Indirect Liquefaction of Coal-Biomass Mixture for Production of Jet Fuel with High Productivity and Selectivity

Final Scientific/Technical Report

Reporting Period Start Date: 10/01/2014

Reporting Period End Date: 12/31/2017

Santosh K Gangwal and Kevin McCabe

March 2018

DOE Award Number: DE-FE0024083

Southern Research
5201 International Drive, Durham, NC 27712

Disclaimer

Table of Contents

Abstract

Coal to liquids (CTL) and coal-biomass to liquids (CBTL) processes were advanced by testing and demonstrating Southern Research's sulfur tolerant nickel-based reforming catalyst and Chevron's highly selective and active cobalt-zeolite hybrid Fischer-Tropsch (FT) catalyst to clean, upgrade and convert syngas predominantly to jet fuel range hydrocarbon liquids, thereby minimizing expensive cleanup and wax upgrading operations. The National Carbon Capture Center (NCCC) operated by Southern Company (SC) at Wilsonville, Alabama served as the host site for the gasifier slip-stream and simulated syngas testing/demonstration.

Reformer testing was performed to (1) reform tar and light hydrocarbons, (2) decompose ammonia in the presence H_2S, and (3) deliver the required H_2 to CO ratio for FT synthesis. FT Testing was performed to produce a product primarily containing C5-C20 liquid hydrocarbons and no C21+ waxy hydrocarbons with productivity greater than 0.7 gC5+/g catalyst/h, and at least 70% diesel and jet fuel range (C8-C20) hydrocarbon selectivity in the liquid product. A novel heat-exchange reactor system was employed to enable the use of the highly active FT catalyst and larger diameter reactors that results in cost reduction for commercial systems.

Following laboratory development and testing, SR's laboratory reformer was modified to operate in a Class 1 Div. 2 environment, installed at NCCC, and successfully tested for 125 hours using raw syngas. The catalyst demonstrated near equilibrium reforming (~90%) of methane and complete reforming/decomposition of tar and ammonia in the presence of up to 380 ppm H_2S.

For FT synthesis, SR modified and utilized a bench scale skid mounted FT reactor system (SR-CBTL test rig) that was fully integrated with a slip stream from SC/NCCC's transport gasifier (TRIG). The test-rig developed in a previous project (DE-FE0010231) was modified to receive up to 7.5 lb/h raw syngas augmented with bottled syngas to adjust the H_2/CO molar ratio to 2, clean it to cobalt FT catalyst specifications, and produce liquid FT products at the design capacity of up to 6 L/day. Promising Chevron catalyst candidates in the size range from 70-200 µm were loaded onto SR's 2-inch ID and 4-inch ID bench-scale reactors utilizing IntraMicron's micro-fiber entrapped catalyst (MFEC) heat exchange reactor technology.

During 2 test campaigns, the FT reactors were successfully demonstrated at NCCC using syngas for ~420 hours. The catalyst did not experience deactivation during the tests. SR's thermo-syphon heat removal system maintained reactor operating temperature along the axis to within ±4 °C. The experiments gave a steady catalyst productivity of 0.7-0.8 g/g catalyst/h, liquid hydrocarbon selectivity of ~75%, and diesel and jet fuel range hydrocarbon selectivity in the liquid product as high as 85% depending on process conditions.

A preliminary techno-economic evaluation showed that the SR technology-based 50,000 bpd plant had a 10 % lower total plant cost compared to a conventional slurry reactor based plant. Furthermore, because of the modular nature of the SR technology, it was shown that the total plant cost advantage increases to >35 % as the plant is scaled down to 1000 bpd.

Acknowledgements

The support for this project by the US Department of Energy/ National Energy Technology Laboratory (DOE/NETL), Southern Research (SR), Chevron, Precision Combustion Inc. (PCI) and Intramicron under Cooperative Agreement DE-FE0024083 is gratefully acknowledged. As the NETL project manager, Mr. John Rockey and Dr. Venkat Venkataraman provided suggestions and guidance throughout the project.

The Chevron catalyst and associated technical support throughout the project was provided by Drs. Kandaswamy Jothimurugesan (Jothi) and Robert (Bob) Saxton of Chevron Energy Technology Company in Richmond, Ca. The catalyst was provided free of cost to the project by Chevron. Drs. Paul Dimick, Hongyun Yang and Bruce Tatarchuk of Intramicron packed the SR reactors with the MFEC media and provided support as needed during the project.

PCI conducted lab-scale reformer testing and provided noble metal-based reforming catalyst supported on their patented metal Microlith for simulated lab-scale testing. John Carroll, John Socha, Patrick Crossley, Bob Lambert, Scott Machovec, Barry Shirley, Frank Morton and several other Southern Company/NCCC staff and contractors at Wilsonville helped with the design hazard review, modification of the SR reformer skid and CBTL test-rig and its connection to their TRIG gasifier slipstream and bottled gases, and provided strong support during operation of the system, and throughout the project. Gerry Choi of Nexant provided technical support for the TEA and LCA.

The authors gratefully acknowledges the Southern Research Energy and Environment Division team on this project consisting of Senior Staff, Engineers, and Chemists including Andrew Lucero, August Meng, Patrick Woolcock, Butch Crews, Brittany Basu, Brandon Cline, Chris Cagle, Kelly Mastro, and Zora Govaderica..

Executive Summary

Liquid transportation fuels from coal and biomass have the potential to impact the domestic transportation fuel markets. In the current scenario of low cost natural gas and liquid hydrocarbons from shale fracking operations, small distributed-scale coal to liquids (CTL) and coal-biomass to liquids (CBTL) plants (<1000 barrels/day) at site specific locations such as Alaska, Hawaii, military bases, and rural areas are attractive. In particular the lower risk from smaller investments compared to large scale CBTL plants that can cost billions of dollars can significantly encourage the development of these small-scale distributed plants.

However, further performance improvements and cost reductions are needed to eliminate the size penalties associated with down scaling. Modular factory built plants with standardized designs and use of advanced gasification, cleanup and synthesis technologies to eliminate hard to handle byproducts such as tar, waste water, and waxes have the potential for the needed cost reductions. Cost reductions/efficiency improvements are needed in every major/minor unit operation associated with the CTL process to increase its market acceptance and for the process to realize its full potential.

Using both simulated syngas and raw syngas slip stream from the Southern Company/National Carbon Capture Center (SR/NCCC) TRIG gasifier, this project aims to demonstrate cost reductions in two key CTL unit operations: (1) Syngas upgrading by Auto-thermal reforming (ATR) (2) Fischer-Tropsch (FT) Synthesis. The technologies associated with these unit operations were initially developed under two previous DOE projects. A typical commercial embodiment including the syngas upgrading and FT synthesis technologies is shown in Figure ES-1.

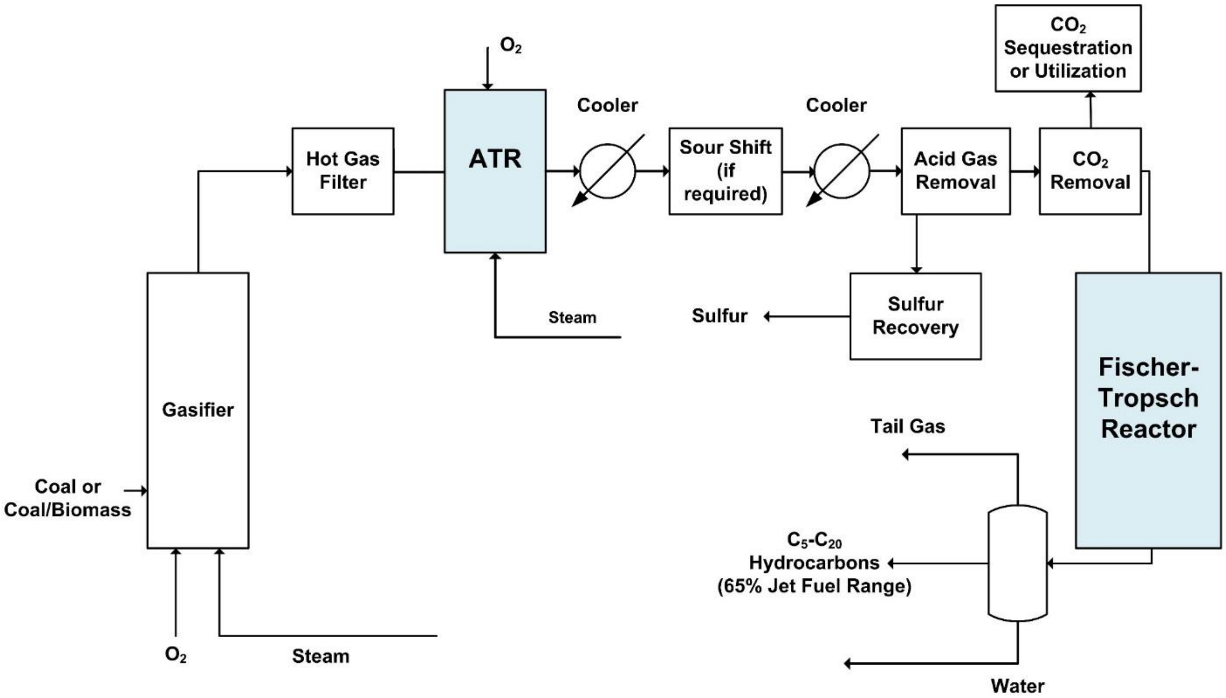


Figure ES-1. CTL commercial embodiment with proposed reformer and FT Technologies

Syngas Upgrading using ATR

Southern Research (SR) had previously developed a sulfur-resistant nickel reforming catalyst under cooperative agreement with DOE (DE-FE0012054). This catalyst operates in the presence of high levels of H_2S and has the potential to combine the following separate steps into a single unit operation (1) reforming of tar and light hydrocarbons, (2) decomposition of ammonia in the presence H_2S, and (3) delivery of the required H_2 to CO ratio syngas for FT synthesis. Laboratory tests with up to 500 ppmv sulfur using simulated TRIG and Lurgi gasifier gases were conducted to demonstrate the performance and durability of the catalyst.

This catalyst was scaled up for field testing at NCCC in this project. SR modified their reformer for Class 1 Division 2 electrical code, and transported and installed it on the gasifier syngas slipstream at NCCC. The gasifier syngas volumetric percent composition for the reforming tests on dry basis was: H2-7.7; CO-8.6; CO2-11.1; CH4-1.1; H2S+COS-0.038; N2-balance. The test was run for 125 hours at 205 psig and 850-900°C at a space velocity of 8,000 scc/(g catalyst.h) with 15 to 30 volume % steam.

Results indicated high reforming of methane (up to 90%) and complete reforming of tar and ammonia in the presence of 380 ppm H_2S+COS. The experiments demonstrated a strong effect of temperature on reforming catalyst performance as a temperature drop of 50°C dropped methane conversion from ~90% to ~60%, but conversion quickly recovered when the temperature was increased again. SR also demonstrated control of the H_2 to CO ratio leaving the reformer at 2:1 by manipulating the water (steam) flow to the reactor (thus delivering the ability to eliminate downstream requirement of water gas shift. The catalyst did not indicate any sign of deactivation and the test was considered a success, delivering on tar and ammonia destruction, and increasing the hydrogen to the required H2/CO ratio.

Fischer-Tropsch

SR previously worked with Chevron and Intramicron to also develop a selective FT synthesis technology under cooperative agreement with DOE (DE-FE0010231). A bench-scale skid-mounted reactor system was installed at NCCC for this work. The selective FT technology uses Chevron's highly selective and active cobalt-zeolite hybrid catalysts in particulate form (70-200 μm) loaded on to Intramicron's thermally conductive copper microfiber called microfiber entrapped catalyst (MFEC) in fixed-bed reactors equipped with a thermal syphon heat removal system designed by SR. High thermal conductivity and small catalyst particles used in MFEC coupled with superior heat management using a thermal syphon system allows rapid heat removal from the catalyst to the reactor wall and from the reactor wall to the jacketed boiling water.

This system has the ability to maintain nearly isothermal conditions for the highly exothermic FT reaction process even while using Chevron's highly active catalysts. The Co-zeolite hybrid catalyst coupled with superior heat management using MFEC and thermal syphon results in predominantly C5-C20 liquid hydrocarbon production with high productivity and selectivity. Furthermore, the system eliminates the production of light gases (C1-C4) and hard to handle solid waxes, thereby minimizing upgrading and tail gas recycle/disposal requirements resulting in cost effective production of the desired liquid hydrocarbons in the C5-C20 diesel and jet fuel range.

In this project, following extensive laboratory screening tests of Chevron Co-zeolite catalysts and required modifications of the bench-scale system at NCCC, the best FT catalyst was selected and two FT field tests were carried out using syngas at NCCC in conjunction with their gasification campaigns during the fall of 2015 and the spring of 2017. The tests were conducted at a range of conditions shown in Table ES-1.

Table ES-1. Nominal Experimental Conditions for FT Field Tests

Syngas composition	H2/CO = 2 with 15-50 % N2 diluent
Reactor diameter	2 inch and 4 inch
Catalyst loaded	300 to 500 g
Pressure	200-280 psig
Temperature	240-250
Space velocity	11,000 to 15,000 scc/(g catalyst.h)

Fall 2015 Test: In this test, the 2 inch FT reactor loaded with 300 g of the 100-200 μm FT catalyst was run at conditions provided previously in Table 1. The CO conversion, methane selectivity and C1-C4 selectivity are shown in Figure 34. The liquid selectivity by difference stayed very constant throughout the run at >77 %. Liquid productivities greater than 0.7 g/g cat/h as well as >65% jet fuel range hydrocarbons were consistently achieved. Both are project objectives thus the test was considered a success.

Spring 2017 Test: This test was conducted in a 4.0 inch FT reactor loaded with 450 g of the more active 60-150 μm size FT catalyst. Results indicated similar catalyst productivity and liquid hydrocarbon selectivity but higher jet fuel selectivity than the previous test. Liquid hydrocarbon distribution measurements for 2017 samples indicated the jet fuel range hydrocarbon selectivity was ~75% with almost nothing detected above C22. Our lab measured up to 35% olefins in these samples, but ASTM specifications for jet fuel limit olefins to less than 1%. SR developed a simple process to reduce olefins down to the required ASTM specifications while further increasing the jet fuel selectivity to 87 %, which significantly exceeded the project objective.

Techno-economic Evalaution

Economic performance of 1000 to 50,000 bpd plants utilizing the SR technologies was compared with a baseline coal-to-liquids plant (CTL) with carbon capture rates of more than 90%. The baseline plant was taken from a Nexant report to SR under DOE Cooperative Agreement DE-FE0012054. The capital costs generated for the tubular FT reactors were based on the estimates developed by Prakash and Bendale [DOE/PC/89870-T1 (Suppl.)(DE92011812)].

The comparison of the total plant cost for the conventional case and the cases employing advanced SR technologies is shown in Table ES-2. SR is presently developing a modular gasification system (under DOE Cooperative Agreement DE-FE0031531) that would be well suited to the selective SR coal to jet fuel/diesel technology developed in this project at small scales of about 1000-5000 bpd or even smaller. Preliminary TEA results (Table ES-2) indicate that the total plant cost based on advanced technologies including SR's modular gasifier and selective FT can significantly reduce the cost of indirect liquefaction.

Table ES-2. Comparison of Total Plant Cost (TPC)—Conventional FT vs Advanced Modular system with SR FT and Gasifier

Plant Size	Conventional FT (Million $)	Advanced SR ATR + Selective FT (Million $)	Advanced SR Selective FT and Modular Gasifier (Million $)	Percent total plant cost reduction
50,000 bpd	4,797	4,299		10.4
5000 bpd	1,205		827	31.4
1000 bpd	458.8		294.7	35.8

The costs in Table ES-2 are preliminary and scaled down from the 50,000 bpd costs by the six-tenth rule except where applicable. They are provided for comparative purpose only and only to illustrate the potential for lower costs as we scale down. It is to be noted that the percent capital cost reduction for the 1000 bpd plant is actually higher than the 5000 bpd plant illustrating the advantages of factory built modular construction which is suitable for the small scale SR technology-based FT system developed in this project.

Conclusions

- Based on results of a slip stream test at NCCC, a sulfur-tolerant nickel-based reforming catalyst prepared by Southern Research was shown to reform light hydrocarbns, tar, and ammonia in the presence of high levels (380 ppmv) of H2S and COS. This catalyst outperformed noble metal-based catalysts at such high sulfur concentrations.
- In lab-scale tests, Chevron's Co-zeolite hybrid FT catalysts consistently performed at hydrocarbon productivities >0.7 g/g cat/h with very high durability and liquid selectivity >75 %. The jet fuel selectivity in the liquid was consistently >65 %
- Chevron catalysts in 70-200 micron range were successfully supported on IntraMicron MFEC packing in 2 inch and 4 inch diameter fixed bed reactors.
- The thermally conductive copper-based MFEC along with SR's thermal syphon system was able to maintain near isothermal FT reactor conditions in the 2 and 4 inch reactors by efficiently removing reaction heat.
- Based on a preliminary TEA, the SR advanced technologies developed in this project combined with other advanced technologies being developed has the potential to reduce capital costs over conventional FT-CTL technology by over 35 % in small modular plants smaller than 1000 bpd.

Recommendations

- The FT and ATR technologies have sufficiently advanced in this project and should be scaled up to pilot-scale demonstration of 5-20 bpd.
- Rigorous TEA should be conducted for small modular 100-500 bpd distributed plants using these technologies to evaluate the cost advantages of factory built small modular plant components

Introduction

Liquid transportation fuels from coal and biomass have the potential to impact the domestic transportation fuel markets. In the current scenario of low cost natural gas and liquid hydrocarbons from shale fracking operations, small distributed-scale coal to liquids (CTL) and coal-biomass to liquids (CBTL) plants (50-100 barrels/day) at site specific locations such as Alaska, Hawaii, military bases, and rural areas are attractive. In particular the lower risk from smaller investments compared to large scale CTL plants that can cost billions of dollars can significantly encourage the development of these small-scale distributed plants.

However, further performance improvements and cost reductions are needed to eliminate the size penalties associated with down scaling. Cost reductions/efficiency improvements are needed in every major/minor unit operation associated with the CTL process to increase its market acceptance and for the process to realize its full potential. Modular factory built plants with standardized designs and use of advanced gasification, cleanup and synthesis technologies to eliminate hard to handle byproducts such as tar, waste water, and waxes have the potential for the needed cost reductions.

This project aimed to demonstrate cost reductions in two CTL unit operations. First, Southern Research (SR) sulfur-resistant nickel reforming catalyst was demonstrated using SR's laboratory-scale reformer to clean and upgrade raw syngas. Second, Chevron's liquid-selective cobalt-zeolite hybrid Fischer-Tropsch (FT) catalyst loaded onto Intramicron microfiber copper packing was demonstrated to produce diesel and jet fuel from syngas. Reformer testing was performed to combine the following steps (1) reforming of tar and light hydrocarbons, (2) decomposition of ammonia in the presence H_2S, and (3) delivery of the required H_2 to CO ratio syngas for FT synthesis. FT Testing was performed to produce a product primarily containing C5-C20 liquid hydrocarbons and no C21+ waxy hydrocarbons. A novel heat-exchange reactor system was employed to enable the use of the highly active FT catalyst and larger diameter reactors that results in cost reduction for commercial systems.

The process envisioned based on these innovative operations reduces the number of syngas cleaning steps by destroying tars and reforming hydrocarbons before cooling the syngas, eliminates costly upgrading of wax produced, and reduces the height and number of FT reactor tubes, resulting in improved economics for CTL-based jet fuel production. This not only allows for CTL/CBTL to be cost competitive at typical large scales, but also makes it viable at smaller scales than previously possible.

Objectives

The purpose of this project is to reduce the costs and accelerate commercialization of coal to liquid (CTL) process for converting coal and coal-biomass mixtures to JP-8 jet fuel. The proposed process reduces the number of parasitic syngas cleaning steps by destroying tars and reforming hydrocarbons before cooling the syngas, eliminates costly upgrading of wax produced in conventional indirect liquefaction processes through the use of a multifunctional catalyst, and reduces the height and number of FT reactor tubes, resulting in improved economics for CTL-based jet fuel production. These improvements directly reduce capital costs of indirect CTL processes, resulting in significantly improved economics and cost competitiveness of CTL when compared to petroleum refining. This not only allows for CTL to be cost competitive at typical large scales, but also opens up opportunities for CTL to be viable at smaller scales than previously considered. The project will move the proposed pressurized, high temperature autothermal reformer (ATR) and FT technologies through bench scale development, with the goal to be ready for integrated pilot / demo scale efforts by the end of the project, accelerating potential commercialization of CTL and CBTL.

Specific objectives of the project are:

- Improve a compact, pressurized, high temperature autothermal reformer (ATR) to (1) reform tar and light hydrocarbons, (2) decompose ammonia in the presence H_2S and other coal syngas contaminants, and (3) deliver the required hydrogen (H_2) to carbon monoxide (CO) ratio for Fischer-Tropsch (FT) synthesis. The ATR research is focused on developing improved reforming catalysts for lower cost and improved durability in the presence of syngas contaminants, and demonstrating the performance of the ATR on both simulated syngas and gasifier-derived syngas;
- Test a second generation cobalt-zeolite hybrid Fischer-Tropsch catalyst that will produce hydrocarbon product containing at least 75 % C5-C20 hydrocarbons, no C21+ waxy hydrocarbons, productivity greater than 0.7 gC5+/gcat/h, and at least 65% jet fuel range (C8-C15) hydrocarbon selectivity in the C5 to C20 product;
- Incorporate a novel and efficient heat-exchange reactor system at bench scale to enable the use of the highly active and productive catalyst and larger diameter reactors;
- Examine the resulting product fuels according to JP-8 specifications (MIL-DTL-83133) and determine requirements to make them compatible with a jet fuel blend.
- Compare the economic performance of the integrated process to petroleum-based jet fuel with a techno-economic analysis (TEA)

Technology Background and Description

Coal is the most plausible fuel for replacing petroleum as a source of transportation fuels and has the potential to impact the domestic transportation fuel markets. As an alternative to oil, the US has an abundant supply of proven coal reserves that can last for over 200 years. The infrastructure for coal mining and supply is quite good because of its significant use to produce electricity. Coal is also competitive in price but increasing its use for converting coal to liquids (CTL) in addition to electricity is not sustainable due to increased CO_2 emissions that contribute to global climate change. Social acceptance is also an issue with increased coal use due to increased mining operations. Initial markets must be established to demonstrate impacts and acceptance of CTL fuels.

CTL has been commercially available via the gasification/Fischer-Tropsch (FT) route for over 60 years. However, there are no commercial plants that make fuels and chemicals from coal in the US (except Eastman's coal to chemicals complex in Kingsport). This is due to a combination of several reasons including economics with respect to petroleum and fracking operations, high capital costs involved, and environmental and social acceptance. Large scale CTL can be commercially deployed but will not be until large scale carbon capture and storage (CCS) is commercially demonstrated.

Further performance improvements and cost reductions in CTL plants are needed to reduce investor risk in these plants that can cost over a billion dollars. Although, several CTL projects were previously proposed for future development, none are currently in production in the U.S. Cost reductions/efficiency improvements are needed in every major/minor unit operation associated with the CTL process to increase its market acceptance and for the process to realize its full potential.

In the current scenario of low cost petroleum, natural gas and liquid hydrocarbons from shale fracking operations, small distributed-scale coal to liquids (CTL) and coal-biomass to liquids (CBTL) plants (<1000 barrels/day) at site specific locations such as Alaska, Hawaii, military bases, and rural areas are attractive. In particular the lower risk from smaller investments compared to large scale CTL plants that can cost billions of dollars can significantly encourage the development of these small-scale distributed plants. Modular factory built plants with standardized designs and use of advanced gasification, cleanup and synthesis technologies to eliminate hard to handle byproducts such as tar, waste water, and waxes have the potential for the needed cost reductions.

Using both simulated syngas and raw syngas slip stream from the Southern Company/National Carbon Capture Center (SR/NCCC) TRIG gasifier, this project aims to demonstrate cost reductions in two key CTL unit operations: (1) Syngas upgrading by Auto-thermal reforming (ATR) (2) Fischer-Tropsch (FT) Synthesis. The technologies associated with these unit operations were initially developed under two previous DOE projects. A typical commercial embodiment including the syngas upgrading and FT synthesis technologies is shown in Figure 1.

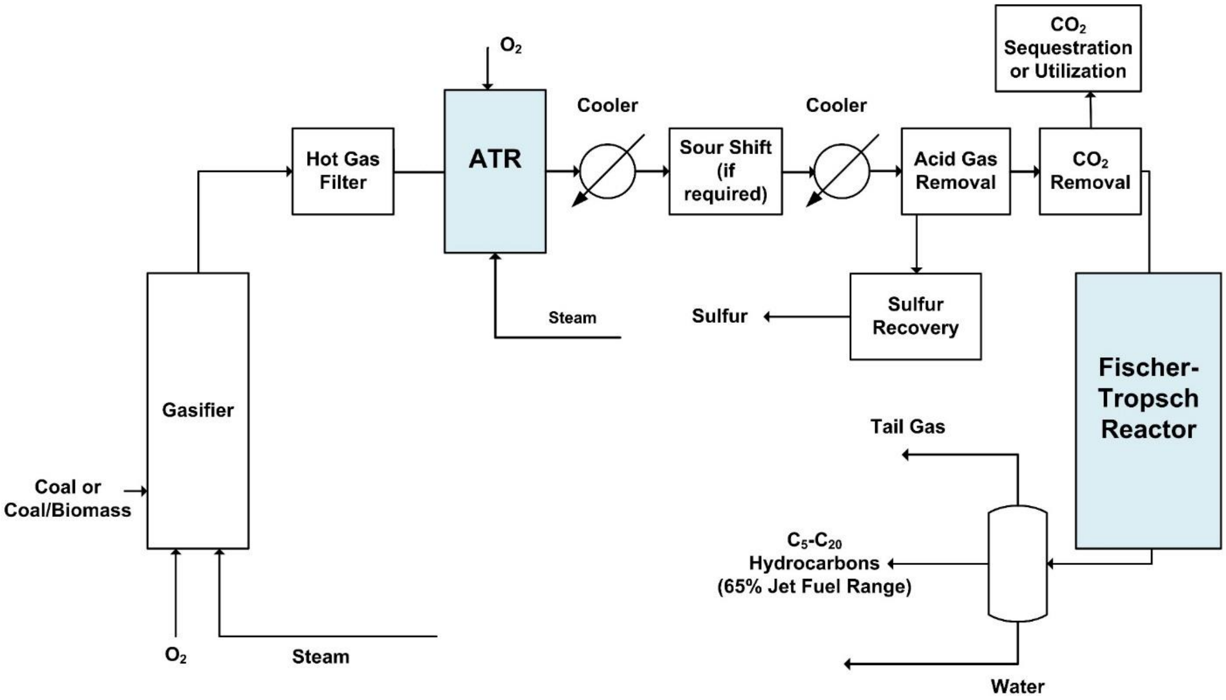


Figure 1. CTL commercial embodiment with proposed reformer and FT Technologies

As shown in Figure 1, hot syngas upgrading is conducted following particulate removal. The heat needed for the ATR can be obtained by recycling the FT tail gas. Background of the two technologies is briefly presented below.

Syngas Upgrading using ATR

Southern Research (SR) developed a sulfur-resistant nickel reforming catalyst under a previous cooperative agreement with DOE (DE-FE0012054). Complete details are available in the final report. This catalyst operates in the presence of high levels of H_2S and has the potential to combine the following separate steps into a single unit operation (1) reforming of tar and light hydrocarbons, (2) decomposition of ammonia in the presence H_2S, and (3) delivery of the required H_2 to CO ratio syngas for FT synthesis. Laboratory tests with up to 500 ppmv sulfur using simulated TRIG and Lurgi gasifier gases were conducted to demonstrate the performance and durability of the catalyst.

Examples of performance of the catalyst are provided in Figures 2 to 4. As seen in Figure 3, SR developed several Ni-based catalysts that showed significantly higher methane reforming and hydrogen increase compared to a commercial reforming catalyst and catalysts from literature. Furthermore the catalysts fully decomposed ammonia and reformed toluene, a tar simulant. The best performing SR catalysts were then tested for durability at various process conditions and in the presence of up to 500 ppmv of H2S. As shown in Figure 4, the catalyst showed methane reforming performance durability irrespective of pressure, space velocity, and gas composition. Finally Figure 5 demonstrates the catalyst's durability in the presence of 500 ppmv H2S at elevated pressure. Based on these results, and results from catalysts provided by PCI, this catalyst was selected for testing in this project with actual gasifier gas

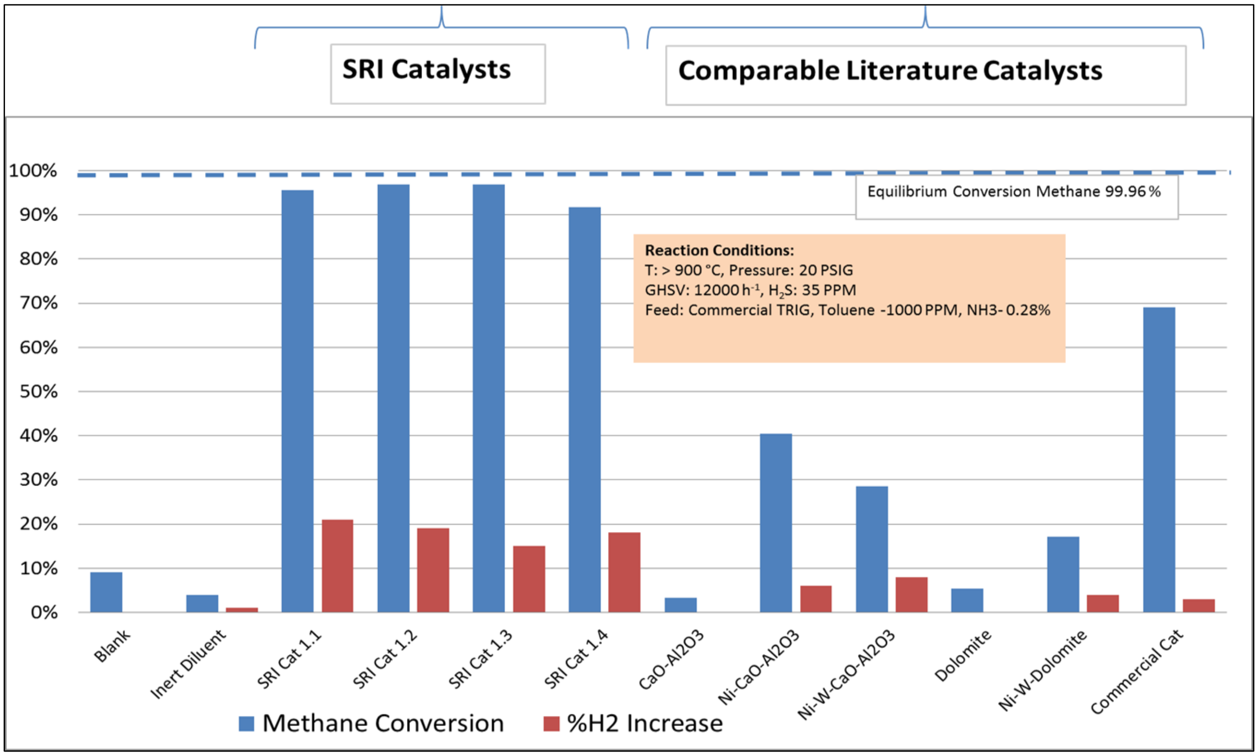


Figure 2. Performance of SR Ni catalysts compared to literature and commercial catalysts

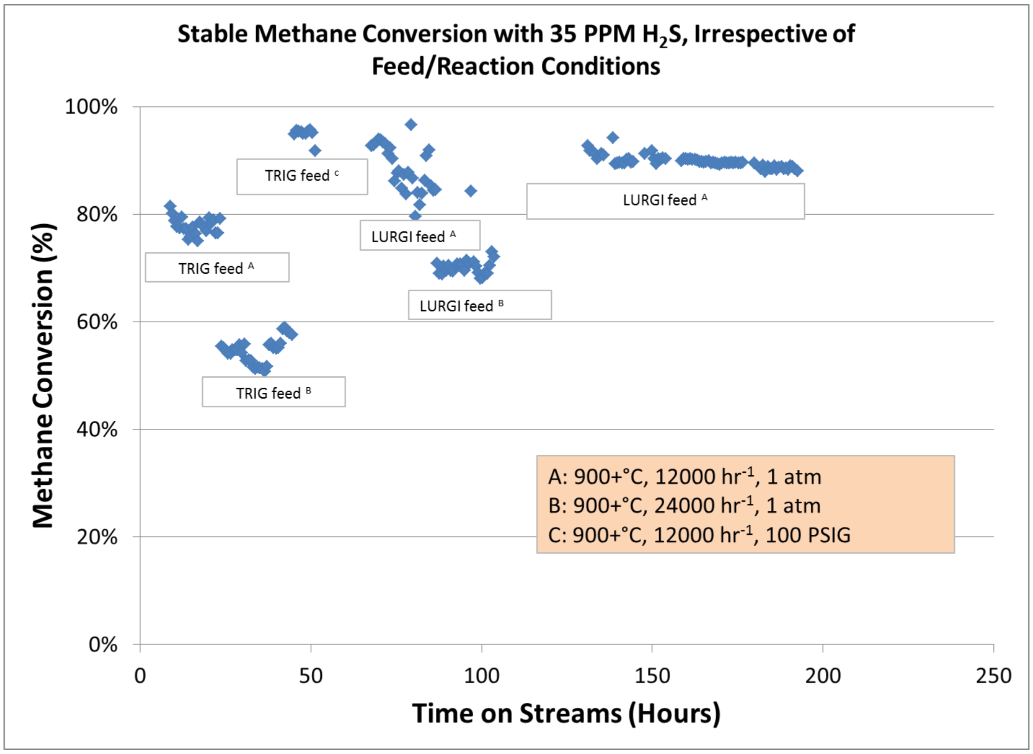


Figure 3. SR Ni catalyst durability in Lurgi and Trig gas feeds at various conditions

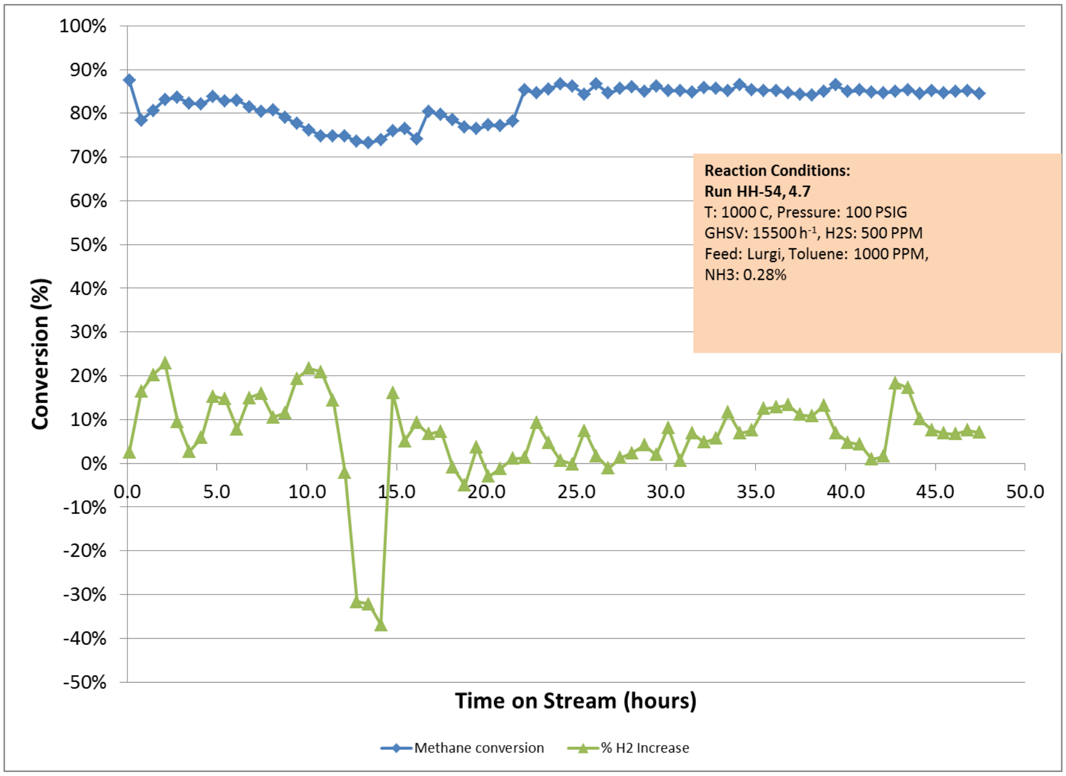


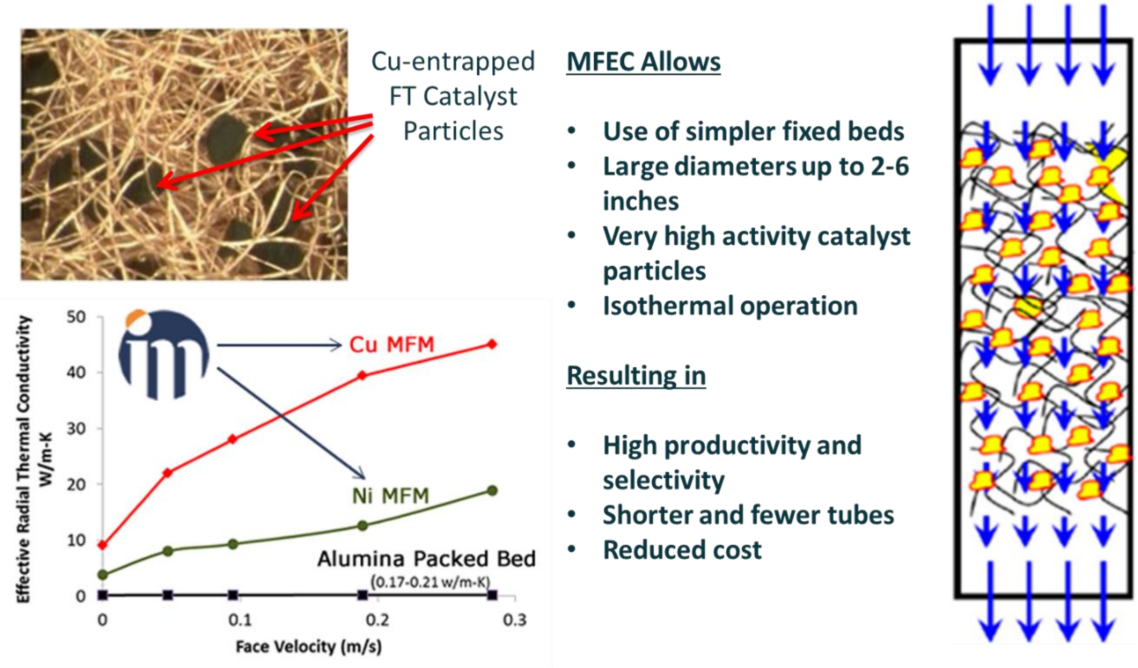
Figure 4. SR Ni reforming catalyst methane conversion durability in 500 ppm H_2S

FT Synthesis

SR worked with Chevron and Intramicron to also develop a selective FT synthesis technology under a previous cooperative agreement with DOE (DE-FE0010231). Complete details are available in the final report. The selective FT technology uses Chevron's highly selective and active cobalt-zeolite hybrid catalysts in particulate form (70-200 µm) loaded on to Intramicron's thermally conductive copper microfiber in 2 to 4inch diameter fixed-bed reactors equipped with a thermal syphon heat removal system designed by SR.

The FT reactor system with copper microfiber-entrapped catalyst (MFEC) has the ability to maintain nearly isothermal conditions for the highly exothermic FT reaction process even while using Chevron's highly active catalysts. The Co-zeolite hybrid catalyst coupled with superior heat management using MFEC and thermal syphon results in predominantly C5-C20 liquid hydrocarbon production with high productivity and selectivity. Furthermore, the system eliminates the production of light gases (C1-C4) and hard to handle solid waxes, thereby minimizing upgrading and tail gas recycle/disposal requirements resulting in cost effective production of the desired liquid hydrocarbons in the C5-C20 diesel and jet fuel range.

High thermal conductivity and small catalyst particles used in MFEC coupled with superior heat management using a thermal syphon system allows rapid heat removal from the catalyst to the reactor wall and from the reactor wall to the jacketed boiling water. The system advantages are illustrated in Figure 5.



MFEC Allows

- Use of simpler fixed beds
- Large diameters up to 2-6 inches
- Very high activity catalyst particles
- Isothermal operation

Resulting in

- High productivity and selectivity
- Shorter and fewer tubes
- Reduced cost

Figure 5. Advantages of MFEC due to superior heat management

FT tests were conducted using a 4 liter/day skid-mounted 2 inch diameter fixed-bed reactor system installed on a slipstream from the NCCC TRIG gasifier. A simplified flow diagram of the system is shown in Figure 6 and a photograph of the system is shown in Figure 7. The skid was designed with walk in and around capability and conformed to Class 1 Division 2 electrical code

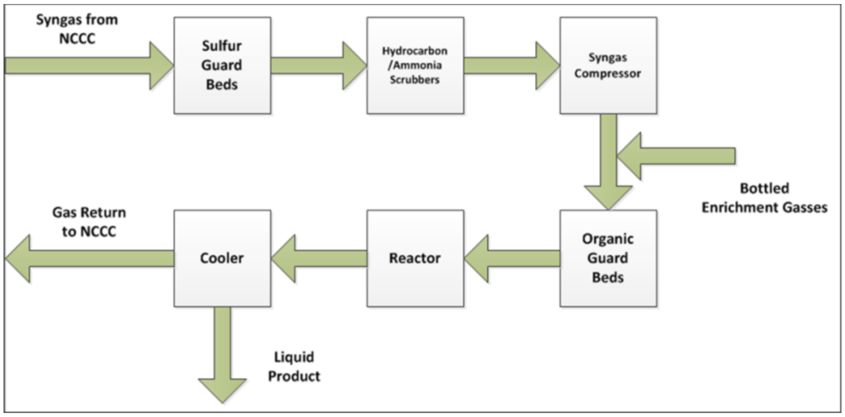


Figure 6. Schematic of FT skid-mounted system installed at NCCC

.

Figure 7. FT skid-mounted system in position at NCCC (walk-in and around capability)

It had a footprint of 16 ft by 8 feet and it was 10 feet tall. As seen in Figure 7, the FT reactor, product collection, and PLC panel is on the right where as the gas cleanup system is on the left. The PLC was used to collect and transmit data to an adjascent control trailor, and the process was controlled using Labview software. Also, gas samples were sent to a separate anlytical trailor where the feed gas and tail gas were analyzed using a continuous H2-CO-CO2 analyzer and an online gas chromatograph (GC).

During a typical run with gasifier syngas, bottled gases were begun first through the FT reactor to reach a steady state. Then gasifier syngas was brought in to replace a portion of the bottled syngas as follows. Typically, a 3 to 5 lb/hr raw/warm syngas slip stream from the air blown NCCC TRIG gasifier was desulfurized using a sorbent/catalyst system that removed both H2S and COS. The gas was then chilled and scrubbed to remove heavy hydrocarbons and ammonia. It was then compressed to the required FT pressure, mixed with H_2 and CO from bottled gases, as indicated above. This was done to increase its H_2/CO ratio to 2 and enrich it to simulate an oxygen-blown gasifier. The mixed gas (gasifier syngas and bottled syngas) was then sent to a series of guard beds for final polishing. It then entered the 2 inch diameter (with a 4 inch jacket) fixed-bed MFEC FT reactor with the water-based thermo-syphon heat removal system.

Chevron catalyst was packed in the reactor using Intramicron's microfiber-entrapped catalyst (MFEC) packing to facilitate rapid radial and axial heat transfer during reaction. The reaction heat was transferred rapidly to the reactor wall and then removed from the walls by boiling circulating water in the jacket produced by the thermo-syphon system. The run began with re-reduction and activation of the catalyst in-situ followed by slow increase of temperature and pressure to the desired operating conditions. Once the catalyst reached steady state using bottled syngas, a portion of the bottled syngas was replaced by gasifier syngas. Gasifier syngas using coal was used first followed by gasifier syngas using coal + biomass.

A test was run for over 320+ hours including 70+ hours with Powder River basin (PRB) coal-derived syngas and 70 + hours with 80 % PRB coal and 20 % biomass-derived syngas. Ground hardwood pellets were used as the biomass fuel. Smooth operation with a seamless switch between various sources of syngas/fuel was achieved successfully demonstrating the design production rate of >> 2 L/day with about 75 % carbon selectivity to liquids. Results summarizing the process conditions, conversion and selectivities are provided in Figure 8. Efficient heat removal and hydrocarbon productivities >>0.7 g/g catalyst/h were demonstrated. The liquid product produced was nearly wax-free. The small catalyst deactivation that was observed over the duration of the test was linked to traces of sulfur in the syngas accumulating on the catalyst. Sulfur levels of up to 164 ppmw were found on the used catalyst. Since a hot polishing bed followed by a low temperature polishing bed was used for efficiently removing H_2S and COS to ppb levels from syngas, it is possible that sulfur found on the catalyst potentially came from other sulfur species such as mercaptans, sulfides and/or thiophenes. Considering that sulfur is a strong poison to cobalt catalysts, the Chevron cobalt-zeolite hybrid catalyst exhibited significant resistance to sulfur.

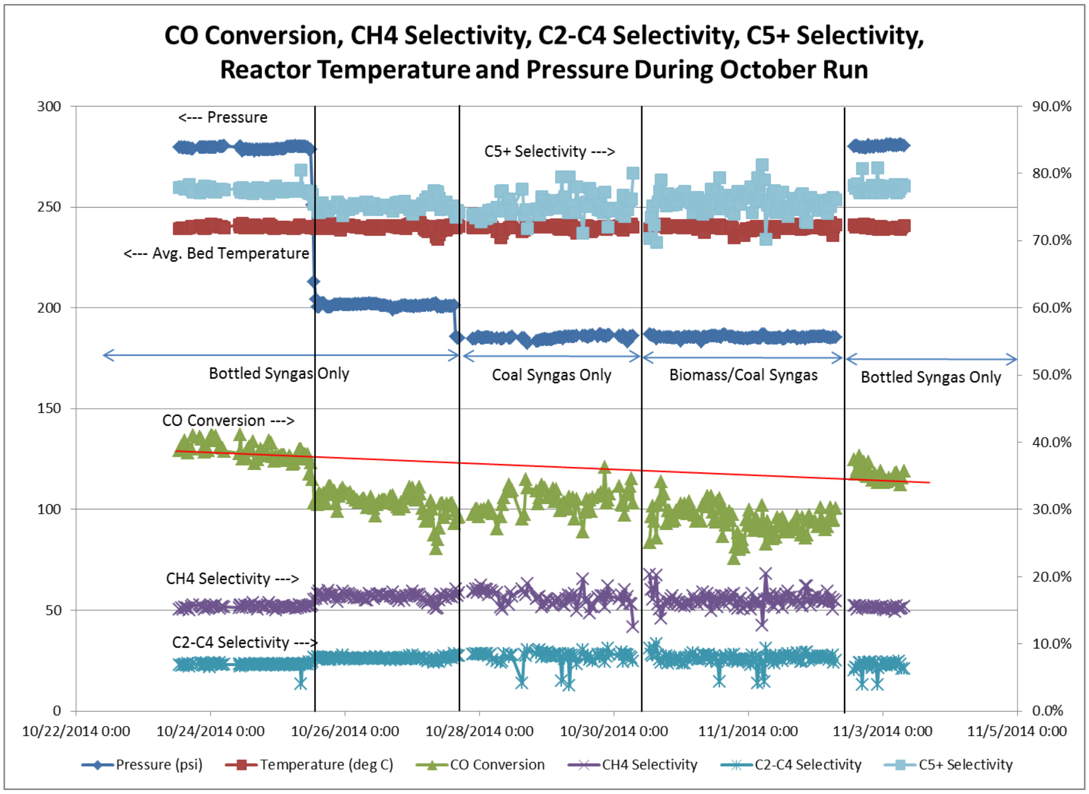


Figure 8. Conversion and selectivity results of FT slip stream test

Comparative analyses of products from the CTL and CBTL test runs using PRB coal and ground wood pellets did not show significant differences between the productivity, selectivity, and distribution of liquid products, probably due to similarity of the compositions of the coal and biomass. Based on these results, Chevron modified the catalyst for maximizing jet fuel selectivity and this modified catalyst was chosen for testing in this project.

Description of Experimental Setup

Initial screening tests were conducted in a laboratory setting to select catalyst for the field testing at NCCC. The lab-scale and field test equipment and test conditions are described below

Lab Scale Systems

Reformer

Lab-scale reforming tests were conducted both using SR's nickel-based catalyst and proprietary catalysts provided by Precision Combustion, Inc (PCI). The PCI catalysts were noble metal-based (e.g. platinum, rhodium and ruthenium) and comprised of these noble metals coated on thermally conductive, inert metal meshes that are named Microlith by PCI. The tests were conducted using SR's lab-scale reformer shown in Figure 9.

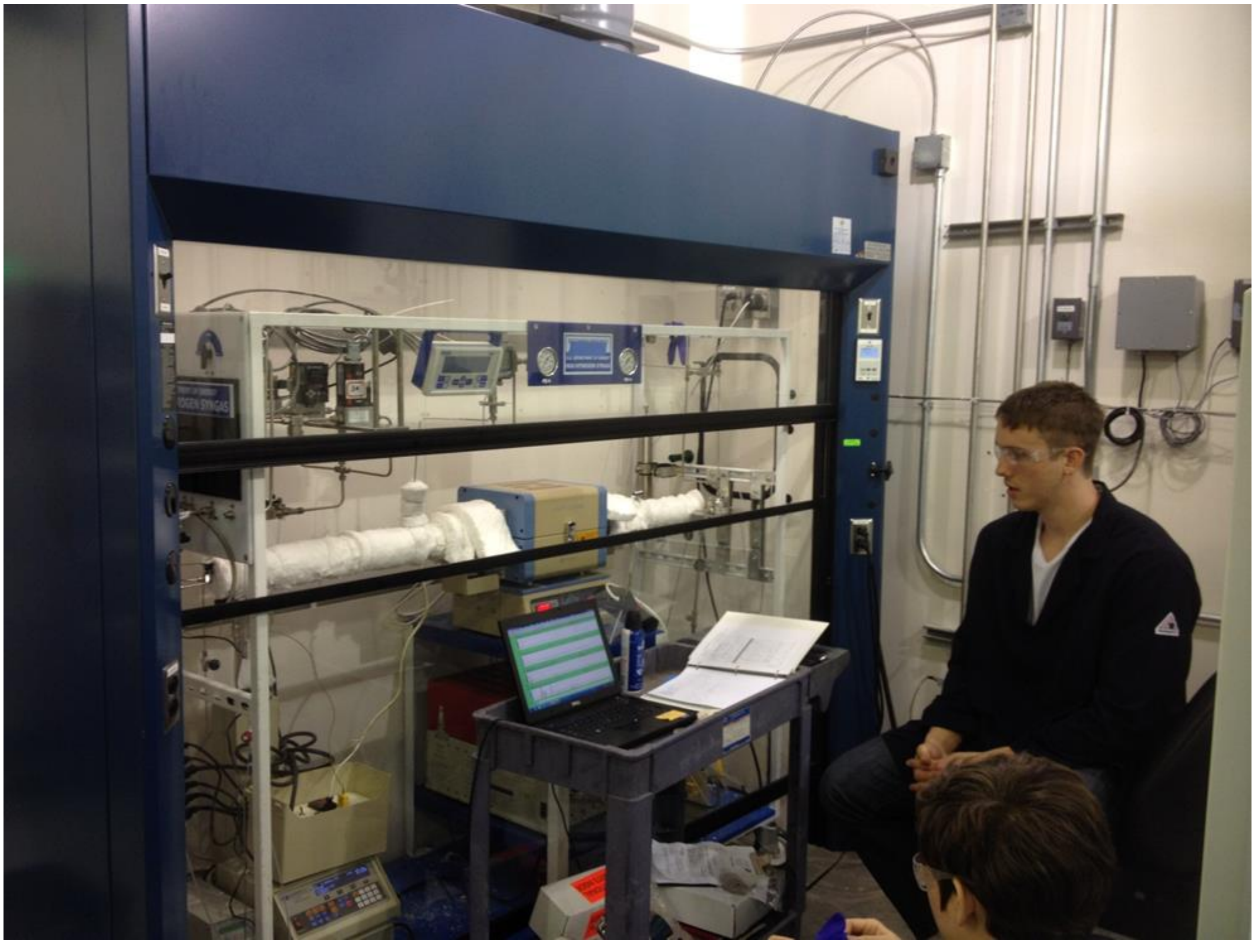


Figure 9. Photograph of laboratory-sale reformer system.

The reactor was installed in a hood and was designed for operations up to 200 psig with syngas containing up to 500 ppm H_2S. Simulated TRIG gas mixture (COS-0.003%, H_2S+COS- up to 500 ppmv, C_3H_8-0.322%, CH_4-2.83%, He-5.0%, CO_2-9.26%, H_2-12.74%, CO-19.06%, N_2-50.76%) was used for the tests with helium and nitrogen as internal standards. As illustrated in Fig. 10, a high-temperature tube reactor (½ inch) was loaded with noble metal-coated Microlith disks sandwiched between inert α-alumina particles. The length of the Microlith loading was measured to calculate the total catalyst volume and gas space velocity. In a typical experiment, the tube reactor was first preheated to 950 ˚C under H_2 flow and it was stabilized at this temperature for ~2 hrs. The simulated syngas with contaminants and FT light hydrocarbon surrogate, propane, was fed into the compact ATR reactor using a mass flow controller. Due to moisture intrusion into the gas line, the controller's O-ring deteriorated by wet H_2S over time and it affected flow consistency. The mass flow controller was hence calibrated daily. Water and toluene were vaporized and fed into the reactor using an Eldex pump and a syringe pump respectively. After reforming, the moisture was condensed from the vapor stream and the resulting dry gas composition was analyzed using a micro-GC.

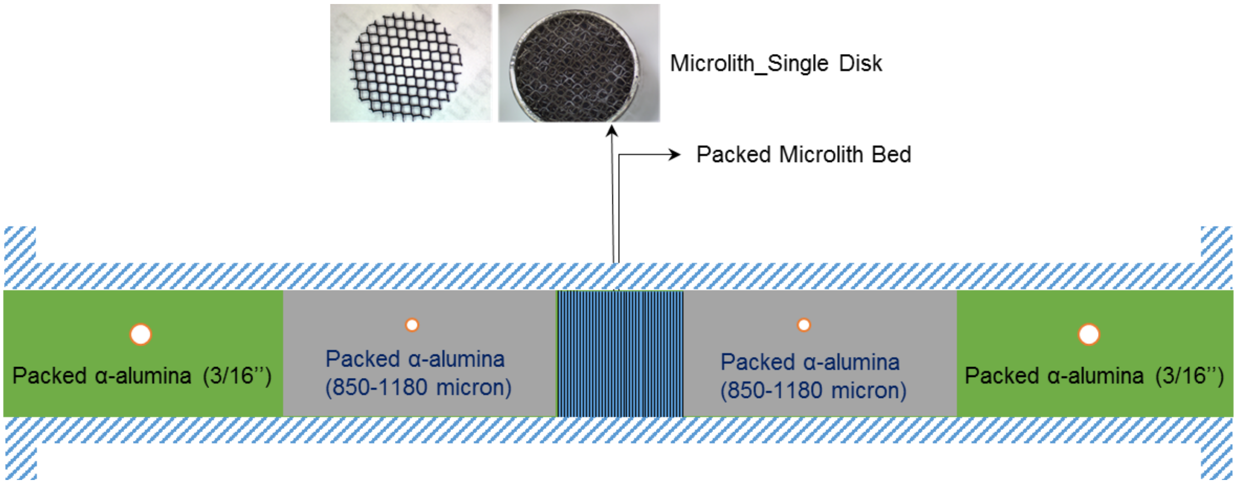


Figure 10. Schematic drawing of reformer reactor.

A number of issues were initially encountered with the mass flow controllers for the lab reformer system and were corrected. Following shakedown, a number of catalysts supplied by PCI were tested. Also, a Microlith coated using SR's sulfur tolerant Ni-based catalyst was tested.

Fischer-Tropsch

Lab-scale FT tests were conducted using catalysts provided by Chevron both in packed bed as well as MFEC configuration. Chevron provided four proprietary FT catalyst formulations at two particle sizes (60-130 µm and 100-200 µm) to SR for selective FT testing. These catalysts were expected to be highly selective for production of jet fuel range hydrocarbons with no solid wax formation. Selected FT catalysts were also sent to IntraMicron for the preparation of MFEC reactors. Inert α-alumina particles (500-710 µm) were used as inert filling in the tubular reactors.

High purity syngas mixtures (H_2/CO mole ratio of 2, UHP grade) were used as the FT feed. Gas contaminants, if any, were pre-removed using appropriate guard beds before feeding into the FT reactor. About 15 vol. % nitrogen was added into the syngas as internal standard.

A ½ inch and a 1 inch tubular reactor were used for packed bed and MFEC tests, respectively. As shown in Fig. 11, the reactor had FT catalyst packed in the upper portion of the reactor and inert α-alumina loaded on the two sides of the catalyst. Compressed glass wool was inserted into the top and bottom of the reactor for bed support. A four-point type K thermocouple was placed in the middle of the reactor to measure the inert top, catalyst top, catalyst bottom and inert bottom temperatures. Three band heaters surrounded the reactor to control the catalyst temperature at the desired level. An aluminum round bar was placed between the reactor tube and band heaters to ensure rapid heat transfer. The MFEC reactors were sent to IntraMicron for loading with the same configuration shown in Fig. 11

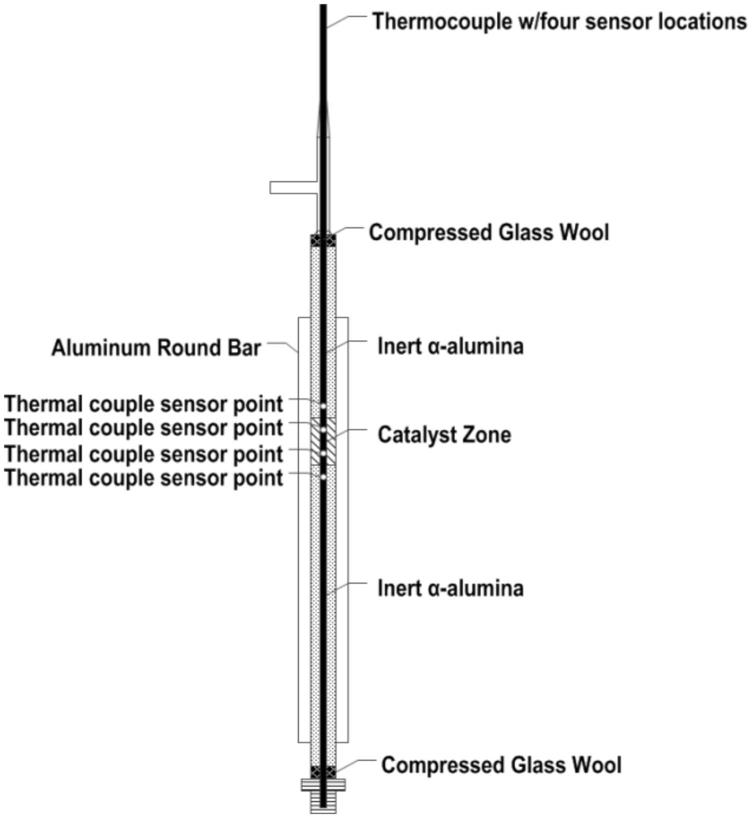


Figure 11. Schematic drawing of FT reactor

A micro-reactor system (Figures 12a and 12 b) was designed and constructed for parametric tests of various FT catalysts. The reactor system consisted of a gas delivery system, the FT reactor, a product separation/collection system, and a gas analysis system. The syngas was metered via a mass flow controller. It was heated to designated temperature using the band-heaters at the top of the reactor tube and was converted to hydrocarbons and water on the catalyst. After leaving the reactor, wax products, if any, were condensed in a hot trap (140 °C). Other light hydrocarbons in the product vapor stream were then chilled to 5 °C with a spiral tube installed in a cold ethylene glycol bath. The cold separator collected water and C_4-C_{20+} liquid products. The remaining gas was then filtered through a coalescing filter to remove entrained liquid droplets and was sent to a Micro GC (Inficon Fusion) for composition analysis. The micro-GC was calibrated 3 times a week to ensure consistent data acquisition. An automated VCR control valve and a back-pressure regulator were used in series to control the reactor pressure.

The FT catalyst was first reduced using ultra-high purity hydrogen and then activated using syngas according to the procedures provided by Chevron. After activation, the reactor was operated under baseline conditions (240-245 °C, 280 psig, and 13,000 sccm/g/hr space velocity) for a minimum of 72 hours to acquire initial catalyst performance. The reactor temperature and space velocity (SV) were then varied to study their effects on syngas conversion and selectivity to liquids and jet fuel range hydrocarbons. Reactor conditions were periodically switched back to the baseline conditions to check the catalyst activity during the parametric study. The liquid samples from the wax trap and the condenser were collected every 24 hours for composition analysis using simulated distillation.

Figure 12a. FT lab-scale reactor system

Liquid products from the wax trap and the condenser were collected in a glass vial (20 ml) and an instant phase separation with two cloudy phases can be seen after sample collection. The top phase is an organic phase contains light hydrocarbons (C_5-C_{25+}) and the bottom phase contains essentially water. The liquid products were allowed to sit under room-temperature for a minimum 24 hrs to ensure complete phase separation. In most cases, the cloudy phase became clear after the stabilization step. The phase separated sample was then transferred to a separation funnel). The bottom aqueous phase was stored at room temperature. The top organic phase was stored in a 4 °C refrigerator for analysis.

Quantitative carbon number distribution analyses on the FT organic phase were performed according to the modified ASTM D2887 and the ASTM D5442 methods. The liquid samples were filtered through a 0.25 μm PTFE filter and 0.5 μL of sample was injected into a

GC-FID (Agilent 7890B) for simulated distillation analysis. A Restek column (Rtx 5- 30m x 0.32 mm x 0.25 µm) was used for sample separation. The GC oven temperature started at -20 °C and ramped 8 °C/min to 20 °C and then ramped 12 °C/min to 325°C. The detector and injection temperature was set to 350 °C and 275 °C respectively. The GC carrier gas was set to 4.5 mL/min, and a split ratio of 16:1 was used. The quantitative analyses were achieved by calibrating the GC using paraffin standard mixes purchased from Restek. A linearity test was performed before each analysis using a decane standard mixed with hexadecane.

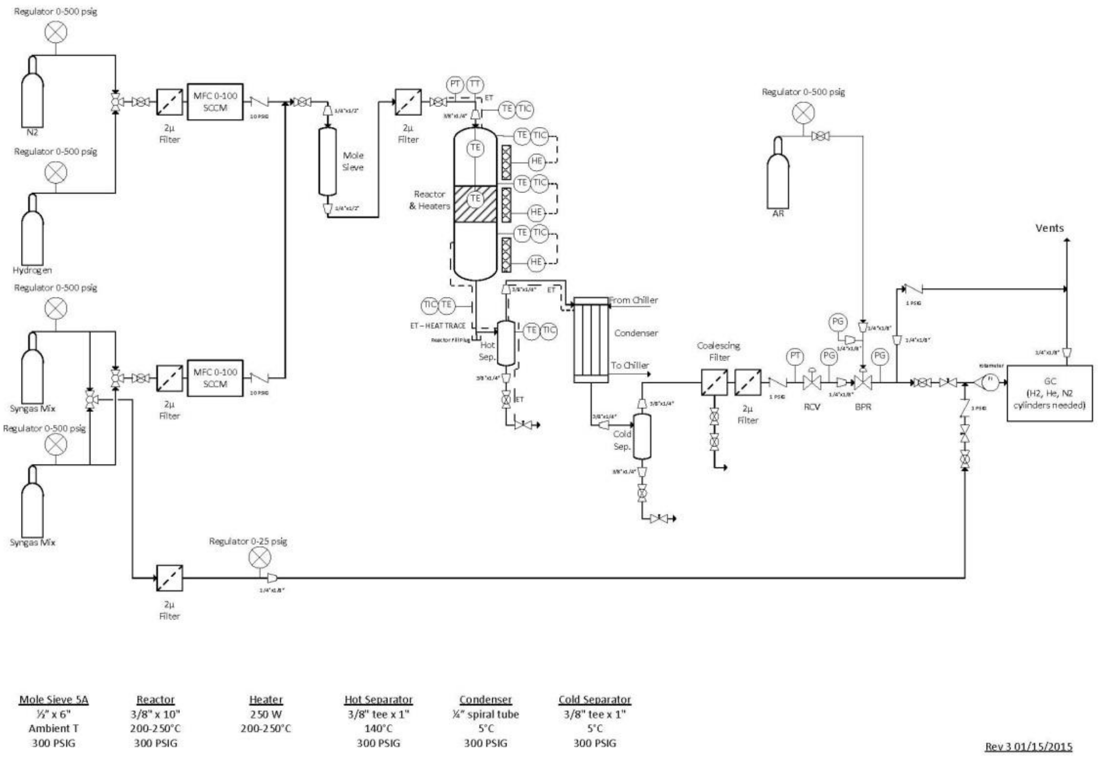


Figure 12 b. FT lab scale reactor system process flow diagram

Field Test Systems at NCCC

Reformer

The original project plan called for PCI to develop a bench-scale auto-thermal reformer (ATR) system and install it on a gasifier slipstream at NCCC. However for reasons beyond SR's control and budget constraints, PCI could not deliver the system. PCI provided a final report of their efforts which is attached as Appendix 1. As a backup plan for reformer field testing with actual gasifier gas, SR undertook to modify the lab-scale reformer (Figure 9) for Class 1 Division 2 electrical code, , and transported and installed it on the gasifier syngas slipstream at NCCC. The system as installed at NCCC is shown in Figures 13 and 14. As seen in Figure 14, the reformer was installed in close vicinity to the previously installed FT skid that was connected to the NCCC gasifier slip stream. .

Figure 13. Lab-scale reformer installed at NCCC

The reformer was modified for remote operations at NCCC using in house machining, fabrication, welding and other capabilities. The reactor was installed in a purged box to meet Class 1 Div. 2 electrical requirements. The close vicinity with SR's FT skid allowed efficient use of existing infrastructure including the trailer for remote operation and the the analytical equipment housed in the gas analysis trailer. After addressing safety issues raised by NCCC, SR completed necessary wiring and shipped the unit to NCCC for installation in January 2017 and completed installation with the help of NCCC contractors.

SR initiated reformer shakedown operations in conjunction with a NCCC gasifier run on March 31, 2017. The SR Ni-based sulfur tolerant catalyst was used for the reforming test. Initial operations led to issues of flow control and an intermittent problem with a thermocouple that was used to control the temperature of the reactor. With the support of NCCC, SR was able to correct these issues and successfully operated the reformer skid for about 125 hours on raw gasifier syngas.

The gasifier syngas volumetric percent composition for the reforming tests on dry basis was: H_2-7.7; CO-8.6; CO_2-11.1; CH_4-1.1; H_2S+COS-0.038; N_2-balance. The test was run at 205 psig and 850-900°C at a space velocity of 8,000 scc/(g catalyst.h) with 15 to 30 volume % steam.

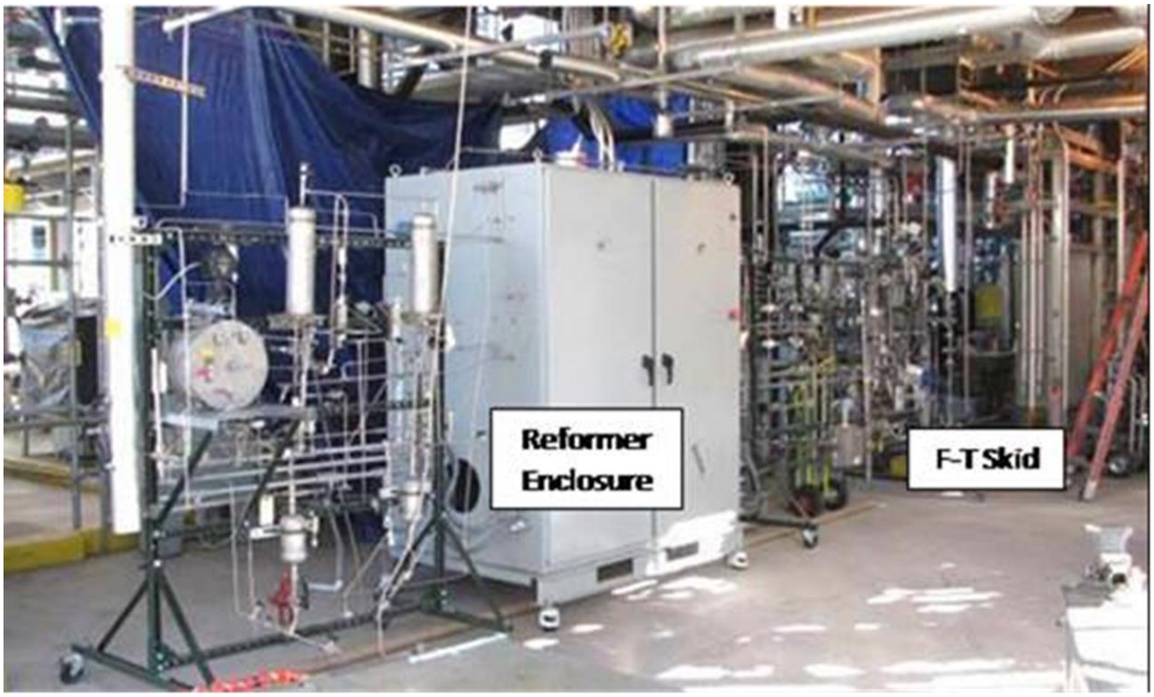


Figure 14. Reformer housed in cabinet installed alongside SR FT skid

Fischer-Tropsch

Two FT field tests were carried out using syngas at NCCC in conjunction with their gasification campaigns during the fall of 2015 and the spring of 2017. In the fall 2015 test, the existing skid (Figures 6 and 7) underwent several modifications prior to the test campaign. The best performing Chevron Co-zeolite hybrid catalyst in the 100-200 µm size range selected based on the lab-scale screening tests was loaded in a 2 inch diameter FT reactor with MFEC packing for this test. The modifications are listed below:

- Replace 30 slpm H_2 mass flow controller (MFC) with 100 slpm MFC
- Replace sorbent in polishing beds
- Install new center point thermocouple in FT reactor
- Reinstall reactor and wax trap
- Several proprietary modifications to thermo-syphon system and steam drum to further improve temperature control
- Replace coalescing filters

After the modifications were made and commissioned, the skid was started up for testing. The FT catalyst was then conditioned and activated according to a proprietary procedure provided by Chevron prior to beginning the FT synthesis

For the spring 2017 test, the FT skid was scaled up for a run with a 4 inch diameter FT reactor with 50 % more of the best performing jet fuel-selective catalyst on MFEC packing but with catalyst particles in the 60-150 μm size range. The modified FT with the 4 inch diameter reactor installed and the 2 and 4 inch reactors are shown in Figures 15 to 17. The unit that was originally designed for 4 liter/day liquid hydrocarbon products using 3-5 lb/h syngas was modified for operation at 50 % higher capacity (6 liter/day using 4.5-7.5 lb/h syngas) to enable

Figure 15. FT skid with 4 inch diameter reactor installed

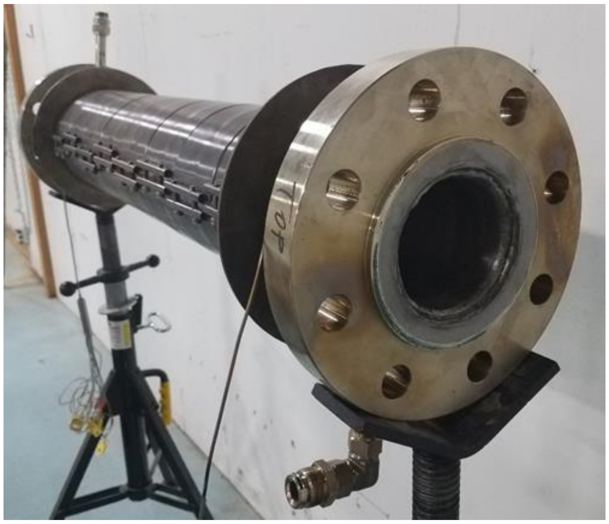


Figure 16. Reactor (4 inch diameter) shown without vented enclosure

the use of the 4 inch diameter FT reactor with 50 % more catalyst. The objective in going to larger diameter reactor was to demonstrate efficient heat management with MFEC even for larger diameters up to 4 inch that could enable the use of significantly fewer tubes in a commercial embodiment.

The 4 inch reactor also integrated a steam jacket similar to the previous design, as well as utilized similar electrical heating elements as were used on the previous design. Also, as with the 2 inch diameter reactor used for previous tests, the 4 inch reactor also had a separate enclosure around it so that the electrical heating elements meet Class 1 Div. 2 requirements. The cooling system for the reactor was evaluated to ensure that the process could remove heat generated with the 50 % higher and higher activity (smaller size catalyst) catalyst used for testing. The sampling system was also evaluated and two new sampling vessels were obtained for the expected increase in liquid production. The simulated syngas feed system was also analyzed for delivering the additional feed, and a new mass flow controller was obtained for carbon monoxide. Finally, it was determined that the backpressure control valves would be inappropriately sized for the two flow cases (activation and operations), so an additional backpressure control valve was obtained in order to allow optimum control of pressure during all phases of the testing.

Figure 17. FT reactors (2 inch) in shipping boxes

The catalyst activation and FT testing with the 4 inch diameter reactor was conducted in a similar fashion as the earlier test with the 2 inch diameter reactor. The tests were conducted at a range of conditions shown in Table 1. Results of the field tests are presented and discussed in the Results and Discussion section.

Table 1. Nominal Experimental Conditions for FT Field Tests

Syngas composition	$H_2/CO = 2$ with 15-50 % N_2 diluent
Reactor diameter	2 inch and 4 inch
Catalyst loaded	300 to 500 g
Pressure	200-280 psig
Temperature	240-250
Space velocity	11,000 to 15,000 scc/(g catalyst.h)

Results and Discussion

Lab-Scale Testing

Reformer

The lab-scale reforming reactor was commissioned to ensure its safe operation and accurate data acquisition. An initial shakedown test was conducted during which a number of experimental problems including a faulty mass flow controller were corrected. All flow, temperature and pressure control instruments and gas chromatographs (GCs) were calibrated and evaluated for accuracy. Following shakedown **several tests** were conducted with selected catalysts to evaluate the effects of process variables. The simulated TRIG feed gas composition for these tests on dry basis was H_2S+COS- up to 500 ppmv, C_3H_8-0.322%, CH_4-2.83%, He-5.0%, CO_2-9.26%, H_2-12.74%, CO-19.06%, N_2-50.76% with a feed H2/CO ratio of ~0.67. Steam feed was varied from 10 to 40 volume %. Results from five most relevant tests are described below.

Test 1: A baseline reforming catalyst (PCI-1) was tested first with simulated syngas (10 % steam) at various temperatures. As shown in Figure 18, a rapid methane conversion decrease (from 96% to 84%) was observed in the first 150 hours at 950 ˚C. When the temperature was increased to 975 ˚C, the conversion went back up to 96% but it decreased to 79% when temperature was cycled back to 950 ˚C. At lower temperature (925 ˚C), the methane conversion dropped significantly to 60% but increasing temperature back to 950 ˚C increased it to 77.4%. The observed conversion drop at lower temperature could be attributed to (1) the temperature effects on methane reforming and (2) the catalyst deactivation. Unlike methane, propane was completely reformed under all applied conditions. At a steam concentration of 20%, the H_2/CO ratio did not vary significantly with temperature and stayed in the range of 1.2 to 1.3. This H_2/CO ratio is significantly lower than the target ratio of 2 for FT synthesis. The test was terminated after 350 hr as the catalyst showed significant deactivation and some coke formation was observed on the spent catalyst due to the low steam concentration. Further optimization and a higher steam concentration was implemented to reduce coke formation and increase H_2/CO ratio in Test 2.

Test 2: In order to evaluate the effect of increase in steam, another reforming test (Figure 19) was conducted using the same PCI-1 catalyst and simulated syngas under varied temperatures and steam concentrations. In this trial, SR also increased the gas space velocity by 20% as instructed by PCI to enhance the catalyst stability. As shown in Fig. 15, the overall test lasted over 680 hours without significant catalyst deactivation. Overall, the methane conversion decreased from 99% to 87% but the first 300 hours experienced only a 3% methane conversion drop. Increasing the steam concentration showed significant effect on H_2/CO while temperature had no effect on it. It was observed that steam concentration can be set at 35% with this syngas composition to achieve H_2/CO ratio of 2 at the exit.

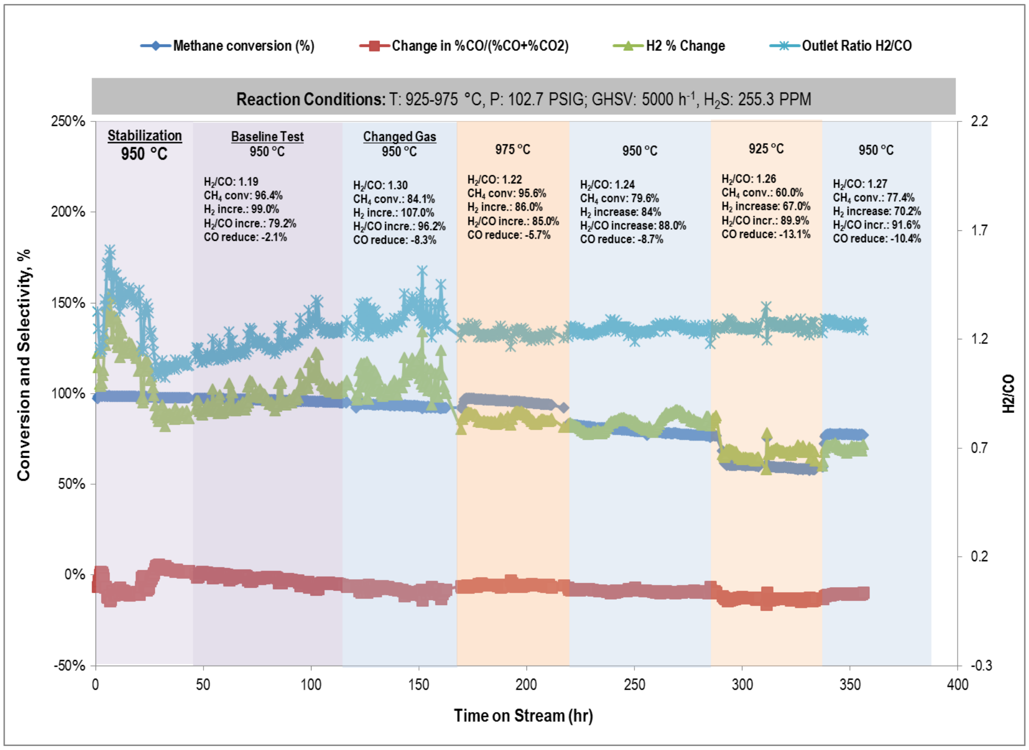


Figure 18. Reforming conversion and selectivity with (baseline PCI Microlith catalyst)

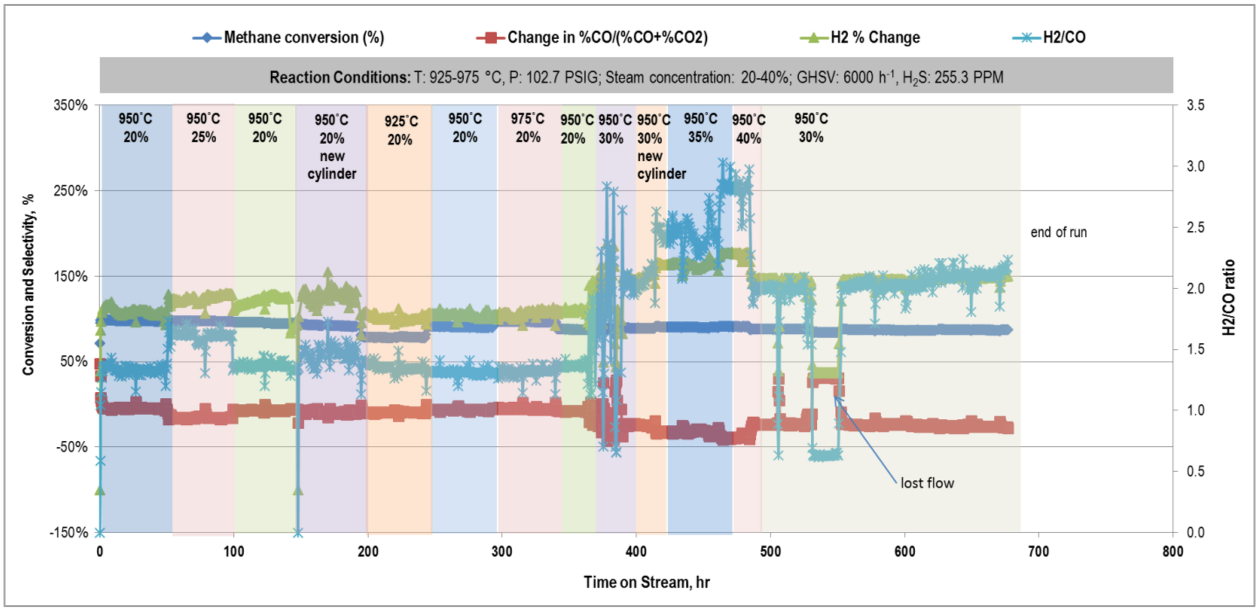


Figure 19. Reforming conversion and selectivity (baseline testing with higher steam).

Test 3: SR Ni-based sulfur tolerant reforming catalyst coated by PCI on Microlith was selected for testing in Test 3. Results are shown in Figure 20. The feed gas composition was same as Test 2 but the temperature was increased by 50°C and the space velocity was reduced by half. The results showed higher CO conversion indicating high WGS activity, but reduced methane conversion (below 50% consistently) and corresponding reduction in hydrogen change. Due to poor performance, the test was concluded shortly after 70h. Compared to results of packed-bed testing (Figures 2 and 3), the poor performance of the catalyst coated on the Microlith is attributed to loss of the active catalyst phase during the catalyst preparation.

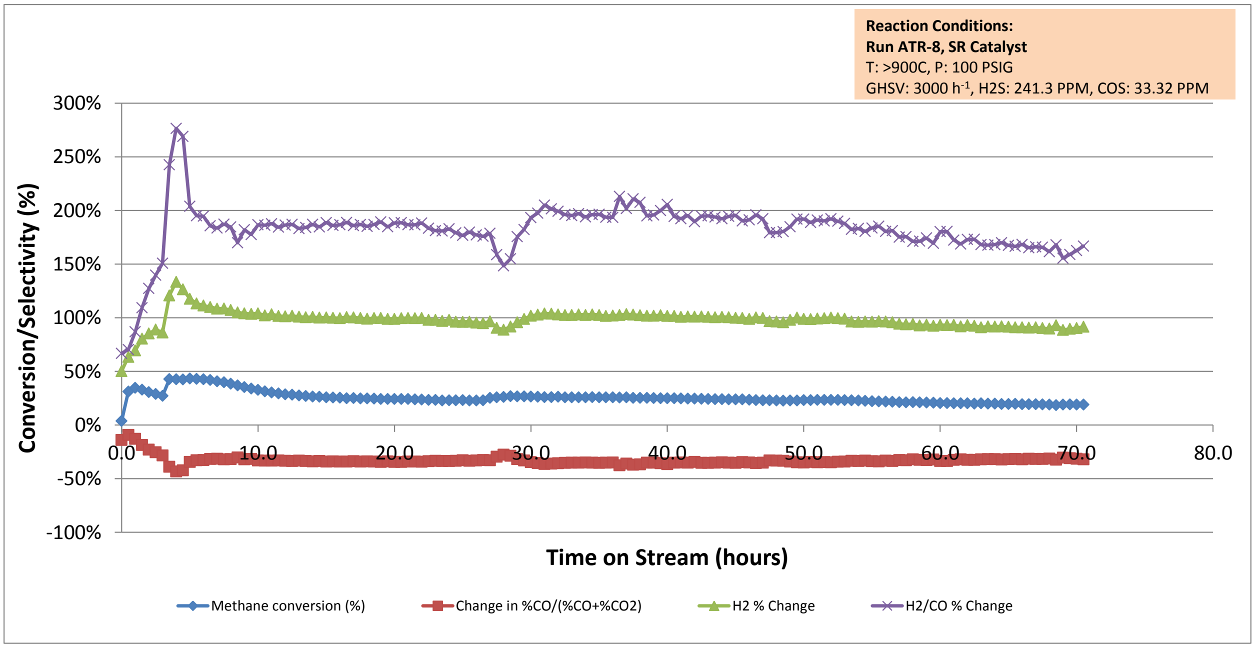


Figure 20. Test of SR sulfur tolerant Ni-based catalyst coated on PCI Microlith

Test 4: Results from PCI catalyst 2 (ATR-9 run) are shown in Figure 21. The reaction was started at a similar condition as the previous PCI catalyst test. However, given the steadily decreasing methane conversion activity, the temperature was increased by 50C. Despite a decrease in WGS activity at the higher temperature, the H_2/CO ratio remained suitable at just over 2.0 and the methane conversion recovered to nearly 100% and remained high for the duration of the experiment. The H_2 increase and WGS activity also remained high for the duration of the trial and the catalyst was considered a success after 350 h on stream with a termination of the experiment shortly thereafter.

Test 5: Results of testing of PCI catalyst 3 are shown in Figure 22. Initial temperatures were increased 50^{o}C due to the success of previous tests, and space velocity was held initially consistent with those conditions that existed during previous tests. The H_2/CO concentration again increased to 2.0, and the conversion of methane also increased to nearly 100% for the initial phase of the run. Following the first four days of trials, the space velocity was reduced by 25% to determine if lower velocities were still successful. The reduction in hydrogen around day three was corrected with a GC recalibration when the space velocity was altered. A pump malfunction around 250h resulted in a period of dry reforming. However, the methane reforming (dry) continued, albeit slightly reduced due to a reduction in steam available for the WGS. When steam flow was reintroduced the catalyst activity returned to normal. The duration of the test beyond 300 h was considered successful and the test was concluded after a few days of validating continued activity.

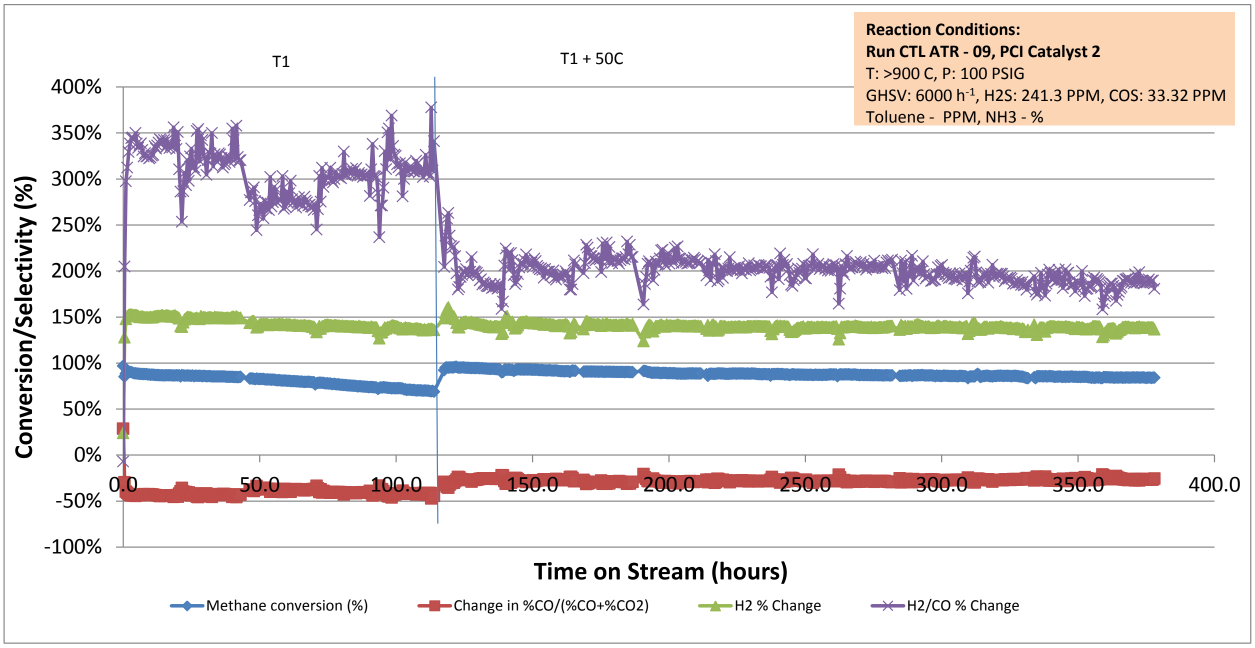


Figure 21. Reforming test with PCI Catalyst 2

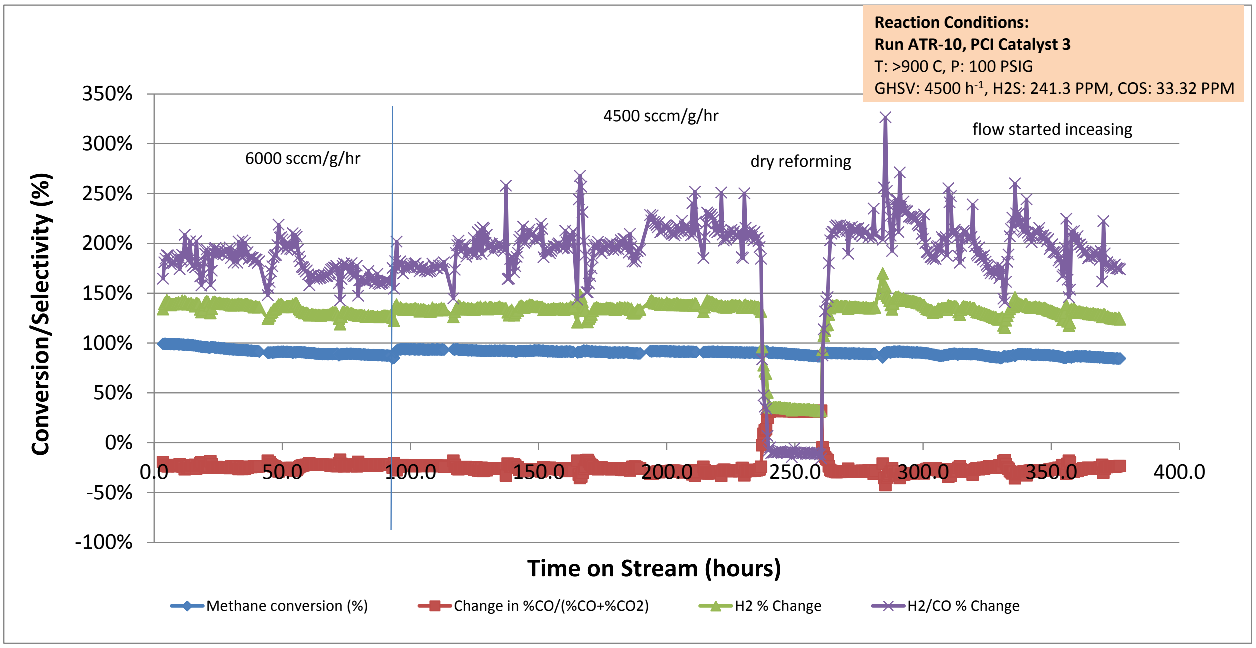


Figure 22. Reforming test with PCI catalyst 3

Based on these tests, the PCI 2 and PCI 3 catalysts were selected for field testing. However, as noted previously, PCI could not deliver the bench-scale reformer with the selected catalyst loaded due to budget constraints. Thus the backup plan was implemented consisting of modifying the SR laboratory reformer and using the SR Ni catalyst in packed bed configuration for field testing.

Fischer Tropsch

Several lab-scale catalyst screening tests were conducted in fixed-bed and MFEC reactors to evaluate the FT catalysts (4 formulations and two particle sizes) provide by Chevron. These experiments aimed to identify at least one FT catalyst that achieves at least 75% liquids with at least 65% jet fuel selectivity with no C_{21+} wax formation and with liquid productivity > 0.7g C_{5+}/g cat/hr. The important results are presented below.

FT Tests in Fixed Bed Reactor: Based on Chevron's recommendation, a jet fuel selective Co-zeolite hybrid catalyst (100-200 μm) was packed in a ½ inch diameter reactor and tested at condition outlined in experimental section. The catalyst bed was diluted with inert α-alumina to prevent hot spots. The inert to catalyst weight ratio was 5. The reactor pressure and space velocity were at 280 psig and 13,000 scc/g/hr during the entire test. The reactor temperature was varied to investigate its effect on the catalyst selectivity and liquid composition. Table 2 summarizes the average CO conversion, FT selectivity and productivity during steady-state operation and Figure 23 shows real-time conversion and selectivity profiles as a function of time on stream (TOS). The initial 100-150 hrs operation had CH_4 peak co-eluted with CO peak on the GC so the data is not included.

Initial test at 240 °C showed that the CO conversion (~35%) was lower than expected value of 45-50% and this could be attributed to the heavy wax accumulation within the catalyst pores typically occurring at low temperature; the methane and liquid selectivity (~15% and 73% respectively) were consistent with the results suggested by Chevron. The liquid productivity of C_{5+} hydrocarbons (0.64 g/gcat/hr) was lower than the target of 0.7 g/gcat/hr. The weight fraction of jet fuel range hydrocarbons in the liquid product (~72%), was however higher than the target value of 65%.

When temperature was increased from 240 to 245 °C, the CO conversion increased to ~45% and leveled off as temperature was further increased to 248 and 250 °C. The methane selectivity also went up slightly at higher temperature (248 and 250 °C). The liquid and jet fuel selectivity were not affected by temperature. In addition, higher temperature resulted in liquid productivity 0.7 g/gcat/hr, the target value. At optimum temperature, the catalyst showed ~45% CO conversion, ~73% liquids selectivity with ~70% jet fuel selectivity and a liquid productivity of ~0.8 g C_{5+}/gcat/hr. These values significantly exceeded targets

The FT liquids generated at different temperatures were collected from the wax trap and the condenser after the reaching steady-state. No solid waxes were observed from the collected samples. The hydrocarbon mixtures were separated from water and injected into a GC-FID for simulated distillation analysis as shown in Figure 24.

As presented in Table 2, the overall jet fuel selectivity (C_8-C_{16}) was not affected by the reaction temperature and it stayed constant at ~70%. The results shown in Fig. 24, however reveals that the carbon number distributions of FT liquid varied somewhat with temperatures. In general, lower temperature as expected reduced the generation of C_5 to C_{10} fraction but increased the formation of C_{12+} fraction. Within jet fuel range (C_8 to C_{16}), the C_8 to C_{10} fraction was significantly higher at higher temperatures (248 and 250 °C) than that at lower temperature (240 and 245 °C) and this was accompanied by a reduction of the C_{12} to C_{16} fraction.

Table 2. FT catalyst performance in fixed-bed reactor (reactor held at 280 psig and 13, 000 sccm/g/hr).

Temp, °C	TOS, hr	CO Conv., %	CH_4 Sel., %	C_2-C_4 Sel., %	CO_2 Sel., %	Liquid Sel., %	Jet Fuel Sel.,%	Liquid Productivity, gC_{5+}/gcat/hr
240	180-220	35.2	14.6	12.1	0.3	73.0	72.0	0.64
245	230-305	44.2	14.7	11.3	0.3	73.7	71.1	0.81
	310-430	39.2	14.2	12.9	0.3	72.6	71.5	0.72
248	760-830	45.2	16.8	11.3	0.6	71.3	71.1	0.81
250	431-525	44.3	14.6	11.7	0.3	73.4	71.0	0.81
	580-740	42.2	16.1	12.4	0.3	71.2	71.7	0.74

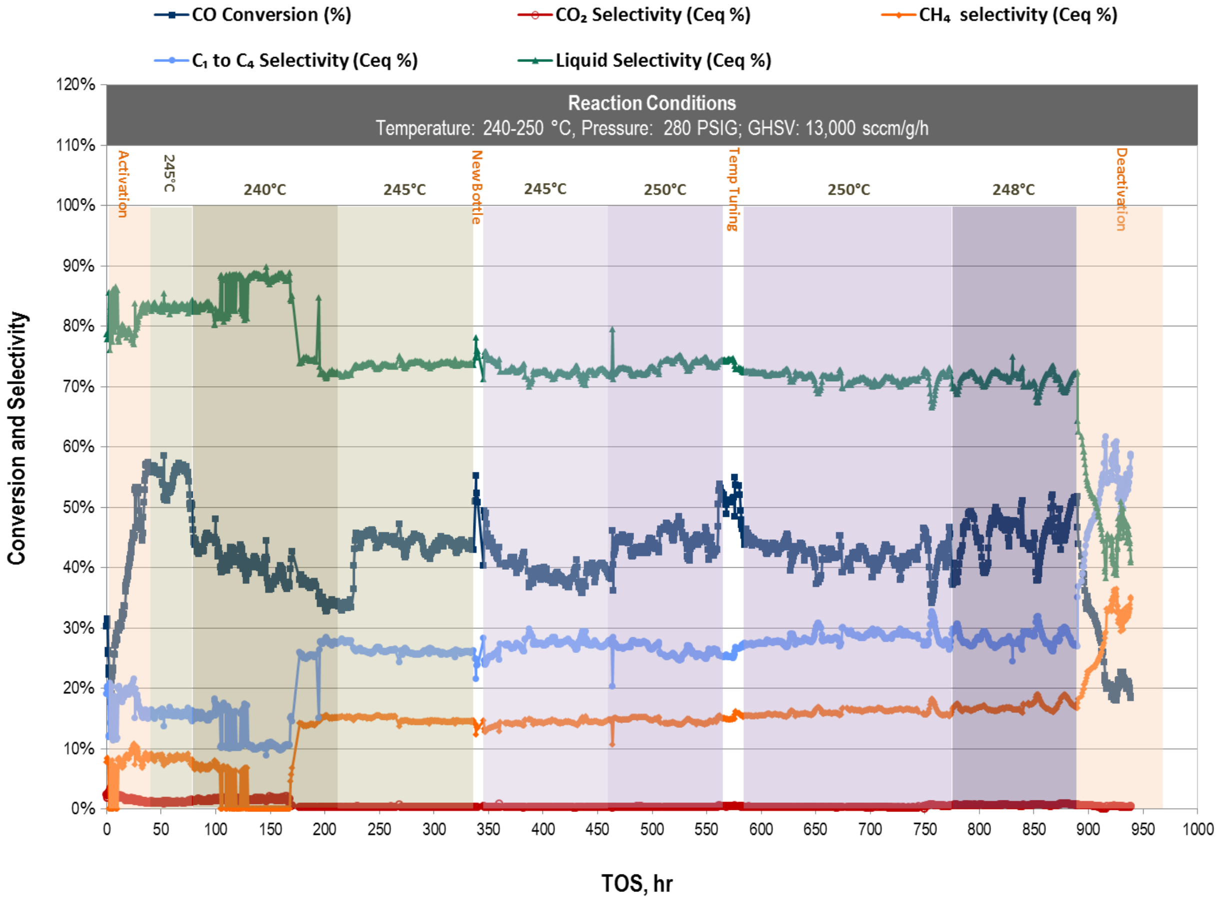


Figure 23. FT conversion and selectivity in fixed-bed reactor.

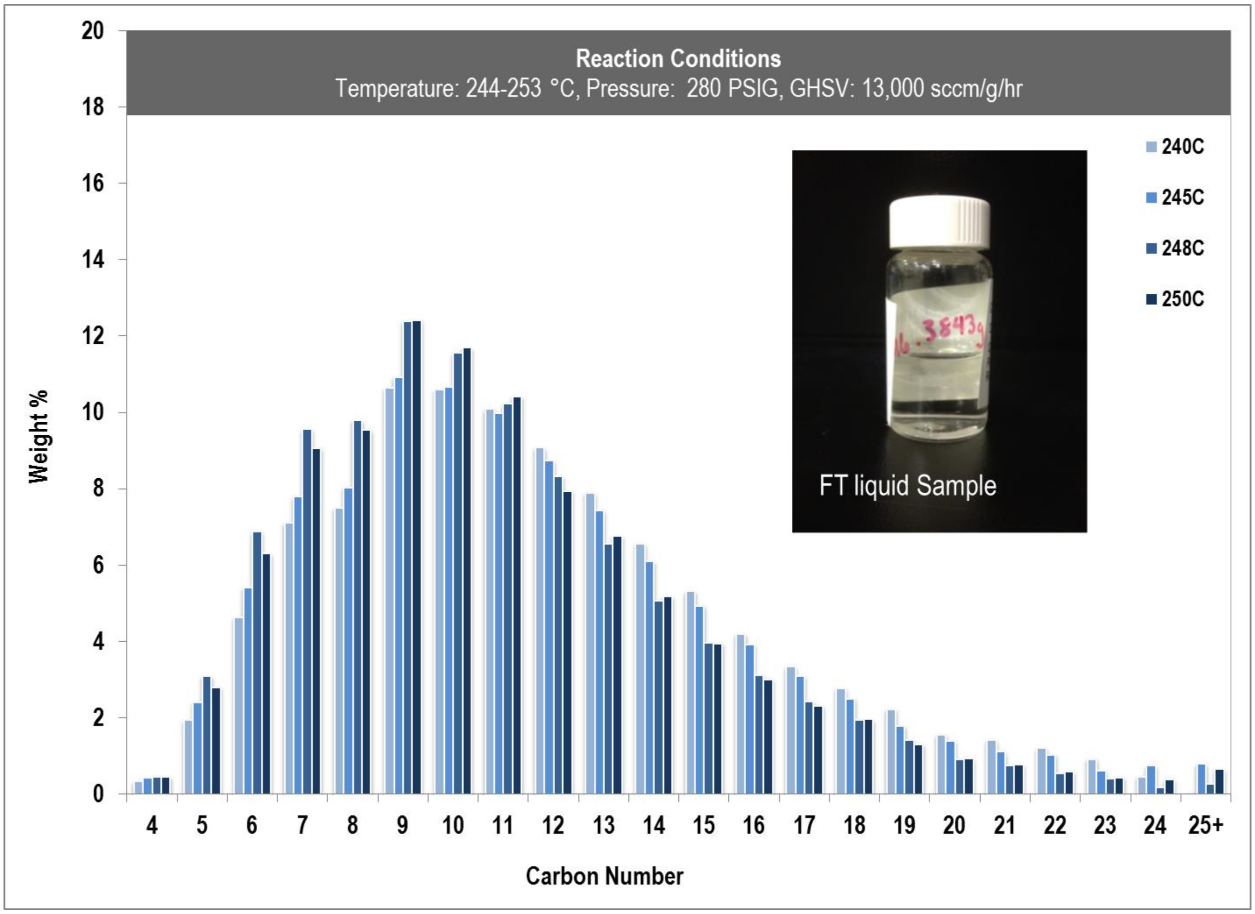


Figure 24. Carbon number distributions of liquid products as a function of temperature

Although overall jet fuel selectivity was not affected by temperature, there was higher CO conversion and lower formation of C_{20+} fraction at higher temperature Thus the optimal FT temperature was determined to be in the 245-250 °C range for pressure and space velocity at 280 psig and 13, 000 scc/g/hr, respectively.

FT Tests in MFEC Reactor: Microfibrous entrapped catalyst (MFEC) reactors were prepared by IntraMicron, Inc. using the same catalyst tested in the fixed-bed reactor. MFEC reactors simultaneously addresses the issues related to heat transfer, process intensification, and product selectivity of Fischer-Tropsch synthesis. it is not practical at commercial scale to have reactor tubes containing 5 times more inactive alumina mixed with the catalyst to prevent hot spots in fixed-bed reactors. With the improved heat transfer characteristics, MFEC reactors can provide very uniform temperature profiles inside the reactor. MFEC reactor

The MFEC reactor was connected to the lab-scale FT skid and tested at a pressure at 280 psig. Reaction temperature and space velocity were varied to investigate their effects on catalyst performance. Based on the fixed bed test, the test was started at 244 °C. The temperature was then increased from 244 to 253 °C and two space velocities, 13,000 and 17,000 sccm/g/hr were tested under two temperature settings (245, 250 °C). During the space velocity test, the reaction conditions were brought back to the baseline conditions (245 C and 13,000 sccm/g/hr) to check if the catalyst still preserves its initial activity after the change.

Table 3 summarizes the average CO conversion, FT selectivity and productivity during the steady-state operation. Figure 25 shows a real-time conversion and selectivity profile as a function of TOS. MFEC generally gave similar CO conversion to that obtained from fixed-bed reactor. The liquid selectivity (~73%), jet fuel selectivity (~70%) and liquid productivity (~0.8 $gC_{5+}/gcat/hr$) are also similar to that achieved in the fixed-bed trial. The overall FT test continued for ~840 hours and was considered a success.

Table 3. FT catalyst performance in MFEC reactor.

Temp °C	SV scc/g/h	TOS, h	CO Conv. %	CH_4 Sel. %	C_2-C_4 Sel. %	CO_2 Sel. %	Liquid Sel., %	Jet Fuel Sel. %	Liquid Productivity ,$gC_{5+}/gcat/hr$
244	13000	80-185	47.7	14.9	10.2	0.6	73.4	69.9	0.87
245	13000	190-305	43.3	14.3	11.3	0.5	73.9	69.7	0.80
245	17000	310-358	30.5	14.9	13.8	0.4	73.0	72.0	0.55
245	13000	367-410	37.8	14.6	11.5	0.5	73.3	70.4	0.69
248	13000	420-520	42.2	15.2	11.9	0.6	72.3	68.5	0.76
250	13000	530-595	43.6	15.4	11.9	0.6	72.0	69.2	0.78
250	17000	600-670	33.0	16.1	12.6	0.5	70.9	70.3	0.58
250	13000	680-715	41.3	15.8	12.2	0.6	71.4	70.1	0.73
253	13000	725-825	45.3	16.7	12.8	0.8	69.7	69.9	0.79

High space velocity reduced the CO conversion as expected leading to low liquid productivity and increased the C_2-C_4 gas selectivity but the liquid selectivity did not appear to change significantly. Space velocity >13,000/h is clearly not favored in achieving the desired catalyst performance.

Figures 26 and 27 show carbon distribution data of the liquid fuel collected from the MFEC test. As shown in Fig. 26, high temperature favored the formation of C_5-C_9 hydrocarbon and decreased the fraction of C_{12+}. A small amount of C_{21+} fraction (<5%) was obtained at 250 °C and 253 °C. As shown in Fig. 9, high space velocity significantly reduced the C_5-C_7 light fraction but increased the C_9-C_{13} jet fuel cuts. The reduced light fraction at high SV could be explained by less catalytic cracking of hydrocarbon products on the zeolite due to reduced reaction time.

Figure 28 compares the carbon distribution of liquid products obtained from fixed-bed and MFEC reactor. The carbon distribution of liquid fuel generated at 245 °C did not show significant difference between fixed-bed and MFEC reactor. At 250 °C, however, the MFEC reactor generated higher amount of C_{14+} but lower C_9-C_{12} cuts jet fuel. The larger diameter of MFEC reactor and different testing history may be the reason for this difference.

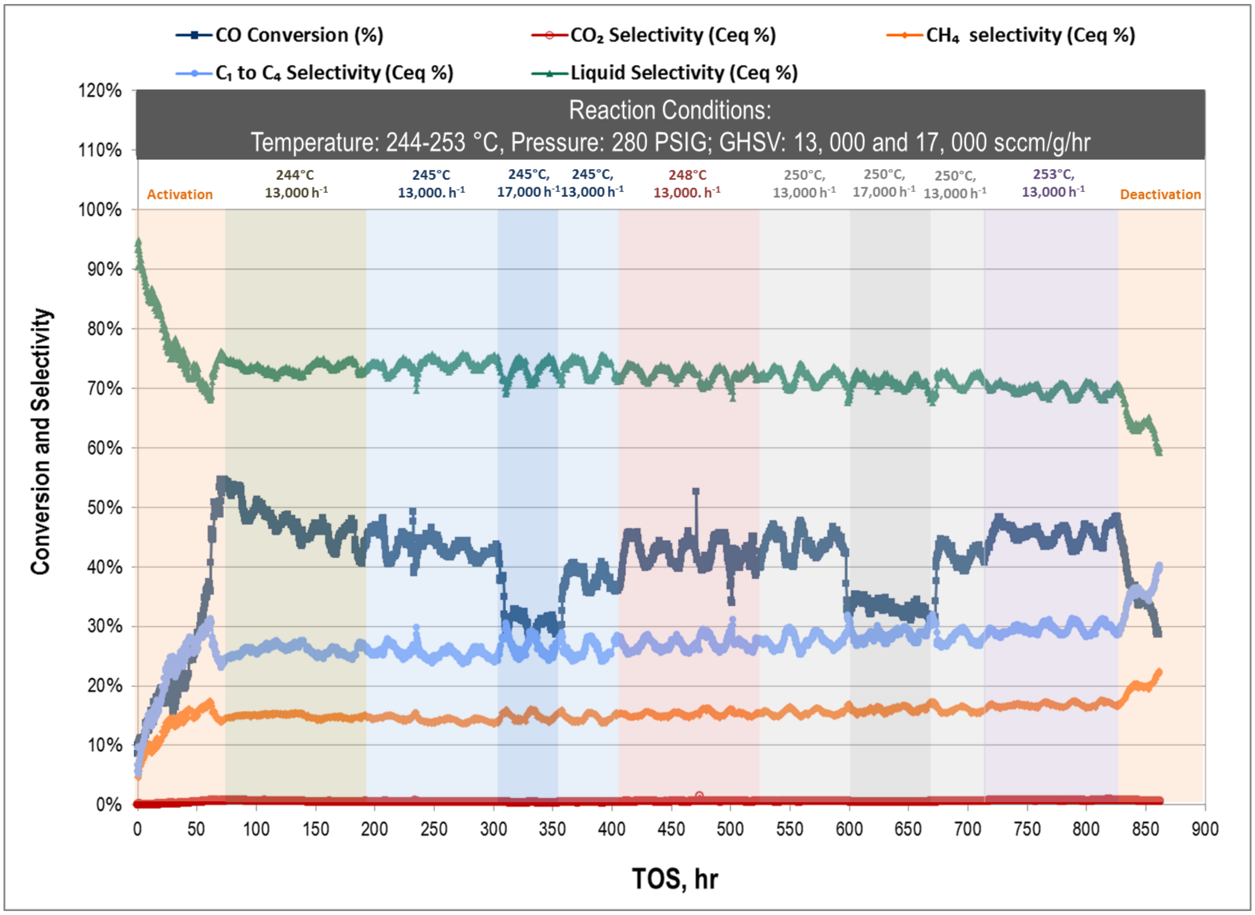
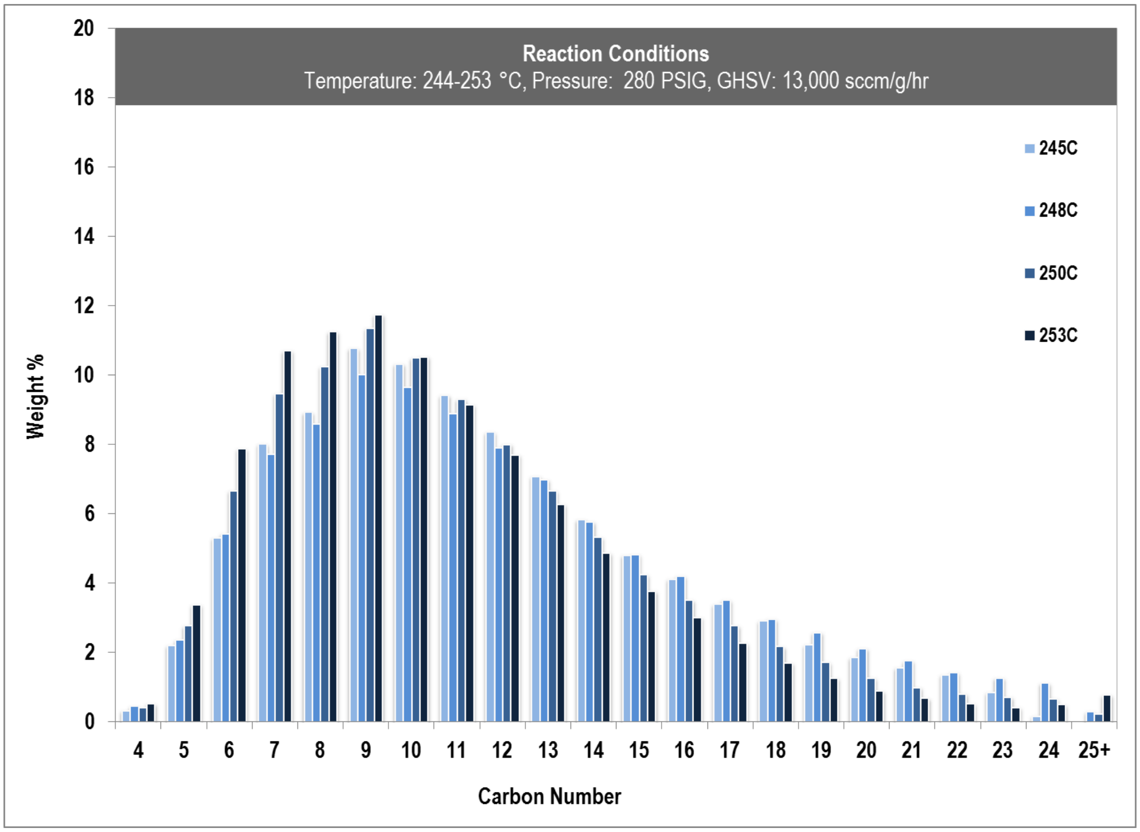


Figure 25. FT conversion and selectivity in MFEC reactor

Table 4 summarizes the straight chain fraction detected in the FT liquid products at different temperature and space velocities. At 13,000 sccm/g/hr, the straight chain fraction decreased with an increase in temperature but there was no effect of temperature at high SV of 17, 000 sccm/g/h. This result is consistent with less catalytic cracking at higher space velocity.

Table 4. Fraction of straight chain hydrocarbons in liquid product.

	Straight Chain Fraction, %
244 °C, 13,000 scc/g/hr	40.0
245 °C, 13,000 scc/g/hr	38.5
248 °C, 13,000 scc/g/hr	36.1
250 °C, 13,000 scc/g/hr	36.1
253 °C, 13,000 scc/g/hr	35.6
245 °C, 17,000 scc/g/hr	32.6
250 °C, 17,000 scc/g/hr	33.3



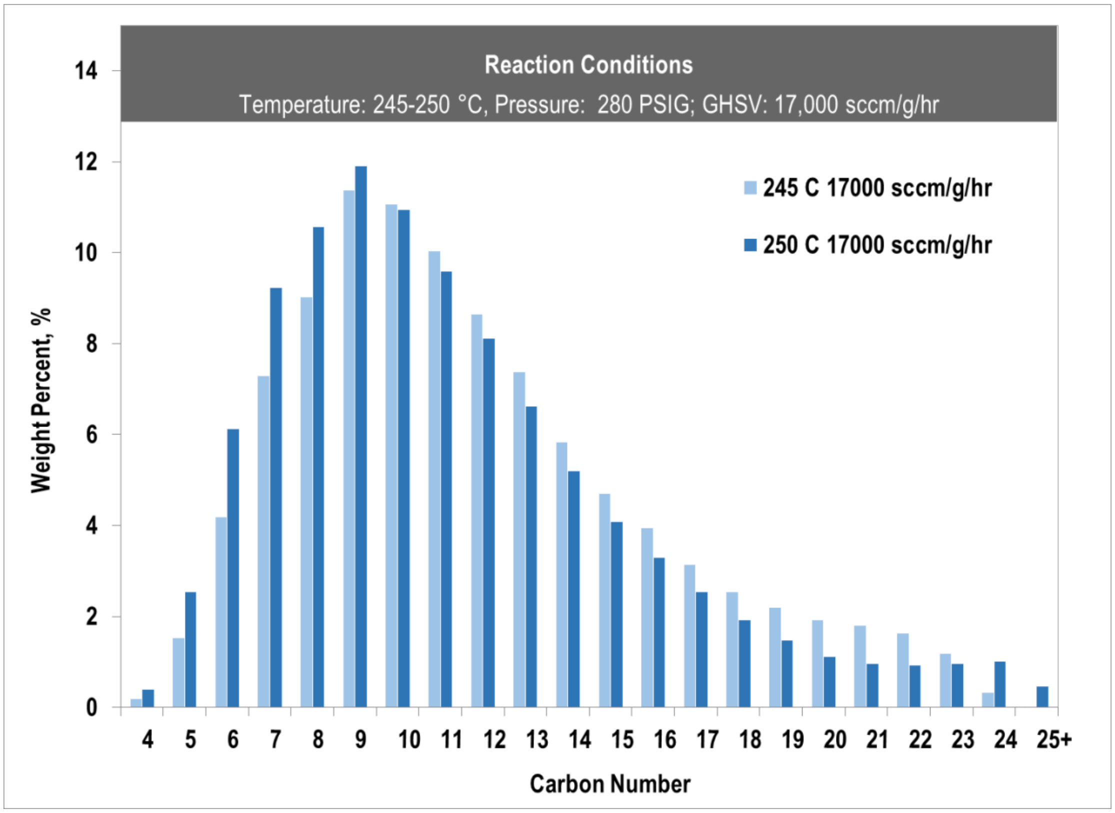
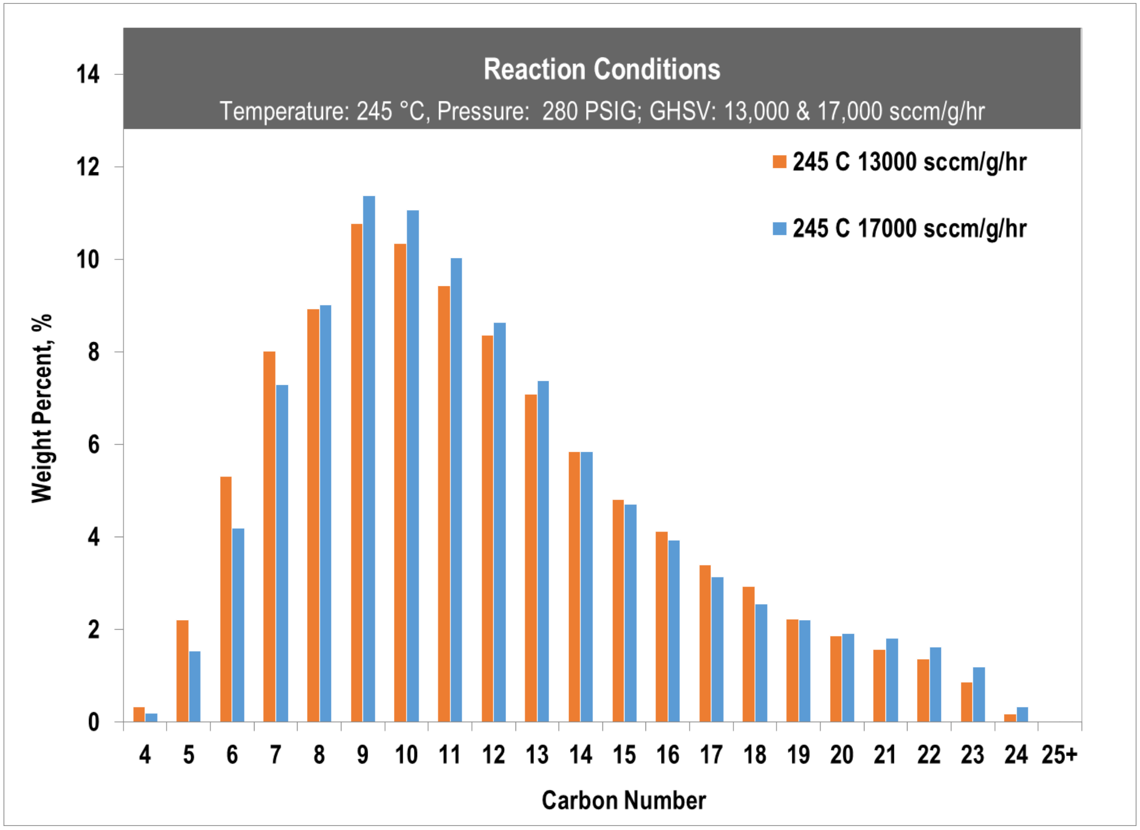


Figure 26. Carbon distribution of FT liquid fuel at varied temperatures and space velocity (MFEC reactor).



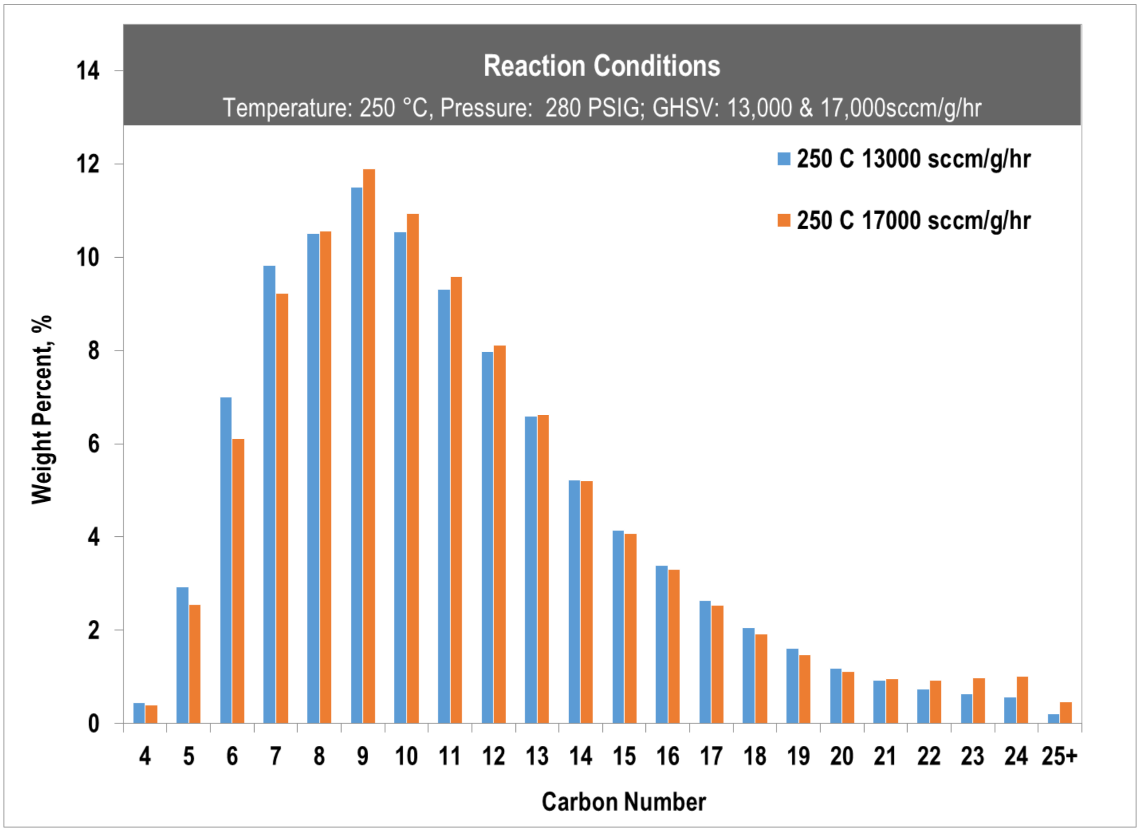
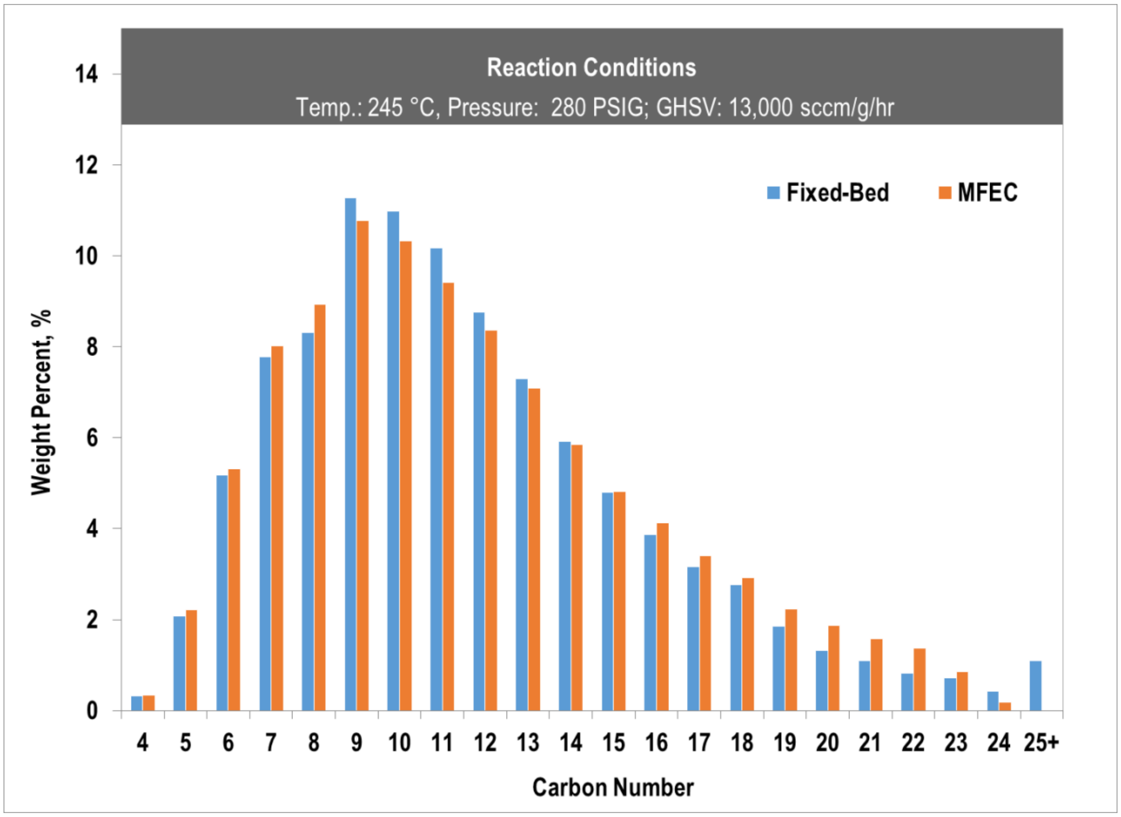


Figure 27. Effect of space velocity on carbon distribution of FT liquid product.



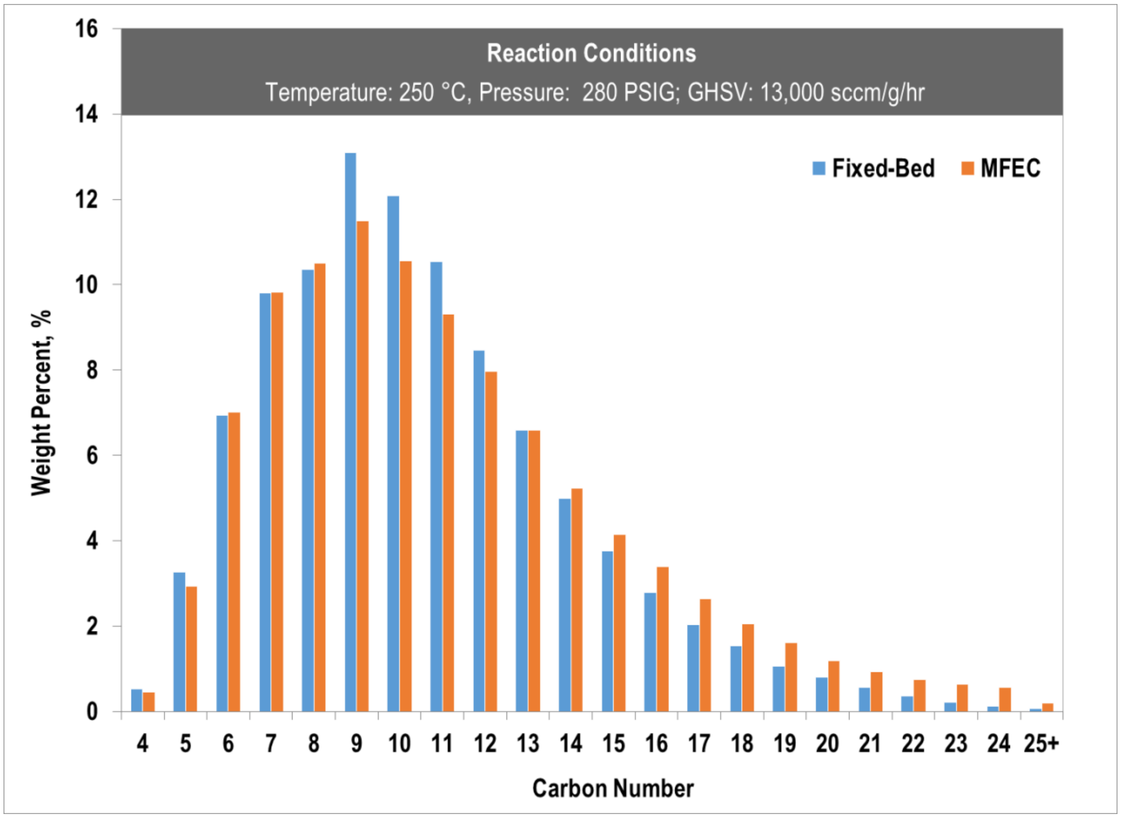


Figure 28. Comparison of carbon distribution of FT liquid product produced from fixed-bed and MFEC reactor.

FT Tests with Fine Catalyst particles: In addition to the 100-200 µm catalyst, Chevron also prepared and sent 3 jet-fuel selective catalyst in the 60-130 µm size range prepared by spray drying. SR evaluated these catalysts in MFEC reactor. From 7 separate tests with these catalyst candidates, only one catalyst showed potential to meet targets.

Fig. 29 summaries the FT results using this catalyst in the MFEC reactor. After activation and stabilization, the catalyst showed expected conversion but higher liquid selectivity (average CO conversion-34.7%; CH_4 selectivity-14.6%, C_2-C4 selectivity-10.4, CO2 selectivity-0.44 and liquid selectivity 75.0%). The CO conversion, however, kept trending down after stabilization.

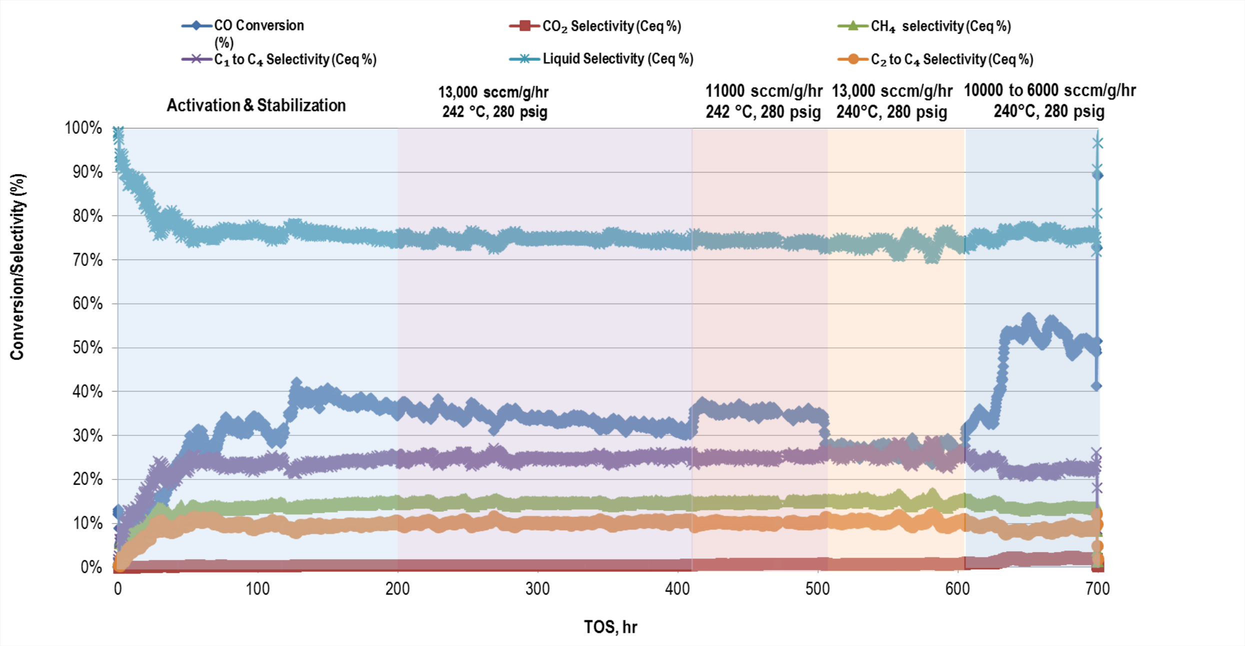


Figure 29. FT conversion and selectivity in the MFEC reactor using a catalyst in small particle size.

SR investigated the effect of space velocity on the catalyst performance. Upon reducing the SV from 13,000 to 11, 000 scc/g/hr, the CO conversion increased to ~37% but the selectivity values were not affected. After cycling the back to 13, 000 scc/g/hr, the CO conversion reduced to <30% indicating a slow loss of catalyst activity. Towards the end of the test, Chevron suggested SR to achieve 50% CO conversion by further reducing the gas space velocity. As shown at the right of Fig. 29, an increasing trend can be observed when slowly dropping the SV from 13, 000 scc/g/hr. The CO conversion reached the ~50% target at SV of 6,000 scc/g/hr and conversion appeared more stable under these conditions.

Fig. 30 summarizes the compositions of the liquid products collected during TOS of 200-600 hrs Overall, the liquid selective to C_8-C_{16} fraction was above the 65% target and no significant variance was observed with different space velocities. However, at the same space velocity of 13, 000 scc/g/hr, the liquid fuel collected from later testing period showed a significant reduction on the C_5-C_7 cuts while C_{10}-C_{24} cuts increased. The difference may be attributed to slow catalyst deactivation during the extended testing period.

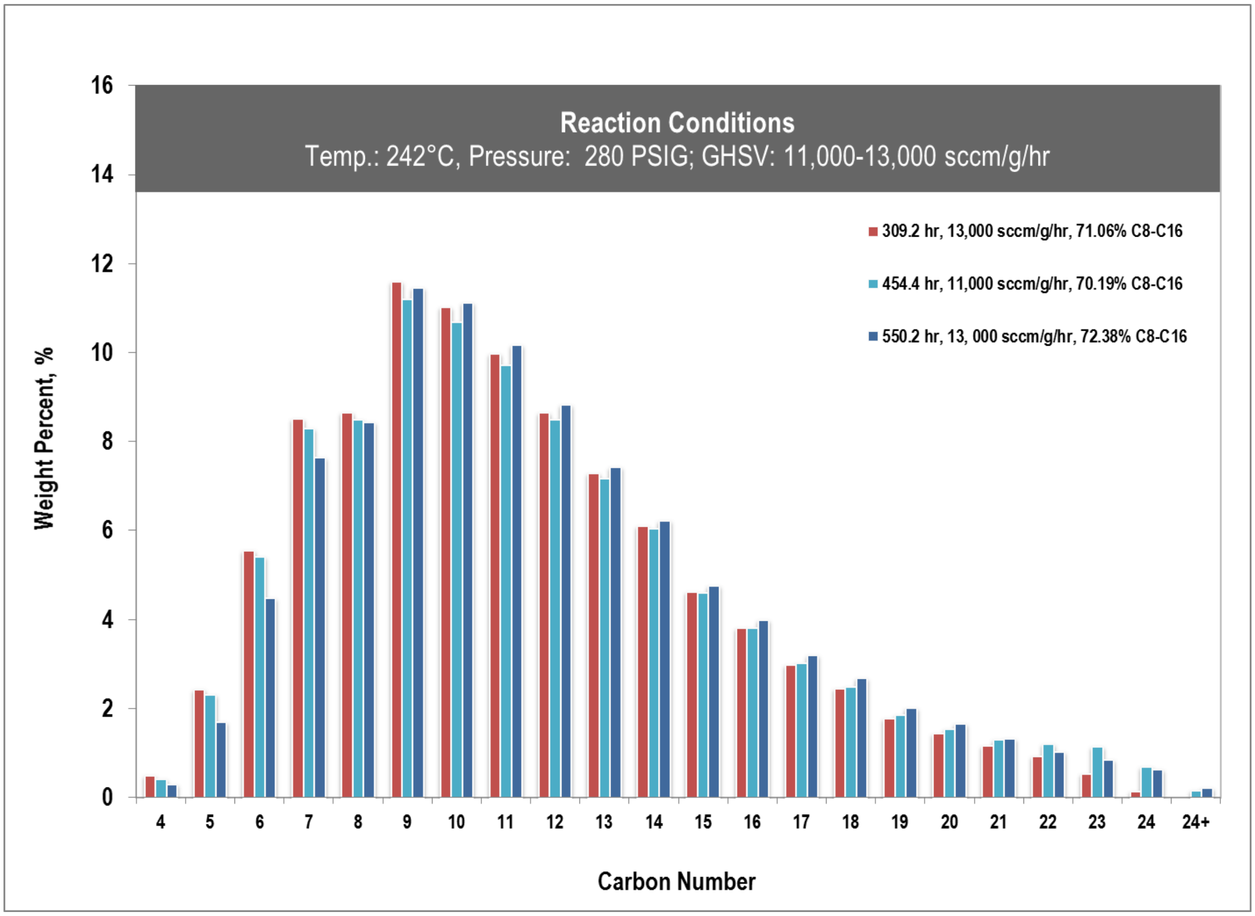


Figure 30. Carbon distribution of FT liquid product produced from MFEC reactor using small particle catalyst at 11,000 scc/g/hr and 13, 000 scc/g/hr.

Fig.31 summarizes the liquid composition during the low space velocity period (TOS of 600 to 700 hr) to achieve 50% CO conversion. The catalyst maintained consistent activity during this period. The results indicate that the lower space velocity slightly decreased overall jet fuel selectivity (C_8-C_{16}) from 72% to 70%. However, as expected, the C_5-C_7 cut increased significantly while C_9-C_{12} cut decreased.

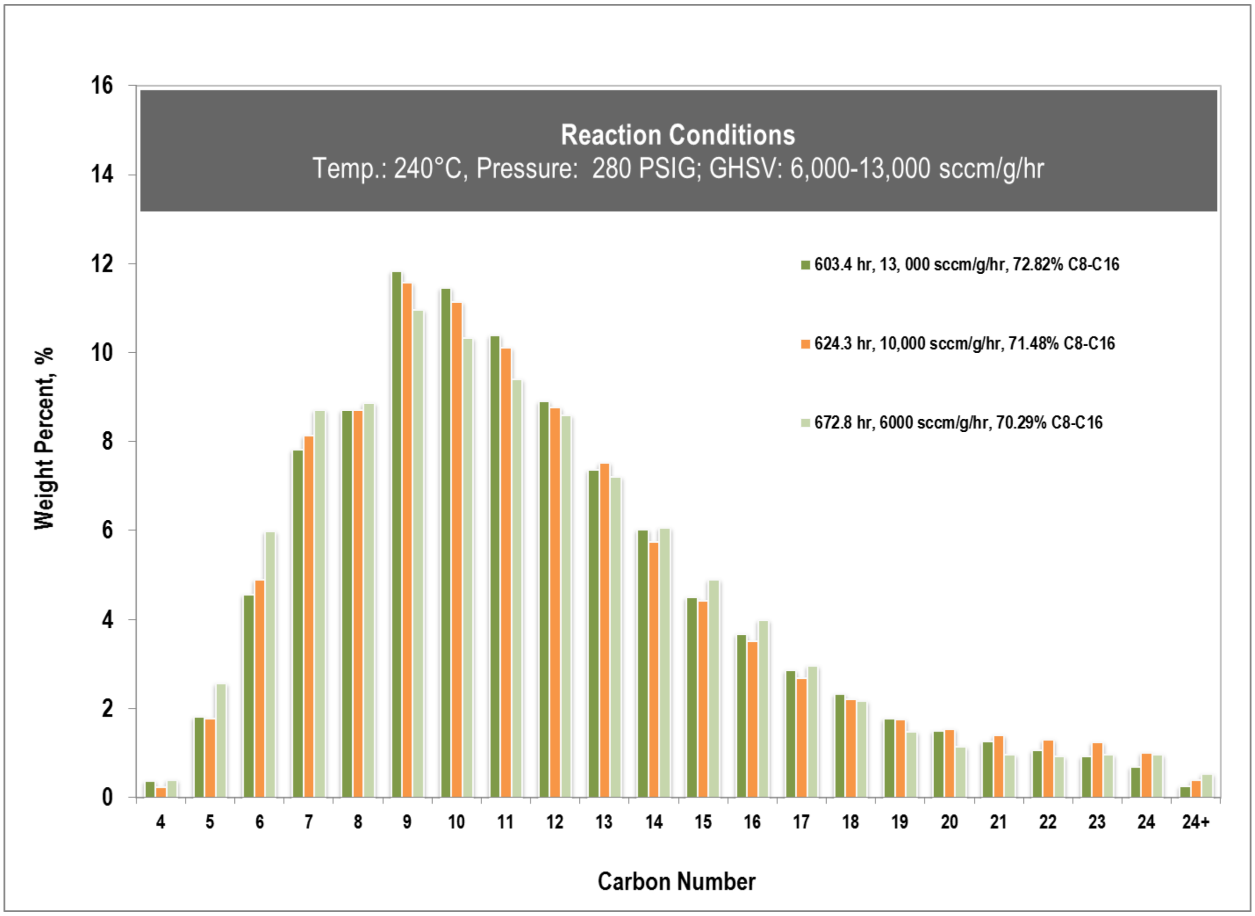


Figure 31. Carbon distribution of FT liquid product produced from MFEC reactor using small particle catalyst at reduced space velocity (from 13,000 to 6000 scc/g/hr).

Field Testing

Reformer

Field testing of the reformer was conducted during the fall of 2017 in conjunction with a gasifier test at NCCC. As indicated in the Experimental section, SR modified the lab-scale reformer for field testing at NCCC under a Class 1, Division 2 environment. The reformer reactor was loaded with with 10 grams of SR's sulfur-tolerant Ni-based reforming catalyst for the field test. The gasifier syngas volumetric percent composition for the reforming test on dry basis was: H2-7.7; CO-8.6; CO2-11.1; CH4-1.1; H2S+COS-0.038; N2-balance. The test was run at 205 psig and 850-900^{o}C at a space velocity of 8,000 scc/(g catalyst.h) with 15 to 30 volume % steam.

Initial operations proved difficult due to an intermittent problem with a thermocouple that was used to control the temperature of the reactor. With the support of NCCC, SR was able to correct the issue and successfully operate the reformer skid about 125 hours on gasifier derived syngas. Test results are presented in Figure 32. Results indicated high conversion of methane (up to 90%) and near complete conversion of tar and ammonia in the presence of 380 ppm H_2S+COS. The experiments demonstrated a strong effect of temperature on reforming catalyst performance as a temperature drop of 50°C dropped methane conversion from ~90% to ~60%, but conversion quickly recovered when the temperature was increased again. Figure 2 shows this impact of temperature on methane conversion during the experiment. SR demonstrated a second key goal during the experiments by controlling the H_2:CO ratio leaving the reformer at 2:1 by manipulating the water (steam) flow to the reactor (Figure 33), thus delivering the ability to eliminate downstream requirement of water gas shift. The catalyst did not indicate any sign of deactivation and the test was considered a success, delivering on tar and ammonia destruction, and increasing the hydrogen to the required H2/CO ratio.

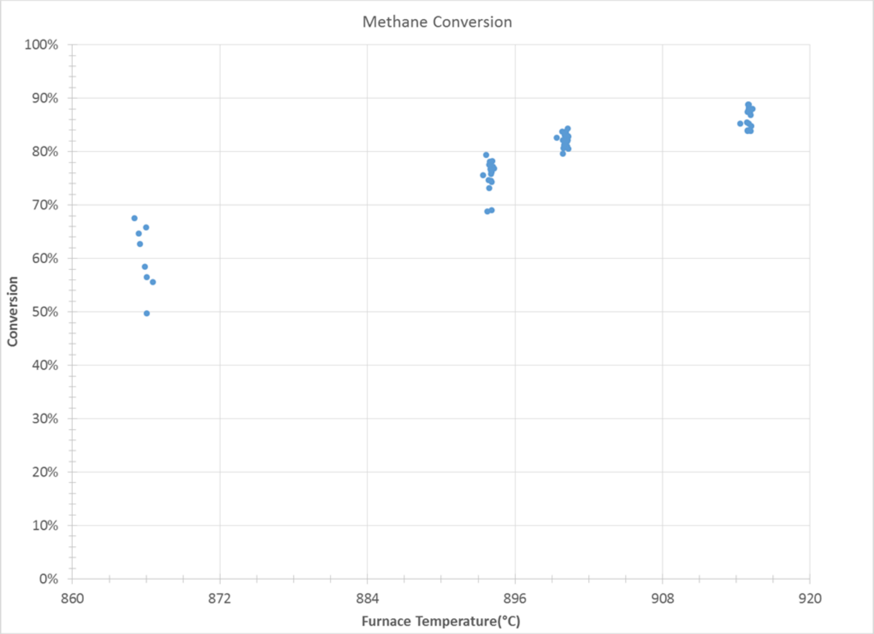


Figure 32. Effect of temperature on methane conversion

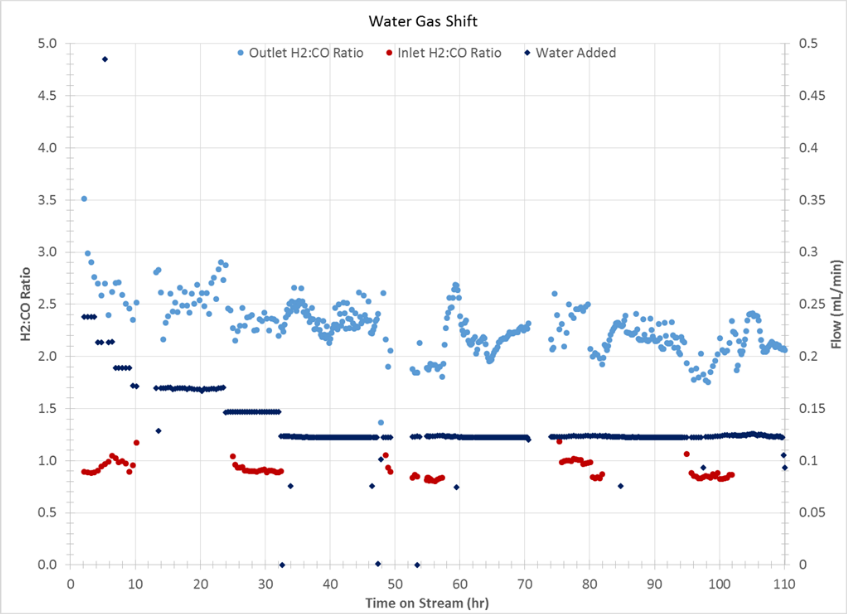


Figure 33. Ability to control H_2:CO ratio by adjusting water flow (steam) to reformer

Fischer Tropsch

Fall 2015 Test: In this test, the 2 inch FT reactor loaded with 300 g of the 100-200 µm FT catalyst was run at conditions provided previously in Table 1. This catalyst was tested successfully both in a fixed-bed reactor and a MFEC reactor in the laboratory as described previously. The FT catalyst was activated using a controlled procedure provided by Chevron. However, during the reduction/activation procedure it appeared that the reactor was prone to high temperature excursion. At the time, these temperatures were taken to be true readings and corrective cooling actions were taken. Later, it was determined that temperature excursions could have been a result of electrical interference in the thermocouple lead wire, and the process was continued.

After the catalyst was activated syngas was brought into the system according to procedure provided by Chevron. The temperature in the reactor was then slowly raised over the course of two days, however, on the first occasion when the reactor temperature reached about 225°C, the top temperature appeared to have an excursion to about 300°C. Then as quickly as the excursion came, it was gone, less than 1 minute up and 1 minute down. A few hours later, another excursion to 260°C occurred, but this was longer, lasting for several minutes and while the temperature was dropping and the gas feed was dwindling, the reactor temperature shot up to 300°C.

After these excursions, there were minor blips in temperature as the reactor was slowly re-heated. Once the reactor was stabilized and was able to run for several hours without anomalous readings, the liquid collection vessel was emptied and a series of experiments were conducted. The experimental conditions for each experiment is listed below in Table 5.

Table 5 Temperature, Pressure, Nitrogen content, and Hours Run for each Experimental Condition

Period Number	N2 (%)	Temp. (°C)	Press. (psig)	Hours Run
1	15.4%	240	250	6.37
2	15.4%	240	235	33.25
3	15.4%	245	235	62.00
4	15.4%	242	240	16.00
5	15.4%	240	240	48.00
6	15.4%	241	240	16.00
7	15.4%	243	240	19.50
8	33.5%	243	280	12.17
9	44.5%	243	280	12.00

The gas flow rates for the various compositions were maintained close to 65 total SLPM while the nitrogen content was changed and the H2/CO were adjusted accordingly (while maintaining a 2:1 H2/CO molar ratio). Gas flows used at various N2 contents are shown in Table 6.

Table 6. Feed Gas Flow

	N2 (SLPM)	H2 (SLPM)	CO (SLPM)
15% N2	9.75	39.20	18.42
34% N2	22.75	31.15	14.08
45% N2	29.90	25.50	11.70

The CO conversion, methane selectivity and C1-C4 selectivity are shown in Figure 34. The liquid selectivity by difference stayed very constant throughout the run at >77 %. Liquid productivities greater than 0.7 g/g cat/h were achieved during the test.

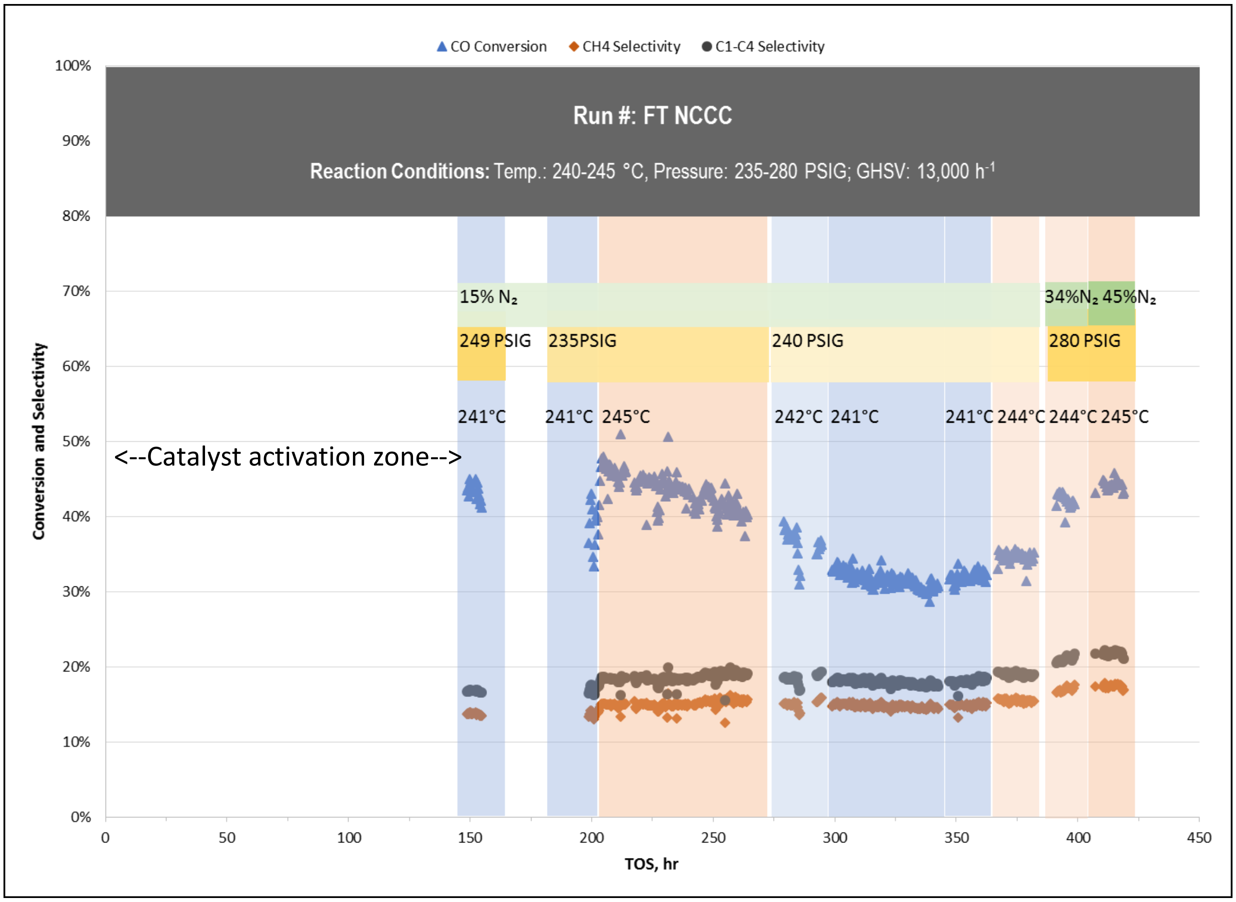


Figure 34. CO conversion and CH4 & C1-C4 selectivities for all experiments

Throughout the experiments the liquid produced from the experiments was collected every 4 hours. The liquids were temporarily stored at the research skid until they could be decanted. A 6 liter separatory funnel was used to separate the water from the liquid hydrocarbons. The entire hydrocarbon sample was retained, while a small 200 ml portion of the water was retained. The remaining water was discarded.

The retained samples were stored until the end of the test campaign in glass jars with Teflon lids. The samples were packaged and shipped to Southern Research where they were analyzed for carbon distribution using a simulated distillation method on a GC. These carbon number distributions are shown in Table 7

Table 7. Carbon Distribution of the Liquid Products

	Temp	Press	C4-C7	C8-C16	C17-C21	C22+
9/25/15 15:28	241.4	248.4	26.2%	69.4%	4.1%	0.5%
9/26/15 16:27	240.7	234.2	18.7%	62.2%	16.0%	3.6%
9/26/15 20:30	240.6	234.9	23.6%	68.6%	7.0%	1.2%
9/27/15 0:30	240.9	233.7	20.8%	65.2%	11.9%	2.5%
9/27/15 4:30	240.6	234.6	21.2%	64.8%	12.1%	2.5%
9/27/15 8:30	240.6	234.0	20.8%	65.5%	11.9%	2.4%
9/27/15 17:30	239.9	234.5	20.8%	64.7%	12.4%	2.6%
9/27/15 21:30	244.6	234.8	21.4%	65.6%	11.5%	2.3%
9/28/15 1:30	244.8	233.1	24.4%	63.0%	11.0%	2.3%
9/28/15 9:30	244.9	234.8	25.0%	64.1%	9.8%	1.8%
9/28/15 13:30	245.3	234.4	26.1%	65.7%	7.6%	1.3%
9/28/15 17:30	245.2	234.9	21.8%	61.1%	15.1%	3.1%
9/28/15 21:52	244.4	236.1	24.1%	64.8%	10.1%	1.9%
9/29/15 2:10	245.3	234.8	24.2%	64.1%	10.4%	2.0%
9/29/15 5:50	245.2	234.8	26.2%	66.8%	6.5%	1.0%
9/29/15 9:50	244.9	234.9	26.2%	67.3%	6.2%	0.8%
9/29/15 13:50	245.0	234.5	23.3%	63.5%	11.8%	2.2%
9/29/15 17:50	245.5	234.7	22.1%	61.0%	14.7%	3.1%
9/30/15 1:50	245.1	234.7	24.2%	64.6%	10.1%	1.9%
9/30/15 5:50	244.9	235.0	25.8%	67.0%	6.8%	1.1%
9/30/15 9:50	244.6	233.6	20.6%	70.1%	8.7%	1.4%
10/1/15 1:50	243.2	240.2	19.5%	61.2%	17.0%	3.7%
10/1/15 5:50	241.7	240.5	20.8%	64.1%	13.2%	2.9%
10/1/15 13:50	242.5	240.4	23.3%	68.8%	7.2%	1.3%

The catalyst was able to produced >0.7 gC5+/gcat/hr, as well as >65% jet fuel range hydrocarbons, both of which are project objectives thus the test was considered a success.

Spring 2017 Test: This test was conducted in a 4.0 inch FT reactor loaded with 450 g of the more active 60-150 µm size catalyst. SR reloaded guard beds, calibrated analytical instruments, finished final leak checks, and initiated FT catalyst activation on March 31. The test period was a shorter 125 hours due to budget constraints. Initial startup of the FT system again proved difficult due to syngas leaks. Again, NCCC personnel supported SR to correct the issue. An abrupt loss of CO on the FT process followed by a later abrupt restart of CO caused a temperature runaway that damaged an estimated 50% of the FT catalyst. Additional abrupt losses of simulated syngas due to area alarms from routine NCCC gasifier facility maintenance also caused operational difficulties and reduced the amount of steady state data. The alarms apparently stemmed from maintenance of a filter just after shift change. The process control system was not programmed to automatically respond to either of these issues. Temperature on 4 inch ID reactor was initially more difficult to control than the 2 inch reactor. Our operating team needed several days to develop new control strategies to operate without constant risk of temperature runaways.

As expected, temperature control was more difficult than previous tests with the 2 inch reactor, but SR successfully tested the catalyst for approximately 125 hours. SR's thermo-syphon system maintained reactor operating temperature along the axis to within ±5 °C. Results indicated similar catalyst productivity and liquid hydrocarbon selectivity but with higher jet fuel selectivity than the previous test.

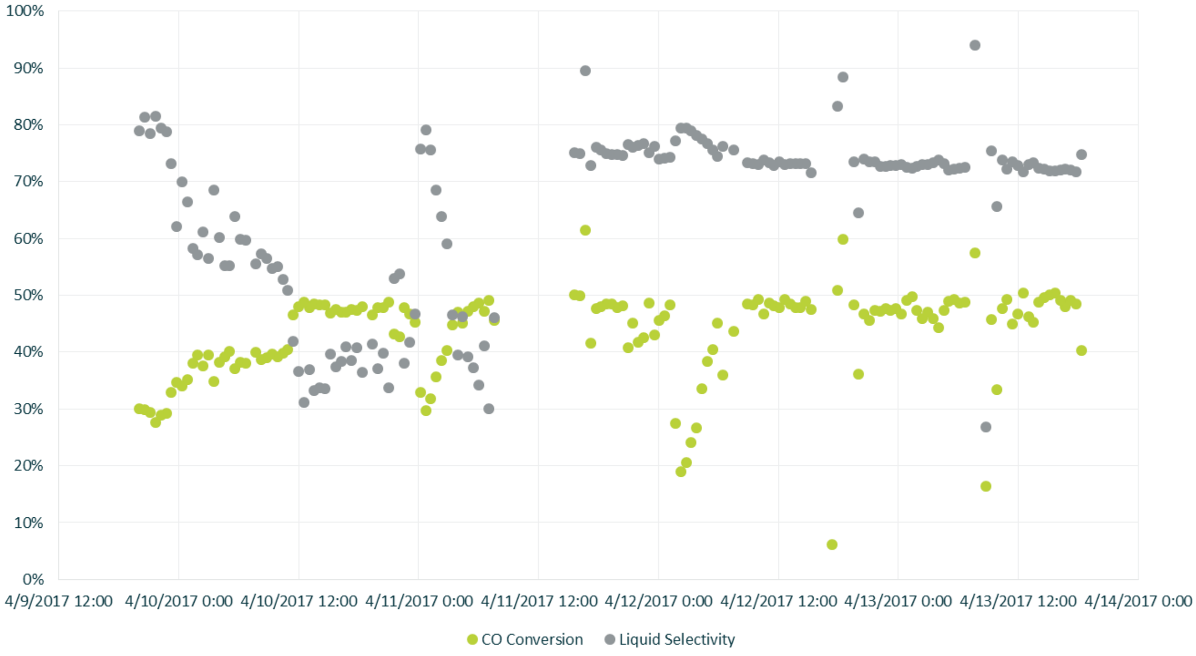


Figure 35. CO conversion and liquid selectivity in test with 4 inch reactor

Liquid hydrocarbon distribution measurements for 2017 samples indicated the jet fuel range hydrocarbon selectivity was ~75% with almost nothing detected above C22 as shown for four separate samples collected during the test in Figure 36; thus the test was considered a major success. Figure 37 shows the jet fuel selectivity for these steady state samples obtained during the run. Our lab measured up to 35% olefins in these samples, but ASTM specifications for jet fuel limit olefins to less than 1%. SR developed a simple process to reduce olefins down to the required ASTM specifications while further increasing the jet fuel selectivity to 87 %. .Figure 38 shows results in which one of the samples was upgraded. In this single step process the jet fuel selectivity increased to >87%. We expect a substantial improvement on the economics of the process based on this development.

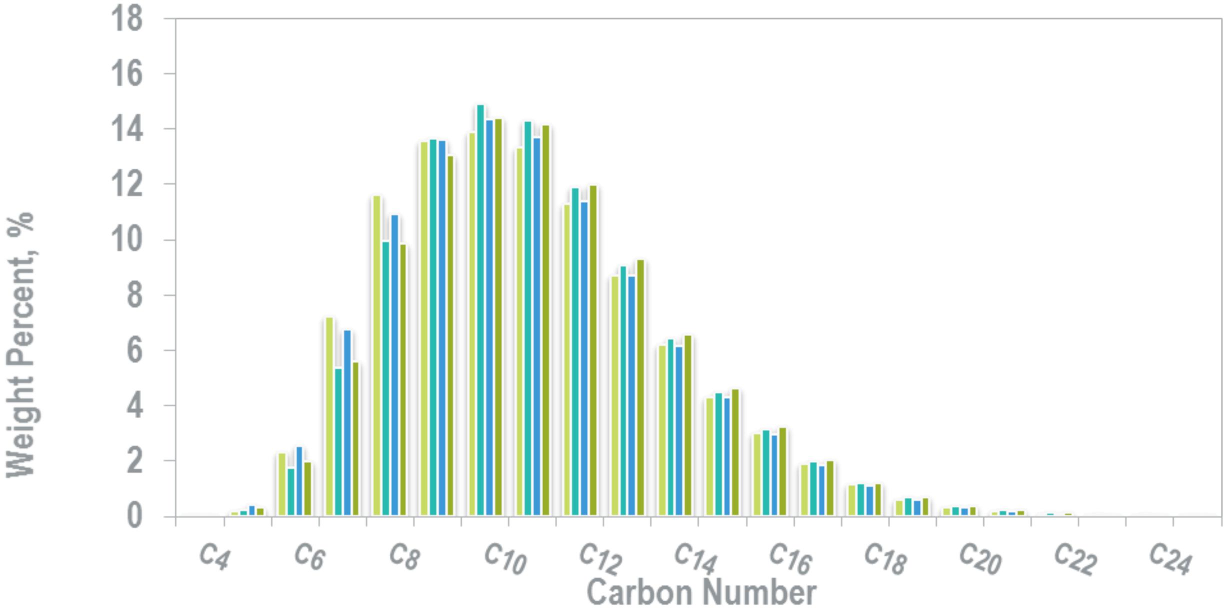


Figure 36. Carbon number distribution for liquids produced in 4 inch FT reactor

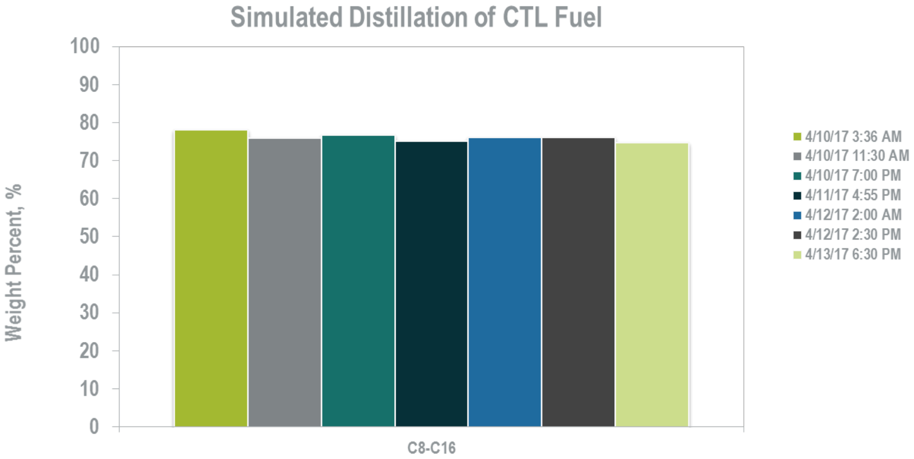


Figure 37. Jet fuel selectivity in steady state samples collected during 2017 experiment

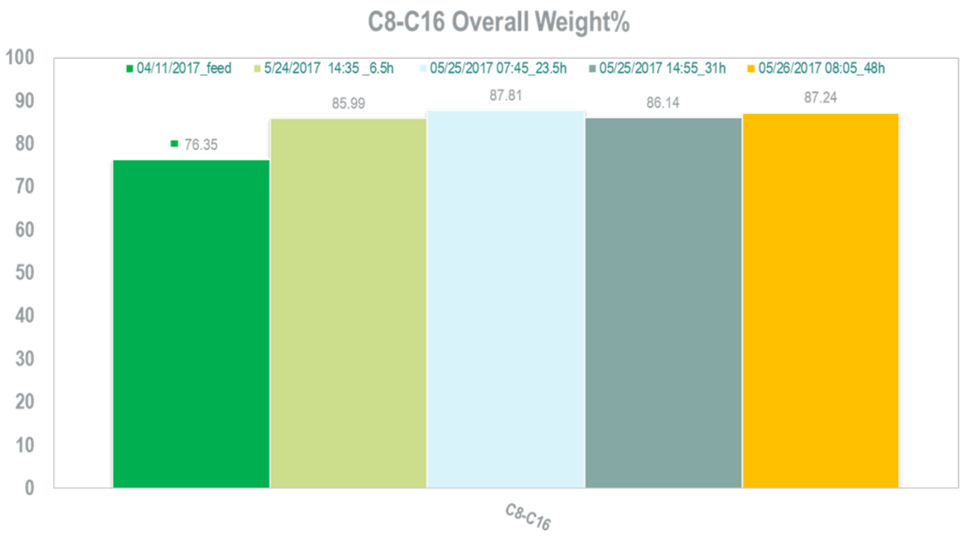


Figure 38. Upgrading process increased jet fuel selectivity to 86%

Preliminary Techno-Economic Evaluation

Economic performance of a 50,000 bpd plant utilizing the SR auto-thermal reformer (ATR) and selective Fischer Tropsch (FT) conversion reactor was compared with a baseline coal-to-liquids plant (CTL), both with carbon capture rates of more than 90%. The baseline plant was taken from a Nexant report to SR under Cooperative Agreement DE-FE0012054 that provides the cost analysis for the Fischer Tropsch (FT) CTL plant, utilizing KBR's Transport Gasifier (TRIG) running PRB coal. The SR technology-based plant was also based on this report, however, the selective FT reactor was substituted for the slurry bed reactors.

A simplified process flow diagram for the SR ATR-FT CTL plant is shown in Figure 39. Aspen plus was used to model the SR FT CTL plant to produce C1-C20 liquid fuels. The products may require a mild upgrading step to saturate olefins but no wax hydro cracking step will be required. The liquid products are separated to produce jet fuel and diesel (C8-C20) while the naphtha (C5-C7) cut was recycled back to the ATR.

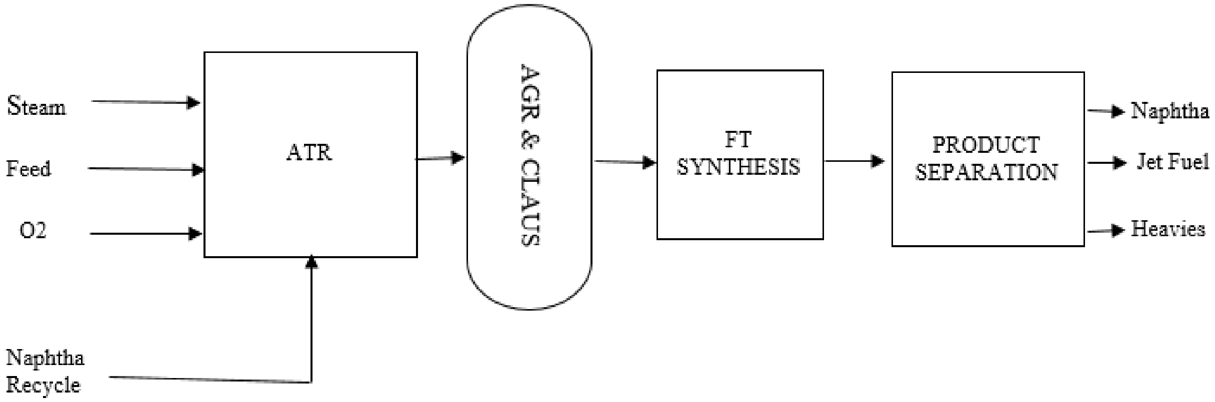


Figure 39. SR's ATR-FT CTL plant simplified process flow diagram

The capital costs generated for the tubular FT reactors were based on the estimates developed by Prakash and Bendale [DOE/PC/89870-T1 (Suppl.)(DE92011812)]. The reactor dimensions were not altered, however, the expected conversion percentage was increased from the 37% found in the report to 50% as a result of the improved heat management of the MFEC. The costs were scaled using chemical engineering plant cost index (CEPCI) values for 1991 and 2011. The installation, engineering, and contingencies for these reactors was assumed to be similar to the slurry reactors and a factor of 1.62 was used to convert bare equipment costs to total plant costs (TPC).

The comparison of the two cases is provided in Tables 8 and 9. In Table 8, the breakdown of the equipment and associated costs are provided and added to come up with a total plant cost (TPC). As can be seen, the SR technology results in a >10 % reduction in TPC even though a 50 % higher cost is assigned to the gasifier and accessories (due to high contingencies assigned to the ATR). Table 9 compares the crude oil equivalent required selling price (RSP) of the Fischer-Tropsch liquid products and the annual revenue requirement (ARR) for the two cases. It can be seen that both are lower for the SR technology case by about 2 %.

Table 8.Total Plant Cost ($K) for 50,000 BPD plants

	Base Case	SR Technology Case
Coal and Sorbent Handling	$135,299	$111,879
Coal and Sorbent Prep & Feed	$457,599	$373,778
Feedwater & Misc BOP Systems	$23,738	$19,474
Gasifier and Accessories	$1,069,989	$1,543,550
Gas Cleanup & Piping	$1,217,683	$914,838
FT-Synthesis and Product Upgrading	$962,481	$654,648
CO2 Removal & Compression	$123,131	$101,224
Combustion Turbine/Accessories	$96,149	$96,149
HRSG, Ducting, & Stack	$124,754	$26,857
Steam Turbine Generator	$121,536	$62,011
Cooling Water System	$52,616	$40,626
Ash/Spent Sorbent Handling system	$133,157	$109,923
Accessory Electrical Plant	$154,246	$121,975
Instrumentation & Control	$37,106	$35,553
Improvements to site	$49,788	$49,517
Buildings and Structures	$37,736	$36,981
Total TPC	$4,797,008	$4,298,983

Table 9. Economic Summary of 50,000 BPD Plants

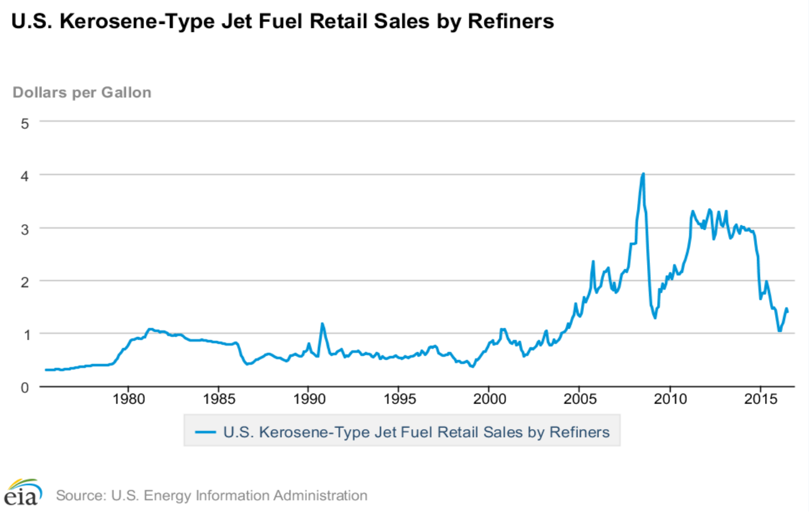
	Base Case	SR Technology Case
TPC (*1000)	$4,797,008	$4,298,983
OWNERS COST(*1000)	$1,061,844	$961,243
TOC (*1000)	$5,858,852	$5,260,226
TASC (*1000)	$7,715,660	$6,033,479
OC_{FIX} (*1000)	$190,158	$184,052
OC_{VAR} (*1000)	$131,893	$120,085
Fuel Cost (*1000)	$231,214	$170,167
Power Export Credit (*1000)	-$163,685	$21,888
RSP ($/gallon)	$2.42	$2.38
ARR (*1000)	$1,666,810	$1,642,921

The methodology for calculating RSP and ARR was as follows. First, owner's cost was added to TPC in Table 9 to come up with the total overnight cost (TOC) for the system. Owner's costs include preproduction costs, inventory capital, initial cost for catalysts and chemicals per design, cost of land (300 acres at $3000 per acre), financing cost (at 2.7 % TPC), and miscellaneous costs (at 15 % TPC). The operation and maintenance (O&M) costs in Table 9 pertain to those charges associated with operating and maintaining the plants over their expected life. These costs include labor (operating, administrative, and support), maintenance, consumables, fuel and waste disposal. There are two components of O&M costs; fixed O&M, which is independent of power generation and FT liquid production, and variable O&M, which is proportional to power generation and FT liquid production. Variable O&M costs were estimated based on 90% capacity factor. The RSP is the minimum price at which the products must be sold to recover the annual revenue requirement (ARR, Table 9) of the plant and was calculated as follows:

$$\text{RSP} = \frac{\text{first year capital charge} + \text{first year fixed operating cost} + \text{fist year variable operating cost}}{\text{annual net Fischer Tropsch Liquid production}}$$

The ARR is the annual revenue needed to pay the operating costs, service the debt, and provide the expected rate of return for the investors, and was calculated as the sum of fuel cost, variable operating cost, fixed operating cost, and annual capital component minus the by-product credits for electric power sale revenues. The annual capital component of the ARR was determined as the product of the total overnight cost (TOC) and the capital charge factor (CCF). The CCF for evaluating the RSP is determined from NETL Power Systems Financial Model (PSFM). Commercial fuels project financial structure is best suited for the FT CTL plant CCF calculation. The estimated CCF using commercial fuels project financial structures used in this study is 0.218.

The FT CTL project is considered economically viable if the market price of the product is equal to or above the calculated RSP. Figure 40 shows the historical retail price of U.S Kerosene-Type Jet Fuel (C8-C16) for the purpose of comparison to our model. It is apparent that at a production capacity of 50,000 BPD, the plant was relatively profitable when compared to U.S jet fuel retail prices in the years between 2010 and 2015.



Source: U.S. Energy Information Administration

Figure 40. Historical prices of U.S kerosene-type jet fuel retail sales by refiners

SR is presently developing a modular gasification system (under DOE Cooperative Agreement DE-FE0031531) that would be well suited to the selective SR coal to jet fuel/diesel technology developed in this project at small scales of about 1000-5000 bpd. Preliminary TEA results (Table 10) indicate that the capital cost based on the modular SR gasifier and other advanced technologies from TDA for air separation and RTI for warm gas desulfurization can significantly reduce the cost of indirect liquefaction.

Table 10. Comparison of Total Plant Cost (TPC) for Small Plants—Conventional FT vs Advanced Modular system with SR FT and Gasifier

Plant Size	Conventional (Million $)	Advanced (Million $)	Percent capital cost reduction
5000 bpd	1,205	827	31.4
1000 bpd	458.8	294.7	35.8

The costs in Table 10 are preliminary and scaled down from the 50,000 bpd costs by the six-tenth rule. They are provided for comparative purpose only and only to illustrate the potential for lower costs as we scale down. It is to be noted that the percent capital cost reduction for the 1000 bpd plant is actually higher than the 5000 bpd plant illustrating the advantages of factory built modular construction which is suitable for the small scale SR technology-based FT system.

Conclusions and Recommendations

Conclusions

- Based on results of a slip stream test at NCCC, a sulfur-tolerant nickel-based reforming catalyst prepared by Southern Research was shown to reform light hydrocarbns, tar, and ammonia in the presence of high levels (380 ppmv) of H2S and COS. This catalyst outperformed noble metal-based catalysts at such high sulfur concentrations.
- In lab-scale tests, Chevron's Co-zeolite hybrid FT catalysts consistently performed at hydrocarbon productivities >0.7 g/g cat/h with very high durability and liquid selectivity >75 %.
- The jet fuel selectivity in the liquid was consistently >65 %
- Chevron catalysts in 70-200 micron range were successfully supported on IntraMicron MFEC packing in 2 inch and 4 inch diameter fixed bed reactors.
- The thermally conductive copper-based MFEC along with SR's thermal syphon system was able to maintain near isothermal FT reactor conditions in the 2 and 4 inch reactors by efficiently removing reaction heat.
- Based on a preliminary TEA, the SR advanced technologies developed in this project combined with other advanced technologies being developed has the potential to reduce capital costs over conventional FT-CTL technology by over 35 % in small modular plants smaller than 1000 bpd.

Recommendations

- The FT and ATR technologies have sufficiently advanced in this project and should be scaled up to pilot-scale demonstration of 5-20 bpd.
- Rigorous TEA should be conducted for small modular 100-500 bpd distributed plants using these technologies to evaluate the cost advantages of factory built small modular plant components.

Appendix 1: Final Project Report by PCI

Precision Combustion, Inc.
Subcontractor to Southern Research Institute
Period of Performance: Nov 26th, 2014 – March 31st, 2017
Subcontract No. 14364 – DOE - 111814

FINAL REPORT

Principal Investigator: Jeffrey G. Weissman

Business Contact: John Scanlon

Southern Primary Contact: Santosh Gangwal

Table of Contents

Project Summary

Precision Combustion Inc. (PCI) proposed to optimize heterogeneous catalysts for and build an oxy-blown autothermal reformer (ATR) for Southern Research (Southern) as a subcontract to Southern's bio-coal to FT-liquids project. The overall project goal was to convert coal-gas, as supplied by National Carbon Capture Center's (NCCC) coal gasifier, into a H_2 and CO containing syngas suitable for use as a feed to a downstream Fischer-Tropsch unit. Syngas exiting the ATR would be at proper temperature, pressure, and H_2/CO ratio to directly feed into a Fisher-Tropsch upgrading unit. The ATR was to be based on a prior PCI oxyblown design with minor design modifications, part sourcing or manufacturing, and controller and system programming, with performance qualification to take place at PCI's site. Additional work related to catalyst cost reduction and use of Southern's ATR catalyst were also proposed. The outcome was to be a techno-economic analysis of the feasibility of using PCI's ATR system and reduced cost catalyst for use in a large scale, 10,000 to 50,000 barrel-per-day, coal-gas to fuels project.

A catalyst with reduced cost was found to be acceptable for the intended application, exhibiting very good resistance to the sulfur levels and operating temperatures expected. Although overall catalyst activity as measured under rigorous testing conditions was less than for the standard catalyst, the activity level was determined to be more than adequate for the coal-gas conversion operation.

ATR design and fabrication were changed significantly from as proposed, due to the requirement to meet strict NCCC safety standards. Changes included: requirement for a code-stamped reactor pressure vessel, change from oxygen-blown to air-blown operation thereby requiring significantly higher flow rates (as compared to original concept) due to nitrogen dilution, need for specific requirements for pressure relief valves, with specific functionalities, and extensive mechanical and electrical changes to comply with Class 1, Division 2 area classification requirements as specified by NCCC, and the need to provide equipment installed in an inert-gas purged enclosure, plus related changes to control and operation. These changes required extensive re-engineering and redesign of the ATR system, eventually involving multiple iterations. The result was that the entire ATR system and many of the subsystems, controls, and components were designed specifically for this project. The magnitude of the changes resulted in a situation such that hardware could not be delivered within the confines of the existing project.

Most design and control related activities were finished; some details related to installation in the purged enclosure or use at NCCC remains to be finalized. An extensive HAZOP review and resulting detailed level of response, including flow and hazardous conditions calculations, were completed. The code-stamped pressure vessel for use at the ATR reactor was built and delivered, as were some of the reactor internals and balance of plant equipment. Many of the long-lead time equipment were purchased and delivered as well.

Results

Reduced cost contaminant tolerant ATR catalyst development

Extensive catalyst testing was required in order to validate the best two low-cost options for replacement of our standard, higher cost catalyst formulation. As proposed by PCI, 500-hour essentially unattended durability tests on each catalyst formulation were to be conducted. However, this led to out-of-spec and thermally hazardous catalyst testing conditions, requiring the use of more complex and labor-intensive testing protocols, as well as validation of the new testing procedure. The outcome of this improved testing procedure was qualification of two compositions that should meet long term performance requirements at a much reduced costs while performing to specifications with high sulfur feeds.

Prior to this project, PCI had developed a bench scale methane partial oxidation test for evaluation catalysts. Catalysts were tested in a kinetically limited regime, close to but not at equilibrium performance, in order to permit discrimination between catalyst samples and treatments, i.e. impact of feed contaminants or catalyst compositions on catalytic activity.

In brief, the test procedure is: load catalysts into the tubular reactor held in a temperature controlled furnace. Catalyst back face and center temperatures are measured, as well as furnace temperature. A pre-mixed flow of 22.5 slpm air and 7.25 slpm methane (standard taken at 1 atm., 70 °F) was passed over the catalyst, giving a space velocity, at standard conditions, of ~1,600,000/hr at an O/C mole ratio of 1.30. Furnace temperature is ramped down from 950 °C, in 50° increments, to about 650 °C; typical catalyst center temperatures vary from 960 to 910 °C, largely as a result of the reaction exotherm and the high rate of enthalpy released by the reaction, as compared to furnace energy input. A slip-stream of exit gas was drawn into a micro-GC, at ~100 cm³/min, after passing through a drying tube. Produced gases are analyzed for H_2, O_2, N_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_3H_6, and C_3H_8 content. Carbon balances are closed to within 1%.

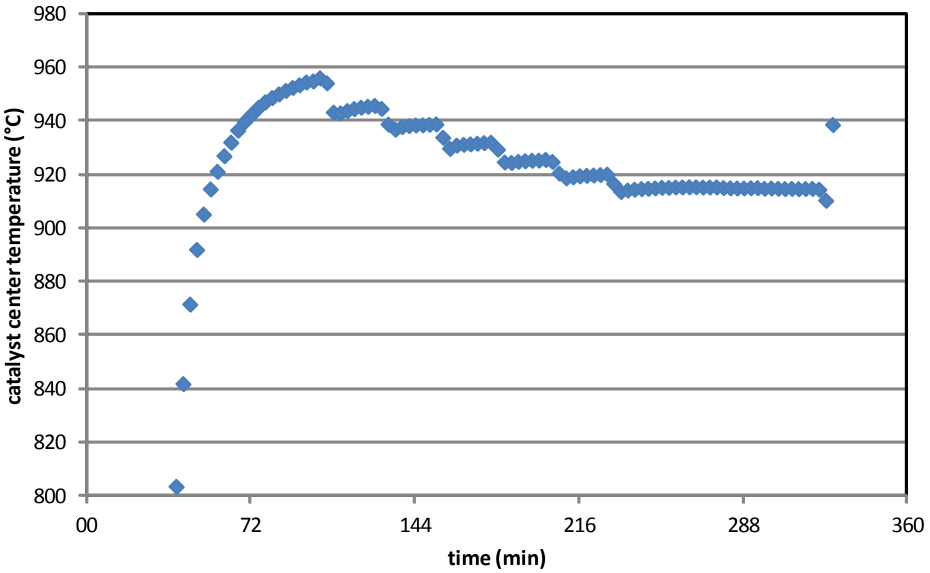


Figure 1: Temperatures recorded during testing of baseline catalyst

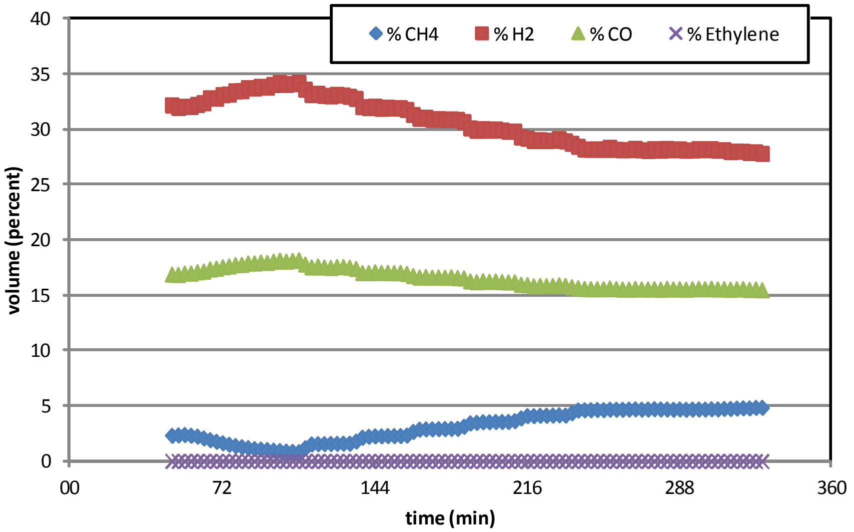


Figure 2: Methane, H_2, CO and C_2H_4 concentrations measured during testing of baseline catalyst

Data was plotted as 1/T (T in K) vs. ln(k) to give Arrhenius plots to aid in comparing catalysts, using simple first order kinetics, where $-k = k_0 \exp(-E_a/RT)$ to determine activation energy, E_a, of the rate limiting step and kinetic factor k_0. The rate limiting is assumed to be related to the number of catalyst activity sites, which is reflected in k_0, and so is a measure of catalyst performance, provided the same rate-limiting step is controlling, if E_A is similar for a given set of catalysts under comparison.

Once E_A and k_0 are known, then the reactor design equation which related activity, space velocity (SV) and conversion (X) can be used for reactor sizing, and also for predicting reactor behavior as a function of catalyst deactivation or age: $k = \mathrm{SV} \ln(1/(1-X))$.

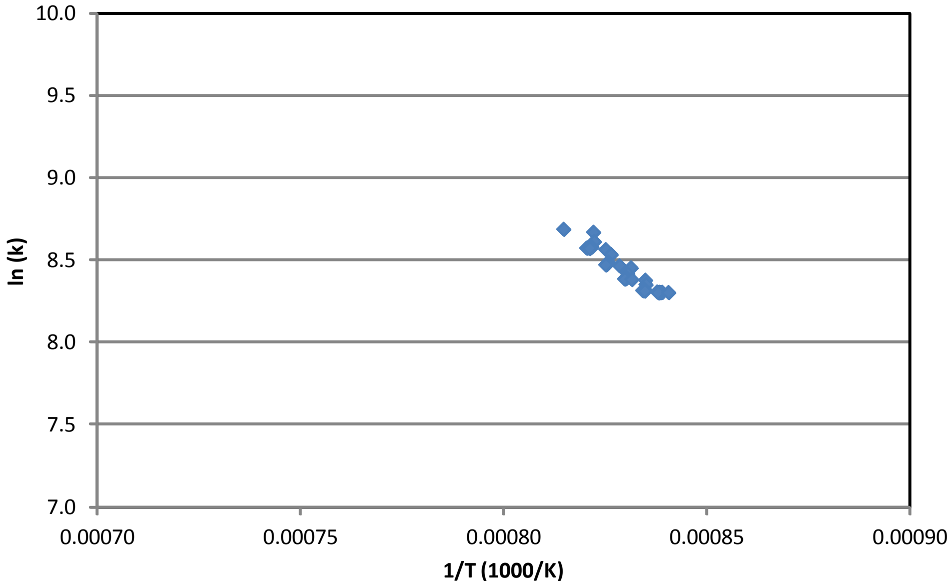


Figure 3: Arrhenius plot for baseline catalyst

Thus while a catalyst may have a lower value of k_0 as compared to the baseline, sufficient activity may still be present so that for a given operating temperature, space velocity and catalyst age, design criteria, conversion for example, can still be met. In other words, the reactor is overdesigned for a fresh catalyst, in order to account for catalyst aging while still being able to meet performance and product quality specifications. The extent of overdesign is greater for the baseline catalyst. Alternatively, a less expensive but less active catalyst may need a larger reactor or operate at a lower SV to achieve the same level of performance.

Once we construct the full scale reactor and evaluate its performance, these kinetic values will be used to determine if any of the lower cost alternatives will be able to meet product quality specifications at the same space velocity while meeting durability specifications.

Sulfur Rapid Aging Testing

Catalysts were evaluated for initial performance, as in Figure 3, exposed to H_2S, then evaluated for short-term aged performance. 16 hours of exposure to sulfur was through the use of 60 ppm H_2S at the catalyst inlet, by blending H_2S with air. Exposure to H_2S resulted in an increase in catalyst center temperature of over 200 °C or more and decrease in methane conversion, as listed in Table 1 for the baseline catalyst. The catalyst exhibited significant deactivation as a result of sulfur exposure, reflected in the plot in Figure 4. The similar slopes in the two curves suggest that the deactivation mechanism is loss of catalytic active sites, likely due to sintering. Similar behaviors were observed for all catalysts before and after H_2S exposures.

During full scale operation (5 kW or greater) temperature is controlled at +/- 975 °C, by adjusting the O/C ratio. As a consequence, even during exposure to sulfur, the catalyst does not experience the high temperatures observed in the bench scale testing. During the bench scale testing catalysts experienced unknown extent of aging, we will need to conduct durability tests on full scale catalysts, and then measure the activity, as a function of time-on-stream, to correlate deactivation seen here to actual durability.

Table 1. Change in baseline catalyst performance during and after 60 ppm H_2S exposure

	adiabatic temperature (°C)	methane conversion
initial (furnace off)	915	80.6 %
during H_2S	1099 - 1158	53.3 - 43.7 %
final (H_2S off, furnace off)	959	68.5

.

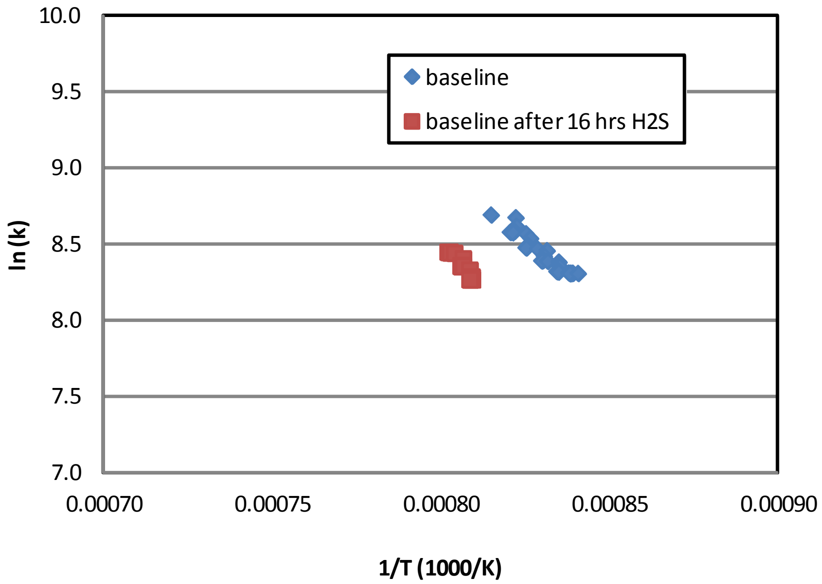


Figure 4: Arrhenius plot for baseline catalyst before and after 16 hour 60 ppm H_2S exposure

Catalyst Evaluation

Machine coating catalysts is only practical at a production-scale. Catalysts were hand coated onto small lots for purpose of bench scale screening. A baseline catalyst was also hand coated for comparison purposes. A small decrease in performance for hand coated equivalent catalysts was noted. Once suitable compositions are identified, machine-coated samples were produced for testing in the full scale reactor.

Samples prepared include reduced active metal content, replacement of part of the active metal with co-catalyst, and modifications to the support composition aimed at improving the stability of the catalyst samples; additional samples for comparison purposes were also prepared; these are summarized in Table 2. Figure 5 compares performances of PCI standard (baseline) catalysts tested before and after exposure to 16 hours of sulfur, showing that machine coating yields a somewhat better performing catalyst. We expect the difference between hand and machine coating to be similar regardless of composition variations.

Table 2. Summary of compositions tested.

#	coating method	wt. loading (% of base)		support	comments
		catalyst	co-catalyst		
1	machine	100		standard alumina	
2	hand	100		standard alumina	
3	hand	25	75	standard alumina	
4	hand	25	75	alumina mod 1	
5	hand	100		alumina mod 2	
6	hand	25	75	alumina mod 3	
7	hand	25		standard alumina	
8	hand	5	95	standard alumina	
9	machine		100	standard alumina	in-situ air 1 hr 575 °C prior to testing
10	machine		100	standard alumina	in-situ H2 1 hr 675 °C prior to testing
11	machine	100	100	standard alumina	
12	hand	100		alumina mod 4	
13	hand	25	75	alumina mod 4	

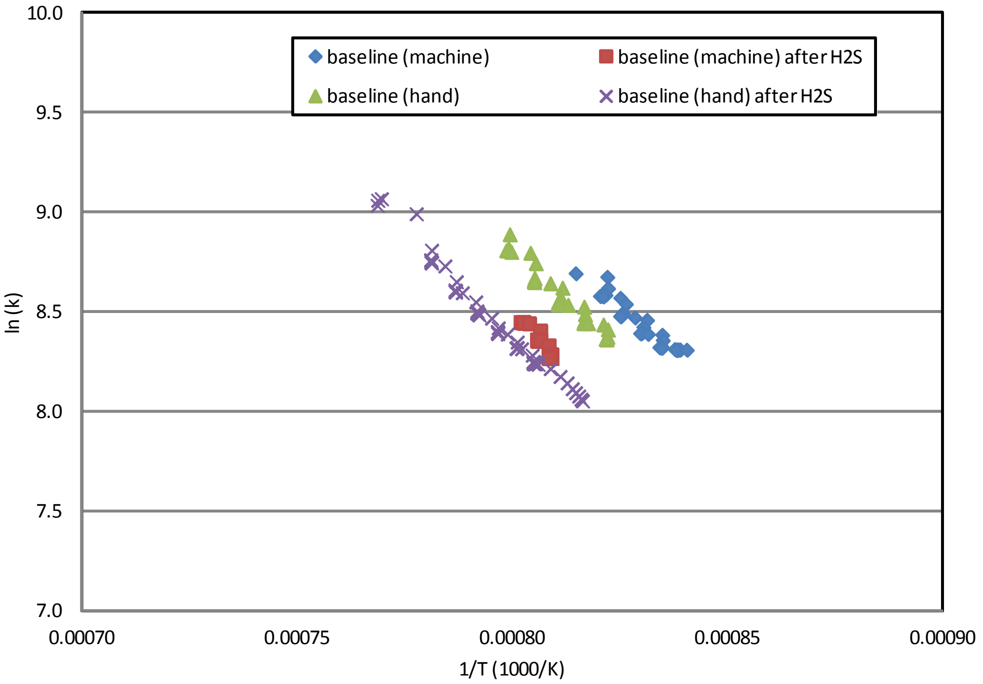


Figure 5 Comparison of baseline catalysts prepared by machine, 1, or hand, 2, before and after sulfur exposure.

Catalyst Rankings Arrhenius parameters E_A and k_0 were determined for each of the catalysts listed in Table 1 before and after sulfur testing, based on straight-line best fit to the data expressed as ln(k) vs. 1/T data. Catalyst performance was then expressed as the operating temperature required for the catalyst to achieve 85 % methane conversion at the standard conditions, as measured at the start of test, and after 16 hours of H_2S exposure, after the H_2S flow was halted. These values, plus samples delivered to SR, are listed in Table 3.

Active metal-only samples delivered to Southern Research are the baseline, 1, and its hand-coated equivalent, 2. Samples 5 and 12 will not have any advantage over sample 1 as they have the same active metal content, but with a more complex support material and lesser performance. Amongst the reduced active metal content samples, sample 7 was the next best performing catalyst after the 100 % active metal content catalysts, and so was selected for further testing by SR. Sample 6, and its equivalent sample 3 were also selected for evaluation at SR.

Table 3. Summary of catalyst activities before and after exposure to H_2S rapid aging testing. Samples with no aged ranking exhibited operating temperatures in excess of 1200 °C during H_2S testing, these tests had to be halted due to safety concerns.

	85 % conversion temperature (°C)				wt. loading			
#	initial	following 16 hrs H2S exposure	aged rank	coating method	catalyst	co-catalyst	support	sent to SR
1	933	975	1	machine	100		standard alumina	✓
2	951	987	2	hand	100		standard alumina	✓
3	1010	ND		hand	25	75	standard alumina	✓
4	1021	1074	7	hand	25	75	alumina mod 1	
5	972	1005	3	hand	100		alumina mod 2	
6	1007	1072	6	hand	25	75	alumina mod 3	✓
7	1009	1061	5	hand	25		standard alumina	✓
8	1113	ND		hand	5	95	standard alumina	
9	1089	ND		machine		100	standard alumina	
10	1002	ND		machine		100	standard alumina	
11	931	ND		machine	100	100	standard alumina	
12	956	1043	4	hand	100		alumina mod 4	
13	997	1179	8	hand	25	75	alumina mod 4	

ATR Design and Engineering

We planned to use our existing oxy-blown ATR designs for this project. Changes to the design intent – including switching from oxy-blown to air-blown operation, need to meet specific NCCC safety, hazardous gas containment, and operational requirements, and change to testing modes and feed input streams combined to result in extensive design changes. The ultimate impact was that we needed to design the ATR system from scratch, as none of our existing designs were suitable for this project. Extensive engineering and controls programming were then required to complete the design to the extensively revised project requirements.

We completed all necessary calculations for the new design – including process modeling to find preliminary flow rates and heat exchanger requirements. We designed a new reactor vessel that was custom fabricated for us to meet NCCC-required code-stamped requirements. We completed and continuously revised P&ID and wiring diagrams. We determined all needed I/O for communications between the control computers, hardware, Southern's hardware external to our ATR system, and to certain NCCC control points. We began building LabVIEW-based control software for operating the ATR system. We designed engineered and prepared drawings for some of the reactor internal parts and steam generators; these parts were fabricated.

Major design changes are listed as follows; note that changes to equipment specification and function were made throughout the entire course of the reactor build portion of the project.

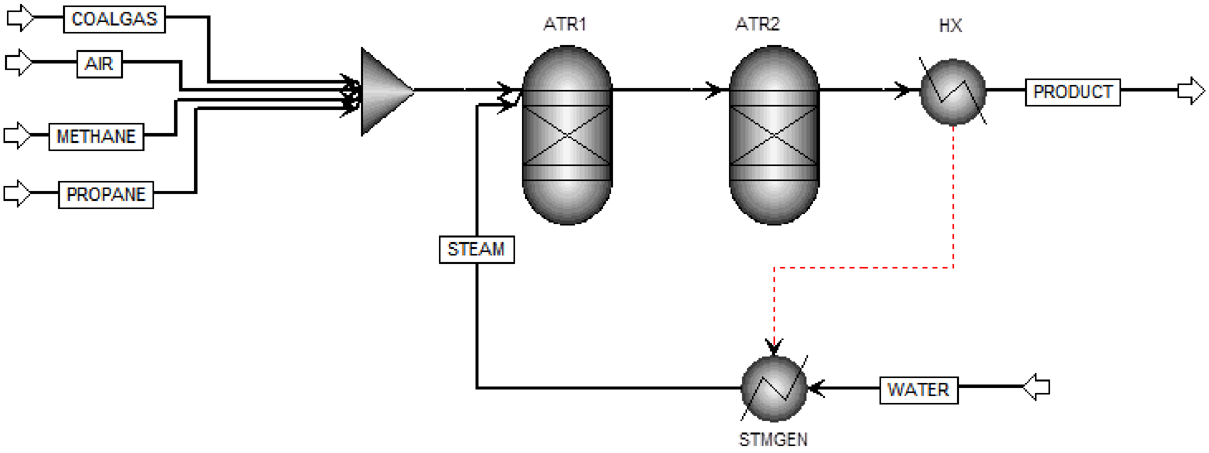
- No support cart redesign or changes were planned within the program, but subsequent requests and changes (included below) from Southern required significant cart modifications for operation at NCCC.
- PCI was informed by Southern of the need to comply with Class I Div. 2 area code, NFPA requirements for NG, and IRI compliance, as well as with safety and operational requirements specific to the NCCC test site, as well as with site-specific feed gas compositions and flow rates for testing at Southern and NCCC. These compliance issues and process changes also necessitated the need for detailed calculations to support subsequent design and hardware decisions.
- PCI was informed by NCCC for the need to have a code-stamped reactor pressure vessel.
- PCI was informed that the oxidant would be air and not oxygen. Together with other changes, including mid-term changes in testing plan, this resulted in changes to design, controls and operational features that were not anticipated in the proposal or included in the contract.
- PCI was informed that the planned testing at Southern on simulated syngas would not take place.
- The overall impact was the need for a complete redesign of PCI existing hardware, as well as specification and sourcing of components unique to this project - including a code-stamped pressure vessel and major changes to design related to the pressure vessel. (PCI normally has not had to provide code-stamped vessels, but have provided computational analysis showing the safety and integrity of pressure vessels.) In the end, the required pressure vessel was changed to a completely new design, requiring design and mechanical optimization with the

supplier in order to achieve the desired performance, beyond what was specified in the first change order. In addition, the reactor internal components had to be modified and analyzed to function properly for air and in the new pressure vessel design.

We used ASPEN process modeling software, and assuming thermodynamic chemical equilibrium at the ATR exit, to determine expected inlet and outlet flow rates fluid streams to the ATR. These calculations were performed assuming the following NCCC PRB coal-gas composition:

	PRB coal (wet)
H_2	0.068
CO	0.084
CO_2	0.087
N_2	0.650
CH_4	0.012
H_2O	0.100
Ar	0.004
H_2S	0.00032
C_2H_6	0.000

The process model split the ATR into two steps, analogous to actual ATR operation: in the first, reactants are brought to Gibbs-free energy minimization equilibrium at 950 °C; in the second step, these products are brought to water-gas shift equilibrium at 750 °C, the temperature at which, in our experience, gas-phase water gas shift will equilibrate at. Below 750 °C, no further changes to CO, CO_2, H_2, and H_2O concentrations will occur in the gas-phase. We used this process model to do these calculations:



Thermal integration of the steam generation is by heat exchanger with the ATR outlet, assuming product exit temperature of 350 °C. Flow rates for feed steams to the ATR were then calculated for all major operating modes:

Case	methane ATR	at SR	at NCCC	at NCCC, no CO, no H2	at NCCC, no CO, no H2 - 50 kWth
coal gas in (NLPM)		427.4	536.8	536.8	418.9
suppl. H2 in (NLPM)		80.8	44.1		
suppl. CO in (NLPM)		120.6	75.6		
suppl. propane in (NLPM)			5.9	31.1	24.3
suppl. water in "(NLPM)"		53.8			
steam in (g/min)	59.8	105.0	104.0	65.6	51.2
air in (NLPM)	247.9	265.9	173.2	335.7	261.9
CH4 in (NLPM)	80.2				

Subsequent design changes necessitated adjustments to these flow rate values. The final values for ATR operating modes based are listed below:

Case		**PCI Normal**	**PCI Max**	**PCI startup**	**NCCC normal**	**NCCC max**	**NCCC no add H2/CO normal**	**NCCC no add H2/CO max**	**NCCC startup**
Fluid Phase		vapor	vapor	vapor	vapor	vapor	vapor	vapor	vapor
Fluid Major components		H2, H2O, CO, CO2, N2	H2, H2O, CO, CO2, N2	H2, H2O, CO, CO2, N2, CH4	H2, H2O, CO, CO2, N2	H2, H2O, CO, CO2, N2	H2, H2O, CO, CO2, N2	H2, H2O, CO, CO2, N2	H2, H2O, CO, CO2, N2
Flow Rate	lb/hr	54.29	59.72	29.41	133.08	146.39	145.40	159.94	35.03
Inlet Pressure	PSIA	175.3	175.3	175.3	175.3	175.3	175.3	175.3	175.3
Delta P	Psid								
Temperature	Deg F	752	752	752	752	752	752	752	752
Molecular Weight	g/mol	19.21	19.21	20.14	24.41	24.41	23.93	23.93	20.53
Fluid density (operating conditions)	lb/ft^3	0.3012	0.3012	0.3155	0.3828	0.3828	0.3750	0.3750	0.3214
viscosity	cp	0.0303	0.0303	0.0297	0.0310	0.0310	0.0310	0.0310	0.0304
Ratio of specific heats		1.93	1.93	1.92	1.88	1.88	1.92	1.92	2.01
Estimated Cv	J/mol/K	16.77	16.77	17.13	18.05	18.05	17.13	17.13	15.21

We prepared and updated P&ID diagrams in order to capture the most recent changes to process, process flows and design requirements. Appendix I tabulates major revisions to the P&ID document. A tabulation of major additional work requests and their impact on the design process in listed on Appendix II. Considerable effort was made in developing control code using LabVIEW process control software; first for operation at PCI, Southern and NCCC, and then later for operation at only PCI and NCCC. The control software will need to operate the ATR in cold-start, warm-start, steady operation, transient operation, normal shut-down, and emergency shut-down modes for all of the operating modes intended. Software will also need to collect inputs and outputs from a large number of devices supplied by both PCI and Southern, as well as provide control inputs and outputs to NCCC safety devices. A comprehensive list of control variables is given in Appendix III. Data acquisition inputs and outputs are also listed in Appendix III.

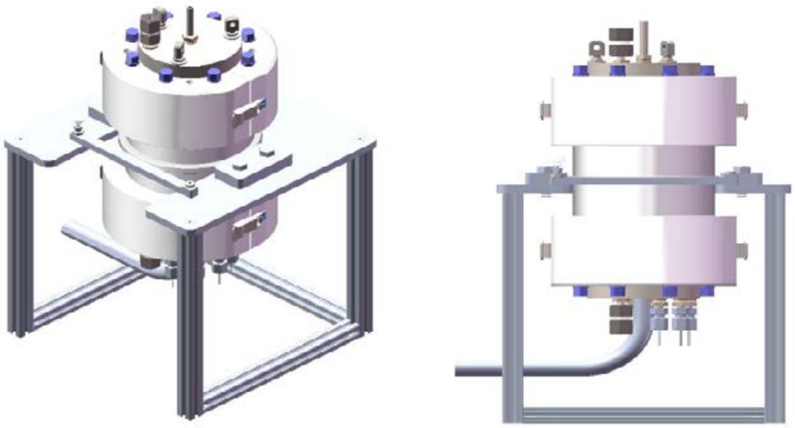
Additional sizing and design exercises, needed to meet additional safety or processing requirements, included:

- ATR heat release was estimated in order to determine appropriate cooling rates for the ATR enclosure. The incoming and outgoing enthalpy of the inlet and product streams, the difference should be the total heat needed to be rejected, which for the NCCC case is about 6 kW, or 20,500 BTU/hr. This does not take into account heat coming from steam generators, but did assume incoming water was liquid at 80 °F. Nitrogen flow will depend on the inlet and outlet temperature of the N_2. Assuming NCCC in summer time, an inlet N2 temperature of 90-100 F may not be unreasonable. For inlet and outlet cooling N_2 temperatures of 90 and 120 °C, a cooling flow of 638 SCFM is required; for 70 and120 °C, 383 SCFM is required. Assuming a maximum APU temperature of 50 °C and ambient temperature of 40 °C, and APU releases 256 BTU/hr maximum, based on suppliers specifications, then a flow of 12.7 SCFM additional N_2 is required to cool the auxiliary power unit (APU).

- For HAZOP review we were asked to size relief valves. This was also needed to provide input into design requirements and sourcing.
- Also for HAZOP review, the expected velocities in process fluid steams were calculated, summarized in Appendix V.

Included in the development of the LabVIEW control software were programming sequences for LABVIEW control, which are the starting point for preparing an operator’s manual.

Hardware Design We needed to design from scratch many components, as our existing designs would not be compatible with NCCC requirements. We contracted to Parr instruments to build a code-stamped pressure vessel that will be NCCC requirements. Drawings of the reactor prepared by Parr Instruments for PCI approval and based on PCI provided specification are presented below:



Safety Planning and HAZOP Review

Several video conferences were held between PCI, Southern and NCCC to review possible failure modes and corrective actions. Major outcomes including requests from NCCC to provide an ‘operation philosophy’ document, calculate lower explosive limits of various gas steams in the event of a leak, and pressure relief and relief valve calculations. All of these were completed and the results shared with Southern and/or NCCC as appropriate. Results of these meetings contributed to many of the design and equipment changes.

A detailed ‘Operation Philosophy’ was prepared on the behest of NCCC in preparation for the HAZOP review.

NCCC requested that we calculated % approach to lower explosive limit (LEL) if a leak occurred in various locations in the ATR, the results of which are summarized:

Purge Air Flow	638	scfm	
	18066.1503	slpm	
	24.14551838	lt / mol @ 21.1 °C	
	748.2196081	g.mol/min	
Gas Flow Scalar	1.1	fraction of nominal gas flow	
	ATR Exhaust Leak		
Methane ATR Normal	24.39	% of LEL for H2	at PCI Only
Methane Startup	11.01	% of LEL for H2	at PCI Only
NCCC Normal	21.26	% of LEL for H2	
NCCC no H2-CO	20.78	% of LEL for H2	
NCCC Propane Startup	13.62	% of LEL for H2	
Assumes Steady State Flow			
Does not account for temporarily high flow rates due to depressurization			

For the HAZOP review, 65 potential deviations from design intent were examined, including cause of and impact of such events as high flow, low or no flow, high pressure, high temperature, misdirected flow, reverse flow, low flow or wrong gas composition; these are summarized in Appendix IV. Many of these results in design changes that were not anticipated in the work plan as stated in our subcontract. We were also asked to perform pressure relief calculations to assure that relief and safety valves are properly sized; the results of which are given in Appendix V.

ATR System Fabrication and Commissioning

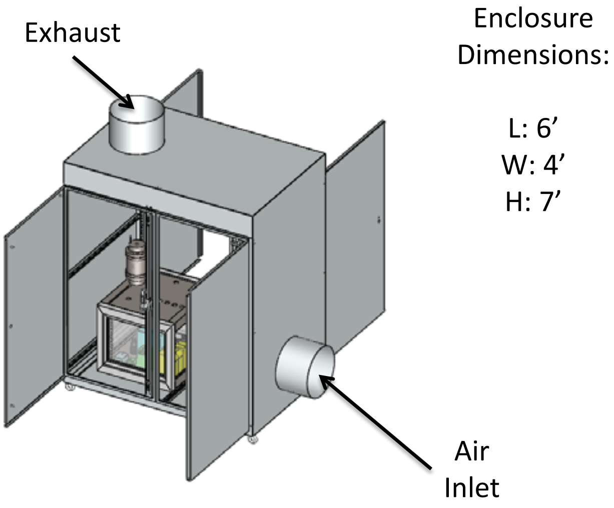
Significant design work entailing the need for an inert-gas enclosure was complete. We worked with Southern to select an enclosure, and we engineered many aspects of components to have correct form, fit and function when installed in the enclosure. We commissioned and received the code-stamped reactor vessel, and we began fabrication of some of the reactor internals and external components. No testing of any of these items was completed.

After contract approval, an additional subtask related to material receiving and tracking was required for inventory control purposes. Additional work was incurred resulting in work expanding significantly when the team determined that the proposed cart for operating the ATR was not acceptable for NCCC testing requirements. The expansion included new design effort for the cart including specifications for Southern ordering (which purchased the components for PCI), and control design and software modifications. Many added hours were spent sourcing hardware due to the need for multiple rounds of specifications, especially related to selection and sourcing of back pressure valves, relief valves, equipment enclosures, and electrical / power supplies that meet NCCC's requirements.

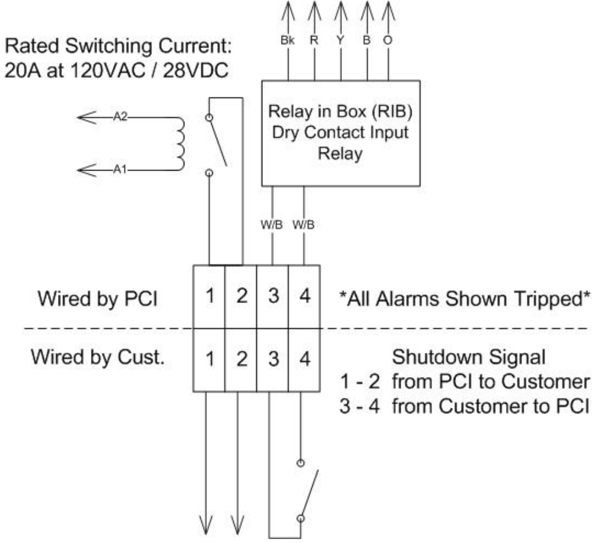
As a consequence of the changes in scope, our work on the reactor was expanded and would have cost more than originally intended. The redesigned reactor system had significantly more structural content, controls and safety features than normally included in our design and scale of similar prototype reactors.

Images of the code-stamped ATR pressure vessel manufactured by Parr Instruments using design and specifications provided by PCI:

A purged enclosure was specified in which to install the ATR and control equipment, design intent, ventilation interface, and electrical interface, details on the design are given in Appendix VI. The layout of ATR and planned air inlet and exhaust inside of purged enclosure:



Electrical interface between PCI controlled electronics and NCCC provided power connections are given below, while preliminary wiring diagrams are given in Appendix VII.



Permitting

Based on guidance provided by Southern, a review of PCI's intended operations, at PCI's facility, was conducted, no new permitting requirements were determined to be needed, and this was considered completed and notice sent to this effect to Andrew Lucero on August 25, 2015, and reported as complete.

Subsequent to this, we were asked by Southern and also as an outcome to the HAZOP review, to provide significant details on the nature, composition, pressure, and temperatures of planned and unplanned (i.e. release valve openings or line breaks) flows coming from our equipment when installed at NCCC on an on-going basis. Additionally, we were asked to provide information on power requirements and electrical hazards. These activities were considered to be part of permitting, and in cases involved considerable engineering time to determine impact of unplanned events and safety relief scenarios. Some of this information is covered in Appendices VI, VII, and VIII.

Appendix I: P&ID revision history in response to design changes

Rev. #	Date	Comments
1	4/1/2015	preliminary based on prior design
2	4/2/2015	add PRV
3	4/15/2015	add N2 inlet with control and heater
4	4/23/2015	add CO and H2 inlets with control
5	5/12/2015	delete CO and H2 inlets and control
6	9/23/2015	add second steam generator
7	10/12/2015	add steam gen relief orifice; add double block/bleed on NG inlet with leak test valves
8	10/26/2015	add ATR outlet GC sample line; add outlet HV bypass; add inlet NG HV bypass
9	11/18/2015	add N2 and air HV above/below MFC's, removed gas inlet vent lines and valves
10	2/8/2016	added water drain HV's; add external control I/O control points; added steam gen pressure relief valve
11	2/11/2016	added external control I/O points
12	3/28/2016	move water inlet control valves

Appendix II: List of additional work requested and impact

Additional work process, procedures, and design changes not in original statement of work and that had a significant impact on work required:

	Project Changes From Contract	**Impact on Work Plan**
1	Required on site operation by PCI personnel	
2	Change to High Pressure Code-Stamped Vessel	Internal structure design changes
3	Class I Div 2 Area Rating	Specify all electrical components to be explosion proof
4	Change system to be located inside a purged enclosure	Re-specify all electrical components to not be explosion proof
5	Spec Propane Line at 200 °F	
6	Change Propane Flow control from PCI to SR	
7	Add dedicated Vent Line	
8	Add Nitrogen Line	
9	Add CO Line	
10	Add H2 Line	
11	Remove CO Line	Negates Time spent adding CO Line
12	Remove H2 Line	Negates Time spent adding H2 Line
13	Spec Coal Gas Line at 200 °F	
14	Change NG Valve Train to be NFPA Compliant	Time Researching NFPA Spec
15	Change NG Valve Train to be IRI Compliant	Time Researching IRI Spec
16	Change Coal Gas Line Temperature to 600 °F	
17	Modify Proposed NG Valve Train for IRI/NFPA86 Compliance	Remove Hand valves from P&ID
18	System will not be tested at SR	Remove all hardware that was required by IRI/NFPA and needed
19	Remove all Combined Vent Valves	
20	Directly Wire some of SR's valves into PCI's cRIO	
21	Have LabVIEW Shared Variables	Explore what is required to share variables

Appendix III: Control variables

A list of control variables for inputs and outputs from LabVIEW control software for both PCI ATR components and Southern components.

Southern to PCI:

Variable Name	Type	Subtype	Representation	Units	Description
Syngas Ctrl FB	Scalar		SGL	SLPM	Indicated flow of SYN Gas
Syngas Content FB	Cluster				
Coal Gas FB		Scalar	SGL	SLPM	Indicated flow of Coal Gas
H2 FB		Scalar	SGL	SLPM	Indicated flow of H2
CO FB		Scalar	SGL	SLPM	Indicated flow of CO
H2+H2S FB		Scalar	SGL	SLPM	Indicated flow of H2+H2S
Toluene FB		Scalar	SGL	g/min	Indicated flow of Toluene
Propane FB	Scalar		SGL	SLPM	Indicated flow of Propane
Water Pump Enable FB	Scalar		Boolean	True = On	Indicated Water Pump State
Syngas Isolation FB	Scalar		Boolean	True=Open?	Indicated Syngas Isolation valve position
Syngas Bypass FB	Scalar		Boolean	True=Open?	Indicated Syngas Bypass valve position
Propane Shutoff 1 FB	Scalar		Boolean	True=Open?	Indicated Propane Shutoff valve #1 position
Propane Shutoff 2 FB	Scalar		Boolean	True=Open?	Indicated Propane Shutoff valve #2 position
GC Sampling Location	Scalar		???		Need to indicate sample feed line (i.e.: inlet, outlet, calibration)
GC Output Data	Cluster				
H2		Scalar	SGL	%	
N2		Scalar	SGL	%	
CH4		Scalar	SGL	%	
CO		Scalar	SGL	%	
CO2		Scalar	SGL	%	
C3H8		Scalar	SGL	%	
H2S		Scalar	SGL	%	
COS		Scalar	SGL	%	
Ar		Scalar	SGL	%	

PCI to Southern

Variable Name	Type	Subtype	Representation	Units	Description
SYN Gas Ctrl SP	Scalar		SGL	SLPM	Requested Flow of SYN Gas

Syn Gas Content SP	Cluster				
Coal Gas SP		Scalar	SGL	SLPM	Requested Flow of Coal Gas
H2 SP		Scalar	SGL	SLPM	Requested Flow of H2
CO SP		Scalar	SGL	SLPM	Requested Flow of CO
H2+H2S SP		Scalar	SGL	SLPM	Requested Flow of H2+H2S
Toluene SP		Scalar	SGL	g/min	Requested Flow of Toluene
Propane SP	Scalar		SGL	SLPM	Requested Flow of Propane
Water Pump Enable SP	Scalar		Boolean	True = On	Requested Water Pump State
Syn Gas Temp FB	Scalar		SGL	°C	Indicated Syn Gas Temperature
Propane Temp FB	Scalar		SGL	°C	Indicated Propane Temperature
Air PSL	Scalar		Boolean	True = on	Air Pressure Below low limit
Coal Gas PSL	Scalar		Boolean	True = on	Coal Gas Pressure below low limit
Propane PSL	Scalar		Boolean	True = on	Propane pressure below low limit
Propane PSH	Scalar		Boolean	True = on	Propane Pressure above high limit
Nitrogen Mass Flow Rate	Scalar		SGL	SLPM	Flow signal from MFC
Air Mass Flow Rate	Scalar		SGL	SLPM	Flow signal from MFC
Water Mass Flow Rate 1700	Scalar		SGL	SLPM	Flow signal from MFC
Water Mass Flow Rate 1710	Scalar		SGL	SLPM	Flow signal from MFC
ATR Inlet Pressure FB	Scalar		SGL	PSIG	PT-5500
ATR Outlet Pressure FB	Scalar		SGL	PSIG	PT-5005
Steam Temperature 1	Scalar		SGL	°C	TE-1701
Steam Temperature 2	Scalar		SGL	°C	TE-1702
Steam Temperature 3	Scalar		SGL	°C	TE-1703
Syngas Out	Scalar		SGL	°C	TE-5000
ATR-5500 Inlet Temperature	Scalar		SGL	°C	TE-5500
ATR-5500 ID Temperature #1	Scalar		SGL	°C	TE-5501
ATR-5500 ID Temperature #2	Scalar		SGL	°C	TE-5502
ATR-5500 MID Temperature #1	Scalar		SGL	°C	TE-5503
ATR-5500 MID Temperature #2	Scalar		SGL	°C	TE-5504
ATR-5500 OD Temperature #1	Scalar		SGL	°C	TE-5505
ATR-5500 OD Temperature #2	Scalar		SGL	°C	TE-5506
ATR-5500 Steam Temperature	Scalar		SGL	°C	TE-5507
ATR-5500 Air/Nitrogen Inlet Temperature	Scalar		SGL	°C	TE-5508

N2/Air Heater Temperature FB	Scalar		SGL	°C	TIC-1611
Steam Generator 1 FB	Scalar		SGL	°C	TIC-1700
Steam Generator 2 FB	Scalar		SGL	°C	TIC-1710

Data acquisition inputs and outputs (channel and slot assignments not listed):

Name	**Type**	**Device**	**Scaled Range**	**Scaled Units**	**Raw Range**	**Raw Units**	**Notes**
Air SP	AO	MFC		slpm	0 to 5	Volts	MFC-1600 SP
N2 SP	AO	MFC		slpm	0 to 5	Volts	MFC-1500 SP
Water 1 SP	AO	MFC		g/min	0 to 5	Volts	MFC-1700 SP
Water 2 SP	AO	MFC		g/min	0 to 5	Volts	MFC-1710 SP
Coal Gas CTRL SP	AO				0 to 5	Volts	SRI Process
Propane CTRL SP	AO				0 to 5	Volts	SRI Process
NG SP	AO	MFC		slpm	0 to 5	Volts	MFC-1300 SP
ATR Pressure CTRL	AO				0 to 5	Volts	PC-5005 SP
N2/Air Heater SP	AO	Heater			0 to 5	Volts	HE-1611 SP
Steam Gen 1 Temp SP	AO	Heater			0 to 5	Volts	HE-1700 SP
Steam Gen 2 Temp SP	AO	Heater			0 to 5	Volts	HE-1710 SP
Air FB	AI	MFC		slpm	0 to 5	Volts	MFC-1600 FB
N2 FB	AI	MFC		slpm	0 to 5	Volts	MFC-1500 FB
Water 1 FB	AI	MFC		g/min	0 to 5	Volts	MFC-1700 FB
Water 2 FB	AI	MFC		g/min	0 to 5	Volts	MFC-1710 FB
Coal Gas CTRL FB	AI				0 to 5	Volts	SRI Process
Propane CTRL FB	AI				0 to 5	Volts	SRI Process
NG FB	AI	MFC		slpm	0 to 5	Volts	MFC-1300 FB
ATR Inlet Pressure FB	AI	Sensor		psi		Volts	
ATR Outlet Pressure FB	AI	Sensor		psi		Volts	
Enclosure CO LVL FB	AI	Sensor			1 to 5	Volts	CO-004 (Requires 250 ohm resistor)
Enclosure COMB FB	AI	Sensor			1 to 5	Volts	GAS-006 (Requires 250 ohm resistor)
ATR Fuel Power	AI	CTRL			0 to 5	Volts	
N2/Air Heater Enable	DO	Relay	On/Off		0 / 5	Volts	HE-1611 Enable
ATR Steam Gen Enable #1	DO	Relay	On/Off		0 / 5	Volts	HE-1700 Enable
ATR Steam Gen Enable #2	DO	Relay	On/Off		0 / 5	Volts	HE-1710 Enable
ATR Igniter	DO	Relay	On/Off		0 / 5	Volts	Pilot Relay IGN-5500

CO2 Process Flow Shutoff	DO	Signal	On/Off		0 / 5	Volts	XV-345 [SRI] (Option)
N2 Process Flow Shutoff	DO	Signal	On/Off		0 / 5	Volts	XV-355 [SRI] (Option)
Water Process Flow Shutoff	DO	Signal	On/Off		0 / 5	Volts	XV-365 [SRI] (Option)
Water Pump Enable	DO	Signal	On/Off		0 / 5	Volts	--- This is going to be a 24 V DC coil contactor
UPS Shutdown	DI		On/Off		0 / 5	Volts	UPS-5100
E-Stop Switch	DI	Switch	On/Off		0 / 5	Volts	
Alarm	DO		On/Off		0 / 5	Volts	Send 5VDC signal unless in Shutdown mode
Facility Safety	DI		On/Off		0 / 5	Volts	Customer supplies 5 volt signal - if it goes away, then Shutdown
5V Supply	DO		On/Off		0 / 5	Volts	Supply for cRIO Stop
cRIO Stop	DI	Switch	On/Off		0 / 5	Volts	Connect with push button switch to 5 Volt Supply
Syngas Temp	TC			deg C			TE-1201
Propane Temp	TC			deg C			TE-1401
Steam Temperature 1	TC			deg C			TE-1701
Steam Temperature 2	TC			deg C			TE-1702
Steam Temperature 3	TC			deg C			TE-1703
Syngas Out	TC			deg C			TE-5000
ATR-5500 Inlet Temperature	TC			deg C			TE-5500
ATR-5500 ID Temperature #1	TC			deg C			TE-5501
ATR-5500 ID Temperature #2	TC			deg C			TE-5502
ATR-5500 MID Temperature #1	TC			deg C			TE-5503
ATR-5500 MID Temperature #2	TC			deg C			TE-5504
ATR-5500 OD Temperature #1	TC			deg C			TE-5505
ATR-5500 OD Temperature #2	TC			deg C			TE-5506
ATR-5500 Steam Temperature	TC			deg C			TE-5507
ATR-5500 Air/Nitrogen Inlet Temperature	TC			deg C			TE-5508
N2/Air Heater Temperature FB	TC			deg C			TIC-1611

Steam Generator 1 FB	TC			deg C			TIC-1700
Steam Generator 2 FB	TC			deg C			TIC-1710
Syngas Heat Trace FB	TC			deg C			TE-305 (SRI)
Mixing Panel Heat Trace FB	TC			deg C			TE-345 (SRI)
Propane Heat Trace FB	TC			deg C			TE-705 (SRI)
Air PSL	DI	Switch	On/Off		off < 5 / on > 10	Volts	TBD (SRI)
Coal Gas PSL	DI	Switch	On/Off		off < 5 / on > 10	Volts	PSL-302 [SRI]
Propane PSL	DI	Switch	On/Off		off < 5 / on > 10	Volts	PSL-702 [SRI]
Propane PSH	DI	Switch	On/Off		off < 5 / on > 10	Volts	PSH-707 [SRI]
NG Process Flow Shutoff	DO	Solenoid	On/Off		0 / 24	Volts	XV-1300
N2 Process Flow Shutoff	DO	Solenoid	On/Off		0 / 24	Volts	XV-1500
Air Process Flow Shutoff	DO	Solenoid	On/Off		0 / 24	Volts	XV-1600
Water 1 Process Flow Shutoff	DO	Solenoid	On/Off		0 / 24	Volts	XV-1700
Water 2 Process Flow Shutoff	DO	Solenoid	On/Off		0 / 24	Volts	XV-1710
Steam Process Flow Bypass	DO	Solenoid	On/Off		0 / 24	Volts	XV-1720/1721
Syngas Isolation	DO	Solenoid	On/Off		0 / 24	Volts	XV-300 [SRI]
Syngas Process Flow Bypass	DO	Solenoid	On/Off		0 / 24	Volts	XV-305 [SRI]
H2 Process Flow Shutoff	DO	Solenoid	On/Off		0 / 24	Volts	XV-315 [SRI]
CO Process Flow Shutoff	DO	Solenoid	On/Off		0 / 24	Volts	XV-325 [SRI]
H2 W/H2S Process Flow Shutoff (pending)	DO	Solenoid	On/Off		0 / 24	Volts	XV-345 [SRI] [Pending]
Propane Process Flow Shutoff #1	DO	Solenoid	On/Off		0 / 24	Volts	XV-704 [SRI]
Propane Process Flow Shutoff #2	DO	Solenoid	On/Off		0 / 24	Volts	XV-706 [SRI]

Appendix IV: Results of HAZOP review

The following summarized PCI's actions to undertake to remedy or reduce the risk from any of these deviations.

Node	**Deviation**	**Design Intent**	**Cause**	**Safe Guards/Controls that Prevent Cause**	**Corrective Actions**
Coal Gas Inlet	No Flow of Coal Gas	500 slpm	1) Incorrect Coal Gas Control Signal (FE300 Incorrect) 2) Problem with CV300 3) Incorrect Manual Valves 301 or 303 4) Debris or malfunction of XV305 5) low supply pressure < ATR operating pressure) 6) No Flow from upstream (gasifier)	Major Impacts on ATR Node 1) Alarm on Flow from Gasifier 2) SOP indicating adjustments to operating parameters indicating necessary changes 3) ATR control program to include appropriate adjustments	Make sure that the ATR controls will perform controlled shutdown if the Coal Gas Flow drops to zero
Coal Gas Inlet	Coal Gas High Temp	600 F	High temperature from upstream node	Either Design for 900F feed or install interlock to shut down flow above valve high temperature	Check that our coal gas inlet plumbing can handle 900F
NG Inlet					Review Gas Train for NFPA compliance
Nitrogen / Air Inlet	N2 Low Flow	400 slpm	Incorrect Set point on Mass Flow controller Incorrect supply pressure MFC Malfunction	1) overtemp on heater 2) interlock on flow enabling heater if flow is sufficient	Overtemp and Low Flow Heater Protection
Nitrogen / Air Inlet	Air Low Flow	400 slpm	Incorrect Set point on Mass Flow controller Incorrect supply pressure MFC Malfunction	1) overtemp on heater 2) interlock on flow enabling heater if flow is sufficient	Overtemp and Low Flow Heater Protection
Nitrogen / Air Inlet	N2 No Flow		Incorrect Set point on Mass Flow controller Incorrect supply pressure MFC Malfunction Hand valves set incorrectly Solenoid valve malfunction	1) overtemp on heater 2) interlock on flow enabling heater if flow is sufficient 3) SOP for hand valves	Overtemp and Low Flow Heater Protection
Nitrogen / Air Inlet	Air No Flow		Incorrect Set point on Mass Flow controller Incorrect supply pressure MFC Malfunction Hand valves set incorrectly Solenoid valve malfunction	1) overtemp on heater 2) interlock on flow enabling heater if flow is sufficient 3) SOP for hand valves	Overtemp and Low Flow Heater Protection

Nitrogen / Air Inlet	Breach		Breach	CO and flammable gas sensors tied to alarm and shutdown of system.	Make sure that the ATR controls will cut all fuel flow when environmental sensors alarm
Water Inlet	Breach		Breach	CO and flammable gas sensors tied to alarm and shutdown of system.	Make sure that the ATR controls will cut all fuel flow when environmental sensors alarm
Water Inlet	High Pressure	300 psig	Problem with CV501 or controls	Specify maximum pump delivery pressure so that it won't damage MFC.	Communicate to SRI a Maximum operating supply pressure for the water MFC
Water Inlet	Low ambient Temperature	300 psig	Low ambient temperature	Install freeze protection. Insulation or insulating blankets. Possible heat trace.	Examine freeze protection options
Gas Exit from ATR	High Flow		High flow from upstream node		Make Sure that the pressure relief valve is sized so that it doesn't dump pressure too quickly?
Gas Exit from ATR	High Flow		loss of instrument air to PCV5003 (HV800)	Pressure switch on instrument air to shut down ATR. Lockable HV 800 and 801 to correct positions while operating.	Lockable Hand Valves
Gas Exit from ATR	Low Flow		PRV undersized	Design specification on PRV (not oversized or undersized). Ensure downstream piping rated for expected temperatures.	Make Sure that the pressure relief valve is sized properly and possibly to handle temperature
Gas Exit from ATR	No Flow		HV5001 closed	SOP to include positions for all valves during operations. Consider lockable valve - locked open during operations.	Lockable Hand Valves
Gas Exit from ATR	Reverse Flow / Misdirected Flow		HV 5005 opened during operation	SOP to include positions for all valves during operations. Consider lockable valve - locked open during operations.	Lockable Hand Valves
Gas Exit from ATR	High Temperature		High temperature from upstream node	TE 5000 tied to shutdown if gas leaving ATR gets too hot. Several TCs in previous node shut down on overtemp.	TE5000 high temp shutdown
Gas Exit from ATR	Low ambient Temperature		low ambient temperature	Install pressure transmitter draining into pipe. Make sure line to pressure transmitter can't collect water.	Have pressure transmitters mounted high

Appendix V: Results of pressure relief calculations

Calculation for the safety valve downstream of the ATR and ahead of the back-pressure regulator:

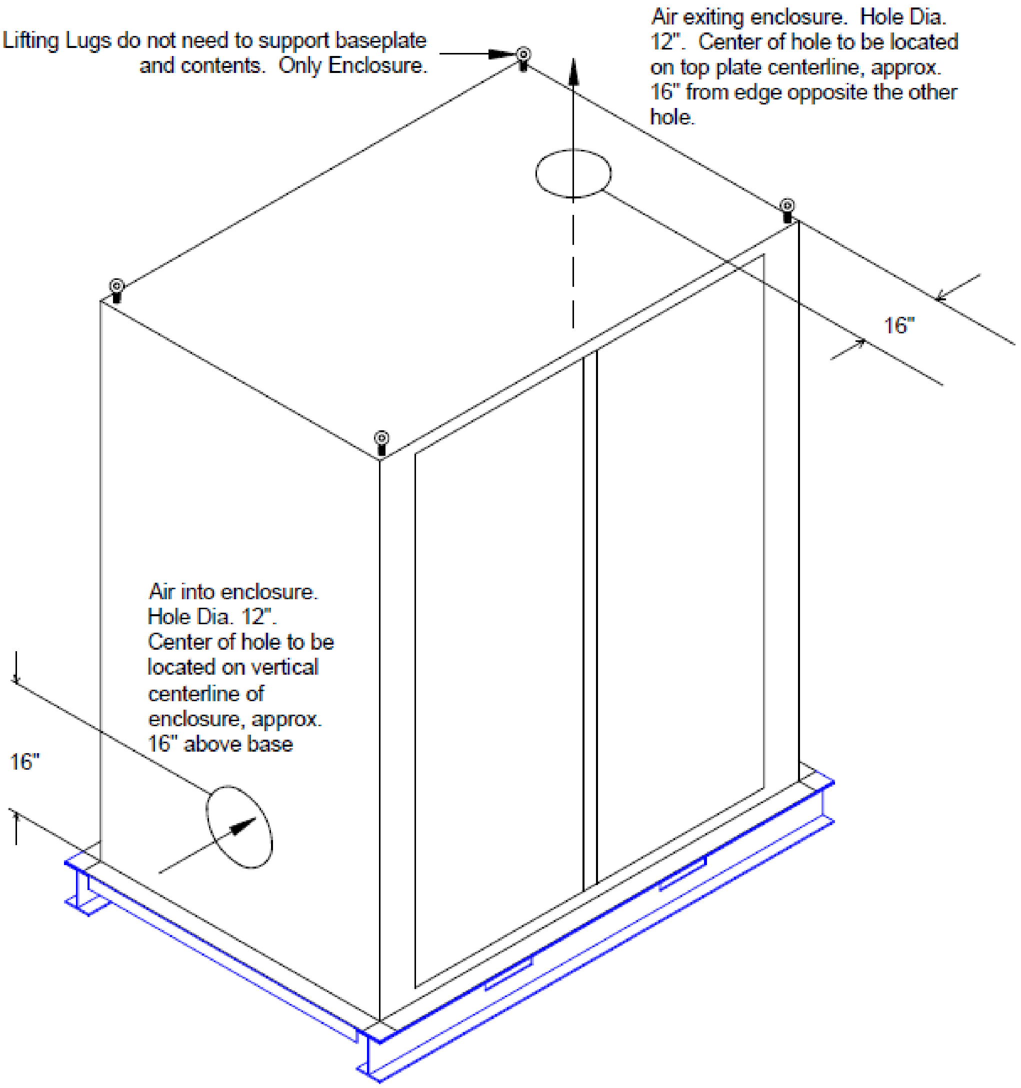
PSV-710		
Assume: 1ft section of pipe between the pressure regulator and the first safety shut-off valve. Propane regulator pressure set to 210 PSIG or 225 PSIA		
Heat Rate of Heat Trace	W/ft	16.0
Length of Tube	ft	1.0
Heat Rate of Heat Trace	W	16.0
Heat Rate of Heat Trace	BTU/hr	54.6
Heat of Vaporization @ 347 PSIA	BTU/lb	104
Vaporization Rate:	lb/hr	0.526
Vaporization Rate:	lb/s	0.00015
Maximum allowable operating pressure	PSIG	225
MAWP or Maxiumum allowable SET pressure	PSIG	250
Maximum alllowable relieving pressure	PSIG	333
Maximum alllowable relieving pressure	PSIA	347
cp =	BTU/lbm*R	0.74462
cv =	BTU/lbm*R	0.44827
cp/cv =		1.6611
T - operating temp	deg F	200
T - operating temp	R	660
R	lbf.ft/(lbmol.R)	***1545***
660	lbm-ft/lbf-s2	***32.2***
C =	(lbm*lbmol*R)^0.5/s*lbf	0.145
z		1
A	in2	1.13E-05

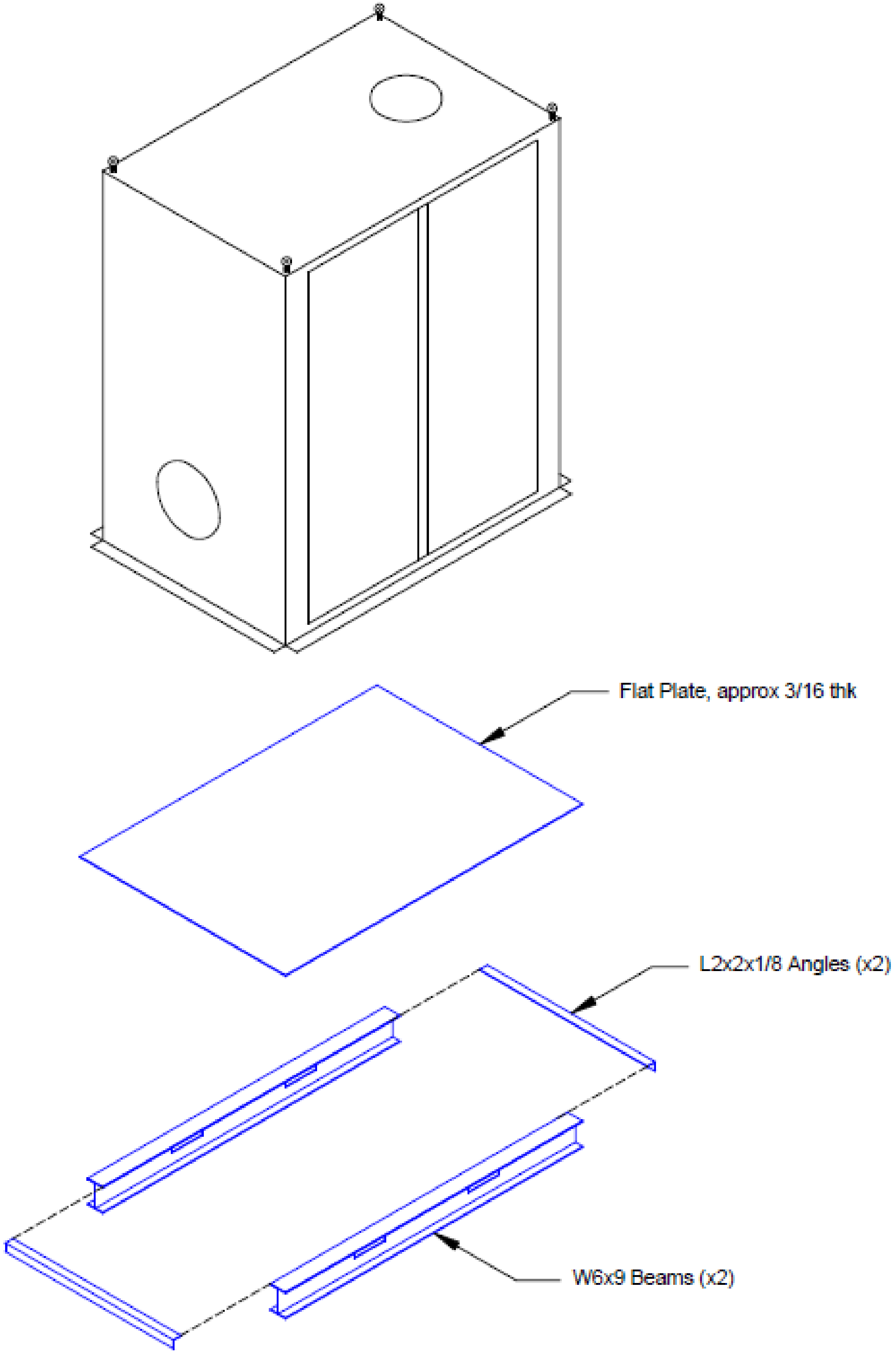
For the relief valve between the steam generators and the ATR reactor:

HE-1700 + HE-1710		
Assume: Both Steam Generators filled with water and full heater power used to vaporize into steam. Each steam gen has 20ft of tube and 8kW total power.		
Solution: Specify the pressure relief valve based on the set pressure of 450psig and a flow rate of 80 lb/h. Needs to be ASME Section I compliant.		
Heat Rate of Heat Trace	W/ft	400.0
Length of Tube	ft	40.0
Heat Rate of Steam Gen	W	16000.0
Heat Rate of Steam Gen	BTU/hr	54594.2
Enthalpy Saturated Liquid	BTU/lb	457.42
Enthalpy Saturated Vapor	BTU/lb	1206.0
Heat of Vaporization @ 455 PSIA	BTU/lb	749
Vaporization Rate:	lb/hr	73
Vaporization Rate + 10%:	lb/hr	80.22344172
Vaporization Rate:	lb/s	0.02228
Maximum allowable operating pressure	PSIG	225
MAWP or Maximum allowable SET pressure	PSIG	250
MAWP or Maximum allowable SET pressure	PSIA	264.696
MAWP to MaxP		1.1
Maximum allowable relieving pressure	PSIG	275
Maximum allowable relieving pressure	PSIA	290
Maximum allowable relieving pressure	lb/ft2A	41716
cp (vapor)=	BTU/lbm*R	0.87668
cv (vapor)=	BTU/lbm*R	0.56139
cp/cv =		1.5616
M, Molecular Weight	g/mol	18.01528
T - operating temp	deg F	469.09
T - operating temp	R	929
R	lbf.ft/(lbmol.R)	***1545***
660	lbm-ft/lbf-s2	***32.2***
C =	(lbm*lbmol*R)^0.5/s*lbf	0.103
z, Compressibility Factor		0.850223
Kd, Discharge Coefficient		0.878
Kb, Back Pressure Correction		1
A	ft^2	0.00003928
A	in^2	0.005656212

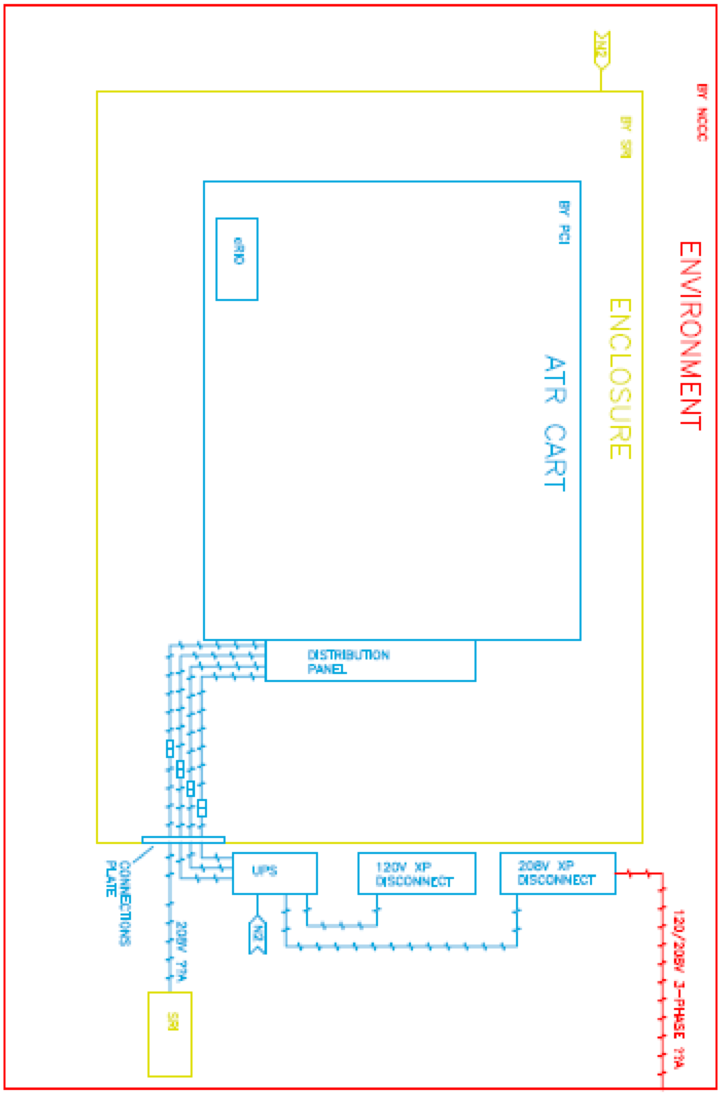
Appendix VI: Design Details for purged reactor enclosure

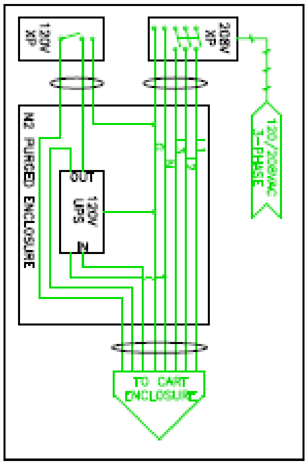
1. Enclosure nominal dimensions: 6' W x 7' H x 4' D
2. Internal dimensions (supporting substructure included) cannot be smaller than 5' 11" W x 6' 11" H x 3' 11" D.
3. Double doors needed on both long sides of cabinet
4. Center-posts for doors must be removable
5. Enclosure Flanges should be turned outward
6. 4-point lifting-lugs on cabinet top
7. Each W6x9 beam should have cutouts for forklift access at the top of the web
8. Enclosure must bolt through the flat plate AND supporting beam below.
9. Enclosure will be purged with approx 900 CFM ambient air, entering near bottom center of one side, exiting near opposite edge of enclosure top.



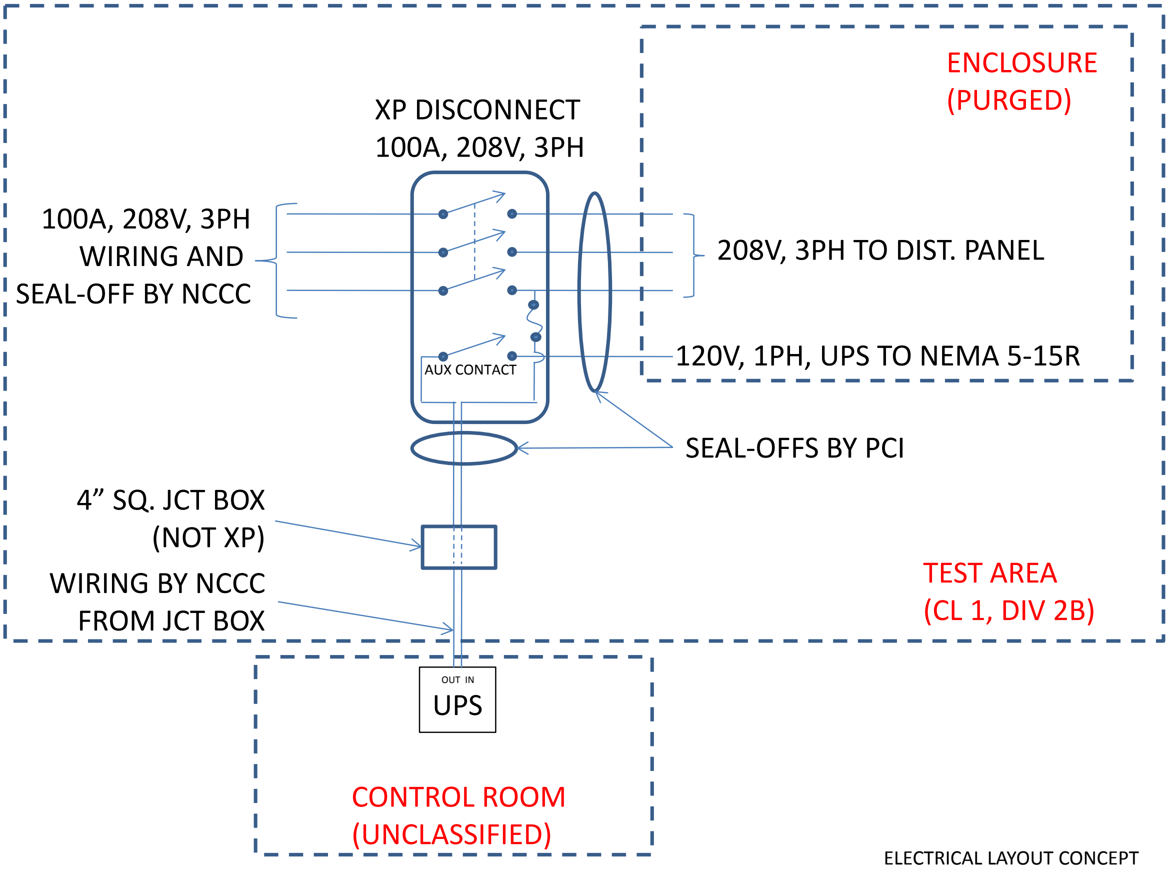

Flat Plate, approx 3/16 thk
L2x2x1/8 Angles (x2)
W6x9 Beams (x2)

Appendix VII: Preliminary wiring diagrams





THIS PRINT AND THE INFORMATION CONTAINED IN IT IS THE PROPERTY OF PRECISION COMBUSTION, INC. IT IS CONSIDERED PROPRIETARY IN NATURE AND MAY NOT BE USED OR DISCLOSED OUTSIDE OF PCI EXCEPT UNDER PRIOR WRITTEN AGREEMENT.



ELECTRICAL LAYOUT CONCEPT
R. MASTANDUNO 8 MARCH 2016