Project Title

Small-scale pilot plant for gasification of coal and coal/biomass blends and conversion of derived syngas to liquid fuels via Fischer-Tropsch synthesis

Final Technical Report

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DISCLAIMER

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Coal gasification, gas clean-up processes and coal/biomass-to-chemicals represent fruitful fields of research and investigation for UK's Center for Applied Energy Research – and the facility made possible through this grant will be an important syngas production facility for a variety of future and complimentary research. This project benefited greatly from CAER's strong collaborations in China. The authors wish to acknowledge the outstanding contribution of GONG, Xin, YU Guangsuo, WANG Fuchen, GUO Qinghua, XU Jianliang and GONG Yan of the China Ministry of Education's Key Laboratory of Coal Gasification, East China University of Science and Technology; WANG Qiuming and TAO Li of the China Electronics and Engineering Design Institute, and REN Xiangkun of Beijing Baota Sanju Energy Science & Technology Co. Ltd. The authors also wish to acknowledge our North American contributors as well, including Ravine Dave, Danielle DeSousa and Leisl Dukhedin-Lalla of ZETON, Inc., Burlington, Canada, and CAER's research and facilities staff, Burt Davis, Gary Jacobs, Dennis Sparks, Will Shafer, Jack Groppo, Robert Hodgen, Steve Summers, Allen Howard, Lamont Bond, Mark Dunavent, Otto Hoffmann, Len Goodpaster, Marshall Marcum, Jake Brumback, Brad Irvin, Kwabena Darkwah and Tate VanHoose.

ABSTRACT

This report describes the second phase of a project to design, construct and commission an integrated coal/biomass-to-liquids facility at a capacity of 1 bbl. /day at the University of Kentucky Center for Applied Energy Research (UK-CAER) – specifically for construction, commissioning and operating of the downstream process units for water-gas-shift, Fischer-Tropsch synthesis and balance of plant [BOP]. The deliverables from the operation of this pilot plant is firstly the liquid F-T products and finished fuels which are of interest to UK-CAER's academic, government and industrial research partners. Going forward the facility will produce research quantities of F-T liquids and finished fuels for subsequent Fuel Quality Testing, Performance and Acceptability. Moreover, the facility is expected to be employed for a range of research and investigations related to: Feed Preparation, Characteristics and Quality; Coal and Biomass Gasification; Gas Clean-up/ Conditioning; Gas Conversion by -F-T Synthesis; Product Work-up and Refining; Systems Analysis and Integration; and Scale-up and Demonstration. Environmental Considerations - particularly how to manage and reduce carbon dioxide emissions from CBTL facilities and from use of the fuels will be a primary research objective. The results of this second phase study include the FEED study and detailed engineering design of the downstream processing units and BOP, the selection of a range of technologies and technology vendors, the as-built plant - its equipment and capabilities, and the results of two trial production runs, one with coal only and one with a coal/biomass blend. These are described in detail in this report.

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EXECUTIVE SUMMARY

Project Objectives

The overarching objective of this project was to advance the second phase of the design and commissioning of an integrated coal/biomass-to-liquids (CBTL) facility at a capacity of 1 bbl./day – specifically for commissioning of the downstream process units for water gas shift, Fischer-Tropsch synthesis and balance of plant [BOP]. The results include the detailed engineering design of the downstream processing units, the selection of a range of technologies and technology vendors, the as-built plant - its equipment and capabilities, and the results of two initial production runs, one with coal only and one with coal/biomass. In addition, the research objectives of the production runs were to compare the compositions of F-T liquids produced from syngas derived from coal-only versus coal/biomass, to assess the economics of the pilot plant, and investigate feed preparation, with emphasis on torrefied biomass.

Main Outcome - A Long-term Platform for Future Research

Beyond the specific technical results discussed below, the main outcome was to finish the coal/biomass-to-liquids (CBTL) facility. Going forward the facility will be an important syngas production facility for a variety of future and complimentary research. With respect to on-going research, environmental considerations, particularly how to manage and reduce carbon dioxide emissions from CBTL facilities and from use of the fuels, will be a primary research objective. Moreover, the facility was purposely designed for modular, skid-mounted processing units, anticipating frequent change-outs; "plug and play"; and future re-purposing. In this respect, the gasifier was purposely designed to provide twice the flows needed for the F-T refinery section to accommodate other slipstream studies; that being at a capacity of 2 bbl. /day gas output [1 ton coal-biomass feed/day; 179 lb./hr. total flow; 65 lb./hr. CO; 3.49 lb./hr. H_2]. The facility has been designed to permit maximum flexibility with the view that it will be an important syngas production facility for a variety of complimentary research, including, for example, as a mid-capacity test facility for first-of-kind carbon capture technologies. The CBTL facility has already attracted two awards from DOE: one directed to improvements for staging the gasifier and adding a fifth burner; a second related to a FEED study and preliminary design of a small, modular gasifier for Combined Heat and Power (CHP). In addition, a number of subscribers and research partners have expressed interest in employing the facility for studies related to, among other topics, membranes for CO_2 separation, improved water-gas-shift catalysts, and sensors and controls for gasification.

Results and Conclusions

1) Feed Handling and Preparation Studies

Significant work on coal slurry preparation resulted in stable slurries of up to 60wt% coal (40wt% water), although slurries with lower solids contents were utilized during production runs to aid in ease of operation and prevent plugging of process lines. In addition, coal/biomass slurry preparation was investigated. The initial goal was to utilize a coal/biomass mix of 10% torrefied wood and 90% coal to make liquid fuels [diesel, etc.] competitive "well-head to wheels" with petroleum on a CO_2 basis. However, coal/biomass slurry preparation was significantly more challenging than coal-only slurries, owing to serious viscosity and pumpability issues associated with torrefied wood at even low weight percent mixtures. A 10 wt% torrefied biomass addition absorbed all of the free water in the slurry, resulting in a thick slurry paste that could neither be tested with a viscometer nor pumped. Similarly, 5 wt% torrefied wood had a viscosity 50% higher than the coal-only slurry and a 1 wt% torrefied wood slurry had a 10% higher viscosity compared to coal. As a consequence, the coal/biomass slurry utilizing 5 wt% torrefied wood required considerable dilution with more water than the coal-only slurry [an

increase from 40 wt% water to 50 wt% water]. This resulted in substantial penalties, among them, a ~20% drop in overall heating value of the slurry for which additional natural gas was required to maintain gasifier operating temperatures. Much work remains to improve the feed-ability of coal/biomass mixtures, including investigations of potentially hybrid dual-feed systems for both wet and dry feeding.

2) Summary Comparison of Coal-only and Coal/Biomass Production Runs

A direct comparison of the coal-only and coal/biomass production runs could not be made because of differing feedstock and operating conditions employed for the two runs. For the gasification section, process conditions were relatively similar, except for the addition of biomass in the feed slurry and the additional natural gas needed to maintain temperature of the system. The syngas produced was also similar in nature except that flow rate was lower for the coal/biomass operation and concentrations of H_2, CO and CO_2 were slightly lower. It is interesting to note that the H_2/CO ratio out of the gasifier for both operations was almost identical. WGS reactor temperature was higher for the coal/biomass operation which resulted in higher H_2/CO ratios downstream. AGR operation was basically identical for both sets of operation data, with removal of more than 97% of the CO_2 from the shifted gas. Finally, the F-T conditions were different enough that conversion and selectivity between the two operations was significantly impacted. The coal biomass had a much higher H_2/CO inlet ratio, lower pressure and higher operating temperature than the coal only run. These factors all contributed to higher CO conversion, while also preferentially producing shorter chain hydrocarbons for the coal/biomass F-T operation. Based on significant experience in the F-T field, had the operation conditions (pressure, temperature and inlet H_2/CO ration) been the same for both operations then the product conversion and selectivity's would have been identical. Accordingly, all differences in data can be easily attributed to the different operating conditions. And, owing to these differences in operating conditions and feedstocks, a direct comparison between runs with regards to CO_2 emissions and product yield and selectivity could not be made based on the initial runs. Nevertheless, feed, product data and emissions are discussed below.

For the coal-only run, a feed of 0.61 TPD coal and 0.41 TPD water was utilized. For the coal/biomass run, 0.36 TPD coal, 0.02 TPD torrefied biomass and 0.36 TPD water were used. The coal-only run consumed 0.11 tons of NG per barrel of products compared to 0.13 tons of NG per barrel of products for the coal-biomass run [greater NG was required because of the greater amount of dilution (water) needed for the coal/biomass run]. For the coal-only run, 0.16 BPD of naphtha and 0.16 BPD diesel was produced. Product yields were higher for the coal-biomass process, at 0.22 BPD of naphtha and 0.18 BPD diesel. The higher product yields in the coal-biomass run relative to the coal-only run can be attributed to the different operating conditions of the WGS and F-T reactors, which produced higher conversions. The light products (C1 - C5) accounted for 61.2% and 69.5% (on BPD basis) of the total products, emphasizing the importance of recycling the lights to produce higher hydrocarbon-chained products (naphtha and diesel). The CO_2 released for the coal-only and coal/biomass runs were 0.77 and 0.72 TPD, respectively, representing 1.22 and 0.83 tons of CO_2 per barrel of total product produced. The lower amount of CO_2 released from the coal/biomass run versus the coal only run is the result of the higher addition of NG feed for the coal/biomass run, such that the differences in CO_2 emissions between the runs is negligible.

3) Economics of the Pilot Plant

Operating costs includes a labor cost of $3000 per barrel of product (for a crew of 3 shifts with 2 technicians per shift) and $800 per barrel for maintenance and materials costs. The purchase cost of the Coal was $91.7 per ton and torrefied wood Biomass at $737.4 per ton. The variable operating costs included the cost of Coal at $89.72 per barrel and $56.62 per barrel for Coal/Biomass. Electricity and water were used at $186.4 per barrel and $73 per barrel, respectively. The pilot plant required a capital investment of $5.3M for site improvements, buildings and structures, and equipment costs for the upstream and downstream process units.

REPORT DETAIL

Project Objective

The overarching objective of this project was to advance the second phase of the design, construction and commissioning of an integrated coal/biomass-to-liquids (CBTL) facility at a capacity of 1 bbl./day at the University of Kentucky (UK-CAER) – specifically for construction, commissioning and operations of the downstream process units for water gas shift, acid gas removal and Fischer-Tropsch synthesis, as well as the balance of plant [BOP]. The main results of this second phase study include the FEED study and detailed engineering design of the downstream processing units and BOP, the selection of a range of technologies and technology vendors, the as-built plant - its equipment and capabilities, and the results of two initial production runs, one with coal only and one with a coal/biomass blend.

Specific research objectives of the project were:

- To compare the compositions of F-T liquid fuels produced from coal-derived syngas with those produced from syngas derived from a coal/biomass mixture, whereby biomass in the amount up to 10% (torrefied basis) is added to the pulverized coal. Compositions of the products were assessed following a straight run through the F-T reactor, as well as after the heavier products (e.g., waxes) are processed in a standalone hydrocracker.
- Assess the economics of the process to compare what the cost is of adding biomass to coal for the purpose of limiting net CO_2 emissions to the environment.
- Investigate feed handling and preparation, with emphasis on torrefied biomass.

Principal Tasks

- Task 1.0 Project Management
- Task 2.0 - Acquisition, Preparation and Handling of Feed stocks – Coal and Biomass:
- Task 3.0 Detailed Design, Fabrication and Delivery of a Modular Fischer-Tropsch Reactor, Water-gas-Shift Reactor and Balance of Plant
- Task 4.0 Installation, Shakedown and Commissioning
- Task 5.0 - Integrated Runs and On-going Research Related to the Production of Liquid Fuels from Coal and Biomass:

Experimental Methods/Equipment Used

1) General Scheme, Process Units, Capacities and Stream Flows

The main process units of the UK's CBTL facility consist of feed preparation [coal/biomass water slurry], gasification, syngas cleaning and conditioning, water-gas-shift, and gas-to-liquids by F-T synthesis. A Phase I grant [no. DE-FC26-08-NT05988] made possible the construction of the refinery building, and fabrication of the upstream processing units for coal/biomass water slurry feed preparation; coal/biomass gasifier for syngas production; and an aqueous amine-based stripper/scrubber and an activated carbon bed for gas cleaning and conditioning. This second grant [DEFC2612FE0010482] provided for fabrication, installation and commissioning of the downstream refinery units: water-gas shift reactor for adjustment of H_2:CO ratio, a micro-

channel reactor for FT synthesis and the balance of plant [BOP]. The second grant also provided funding for operation of the full facility.

Operation of the F-T PDU Facility has the capability of producing approximately 1 barrel per day of mixed hydrocarbon fuels and feed stocks ranging from diesel, gasoline, naphtha, and waxes and light gases. Streams flows are shown in **Figure 1** using coal as the feedstock. The gas compositions provided are in weight %.

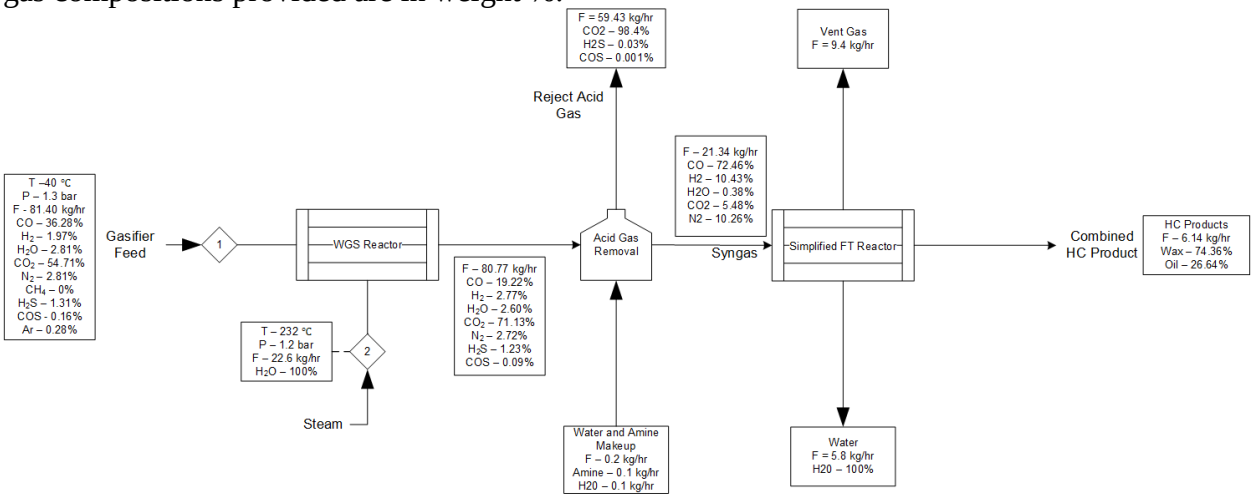


Figure 1: Simplified Process Flow Sheet – Unit Processes and Output

2) Coal/Biomass Slurry Preparation System and Gasifier

As reported previously for a Phase I grant [no. DE-FC26-08-NT05988], substantial savings were achieved in the foreign-sourcing of a much cheaper and still proven gasifier than that which could be sourced domestically. This included all the associated coal handling and preparation equipment. UK-CAER made the choice to utilize a gasifier designed and fabricated by the China Ministry of Education's Key Laboratory of Coal Gasification, East China University of Science and Technology [ECUST].

ECUST, along with Yankuang Lunan Chemical Fertilizer Plant and China Tianchen Engineering Corporation Co. Ltd (TCC) have developed the coal-water slurry gasification technology with opposed multi-burners (OMB). A general flow schematic of the ECUST-OMB technology is shown in **Figure 2**, which is based on the principle that impinging flows strengthen the mixing of the particles during the gasification process. Successive field deployments and industrial demonstrations of larger and larger capacity gasifiers have led ECUST's OMB gasification technology to become one of the leading technologies in the world market (1).

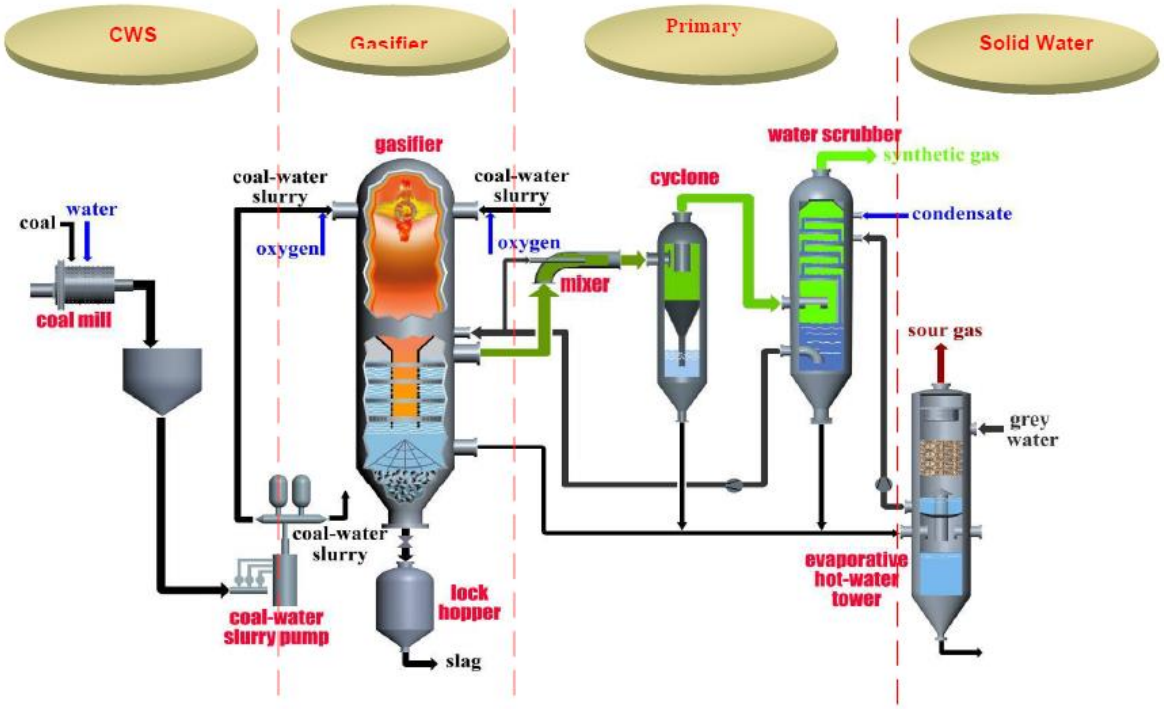


Figure 2: Schematic - ECUST OMB gasification process

The system includes: 1.) Coal water slurry preparation system (mill, CWS tank, additive container); 2.) Raw material supply system (CWS pump, O_2 dewar tank, flow meters, oil tank and pump); 3.) Gas purge and protection system; 4.) Gasification section (stainless gasifier, refractory brick, slag container, burner); 5.) Flame monitoring system; 6.) Gas composition and temperature analysis system; and 7.) Emergency control and shutdown system. ECUST's OMB gasification technology involves using four symmetrically opposite burners to introduce the coal/water slurry to the gasifier in order to produce syngas. This system can produce enough slurry for the gasifier to consume 1 ton of dry coal per day during standard operation which produces approximately 179 lbs/hr of high quality syngas. Under normal operation, the H_2/CO molar ratio produced in the syngas will be ~0.75/1. OMB technology has many advantages over typical entrained flow gasification systems, such as: improved flow distribution, enhanced residence time, and carbon conversion, high syngas production with low coal/oxygen consumption, wide capacity range (40-120% of rated capacity) and low process pressure drop along with low operating pressures (30 psi).

The first step of the process involves adding raw coal to the feed preparation unit which allows UK-CAER to produce the required slurry on site. In the feed preparation unit as shown in **Figure 3**, the coal is weighed and then introduced to the ball mill where the particle size is reduced while simultaneously being mixed with water of an appropriate amount. A small amount of additive is also added in this step to reduce surface tension and help increase the pumpability of the slurry. After blending, the Coal Water Slurry (CWS) is stored in a tank and kept suspended with a mixer. Once the slurry is prepared, it is then introduced concurrently with oxygen to the gasifier via the four burners.

Figure 3: Photo/Illustration of Feed Preparation

Figure 4 includes a photograph of the installed OMB gasifier, which stands 25 ft. tall and is 6ft in outside diameter. The gasifier consists of two parts: the gasification chamber (where the slurry reacts) and the quench chamber (where the reaction is extinguished). Upon entering the gasification chamber, the coal-water slurry and oxygen react to produce crude syngas and molten ash, which then passes to the quench chamber through a cross flow water spray and subsequent water bath. This acts as a first wash for the raw syngas and removes large ash particles while also quickly removing heat. Moreover, the syngas is completely saturated in this step due to the requirements of downstream purification processes. After the washed syngas leaves the quench chamber, it proceeds to the primary purification section. Here the syngas passes through a water scrubber, which removes about 80% of the unconverted particles and remaining ash. The water scrubber is the last step in the gasification process before the syngas continues downstream to the WGS unit for further processing.

Figure 4: Photo - OMB Gasifier

3) Water Gas Shift Reactor

Syngas from the OMB gasifier is sent to the WGS section. First, the syngas goes through 10 micron filters to remove any remaining particulates in the gas stream. Then a control valve is utilized to send the required amount of syngas to the WGS unit while the rest is sent through a bypass where it will be mixed back with the shifted gas again before exiting the module. Syngas proceeding to the WGS reactor then passes through an electric pre-heater. In the electric pre-heater, syngas is mixed with steam in the appropriate ratio, heated to 240^{o}C and then introduced to the WGS reactor itself. The WGS is a packed bed type of reactor that utilizes a commercial sour shift catalyst to perform the reaction. The shifted gas exits the WGS where it is then cooled, excess water is condensed in a knockout pot, mixed with the bypass gas and then finally sent downstream to the AGR system. The WGS reactor can be seen in **Figure 5**. A simplified block flow diagram depicting the process is shown in **Figure 6**.

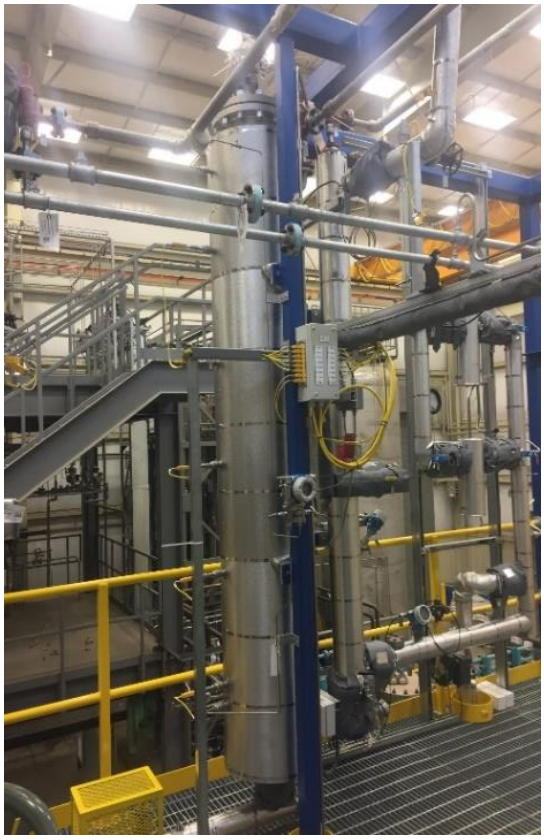


Figure 5: Photo of WGS Reactor

The WGS system has the ability to take a syngas with an H_2/CO molar ratio of approximately 0.75:1 and produce a H_2/CO molar ratio of up to 11:1. As mentioned previously, there is a controllable by-pass valve that provides precise control of the WGS reactor output. The valve can be manually controlled by the operator setting the desired H_2/CO ratio or it can be automatically controlled using the online GC and DeltaV operating system. Designing the WGS in such a manner, allows the facility to be operated flexibly depending on the downstream requirements. For example, the facility is currently designed to produce fuels from F-T using a cobalt catalyst which prefers H_2/CO concentrations of approximately 2. However, with this design, an iron catalyst could be used in the F-T reactor (H_2/CO ~ 0.75), or the facility could be used to produce chemicals or for poly-generation (H_2/CO > 2). After the shifted-gas exits the process, it is then sent to the acid gas removal system for compression and cleaning before it is delivered to its final destination in the F-T unit.

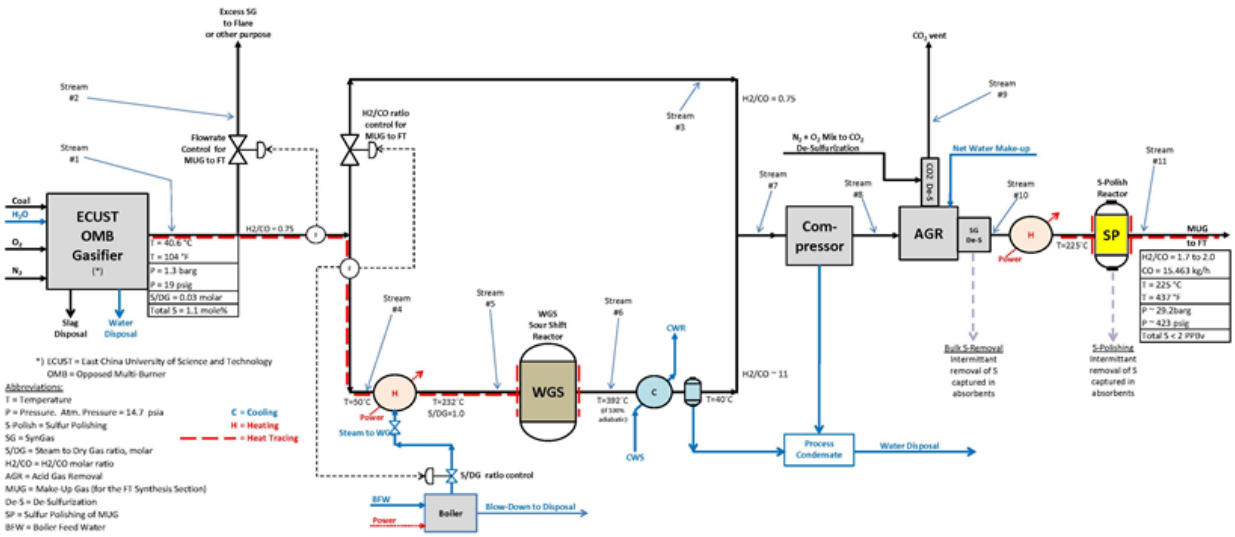


Figure 6: WGS Simplified Block Flow Diagram

4) Acid Gas Removal Plant

After leaving the WGS, the shifted gas proceeds to the acid gas (CO_2 and sulfur compounds) removal system, as shown in the process flow diagram as **Figure 7**. The first step in the AGR is compression of the shift gas up to 450psi utilizing the Howden Burton Corblin metal diaphragm compressor. Compressed gas exits the compressor and proceeds to the absorption column where an aqueous amine solvent strips acid gas out of the shifted gas in a counter current flow method. The cleaned gas proceeds through a hydrolysis reactor to convert COS to H_2S and CO_2, as well as activated carbon beds to reduce the sulfur concentration below 1ppmv before it is finally sent downstream to the F-T module. Meanwhile, the rich amine solvent loaded with acid gas is sent to the ambient pressure stripping column. The stripping column is also heated to approximately 80°C to assist in regenerating the amine solvent. Lean amine solvent is then pumped back to the absorber to begin another cycle of acid gas removal. The rejected acid gas out the top of the stripper also passes through a set of three activated carbon beds to capture H_2S and exits the process through the flare system. Photos of the AGR modules and the activated carbon bed used for sulfur removal is shown in **Figure 8.**

UK-CAER has over 15 years of experience with similar aqueous amine capture systems. Since this system is used mainly to clean the gas to F-T specifications, the removal of sulfur is of greatest importance. Sulfur has the ability to cause significant and irreversible damage to the F-T catalyst at even very low concentrations. Therefore, process guarantees were required from the manufacturer of this system for the cleaned gas of 95% CO_2 capture and simultaneous removal of H_2S to below 1ppmv.

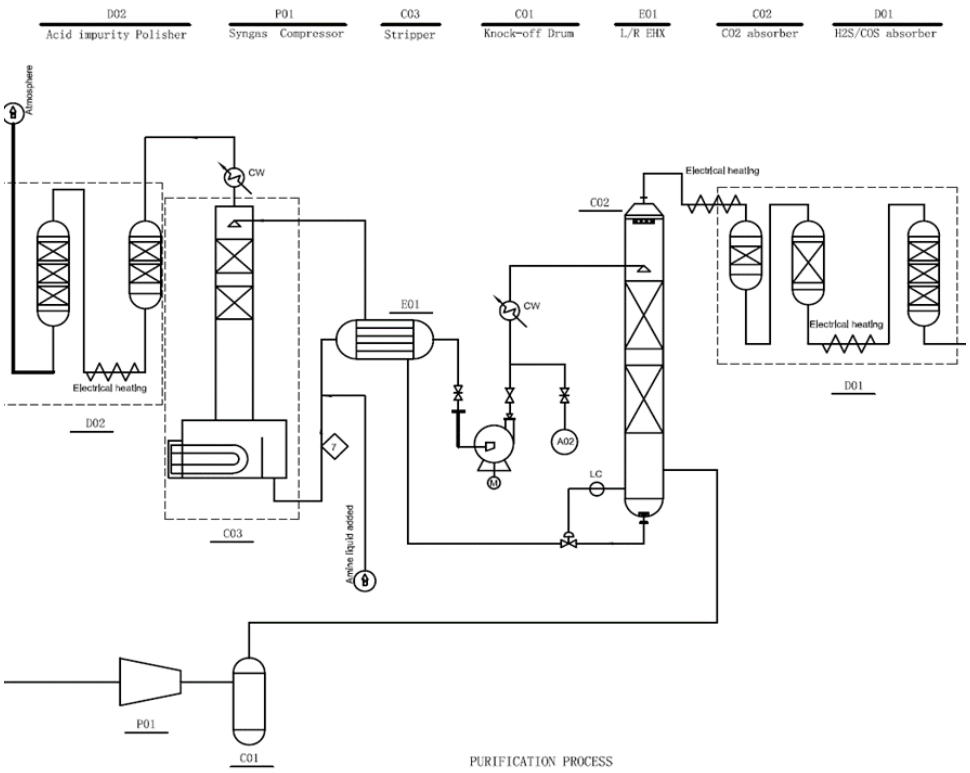


Figure 7: Process Flow Diagram for Acid Gas Cleanup

Figure 8: Photo - Acid Gas Removal Unit (left) and Activated Carbon Bed (right)

5) Micro-channel Fischer-Tropsch Synthesis Reactor

The F-T reactor can be seen in **Figure 9 (left)**, below. The F-T reactor, itself, is a Chart Energy microchannel design capable of handling Fe or Co catalysts with production capability of 1 barrel of liquids per day. This type of F-T reactor is an aluminum heat exchanger that is packed with catalyst on the process side, while the other side of the exchanger is hot oil coolant. Since the reactor is made of aluminum, there is the potential for integrity issues at high temperatures and pressures. Therefore, the system requires a pressurized hot oil system that maintains the pressure of the oil coolant side of the exchanger identical to that of the process side, while also removing heat from the exothermic reaction (see photo in **Figure 9 (right)**.

Once the cleaned syngas exits the AGR, it is introduced to the F-T section. A process flow diagram of the F-T section is shown in **Figure 10**. First, the gas is sent through a sulfur polishing reactor that uses a zinc based absorbent to ensure that no sulfur components enter the F-T reactor and subsequently poison the catalyst. Next, the polished gas, at approximately 450psi, is pre-heated with an electric heater to a reaction temperature around 210-225℃ and then enters the Chart Energy microchannel heat exchange F-T reactor where it reacts with a cobalt based catalyst to produce a range of hydrocarbon products. The unconverted gas and F-T products exit the once through reactor and are cooled to 150℃ in the hot effluent separator. This separator condenses the heavy waxes and stores them for future processing, while the rest of the gas continues downstream. The remaining gas is cooled to 5℃ to condense the liquid oil products and water in the light effluent separator. The light effluent separator can then partition the water and liquid oil products using density differences. The liquid oil is then transferred to a drum for final storage. Meanwhile, the water is recycled and employed elsewhere in the plant. All remaining gas then exits facility via the flare. This exit/tail gas generally consists of inert components, unconverted syngas, and lighter hydrocarbons such as methane, propane, etc.

Figure 9: Photo of F-T Reactor (left) and Pressurized Hot Oil System (right)

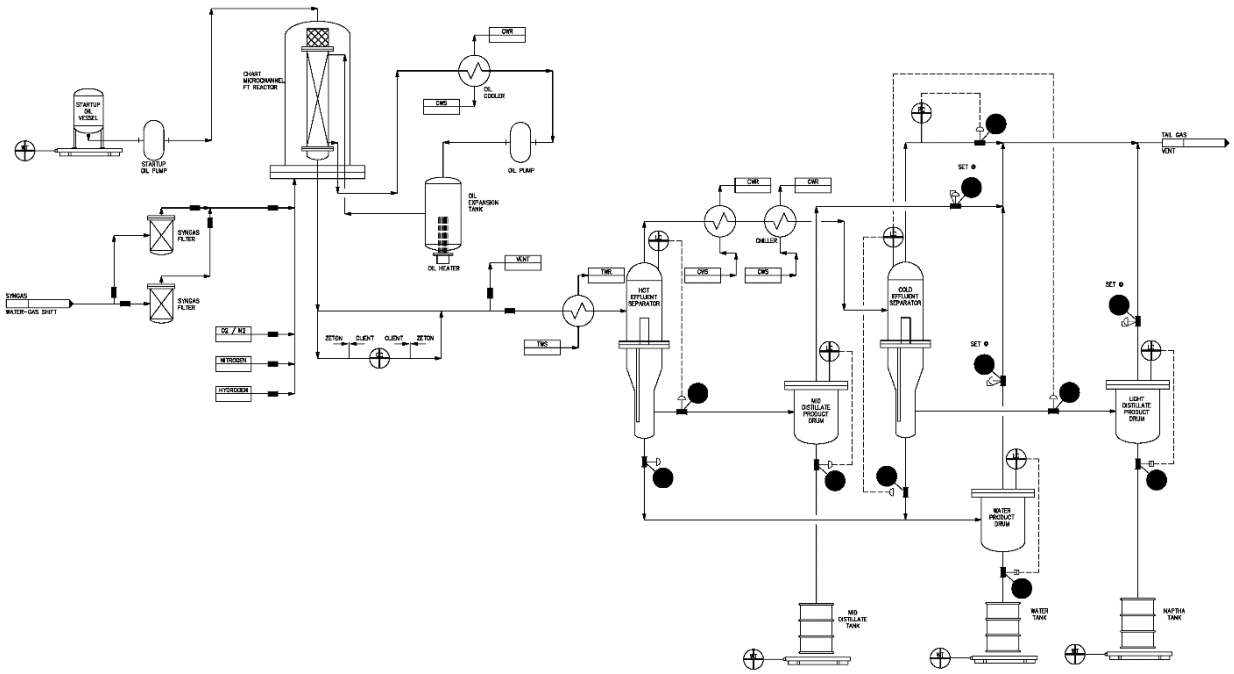


Figure 10: Process Flow Diagram of F-T Section

6) Balance of Plant

The plant complex includes ancillary systems for power generation, utilities, effluent treatment, ash disposal, operation control, safety control, and analytical systems. Mechanical systems include nitrogen, hydrogen, oxygen, carbon dioxide, natural gas, domestic water, sanitary piping, and general use compressed air piping. Analytical capabilities include an online Gas Chromatograph (GC) with five sample ports for real-time gas composition measurements. The GC is also integrated with the DeltaV control system for recording data, and operator feedback. The Emerson (Rosemount Analytical) 1500XA online GC has the ability to handle eight process sample lines and provides optimal reliability and flexibility. The GC is currently equipped to measure five gas samples throughout the facility: syngas out of the gasifier, shift gas out of the WGS, syngas into the AGR, cleaned gas out of AGR, and lastly, the tail gas out of the F-T. Photos of a selection of the BOP systems are shown in **Figure 11**.

Figure 11: BOP systems (Left to Right): Oxygen Gas, Nitrogen Generator and Air Compressor, Crane, Chiller, Flare and Gas Chromatograph

RESULTS AND DISCUSSION

Main Outcome – A Long-term Platform for Future Research

Coal gasification, gas clean-up processes and coal/biomass-to-chemicals represent fruitful fields of research and investigation. Beyond the specific technical outcomes and results of this project which are discussed below, the main outcome was to finish the design, construction and commissioning of an integrated coal/biomass-to-liquids (CBTL) facility at a capacity of 1 bbl./day at the University of Kentucky Center for Applied Energy Research (UK-CAER). Such a facility has required significant lead time for environmental review, architectural/building construction, and EPC services for the design and fabrication of the principal refinery units. Going forward the facility made possible through this grant will be an important syngas production facility for a variety of future and complimentary research. With respect to on-going research, environmental considerations, particularly how to manage and reduce carbon dioxide emissions from CBTL facilities and from use of the fuels, will be a primary research objective. In addition, research at this new CBTL facility will focus on: Feed Preparation, Characteristics & Quality; Coal & Biomass Gasification; Gas Clean-up/Conditioning; Gas Conversion by F-T Synthesis; Product Work-up and Refining; and Systems Analysis and Integration.

Moreover, the facility was purposely designed for modular, skid-mounted processing units, anticipating frequent change-outs; "plug and play"; and future re-purposing. In this respect, the gasifier was purposely designed to provide twice the flows needed for the F-T refinery section to accommodate other slipstream studies; that being at a capacity of 2 bbl. /day gas output [1 ton coal-biomass feed/day; 179 lb./hr. total flow; 65 lb./hr. CO; 3.49 lb./hr. H_2]. For research purposes the gasifier can run in a range of 40-120% of its rated capacity which provides the ability to ramp up/down and provide slipstreams for multiple downstream units. The facility has been designed to permit maximum flexibility with the view that it will be an important syngas production facility for a variety of complimentary research, including, for example, as a mid-capacity test facility for first-of-kind carbon capture technologies.

On an on-going basis, the know-how, show-how associated with the facility is expected to be a key benefit, which can be used as test beds for new technologies and concepts at a level of expenditure that is affordable. It will provide open-access facilities and information in the public domain to aid the wider scientific and industrial community, and a means to independently review vendor claims and validate fuel performance and quality. The facility will be used to build up human capital – the future generation of skilled energy technologists, engineers and operating personnel that will be needed to sustain a CBTL industry. And, one of the best ways of creating this skills base is to stimulate and fund RD+D at appropriate institutions which have the facilities to teach and train students in the practical application of science and engineering.

The CBTL facility has already attracted one new award from DOE directly related to improvements for staging the OMB gasifier and adding a fifth burner. UK-CAER's entry into gasification technologies also led to a second award from DOE for a FEED study and preliminary design of a small, modular gasifier for CHP. In addition, a number of subscribers and research partners have expressed interest in employing the facility for studies related to,

among other topics, membranes for CO_2 separation, improved water-gas-shift catalysts, and sensors and controls for gasification.

Specific Technical Results and Outcomes

1) Feed Handling and Preparation Studies

1.1. Source Coal and Biomass

Coal was sourced from Illinois Basin coals purchased from Alliance Coal. Specification and composition of the coal are shown below in **Table 1**. The coal was specified for two main features: ash fusion temperature and sulfur content. The ash fusion point is important because the gasifier must be operated above the ash fusion point so that the slag flows as a liquid down the walls. If this is not done, then it is possible the slag will become a solid and has the potential to clog the exit of the gasifier. In addition, the upper temperature limit is set by the refractory properties. Therefore, using the Gibson Mine coal provided a reasonable range for operation temperature. As for the sulfur content, this coal has a relatively low amount which eased the duty of the AGR and sulfur polishing beds downstream to meet the F-T system maximum sulfur requirements.

Coal Analysis for Gibson Mine, Indiana

Heating Value	BTU/lb	
Gross Calorific Value	16,624	

Ash Fusion Temperatures	Fahrenheit	Celsius
Initial temperature (reducing)	2011	1099
Softening Temperature (reducing)	2155	1179
Hemispherical Temperature (reducing)	2393	1312
Fluid Temperature (reducing)	2464	1351
Initial temperature (oxidizing)	2051	1122
Softening Temperature (oxidizing)	2189	1198
Hemispherical Temperature (oxidizing)	2272	1244
Fluid Temperature (oxidizing)	2502	1372

Proximate	%
%Ash	7.09
%Moisture	9.71
%Volatile Matter	31.62
%Fixed Carbon	51.58

Ultimate	%
%Carbon	67.22
%Hydrogen	5.62
%Nitrogen	1.33
%Total Sulfur	1.26

Major Ash Components	%
$\%SiO_2$	44.68
$\%Al_2O_3$	20.57
$\%Fe_2O_3$	26.19
%CaO	2.1
%MgO	0.79
$\%Na_2O$	0.98
$\%K_2O$	2.42
$\%P_2O_5$	0.02
$\%TiO_2$	1.19
$\%SO_3$	1.45

Minor Ash Components	Ppm
V	199
Cr	133
Mn	126
Co	62
Ni	148
Cu	139
Zn	266
As	191
Rb	110
Sr	1015
Zr	224
Mo	22
Cd	5
Sb	5

%Oxygen	17.48	Ba	1.30%
		Pb	58

Table 1: Coal Composition

As for the torrefied biomass, an exhaustive search was performed for a supplier. The challenge was finding a supplier who could produce torrefied biomass on the tons' scale. Utilizing existing UK-CAER contacts in the biomass field, Amaron Energy was contracted to produce the five tons of torrefied biomass required. The composition of the torrefied biomass procured is shown in **Table 2**.

Analysis of Torrefied Biomass

Heating Value	**BTU/lb**		**Major Ash Components**	**%**
Gross Calorific Value	9255		$\%SiO_2$	27.27
			$\%Al_2O_3$	10.70
Ash Fusion Temperatures	**Fahrenheit**	**Celsius**	$\%Fe_2O_3$	13.31
Initial temperature (reducing)	2045	1118	%CaO	18.25
Softening Temperature (reducing)	2084	1140	%MgO	4.67
Hemispherical Temperature (reducing)	2105	1152	$\%Na_2O$	4.64
Fluid Temperature (reducing)	2151	1177	$\%K_2O$	5.67
			$\%P_2O_5$	1.35
Proximate	**%**		$\%TiO_2$	3.36
%Ash	1.54		$\%SO_3$	8.50
%Moisture	3.62		$\%Al_2O_3$	10.70
%Volatile Matter	73.88		$\%Fe_2O_3$	13.31
%Fixed Carbon	20.96		%CaO	18.25
			%MgO	4.67
Ultimate	**%**		$\%Na_2O$	4.64
%Carbon	56.58		$\%K_2O$	5.67
%Hydrogen	6.06		$\%P_2O_5$	1.35
%Nitrogen	0.00		$\%TiO_2$	3.36
%Total Sulfur	0.03		$\%SO_3$	8.50
%Oxygen	35.79			

Table 2: Torrefied Biomass Composition

1.2. Coal and Coal/Biomass Slurry Preparation

The coal slurry preparation was relatively simple and straight forward. Slurry for the coal-only run was prepared utilizing the feed preparation unit in a 60 wt% solids and 40 wt% water ratio. The solids in this case was 59% coal and 1% limestone. The limestone was added to help lower the ash fusion temperature slightly to reduce the chance of plugging the gasifier. An additive, Daracem 55, was also added in a concentration of 0.5wt% to the prepared slurry in order to help keep the solids suspended and prevent settling.

The coal/biomass slurry preparation was much more challenging**.** Significant investigative work was performed to look at biomass utilization in the gasifier feed with an emphasis on slurry preparation using biomass at up to 10 wt% (90 wt% coal) - to make liquid fuels [diesel, etc.] competitive "well-head to wheels" with petroleum on a CO_2 basis. Initially, torrefied wood was used to look at the effect on the viscosity which can then be directly correlated to the

pumpability of the solution. A range of slurries with torrefied wood and coal blends were prepared but maintained at constant solids (coal/biomass) to water ratio of 60 wt% solids to 40 wt% water. In addition, a control slurry with coal only was mixed for comparison purposes.

The results of these experiments are shown in **Figure 12**. From the results, it was observed that at 10 wt% torrefied biomass, all of the free water was absorbed by the biomass. This resulted in a thick slurry paste that could neither be tested with a viscometer nor pumped. Meanwhile, the 5 wt% torrefied wood sample had a viscosity 50% higher than the coal only control slurry, and the 1 wt% torrefied wood slurry had a 10% higher viscosity compared to the control. From these experiments, it was obvious that both the 10 wt% and 5 wt% torrefied biomass slurries could not be utilized with the UK-CAER gasification unit because they would be un-pumpable. It was possible to use the 1 wt% torrefied biomass slurry on the current system, however at such low concentration the improvement on the CO_2 footprint would be minimal.

Therefore, it was decided that the 5 wt% solution would be diluted with enough water to make it pumpable for utilization in the gasification system. After much testing, the final torrefied biomass slurry for utilization with the current UK-CAER gasification system, had the following properties: 50 wt% solids (95 wt% coal and 5 wt% torrefied biomass) and 50 wt% water. This corresponds to about 20% reduction in the heating value of the feed, which then has to be made up with additional fuel to maintain the gasifier temperature during operation. It should also be noted that both limestone and additive concentrations were used in the same proportion as the coal-only feed.

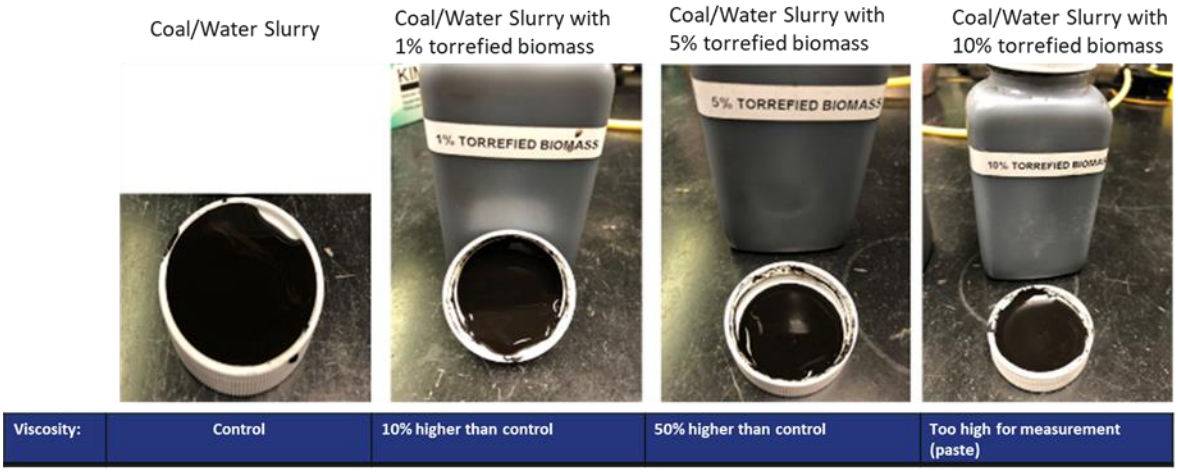


Figure 12: Coal/Biomass Slurry Preparation Characterization

Further lab scale experiments were performed on raw biomass. Sawdust and corn flour were tested because both are local products obtained easily and quickly. The raw biomass slurry testing was conducted exactly the same as for the torrefied biomass. The results were very similar to the torrefied woods results shown previously. The only difference between the two results was that the raw biomass had a much higher water concentration than the torrefied wood (since the raw biomass had not been through the torrefaction process) which made the resulting solutions higher in moisture. Once corrected for the moisture content, the results were basically identical.

Based on the above information, a decision was made to utilize the torrefied biomass feed because the properties of the torrefied biomass were closer to that of the coal than the green biomass (which made process operations more straightforward). The final slurry was prepared with a 5 wt% torrefied biomass/95 wt% coal in a 50:50 mixture with water for the final coal/biomass run. This slurry provided the best balance for maintaining heating value of the slurry while limiting the viscosity issues of the feed to make sure the slurry could be properly pumped into the gasifier. Overall, the blending of biomass to reduce CO_2 sounds good in theory but the pump-ability issue along with the heating value reduction make it a real challenge.

2) FT Catalyst Studies

2.1. Initial Screening/Optimization of Cobalt Fischer-Tropsch Catalyst

A sample of UOP alumina pellets was obtained for use as a potential support of cobalt nanoparticles for the F-T Compact Heat Exchange Reactor (CHER). The support was found to have a surface area that was too high such that interactions between cobalt oxides and the support would lead to inadequate % cobalt reduction. Moreover, the pores were too narrow, such that supported cobalt particles would likely be too small (e.g., a high fraction < 4 nm), making them susceptible to oxidation by H_2O under Fischer Tropsch Synthesis (FTS) conditions. An investigation was made to improve the alumina characteristics by calcination at high temperature, which at high temperature decrease the surface area (potentially lessening interactions between cobalt oxides and the support) and increase the pore diameter (potentially leading to larger, more stable cobalt nanoparticles less susceptible to oxidation under FTS conditions).

UOP Advanced Specialty Gas Equipment Al_2O_3 (Molsiv Adsorbents Activated Alumina D – 201 5 x 8, Aluminum Oxide (non-fibrous (1344-28.1) <97%, Water (7732-18-5) < 10%) was dried at 100^{o}C overnight. Samples were calcined at 350^{o}C, 400^{o}C, 500^{o}C, 600^{o}C, or 650^{o}C for 4 h and characterized for their BET surface area and porosity characteristics. A sample of alumina was crushed and sieved to 90 – 125 microns and calcined at 650^{o}C for 4 h; the amount was 50 g.

This alumina was used to prepare a 0.1%Pt-15%Co/Al_2O_3 catalyst. A 3-step incipient wetness impregnation procedure was used, such that 12.1 g of $Co(NO_3)_2$*$6H_2O$ was added in a loading solution of 13.24 ml in each step, with interval drying in a rotary evaporator under vacuum at temperatures ranging from 80 – 100^{o}C. Then, 0.095 g of tetraamine platinum (II) nitrate was impregnated using 13.24 ml of loading solution. The catalyst was dried in the rotary evaporator and calcined at 350^{o}C for 4 h (5 h ramp from 20^{o}C to 350^{o}C).

2.2. Production and Testing of Large Test Batch

100 kg of alumina pellets for the project were subsequently shipped to Applied Chemical (4350 Helton Drive, Florence, AL 35630) and an industrial-style test batch of 0.1%Pt-20%Co/Al_2O_3 was produced for the purpose of later characterization and testing in a 1’ CHER and 1 L continuously stirred tank reactor (CSTR).

A test batch of 0.1%Pt-15%Co/Al_2O_3 catalyst was made, but only a temperature programmed reduction experiment and porosity measurements were made.

A barrel of 100 kg of Clariant Al_2O_3 (Actisorb 100-1 1/8" extrudates) was shipped to Applied Chemicals Inc. (ACT) (4350 Helton Drive, Florence, AL 35630) for the preparation of test batches and the final pilot plant batch (future). The initial test batch involved ACT's 100 N fluid bed to coat 1 lb of alumina with cobalt nitrate hexahydrate/tetraamineplatinum(II) nitrate according to the following scope:

- 1 lbs of sieved (range to be provided by University of Kentucky) aluminum oxide was coated with an aqueous solution of cobalt nitrate hexahydrate and tetraamineplatinum (II) nitrate using the formulation provided by the University of Kentucky.
- A lab scale fluid bed was used in the testing.
- An alternative mixer/drying system was also tested.
- The final coated material contained 20 wt% cobalt on a calcined catalyst basis, assuming: $\%Co = (Co^0)/(Co_3O_4 + PtO_2 + Al_2O_3) \times 100\%$
- The catalyst was promoted with Pt using an aqueous solution of tetraamineplatinum(II) nitrate at a loading of 0.1% on a calcined catalyst basis, assuming: $\%Pt = (Pt^0)/(Co_3O_4 + PtO_2 + Al_2O_3) \times 100\%$
- Flow rates and parameters to keep agglomeration at a minimum during the coating process were identified.
- All testing and process development formulas and procedures were determined with commercialization in mind, focusing on low cost alternatives and methods.
- The catalyst was calcined in air, in flowing air, at 350^{o}C for 4 h. The temperature ramp for the resulting product was no faster than 1^{o}C per min.
- The product was screened to determine the amount of oversize and undersize after the coating process following calcination.

BET and BJH measurements were conducted using a Micromeritics 3-Flex system. Samples were outgassed overnight at 160^{o}C to approximately 50 mTorr. Temperature programmed Reduction (TPR) profiles were obtained using a Zeton Altamira AMI-200 unit. Calcined fresh samples were first heated and purged in flowing argon to remove traces of water. TPR was performed using 30 mL/min of a 10%H_2/Ar mixture referenced to argon. The ramp rate was 10 ^{o}C/min from 50 to 900+ C. Hydrogen chemisorption measurements were performed using a Zeton Altamira AMI-200 unit, which utilizes a thermal conductivity detector (TCD). The catalyst was activated at 350^{o}C for 10 h using a flow of pure hydrogen and then cooled under flowing hydrogen to 80-100^{o}C. The sample was then held under flowing argon to prevent physisorption of weakly bound species prior to increasing the temperature slowly to the activation temperature. At that temperature, the catalyst was held under flowing argon to desorb the remaining chemisorbed hydrogen so that the TCD signal returned to the baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibrated hydrogen pulses.

Prior to experiments, the sample loop was calibrated with pulses of nitrogen in helium flow and compared against a calibration line produced from gas tight syringe injections of nitrogen under helium flow. After TPD of hydrogen, the sample was re-oxidized at the activation temperature by injecting pulses of pure oxygen in helium referenced to helium gas. After oxidation of the cobalt metal clusters, the number of moles of oxygen consumed was determined, and the percentage reduction was calculated assuming that the Co^0 re-oxidized to Co_3O_4. While the

uncorrected dispersions (uc) are based on the assumption of complete reduction, the corrected dispersions (c), include the percentage of reduced cobalt as follows: $\%D_{uc}$ = (# of Co^0 atoms on surface X 100%)/(total # Co atoms)$\%D_c$ = (# of Co^0 atoms on surface X 100%)/[(total # Co atoms)(fraction reduced)]

Initial investigation shows that the dried UOP Al_2O_3 had a high surface area of 337.7 m^2/g and an average pore diameter of 4.48 nm. It is known from prior CAER research that supports having a high surface area result in a significant problem regarding cobalt oxide reduction, due to the strong interaction between cobalt oxides and alumina support. Moreover, upon activation in hydrogen and exposure of cobalt nanoparticles to realistic Fischer-Tropsch synthesis conditions (e.g., 50+ % conversion), cobalt clusters having domains of < 4 nm have been suggested to oxidized by intrinsically produced. Therefore, the pore size was deemed to be too narrow.
By increasing the calcination temperature, **Figure 13** shows that the surface area and porosity characteristics of the alumina became more favorable. The surface area decreased to 233.2 m^2/g (650°C calcination) and the average pore diameter increased to 5.5 nm. Note the surface area is still considered to be higher and the pore diameter smaller than our preferred powder support, Catalox 150 g-Al_2O_3 (140.2 m^2/g, 10.2 nm diameter).

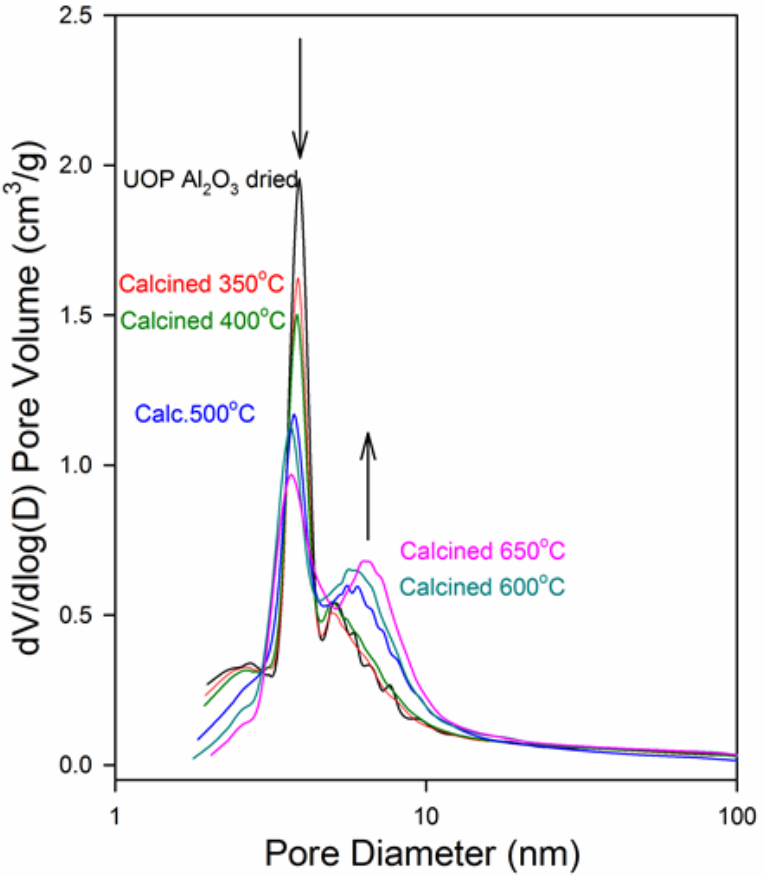


Figure 13: BJH desorption branch pore size distribution as a function of calcination temperature for UOP Al_2O_3 pellets

Adding 15%Co and 0.1%Pt to the support resulted in changes in the surface area and porosity. The surface area decreased from 233 to 154 m^2/g. If alumina is considered to be the main

contributor to the area, then, if there is no significant pore blocking, one would expect the surface area to decrease to: 15 * 1.333 (accounting for Co_3O_4 in calcined catalyst) = 20 %; (1 - 0.2) * 233.2 = 186.6 m^2/g. The measured value was 154 m^2/g, suggesting that some pore blocking did occur. **Figure 14** suggests that the narrower pores tended to be filled first, shifting the pore diameter to a higher value (from 5.5 nm to 6.6 nm).

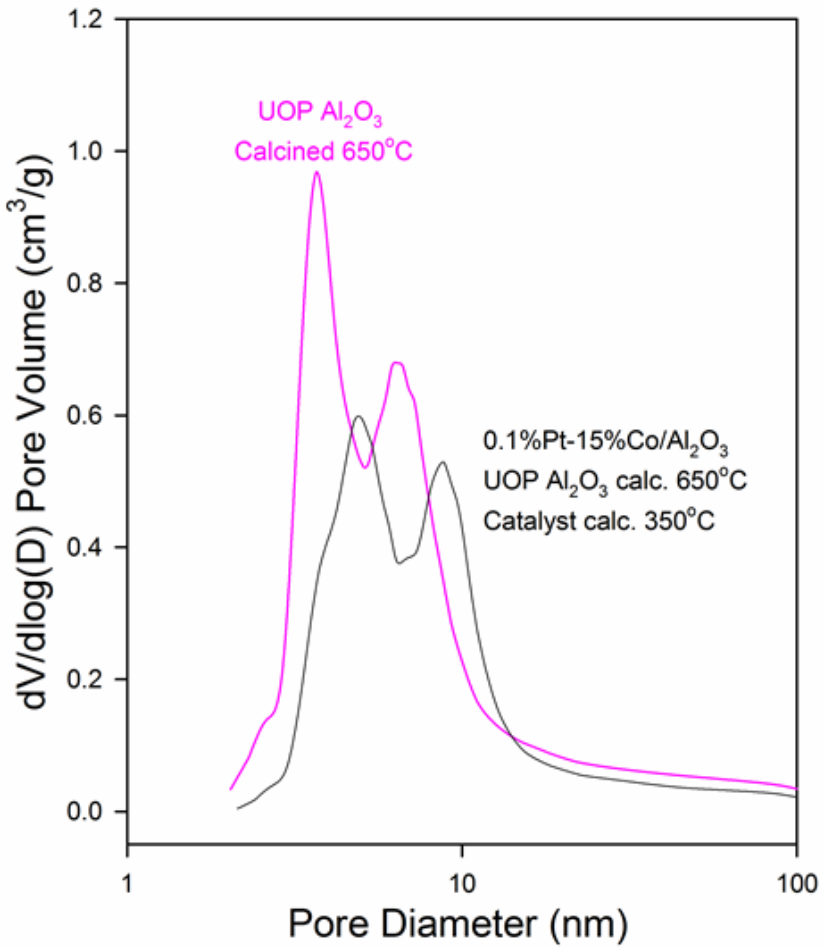


Figure 14: BJH desorption branch pore size distribution of UOP Al_2O_3 calcined at 650°C and 0.1%Pt-15%Co/Al_2O_3 (Al_2O_3 calc. 650°C, 4 h and catalyst calc 350°C, 4 h

Figure 15 shows the H_2-TPR profile of the catalyst. For a typical un-promoted catalyst, the first peak of reduction, characteristic of $Co_3O_4 + H_2 \rightarrow 3CoO + H_2O$ occurs in the range of 300-350°C, while that of $3CoO + 3H_2 \rightarrow 3Co^0 + 3H_2O$ is three times that of the first peak and extends up to 800°C. With the 0.1%Pt promoted catalyst, the first peak of reduction was shifted to slightly lower temperature (225 – 325°C) and the second peak was completed slightly below 600°C. This is in agreement with our XPS and synchrotron characterization studies, which suggest Pt reduces at a lower temperature than Co, promoting either a H_2 dissociation and spillover mechanism, or a chemical effect, to facilitate the reduction of cobalt oxides interacting with the support. Some cobalt was sacrificed to the support as irreducible cobalt aluminate, as a peak was beginning to form in TPR above 800°C.

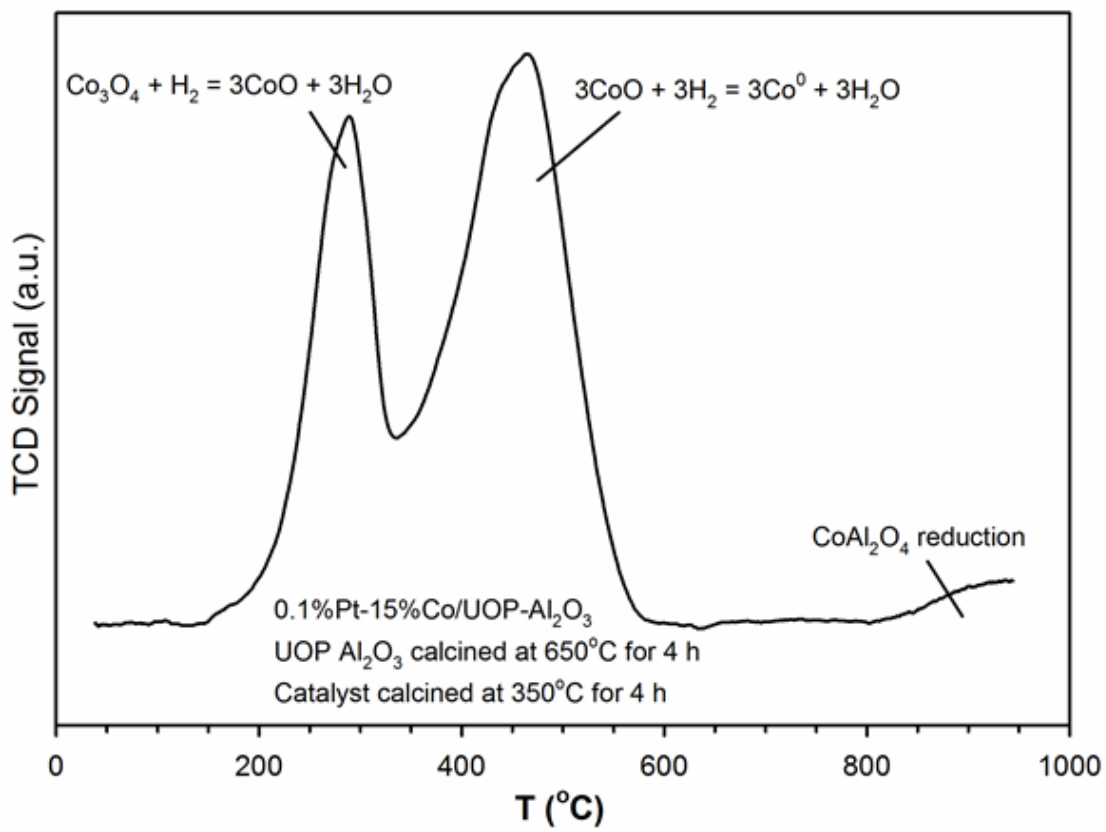


Figure 15: TPR profile of 0.1%Pt-15%Co/UOP-Al_2O_3, with UOP Al_2O_3 calcined at 650°C for 4 h and the catalyst calcined at 350°C for 4 h

Initial investigation shows that the Clariant alumina had a lower surface area than the UOP alumina. Moreover, **Figure 16** shows that the distribution of pores was narrower, with the average diameter being 7.54 nm. Adding Co and Pt to the catalyst did not result in any significant shift in the pore distribution, suggesting uniform filling of pores. Adding 20% Co is equivalent to adding 26.7% cobalt oxide, such that if alumina is the primary contributor to surface area, one would expect a decrease of (1 – 0.267) *258.9 = 189.7 m^2/g. The actual value was 176.3 m^2/g, suggesting that pore blocking was only slight.

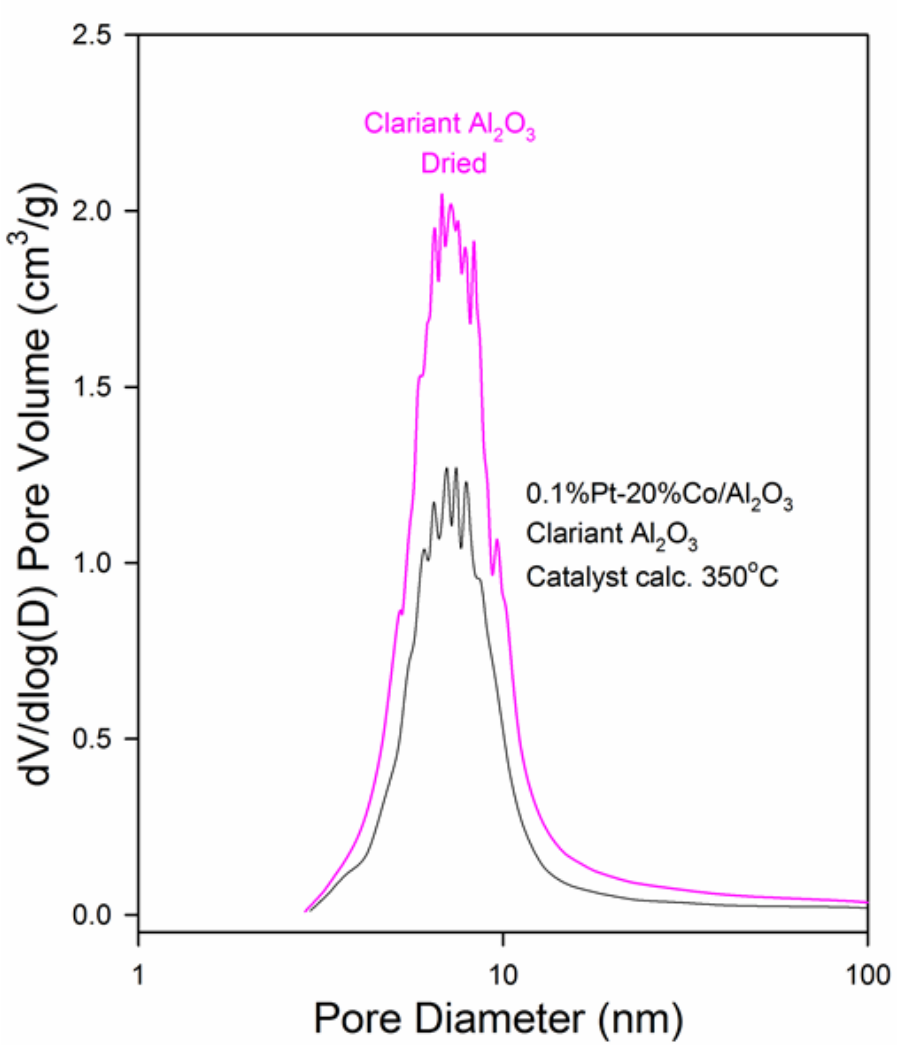


Figure 16: BJH desorption branch pore size distribution of Clariant Al_2O_3 (dried) and 0.1%Pt-20%Co/Al_2O_3 (calc 350°C, 4 h

Figure 17 shows that the cobalt oxides reduced in a similar range as observed with the UOP alumina supported cobalt catalyst (225-325°C for Co_3O_4 to CoO, and CoO reduced to Co^0 below 600°C). In contrast, however, no significant peak for cobalt aluminate reduction was noted in the observable TPR range. Using a standard reduction temperature 350°C for 10 h, Table 3 indicates that close to 30% of the cobalt oxide reduced, with a % dispersion of 15.7% and an average diameter of 6.6 nm. Note that ICP results for the catalyst showed 24.42% cobalt and 0.12% platinum, relatively close to the nominal values.

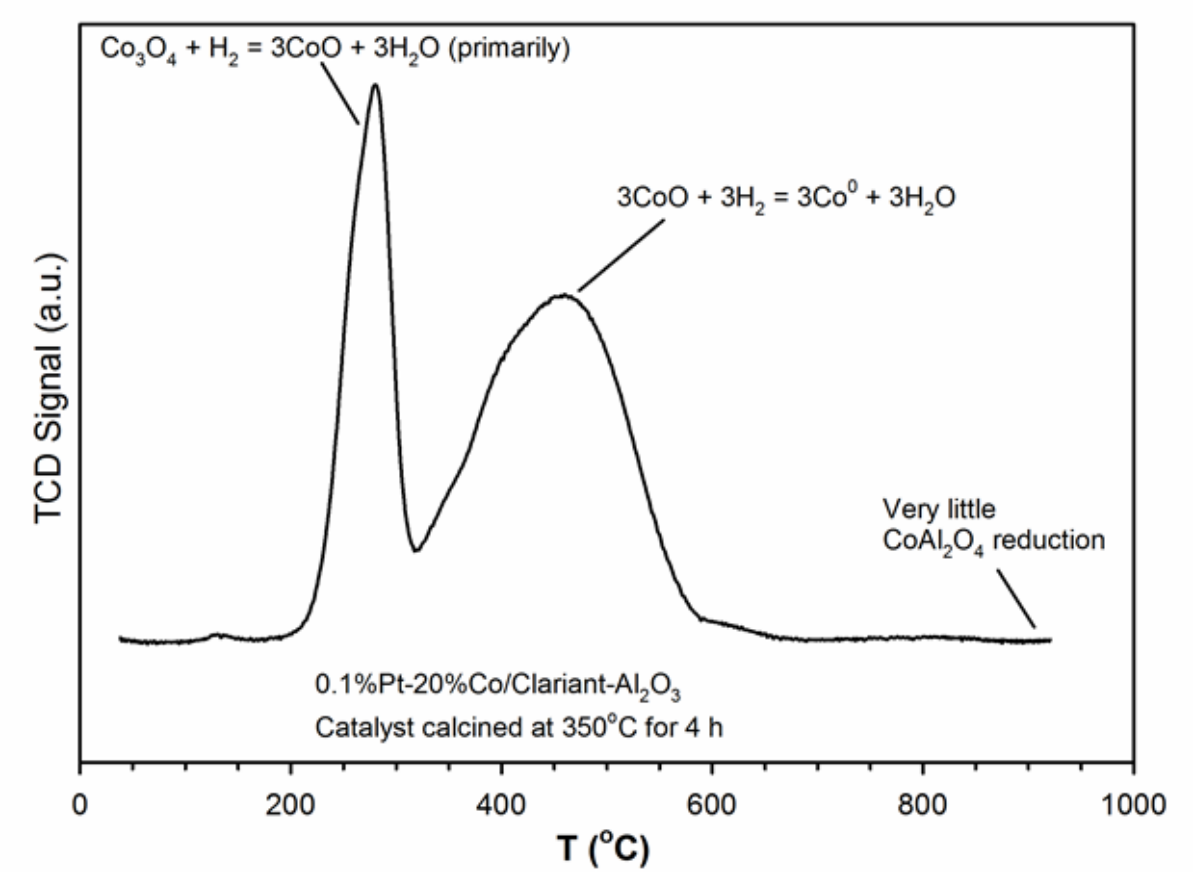


Figure 17: TPR profile of 0.1%Pt-20%Co/Clariant-Al_2O_3, catalyst calcined at 350°C for 4 hours.

2.3. Comparative Runs on Lab-scale CSTR and Fixed-bed Reactors to Validate F-T Catalyst Performance

A one-pound sample of the F-T catalyst production batch was run in the small channel reactor at 150 psig due to the pressure limitations of the small lab reactor. The same catalyst was run in a Continuously Stirred Tank Reactor (CSTR) at 150 and 400 psig, the approximate pressure used for the pilot scale unit, using Polywax 3000 as the startup solvent. In both the CSTR and micro-channel reactors, the reaction temperature, space velocity and H_2/CO ratio used were 205-230 °C, 3.0 NL/gcat/h and H_2/CO = 1.7.

For the CSTR runs, the catalyst was activated by hydrogen in a fixed-bed reactor using 6 hours to heat from room temperature to 350°C; the catalyst was held at 350°C for 24 h. The reduced catalyst was transferred under N_2 pressure to the 1-liter CSTR which contained about 300g molten PW-3000 as a startup solvent. The catalyst after transfer was reduced again in flowing hydrogen for 24 hours at 230°C.

The activation in the small channel reactor was conducted in-situ with flowing hydrogen. The sample was heated in dry nitrogen to about 150°C to remove water and then the gas flow was switched to hydrogen. The sample was heated at about 2°C/minute to 350°C and held at this temperature for approximately 10 hours.

Additionally, for the CSTR operation runs, the reactor was heated to about 170^{o}C while feeding only hydrogen and then CO was added to the feed stream and the flow of CO adjusted to give a H_2/CO ratio of 1.7. The reaction temperature was gradually heated to the set temperature shown in **Figure 18** below (i.e. 205, 215, 223, 230 ^{o}C). Samples were collected daily and after a period of time (3-8 days) at one temperature. Subsequently, the temperature was increased and the run continued at the next higher temperature. **Figure 18 and Figure 19** show the results of the lab scale CSTR run. Further analysis of the CSTR lab scale operation showed that the CO conversion was slightly higher at 150 psig than at 400 psig and the methane selectivity was lower (shown in **Figure 20**).

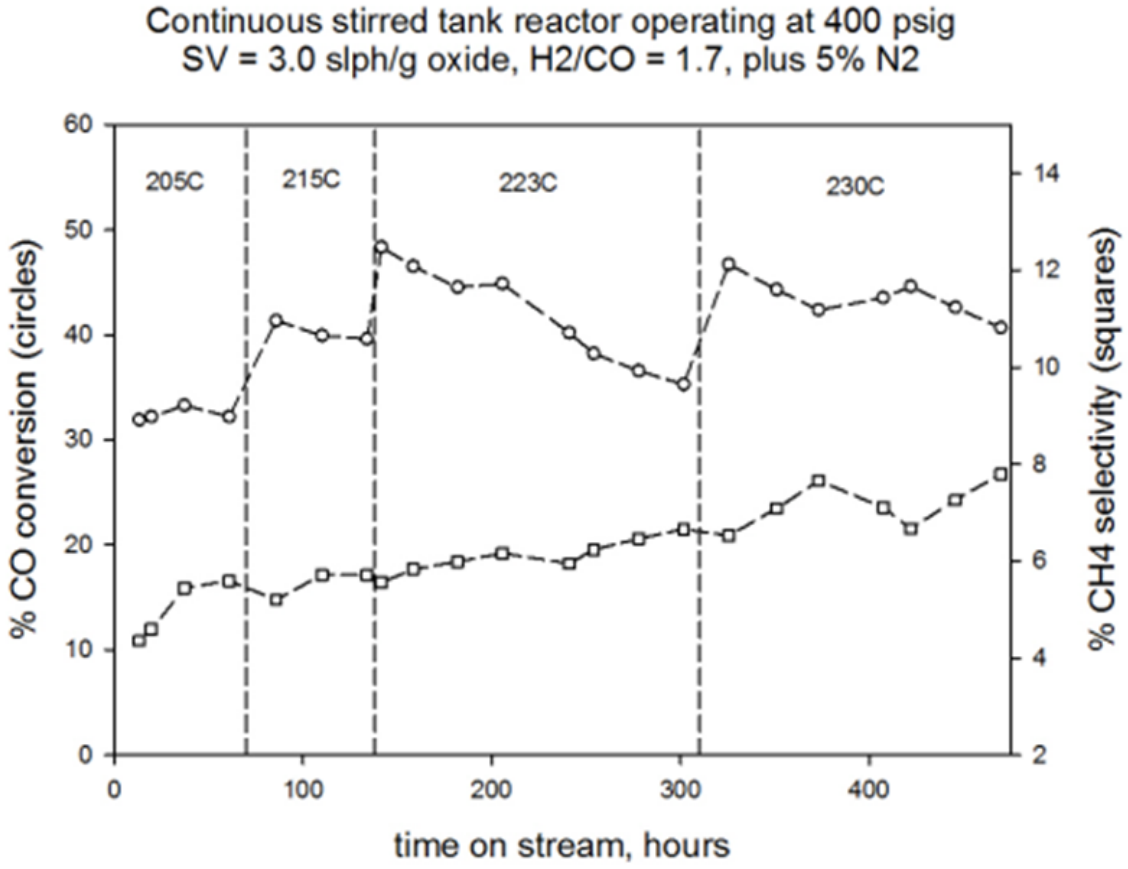


Figure 18: CO Conversion and Methane Selectivity for Operation at 400psig in the CSTR

Index	TOS (hrs)	Light Gas	Gas	Gasoline	Diesel	Wax	C5+	C12+
7.000	133.917	5.663	9.114	20.036	22.377	42.811	85.223	65.188
9.000	158.333	5.351	8.158	26.112	25.532	34.847	86.491	60.379
11.000	205.500	6.274	8.838	22.079	29.120	33.689	84.888	62.809
15.000	301.700	10.119	14.383	27.605	26.298	21.596	75.499	47.894
17.000	350.917	8.207	10.875	24.980	24.393	31.545	80.918	55.938
21.000	445.500	11.740	15.453	31.614	23.968	17.225	72.807	41.193

Notes: All composition groups are in weight percent.

Light Gas: C1
Gas: C2 - C4
Gasoline: C5 - C12
Diesel: C12 - C18
Wax: C19+

Figure 19: Product Distribution for Operation at 400psig in the CSTR

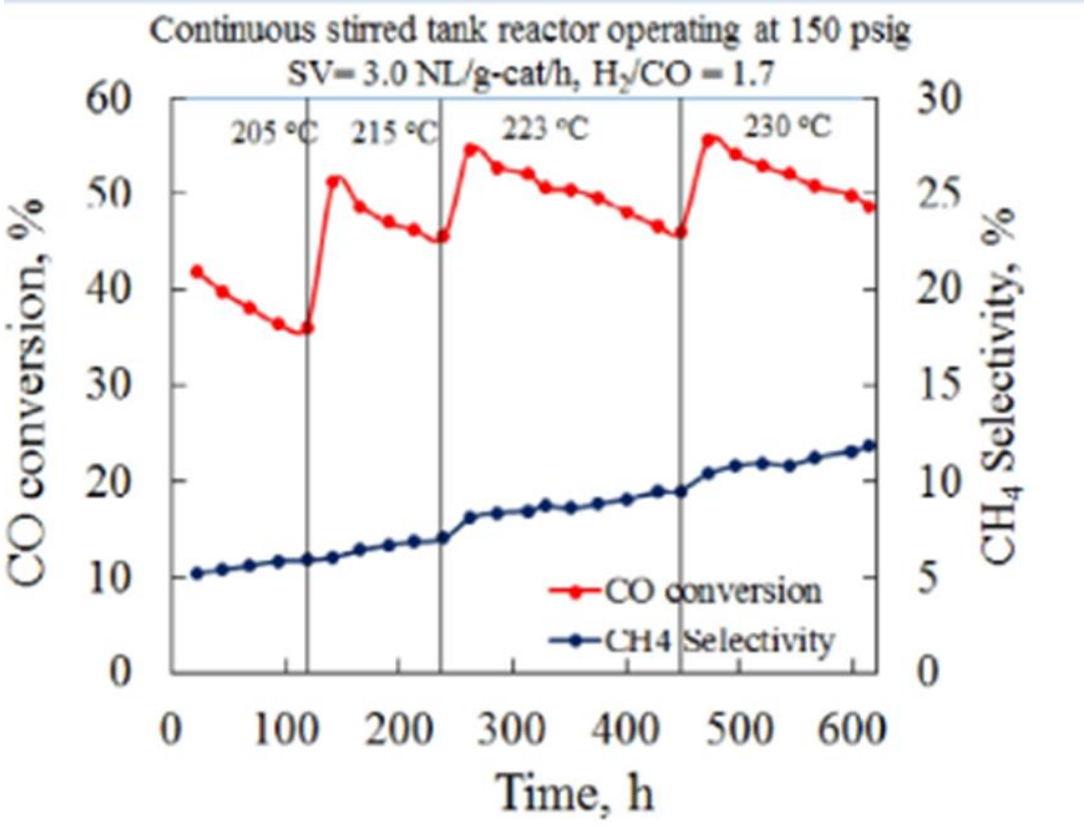


Figure 20: CO Conversion and Methane Selectivity for the CSTR at 150psig

For the run in the small channel reactor a light oil was added to the hydrogen stream until liquid was collected in the product trap. At this point, the hydrocarbon flow was reduced to a flow that gave about 2 carbon% flow of oil added to the reaction mixture and then CO flow was started at about 170°C. The temperature was then gradually increased to the first set-point temperature. After about 2 days run, the flow of oil was terminated. Samples were collected on a daily basis. Results are shown in **Figure 21 and Figure 22.**

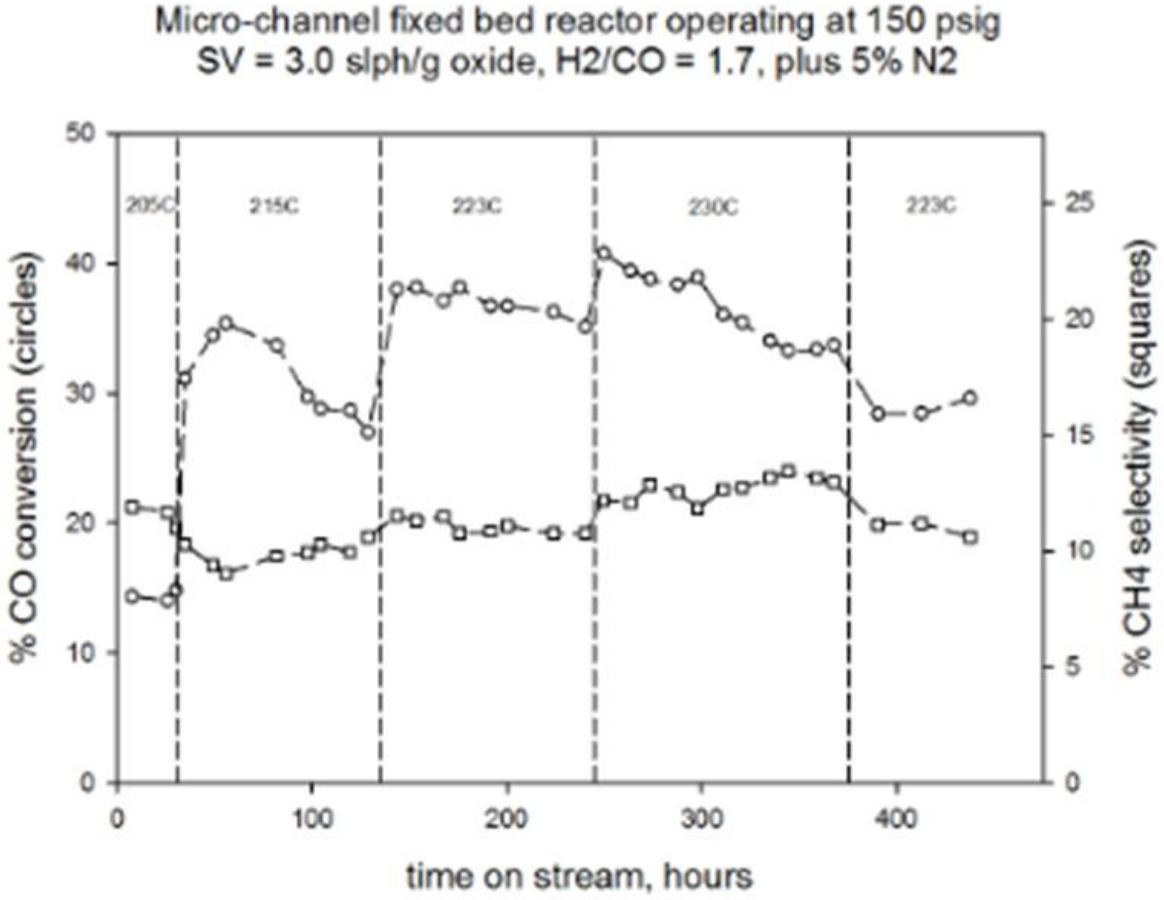


Figure 21: CO Conversion and Methane Selectivity for Lab-Scale Small Channel Reactor at 150°C

Index	TOS (hrs)	Light Gas	Gas	Gasoline	Diesel	Wax	C5+	C12+
7	55.60	4.496	4.228	23.320	32.882	35.074	91.276	67.956
14	153.25	6.513	6.456	30.319	31.358	25.354	87.031	56.712
19	223.90	13.130	12.805	31.102	23.887	19.077	74.065	42.964
23	273.50	8.176	7.527	36.639	29.586	18.072	84.297	47.658
27	320.65	7.989	7.001	35.898	29.748	19.365	85.010	49.112
31	367.50	7.276	6.308	36.095	30.293	20.027	86.416	50.321
34	437.60	13.816	12.644	30.143	25.439	17.957	73.539	43.396

Notes: All composition groups are in weight percent.

Light Gas: C1
Gas: C2 - C4
Gasoline: C5 - C12
Diesel: C12 - C18
Wax: C19+

Figure 22: Product Distribution for Lab Scale Small Channel Reactor

The CO conversion in the small channel reactor was about 25% lower than for the CSTR for the same reaction temperature and the methane selectivity (e.g. formation) was higher (about 10% versus about 6%) for the CSTR at 215ºC. The alpha values of the products are similar and what is expected for a cobalt catalyst (0.92-0.90, **Figures 23 and 24**). However, these differences in product/process data can be attributed to the minor differences in operating conditions between the lab scale units. It is assumed, that all conditions being equal, would produce exactly the same products.

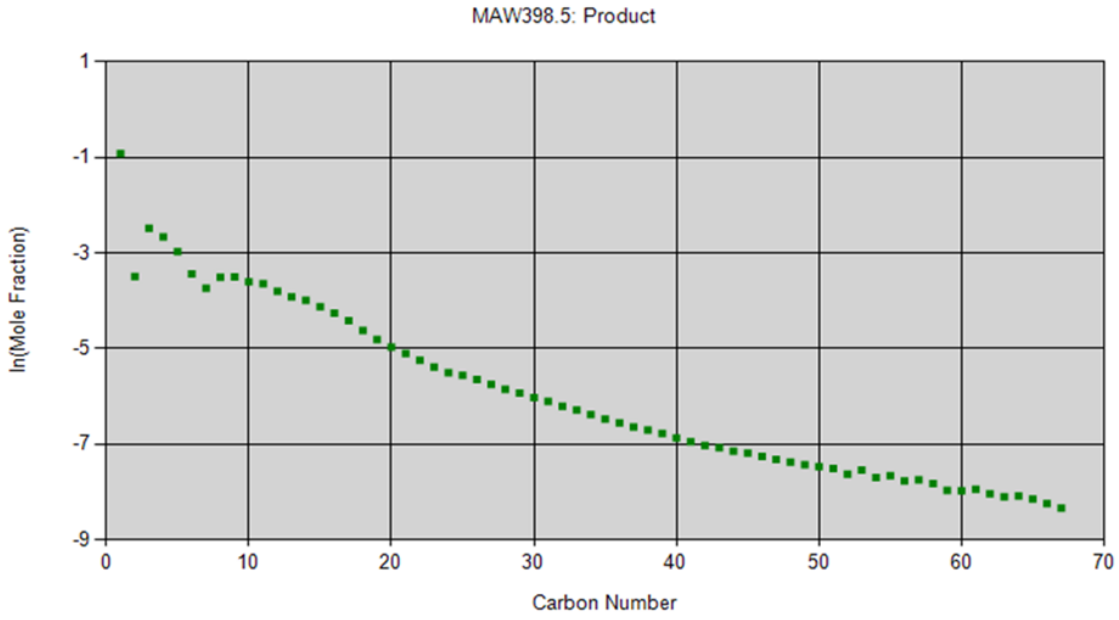


Figure 23: Alpha Plot for CSTR Operation at 150psig (α_{c10+} = 0.92)

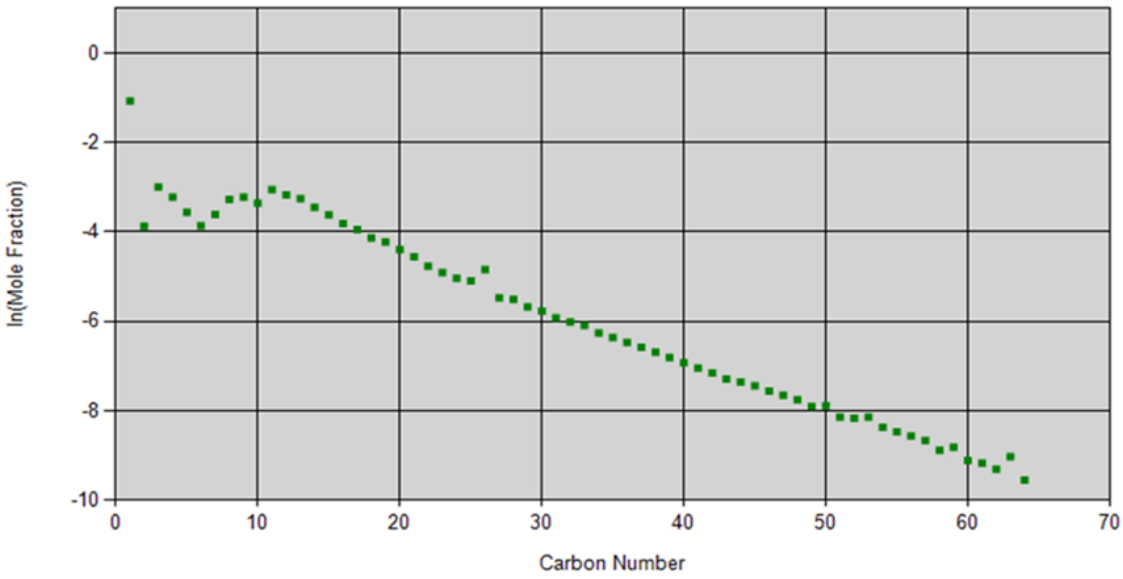


Figure 24: Alpha Plot for Lab Scale Small Channel Reactor Operation at 150psig (α_{c10+} = 0.90)

To summarize, normally less than 10% methane selectivity is ideal for lab scale production runs. The catalyst produced at the bulk/pilot scale, that was developed in-house, is known to normally produce this result in the lab. However, during the scale-up some differences during the reduction of the cobalt produced large particles and thus produced higher methane selectivity's for the final production catalyst. It should be noted, that UK-CAER did contact some commercial vendors to purchase the catalyst but all of them declined to sell it for fear of losing control of their data/results. In the future, UK-CAER will certainly continue to improve the F-T catalyst with new formulation or methods and will work with the chemical supplier to improve the production methods already in use.

3) Design, Fabrication, Installation and Commissioning of Downstream Refinery Units for WGS, F-T and BOP

3.1. Design and Fabrication

The UK-CAER team began process design work by contracting Zeton Inc, with the assistance of Stovlbaek Consulting to complete the preliminary engineering design of the downstream components. In addition, Chart Energy was contracted to provide the Fischer-Tropsch reactor and associated design. The first item for the initial engineering design was to finalize the location of the WGS unit in the process chain. Three alternative configurations for placement of the WGS shift unit were discussed. Originally the WGS, was planned for placement after the AGR, however after rounds of design iterations the WGS was placed after the gasifier (before the AGR) because it offered the most advantages in the overall process scheme. Those reasons are summarized below:

- This location would require a Sour Shift (SS) Cobalt-Molybdenum (CoMo) based catalyst. This catalyst is not negatively affected by high sulfur containing syngas (SG), it actually

requires a certain minimum S-content around ±300 ppmv to maintain a sulfided state of the CoMo to be active for promoting the WGS reaction as well as the COS hydrolysis reaction. If not completely sulfided, it can promote the undesired methanation reaction. The SG at this location contains plenty of sulfur, about 1 mole %.

- The SS catalyst has the advantages of being able to operate at much lower feed temperature than the HTS catalyst, down to 200 °C (needs to be min. 20 °C above the dew point), and lower steam to dry gas ratio.
- The potential for forming Boudouard carbon in the WGS feed preheater at this location is lower than both other locations evaluated, due to the low pressure (1.2 barg). The Boudouard equilibrium temperature Teq = 660 °C at S/DG =1.
- The methane decomposition potential is essentially zero due to the metal surface passivation effect of the high S-content.
- The low pressure at this location will lead to a reasonable proportioned shape reactor design even at this small pilot rate scale while achieving a reasonable Superficial Velocity (SV).
- The low pressure at this location will accommodate a low pressure package boiler to provide the steam required for the WGS reaction. Significantly less expensive than the other locations evaluated.
- The CO_2 product from the WGS reaction will be removed in the downstream AGR.

Completion of the preliminary design by Zeton occurred in early 2015 with all applicable design documents, such as, process flow diagrams, process and instrumentation diagrams, flows, equipment data sheets, general arrangement drawings and a +/-10% cost estimate. The cost estimate for the final detailed design, fabrication and delivery was $1.7million. Meanwhile, Chart Energy completed the detailed design and fabrication of the FT reactor, which was subsequently delivered to UK-CAER.

As part of the detailed design, UK-CAER also contracted Bluefield Process Safety to perform a full process hazards and operability analysis, flare and gas relief evaluation, as well as a gas monitoring plan. A team from UKY and Zeton Inc. completed a Process Hazard Analysis (PHA) of the Gasifier/F-T/AGR Plant in the form of a Hazard and Operability Review (HAZOP). The review addressed the 39 piping and instrument diagrams (P&IDs) that described the process in the Gasifier/F-T/AGR Plant. Altogether, 182 nodes were reviewed, resulting in 146 recommendations of items that were incorporated into the detailed design. Based upon the relief sizing calculations, the following recommendations were made: Installation of relief devices and subsequent piping systems to the recommended sizes for T-302, P-302, P-202, P-201A, P-201B, P-201C, and P-201D. An inventory was made to confirm spares that are needed onsite for those devices in which chattering is to be accepted. In addition, the locations of the CO gas monitors were determined for 7 locations throughout the plant.

At the end of the detailed design and fabrication by Zeton, team members from UK-CAER took a visit to the module construction location for a final process review and site visit. From the review, progress was proceeding as planned and on schedule. UK-CAER also performed a Factory Acceptance Test (FAT) at Zeton, as part of the standard process. Some minor concerns were discovered, and subsequently corrected by Zeton. Photos from the FAT are shown in **Figure 25**.

Figure 25: FAT Site Photos

Based on the FAT review, the three main changes made:

- On bypass loop around the WGS unit, there was no drain. The unit will probably have lots of water carryover from gasifier sections. Zeton issued a valve and UK installed drain port to condensate tank from the bypass line to fix this issue.
- During the interlock of the system due to high/low differential pressure between the F-T and hot oil system, the controls would depressurize the reactor side which would likely cause the F-T reactor internals to be severely damaged. Solution was to have the control system determine the lowest pressure between reactor and hot oil package and then set the pressure

controller on both sides to the lowest pressure. This will allow the system to depressurize safely and then let operator manually bring it back online or perform full shutdown.

- Similar to case above during emergency stop (and all interlocks that trip emergency shutdown), original control design would shut down the hot oil system and F-T but would allow F-T side to depressurize. As a solution Zeton had to rewire controls to make sure both loops stay functional during emergency shutdown to prevent reactor damage.

3.2. Installation

After delivery, site installation and construction of the WGS/F-T modules started in earnest. UK-CAER with the help of the site contractor, EC Matthews, unloaded the modules, installed them on to their foundations and reconnected major equipment. Mechanical, electrical and controls work proceeded in parallel, as possible. There was a substantial amount of mechanical pipe work to complete. Mechanical work included, flanges, welding, soldering, and tubing. A full list of all the mechanical items is shown below:

- Inter-module pipping connections: 15 pipe and tube sections that had to be reconnected (disconnected for shipping)
- Process tie ins: Gasifier to WGS, WGS to AGR, AGR to F-T; and
- Auxiliary Components: Nitrogen, Air, cooling water, drains, vent line, flare line, bottled nitrogen, hydrogen, and O_2/N_2 cylinders.

While the mechanical work proceeded, electrical and controls work also proceeded. For the electrical, only 3 main feeds were required. The modules required a 480V, 208V, and 120V tie-in and the power was pre-wired to distribute throughout the module without any further connections. However, the controls aspect was slightly more complicated. The controls work required the following items:

- Reinstallation of 39 instruments: These are instruments that had to be unconnected for transport;
- Connecting module controls to control room; and
- Addition of 8 CO alarms to the WGS/F-T control system.

Photos of the installation work are shown in **Figure 26**.

Figure 26: Mechanical, Electrical and Controls Installation

3.3. Commissioning

After all of the installation work was completed, extensive effort began on the shakedown and commissioning. Four main items were accomplished: 1.) control system check out, 2) loading of the WGS and Sulphur polishing beds, 3) Syngas compressor startup and testing, and 4) pressurized hot oil system startup and testing. The control system check-out went smoothly and all instruments worked as expected. Once the instrumentation and controls had been checked and tested, loading of the WGS and Sulphur polishing reactor beds was completed. The design can be seen in **Table 3** below, along with the results of the loading. Some photos of the catalyst, reactors and loading are shown in **Figure 27** below.

Meanwhile, the syngas compressor was started up and tested using nitrogen gas. The compressor was able to compress the gas to 425 psi and all components performed as expected. In addition, interlocks and safety mechanisms were tested for functionality and also performed as expected. The last main item from the commissioning of the WGS/F-T module was the pressurized hot oil system. Testing of the hot oil system occurred at 100℃ and over 200psi. While this was not tested at expected operating conditions, the test conditions provided the opportunity to learn the system and successfully proved functional operation.

Final commissioning work then proceeded to complete the controls and instrumentation work which focused on the continuous historian (DeltaV data recording), GC controls/data integration and minor controls updates. An Emerson technician set-up up and calibrated the GC, and provided training.

UKY/CAER Coal to Fisher Tropsch PDU
V-150 and V-300 Catalyst Loading Results
June 2, 2017

NOTE: Results are presented BOTTOM-UP in the tables in this sheet

V-150 Sour Shift
Loading measurements May 17, 2017

		Outage from top flange			A Zone Length	A Zone Volume	Zone Description	B Design (*) Zone Length	A - B Actual Deviation Zone Length
		Feet	Inches	Feet decimal	Feet	cuft		Feet	Feet
BOTTOM	Empty Rx	8	10	8.83	8.83	5.23	Empty Reactor length from top flange		
	Bottom 1/2" Denstone 99 Balls	8	6	8.50	0.33	0.20	Bottom 1/2" Denstone 99 Balls	0.33	0.00
	Bottom 1/4" Denstone 99 Balls	8	2	8.17	0.33	0.20	Bottom 1/4" Denstone 99 Balls	0.33	0.00
	Catalyst SSK-10	3	1	3.08	5.08	3.01	Catalyst SSK-10	5.10	-0.02
	Top 1/2" Denstone 99 Balls	2	9	2.75	0.33	0.20	Top 1/2" Denstone 99 Balls	0.33	0.00
	Top GSSK	1	9	1.75	1.00	0.59	Top GSSK	1.00	0.00
TOP	Inlet nozzle bottom	0	3.25	0.27	1.48	0.88	Space from bottom of nozzle to top of GSSK	1.50	-0.02
					0.27	0.16	Length of nozzle tip inside Rx, below top flange	0.33	-0.06
				Sum Zones	8.83	5.23	Sum Zones	8.92	-0.09

ID = 10.42 inches
A = 0.592 sqft

Comments to Loading results:
The loading is a perfect match of the design loading,
Rev. 11 of June 8, 2016.

*) Catalyst loading Design Rev. 11 of June 8, 2016. Attached as Page 2.

V-300 Sulfur Polishing
Loading measurements May 16 and 17, 2017

		Outage from top flange			A Loaded Zone Length	A Loaded Zone Volume	Zone Description	B Design (*) Zone Length	A - B Actual Deviation Zone Length
		Feet	Inches	Feet decimal	Feet	cuft		Feet	Feet
BOTTOM	Empty Rx	8	11	8.92	8.92	1.61	Empty Reactor length from top flange		
	Bottom 1/2" Denstone 99 Balls	8	4	8.33	0.58	0.11	Bottom 1/2" Denstone 99 Balls; req. for cover bottom nozzle	0.33	0.25
	Bottom 1/4" Denstone 99 Balls	7	11.75	7.98	0.35	0.06	Bottom 1/4" Denstone 99 Balls	0.33	0.02
	Catalyst/Absorbent HTZ-51	2	5.875	2.49	5.49	0.99	Catalyst/Absorbent HTZ-51	5.50	-0.01
	Top 1/2" Denstone 99 Balls	1	11.875	1.99	0.50	0.09	Top 1/2" Denstone 99 Balls	0.50	0.00
TOP	Inlet nozzle bottom	0	6.375	0.53	1.46	0.26	Space from bottom of nozzle to top of 1/2" balls	1.50	-0.04
					0.53	0.10	Length of nozzle tip inside Rx, below top flange	0.33	0.20
				Sum Zones	8.92	1.61	Sum Zones	8.49	0.43

ID = 5.761 inches
A = 0.181 sqft

Comments to Loading results:
The main deviance from the design loading is related to the inlet and exit nozzles being about 2.5" longer than the basis applied for the loading design. This required a 7" layer of the bottom 1/2" balls, instead of the 4" design, to cover the bottom exit nozzle, . Most importantly: The catalyst zone, other support ball zones and the top inlet gas disengagement zone are matching the design.

*) Catalyst loading Design Rev. 11 of June 8, 2016. Attached as Page 2.

Table 3: WGS Catalyst Loading Design and Results

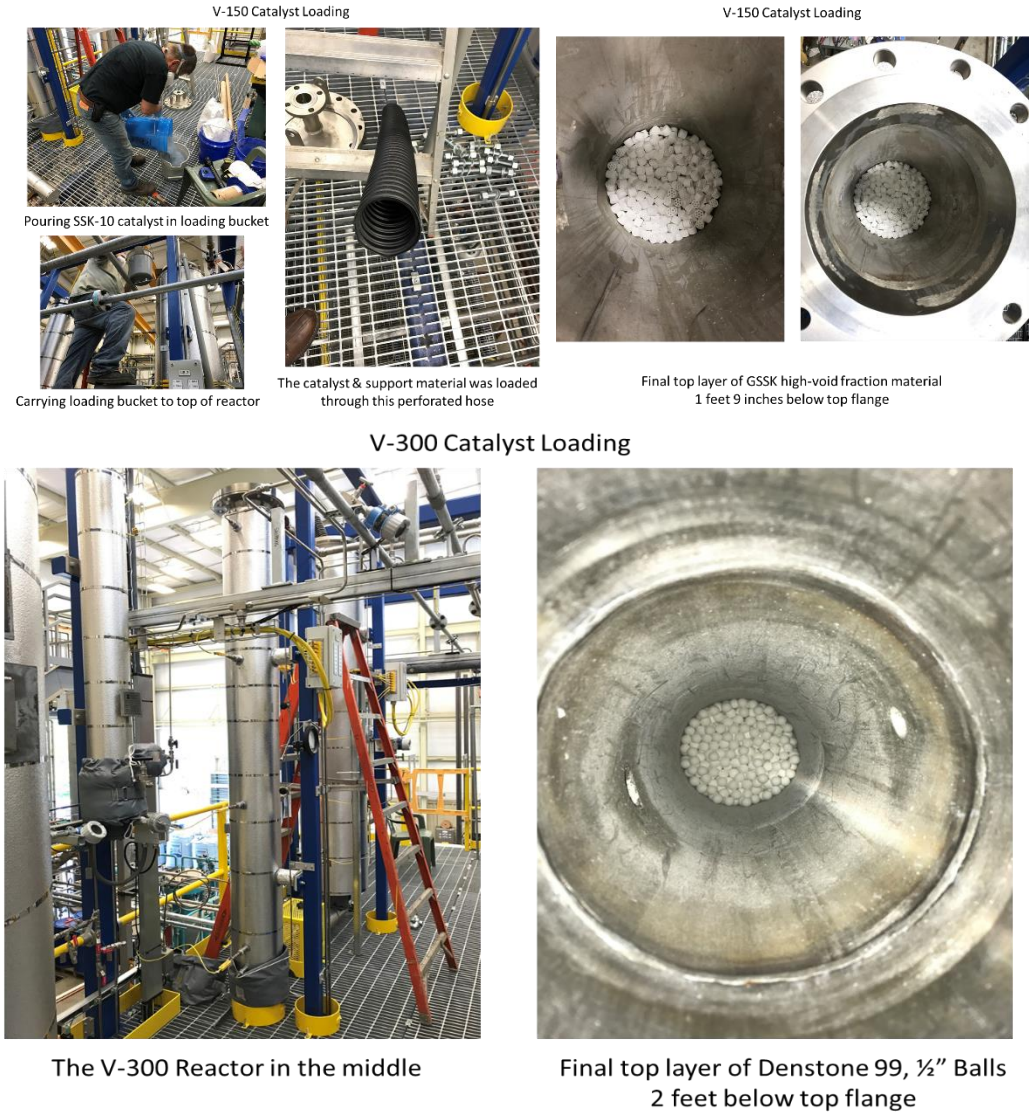


Figure 27: Photos of WGS and Sulphur Polishing Bed Catalyst Loading

While the WGS and Sulphur polishing bed had already been loaded with catalyst during the aforementioned site visit, the F-T reactor loading still remained. Leaning on past experience from the dealing with the lab scale Chart Energy microchannel reactor, catalyst loading was attempted using 100-150 micron catalyst particles. During this initial loading, significant vibration was used to help pack the channels evenly. However, after a flow test it was determined that the pressure drop across the reactor was much too high which resulted in zero gas flow through the bed at expected operating conditions. It should be noted here that on the lab scale reactor the UK-CAER team saw little to no pressure drop issues. This is likely due to the fact that the pilot scale version has over 5 times the length of bed compared to the ones in operation in the lab as well as the difference in particles sizes and loading techniques (vibration) at the large scale which caused the catalyst to pack tighter.

A significant amount of consultations took place with Zeton, Stovlbaek Consulting, Chart Energy and the in-house UK-CAER F-T team. From these discussions, it was determined that the catalyst was packed too well, and had to be reloaded. For the reloading, it was determined that the following steps should be taken: bigger particle sizes, less/no vibration during loading, and use of 500 micron glass beads as an initial layer to protect the mesh screen at the outlet from plugging. Based on this information, the already loaded catalyst was removed, the reactor cleaned and then new catalyst particles with sizes above 150 micron were loaded with a layer of 500 micron glass beads loaded first. The final result was approximately 20.6 lbs of catalyst added to the reactor. Flow testing of this produced a pressure drop of ~ 50psi at operating flow/conditions which, while still high, was within acceptable limits. Finally, after loading was complete, the catalyst was activated over the course of ~5 days using pure H_2. The F-T reactor was left with a blanket of hydrogen to keep the catalyst ready for operation and prevent oxygen/air from entering the reactor and subsequently oxidizing the catalyst.

The only part remaining of the commissioning work was the activation of the WGS catalyst which had been previously loaded into the WGS reactor. This was accomplished via a ~2 day procedure under the supervision of Stovlbaek consulting. This procedure required the use of bottled H_2S and the in-house nitrogen generator. Activation of the WGS catalyst was successful and the WGS unit was ready for operation. Activation procedures are shown here below in **Table 4**. The basic premise of the activation was to introduce the H_2S at specific concentrations while slowly increasing temperature at planned levels. Monitoring the breakthrough of H_2S was utilized to determine when the reaction was complete. This was accomplished by metering the H_2S input and utilizing the GC on the outlet. Once the outlet reached the same concentration as the inlet, at the max temperature, the reaction was considered complete.

WGS Catalyst Activation Sulfiding Timeline

10,000 - 20,000 ppmv (1-2 mole %) H2S and 10% H2 in N2 + H2 (*)

Rev. 3 -- October 24, 2017

Time Period Begin - End Hours from start	Action	Critical
WGS Ready State = WGS under N2 blanket, preheated by heat tracing of top catalyst bed to 90-100 °C		Turn-on JEM Heat Tracing at least 12 hours prior. SP: 80/80/105 °C
0 - 1	START N2 flow through WGS by-pass. Add H2 and min. H2S for achieving 10% H2, 1-2% H2S	Max 8.5 ACFM N2 (0.4 barg) to WGS with no other active consumers
1 - 2	When target gas composition verified by GC, gradually re-direct flow through E-130 at setpoint 100 °C	
2 - 3	Increase H2S towards 2% (20,000 ppmv), while maintaining stable max 100 °C catalyst temperatures	Max 100 °C catalyst temperature
3 - 4 4 - 5 5 - 6 6 - 7 7 - 8	PHASE 1: Sulfiding at 100°C assuming 75% S-absorbtion efficiency Approx. max 6 hours duration Range: 4 - 6 hours The duration of his stage may be longer or shorter than indicated.	MAX 100 °C CATALYST TEMPERATURE All catalyst temps must be min 20 °C above dew point
8 - 9	When the WGS delta S approaches zero, start heating towards 300 °C at max 15 °C/h	Syncronized increasing E-130 and Heat Tracing setpoints
9 - 10 10 - 11 11 - 12 12 - 13 13 - 14 14 - 15 15 - 16 16 - 17 17 - 18 18 - 19 19 - 20 20 - 21 21 - 22 22 - 23 23 - 24	PHASE 2 Sulfiding at >100°C Gradually increase catalyst temperatures towards 300 °C at max 15 °C/h *) Based on N2+H2 = 20 Nm3/h containing 10% H2 and 10,000-20,000 ppmv H2S NOTE: H2S may be reduced to 10,000 ppmv (1%) depending on development PRECAUTION: SULFUR BREAK-THROUGH MUST BE MAINTAINED AT ALL TIMES. If the Sulfur at the exit drops significantly, stop heating. Wait until the sulfur exit starts increasing, then continue heating. Due to these precautions, the duration of this stage may be longer or shorter than indicated.	SULFUR BREAK-THROUGH MUST BE MAINTAINED AT ALL TIMES.
24 - 25 25 - 26 26 - 27 27 - 28	PHASE 3 Sulfiding Completion: Hold top catalyst bed temperature at 300 °C for 4 hours to complete the Sulfiding.	If 300 °C cannot be reached, the maximum possible temperature will have to suffice.
28 - TBD	SULFIDING COMPLETE --> SHUT-DOWN	Follow specific procedures

Nm3/h = Normal cubic meters per hour at standard conditions 0 °C, 1 atm abs. N2 ACFM = Actual Cubic Feet per Minute at approx 25°C and 0.4 barg

Table 4: WGS Catalyst Activation Procedure

3.4. Start-up

Upon completion of installation and commissioning, final startup activities needed to be performed. The startup activities consisted mainly of: operator training, confirmation and verification of each process unit, simultaneous operation of all process units together, and development of analytical sampling and processing techniques.

The gasification system, as the workhorse of the facility, is the most critical process unit. Therefore, a significant portion of the start-up work was spent on the gasification system. The gasification unit was operated many times to generate baseline data and prove that unit can be operated in a safe and consistent manner. Some general data is presented in **Figure 28 and 29**, with corresponding results summarized in the text below.

Generally, the system was stable for the entire testing operation. The feed for this operation was roughly 35% coal in the slurry and 65% water for easier operation and as a learning experience for stable operation. Ideally, this would have been reversed and we would like closer to 60% coal in the slurry. As result of the loss in heating value, we had to co-fire a small amount of natural gas to maintain heat. Based on the data, this was around 15% of the total heating value input. The temperature measurement displayed in the **Figure 28** is from the thermocouple located directly above the reaction zone, as measured at the refractory wall. Thermocouples generally measure right at refractory wall due to the slagging characteristic the refractory wall temperature is the critical temperature for slagging gasifiers. Temperature was generally stable within a 50°C range during the operation. One important lesson learned from this operation was the need to replace the thermocouple in the gasifier. As noted with the red circles on the temperature plot, the thermocouple experienced several instantaneous drops in temperature during the operation which was not realistic. These occurred due to a bad thermocouple and as a result the thermocouple was replaced with a more resilient model. Pressure was fairly stable during the operation.

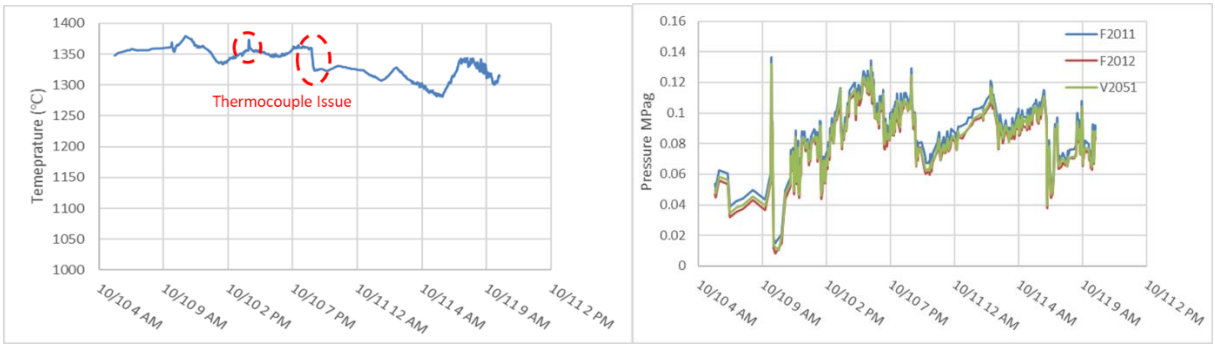


Figure 28: Experimental Data from Initial Coal-only Run of the Gasification Unit Temperature and Pressure

As shown in **Figure 29**, the plots of the H_2 and CO concentrations in the syngas have two separate data points each as a result of data from the initial testing with our GC. This work served two main purposes: gasification system performance and analytical techniques utilizing the GC. In order to become more familiar with the unit and run a steady state operation (maintain composition), multiple sample points were used to test both systems. As expected, there was good agreement between the data sets. In the top plots of **Figure 29**, it is possible to observe that normal gasification started around 9PM and the concentration of both H_2 and CO components

went from near zero to the expected range. The concentrations were maintained in the expected range until around 3AM when the concentrations of both H_2 and CO began to drop. The reason the concentrations of both components started falling was due to the fact that one of the 4 feed pumps failed, resulting in a ¼ of fuel input being lost while the oxygen feed was left unchanged. As a result, the fuel/oxygen ration began to drift from the gasification conditions to combustion conditions. The bottom plot of **Figure 29**, shows the critical syngas composition factor of the H_2/CO molar ratio. For this operation, the ratio was stable throughout the operation around 1.1/1. This ratio is higher than expected for coal gasification (likely due to the co-firing of coal and natural gas) but the ratio is within the expected range based on those conditions. It is also interesting to note that the ratio barely changed during the unstable operation period, meaning H_2 and CO were almost always present in the same ratio.

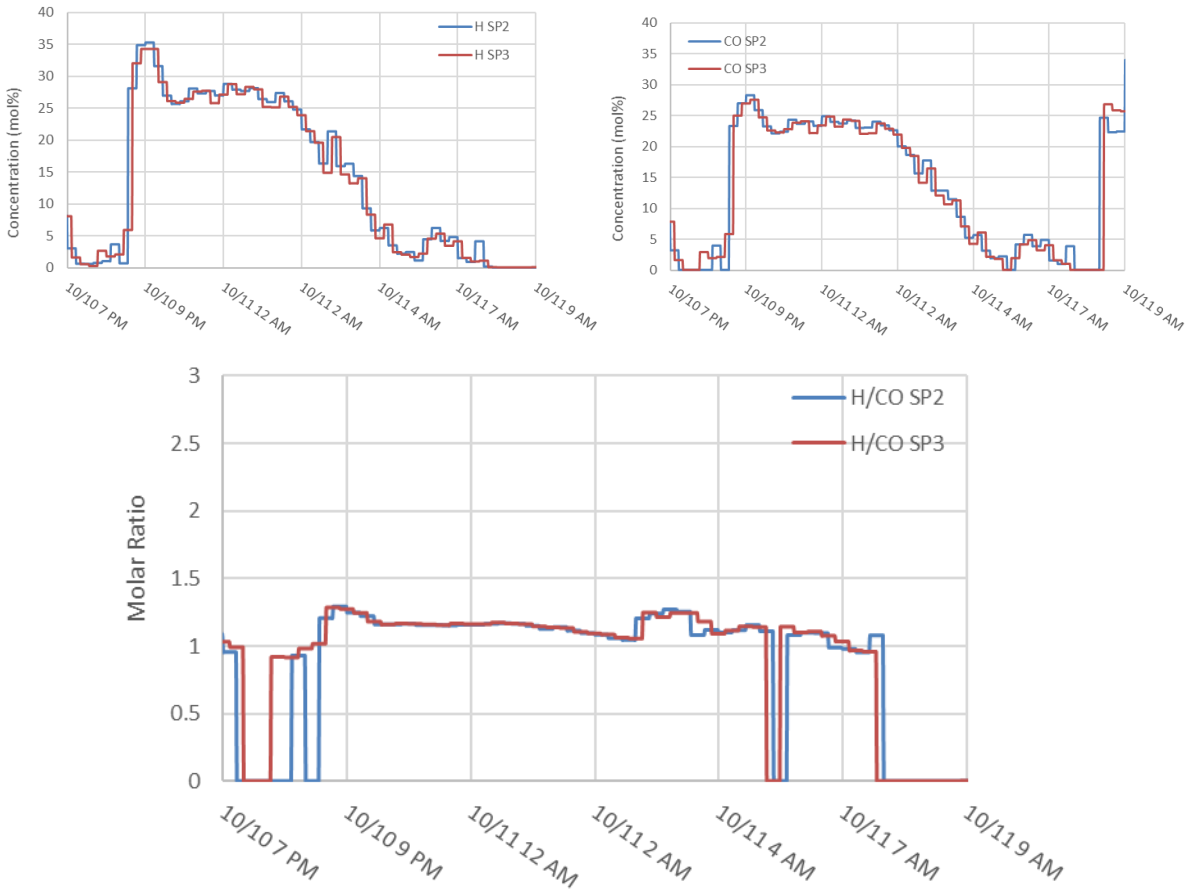


Figure 29: Experimental Data from Initial Coal-only Run of the Gasification Unit Availability, CO, and H_2/CO Ratio

Based on the above results, the gasifier temperature profile, hydraulic operating conditions, H_2/CO ratio were all verified successfully. In addition, stable operation of the system was performed for extended periods proving the gasifier was ready for full operation. Lastly, it was also possible to prove the GC was accurate and results were precise. In addition, as with any system, significant insights and knowledge were gained during the initial operation campaigns. A number of modifications and improvements were made to the gasification unit based upon the insights and knowledge gained. These modifications included: adding a blower to provide

evaporative cooling in quench water (water temperature was too high), new quench pumps to handle higher operating temperature of the quench water, modified burners with proper atomization and burner dynamics, new thermocouples to handle the slagging in the gasification unit, and a new knockout pot with mist eliminator to prevent particulates from proceeding downstream. Upon completion of the modifications, a final test run of the gasification unit was then performed successfully.

Once the gasifier system performance and stability was adequately demonstrated, the other main process units had to be completed as well. In order to accomplish this, the gasifier was operated to produce a stable syngas for downstream testing purposes. First, the WGS was verified. Results of this testing, was fairly straightforward and the WGS operated as expected. The main outcomes with respect to the WGS unit were the following: proof that the H_2/CO outlet ratio could reach at least 2/1; stable extended period of operation was proven; and control of the H_2/CO ratio could be performed thermally (i.e. higher temperature produced higher H_2/CO ratio for the same inlet feed conditions, and vice versa). The syngas from the WGS then went to the AGR, where typical operating conditions yielded better than design results. The AGR was also successfully operated for an extended period in a stable manner. This particular system was the easiest to operate due to extensive operator experience with similar systems, so startup on the AGR was quick and straightforward. The last process unit that needed to be tested was the F-T. Once again, owing to UKy-CAER's over 30 years plus experience with smaller F-T process units, the startup of this particular unit was also simple. The only item that required additional attention was the product separation vessels. However, after operators familiarized themselves with the new hardware everything proceeded smoothly. The F-T reactor itself was similar to the lab scale units already possessed at UKy-CAER and operated as expected, with the added convenience of automatic controls from a central control system. At this point, the full system was tested utilizing syngas and was considered ready for the first full run campaign.

4) Production Runs of the Integrated Refinery

4.1. Run 1 - Coal-only Run

Gasification

First, the gasifier was carefully pre-heated using natural gas to ~1400℃ over the course of 5 days in order to prevent damage to the refractory. Once the gasifier internals reached 1400℃, as measured by thermocouples, the coal/water slurry feed and appropriate amount of oxygen were introduced to the system. The slurry for this particular run was 55wt% coal and 45wt% water, which is slightly higher in water content than optimal. The additional water assisted stable operation by decreasing viscosity of the slurry and helped prevent clogging. However, due to the higher water content, the slurry cooled the gasifier. To counter this cooling, a small amount of natural gas was co-fired to maintain the temperature of the gasifier at optimal levels and facilitate stable operation. The amount of natural gas added was approximately 15% of the total heating value of the feed (coal accounted for 85% of the total heating value).

Once the gasification reaction was stable, the pressure was then increased to normal operating pressure of 0.1 MPag. The gasification system was then operated continuously in a stable manner

for over 68 hours. From **Figure 30** below, both temperature and pressure remained relatively stable during the entire campaign.

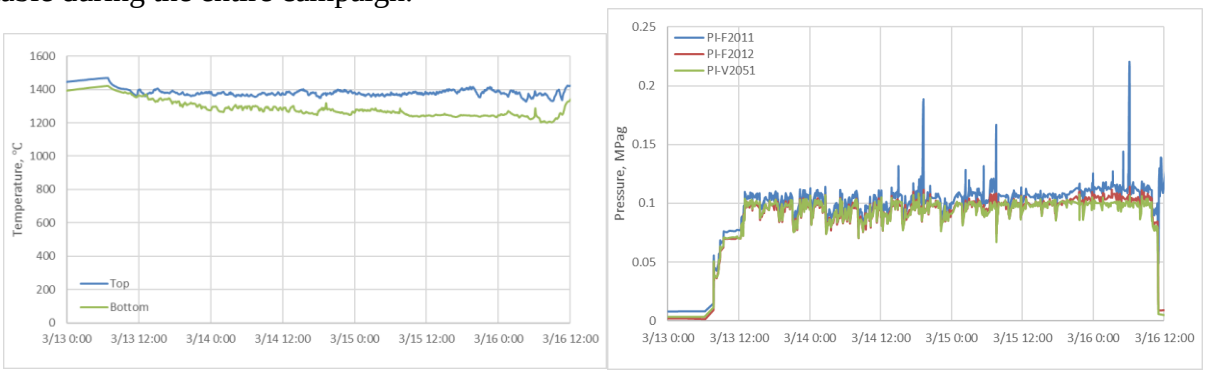
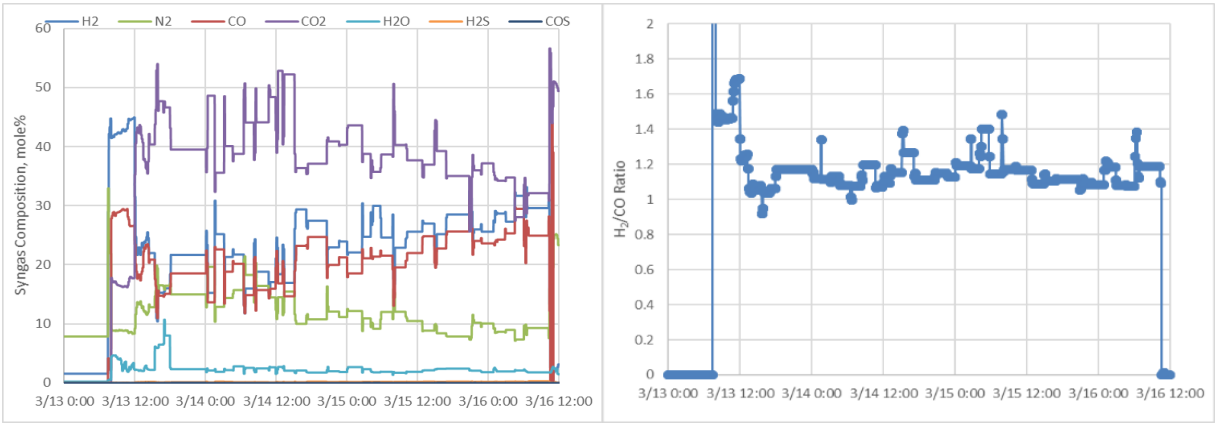


Figure 30: Temperature and Pressure Data of the Gasifier

Syngas quality was analyzed using an online gas chromatograph and the results are presented in **Figure 31**. The composition of the syngas was consistent for the full operating time period (mole %): 40% CO_2, 25% H_2, 23% CO, 10% N_2, 0.2% H_2S and 0.02% COS (top left of **Figure 31**). An additional parameter that is crucial for downstream utilization is the H_2/CO molar ratio. The molar ratio was between 1 and 1.2 throughout (top right of **Figure 31**), while the gasifier was able to consistently produce approximately 40 m^3/hr (bottom left of **Figure 31**) of syngas for downstream utilization. The H_2/CO ratio was higher than would have been observed with a coal only feed due to the addition of natural gas to maintain gasifier operation temperature. It was however, well within the range expected utilizing the aforementioned feeds. The bottom right plot in **Figure 31** shows the carbon conversion for the operation. As can be seen, the conversion was slightly lower than expected around 70%. However, this is near the design conversion for the pilot scale unit and the deviation is likely attributed to imperfect burner atomization and associated burner dynamics.



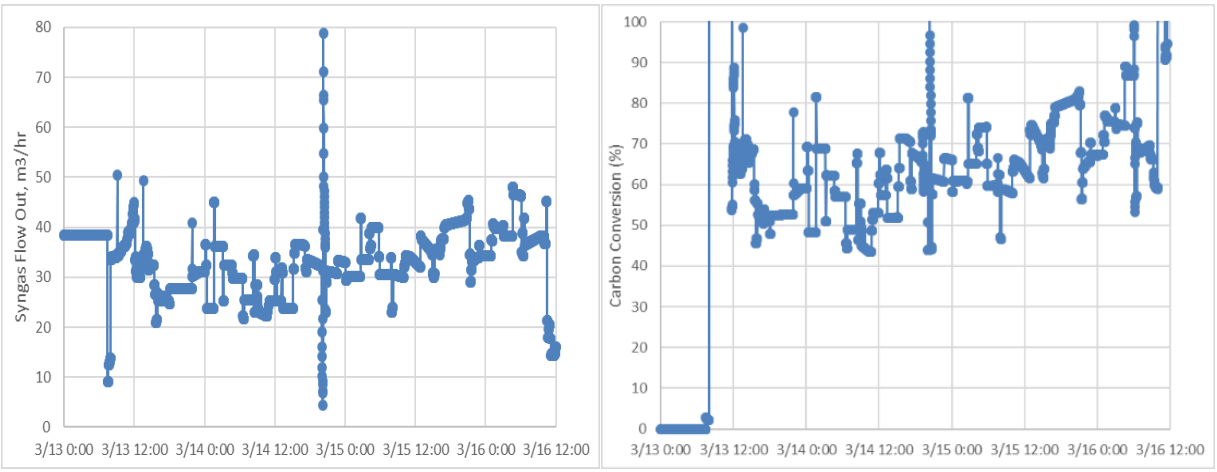


Figure 31: Syngas Composition, Quality, Production Rate and Conversion Data from the Gasifier

Water-gas Shift

Once the syngas exited the gasifier, it proceeded to the WGS unit. In order to facilitate consistent and steady operation of the WGS, the following parameters were controlled: syngas flow into WGS reactor, steam into WGS reactor, and steam to dry gas volume ratio. A steam to dry gas volume ratio of approximately 1 is ideal to promote the WGS reaction for the UK-CAER pilot system which corresponded to controlling the syngas flow into the WGS at 22 kg/hr. with a steam flow of 12-14kg/hr. With these parameters tightly controlled, the bypass around the WGS unit, and the pressure were allowed to fluctuate. As can be seen in **Figure 32**, the inlet process conditions as described above were consistent during the full operation timeframe.

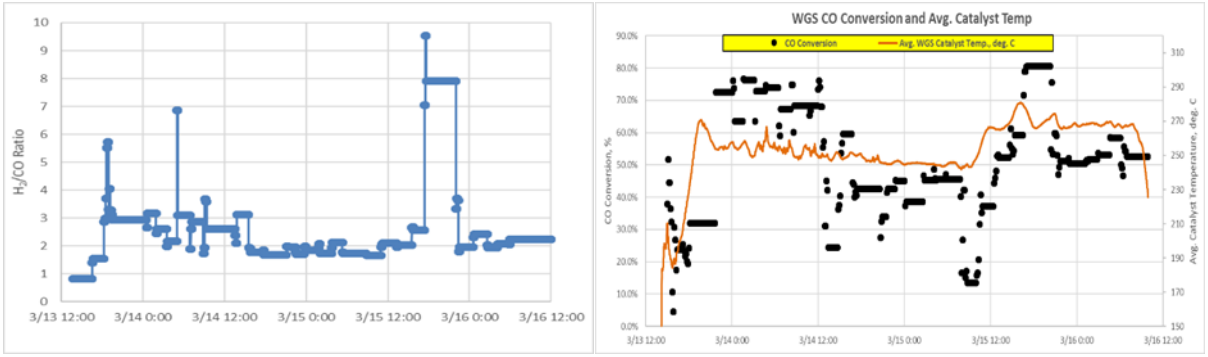


Figure 32: WGS Feed Conditions

The F-T unit for this particular operation utilized a cobalt based catalyst and as a result, the WGS must produce an outlet H_2/CO ratio of ~2 for optimum downstream liquids production. Based on the constant inlet conditions, while also letting the bypass flow vary as needed to maintain those inlet conditions, an outlet H_2/CO concentration of near 2 was produced from the WGS module during the whole operation as can be seen in the left plot of **Figure 32**. This could not be accomplished without modifying temperature of the reactor. Based on the operational knowledge, the temperature of the WGS reactor bed was used as a control point to increase/decrease the outlet H_2/CO. The right plot in **Figure 32** helps to illustrate this point. Notice the large spike in outlet H_2/CO ratio around 18:00 on 3/15/2018 (left plot), which

corresponds to the increase in catalyst bed temperature from 235℃ to 290℃. Then it is also possible to see that as the catalyst bed was cooled back to 250℃, the H_2/CO ratio returned to around 2. This short period of increased temperature was done as a test to see the capabilities of the system. Test results verified that the WGS can produce syngas H_2/CO ratios of up to ~10/1, as designed. Shift gas produced from the WGS module proceeded downstream to the compressor and AGR module for cleaning.

Acid Gas Removal

Shifted gas from the WGS unit enters the AGR module after being compressed with a diaphragm compressor from ~15psi to ~375psi. The AGR system was designed with a guaranteed to remove at least 95% CO_2 and H_2S to below 1ppm. For the operation period, the regeneration temperature in the stripper was controlled at 70℃ (top plot of **Figure 33**) while the liquid recirculation rate was varied to try and reduce the energy penalty associated with capture (bottom plot of **Figure 33)**.

For most of the operation period, the liquid recirculation was kept constant at 0.8 m^3/hr. However, near the end of the operation the recirculation rate was reduced while continuing to monitor CO_2 capture. CO_2 capture data is shown in **Figure 34**, where it can be seen that even at lower circulation rates the CO_2 capture was largely unaffected. This can be attributed to two main factors. First, the gas flow into the AGR was a little more than half of the design flow rate and secondly, the fact that the AGR unit was overdesigned in order to guarantee the process could meet the design specifications of 95%+ capture. Both of these items would contribute to high capture even at lower liquid circulation rates. Reducing the recirculation rate, successfully demonstrated that a lower energy penalty could be achieved as compared to design conditions while still maintaining sufficient capture for downstream utilization in the F-T. However, it should be noted that CO_2 is not the primary concern for syngas cleaning when using an F-T system downstream. For the F-T unit, CO_2 acts mainly as an inert, which could cause a slight drop in efficiency of the system but would otherwise have no adverse effects on the catalyst. Therefore, the primary concern for gas cleanup is the sulfur based components. Even as little as 200ppb H_2S has been shown to poison most F-T catalysts. With that in mind, the cleaned outlet gas was also monitored for H_2S. Unfortunately, the online GC was unable to measure H_2S concentration in the expected outlet range (below 1ppm), so samples had to be tested manually using Drager tubes. Samples were tested throughout and never had a response above 0.2ppm. Once the cleaned syngas was determined to meet/exceed the requirements of below 1ppm as in the process guarantee conditions, the gas was sent downstream to the F-T unit for conversion to fuels.

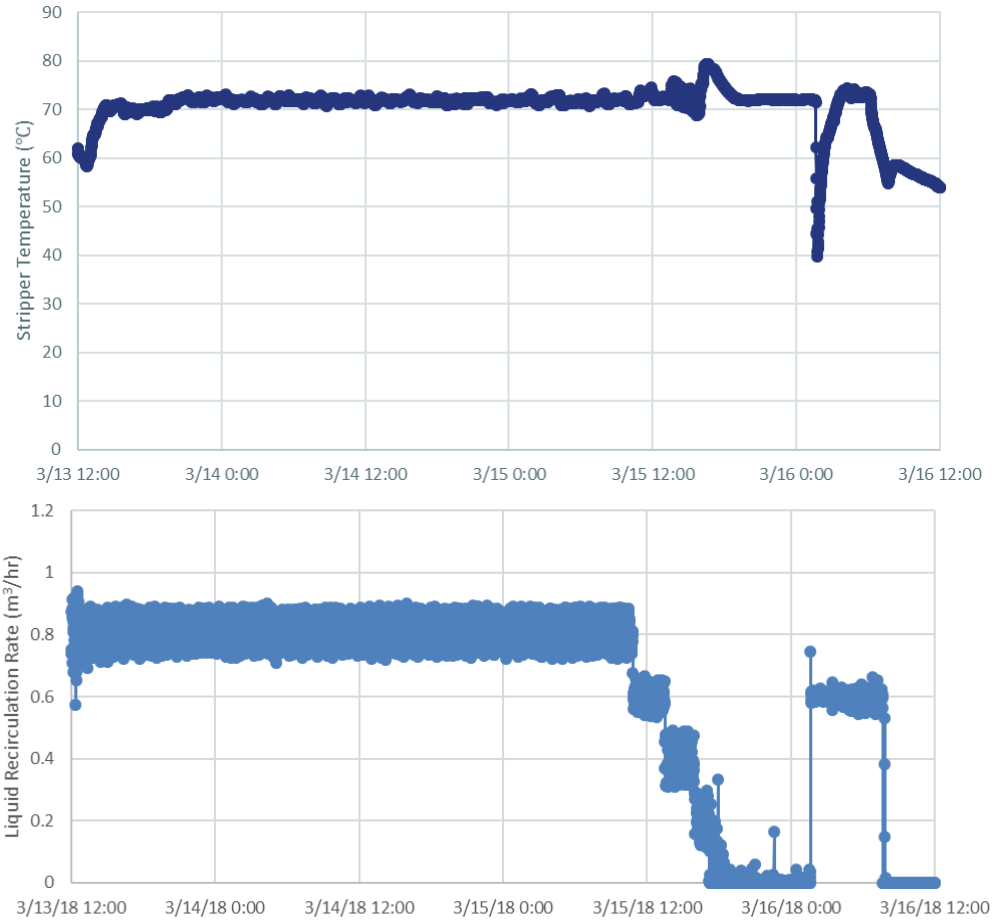


Figure 33: Stripper Regeneration Temperature and Amine Circulation Rate

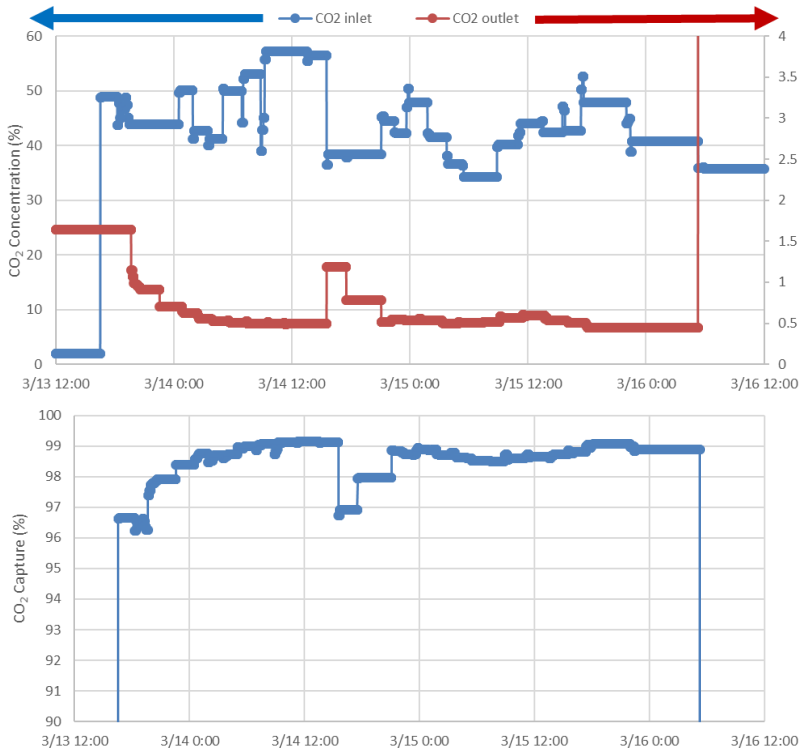


Figure 34: CO_2 removal using the AGR

Fischer-Tropsch Synthesis and Product Output

Cleaned gas then entered the F-T section where a nickel based guard column removed any residual H_2S and then proceeded through the F-T reactor. Conditions for this operation were maintained around 25 bar and 215°C. The process data for these parameters is shown in **Figure 35**. Both parameters maintained small fluctuations from their set points. It can be observed that the temperature of the F-T reactor was modified three times during the sequence in order to control product output.

Operation of the F-T reactor consisted of two main variables for controlling the product and conversion. **Figure 36** shows two plots depicting the relationship between temperature and inlet H_2/CO molar ratio as well as its effect on the products. The left plot shows that temperature and conversion/selectivity are strongly correlated. At higher temperatures, conversion is higher, while methane and carbon dioxide selectivity also increase. At lower temperatures, the opposite trend is true. Similarly, in the right plot of **Figure 36**, an increase in the inlet H_2/CO molar ratio corresponds to higher conversion and methane selectivity. This knowledge will allow for tighter control of the product slate in future operations. Another important qualitative item gained from this operation was the knowledge that the microchannel heat exchange reactor is safe and easy to operate. This also corresponds to the fact that even at very high conversions, the reactor was able to sufficiently remove enough heat to prevent runaway which could have potentially damaged the reactor and/or the catalyst.

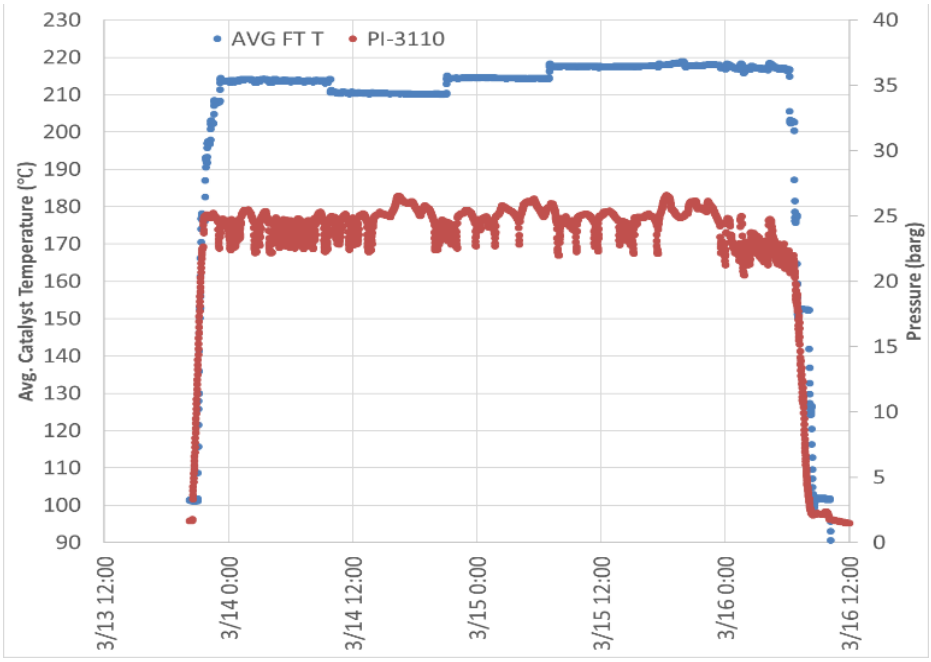


Figure 35: Temperature and Pressure of the FT reactor

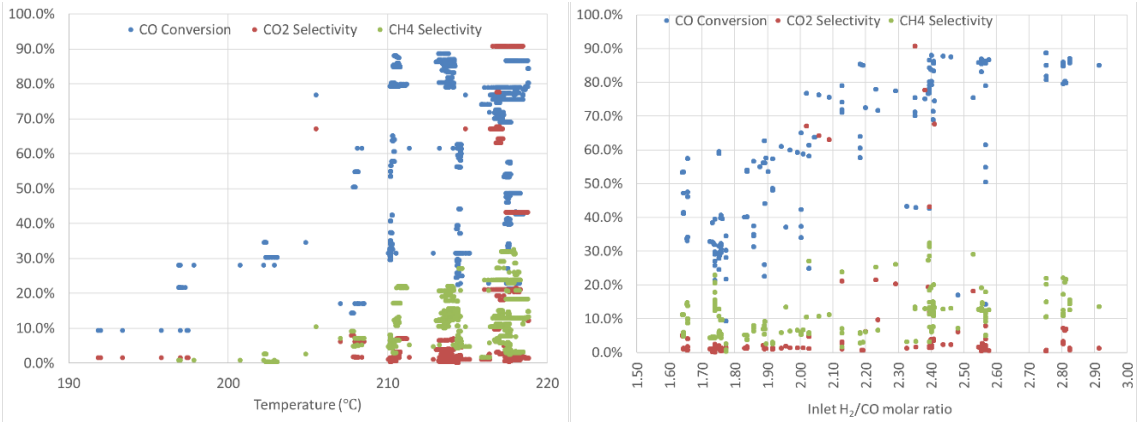


Figure 36: Temperature and Inlet H_2/CO Ratio correlation with Conversion and Selectivity

Once the liquid hydrocarbons had been produced in the F-T reactor, the products and any unconverted gas proceeded to the collection traps. The first trap was set at 150℃ to condense the heavier wax products, while the second trap was set at 5℃ to capture the liquid oil products and water. The products were then separated and stored in drums for later analysis. The light products (methane, ethane, etc.) were not capture and sent to flare. For the full operation period of the F-T unit (55 hours), there were 27.25 kg of wax, 31.25kg of oil and 57.50kg of water produced. A photo of the products is shown in **Figure 37.** Average conversion for this particular system operation was approximately 60%. Simulated distillation analysis was performed on a sample of the wax and oil products. The results of this analysis is also shown in **Figure 37**. The wax consisted of mainly hydrocarbon chains from C15-C41, and the oil consisted of hydrocarbon chains from C8-C19.

Some of the wax produced was sent to the lab-scale hydrocracking system for a processing study and the results of that study are presented in **Section 5** below.

Wax

Component	Area %	Component	Area %
C14 alkane	1.00	C33 alkane	2.61
C15 alkane	2.19	C34 alkane	2.34
C16 alkane	1.75	C35 alkane	2.31
C17 alkane	2.79	C36 alkane	2.00
C18 alkane	3.21	C37 alkane	1.78
C19 alkane	3.46	C38 alkane	1.57
C20 alkane	3.39	C39 alkane	1.38
C21 alkane	3.36	C40 alkane	1.21
C22 alkane	3.34	C41 alkane	1.04
C23 alkane	3.37	C42 alkane	0.94
C24 alkane	3.56	C43 alkane	0.82
C25 alkane	3.77	C44 alkane	0.72
C26 alkane	4.28	C45 alkane	0.63
C27 branched alkanes	1.13	C46 alkane	0.68
C27 branched alkanes	1.47	C47 alkane	0.52
C27 branched alkanes	1.63	C48 alkane	0.50
C27 branched alkanes	2.20	C49 alkane	0.40
C27 alkane	5.32	C50 alkane	0.32
C28 branched alkanes	1.89	C51 alkane	0.30
C28 branched alkanes	0.93	C52 alkane	0.21
C28 branched alkanes	6.00	C53 alkane	0.20
C28 alkane	4.04	C54 alkane	0.15
C29 alkane	3.66	C55 alkane	0.14
C30 alkane	3.24	C56 alkane	0.08
C31 alkane	3.08	C57 alkane	0.13
C32 alkane	2.82	C58 alkane	0.07
		C59 alkane	0.10

Oil

Component	Area %
C8 alkane	9.86
C9 alkane	13.55
C10 alkane	13.88
C11 alkane	12.55
C12 alkane	11.45
C13 alkane	9.86
C14 alkane	8.02
C15 alkane	6.12
C16 alkane	4.50
C17 alkane	3.15
C18 alkane	2.15
C19 alkane	1.45
C20 alkane	0.97
C21 alkane	0.68
C22 alkane	0.49
C23 alkane	0.39
C24 alkane	0.27
C25 alkane	0.21
C26 alkane	0.16
C27 alkane	0.28

Figure 37: FT Product Characterization

4.2. Run 2 - Coal/Biomass Run

Gasification

After much testing (as reported earlier), the final torrefied biomass slurry for utilization with the current UK-CAER gasification system, had the following properties: 50 wt% solids (95 wt% coal and 5 wt% torrefied biomass) and 50 wt% water. This slurry also had 1 wt% limestone and 0.5 wt% Daracem 55 additive. Due to the higher water content of this slurry, it corresponds to a roughly 20% reduction in the heating value of the feed. Natural gas was added to maintain the gasifier temperature during operation. For this operation, coal was 72% of the total heating value, biomass 3% and natural gas was 25%.

Similar to the coal-only run, first, the gasifier was carefully pre-heated using natural gas to ~1400°C over the course of 5 days in order to prevent damage to the refractory. Once the gasifier internals were stable at 1400°C the gasification operation started. Once the gasification reaction was stable, the pressure was then increased to normal operation pressure of 0.1 MPag. The gasification system was then operated continuously in a stable manner for over 24 hours. From **Figure 38** below, it is easy to see that both the temperature (top left) and pressure (top right) remained relatively stable during the entire campaign just as in the coal only campaign. In the bottom plot of **Figure 38**, the amount of each fuel as percentage of the heating value for this operation is shown. Syngas quality was then measured and the data is presented in **Figure 38**.

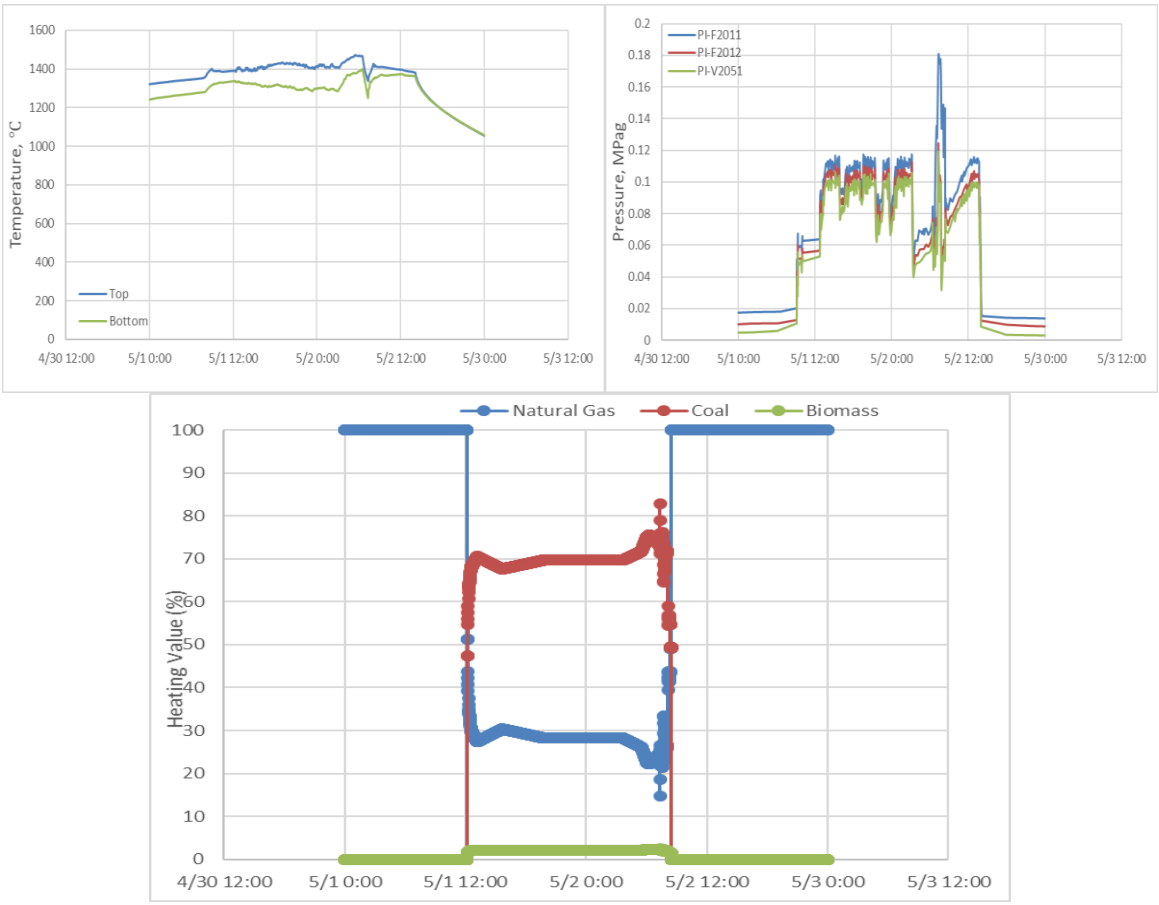


Figure 38: Temperature, Pressure and Heating Value of the Gasifier with Coal/Biomass Slurry

The composition of the syngas was similar to the coal only run and was consistent for the entire operation period: 36% CO_2, 22% H_2, 20% CO, 17% N_2, 0.15% H_2S and 0.01% COS (top left plot of **Figure 39**). However, due to the increased amount of natural gas and decreased amount of coal for coal/biomass run (as compared to the coal-only run) the amount of CO_2, as a percentage of the syngas, was lower for the coal/biomass run than the coal-only operation. However, the H_2/CO molar ratio was 1.1 (top right plot of **Figure 39**) at nearly 25 m^3/hr (bottom left plot of **Figure 39),** which are nearly identical to the coal-only run. The bottom right plot in **Figure 39**, depicts the carbon conversion during operation which was around 60% as expected based on previous gasifier operation.

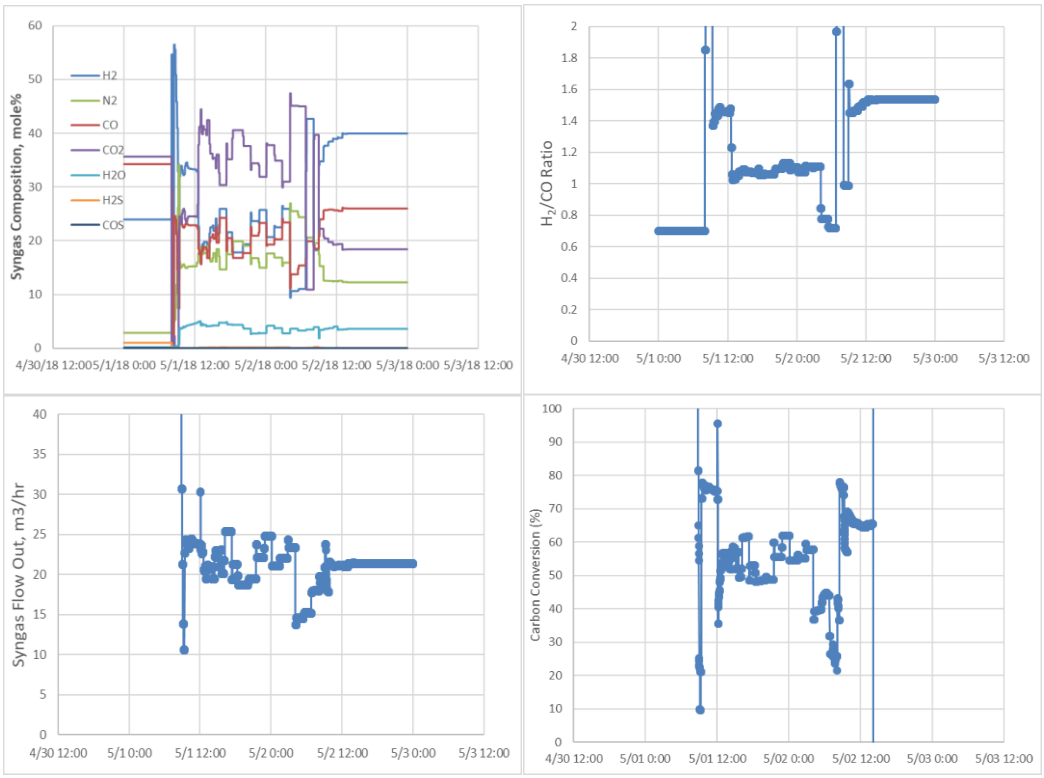


Figure 39: Syngas Composition, Quality, Production Rate and Conversion Data from the Gasifier for Coal/Biomass Slurry

Water-gas Shift

At this point on, there was very little difference in operation for the coal only operation and coal/biomass operation. The syngas compositions exiting the gasifier for both the coal only and coal/biomass were very similar. So, from the WGS component and further downstream the operational results are expected to be nearly identical.

After the syngas exited the gasifier, there was relatively little difference in operation of the full system. The syngas proceeded to the WGS. Similar operation controls were maintained: syngas flow into WGS reactor, steam into WGS reactor and steam to dry gas volume ratio. The flows for this operation were 22 kg/hr syngas into the WGS, with a steam flow of 12-14kg/hr. With these parameters tightly controlled, the bypass around the WGS unit, and the pressure were allowed to fluctuate. Even though those parameters were allowed to fluctuate, they stayed stable. As can be seen in **Figure 40**, the inlet process conditions as described above were once again consistent during the full operation timeframe.

The goal for this operation was to produce a syngas with an H_2/CO ratio of 2/1 for downstream utilization in the F-T reactor. In practice, however, the actual output was slightly higher at ~2.5/1 for the full operation. This can be observed in the plot of **Figure 41**. Experimental results for the WGS unit, showed that coal/biomass syngas behaves similarly to the coal only syngas which was expected. Shift gas produced from the WGS module proceeded downstream to the compressor and AGR module for further processing.

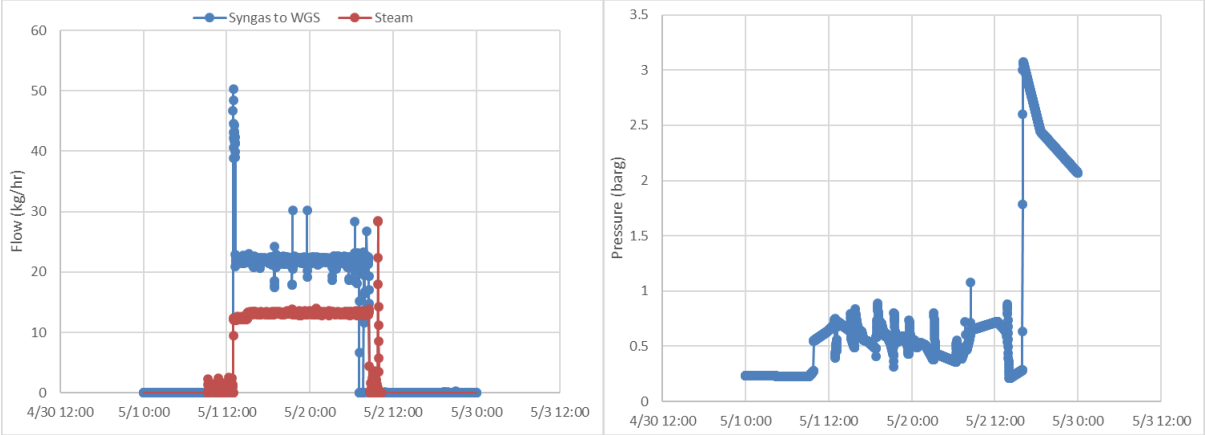


Figure 40: WGS Feed Conditions for Coal/Biomass Run

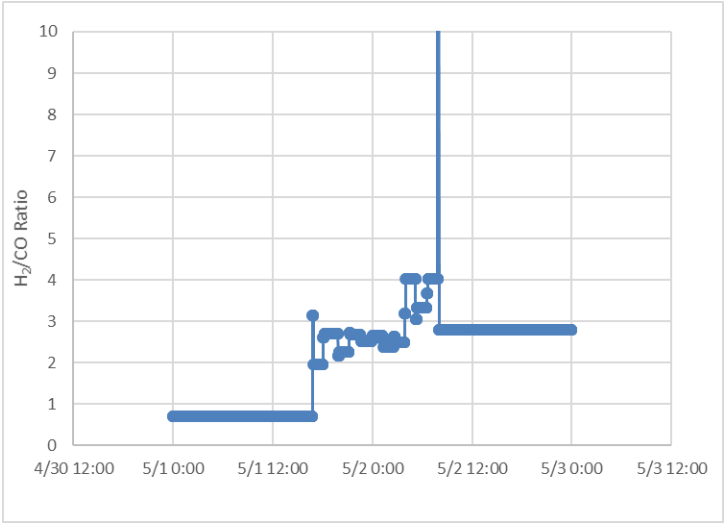


Figure 41: WGS Shifted Gas Outlet Composition for Coal/Biomass Run

Acid Gas Removal

Shifted gas from the WGS unit entered the AGR module after being compressed with a diaphragm compressor from ~15psi to ~300psi. The AGR system was designed with a guaranteed to remove at least 95% CO_2 and H_2S to below 1ppm. For the operation period, the regeneration temperature in the stripper was controlled at 70°C (top plot of **Figure 42**). Process data for these two items is shown in **Figure 42**. Even though the pressure was lower for this coal/biomass operation, the regeneration temperature and amine circulation rate were controlled at the same conditions as the coal only campaign.

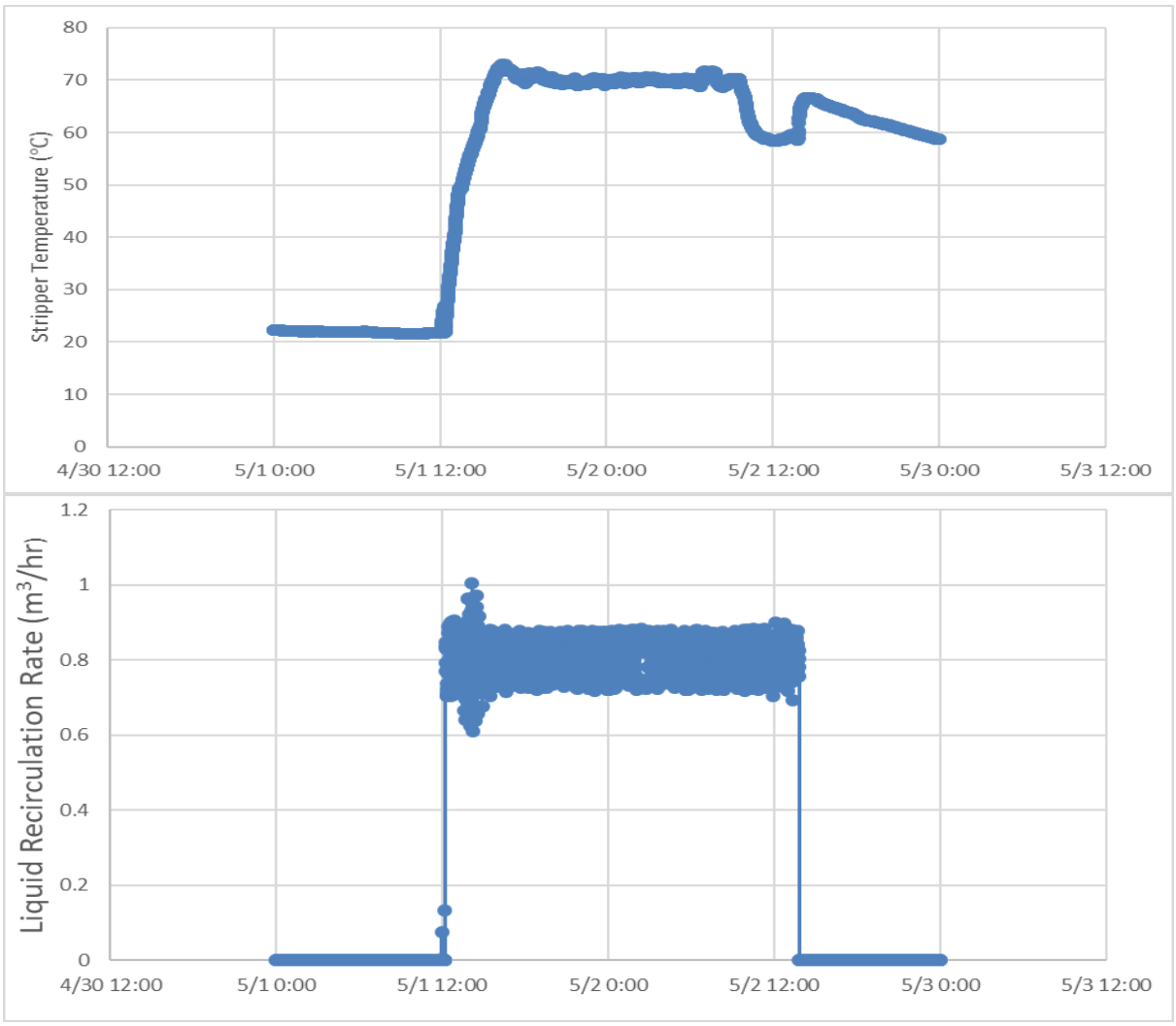


Figure 42: Stripper Regeneration Temperature and Amine Circulation for Coal/Biomass Run

CO_2 capture data is shown in **Figure 43**. After the first couple of hours, due to plant start-up and the time for the process to get to steady state operation, the CO_2 capture was much better than 95% for the operation period. The CO_2 capture was slightly lower than the coal only operation. However, if the lower operation pressure in the absorber is accounted for, there is relatively no difference between the coal only and coal/biomass operation. Carbon capture requirements and, more importantly, sulfur capture requirements were met. The cleaned syngas was then sent downstream to the F-T module.

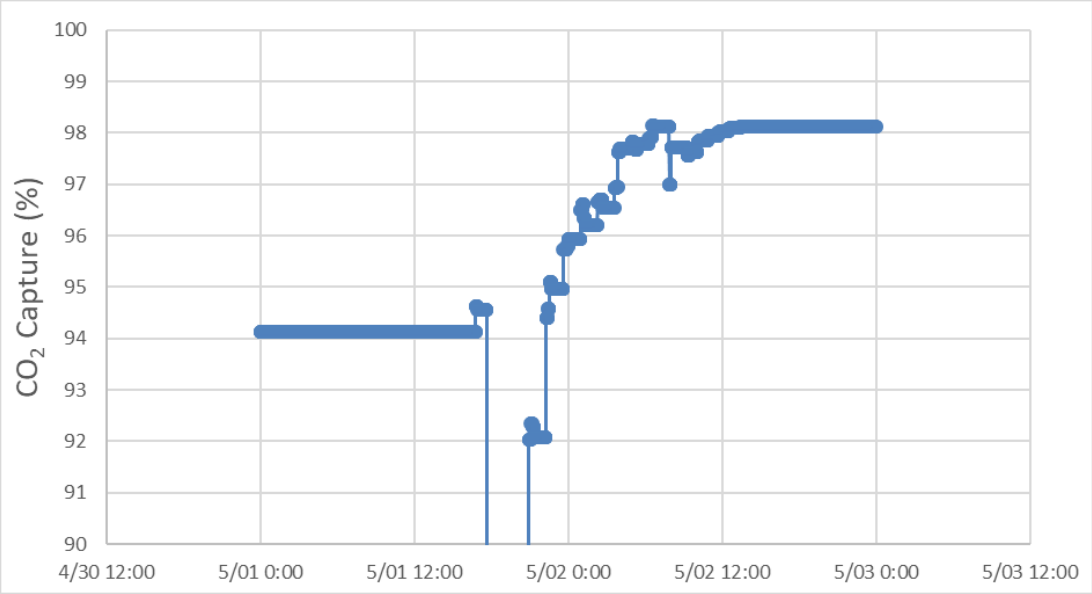


Figure 43: CO_2 removal using the AGR for the Coal/Biomass Run

Fischer-Tropsch Synthesis and Product Output

As previously mentioned, by the time the syngas reaches this portion of the process it is identical to the syngas from the coal only operation. The syngas only contains H_2 and CO in the proper ratio around 2/1, as well as small amounts of residual CO_2 and N_2. The cleaned syngas from coal/biomass then entered the F-T section where a nickel based guard column removed any residual H_2S and then proceeded through the F-T reactor. Conditions for this operation were maintained around 20 barg and 220°C. The process data for these parameters is shown in **Figure 44**. Both parameters were maintained with small fluctuations from their set points. These conditions were similar, but also slightly different than the coal only operation. This small difference in operating conditions could potentially make a much larger impact on the F-T product slate and composition.

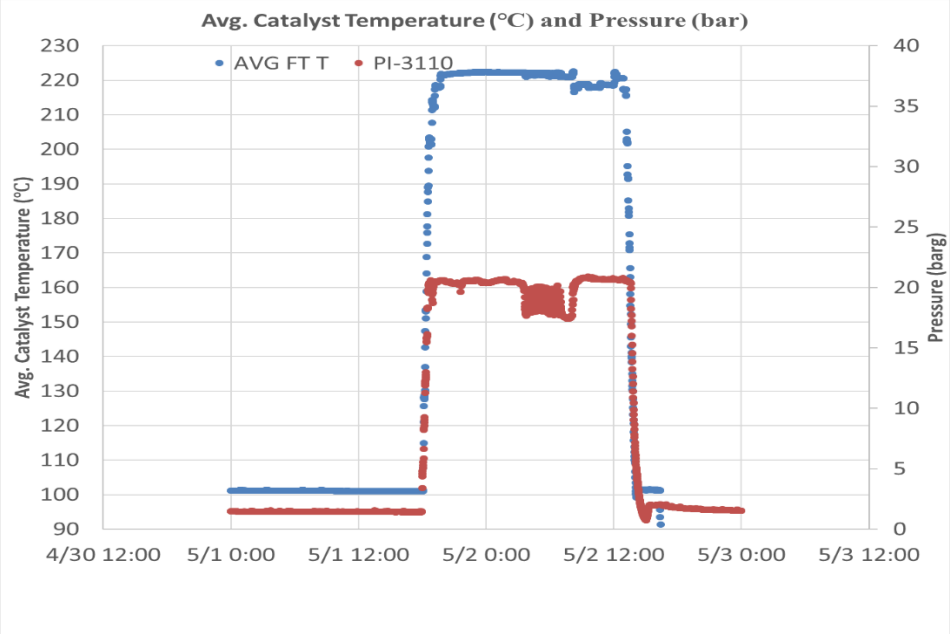


Figure 44: Temperature and Pressure of the F-T Reactor for the Coal/Biomass Run

Operation of the F-T reactor consisted of two main variables for controlling the product and conversion. **Figure 45** shows two plots depicting the relationship between temperature and inlet H_2/CO molar ratio as well as its effect on the products. The left plot shows that temperature and conversion/selectivity are strongly correlated. At higher temperatures, conversion is higher, while methane and carbon dioxide selectivity also increase. At lower temperatures, the opposite trend is true. Similarly, in the right plot of **Figure 45**, an increase in the inlet H_2/CO molar ration corresponds to higher conversion and methane selectivity. In general, the F-T reactor was operated at higher conversions for the coal/biomass operation which would selectively favor more of the shorter chain hydrocarbon products. The average conversion for this particular run was approximately 80%.

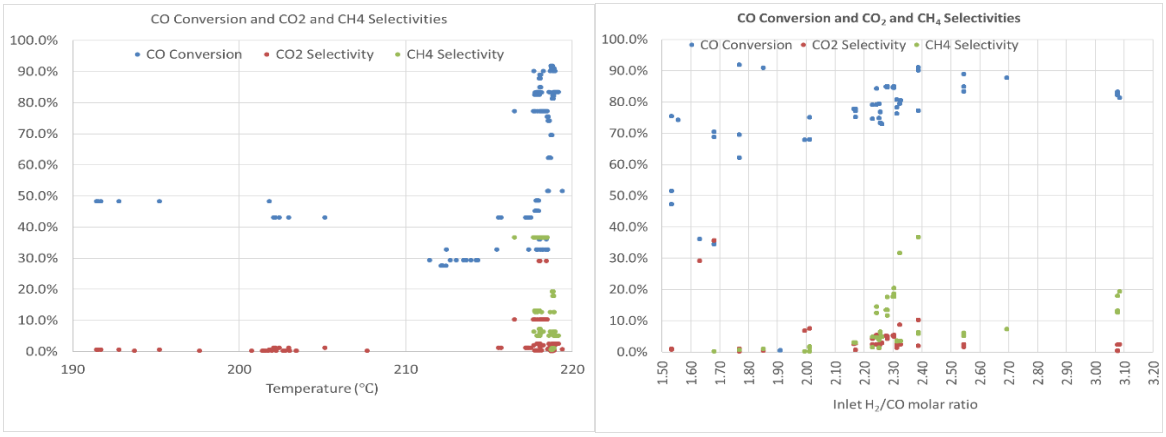
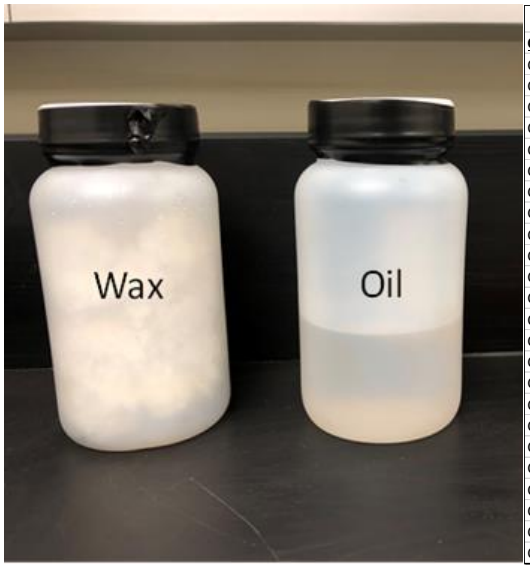


Figure 45: Temperature and Inlet H_2/CO Ratio Effect on Conversion and Selectivity for the Coal/Biomass Run

Once the liquid hydrocarbons had been produced in the F-T reactor, the products and any unconverted gas proceeded to the collection traps. The first trap was set at 150°C to condense the

heavier wax products, while the second trap was set at 5°C to capture the liquid oil products and water. The products were then separated and stored in drums for later analysis. The light products (methane, ethane, etc.) were not capture and sent to flare for disposal. For the full operation period of ~19 hours, there were 11.20 kg of wax, 6.3kg of oil and 24.30kg of water produced. A picture of the products is shown in **Figure 46.** Simulated distillation analysis was performed on a sample of the wax and oil products. The results of this analysis is also shown in **Figure 46**. The wax consisted of mainly hydrocarbon chains from C12-C39, and the oil consisted of hydrocarbon chains from C8-C19. It should also be noted that in both the oil and wax products there was a larger percentage of the lighter hydrocarbon chains compared to the coal only operation. This was expected as the operating conditions for this coal/biomass campaign would favor the shorter chains hydrocarbon production due to the lower pressure, higher H_2/CO and higher conversion. In conclusion, for the F-T process, product composition was almost identical. However, due to differing operating conditions the conversion rates and yields were slightly different between the coal only and coal/biomass operation.



Wax				
Component	Area %		Component	Area %
C10 alkane	0.82		C34 alkane	2.16
C11 alkane	0.86		C35 alkane	1.75
C12 alkane	1.19		C36 alkane	1.56
C13 alkane	1.74		C37 alkane	1.37
C14 alkane	2.83		C38 alkane	1.31
C15 alkane	3.77		C39 alkane	1.14
C16 alkane	4.49		C40 alkane	0.97
C17 alkane	4.44		C41 alkane	0.84
C18 alkane	4.28		C42 alkane	0.67
C19 alkane	4.59		C43 alkane	0.65
C20 alkane	4.25		C44 alkane	0.53
C21 alkane	4.28		C45 alkane	0.42
C22 alkane	4.21		C46 alkane	0.37
C23 alkane	4.39		C47 alkane	0.32
C24 alkane	4.60		C48 alkane	0.29
C25 alkane	4.51		C49 alkane	0.25
C26 alkane	4.61		C50 alkane	0.18
C27 alkane	4.50		C51 alkane	0.17
C28 alkane	4.10		C52 alkane	0.13
C29 alkane	3.90		C53 alkane	0.13
C30 alkane	3.56		C54 alkane	0.14
C31 alkane	3.14		C55 alkane	0.17
C32 alkane	2.80		C56 alkane	0.13
C33 alkane	2.49			

Oil	
Component	Area %
C8 alkane	13.13
C9 alkane	14.09
C10 alkane	13.79
C11 alkane	12.85
C12 alkane	11.44
C13 alkane	9.58
C14 alkane	7.87
C15 alkane	5.99
C16 alkane	4.28
C17 alkane	2.89
C18 alkane	1.82
C19 alkane	1.01
C20 alkane	0.64
C21 alkane	0.36
C22 alkane	0.26

Figure 46: F-T Product Characterization for the Coal/Biomass Run

4.3. Comparison of Coal-only and Coal/Biomass Production Runs

Operating Conditions of the Unit Operations

A summary of operating conditions of the unit processes for the two runs is included in **Figure 47** below. For the gasification section process conditions were relatively similar, except for the addition of biomass in the feed slurry and the additional natural gas needed to maintain temperature of the system. The syngas produced was also similar in nature except that flow rate was lower for the coal/biomass operation and concentrations of H_2, CO and CO_2 were slightly lower. It is interesting to note that the H_2/CO ratio out of the gasifier for both operations was almost identical. WGS reactor temperature was higher for the coal/biomass operation which resulted in higher H_2/CO ratios downstream. AGR operation was basically identical for both sets of operation data, with removal of more than 97% of the CO_2 from the shifted gas. Finally, the F-T conditions were different enough that conversion and selectivity between the two operations was significantly impacted. The coal biomass had a much higher H_2/CO inlet ratio, lower

pressure and higher operating temperature than the coal-only run. These factors all contributed to higher CO conversion, while also preferentially producing shorter chain hydrocarbons for the coal/biomass F-T operation. Based on significant experience in the F-T field, had the operation conditions (pressure, temperature and inlet H_2/CO ration) been the same for both operations then the product conversion and selectivity's would have been identical. Accordingly, all differences in data can be easily attributed to the different operating conditions. And, owing to these differences in operating conditions and feedstocks, a direct comparison between runs with regards to CO_2 emissions and product yield and selectivity could not be made based on the initial runs. While a direct comparison could not be made, feed, product data and emissions are discussed below.

Coal Only

Gasifier	
Temperature	1390 ℃
Pressure	1 bar
Coal Feed	.62 TPD
NG Feed	0.08 TPD
Biomass Feed	0 TPD
Syngas Flow Out	35 m^3/hr
Syngas Produced	
H_2	25 mol%
CO	23 mol%
CO_2	40 mol%
H_2S	0.2 mol%
N_2	10 mol%
WGS	
Temperature	250 ℃
Pressure	0.8 bar
H_2/CO average out	2
AGR	
Stripper Temperature	70 ℃
Amine Circulation Rate	0.8 m^3/hr
CO_2 Removal	98.50%
F-T	
H_2/CO inlet	2
Pressure	24 bar
Temperature	215 ℃
CO Conversion	60%
Product	
Wax	0.16 BPD
Oil	0.16 BPD
Water	0.15 BPD

Coal/Biomass

Gasifier	
Temperature	1400 ℃
Pressure	1 bar
Coal Feed	.37 TPD
NG Feed	.12 TPD
Biomass Feed	.02 TPD
Syngas Flow Out	25 m^3/hr
Syngas Produced	
H_2	22 mol%
CO	20 mol%
CO_2	36 mol%
H_2S	0.15 mol%
N_2	17 mol%
WGS	
Temperature	275 ℃
Pressure	0.8 bar
H_2/CO average out	2.5
AGR	
Stripper Temperature	70 ℃
Amine Circulation Rate	0.8 m^3/hr
CO2 Removal	97.0%
F-T	
H_2/CO inlet	2.5
Pressure	20 bar
Temperature	220 ℃
CO Conversion	80%
Product	
Wax	0.22 BPD
Oil	0.18 BPD
Water	0.19 BPD

Figure 47: Comparison Summary of Coal Only and Coal/Biomass Operating Parameters

Process Inputs

For the coal-only run, a feed of 0.61 tons per day (TPD) coal and 0.41 TPD water, representing 59.8 and 40.2 wt. %, respectively. For the coal/biomass run, 0.36 TPD coal, 0.02 TPD torrefied biomass and 0.36 TPD water were used, representing 48.7, 2.6, and 48.7 wt.%, respectively. For the coal/biomass run, 5.3 wt% torrefied biomass was added to the pulverized coal. The coal/biomass run required more water to process than the coal-only run because the coal/biomass was a much thicker slurry to process as was discussed previously. Further, the coal/biomass run required 57.5% more oxygen (TPD basis) relative to the coal-only trial run. Finally, to maintain temperature stability in the gasifier, the production runs were supplemented with a small feed of natural gas. The coal-only run consumed 0.11 tons of NG per barrel of products compared to 0.13 tons of NG per barrel of products for the coal-biomass run [greater additions of NG were required because of the greater amount of dilution [water] needed for the coal/biomass run. The results of the coal-only and coal/biomass run inputs are shown in **Table 5**.

Input	Tons per day (TPD)	Tons per bbl TPB
Coal feed (as received)	0.6173	0.9788
Water	0.4157	0.6591
Oxygen/Air	0.7610	1.2067
NG	0.0739	0.1171
CO_2 released	0.7671	1.2163

Input	Tons per Day (TPD)	Tons per Barrel (TPB)
Coal feed (as received)	0.3677	0.4222
Torrefied Wood (as received)	0.0196	0.0225
Water	0.3677	0.4222
Oxygen/Air	0.7569	0.8690
NG	0.1164	0.1336
CO_2 released	0.7199	0.8265

Table 5: Inputs for Coal-only Run (Left) and Coal/Biomass Run (Right)

Product Slate and Output

Diesel is a more valuable product relative to naphtha because diesel has no sulfur and about 75 cetane number whereas naphtha has a low cetane number. Equivalent diesel is calculated with the assumption that naphtha has a 71 % value relative to diesel. For a feed of 0.61 TPD coal, 0.16 BPD naphtha, and 0.16 BPD diesel were produced, representing 0.27 equivalent diesel (left table in **Table 6**). On the other hand, the 0.36/0.02 TPD coal-biomass process produced 0.22 BPD naphtha, and 0.18 BPD diesel with 0.34 equivalent diesel (right table in **Table 6**).

Outputs	1 BPD
Naphtha (BPD)	0.1555
Diesel (BPD)	0.1624
Naphtha & Diesel (BPD)	0.3179
Equivalent Diesel (BPD)	0.2728
CO_2 released (TPD)	0.7671
Water vapor (TPD)	0.0273

Outputs	1 BPD
Naphtha (BPD)	0.2224
Diesel (BPD)	0.1786
Naphtha & Diesel (BPD)	0.4009
Equivalent Diesel (BPD)	0.3365
CO_2 released (TPD)	0.7199
Water vapor (TPD)	0.0338

Table 6: Product Slate, Equivalent Diesel and CO_2 Produced for Coal-only Run (Left) and Coal/Biomass Run (Right)

A total of 0.63 BPD products were produced from the coal-only run (left table in **Table 7**) whereas the coal/biomass run produced 0.87 BPD (right table of **Table 7**) in a single pass [e.g., no recycle] of the syngas in the F-T process.

Component	BPD
Lights	0.3860
Naphtha	0.0912
Diesel	0.0980
Lub oil	0.0403
Fuel oil	0.0123
Paraffin wax	0.0026
Bitumen	0.0002
Total	**0.6307**

Component	BPD
Lights	0.6055
Naphtha	0.1215
Diesel	0.0776
Lub oil	0.0481
Fuel oil	0.0149
Paraffin wax	0.0031
Bitumen	0.0003
Total	**0.8710**

Table 7: Detailed Product Slate Analysis for Coal-only Run (Left) and Coal/Biomass Run (Right)

The lights (C1 - C5) accounted for 61.2 and 69.5% (on BPD basis) of the total products in the coal-only and coal/biomass runs respectively, emphasizing how imperative it is to recycle the lights in F-T processes to produce higher hydrocarbon-chained products (naphtha and diesel). In a commercial F-T operation, the light gases would be recycled to extinction and eventually converted to heavier hydrocarbons. **Table 8** below show the results of the light products (C1 – C5) being redistributed to the heavy products assuming recycle of the light gases.

Component	BPD
Naphtha	0.1555
Diesel	0.1624
Lub oil	0.1046
Fuel oil	0.0767
Paraffin wax	0.0669
Bitumen	0.0646
Total	**0.6307**

Component	BPD
Naphtha	0.2224
Diesel	0.1786
Lub oil	0.1490
Fuel oil	0.1158
Paraffin wax	0.1041
Bitumen	0.1012
Total	**0.8710**

Table 8: Detailed Product Slate Analysis Utilizing Distribution of the Lights to Heavier Products for Coal-only Run (Left) and Coal/Biomass Run (Right)

The capacity of the F-T synthesis process is half that of the gasification unit. Furthermore, the pressure drop in the F-T bed restricted how much gas could be processed in the F-T unit. Consequently, portions of the syngas from the gasifier were flared. 34.5 % and 28.5% of the gasifier output was flared in the coal-only and coal/biomass production runs, respectively.

Emissions Profile

The net CO_2 released for the coal-only and coal/biomass runs were 0.77 and 0.72 TPD, respectively. This represents 1.22 and 0.83 Tons of CO_2 per barrel of total produced for the coal-only and coal/biomass runs, respectively. For the 5/95 % wt. coal/biomass run, there was 0.39 less tons of CO_2 per barrel relative to the coal-only process. The emissions profile is depicted in **Table 9**. The lower amount of CO_2 released from the coal/biomass run versus the coalonly run is partially the result of the higher addition of NG feed for the coal/biomass run, such that the differences in CO_2 emissions between the runs is negligible.

Emissions	
CO_2 released (TPD)	0.7671
CO_2 released per Barrel of product (TPD per BPD)	1.2163

Emissions	
CO_2 released (TPD)	0.7199
CO_2 released per Barrel of product (TPD per BPD)	0.8265

Table 9: Emissions Profile for Coal-only Run (Left) and Coal/Biomass Run (Right)

5) Hydrocracking Studies

F-T wax from the coal-only run was utilized as a representative sample for use in hydrocracking experiments. The wax produced from both operation runs was almost identical. Therefore, the results presented in this section with regards to the hydrocracking studies, while only performed on the coal-only produced wax, is applicable to both the coal and coal/biomass wax.

Utilizing a platinum/zeolite catalyst, the F-T wax was successfully cracked to gasoline range hydrocarbons. **Figure 48** shows the results from hydrocracking of the wax with the Pt/Zeolite catalyst at two lower operating temperatures, as well as the raw wax for comparison purposes. Both experiments were performed at 450psig. As can be observed, the as produced wax had a product distribution with ~1.4% below C11 (gasoline range), ~35% between C12 and C20 (diesel range), and 65% above C20. In addition, after cracking, over 90% of the resulting

hydrocarbons were in the gasoline range below C10. While this was true for both of the lower operating temperatures tested, the 340℃ temperature produced slightly more of the smaller hydrocarbons, compared to the 320℃ test. Full results showed that 1-5% went to light hydrocarbons (methane, ethane and propane), 90-94% were in the gasoline range and 1-4% remained in the diesel range.

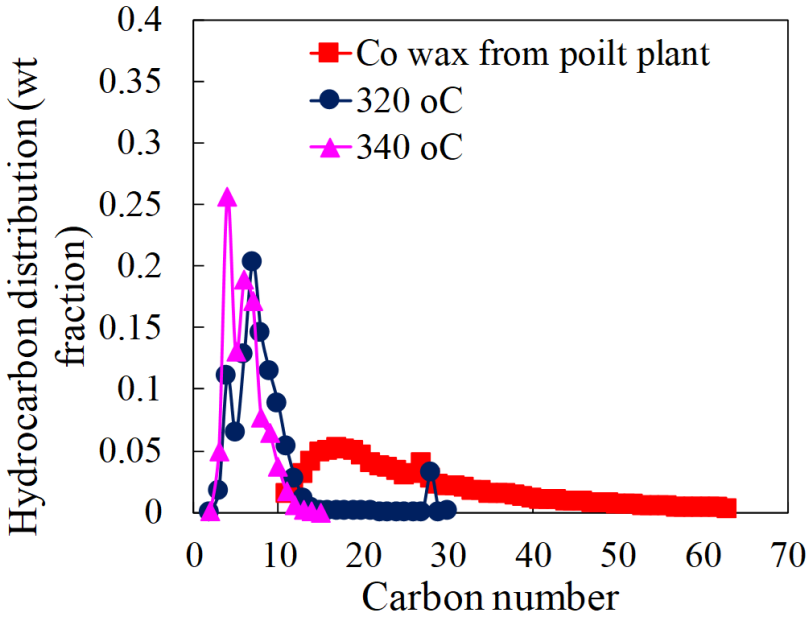


Figure 48: Low Temperature Hydrocracking Experimental Results

Additional experiments were performed at two higher temperatures (360℃ and 380℃), but maintained the 450psig operating pressure. **Figure 49** shows the experimental results for the higher temperature hydrocracking. Similar to the lower temperature results, the higher temperatures both produced at least 90% of the final products in the gasoline range. Although, it also followed the similar trend, that higher temperatures produced relatively more of the lights range hydrocarbons. Results for these two experiments were 7-10% light hydrocarbons, 90-91% gasoline range hydrocarbons and 0-1% diesel range.

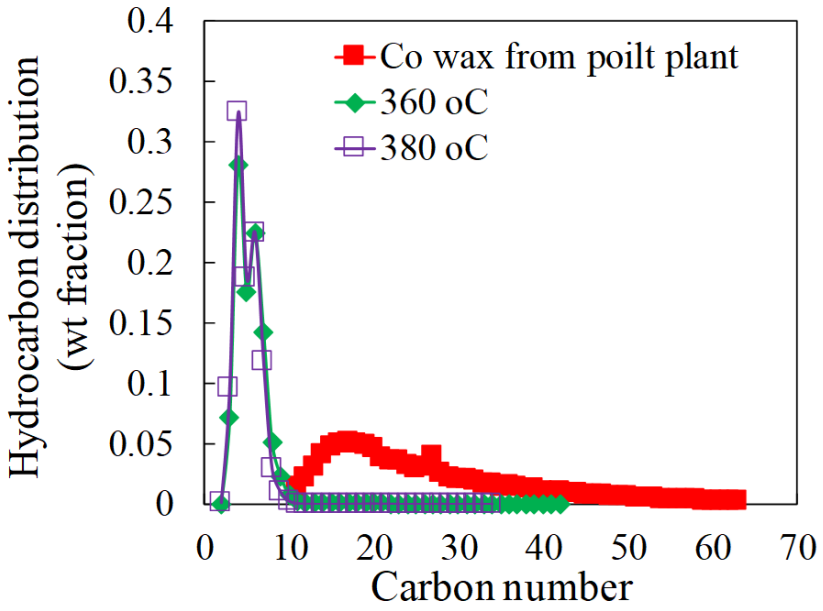


Figure 49; High Temperature Hydrocracking Results

The results of all the hydrocracking testing are summarized in **Table 10** below. The Pt/Zeolite catalyst was highly active and produced conversions above 95% for all conditions tested. The catalyst is also highly selective to produce gasoline range hydrocarbons with greater than 90% selectivity. Lastly, the catalyst was stable over the course of the entire testing period, lasting more than 208 hours.

Temperature, ^{o}C	320	340	340	340	360	380
Pressure, Psig	450	450	450	450	450	450
Time, h	41.9	66.3	89.9	112.7	160.6	208.5
C_{20+} conversion, %	95.4	99.7	100.0	100.0	99.3	99.8
Cracked hydrocarbon distribution, wt%						
C_2-C_3	1.7	4.2	5.0	4.5	7.3	9.8
C_4-C_{11}	90.6	91.1	94.1	94.9	91.0	89.9
C_{12}-C_{19}	4.4	4.5	0.9	0.6	1.0	0.2
C_{20+}	3.3	0.2	0.0	0.0	0.7	0.1

Table 10: Detailed Summary of Hydrocracking Experiments

Data presented in this section, indicate that the Pt/Zeolite catalyst used was able to successfully crack wax to gasoline hydrocarbons. Over the wide temperature range tested, all conditions produced greater than 90% selectivity yield for the gasoline products. Generally, as the temperature was increased, the resulting hydrocracking product was for lower range hydrocarbons. The catalyst produced conversions of greater than 95% of the wax, while

maintaining activity over the entire testing timeline (208+ hours). The catalyst has also been shown to be robust and stable. Lastly, while the focus of this work was to convert the wax products to gasoline range hydrocarbons, future work on conversion to diesel products may be relevant. This would require another catalyst and slightly different operating conditions to complete but this can be done in the future if there is further interest.

6) Economics of the Pilot Plant

The data used in the economic analysis are actual data from the pilot plant. Calculations for the economics of the pilot plant vis-à-vis the coal-only and coal/biomass runs were performed in Aspen Plus (using the actual plant data) to take advantage of the thermodynamic models and property estimation features. Coal and biomass are non-conventional components in Aspen Plus and require properties collectively termed as component attributes in order to characterize these non-conventional components accurately. The component attributes (ultimate and proximate analyses) are then used to estimate additional properties, such as density. These estimated properties are used to convert data from one unit of measurement to another. Simple stoichiometric reactors were used to represent the gasification, AGR, WGS, and F-T processes with yields that reflected the respective product mixes of each process based on the actual plant data. The proximate and ultimate analyses of coal and biomass have been reported in **Table 1 and Table 2**, previously. The particle size distribution data used to model the attributes of coal and biomass are shown in **Table 11**. The particle size distribution was defined as weight fractions per size interval using a 20 µm size range for coal and coal/biomass mixture. The particle size distribution for coal was used for the coal/biomass mixture as well since both were produced on the same milling apparatus.

Particle size distribution

Lower limit	Upper Limit	Weight fraction
0	20	0.5181
20	40	0.2653
40	60	0.1311
60	80	0.0528
80	100	0.0157
100	120	0.0097
120	140	0.0052
140	160	0.0016
160	180	0.0005
180	200	-

Table 11: Particle Size Distribution Analysis

Table 12 shows the operating cost per day and per barrel of products for the coal-only and coal/biomass trial runs. Fixed operating costs included a labor cost of $3000 per barrel of product (for a crew of 3 shifts with 2 technicians per shift) and $800 per barrel for materials and maintenance costs. It should be noted that these are the actual costs associated for operation of

this pilot plant for this operation. It is expected that costs will be higher for future operations, especially longer campaigns, for additional staff and shifts. The purchase cost of the coal was $91.7 per ton and torrefied wood (biomass) at $737.4 per ton. The variable operating costs included the cost of coal at $89.72 per barrel and $56.62 per barrel for coal/biomass. Electricity and water were used at $186.4 per barrel and $73 per barrel, respectively.

Operating Costs (Thou$)

OPEX	$/day - Coal	$/day – Coal/Biomass	$/bbl - Coal	$/bbl – Coal/Biomass
Coal Feed	56.59		89.72	-
Coal/ Biomass Feed		33.71 + 15.60	-	38.70 + 17.91
Catalyst/ Chemicals				
Labor/ Overhead	3000	3000	3000	3000
Administrative				
Maintenance & Materials	800	800	800	800
Other Operating Costs				
Electricity	186.40	186.40	295.55	214.01
Water	72.96	72.96	126.78	91.80
Natural Gas	0.40	0.62	0.63	0.71
Oxygen	102.2	101.6	162.02	116.67
Amine replacement cost @ 2kg per day	6.17	6.17	6.17	6.17
F-T Catalyst replacement cost (@ 0.5 lb per barrel	163.67	163.67	163.67	163.67
Op Costs	**4388**	**4381**	**4644**	**4449**

Table 12: Operating Costs of the Pilot Plant

The data used in this analysis are actual data from the pilot plant and are adequately accurate. However, the simple comparison made here of the economics of the coal-only and coal/biomass trial runs is made without detailed engineering and economic analysis and, are therefore, at best an approximation. As a result of the limitations and/or restrictions placed on the process; the capacity of the gasification unit relative to the capacity of the F-T reactors, pressure drop in the F-T catalyst bed, and the high viscous nature of the coal/biomass feedstock, a direct comparison could not be made between the coal-only and coal/biomass trial runs.

Capital equipment costs for the pilot plant are given below in **Table 13**.

CAPEX	
Gasifier and Coal/Biomass Feed Prep and Handling	$680
Syngas Cleaning – Acid Gas Removal [AGR]	$1,290
Air Separation and Compression	$181
Water-gas- Shift and F-T Synthesis	$2,227
House Gas-Compressed Air/Nitrogen	$94
Instrumentation – Gas Analysis	$114

Buildings and Structures	$1,250
Total Capital Equipment	**$5,836**

Table 13: Capital Costs – 1 BBL/day CBTL Pilot Plant

CONCLUSIONS

Main Outcome - A Long-term Platform for Future Research

Beyond the specific technical outcomes and results of this project which are discussed below, the main outcome was to finish the design, construction and commissioning of an integrated coal/biomass-to-liquids (CBTL) facility at a capacity of 1 bbl./day at the University of Kentucky Center for Applied Energy Research (UK-CAER). Going forward the facility made possible through this grant will be an important syngas production facility for a variety of future and complimentary research. With respect to on-going research, environmental considerations, particularly how to manage and reduce carbon dioxide emissions from CBTL facilities and from use of the fuels, will be a primary research objective. In addition, research at this new CBTL facility will focus on: Feed Preparation, Characteristics & Quality; Coal & Biomass Gasification; Gas Clean-up/Conditioning; Gas Conversion by F-T Synthesis; Product Work-up and Refining; and Systems Analysis and Integration.

Moreover, the facility was purposely designed for modular, skid-mounted processing units, anticipating frequent change-outs; "plug and play"; and future re-purposing. In this respect, the gasifier was purposely designed to provide twice the flows needed for the F-T refinery section to accommodate other slipstream studies; that being at a capacity of 2 bbl. /day gas output [1-ton coal-biomass feed/day; 179 lb./hr. total flow; 65 lb./hr. CO; 3.49 lb./hr. H2]. For research purposes the gasifier can run in a range of 40-120% of its rated capacity which provides the ability to ramp up/down and provide slipstreams for multiple downstream units. The facility has been designed to permit maximum flexibility with the view that it will be an important syngas production facility for a variety of complimentary research, including, for example, as a mid-capacity test facility for first-of-kind carbon capture technologies.

On an on-going basis, the know-how, show-how associated with the facility is expected to be a key benefit, which can be used as test beds for new technologies and concepts at a level of expenditure that is affordable. It will provide open-access facilities and information in the public domain to aid the wider scientific and industrial community, and a means to independently review vendor claims and validate fuel performance and quality. The facility will be used to build up human capital – the future generation of skilled energy technologists, engineers and operating personnel that will be needed to sustain a CBTL industry. And, one of the best ways of creating this skills base is to stimulate and fund RD+D at appropriate institutions which have the facilities to teach and train students in the practical application of science and engineering.

The CBTL facility has already attracted one new award from DOE directly related to improvements for staging the OMB gasifier and adding a fifth burner. UK-CAER's entry into gasification technologies also led to a second award from DOE for a FEED study and preliminary design of a small, modular gasifier for CHP. In addition, a number of subscribers

and research partners have expressed interest in employing the facility for studies related to, among other topics, membranes for CO_2 separation, improved water-gas-shift catalysts, and sensors and controls for gasification.

Specific Results and Conclusions

1) Feed Handling and Preparation Studies

Significant work on coal slurry preparation resulted in stable slurries of up to 60wt% coal (40wt% water), although slurries with lower solids contents were utilized during production runs to aid ease of operation and prevent plugging of process lines. In addition, coal/biomass slurry prep was investigated. The initial goal was to utilize a coal/biomass mix of 10% torrefied wood and 90% coal to make liquid fuels [diesel, etc.] competitive "well-head to wheels" with petroleum on a CO_2 basis. However, coal/biomass slurry preparation was significantly more challenging than coal-only slurries, owing to serious viscosity and pumpability issues associated with torrefied wood at this weight percent. A 10 wt% torrefied biomass addition absorbed all of the free water in the slurry, resulting in a thick slurry paste that could neither be tested with a viscometer nor pumped. Similarly, 5 wt% torrefied wood had a viscosity 50% higher than the coal-only slurry and a 1 wt% torrefied wood slurry had a 10% higher viscosity compared to coal. As a consequence, the coal/biomass slurry utilizing 5 wt% torrefied wood required considerable dilution with more water than the coal-only slurry [and increase from 40 wt% water to 50 wt% water]. This resulted in serious penalties, among them, a ~20% drop in overall heating value of the slurry for which additional natural gas was required to maintain gasifier operating temperatures. Much work remains to be done to improve the feed-ability of coal/biomass mixtures, including investigations of potentially hybrid dual-feed systems for both wet and dry feeding.

2) Summary Comparison of Coal-only and Coal/Biomass Production Runs

For the gasification section process conditions were relatively similar, except for the addition of biomass in the feed slurry and the additional natural gas needed to maintain temperature of the system. The syngas produced was also similar in nature except that flow rate was lower for the coal/biomass operation and concentrations of H_2, CO and CO_2 were slightly lower. It is interesting to note that the H_2/CO ratio out of the gasifier for both operations was almost identical. WGS reactor temperature was higher for the coal/biomass operation which resulted in higher H_2/CO ratios downstream. AGR operation was basically identical for both sets of operation data, with removal of more than 97% of the CO_2 from the shifted gas. Finally, the F-T conditions were different enough that conversion and selectivity between the two operations was significantly impacted. The coal biomass had a much higher H_2/CO inlet ratio, lower pressure and higher operating temperature than the coal only run. These factors all contributed to higher CO conversion, while also preferentially producing shorter chain hydrocarbons for the coal/biomass F-T operation. Based on significant experience in the F-T field, had the operation conditions (Pressure, Temperature and inlet H2/CO ration) been the same for both operations then the product conversion and selectivity's would have been identical. Accordingly, all differences in data can be easily attributed to the different operating conditions. And, owing to these differences in operating conditions and feedstocks, a direct comparison between runs with regards to CO_2 emissions and product yield and selectivity could not be made based on the initial runs.

While a direct comparison could not be made, feed, product data and emissions are discussed below. For the coal-only run, a feed of 0.61 TPD coal and 0.41 TPD water, representing 59.8 and 40.2 wt. %, respectively. For the coal/biomass run, 0.36 TPD coal, 0.02 TPD torrefied biomass and 0.36 TPD water were used, representing 48.7, 2.6, and 48.7 wt.%, respectively. To maintain temperature stability in the gasifier, the production runs were supplemented with a small feed of natural gas. The coal-only run consumed 0.11 tons of NG per barrel of products compared to 0.13 tons of NG per barrel of products for the coal-biomass run [greater additions of NG were required because of the greater amount of dilution [water] needed for the coal/biomass run. For the coal-only run, 0.16 BPD of naphtha and 0.16 BPD diesel was produced, representing 0.27 equivalent diesel. Product yields were higher for the coal-biomass process, at 0.22 BPD of naphtha and 0.18 BPD diesel with 0.34 equivalent diesel. A total product slate of 0.63 BPD products was produced from the coal-only run, whereas the coal-biomass run produced a total product slate of 0.87 BPD in a single pass of the syngas to the F-T process. The higher product yields in the coal-biomass run relative to the coal-only run can be attributed to the different operating conditions of the F-T reactor which produced higher conversions, in addition to the higher input of natural gas that was required for the coal-biomass run. The light products (C1 - C5) accounted for 61.2 and 69.5% (on BPD basis) of the total products, emphasizing the importance of recycling the lights to produce higher hydrocarbon-chained products (naphtha and diesel). The CO_2 released for the coal-only and coal/biomass runs were 0.77 and 0.72 TPD, respectively, representing 1.22 and 0.83 tons of CO_2 per barrel of total product produced. The lower amount of CO_2 released from the coal/biomass run versus the coalonly run is also partially the result of the higher addition of NG feed for the coal/biomass run, such that the differences in CO_2 emissions between the runs is negligible.

3) Economics of the Pilot Plant

Fixed operating costs included a labor cost of $3000 per barrel of product (for a crew of 3 shifts with 2 technicians per shift) and $800 per barrel for materials and maintenance costs. It should be noted that these are the actual costs associated for operation of this pilot plant for this operation. It is expected that costs will be higher for future operations, especially longer campaigns, for additional staff and shifts. The purchase cost of the coal was $91.7 per ton and torrefied wood (biomass) at $737.4 per ton. The variable operating costs included the cost of coal at $89.72 per barrel and $56.62 per barrel for coal/biomass. Electricity and water were used at $186.4 per barrel and $73 per barrel, respectively. The pilot plant required a capital investment of $5.3M for site improvements, buildings and structures, and equipment costs for the upstream and downstream process units.

GRAPHICAL MATERIALS LIST

REFERENCES

1. *State of the Gasification Industry: Worldwide Gasification Database 2014 Update*. **Higman, C.** Washington, DC : Gasification Technologies Conference, 2014.

LIST OF ACRONYMS AND ABBREVIATIONS

AGR: Acid Gas Removal
BET: Brunauer-Emmett-Teller Surface Area Analysis
BJH: Barrett-Joyner-Halenda Pore Size and Volume Analysis
BOP: Balance of Plant
BPD: Barrels Per Day
CBTL: Coal/Biomass to Liquids
CEEDI: China Electronics Engineering Design Institute
CHER: Compact Heat Exchange Reactor
CHP: Combined Heat and Power
CSTR: Continuous Stirred Tank Reactor
CTL: Coal to Liquids
ECUST: East China University of Science and Technology
FAT: Factory Acceptance Test
FEED: Front End Engineering Design
FT: Fischer-Tropsch
FTS: Fischer-Tropsch Synthesis
GC: Gas Chromatograph
ICP: Inductively Coupled Plasma
NG: Natural Gas
OMB: Opposed Multi-Burner
PHA: Process Hazard Analysis
P&ID: Piping and Instrumentation Diagram
RD+D: Research, Development and Deployment
SS: Sour Shift
SV: Superficial Velocity or Space Velocity
TPD: Tons Per Day
TPR: Temperature Programmed Reduction
UKy-CAER: University of Kentucky – Center for Applied Energy Research
WGS: Water-Gas Shift