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

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CFFS Annual Meeting

August 4, 2008

UNCLASSIFIED.
DISTRIBUTION STATEMENT A.
Approved for public release;
unlimited public distribution.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
04 AUG 2008	**Briefing Charts**	**01-01-2008 to 01-01-2008**

4. TITLE AND SUBTITLE
Process Technology for Tunable Fischer Tropsch Synthesis Towards Middle Distillate Fuel Fractions

5a. CONTRACT NUMBER
W56HZV-07-C0721

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Ed Durham; Christopher Roberts

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army TARDEC,6501 East Eleven Mile Rd,Warren,Mi,48397-5000

8. PERFORMING ORGANIZATION REPORT NUMBER
#18977

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army TARDEC, 6501 East Eleven Mile Rd, Warren, Mi, 48397-5000

10. SPONSOR/MONITOR'S ACRONYM(S)
TARDEC

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
#18977

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

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.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**Public Release**	**28**	

Objectives

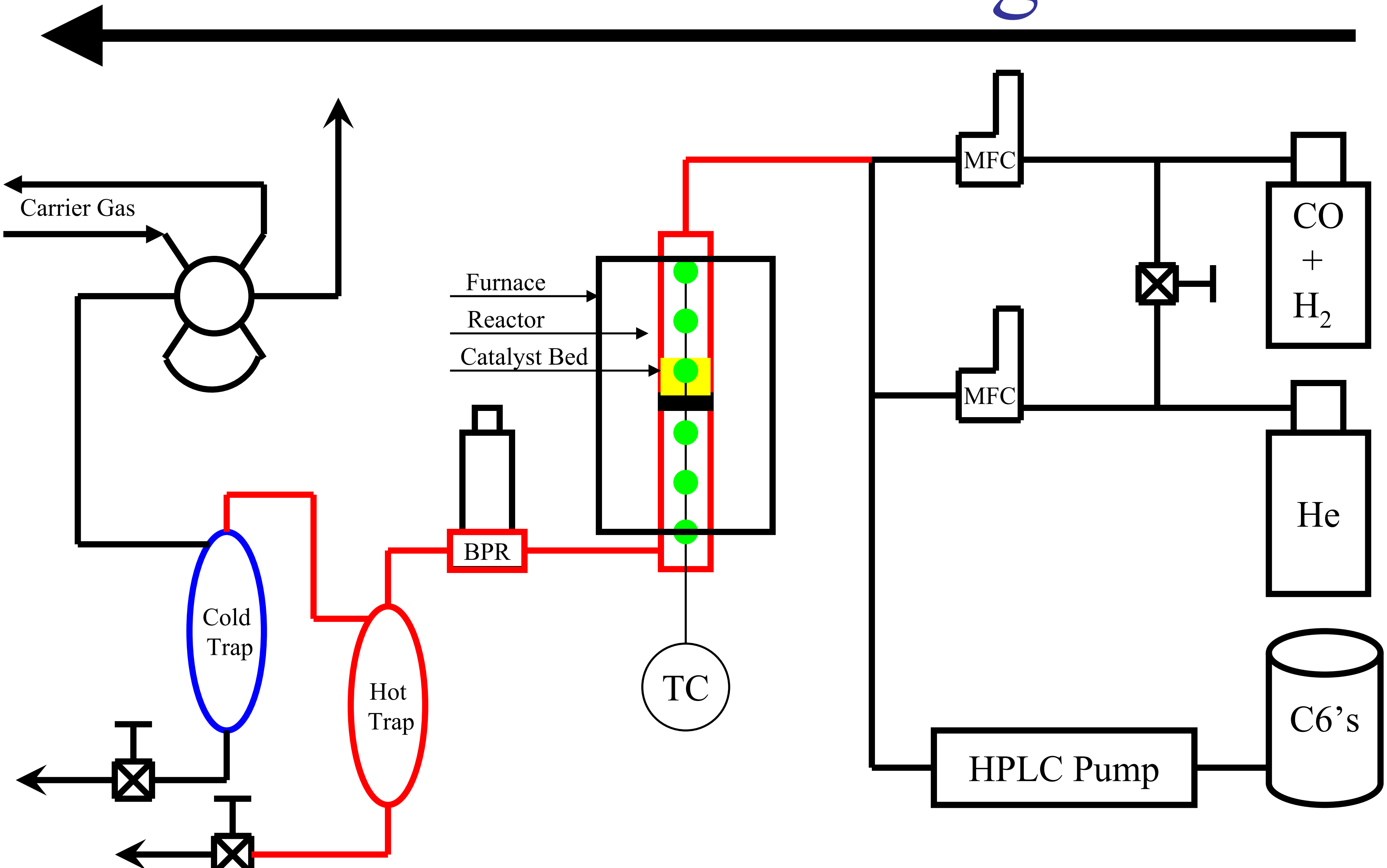
- Develop Fischer Tropsch technologies that target the production of FT SBF through process, catalyst, and reactor improvements.
- Investigate Supercritical Fischer Tropsch Synthesis (SC-FTS) process performance as related to key reaction conditions.
- Develop Fe catalysts that operate over a wider range 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 H_2:CO usage ratio, allowing for a lower H_2: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



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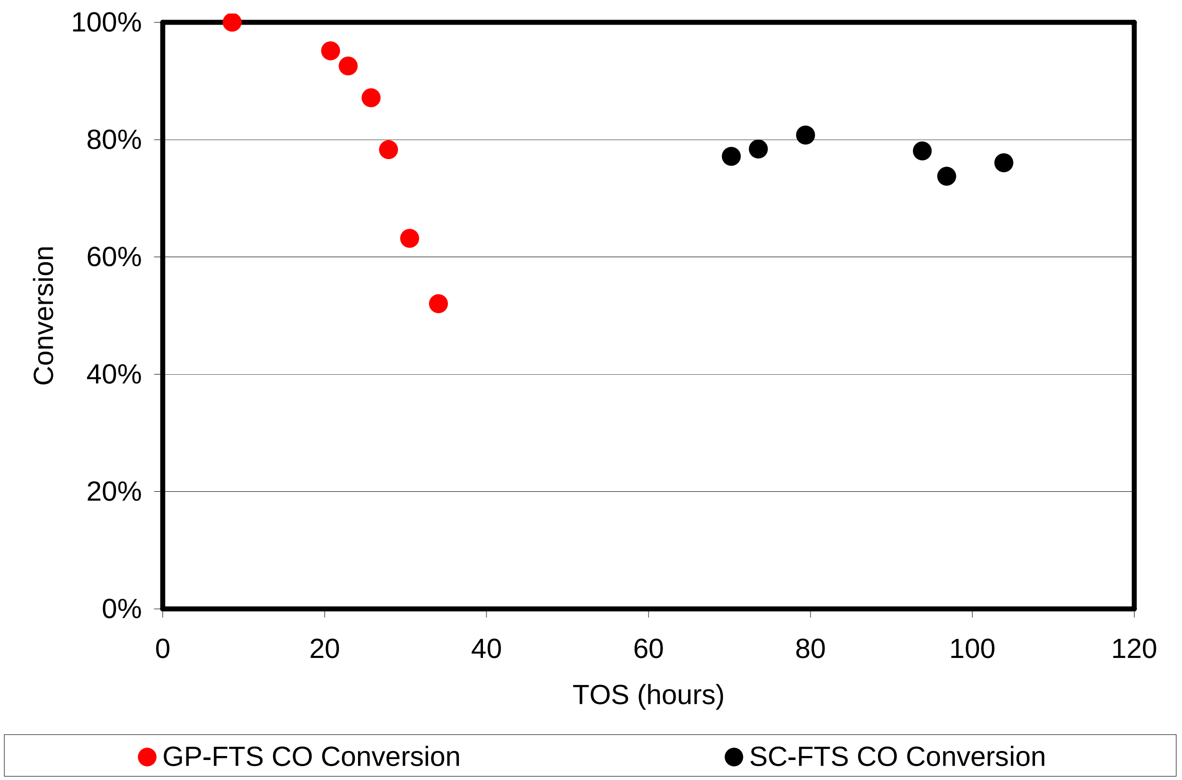
Reactor Re-Design

Cobalt Fischer Tropsch
Gas Phase –v– Supercritical (SC) Phase FTS

- 1.5 g of 20% Co / Al_2O_3
- Catalyst reduced in situ for 4 hours in 50 SCCM hydrogen at T = 400^{o}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^{o}C.
- Syngas: 2% N_2 (internal standard), 31% CO, 67% H_2 (Syngas Ratio = 2.15)

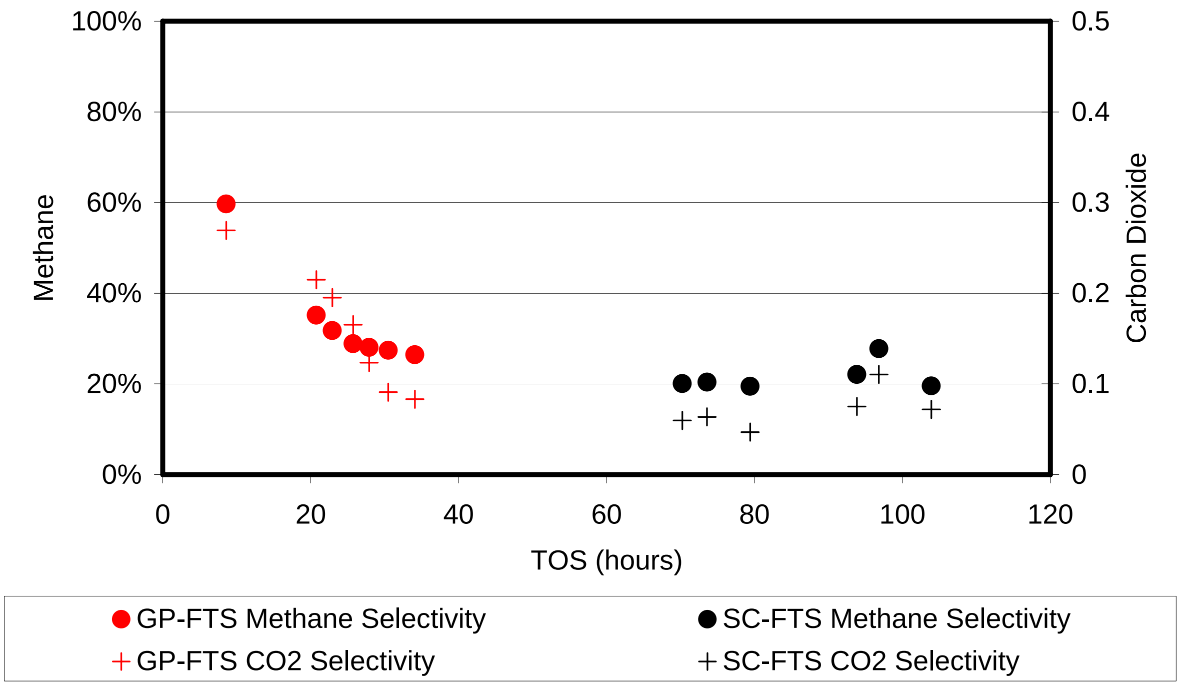
Cobalt Fischer Tropsch

Gas Phase –v– SC Phase: Conversion



Cobalt Fischer Tropsch

Gas Phase –v– SC Phase: Gas Selectivities



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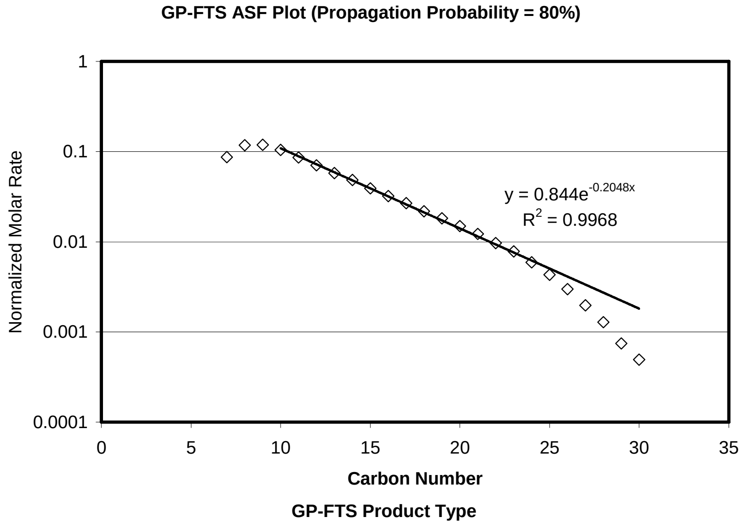
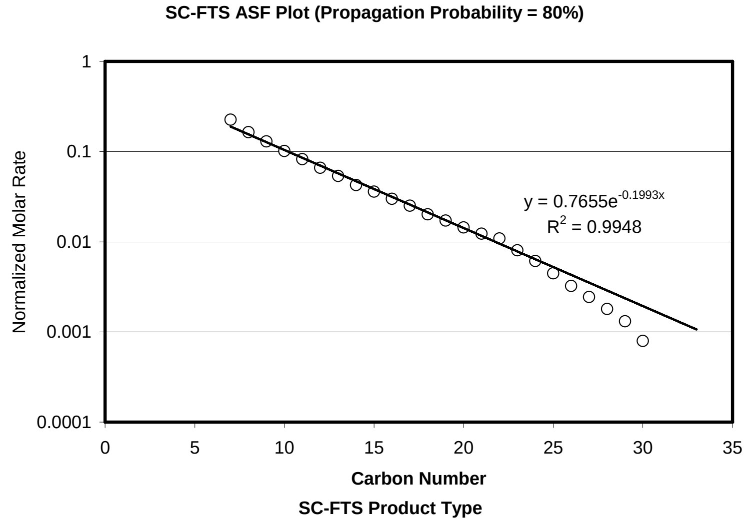
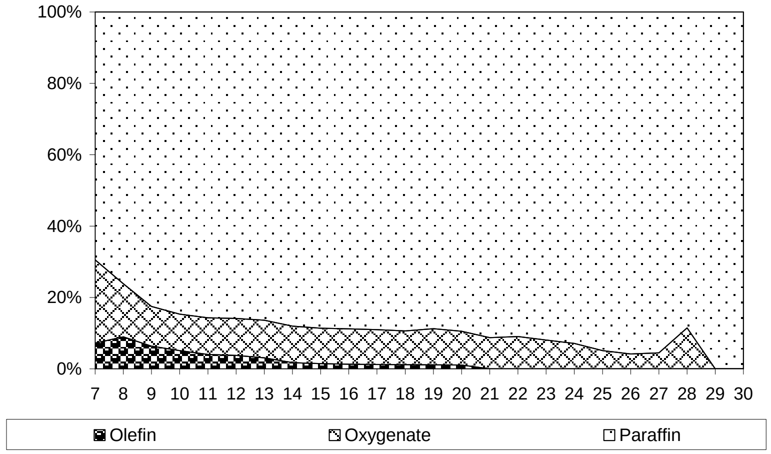
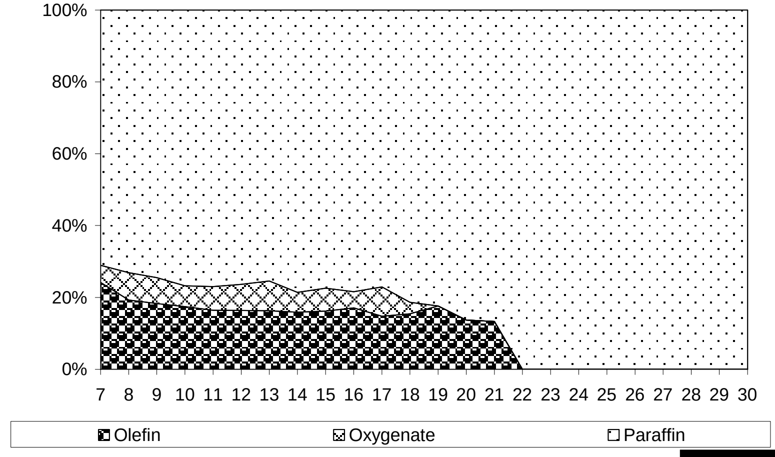
Cobalt Fischer Tropsch

Gas Phase –v– SC: Liquid Product Distribution









Summary from Cobalt Studies

- Redesigned reactor matches previous performance for both GP-FTS and SC-FTS.
  - Lower Methane and CO_2 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^{o}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 80oC then calcined for 1 hour at 350^{o}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°C then calcined for 1 hour at T = 350°C
- Incipient Wetness Used to impregnate Copper Solution onto Iron (Cu / Fe atomic ratio = .01). Catalyst dried overnight at T = 80°C then calcined for 1 hour at T = 350°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°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

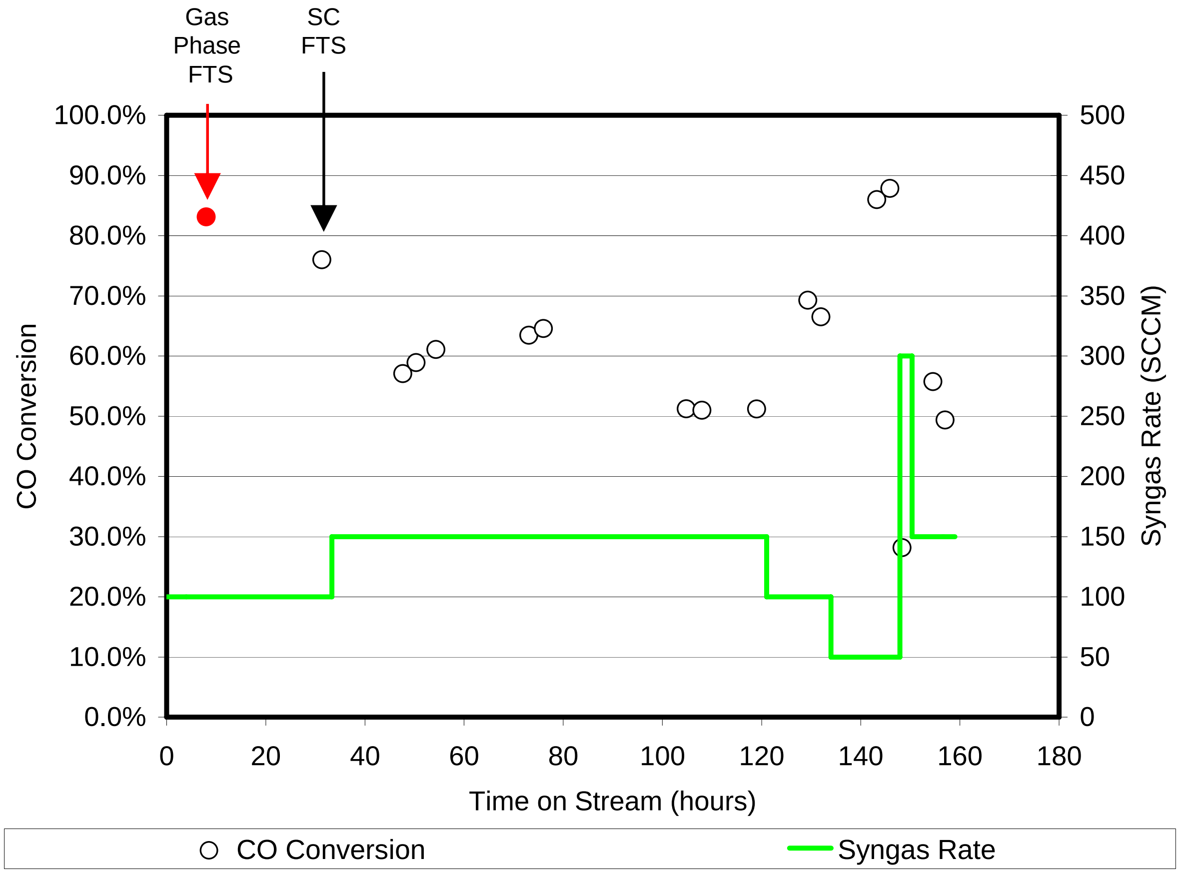
  → Pore Volume ≈ 1.0 mL / g

Fischer Tropsch Parameters

- 2 g of calcined promoted catalyst loaded into reactor
- Syngas is 1.5% N_2, 37.1% CO, 61.4% H_2
  (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^{o}C for most of study

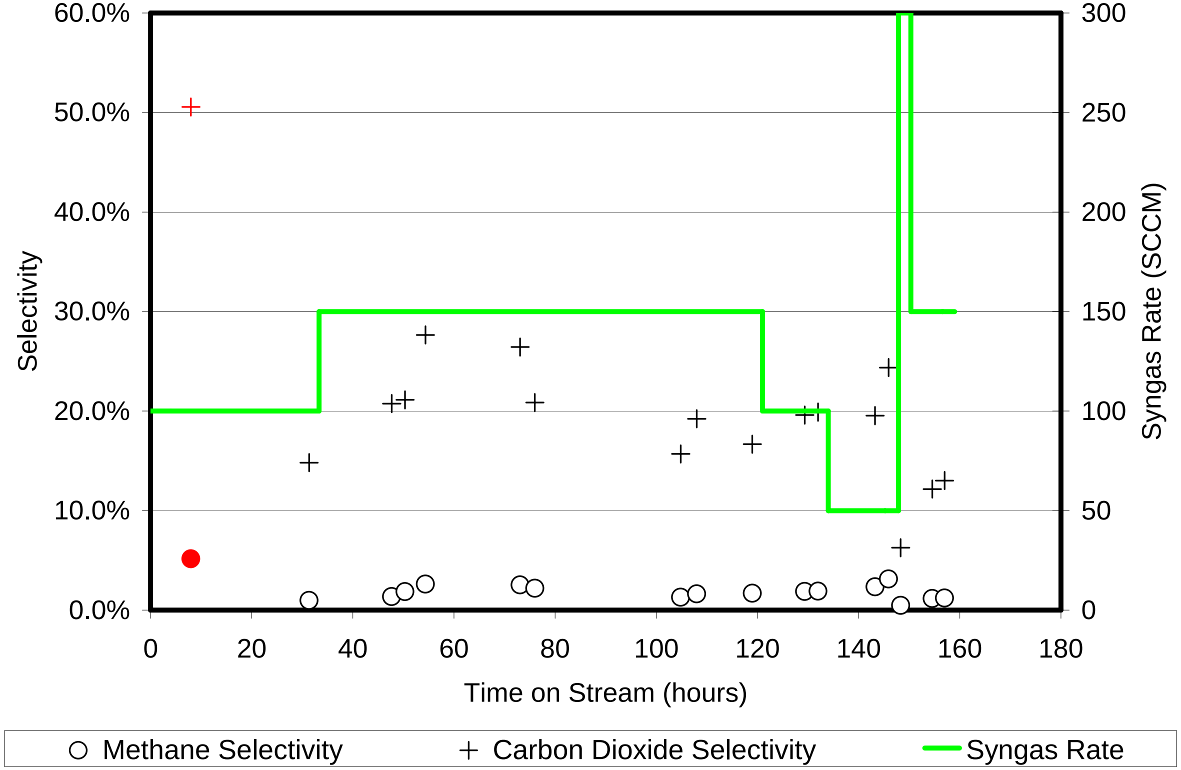
Iron SC-FTS Performance

Conversion



Iron SC-FTS Performance

Methane and CO_2 Selectivity



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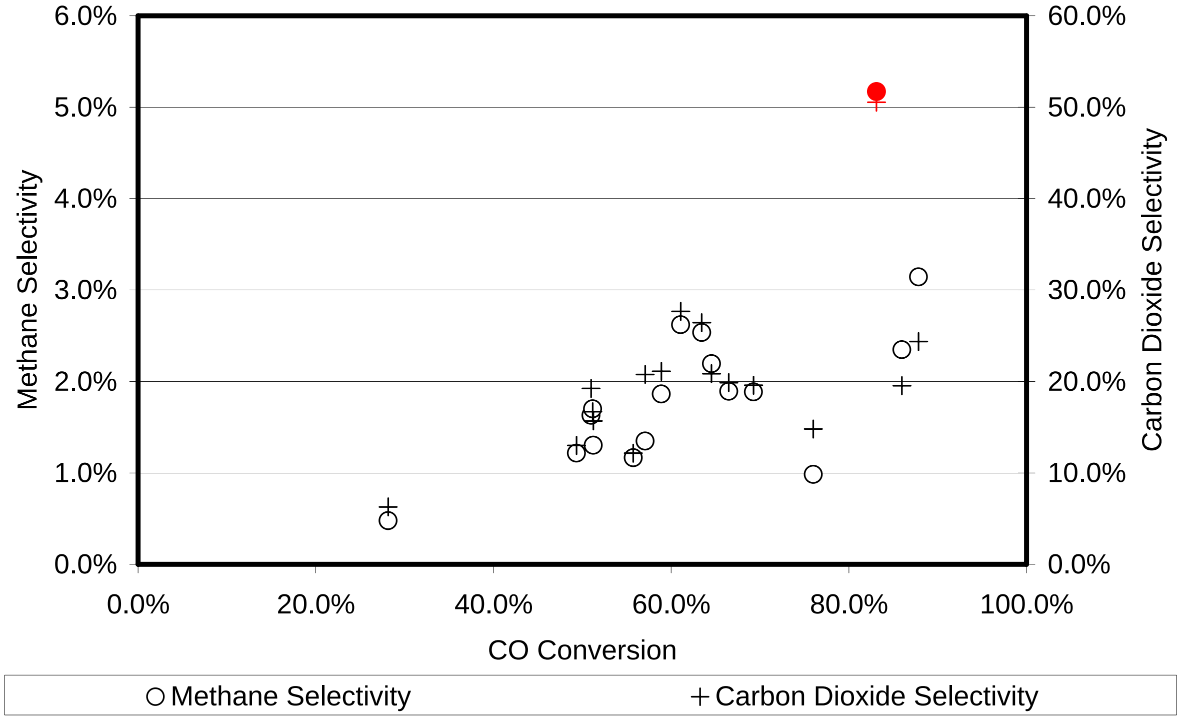
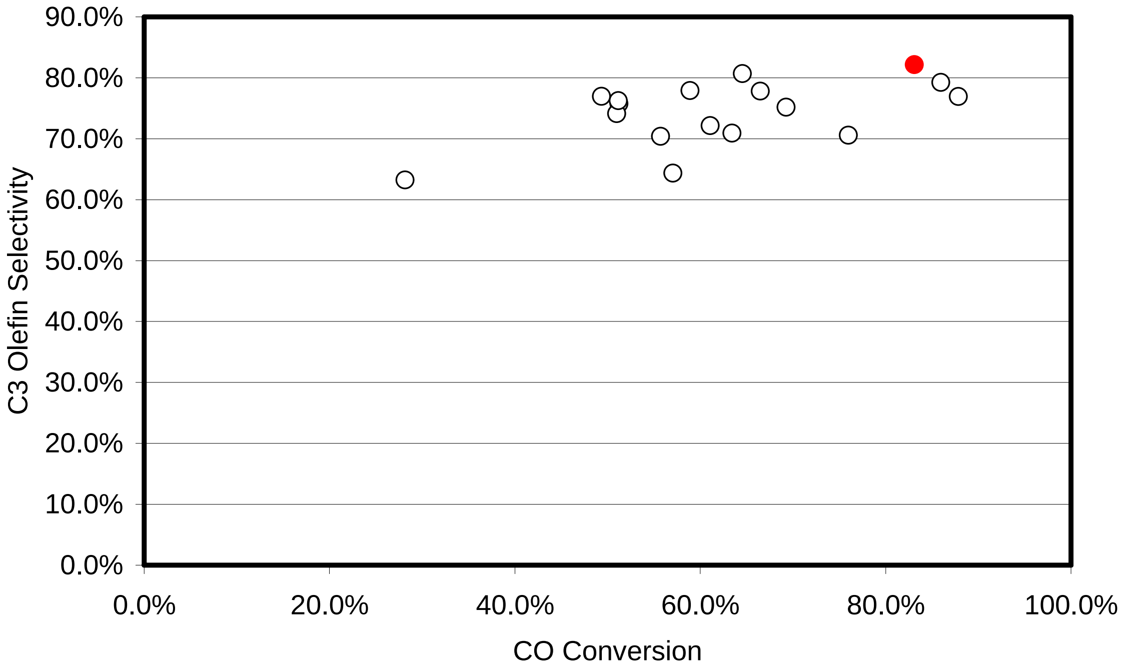
Iron SC-FTS Performance

Selectivity Cross-Plot



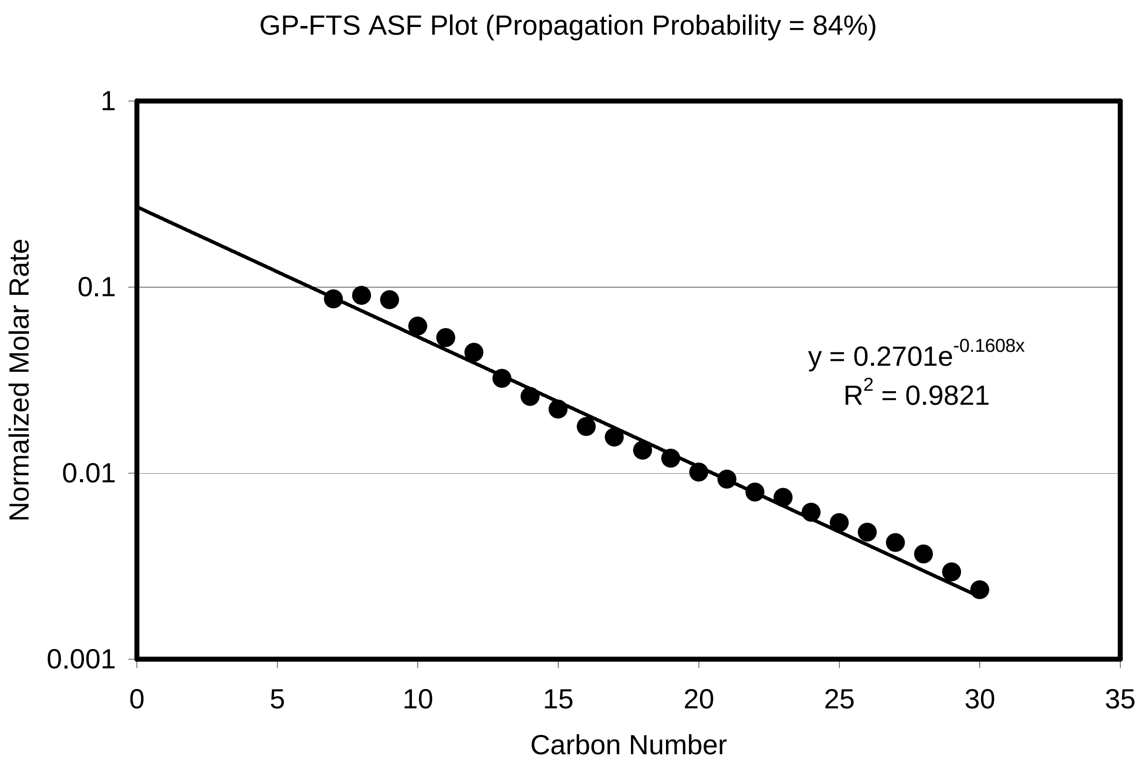
Iron SC-FTS Performance

C3 Olefin Selectivity Cross-Plot



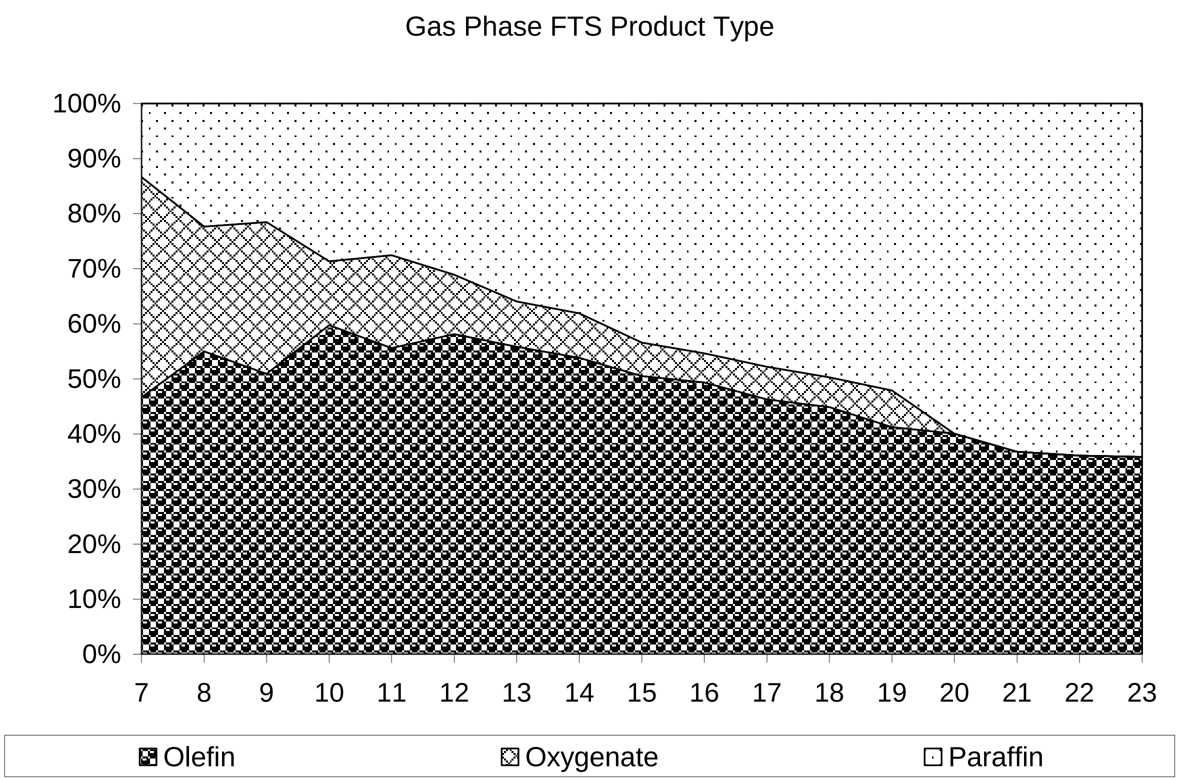
Iron GP-FTS Performance

Liquid Products: ASF Plot

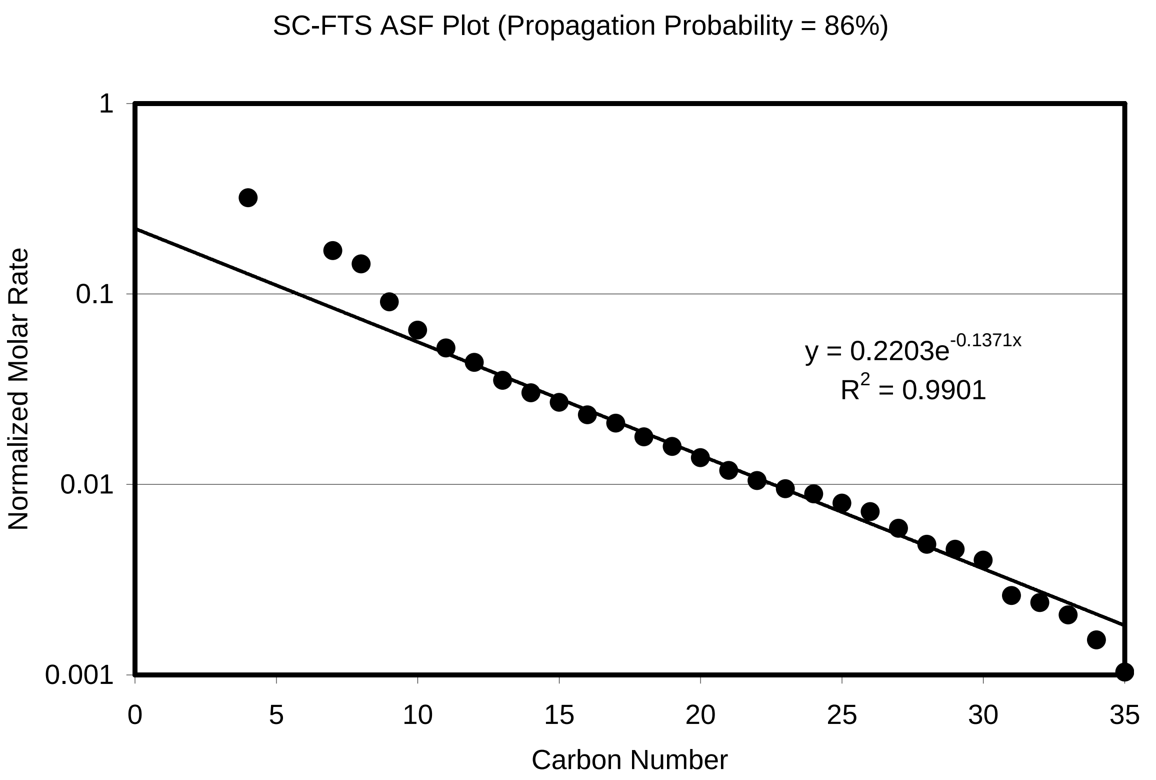


Iron GP-FTS Performance

Liquid Products: Product Type



Iron SC-FTS Performance
Liquid Products: ASF Plot



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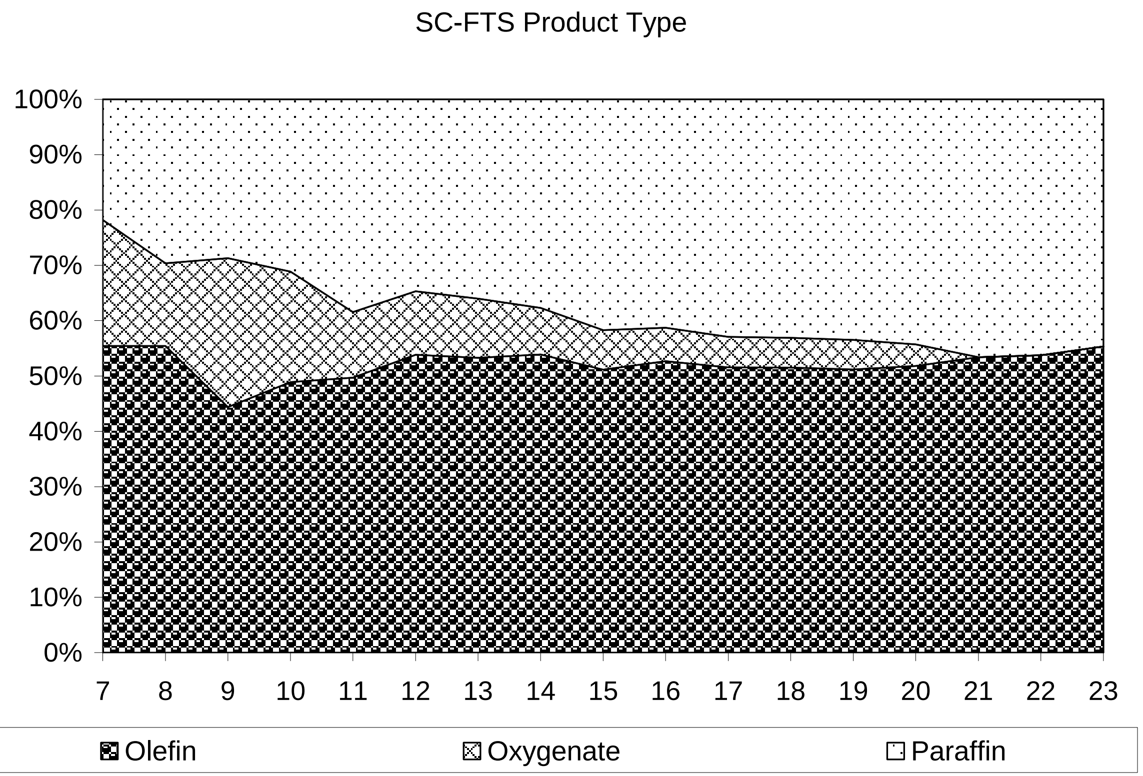
Iron SC-FTS Performance

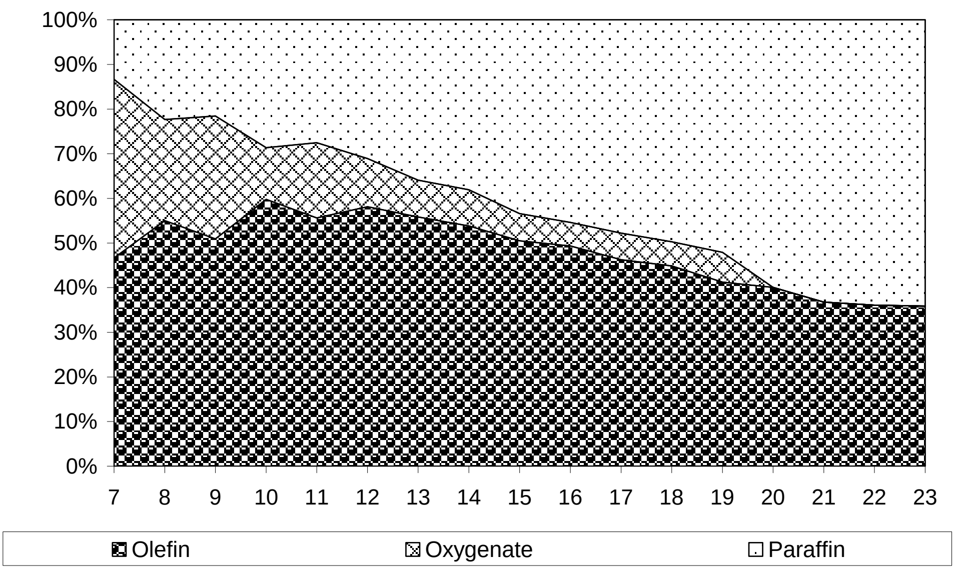
Liquid Products: Product Type



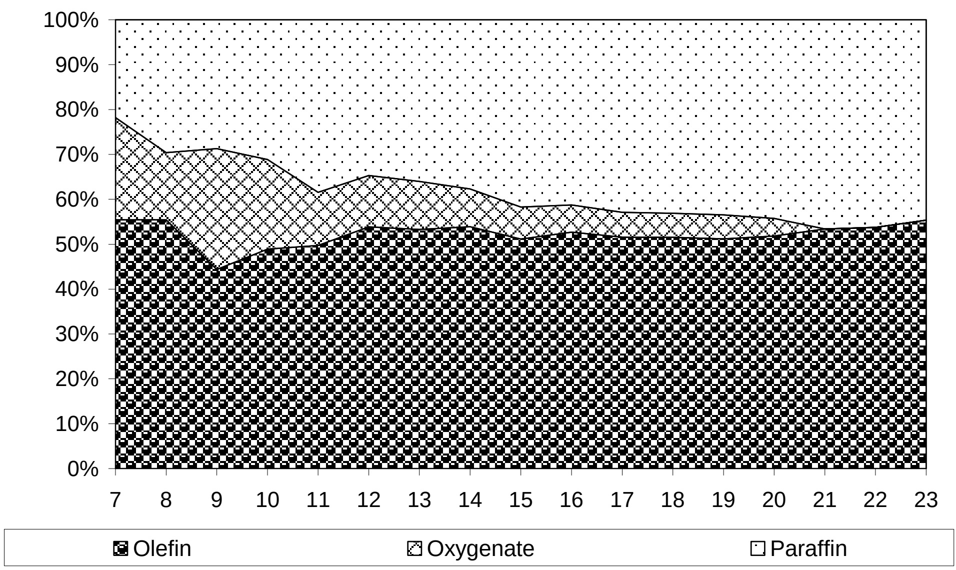
FTS Product Type Comparison

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 demonstated much higher olefin selectivity, chain growth probability, and CO_2 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.

Acknowledgements

- The Consortium for Fossil Fuel Science
- U.S. ARMY TACOM Contract No. W56HZV-07-C-0721

- Brian Schwieker

Questions