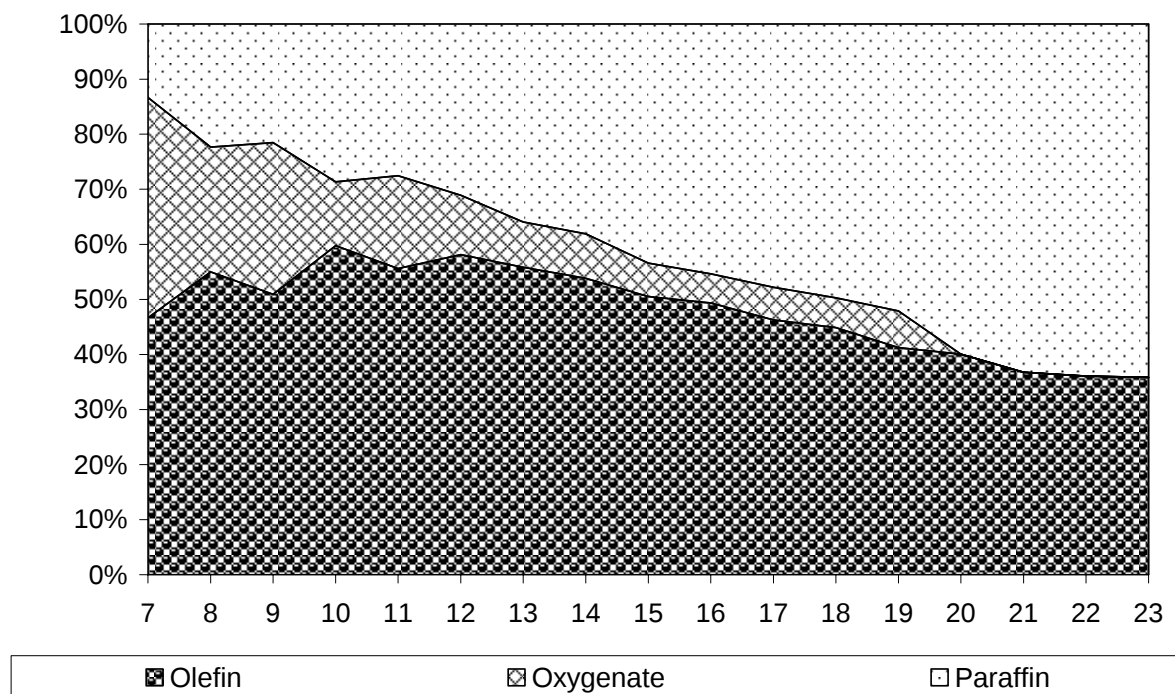




Iron GP-FTS Performance

Liquid Products: Product Type

Gas Phase FTS Product Type

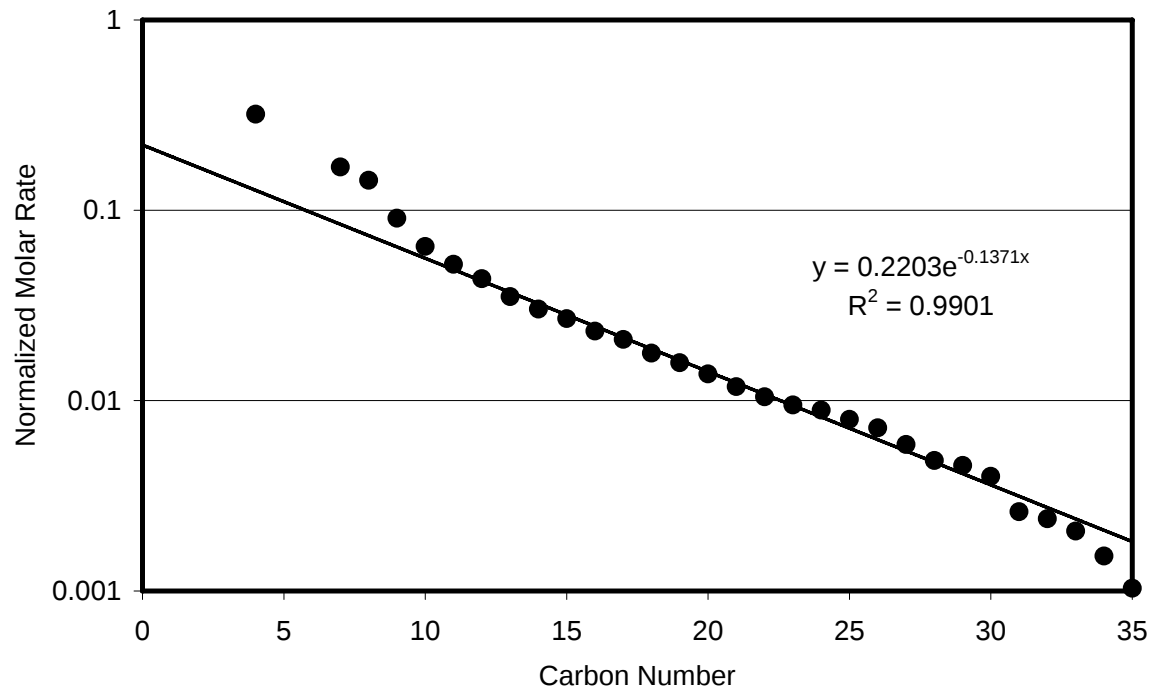




Iron SC-FTS Performance

Liquid Products: ASF Plot

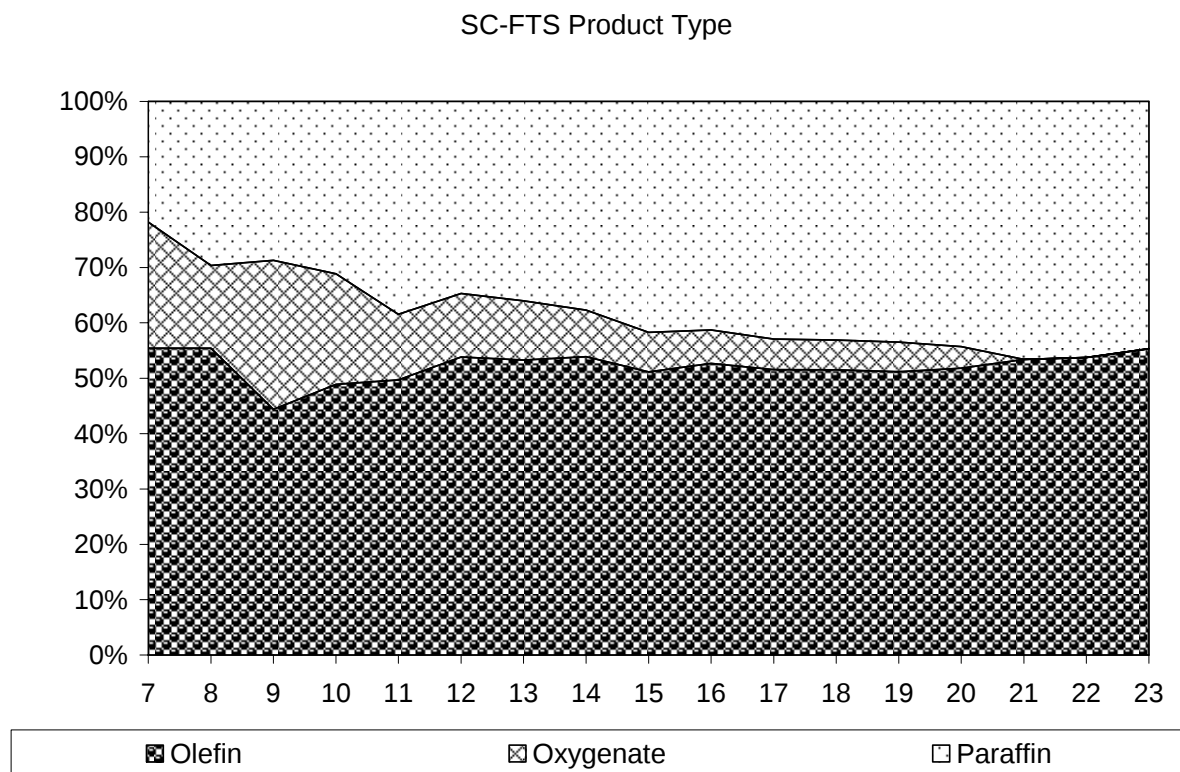
SC-FTS ASF Plot (Propagation Probability = 86%)





Iron SC-FTS Performance

Liquid Products: Product Type

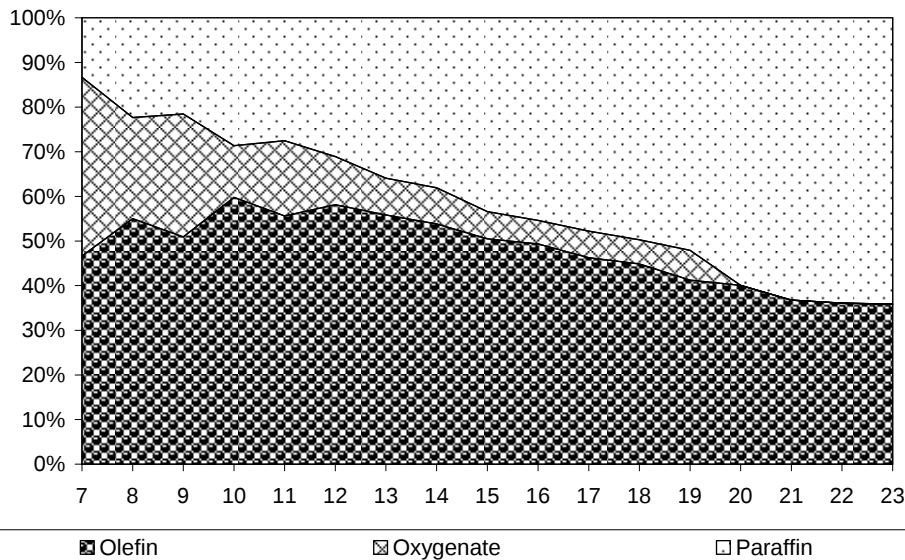




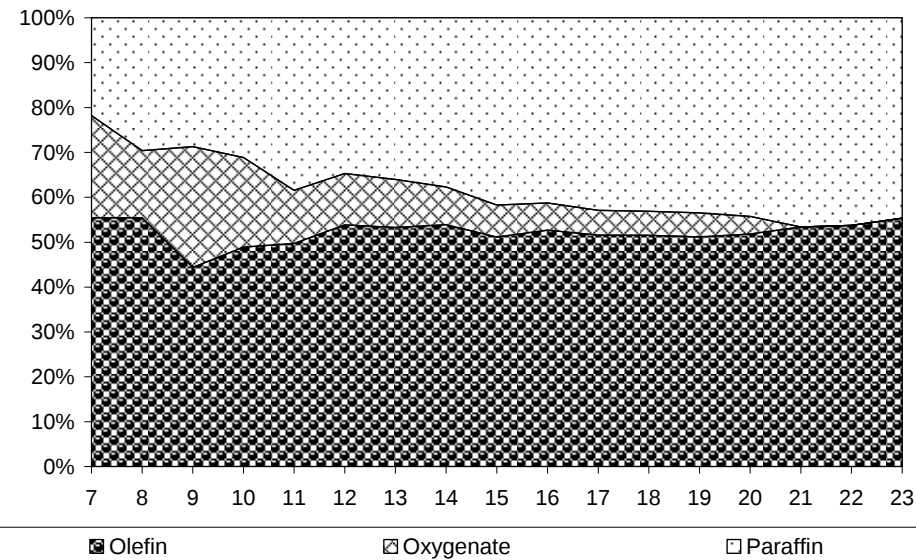
FTS Product Type Comparison

GP-FTS –v- SC- FTS on Iron Catalyst

Gas Phase FTS Product Type



SC-FTS Product Type



- SC-FTS maintains the olefin selectivity in the middle and wax fractions better than GP-FTS.



Conclusions

- We have successfully synthesized an effective iron Low Temperature Fischer Tropsch (LTFT) catalyst and tested it under both gas phase and supercritical phase conditions.
- The iron catalyst demonstrated much higher olefin selectivity, chain growth probability, and CO₂ selectivity than we have observed on cobalt while yielding a lower methane selectivity.
- The benefits of SC-FTS realized with a cobalt catalyst (decreased methane and CO₂ selectivity and enhanced middle and heavy olefin selectivity) were also achieved on this iron catalyst.



Future Work

- Compare Gas Phase and Supercritical Phase for Iron LTFT Operation
- Study the influence of basic process parameters (temperature, pressure, etc.) on process performance.
- Compare traditional Iron FT catalyst with composite nanoparticles on a porous and non-porous support.
- Integrate Iron-Based FT into 3-Bed Reactor that incorporates oligomerization and cracking/isomerization to improve desired product selectivity and quality.



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Questions