U.S. NAVAL RESEARCH LABORATORY

NRL/6360/MR—2022/6

Commissioning of NRL Two-Stage Pilot-Scale CO2 to Hydrocarbons Reactor Skid: Validation of the Fischer-Tropsch Reactor

JAMES R. MORSE

HEATHER D. WILLAUER

Scientific Staff
Materials Science & Technology Division

JEFFREY W. BALDWIN

Functional Materials and Energy Section
Acoustics Division

JOSEPH J. HARTVIGSEN

LYMAN FROST

NATHAN DAVIS

MICHELE HOLLIST

SKYLER VALDEZ

OxEon Energy
North Salt Lake, Utah

October 21, 2022

REPORT DOCUMENTATION PAGE

1. REPORT DATE (DD-MM-YYYY) 21-10-2022	2. REPORT TYPE NRL Memorandum Report	3. DATES COVERED (From - To) 10/01/2021 – 09/29/2022

4. TITLE AND SUBTITLE

Commissioning of NRL Two-Stage Pilot-Scale CO2 to Hydrocarbons Reactor Skid: Validation of the Fischer-Tropsch Reactor

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

James R. Morse, Jeffrey W. Baldwin, Heather D.Willauer, J.J. Hartvigsen*, L. Frost*, N. Davis*, M. Hollist*, and S. Valdez*

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
1P96

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5320

8. PERFORMING ORGANIZATION REPORT NUMBER

NRL/6360/MR--2022/6

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5320

10. SPONSOR / MONITOR'S ACRONYM(S)

NRL 6.1 Base Program

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

12. DISTRIBUTION / AVAILABILITY STATEMENT

DISTRIBUTION STATEMENT A: Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

*OxEon Energy, 257 River Bend Way, North Salt Lake, UT 84054

14. ABSTRACT

To demonstrate the feasibility of CO2 utilization strategies, the design and testing of pilot-scale processes for CO2 hydrogenation at relevant scales is important . To this end, the design, assembly, and testing of a two-stage pilot-scale reverse water gas shift/ Fischer-Tropsch (RWGS/ FT) reactor, capable of generating up to three liters of liquid hydrocarbon products a day using only CO2 and H2 feedstocks, was recently executed. The contents of this Memorandum Report describe the design specifications of the pilot-scale reactor, along with preliminary results of the initial commissioning of the FT portion of this reactor. Initial testing of the FT reactor utilized a closed loop recycle, with the tail gas of the FT reactor recycled back to the inlet of the FT reactor at a 20:1 ratio. The reactor bed was operated at 210 °C, with a reagent feed of syngas flowed at 2 SLPM (H2:CO ratio of 1.8). This resulted in CO and H2 conversions > 80%, with a methane selectivity on the order of 8 to 12%, and yielded a hydrocarbon product distribution peak of C9 or greater. These results meet the expectations and targets that were established for the FT portion of this reactor. The results of this initial commissioning are interpreted and used to inform recommendations for further testing and evaluation of the two-stage WRGS/FT reactor.

15. SUBJECT TERMS

CO2 hydrogenation	Heterogeneous catalysts
Reverse water gas shift	Fischer-Tropsch

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON James R. Morse
a. REPORT U	**b. ABSTRACT** U	**c. THIS PAGE** U	U	13	**19b. TELEPHONE NUMBER** (include area code) (202) 404-3418

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EXECUTIVE SUMMARY

The hydrogenation of CO_2 to liquid hydrocarbon fuels represents an attractive means of CO_2 utilization. With appropriate CO_2 capture technologies, such processes could be applied across a wide range of environments, including in littoral, marine, fixed bases, and remote forward operating locations, thus reducing the logistical burden of liquid fuel delivery and enabling "Freedom of Action" for the Warfighter.

The U.S. Naval Research Laboratory is currently pursuing various research avenues to enable processes and technologies capable of producing fuel from CO_2. Among these research efforts include CO_2 capture, seawater electrolysis, and thermochemical catalyst development. Of similar importance to these fundamental research and development efforts, is the design and testing of pilot-scale processes to demonstrate the feasibility of these technologies at relevant scales. To this end, the design, assembly, and testing of a two-stage pilot-scale reverse water gas shift/ Fischer-Tropsch (RWGS/FT) reactor, capable of generating up to three liters of liquid hydrocarbon products a day using only CO_2 and H_2 feedstocks, was recently executed. The contents of this Memorandum Report describe the design specifications of the pilot-scale reactor, along with preliminary results of the initial commissioning of the FT portion of this reactor. Initial testing of the FT reactor utilized a closed loop recycle, with the tail gas of the FT reactor recycled back to the inlet of the FT reactor at a 20:1 ratio. The reactor bed was operated at 210 °C, with a reagent feed of syngas flowed at 2 SLPM (H_2:CO ratio of 1.8). This resulted in CO and H_2 conversions > 80%, with a methane selectivity on the order of 8 to 12%, and yielded a hydrocarbon product distribution peak of C9 or greater. These results meet the expectations and targets that were established for the FT portion of this reactor. The results of this initial commissioning are interpreted and used to inform recommendations for further testing and evaluation of the two-stage WRGS/FT reactor.

1.0 Background

The orchestration of sustained liquid fuel delivery to the Warfighter represents a tremendous logistical operation and potential strategic vulnerability.[1,2] Accordingly, technologies capable of generating "drop-in ready" fuel at or near the point of use, have been identified as an important focus area.[3]

CO_2 represents an abundant carbon feedstock that is accessible from practically any location on the planet. In particular, the surface of the World's oceans offers a rich supply of CO_2, with concentrations on the order of 100 mg L^{-1} (nearly 140 times greater than the volumetric concentration of CO_2 in the atmosphere).[4] With this in mind, NRL has developed and patented a process and apparatus for the simultaneous extraction of CO_2 and production of H_2 from seawater.[5–10] These gases can be subsequently used as the exclusive feedstocks for the thermocatalytically driven hydrogenation of CO_2 to longer chain liquid hydrocarbons, which could have application in the generation of "drop-in ready" liquid fuels.[11–16]

The thermocatalytically driven hydrogenation of CO_2 to hydrocarbon products requires the initial activation of the energetically stable CO_2 molecule to an intermediate species that can subsequently be hydrogenated and oligomerized. One of the most commonly proposed methods for this initial activation

of CO_2, is to generate carbon monoxide (CO) as in intermediate C_1 species through the reverse water gas shift (RWGS) reaction (Reaction 1).[17–21]

$$(1) \qquad CO_2 + H_2 \rightarrow CO + H_2O, \Delta_R H_{573\ K} = 38\ kJ\ mol^{-1}$$
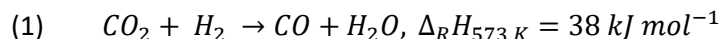
The effluent CO can then be hydrogenated to longer-chain hydrocarbons through the traditional Fischer-Tropsch (FT) synthesis (Reaction 2), which has been performed commercially for nearly a century.[22]

$$(2) \qquad nCO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O, \Delta_R H_{573\ K}, = -166\ kJ\ (mol\ CO)^{-1}$$
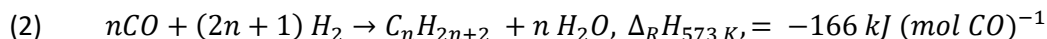
Direct hydrogenation of CO_2 to longer-chain hydrocarbons (CO_2-FTS) can be achieved when both reactions 1 and 2 are performed in tandem within a single reactor, however, kinetic and thermodynamic differences between the two reactions limit the overall efficiency of this one-step process.[15,23] Alternatively, greater overall conversions can be achieved when both reactions are performed independently, under optimized conditions.

To demonstrate the feasibility of CO_2 hydrogenation at relevant scales, a pilot-scale, two stage reactor skid was assembled and tested. The reactor represents the largest, and most mature processes for NRL's "CO_2 to Fuel" program to date, and consists of two, 4 ft. tall reactors connected in series, independently dedicated to the RWGS and FT reactions, respectively. The FTS portion of this reactor utilized a commercially purchased cobalt based catalyst. In this work, we describe the reactor design, commissioning and results of initial testing of the FT portion of this reactor.

2.0 Objective

The objective of this work is to describe the design, assembly, and initial testing results for a pilot-scale reactor skid capable of generating liquid hydrocarbons from CO_2 and H_2 feedstocks. These initial tests verified the performance of the FT portion of the reactor, and bypassed the RWGS reactor. Successful commissioning of the FT portion of this reactor will be defined by the following criteria: > 80% CO and H_2 conversion, > 76% C5+ product selectivity, > 67% C5+ yield, and product distribution C_n peak of C9 or greater. The results of the initial commissioning of the pilot-scale skid are discussed, rationalized, and used to make informed recommendations regarding future reactor tests and modifications.

3.0 Experimental

3.1 Reactor Skid

The 2-stage RWGS/FT reactor skid was assembled by OxEon Energy, and tested at their facility in Salt Lake City, Utah, US, under contract #N00014-20-P-1004. A schematic and images of the reactor can be found in Figures 1 and 2, respectively. Previous FT catalyst testing in an older reactor was conducted in May-July of 2020. The results from this previous testing informed the current 2-stage RWGS/FT reactor design, commissioning, and operations.

Leak checks were conducted by pressurizing the system with nitrogen in July 2021, before addition of catalyst. The initial commissioning of the reactor aimed to demonstrate effective performance of the FT

reactor independently. To evaluate the FT portion of the reactor, the RWGS reactor was left empty and not charged with catalyst. Typical loading of the FT catalyst consisted of roughly 900 g. Preheat conditions were optimized so that syngas enters the catalyst bed at reaction temperature. The reactor is equipped with a 6-point thermocouple profile probe installed along the centerline of the FT reactor. This temperature profile was followed through time, along with the oil heater temperature.

Syngas for the inlet stream was generated in house at the test facility using natural gas processed through an arc plasma reformer. Reactor inlet composition and product streams were characterized by gas chromatography using a combination of GCs (Inficon 3000 MicroGC and Bruker 456), and liquid hydrocarbon product distribution was measured using a Bruker 436 GC configured for simulated distillation.

The syngas entering the reactor was preheated to match the temperature of the reactor bed. Preheating of the syngas in this way maximizes the per pass conversion of the catalyst bed and makes for a more uniform product distribution. Methane make is strongly tied to the maximum temperature in the catalyst bed, with higher temperatures driving the product distributions toward a greater fraction of methane. Reaction rate is also a function of temperature, such that cold zones don't contribute strongly to CO conversion. With the syngas entering the bed at the target reactor temperature, the full bed was able to function at the desired temperature yielding good conversion while minimizing the peak temperature in the bed.

Catalyst bed temperatures were controlled tightly by deliberate adjustment of the temperature of the heating oil in the jacket around the reactor. A range of temperatures were initially explored by slowly ramping the oil heater setpoint up and down. The best results were obtained setting the oil heater at 210 ℃. Higher temperatures strongly increased methane selectivity, while dropping the temperature just 3 ℃ to 207 ℃ allowed wax to deposit too quickly on the catalyst, resulting in large drops in CO and H2 conversion. Unless otherwise stated, for the data described within this manuscript, the oil heater setpoint remained at 210 ℃.

Real-time data analysis was performed using a Visual Basic Application (VBA) code within Excel so that CO & H_2 conversion, and product selectivities could be evaluated in real-time.
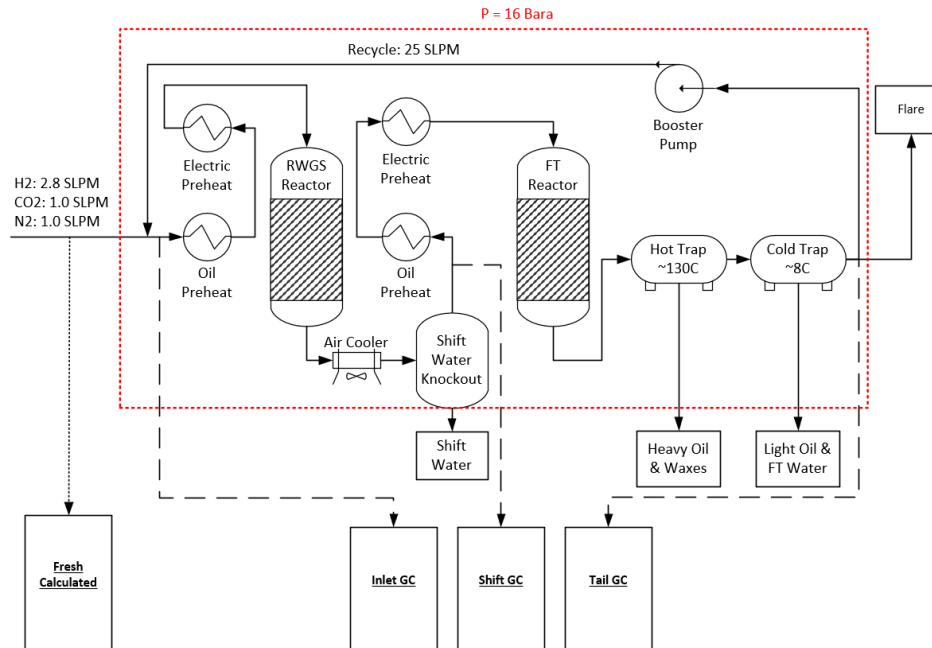
Figure 1: Diagram describing the primary components of the 2-stage FT/RWGS pilot-scale reactor skid, and the positions used for gas sampling

Figure 2. Image of the assembled 2-stage RWGS/FT pilot-scale reactor skid

3.2 FT Catalyst Details

Two cobalt-ruthenium based catalysts supported on alumina were purchased from Verdis Synthetic Fuels and ESM, respectively, and tested as FT catalysts in the 2-stage pilot-scale reactor skid. No significant differences were observed in the performance of these two catalysts. Unless otherwise noted, all data described in this manuscript pertains to the ESM catalyst. FT catalysts were added to the FT reactor along with silicon carbide as a diluent to improve thermal conductivity.

Pretreatment of the FTS portion of the reactor consisted of flowing a syngas blend (roughly 2:1 H_2/CO) over the catalyst bed overnight at 165 °C at a total flow rate of 2 SLPM. The reactor was then heated to an operating temperature of 210 °C under identical gas flow. These temperatures and flow rates were maintained throughout testing, as parameters were varied and data was collected.

4.0 Results and Discussion

4.1 FT Reactor Optimization

To identify conditions that would allow the FT system to reach the required performance, a variety of experimental parameters were evaluated including reactor total pressure, temperature, syngas pre-heat, reactor temperature uniformity, fresh feed flow rate, recycle ratio, and H_2/CO ratio. The temperature, H_2/CO ratio, and recycle ratio were found to be the most significant parameters to achieve low methane selectivity and the desired hydrocarbon distribution with a product distribution peak of C_9 or greater.

To improve total CO conversion and product yields, a closed loop recycling process was employed to reintroduce a portion of the FT tail gas back to the inlet of the FT reactor. The recycle of tail gas to the reactor feed was 7:1 in previous testing. To study the effect of recycle ratio on methane selectivity, the recycle ratio was varied over a several-day period, and it was determined that a recycle ratio of 20:1 maximized metrics on this system. In this case increasing the recycle ratio to 20:1 lowered the methane selectivity by about 1.5%.

The H_2/CO ratio was varied from between 2.0-2.1 in previous testing to as low as 1.7-1.8 in recent testing. By varying the ratio to 1.7, the methane selectivity dropped by over 7%. However, this negatively affected the CO conversion rate. Recognizing that CO was acting as the excess reactant, the H_2/CO ratio was increased to a nominal 1.8, with the CO conversion rate climbing back above the desired 80% target, while the methane selectivity was still significantly reduced from the start of this study.

As described in Section 3.1, the temperature of the heating oil surrounding the FT reactor was maintained between 208 - 210 °C over the course of this work. A series of thermocouples were applied throughout the FT reactor bed to measure the temperature profile across the catalyst bed. This temperature profile is plotted against time for the first three days of commissioning in Figure 3. An image describing the thermocouple naming scheme and location is also provided. This temperature gradient is to be expected of the exothermic FT reaction, with the reaction rate being highest near the inlet of the reactor. The

consistent and relatively narrow temperature distribution demonstrates the effective control of reaction conditions that can be achieved with this reactor configuration and feed gas preheating.
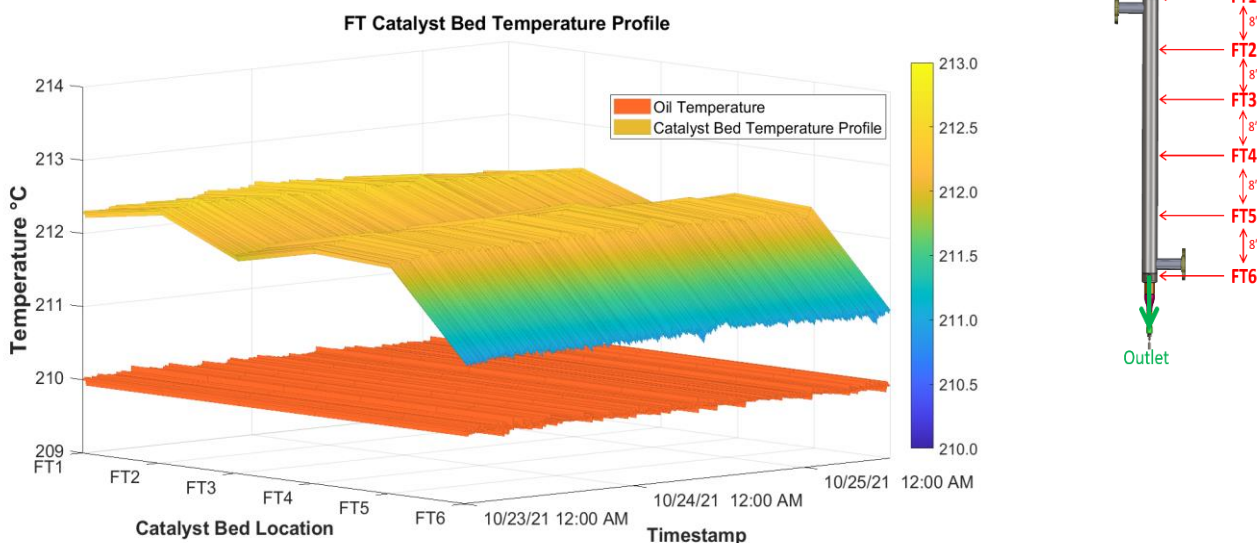

Figure 3. FT Catalyst Bed Temperature Profile

After exploring the individual operating condition sensitivities, the catalyst was conditioned with nitrogen prior to commissioning. This catalyst rejuvenation involved flowing dry nitrogen over the catalyst at a higher temperature and lower pressure to strip wax buildup in the catalyst pores. Such catalyst rejuvenation is an accepted practice, the interval of which depends on the nature of the catalyst and the operating conditions it has seen. After rejuvenation in flowing nitrogen, the system was then run at the optimized conditions detailed below.

4.2 FT Reactor Commissioning

The initial commissioning of the FT portion of this reactor began October 21, 2021 and continued through October 29, 2021. The initial conditions chosen to demonstrate successful commissioning of the FT reactor were applied as follows: H2/CO ratio of 1.79, recycle of 20:1, total syngas fresh feed rate of 2.0 SLPM, cooling jacket oil temperature of 210 °C, and inlet gas pressure of 16 bar.

After this initial period, testing was continued but with reduced cooling jacket oil temperature of 208 °C through November 3, 2021, to try to further improve FT performance. This resulted in slightly inferior performance as compared to the original conditions tested from October 21, 2021 – October 29, 2021, due to a rise in methane selectivity likely caused by a buildup of wax on the catalyst due to the lower temperatures of operation and higher production of wax, overall.

The product carbon number distribution was measured by a gas chromatography (GC) technique known as simulated distillation (SimDis) in which the carbon chain length distribution of mixed oil-wax samples is measured. The SimDis data from eight daily product collections, along with that of a wax sample for

reference, are shown in Figure 4. A vertical red line at C9 is included for reference as the nominal target location of the product distribution peak. All the SimDis curves show a maximum at or above C9.
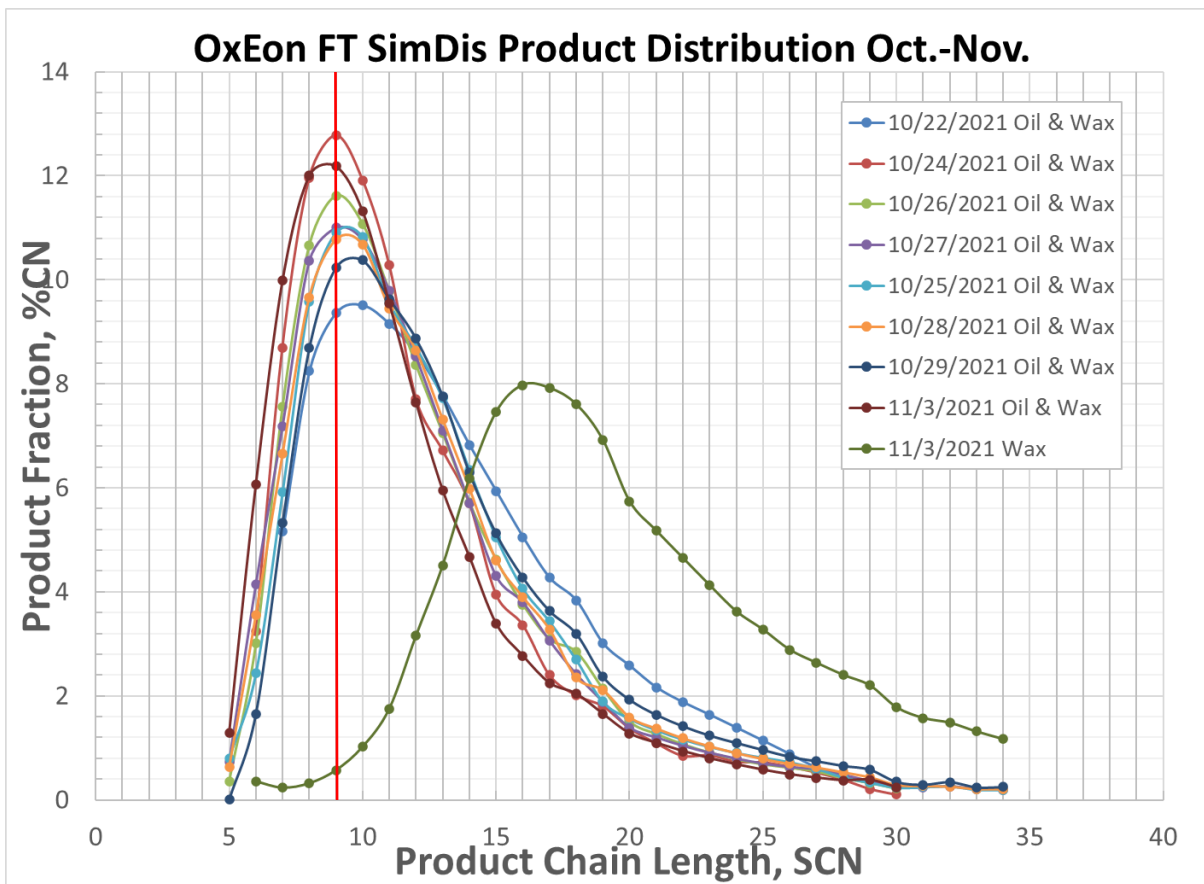

OxEon FT SimDis Product Distribution Oct.-Nov.

Legend:
- 10/22/2021 Oil & Wax
- 10/24/2021 Oil & Wax
- 10/26/2021 Oil & Wax
- 10/27/2021 Oil & Wax
- 10/25/2021 Oil & Wax
- 10/28/2021 Oil & Wax
- 10/29/2021 Oil & Wax
- 11/3/2021 Oil & Wax
- 11/3/2021 Wax

X-axis: Product Chain Length, SCN
Y-axis: Product Fraction, %CN

Figure 4. SimDis Product Distribution (C9 shown with red vertical line)

Time history charts of conversion and selectivity through the initial commissioning period are shown in Figure 5 and the overall results of this initial commissioning are summarized in Table 1 below. The CO and H_2 conversion were > 80% for the entirety of the test. The dips in conversion at regular intervals are due to product collection, as the product collection process is driven by syngas pressure which slightly depressurizes the system. The CO selectivity to C5+ relative to the metric of 76% selectivity is plotted in the upper trace of the 2nd graph, the horizontal line showing the 76% level. The product of CO conversion and selectivity to C5+ is plotted below, with the horizontal line referencing the 67% requirement value. As described previously, the increase in CH_4 selectivity after Oct. 31, 2021 was likely due to the reduced temperature of the catalyst bed, leading buildup of wax on the catalyst.
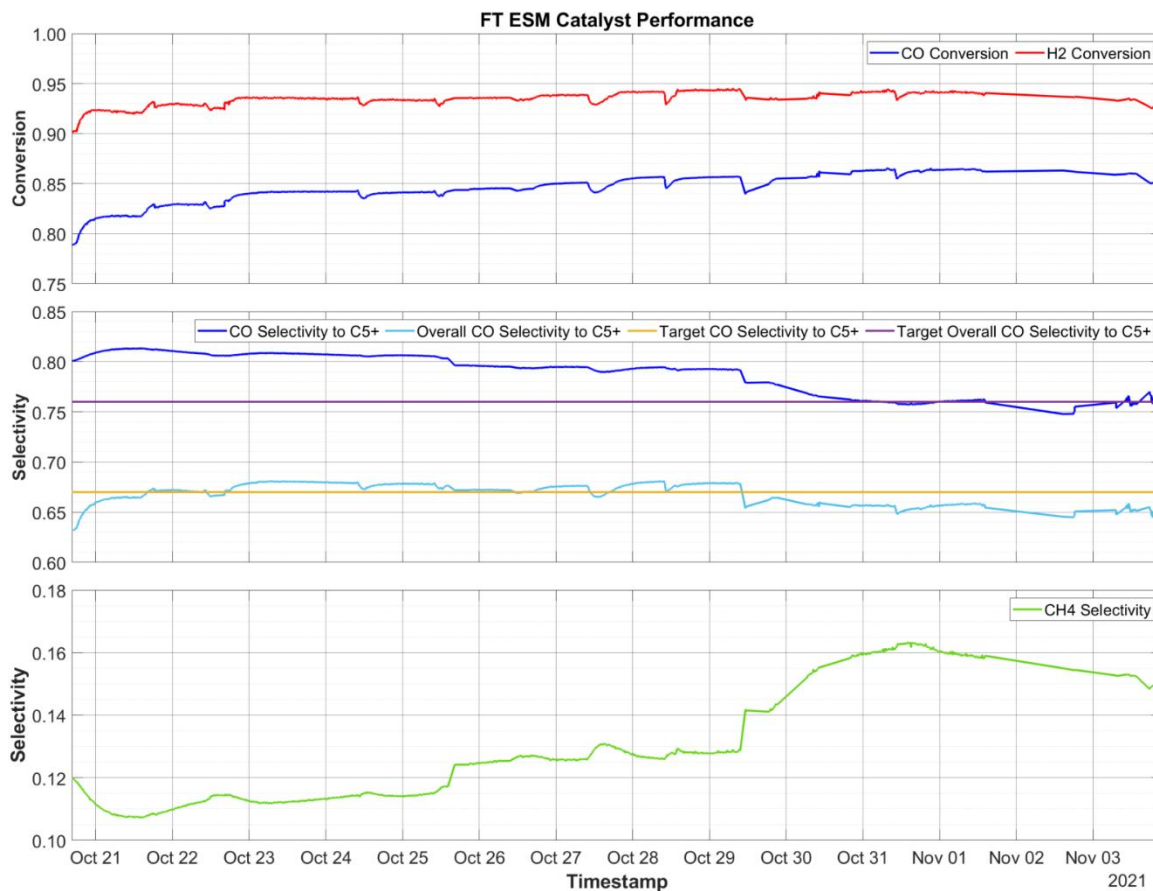
Figure 5. FT Catalyst Performance from October 21, 2021 to November 3, 2021

Table 1. Fischer Tropsch System Test Results

Criteria	Target	Averages 10/21/21-10/29/21	Averages 10/30/21-11/3/21	Overall Averages 10/21/21-11/3/21
CO Conversion	>80%	84.2%	86.1%	84.9%
H_2 Conversion	>80%	93.4%	93.8%	93.6%
CO Selectivity to C5+	>76%	80.2%	75.9%	78.6%
Overall CO to C5+ Yield	>67%	67.4%	65.4%	66.7%
Mass Carbon Balance	>92%	95.8%		
Product Distribution C_n peak	>C9	C9-C10		C9-C10

5.0 Conclusions

Successful commissioning of the FT portion of the 2-stage pilot-scale RWGS/FT reactor was achieved, and the target goals of 80% CO and H_2 conversion, 76% C5+ selectivity, 67% C5+ yield, and product distribution C_n peak of C9 or greater, were all met or surpassed. Stable catalyst bed temperatures with a narrow temperature distribution were achieved by preheating the inlet gasses and diluting the catalyst bed with silicon carbide. Increasing the recycle ratio to 20 allowed for improved CO conversion and reduced CH_4 selectivites. For the cobalt based FT catalyst used in this work, temperatures of 210 °C were found to yield the most ideal results.

6.0 Recommendations

From the results described within this report, we offer the following recommendations in regard to future testing and demonstration of the 2-stage pilot-scale RWGS/FT reactor:

1. While the FT catalyst used in this work was capable of generating results that met the target goals, a different catalyst with reduced methane selectivity could further improve overall FT performance and longevity. A new catalyst with larger mean pore diameter, smaller extrudate diameter and greater concentration of ruthenium dopants has been identified, and is recommended for future FT demonstrations.

2. With the successful commissioning of the FT portion of this reactor, we recommend similar optimization and commissioning of the RWGS portion of this reactor independently. Once both FT and RWGS portions of the reactor have been successfully demonstrated independently, the 2-stage reactor should be commissioned for demonstration of CO_2 hydrogenation to hydrocarbon products by coupling of the two reactors in series.

7.0 Acknowledgements

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