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ABSTRACT

Battelle has demonstrated a novel and potentially breakthrough technology for a direct coal-to-liquids (CTL) process for producing jet fuel using biomass-derived coal solvents (bio-solvents). The Battelle process offers a significant reduction in capital and operating costs and a substantial reduction in greenhouse gas (GHG) emissions, without requiring carbon capture and storage (CCS). The results of the project are the advancement of three steps of the hybrid coal/biomass-to-jet fuel process to the technology readiness level (TRL) of 5. The project objectives were achieved over two phases. In Phase 1, all three major process steps were explored and refined at bench-scale, including: (1) biomass conversion to high hydrogen-donor bio-solvent; (2) coal dissolution in biomass-derived bio-solvent, without requiring molecular H_2, to produce a synthetic crude (syncrude); and (3) two-stage catalytic hydrotreating/hydrogenation of syncrude to jet fuel and other distillates. In Phase 2, all three subsystems of the CTL process were scaled up to a pre-pilot scale, and an economic analysis was carried out.

A total of over 40 bio-solvents were identified and prepared. The most unique attribute of Battelle's bio-solvents is their ability to provide much-needed hydrogen to liquefy coal and thus increase its hydrogen content so much that the resulting syncrude is liquid at room temperature. Based on the laboratory-scale testing with bituminous coals from Ohio and West Virginia, a total of 12 novel bio-solvent met the goal of greater than 80% coal solubility, with 8 bio-solvents being as good as or better than a well-known but expensive hydrogen-donor solvent, tetralin.

The Battelle CTL process was then scaled up to 1 ton/day (1TPD) at a pre-pilot facility operated in Morgantown, WV. These tests were conducted, in part, to produce enough material for syncrude-upgrading testing.

To convert the Battelle-CTL syncrude into a form suitable as a blending stock for jet turbine fuel, a two-step catalytic upgrading process was developed at laboratory scale and then demonstrated at pre-pilot scale facility in Pittsburg, PA. Several drums of distillate products were produced, which were then distilled into unblended (neat) synthetic jet fuel and diesel products for a detailed characterization. Based on a detailed characterization of the synthetic jet fuel, a 20% synthetic, 80% commercial jet fuel blend was prepared, which met all specifications. An analysis of the synthetic diesel product showed that it has the promise of being a drop-in fuel as super-low (less than 15 ppm)-sulfur diesel fuel.

A detailed economic analysis showed that the Battelle liquefaction process is economical at between 1000 metric tons/day (MT/day) and 2000 MT/day. The unit capital cost for Battelle CTL process for making jet fuel is $50K/daily bbl compared to $151K/daily bbl for indirect CTL, based on 2011 dollars. The jet-fuel selling cost at the refinery, including a 12% capital cost factor (which included profit), for the Battelle CTL process is $61/bbl ($1.45/gallon). This is competitive with crude oil price of $48/bbl. At the same time, the GHG emissions of 3.56 MT CO_2/MT fuel were lower than the GHG emissions of 3.79 MT CO_2/MTfuel for petroleum-based fuels and 7.77 MT CO_2/MT fuel for indirect CTL. Thus, the use of bio-solvents completely eliminates the need for carbon capture in the case of Battelle CTL process. The superior economics and low GHG emissions for the Battelle CTL process has thus sparked worldwide interest and some potential commercialization opportunities are emerging.

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1.0 EXECUTIVE SUMMARY

Battelle has demonstrated a novel and potentially breakthrough technology for a direct coal-to-liquids (CTL) process for producing jet fuel using biomass-derived coal solvents (bio-solvents). The Battelle process offers a significant reduction in capital and operating costs and a substantial reduction in greenhouse gas (GHG) emissions, without requiring carbon capture and storage (CCS). The results of the project are the advancement of three steps of the hybrid coal/biomass-to-jet fuel process to the technology readiness level (TRL) of 5. The project objectives were achieved over two phases. In Phase 1, all major process steps were explored and refined at bench-scale, including: (1) biomass conversion to high hydrogen-donor bio-solvent; (2) coal dissolution in biomass-derived bio-solvent, without requiring molecular H_2, to produce a synthetic crude (syncrude); and (3) two-stage catalytic hydrotreating/hydrogenation of syncrude to jet fuel and other distillates. In Phase 2, all three subsystems of the CTL process were scaled up to a pre-pilot scale.

Biomass-Derived Bio-solvents. While the goal of Phase 1 was to identify and prepare 6 hydrogen-donor bio-solvents, we actually prepared a total of over 40 bio-solvents. The raw materials for these, mostly non-edible bio-solvents, are believed to be readily available around the world. In some cases, the biomass feedstocks are commercially available from specialty chemical companies though none have previously been used for CTL processing. In many cases, commercially-available feedstocks had to be modified by Battelle to provide the desired solvation and other physical properties. The most unique attribute of Battelle's bio-solvents is their ability to provide much-needed hydrogen to liquefy coal and thus increase its hydrogen content so much that the resulting syncrude is liquid at room temperature.

Direct Coal Liquefaction. Coal liquefaction tests were done in several different reactor systems. The majority of parametric testing, especially to down-select preferred bio-solvents, was done at Battelle, using a 0.5L autoclave system. The resulting products were analyzed to determine the coal solubility, defined as the yield of THF-soluble fraction. The viscosity of the THF-free syncrude was also measured at 50°C to assess the degree of hydrogen transferred from the bio-solvent to coal-derived liquids. The initial testing was done with a bituminous coal from West Virginia, followed by more extensive testing on an Ohio bituminous coal. The various bio-solvents were compared to tetralin, which is a well-known hydrogen-donor solvent, as well as soybean oil, which was referenced in prior art. The Battelle tests showed that a total of 12 novel bio-solvent met the goal of greater than 80% coal solubility, with 8 bio-solvents being as good as or better than tetralin. On the other hand, soybean oil gave solubility below 70% and the product was very viscous. The viscosity of the product with preferred bio-solvents was an order-of-magnitude lower than with soybean oil. The solubility goal was also met with a sub-bituminous coal from the Powder River Basin. The Battelle parametric testing was supported by microcatalytic-reactor testing by Pennsylvania State University (PSU).

The Battelle CTL process was scaled up to 1 ton/day (1TPD) at a pre-pilot facility operated in Morgantown, WV by Quantex. These tests were conducted, in part, to produce enough material for syncrude-upgrading testing. The Quantex plant required several changes to adequately carry out liquefaction. The preliminary data show that the solubility and syncrude viscosity are comparable to those attained during autoclave testing at Battelle.

Upgrading the CTL Syncrude to Distillates. To convert the Battelle-CTL syncrude into a form suitable as a blending stock for jet turbine fuel, a two-step catalytic upgrading process was developed at laboratory scale and then demonstrated at pre-pilot scale facility operated by Intertek. For the first step (Stage-1), a number of commercially-available hydrotreatment catalysts were tested for removal of heteroatoms, most notably sulfur, nitrogen, and oxygen. A proprietary, sulfided catalyst was selected for demonstration. For Stage-2, two proprietary catalysts for cracking and hydrogenation of Stage-1 product were successfully demonstrated at pre-pilot scale. Several drums of distillate products were produced, which were then distilled into unblended (neat) synthetic jet fuel and diesel products for a detailed characterization.

Characterization of Distillate Fraction as Jet Fuel or Diesel. A synthetic jet-fuel produced from the Battelle CTL process was evaluated by UDRI to determine potential suitability for use in aviation applications. Efforts focused on testing of the specification and limited Fit-For-Purpose (FFP) properties of the neat synthetic fuel and a blend with petroleum-derived aviation fuel, and followed recommended protocols for certification of synthetic fuels for commercial and military applications. Analyses of the neat synthetic fuel indicated it was not feasible to use the current formulation as a direct “drop-in” fuel as a couple of the properties did not conform to required Jet A/JP-8 specification requirements. Overall, the results indicate that the synthetic fuel has the potential for use as a synthetic blending feedstock for aviation applications. Based on the analyses and testing, it appears feasible to make slight modifications to the syncrude upgrading process to better tailor the final synthetic fuel to aviation applications. An analysis of the synthetic diesel product showed that it has the promise of being a drop-in fuel as super-low (less than 15 ppm)-sulfur diesel fuel.

Economic Analysis. A detailed economic analysis was carried out to show that the liquefaction process is economical at between 1000 metric tons/day (MTPD) and 2000 MTPD, which is an order of magnitude smaller than commercially-available indirect CTL processes. The elimination of the need for gaseous hydrogen and a catalyst in the Battelle liquefaction process leads to process simplifications that greatly reduce capital and operating costs. A plant design using 4 Battelle CTL plants and a single syncrude upgrading plant producing 32,000 barrels (bbl) per day of jet fuel (and/or diesel) was compared to a 19,000 MTPD FT-technology based indirect CTL plant producing 50,000 bbl/day (BPD) of jet fuel plus diesel plus naphtha. The unit capital cost for Battelle CTL process is $50K/daily bbl compared to $151K/daily bbl for indirect CTL, using 2011 costing basis required by DOE. The jet-fuel selling cost at the refinery, including a 12% capital cost factor (which included profit), for the Battelle CTL process is $58/bbl ($1.38/gallon). This is competitive with crude oil price of $46/bbl. The selling price for the indirect CTL process was much higher at $95/bbl. An analysis also showed that the unrefined syncrude from the Battelle CTL process could also be sold to petroleum refineries at $32/bbl. No premiums were placed on either the syncrude or the jet fuel or diesel from the Battelle CTL process for having an ~40% bio-content. This however was a major factor in meeting the GHG reduction goals.

Greenhouse Gas (GHG) Analysis. A GHG emissions analysis was performed by Prof Bhavik Bakshi of The Ohio State University (OSU). The total GHG emissions from well (for petroleum) or coal mine/biomass-feedstocks source-to-wheels (e.g., well-to-wheels [WTW] for petroleum-based jet fuel) were estimated. While the baseline WTW value for petroleum-based jet is 3.79 MT CO_2/MT fuel, the Battelle-CTL jet fuel GHG emissions were somewhat lower at 3.56 MT CO_2/MT fuel. On the other hand, the GHG emissions on the same basis for FT-based jet fuel was much higher at 7.77 MT CO_2/MT fuel. For the FT process to meet the Section 526 of EISA 2007 goal of being no worse than petroleum-to-jet baseline, about 90% of the pre-combustion GHG emissions from CTL will need to be controlled by CCS. However, no CCS will be required for the Battelle CTL process.

The superior economics and low GHG emissions for the Battelle CTL process has thus sparked worldwide interest and some potential commercialization opportunities are emerging. Thus, the project goal of demonstrating a fast, straight forward path to commercialization has also been achieved through this project.

2.0 PROJECT OBJECTIVES

Battelle has invented a potentially breakthrough direct coal-to-liquids (CTL) technology using biomass-derived solvents. The objectives of this project were as follows:

1. Advance the Battelle CTL process technology to technology readiness level (TRL) 5, which involved pre-pilot-plant scale testing.
2. Demonstrate that the process is applicable to a variety of coals, achieving at least 80% coal conversion to synthetic crude (syncrude).
3. Demonstrate that the syncrude from the Battelle CTL process can be upgraded to jet fuel and, if desired, diesel.
4. Demonstrate that the process can substantially reduce capital and operating costs of coal-to-jet fuel, making it competitive at today's crude-oil prices.
5. Demonstrate that the process can achieve substantial reduction in greenhouse gas (GHG) emissions without using carbon capture and storage (CCS).

3.0 PROJECT DESCRIPTION

The project objectives were accomplished over a 3-year, 5-task R&D effort to advance the hybrid, direct CTL process for jet fuel to a TRL of 5. The three major Subsystems of the process – biomass to bio-solvent conversion, coal dissolution and demineralization to produce a syncrude, and hydrotreatment/ hydrogenation of the syncrude to jet fuel – were developed and tested in batch/lab-scale, bench-scale, and then at pre-pilot scale. The project objectives were achieved over two phases. In Phase 1, all major process steps were explored and refined at continuous bench-scale, including: (1) biomass conversion to high hydrogen-donor bio-solvent; (2) coal dissolution in biomass-derived bio-solvent, without requiring molecular H_2, to produce a syncrude; and (3) two-stage catalytic hydrotreating/hydrogenation of syncrude to jet fuel and other distillates. In Phase 2, these same process steps were scaled-up to continuous, pre-pilot scale, allowing realistic estimates of process economics and GHG emissions reduction, thus defining the path for widespread process commercialization in a short time period. The process meets the requirements of Section 526 of Energy Independence and Security Act of 2007 (EISA 2007) without requiring CCS, and it should help reduce the dependence on imported petroleum crude for jet fuel production. More information on each task is provided below.

Phase 1

Task 1 - Lab/Bench-Scale Coal Liquefaction and Syncrude Hydrotreating/Hydrogenation. Several combinations of coals and bio-solvents were tested at laboratory- and bench-scale to determine preferred operating conditions for the scale-up of the coal liquefaction Subsystem to 1 ton per day (1 TPD) pre-pilot scale in Task 2. Additionally, a two-stage catalytic system was tested for upgrading the syncrude to jet fuel. Several catalysts were screened at laboratory-scale to determine the preferred conditions for scale-up to one barrel per day (BPD) pre-pilot scale in Task 3. This task was supported by four Battelle subcontractors: Pennsylvania State University (PSU), University of Dayton Research Institute (UDRI), Advanced Research Associates (ARA), and Quantex.

Task 2 – Pre-Pilot-Scale Coal Liquefaction and Syncrude Production. A 1 TPD coal liquefaction pre-pilot plant was tested at the Quantex facility in Morgantown, WV. Several hundred gallons of syncrude were produced for upgrading to jet fuel in Task

Phase 2

Task 3 – Pre-Pilot-Scale Syncrude Hydrotreating /Hydrogenation to Jet Fuel. The syncrude from Task 2 was upgraded to a distillate product, which was fractionated into jet fuel and diesel fractions at the Intertek facility near Pittsburgh, PA, employing catalysts and operating conditions determined in Task 1. The jet fuel was analyzed against the commercial Jet-A specifications. Some “Fuel-fit-for-use” testing was also performed, with the testing conducted by UDRI. A diesel product was also characterized.

Task 4 – Conceptual Plant Design and Process Economics. Battelle completed a comprehensive conceptual plant design and utilized the design for a techno-economic analysis (TEA), following DOE/NETL guidelines.

Task 5 – Greenhouse Gas (GHG) Emission Analysis. A GHG life-cycle emissions analysis was performed, using DOE/NETL and USAF guidelines, to demonstrate progress towards meeting requirement of Section 526 of EISA 2007.

This is a Final Report on the 2-phase project.

4.0 DIRECT CTL BACKGROUND AND DESCRIPTION OF THE BATTELLE CTL PROCESS

4.1 Direct CTL Background

The U.S. DOE-supported direct CTL programs in the 1970s and 1980s included solvent-refined coal (SRC), H-Coal, Exxon Donor Solvent (EDS), and other two-stage liquefaction processes. The DOE's focus was on direct CTL since it had a significantly higher thermal efficiency than indirect CTL using the coal gasification plus Fischer-Tropsch (FT) route. Most R&D and demonstration efforts were stopped in the late 1980s due to escalating cost estimates for CTL and very low petroleum crude prices. During the last decade, CTL has received renewed interest, though the focus of recent R&D has been indirect CTL. In many respects, direct CTL is more appealing than indirect CTL relative to the priority objectives of this project. First, it is possible with direct CTL, by carefully dissolving, depolymerizing, and hydrotreating coal, to produce acceptable jet fuel without blending in petroleum-based jet fuel. Indirect CTL, e.g., via FT route, converts a highly aromatic coal structure to a linear, paraffinic structure, which is unacceptable as JP-8 or Jet-A, as those fuels require a minimum of 8% aromatics, and hence must be blended with petroleum-based jet fuel, per Military (Mil-DTL-83133H w/Amendment 1–Tables A-II & B-II) and Commercial (ASTM D7566-12A–Table 1, Part 2) specifications. Second, a carefully controlled direct CTL process, such as the one Battelle is developing, is thermodynamically more efficient in terms of yield than the indirect CTL approach of converting coal to synthesis gas and then recombining to make condensable liquids. The higher expected thermal efficiency of direct CTL drives a reduction in greenhouse gas (GHG) emissions per gallon of jet fuel produced.

4.2 Battelle's Novel Direct CTL Process

Battelle has developed a hybrid CTL process that uses a significant amount of biomass for direct CTL in its innovative approach. The hybrid CTL process includes three basic steps: (a) biomass conversion to a high hydrogen-donor (H-donor) bio-solvent; (b) coal dissolution in novel biomass-derived solvent without molecular H_2; and (c) syncrude hydrotreating/hydrogenation to jet fuel.

State-of-the-art direct CTL processes first quickly depolymerizes/dissolves the coal, typically in a coal-derived solvent, and then these slowly hydrotreat the solution to break up large molecules, remove heteroatoms (e.g., S, N, O), and increase the H/C atomic ratio. The resulting syncrude can be further refined by hydrotreating to various distillate fuels, a portion of which may be jet fuel. Battelle has investigated ways to overcome several disadvantages of current direct CTL. First, the GHG emissions for current CTL jet fuel are about twice that for petroleum jet fuel, so it would be necessary to capture 90% CO_2 at the CTL plant to meet the CTL GHG emissions reduction goal. Second, a straightforward process for dissolving coal and biomass in a solvent has not been practical, partly because of the high moisture content of biomass. Third, the H/C atomic ratio in a typical bituminous coal is about 0.80, while it is about 1.90 for jet fuel, so a large amount of H_2 must be added to coal, which contributes to high GHG emissions, and drives up capital and operating costs for current direct CTL processes. In particular, with processes that both dissolve coal and hydrotreat in one step, the high temperature (~450°C) and pressure (~2500 psig) requirements make the reactor costs uneconomically high, cause equipment erosion, and utilize H_2 inefficiently due to excessive production of lighter hydrocarbons. Finally, the yield of jet fuel vs. diesel is significantly less in these current direct CTL processes than for FT-based jet fuel production.

To address these concerns, Battelle has developed a hybrid CTL process that uses a significant amount of biomass for direct CTL in an innovative approach, as shown in Figure 1.

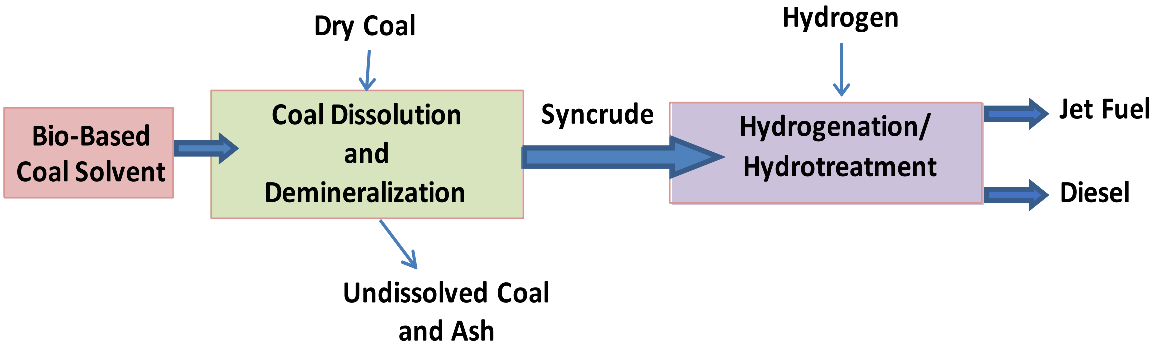

Figure 1. Battelle's novel, direct CTL process proposed by Battelle.

As currently conceived, the Battelle Direct CTL process has three major Subsystems including: (1) biomass conversion to high hydrogen-donor solvent; (2) coal dissolution in biomass-derived solvent without molecular H_2; and (3) 2-stage catalytic hydrotreating/hydrogenation to jet fuel and other distillates. In Subsystem 1, biomass, derived primarily from non-food sources, is converted to a bio-solvent in processing plants that are economical at smaller scale (≤100 TPD). The resulting bio-solvents, with a H/C atomic ratio above about 1.40, are delivered to a larger coal dissolution/demineralization facility (≥1,000 TPD) in Subsystem 2. Based on data on solvent refining of coal published by Longanbach and Chauhan of Battelle in late 1970s, and more recently confirmed by West Virginia University as well as by Battelle project team member Quantex, coal can be dissolved quickly (in <10 minutes) at mild conditions (~400°C and 500-800 psig) with addition of only 0.3–0.5% hydrogen, by weight of coal, which increases the H/C molar ratio from about 0.80 to 0.86 [1-4]. The bio-solvents can be engineered to alter the nature and quantities of the cyclic/aromatic and linear species with desired hydrogen-donor properties.

Based on the low hydrogen-addition requirements to dissolve coal, as little as 10% of bio-solvents based on weight of coal is sufficient without requiring any gaseous H_2, and thus minimizing CO_2 emissions at the CTL plant (Subsystem 2). However, larger amounts of bio-solvent input will not only help meet the GHG reduction goal without CO_2 capture, but also reduce the viscosity of the synthetic crude (syncrude), improving separation of ash and unconverted coal. Further, the larger quantity of bio-solvent helps produce a jet fuel that has a more manageable balance of aromatic and non-aromatic species, thus overcoming a significant limitation of current direct CTL. The solvent/coal weight ratio is expected to be about 2.5, so a portion of the solvent, including some coal-derived liquids, will need to be recycled after solid/liquid separation.

In Subsystem 3, the syncrude from the liquefaction plant can be catalytically hydrotreated/hydrogenated at either a petroleum refinery or a facility dedicated to maximizing jet fuel production. This is the location where all the molecular H_2 will be added. The overall, gaseous H_2 requirements for the Battelle CTL process are expected to be substantially less than for the H-Coal or EDS processes. We also expect the yield of jet fuel to be much higher than from H-Coal or EDS processes.

Battelle's approach is to use novel, biomass-derived solvents with high hydrogen-donor capacity. These bio-solvents can be engineered to have significant amounts of cyclic/aromatic compounds (>20%) and a controllable H/C ratio, with good hydrogen-donor capabilities. The objective was to achieve as good hydrogen donor performance as with the well-known solvent tetralin, used in the EDS process as well as tested for direct CTL for the last 75+ years, but with solvents that are biomass-derived and cheaper than tetralin.

4.3 Potential Benefits of the Battelle Direct CTL Process

Battelle's hybrid CTL process offers these specific advantages: (a) straightforward system integration of proven process steps; (b) improved process reliability due to mild liquefaction operating conditions (less than 800 vs. 2500 psig); (c) elimination of CCS at coal liquefaction site as well at the syncrude refining site; (d) significant reduction in molecular H_2 requirement for syncrude refining; (e) increased aromatic content and density of jet fuel close to that of JP-8; (f) short time period to commercialization; (g) significant reduction in the capital and operating costs; and (h) substantial reduction in GHG emissions.

The Battelle CTL technology helps achieve the GHG emissions reduction goal of this project, unlike state-of-the-art CTL technologies, without requiring CCS. The key reasons for this are as follows:

- A major portion of the coal is replaced by biomass, which will significantly reduce the GHG footprint of this hybrid CTL process.
- The novel biomass-based solvents (bio-solvent) are high in H/C ratio compared to coal. The resulting calculated syncrude H/C ratio, at commercial-scale where some solvent is recycled, is ~1.20, compared to ~0.80 for coal and ~1.60 for crude oil. The single-pass syncrude H/C ratio using no recycle is typically ~1.00. Thus, the H_2 requirements for hydrogenating syncrude to jet fuel (H/C ~1.90) are lowered by as much as 40%, which is a key determinant of GHG emissions during upgrading of syncrude to jet fuel.
- Unlike indirect coal-biomass to liquid (CBTL), where the coal and biomass contributions to jet fuel are only additive or proportionate, Battelle's hybrid, Direct CTL process brings considerable synergy since the bio-solvent carries a significant hydrogen-donor

capability. As a result, up to 90% of the organic fraction of coal can be dissolved without requiring molecular H_2. This means that the GHG emissions in Subsystems 1 and 2 will be less than the GHG credit applicable to the biomass-derived content of the syncrude.

- The ability to operate the coal liquefaction step at mild conditions (~400°C, ~500-800 psig, no gaseous H_2, no catalyst) allows for lower plant-energy requirements leading to further GHG emissions reduction.
- The absence of the vast majority of the mineral matter in syncrude increases catalyst life of the first stage of two-stage hydrotreatment/hydrogenation, which reduces catalyst regeneration requirements, as well as minimizes the wastage of H_2 in producing the lighter, non-jet-fuel fractions.
- The biomass is converted to bio-solvent in small, distributed plants (~100 TPD) near the sources of biomass so the energy and cost required for biomass transport is greatly reduced. Additionally, bio-solvent is easily pumpable compared to cellulosic and other plant biomass. Similarly, smaller coal liquefaction plants (1,000-2,000 TPD) are economical due to use of non-catalytic, mild conditions, so coal transportation energy and cost is reduced as well.

5.0 LAB/BENCH-SCALE COAL LIQUEFACTION

The objectives of this effort were as follows:

- Select various feedstocks for coal liquefaction for exploratory testing
- Demonstrate that at least 80% of coal could be dissolved in biomass-derived solvents
- Perform parametric testing to help identify the preferred operating conditions for scale-up of Subsystems 1 and 2.

5.1 Feedstock Selection

The Battelle CTL process combines coal, coal-derived recycle solvent, and an additional bio-solvent, and then heats the agitated mixture at elevated temperatures and pressures. After the mixture is cooled, mineral matter and undissolved organic matter in coal are removed in a solid-liquid separation step. Finally, the de-ashed, liquefied coal is fractionated in a distillation column to separate the liquefied coal or synthetic crude (syncrude) from the recycle solvent and heavy oil. The heavy oil may be sold as a by-product, or coked to recover more liquefied coal and the coke sold. If desired, the heavy oil may also be hydrocracked with the rest of the syncrude. Other potential, high-value, products from the heavy oil are: (a) binder pitch; (b) anode-grade coke; (c) needle coke; or (d) polyols or other chemicals. The centrifuge cake may be sold as an asphalt additive, burned to generate heat or power, or gasified to generate syngas.

Presented below is a brief discussion of the selection of the three major feedstocks.

5.1.1 Coal

Three coals were selected: (1) a West Virginia (WV) high volatile A, bituminous coking coal[1] from Leer Mine; (2) an Ohio high volatile A, bituminous, coal from Waterloo Coal Company (sample obtained from Bramhi Coal Company), and (3) a Powder River Basin sub-bituminous coal from the Black Thunder Mine. One ton each of the first two coals were acquired and a portion ground to -25 mesh size at Quantex. A drum of the Black Thunder subbituminous coal also was obtained and ground to -25 mesh size at Quantex.

WV Bituminous Coal. During the previous West Virginia University (WVU) coal-liquefaction program, they successfully processed a Lower Kittanning seam, high-volatile A, coking, bituminous coal. Unfortunately, the coal mine in West Virginia where this coal was obtained from has now closed. In reviewing options, Quantex identified a coal from a Lower Kittanning seam about 30 miles from the original site. This coal is from the Leer Mining Complex, located in the town of Grafton in Jackson County, WV; a map showing the location of the mine is presented in Figure 2. The mine is owned by Arch Coal Inc. One ton of this coal was acquired. Four 5-gallon pails of the coal were initially ground by Quantex to a size smaller than 25 mesh

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[1] A high volatile A bituminous coal has a fixed carbon content, on a moisture and ash (MAF) basis, of less than 69 wt%, and volatile matter content, on an MAF basis, of greater than 31 wt%, and a higher heating value (HHV) equal to greater than 14,000 Btu/lb on an MAF basis.

(designated -25 mesh) to support chemical analysis and small scale liquefaction tests. More of this coal was ground to -25 mesh to support the Quantex 1 ton per day (TPD) unit testing.

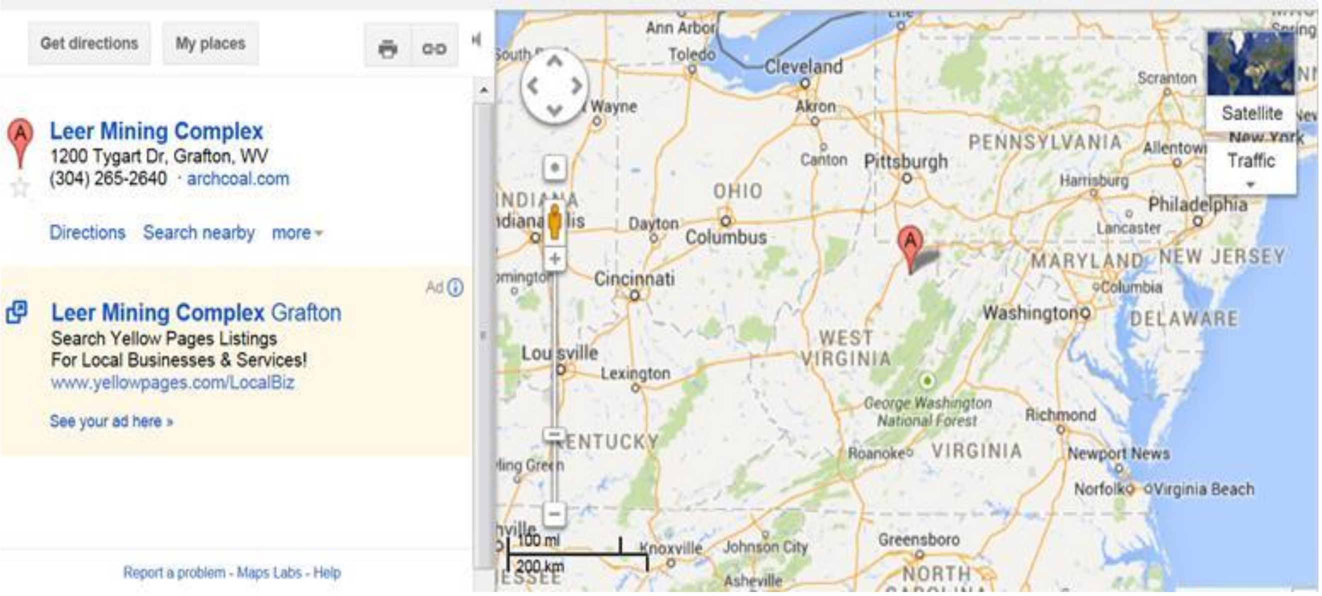

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Figure 2. Location of Leer Mine

Ohio Bituminous Coal. There are three major seams that underlie southeastern OH, western PA and northern OH; see Figure 3. They include the Pittsburgh, Upper Freeport, and Lower Kittanning seams. The Lower Kittanning seam is the largest and is the same seam as was found successful in the WVU liquefaction tests that employed hydrogenated soybean oil [3, 4].

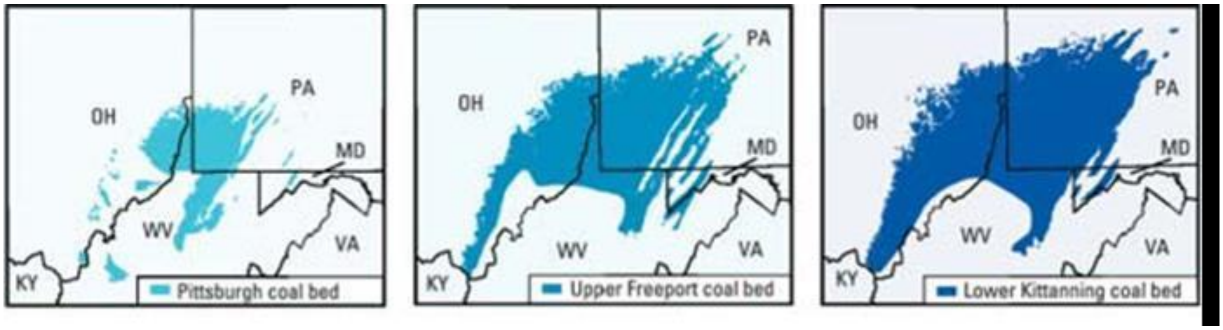


Figure 3. Location of the Lower Kittanning coal seam in PA, OH, and WV

Therefore, the team looked for a Lower Kittanning seam, high-volatile A, coking, bituminous coal in OH and identified existing mines with coal preparation plant in the area. Coal from the Waterloo Coal Plant, was identified. The location of the preparation plant is shown in Figure 4. Leer Coal does not sell directly to the public, but a vendor (Bramhi Coal Company) was identified. Four pails of the Ohio coal were initially ground by Quantex to -25 mesh for analysis and testing. More of this coal was ground to -25 mesh to support the Quantex 1 TPD liquefaction unit testing.

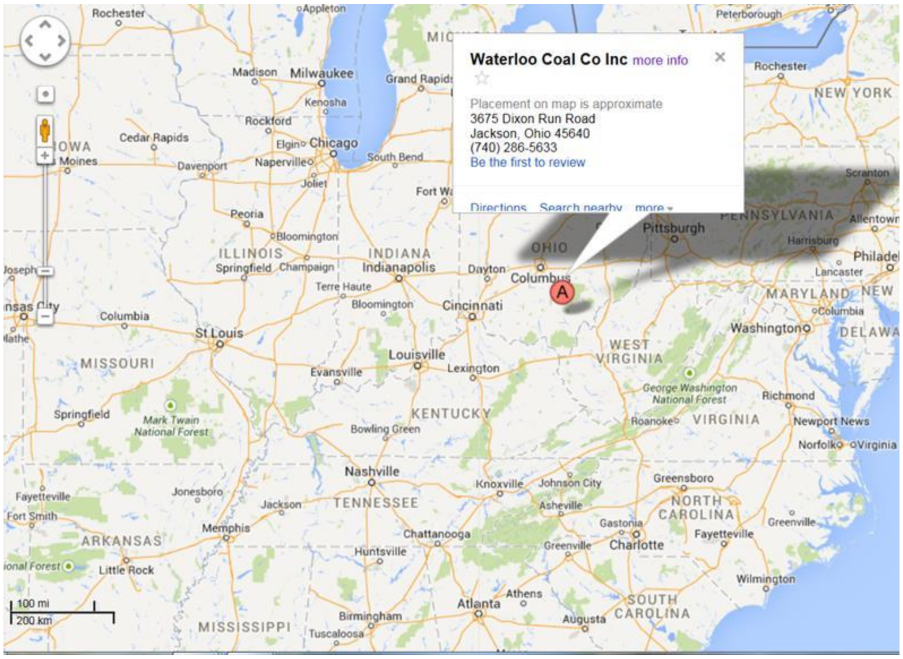


Figure 4. Location of the Waterloo Coal Preparation Plant

Wyoming Subbituminous Coal. WVU also successfully treated lower rank, low-ash coals in their liquefaction process. One of the subbituminous coals processed was Black Thunder coal, surface mined in Wright, WY. The location of the mine is shown in Figure 5 (this figure also shows the mine is located in the Powder River Basin covering southeast Montana and northeast Wyoming).

Figure 5. Location of the Black Thunder Coal Company

Fortunately, this coal is still commercially mined by The Black Thunder Coal Company (owned by Arch Coal, Inc.). A 55-gallon drum of a fresh sample of this coal was obtained.

The Leer (WV) and Waterloo (OH) coals were analyzed for ultimate and proximate analysis, sulfur forms, and Free Swelling Index. The Geisler plasticity was also determined to provide a measure of how easily the coal softens and flows upon heating. Results are shown in Table 1. The analyses are reported on a dry basis, except for moisture content and hydrogen, for which the as received (AR) value is also reported. Typical Black Thunder analyses (obtained from Arch Coal, Inc.) are also included in this table.

Table 1. Coal Analyses

Parameter (Test Method)	Leer Coal Co., WV Coal	Waterloo Coal Co., OH Coal		Black Thunder Coal Co., WY Coal
		Initial Analysis	Repeat Analysis	
Proximate – Dry Basis, Wt%				
Moisture (ASTM D3302)	(4.10 AR)	(8.44 AR)	(9.28 AR)	(27.3 AR)
Ash (ASTM D3174)	11.53	8.90	8.48	7.33
Volatile matter (ASTM D3175)	32.61	40.12	41.40	50.00
Fixed carbon (ASTM D3172)	55.86	50.98	50.12	NR(a)
HHV, Btu/lb (ASTM D5865)	13,431 13,670(b)	NR 13,460(b)	NR 13,410(b)	8,860
Ultimate (ASTM D5373) – Dry Basis, Wt%				
Moisture	(4.10 AR)	(8.44AR)	(9.28 AR)	(27.3 AR)
Ash	11.53	8.90	8.48	7.33
Carbon	74.25	72.84	73.71	NR
Hydrogen(c)	5.32 (5.71 AR)	5.51 (6.31 AR)	5.28 (6.21 AR)	NR
Nitrogen	1.40	1.55	1.56	NR
Sulfur	0.94	2.38	2.17	0.48
Oxygen (by difference)	6.56	8.82	9.20	NR
Sulfur Forms (ASTM D2492) – Dry basis, Wt%				
Total	0.94	2.38	2.17	NR
Pyrite	0.13	1.75	1.46	NR
Sulfate	0.19	0.08	0.10	NR
Organic	0.62	0.55	0.61	NR
Fluidity Measures				
Free Swelling Index (ASTM D720)	7.0	3.0	3.0	0(d)
Gieseler Plasticity (ASTM D2639)				
Max fluidity, DDPM(e)	1404	NA(f)	4	NR
Temp. @ Max. Fluidity, °C	440		420	
Start Temp. (1 DDPM) , °C	402		393	
Final Temp. (1 DDPM) , °C	478		444	
Temperature range, °C	76		51	

(a) NR: Not reported.
(b) Estimated by Dulong formula: HHV = 14,600* C + 62,000* (H – O/8) + 4050* S.
(c) Hydrogen in the water included in the as-received H content.
(d) Expected, like other subbituminous coals, to have a Free Swelling Index (FSI) of approximately zero.
(e) DDPM: Dial division per minute.
(f) NA: Not applicable – the coal was initially found to be non-agglomerating and therefore did not melt or flow; likely oxidized in storage.

Coal parameters expressed on a dry or MAF basis are often used to characterize coal. The coal values on these bases are noted in Table 2.

Table 2. Coal Analyses on a Moisture- and Ash-Free (MAF) Basis

Parameter (Test Method)	Leer Coal Co., WV Coal	Waterloo Coal Co., OH Coal		Black Thunder Coal Co., WY Coal
		Initial Analysis	Repeat Analysis	
Fixed carbon, MAF%	47.31	56.83	55.54	NA
Volatile matter, MAF%	52.69	43.17	44.46	NA
HHV, Btu/lb, MAF%	15,458	13,572	13,448	6,830
Coal Classification	High Volatile A	High Volatile A	High Volatile A	Subbituminous C

5.1.2 Coal-Derived Recycle Solvent

Coal tar distillate (CTD) is used to start the liquefaction process. After a period of time sufficient coal liquids will be generated in the process so they can displace the CTD and very little (≤ 10% based on wt of coal) additional CTD will be required. For the initial liquefaction tests at Battelle, PSU, and Quantex, a Koppers CTD was used. The typical Koppers CTD, used to make carbon black, has a boiling range of 230ºC to 360ºC. However, the Koppers CTD supplied to Quantex a couple of years ago has about 50% boiling above 400ºC, as indicated by the simulated distillation (SimDis) test conducted by PSU (see Figure 6). These two start-up solvents were compared so we could select the correct one for further testing. In any case, this CTD is expected to contain significant quantities of cresol, naphthalene, naphthol, and anthracene.

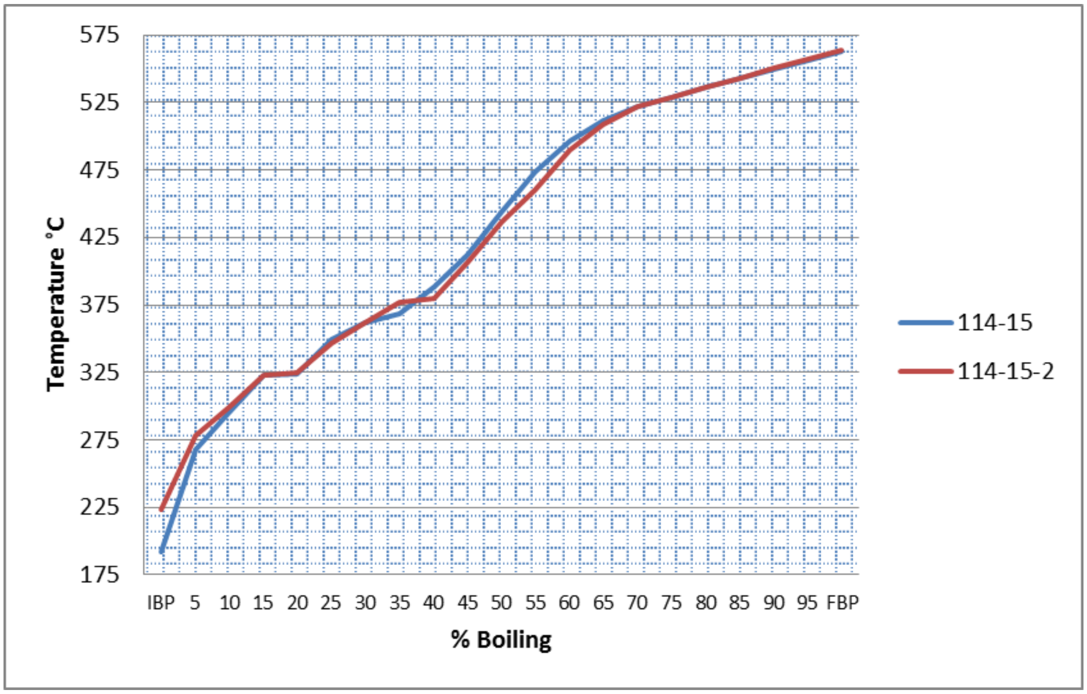


Figure 6. Simulated distillation data for Koppers CTD supplied by Quantex

5.1.3 Bio-solvents

In the initial work at West Virginia University (WVU), a combination of coal, CTD (recycle solvent), and hydrogenated soybean oil was used to liquefy the coal [3, 4]. It is believed by Quantex that the soybean oil facilitated coal depolymerization and the resulting coal dissolution. On the other hand, in Battelle's direct coal liquefaction process, we use a bio-solvent that helps dissolve coal as well as serves as a hydrogen donor to species generated during coal depolymerization/ dissolution. In this fashion, we expect to increase the H/C atomic ratio of coal-derived syncrude without using any molecular hydrogen (H_2). One example of a well-known hydrogen donor-solvent is tetralin, which is expensive and typically not bio-based.

A major effort on this project was the selection, procurement, modification, and liquefaction screening of a number of bio-solvents. Over 40 bio-solvents were prepared and screened. The majority of these bio-solvents were prepared utilizing non-edible biomass, employing proprietary treatment methods. Originally, about 6 bio-solvents were targeted as the testing began with the West Virginia coal. Next, the Ohio coal was tested, during which time many more bio-solvents were identified or became available. As such, most of the bio-solvents were tested on Ohio coal. A very limited amount of testing, with a preferred bio-solvent, was carried out on the Wyoming coal. Some of the bio-solvents were a mixture of two bio-solvents to achieve better hydrogen transfer as well as to facilitate coal depolymerization.

5.2 Laboratory-Scale Coal Liquefaction Testing

5.2.1 Test Objectives

The goal for this effort was to demonstrate the feasibility of Battelle's hybrid, direct CTL process for producing a syncrude using novel bio-solvents without using any molecular H_2. The primary liquefaction testing was performed in Battelle's 0.5 L high temperature, high pressure autoclave in order to achieve a coal solubilization of 80% or greater. Microreactor liquefaction tests were also run at PSU in parallel to Battelle's work to better understand the kinetics of the liquefaction process.

5.2.2 Lab-scale Coal Liquefaction Test Procedures.

The test procedure for the autoclave tests is shown schematically in Figure 7.

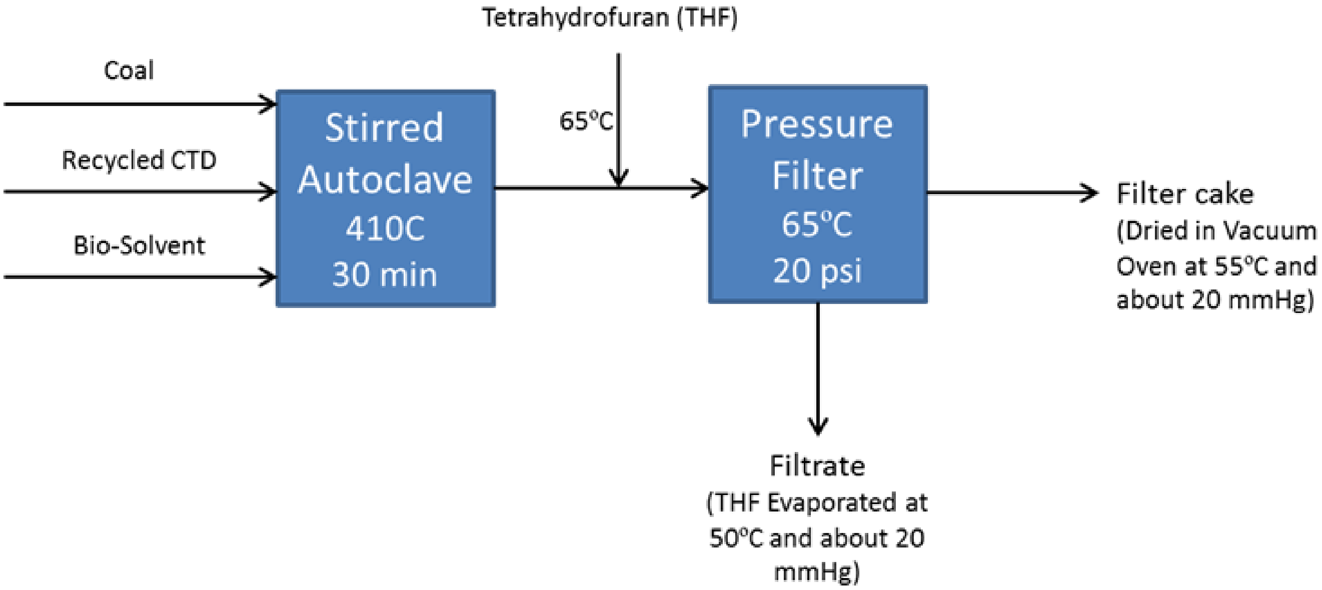


Figure 7. Typical coal-liquefaction processing conditions for 0.5 L autoclave system.

Shown in Figure 8, below, is a photo of the autoclave as well as the 0.5-L cup (i.e., the base of the autoclave).

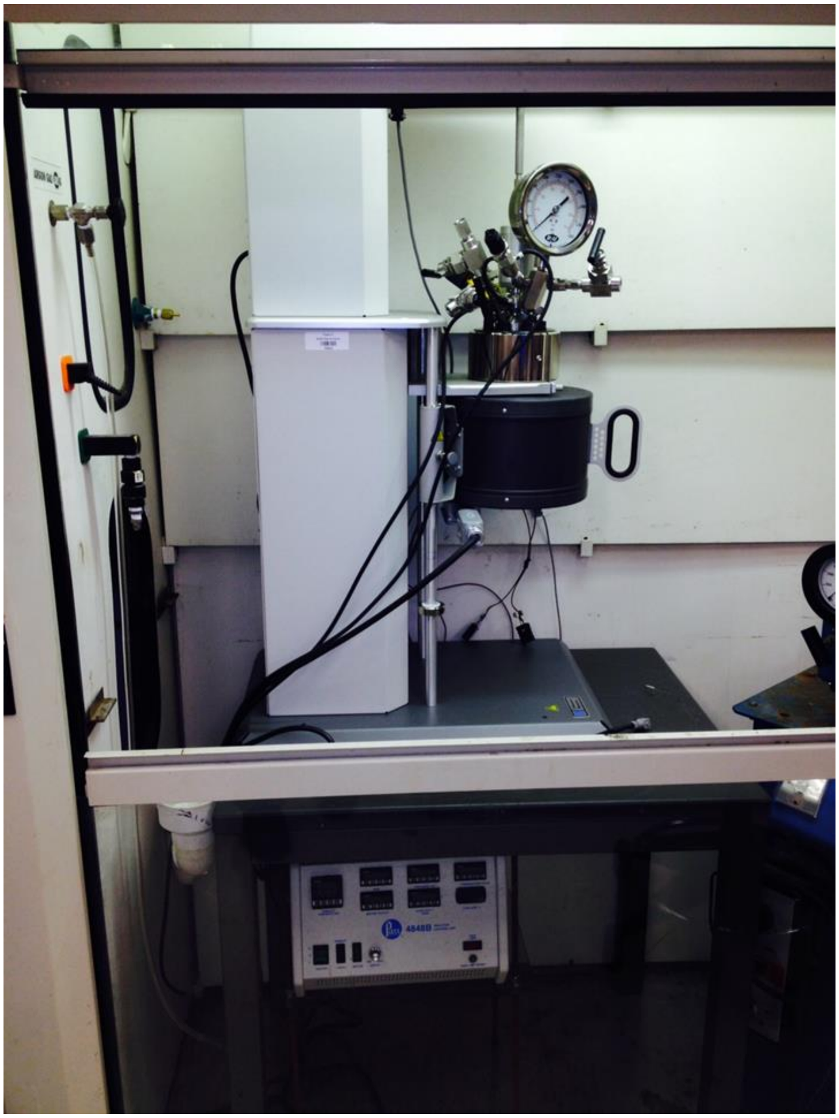


Figure 8. Photograph of 0.5 L autoclave system at Battelle.

After a run, water was passed through a Hastelloy-C coil located within the reactor. This cooled the liquids and allowed us to reduce the pressure to atmospheric level. The retaining bolts were unscrewed and the autoclave head that held the mixing assembly and cooling coil was removed. A low-boiling inert liquid (tetrahydrofuran, THF) was sprayed onto the head, mixing shaft and propeller, and the coil to recover all remnants. Additional THF was added to the cup (the more viscous the product, the more solvent was used).

The contents of the cup were also transferred to a 1 L Erlenmeyer flask. The solution was heated to boiling while being stirred to separate the liquid fraction from the solid particles. This step also speeded up filtration. Once boiling was achieved, it was poured into the top of a pressure-filter. In some cases the Syncrude produced after liquefaction was low viscosity, water-like liquid and was easily transferred. In other cases the product was a thicker, more viscous fluid. In these cases, THF alone could not reduce viscosity enough for effective filtration. For this reason, hot (150°C) dimethylformamide (DMF) was utilized. The recovered liquid and undissolved coal and mineral matter were pressure filtered at up to 40 psig (easy to filter products required less pressure to filter). More inert fluid, THF or DMF, was used to try to recover as much coal material as possible from the filter. The filter cake was washed again with THF and the cake placed in a vacuum oven to remove the wash solvent. The filtrate was placed in an evaporating flask and put in a specialized vacuum heated apparatus called a Rotovap operated at 50°C and 20 mm Hg (20 Torr) for 1 hour. If DMF was used, a specialized Rotovap, called a Kugelrohr, was used at 80°C and ~1 mm Hg pressure. The solvent-free filtrate and filter cake were then weighed.

Provided below is an example run. The following was weighed out into the autoclave cup:

- 88.39 g of as-received Ohio coal (with 8.20 g, 9.28 wt% moisture and 6.80 g, 7.69 wt% mineral matter) ground to smaller than 20 mesh (designated -20 mesh)
- 15.1 g of bio-solvent (i.e., 17 lb/100 lb coal)
- 210.65 g of coal tar distillate (CTD).

This provided a 2.6:1 liquid to as-received (AR) coal ratio. The operating procedure is as follows:

1. Weigh components into autoclave cup, place autoclave cup onto reactor assembly. Inter head with stirred and cooling coil. Tighten vessel retainer and purge with N_2 to remove air.
2. Begin stirring at 360 RPM and heat to 400ºC.
3. Once temperature is reached (approximately 47 minutes), maintain temperature for 30 minutes.
4. Once 30 minutes has passed, cool reactor contents to 80ºC by passing water through the internal cooling coil and vent off gas.
5. Lift autoclave head and rinse with solvent into separate beaker.
6. Combine all material (autoclave cup and rinse fluid) into an Erlenmeyer flask.
7. Heat to boiling with manual stirring and then pour contents into pressure filter containing a10-micron nylon membrane filter; close lid and apply up to 40-psig N_2 pressure; capture filtrate into jar. (With a good bio-solvent, this pressure may be less than 5 psig, indicating low viscosity and ease of filtering).
8. Rinse filter cake with boiling THF solvent into round bottom flask.
9. Evaporate off wash solvent using a Rotovap.
10. Place filter cake into vacuum oven at 60°C and 20-mm Hg vacuum overnight to remove the wash solvent.

In this example, after pressure filtration and solvent removal, 286.56 g of solvent-free liquids and 16.25 g of solvent free filter cake were obtained.

Solubility of coal is defined as 100 minus (the “quantity of filter cake minus coal ash fed” divided by the quantity of moisture, ash free (MAF) coal fed) times 100, or

$$\text{Solubility} = 100 - \frac{\text{Filter cake} - \text{coal ash fed}}{\text{MAF coal fed}} \times 100$$

Or, in more detail

$$\text{Solubility} = 100 - \left\{ \frac{\text{Filter cake} - (\text{coal fed} - \text{coal ash percentage}/100)}{\text{Coal fed} - (\text{coal fed x (coal ash percentage}/100) - (\text{coal fed x (coal moisture percentage}/100)\text{B}} \right\} \text{x}100$$

Using the numbers in our example, solubility was calculated as follows:

$$= 100 - \frac{16.25 - (88.39 * 0.0769)}{88.39 - (88.39 * 0.0769) - (88.39 * 0.0928)} \text{ x } 100$$

$$= 100 - (9.45/73.39) \text{ x } 100 = 87.12 \text{ wt\%.}$$

The filter cake was ashed at 500°C for 240 minutes. The ash content was determined to be 36.9 wt%. We compared this measured ash value to a theoretical solubility versus ash content curve, see Table 3 and Figure 9. The mass balance for this example was 96.4%.

Table 3. Solubility versus Predicted Filter Cake Ash Content

Ohio (Brahmi) Theoretical Ash Content	
% Solubilized	% Ash
0	8.48
25	11.00
50	15.63
60	18.81
70	23.60
75	27.04
80	31.66
85	38.18
90	48.09
95	64.95
100	100.00

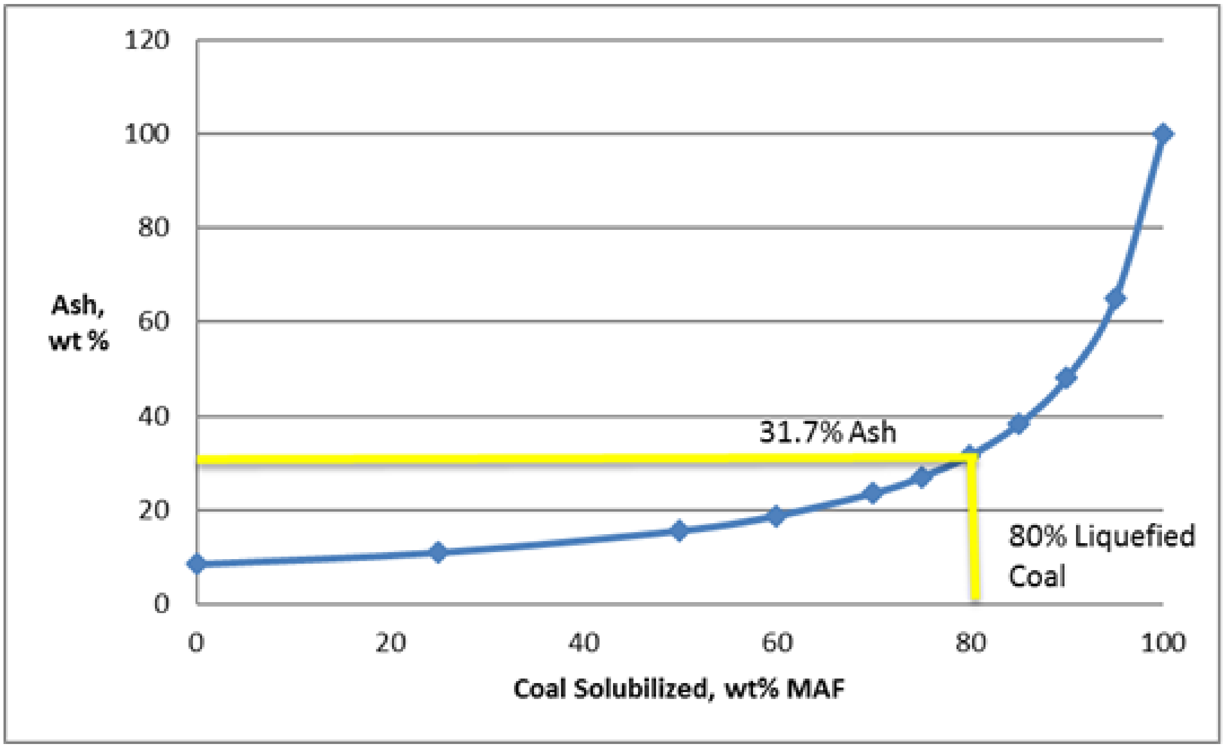


Figure 9. Theoretical solubility versus product (syncrude) ash content.

This relationship was calculated by assuming (1) the mineral matter in the coal equals its ash content, (2) 100 % of the ash in the coal ends up in the filter cake, (3) all of the non-solubilized coal ends up in the filter cake, and (4) no residual coal liquids are retained with the filter cake. So, for 0 wt% solubility, all of the coal would end up in the filter cake and the predicted ash content would be the moisture-free ash content of the coal (8.48 wt%). At 100% solubility, only the ash would be retained in the filter cake, and the ash content of the filter cake would be 100 wt%.

For the measured 36.9 wt% ash content, the predicted solubility was between 84% and 85 %, which is in reasonably good agreement with the calculated value of 87.12 %.

5.2.3 Results for West Virginia (WV) Coal

The reactions were performed following the autoclave procedure described above. The coal was minus 25 mesh with no further treatment. We initially began running reactions at 400ºC for 30 minutes with WV coal and Koppers CTD but found that the resulting syncrude was very viscous and only one candidate bio-solvent performed reasonably well. Because of the higher viscosity of filtrate, we decided that a higher temperature was needed to help depolymerize the coal to a greater degree. We next ran at a temperature of 425ºC. Tetralin performed well at this temperature yielding 86.8% dissolution of coal. However, after running the best bio-solvent at that point (BS-3) at times of 30 min, 60 min, and 90 min, we found that we were getting some coking. This was supported by previous observations at Quantex indicating they had seen coking at temperatures greater than 420ºC. This led us to testing at 410ºC. With Leer coal and Koppers CTD, the best bio-solvent yielded a dissolution value of 86.7%, which is same as for tetralin. At 415ºC the same material gave a dissolution of 85.5%; essentially the same value as at 410ºC. Under these same conditions Tetralin was run twice and gave dissolution values of 84.3% and 86.6% at 415ºC and 410ºC, respectively. From this point onwards, we selected 410ºC as the standard operating temperature for feedstock screening. The liquefaction yields for the several bio-solvents, using WV coal, are compared with soybean oil and tetralin in Table 4. The yields for other bio-solvents were below 50%.

Table 4. Batch Autoclave Coal Liquefaction Screening Results on WV Coal

Solvent	Test No.	Coal Solubilized % MAF Coal	Comments
Soybean Oil (Base Case)	WV-15	76.5 (DMF) 58.9 (THF)	Very viscous; some not miscible with hot THF
Tetralin	WV-18	86.6	Low viscosity; very clean reaction
Bio-solvent #2 (BS-2)	WV-17	53.1	Very viscous; slow to filter in hot THF
BS-3	WV-13	86.7	Lower viscosity; hot THF soluble
BS-9	WV-25	85.5	Medium viscosity; hot THF soluble
BS-10	WV-26	69.8	Clean reaction; readily soluble in hot THF
BS-14	WV-30	56.9	Very viscous; difficult to filter
BS-15	WV-34	87.9	Lower viscosity; readily soluble in hot THF

The data on WV coal showed that the percent solubility of coal, as defined by solubility in hot THF, as well as the viscosity and filtration behavior of the product are highly dependent on the solvent used. For example, the product based on use of tetralin was of a lower viscosity and the product work-up, including dissolution in hot THF and filtration were easy. At the same time, the solubility with tetralin was quite high at 86.6%. Soybean oil base case gave a relatively good dissolution yield at 76.5%, but a stronger solvent (DMF) had to be used and the product was very viscous. After re-extracting the filtrate with hot THF, we found that 23.0% of the filtrate was THF insoluble. Thus, the corrected THF solubility with soybean oil was only 58.9%. On the other hand, three bio-solvents, BS-3, BS-9, and BS-15, provided as high dissolution yields as with tetralin and the products were of lower viscosity and relatively easy to dissolve in hot THF. This result was expected since soybean oil is not an H-donor.

Based on the initial results from 31 autoclave tests, BS-3 (Autoclave Test No. WV-13) and BS-15 (Autoclave Test No. WV-34) appeared to be the best bio-solvents. One of these tests, WV-13, was selected for further analysis of the filter residue and syncrude, which included a portion that will normally be returned to the front-end of the process as the CTD recycle solvent. The ultimate analysis of the filter residue and syncrude, are compared with that of coal and CTD solvent in Table 5.

Table 5. Coal, CTD Solvent, Syncrude, and Filter Residue Analyses for Autoclave Test No. WV-13

Content	Coal Wt%	CTD Solvent Wt%	Syncrude including CTD Solvent Wt%	Filter Residue Wt%
Moisture	4.1	<0.9	<0.7	1.18
Ash	11.06	0.01	0.21	42.36
Carbon	71.2	91.81	89.21	NA[(b)]
Hydrogen	5.35[(a)]	5.71	6.66[(a)]	NA
Nitrogen	1.34	0.91	0.68	NA
Sulfur	0.90	0.67	0.66	NA
Oxygen	6.05[(c)]	1.69[(d)]	2.75[(d)]	NA
Higher Heating Value, BTU/lb	12,880	NA	NA	8,063

(a) Corrected for hydrogen from moisture
(b) NA: Not analyzed
(c) By difference
(d) By ASTM D5373 modified method

A mass balance for Test No. WV-13 shows about 96% closure for filter residue, syncrude, and moisture from feed. The remaining 4% includes losses including some C1-C3 gases vented from autoclave. Based on elemental mass balances, the estimated composition of syncrude, free of CTD solvent, compared with coal, is shown in Table 6.

Table 6. Estimated Composition of Syncrude, Free of CTD Solvent, Compared to Coal, on Moisture-Free (MF) Basis

Content	Coal MF%	Test WV-13 Syncrude MF%
Ash	11.53	0.26
Carbon	74.25	86.29
Hydrogen	5.32[(a)]	7.73
Nitrogen	1.40	0.73
Sulfur	0.94	0.65
Oxygen	6.56	3.90
H/C, Atomic	0.86	1.075

(a)Corrected for hydrogen from moisture.

The results on the WV coal show that coal liquefaction resulted in 98% mineral matter removal and 34% oxygen removal. The calculation for sulfur removal is complicated as the bio-solvent, which becomes part of the syncrude, is free of sulfur. However, based on the types of sulfur present in coal, it is predicted that the liquefaction process removes only the pyritic and sulfate sulfur, but not the organic sulfur. Similarly, no nitrogen removal is expected, as all of the nitrogen is organic nitrogen. The H/C atomic ratio increased by about 25%.

5.2.4 Results for Ohio Coal.

After completing the tests with WV coal, we began testing the Ohio coal. A total of 151 batch tests were carried out. The primary reason for more testing on Ohio coal was that many more bio-solvents became available during Ohio coal testing.

The preferred bio-solvents were compared with tetralin and soybean oil, as shown in Table 7.

Table 7. Batch Autoclave Coal Liquefaction Results on Ohio Coal

Biomass-Derived Solvent	Coal Solubilized %MAF Coal THF Soluble	Viscosity @ 50C cP	Comments
Soybean Oil	66.9	2,100	Selected for Quantex Run #2
Tetralin	84.9	325	
BS-12	88.3	94	
BS-15	86.2	9.2	
BS-15A	85.1	20	
BS-19	84.9	190	
BS-19A	82.0	50	Selected for Quantex Run #3
BS-19B	82.2	31.7	
BS-23	85.2	1632	
BS-25	83.6	1330	
BS-27B	88.2	403	Selected for Quantex Run #4
BS-32	85.5	658	Selected for Quantex Run #5
BS-40D	92.1	639	Selected for Quantex Run #6
BS-41A	90.4	1246	

As shown in Table 7, seven (7) bio-solvents performed as well as or better than tetralin. A total of 11 bio-solvents gave over 80% coal solubility, compared with only 66.9% for soybean oil, which served as the base case. The BS-19A and BS-32 bio-solvents were actually used for larger-scale testing at Quantex. The liquid product from the BS-19A test, called Syncrude 2, was evaluated for lab-scale hydrotreating/hydrogenation. Based on cost considerations, two bio-solvents, BS-27B and BS-32, were down-selected for scale-up in Task 1.03.

5.2.5 Results for Wyoming Coal.

Black Thunder coal was found to be 6% ash and 22.2% water. We ran four tests through our dissolution process. After correcting for moisture content, we ended up using a liquid to coal ratios of 2.5-2.8 and ran at temperatures of 400°C or 410°C for 30 minutes. The bio-solvents used were soybean oil, BS-19A, BS-27, and BS-32. The soybean oil run could not be worked up due to a very thick tar product plugging the filter. We tried using hot THF and hot DMF but the material would still not filter. The reaction with BS-19A went well and produced a low viscosity oil. But, even with THF this material would not filter due to the solid material being more like a tar/thick oil than a solid as seen with other coals. It is believed this reaction would do well with a centrifuge, as used in continuous tests at Quantex. The solid gummed so well that the liquid solvent mixture was decanted. The solid portion was rinsed with hot solvent and continued to show a tar-like consistency. This test with BS-19A calculated to 91.9% solubilized coal. The filtrate was of very low viscosity and this would be expected due to the fact that we did not remove the water from the coal, making our real liquid to coal ratio equal to 2.6 instead of 2.0.

5.2.6 Parametric Testing Results

Effect of Time and Temperature. During early studies on WV coal, temperature was varied from 400°C to 425°C. We began our work at 400°C, but found that we could only obtain good data for one candidate, the BS-3 solvent. The soybean oil and other candidates produced too thick of tars even without removal of the extraction solvents. Because of these issues, we then switched and ran at 425°C. This temperature gave lower viscosity oils, but also gave lower yields. When time was increased from 30 to 90 minutes on the BS-3, the solubilization dropped by 40.0 percent. This meant that we were coking our mixtures at 425°C. This was supported by WVU work which saw coking above 420°C. On the other hand, at 410°C, the same BS-3 solvent solubilized 86.7% of coal. When this temperature was increased to 415°C the solubilization was 85.5%. Therefore, at that time, we settled on a reaction temperature of 410°C. Later on, while working with the Ohio coal, we decided to evaluate lower temperatures due to the belief that no coking would take place at 400°C and below. Based on PSU work (see Section 5.2.7), we also knew that solubility was better at lower temperatures, but typically at longer times. Due to lack of the normal coal tar distillate at the time, we had to use a light coal tar distillate which was known to perform less favorably, but was believed to be acceptable for providing the trends relative to time and temperature. The results are in Table 8 below.

Table 8. Effect of Reaction Time and Temperature for WV Coal Using BS-27 at 29% BS/MF Coal and Lighter CTD

Rank for Solubility	Time, minutes	Temperature, °C	Solubility of Ohio Coal, wt %
1	30	390	73.8
2	10	400	70.7
3	30	400	70.6
4	10	390	65.3

As seen above, there was little difference in the solubility between 390°C at 30 minutes and 400°C at 10 and 30 minutes. However, lower solubility was observed at 390°C and 10 minutes. This suggested that time is more critical when working at lower temperatures. Once we had obtained more of the desired coal tar distillate (CTD), we repeated two tests shown above. The results are shown in Table 9 below.

Table 9. Effect of Temperature on Solubility for Ohio Coal Using Heavier CTD

Rank for Solubility	Time, minutes	Temperature, °C	Solubility of Ohio Coal, wt %	Viscosity, Cp at 50°C
1	45	390	91.0	3309
2	30	400	88.2	403

As expected, the solubilities at 400°C for 30 minutes were quite good with the new, heavier CTD. The solubility was good even at 390°C when time was extended to 45 minutes. However, the reaction is likely not complete as the viscosity was still high. If lower temperature (e.g., 390°C) is desired, a time of 60 minutes or greater is likely needed.

Effect of Bio-solvent. The various bio-solvents have varying degrees of performance based on their potential to dehydrogenate, and thus serve as an H-donor. As seen in Table 7, BS-15 and BS-19 seem to have the greater potential to reduce the final viscosity of the syncrude. Also, based on the molecular structures, BS-9, BS-15, BS-26, BS -27, and BS-32 have the highest potential for dehydrogenation, so it was expected that they would perform well, and which they did. Another surprising matter is that the physical state of the bio-solvent before the reaction does not necessarily effect the final syncrude state. For example, BS-24, BS-27, and BS-19 are solids at room temperature. They were blended with soybean oil in order to maintain them as liquids. However, the non-blended samples produced lower viscosities than after blending with soybean oil. This further confirms that soybean oil, which was tested by WVU and therefore served as a base case, doesn’t transfer hydrogen to depolymerized coal unlike BS-19, BS-24, and BS-27. Some selected comparisons of the novel bio-solvents with soybean oil relative to coal solubility and viscosity of syncrude are shown in Table 10.

Table 10. Effect of Bio-Solvent Type on Coal Solubility and Syncrude Viscosity for Ohio Coal.

	Sol	Viscosity, cP 50C	Comments
Bio-solvent (BS) or Soybean Oil	N/A	N/A	Couldn't dissolve in THF or DMF
Soybean Oil	66.9	2100	Base Case
BS-19A	82.0	50	
BS-19	84.9	190	
Soybean Oil	66.9	2100	Base Case
BS-27A	81.6	693	
BS-27	88.6	46	
Soybean Oil	66.9	2100	Base Case
BS-15A	85.1	20	
BS-15	86.2	N/A	
Soybean Oil	66.9	2100	Base Case
BS-23	85.2	1632	
Soybean Oil	66.9	2100	Base Case
BS-24	76.6	283	
BS-24D	80.1	N/A	Replaced 10% BS-24 with hydrogenated syncrude
Soybean Oil	66.9	2100	
BS-9	85.5	779	WV Coal

Solvent Recycle. We evaluated replacing Koppers CTD with our own syncrude five different times. When we took our syncrude from Run OH-43 and replaced 100% Koppers CTD in run with BS-19A, the coal solubility dropped from 84.5% to 51.0%. Similarly, when we took syncrude from Run OH-60 with BS-24 and replaced 50% Koppers CTD in run with BS-24, the coal solubility dropped from 76.6% to 48.3%. However, when we took syncrude heavies from Quantex Run #3 with BS-19A and replaced 50% Koppers CTD in run with BS-19A, the coal solubility increased from 82.0% to 89.7%. Similarly, when we took syncrude from Quantex Run #3 with BS-19A and replaced 100% Koppers CTD in run with BS-19A, the coal solubility increased from 82.0% to 84.7%. The reason the first two failed when compared to those run with Quantex Run #3 heavies is likely due to the low-boiling fractions being included in the first two. The Quantex Run #3 heavies is the material that passed through the wiped film evaporator (WFE) to remove everything boiling below ~290°C. This means that the material contains everything >290°C boiling point. It is known that heavier coal tar distillate typically solubilizes coal better than lighter fractions. By removing the lighter fractions, we made a better solvent out of our syncrude. Replacement of 10% of the BS-24 with hydrotreated syncrude from Quantex Run #3 improved the coal solubilization from 76.6% to 80.1%, which is due to production of tetralin type of molecules during hydrotreatment. Finally, in Run OH-140, we replaced 50% of the Coppers CTD with centrate from Quantex Run #6A and used Stage-1 product from syncrude hydrotreatment as a H-donor solvent. This reaction resulted in 85.2% coal solubility, indicating that the bio-solvent can be regenerated via syncrude hydrotreatment.

5.2.7 Microcatalytic Reactor Testing at PSU

Test Equipment and Procedure. A series of coal dissolution experiments were performed in vertical tubing reactors (microreactors). Having an internal volume of approximately 25 milliliters (mL), these microreactors are fitted with a pressure gauge, adjustable pressure relief valve and isolation valve. A photograph of a microreactor is shown in Figure 10.

A blend of coal, bio-oil, and coal-derived solvent, having a total weight of approximately 7.50 grams, was loaded into the reactor's body for each test. The reactor was then connected to a gas manifold, pressurized with nitrogen, and tested for leaks. The reactor was vented and again pressurized. This step was repeated two times to purge all air from the reactor. Finally, the reactor was pressurized to the reaction pressure and the pressure relief valve adjusted as necessary. The reactor was then plunged into a preheated sand bath held at the desired reaction temperature. The bath temperature was measured by a thermocouple placed in close proximity to the reactors. Each reactor and its contents were agitated at approximately 200 cycles per minute to promote mixing between the coal, bio-solvent, and coal-derived solvent throughout the test.

After the reaction time had been reached, the reactors were removed from the sand bath and quenched in cold water. Product work-up was similar to typical coal liquefaction product work-up [5]. Any gas products were vented and the solid or liquid by-products were flushed from the reactor with THF. The solution was sonicated for 20 minutes to promote dissolving of the coal dissolution products. THF insolubles were then separated from solution by filtering the THF through glass fiber filter paper having particle retention of 2.2 µm. The filter paper and solids were allowed to dry for 24 hours in a fume hood before being transferred into a glass fiber thimble. The thimble had particle retention of approximately 0.8 µm. Solvent extraction was performed for 24 hours using the THF collected during the previous filtration. The thimble and its contents were dried for 24 hours in a fume hood and then dried under vacuum for at least 1 hour at 110°C. The final weight of the THF insolubles was determined and used in Equation 1 to calculate the percent conversion of the coal on a dry, ash-free basis.

$$Coal\ Conversion\ (wt.\%\ \mathrm{d.a.f.}) = \frac{(Dry\ Coal\ Weight - THF\ Insolubles)}{Dry, Ash-Free\ Coal\ Weight}\ x\ 100$$

The THF solvent was removed from the THF solubles by rotary evaporation combined with final evaporation under vacuum for 1 hour at 70°C.

Figure 10. Microreactor used for coal dissolution experiments.

Coal Dissolution Results. A total of 38 coal dissolution experiments were performed in the microreactors. These experiments were intended as a screening tool to evaluate the effect of different bio-oil solvents, coal-derived solvents, chemical solvents, and operating conditions (reaction temperature and reaction time) in promoting coal conversion. The operating conditions and coal conversion (on a dry-ash free basis) for each microreactor experiment is provided in Table 11. A slight correction (0.1 to 0.2 weight %) for coal conversions reported in the previous quarterly report was made to adjust for coal analysis subsequently determined at PSU. Only the Leer (WV) coal was used in the microreactor testing. The Bramhi (Ohio) coal was used in the large lab reactor testing discussed in Section 5.3.

Table 11. Operating Conditions and Coal Conversions for the Microreactor Experiments on WV (Leer) Coal

Battelle Test # #	PSU Test #	Coal	Coal-derived Solvent	Bio-oil/ Chemical Solvent	Solvent-to-Coal Ratio	Temperature, °C	Residence Time, Minutes	Conversion, Wt. % (MAF)
-----	PSU-1	Leer	QRS	BS-2	2:1	400	60	30.2
-----	PSU-2	Leer	QRS	BS-2	2:1	400	60	40.2
-----	PSU-3	Leer	QRS	BS-2	2:1	385	60	50.5
-----	PSU-4	Leer	Tetralin	Tetralin	2:1	400	60	78.1
-----	PSU-5	Leer	QRS	BS-2	2:1	385	60	48.2
1	PSU-8	Leer	Koppers	BS-3	2:1	415	30	59.9
2	PSU-14	Leer	Koppers	BS-3	2:1	415	60	59.2
3	PSU-17	Leer	Koppers	BS-3	2:1	415	90	53.2
4	PSU-11	Leer	Koppers	Tetralin	2:1	415	30	64.5
5	PSU-7	Leer	Koppers	BS-3	2:1	400	30	59.6
6	PSU-13	Leer	Koppers	BS-3	2:1	400	60	57.9
7	PSU-16	Leer	Koppers	BS-3	2:1	400	90	58.6
8	PSU-10	Leer	Koppers	Tetralin	2:1	400	30	59.9
9	PSU-6	Leer	Koppers	BS-3	2:1	385	30	54.2
10	PSU-12	Leer	Koppers	BS-3	2:1	385	60	62.8
11	PSU-15	Leer	Koppers	BS-3	2:1	385	90	58.5
12	PSU-9	Leer	Koppers	Tetralin	2:1	385	30	58.0
13	PSU-20	Leer	QRS	BS-3	2:1	415	30	62.3
14	PSU-23	Leer	QRS	BS-3	2:1	415	60	58.0
15	PSU-26	Leer	QRS	BS-3	2:1	415	90	60.5
16	PSU-29	Leer	QRS	Tetralin	2:1	415	30	70.4
17	PSU-19	Leer	QRS	BS-3	2:1	400	30	63.0
18	PSU-22	Leer	QRS	BS-3	2:1	400	60	61.3
19	PSU-25	Leer	QRS	BS-3	2:1	400	90	61.9
20	PSU-28	Leer	QRS	Tetralin	2:1	400	30	64.4
21	PSU-18	Leer	QRS	BS-3	2:1	385	30	56.3
22	PSU-21	Leer	QRS	BS-3	2:1	385	60	61.9
23	PSU-24	Leer	QRS	BS-3	2:1	385	90	64.4
24	PSU-27	Leer	QRS	Tetralin	2:1	385	30	55.8
25	PSU-30	Leer	Koppers	BS-19A	2:1	400	30	47.8
26	PSU-31	Leer	Koppers	BS-19A	3:1	400	30	51.5
27	PSU-32	Leer	Koppers	Tetralin	3:1	400	30	66.4
28	PSU-33	Leer	Koppers	BS-19A	2.5:1	400	30	55.1

Table 11. Operating Conditions and Coal Conversions for the Microreactor Experiments on WV (Leer) Coal (continued)

Battelle Test #	PSU Test #	Coal	Coal-derived Solvent	Bio-oil/ Chemical Solvent	Solvent-to-Coal Ratio	Temperature, °C	Residence Time, Minutes	Conversion, Wt. % (MAF)
-----	PSU-13-1	Leer	Koppers	BS-3	2:1	400	60	60.8
-----	PSU-13-2	Leer	Koppers	BS-3	2:1	400	60	60.9
-----	PSU-13-3	Leer	Koppers	BS-3	2:1	400	60	61.8
-----	PSU-34	Leer	Koppers	BS-3	2:1	390	15	55.0
-----	PSU-35	Leer	Koppers	BS-3	2:1	400	15	53.2

The first microreactor test was performed using soybean oil blended with QRS coal-derived solvent. Attempts to separate the solid and liquid products from this test using dichloromethane were not successful, as also observed in Battelle's testing. Therefore, a decision was made to perform the next series of tests using BS-2 followed by recovery with THF. With the exception of PSU-4, the first five tests in this next series were performed using BS-2 blended with the QRS coal-derived solvent. These initial tests were used to develop the protocol for recovering the coal dissolution products from the microreactors and separating the unreacted coal and mineral matter from the liquid products. The highest level of coal conversion using BS-2, 50.5 weight % MAF), was achieved at 385°C with a reaction time of 60 minutes.

Tetralin, a hydroaromatic solvent capable of donating hydrogen to cap free radicals, was used in PSU-4 to compare with the coal conversions achieved with the bio-oils. This test resulted in the highest coal conversion (78.1 wt% MAF) achieved in the microreactor experiments.

Although the microreactors were agitated during each test, a concern was raised regarding the effect of reactor orientation on mixing and coal conversion. Previous coal dissolution studies have used both vertical (see Figure 10) and horizontal reactor bodies. To evaluate the effect of reactor orientation, an experiment (PSU-5) was performed in a horizontal reactor body. The coal conversion of PSU-5 (conversion – 48.2 wt% MAF was compared with PSU-3, the same test performed in a vertical reactor body (conversion – 50.5 wt% MAF). The difference between these tests was 2.3 wt% with the vertical reactor achieving the higher coal conversion. Because the vertical reactor orientation achieved the higher conversion, it was determined that this design did not limit internal mixing and coal conversion. Therefore, continued dissolution testing was performed in the vertical reactor design. Also, an analysis of the liquid products by GC SimDis confirmed that the reactor's orientation did not significantly affect the liquid product's boiling point distribution.

Testing performed at Battelle determined that the coal conversions achieved using BS-3 were greater than those with BS-2. Therefore, Battelle requested that all further testing be performed using BS-3. Several series of tests were then performed varying the reaction temperature, reaction time, and coal-derived solvents in combination with BS-3. Figure 11 shows a plot comparing the percent coal conversion versus temperature for different coal-derived/bio-oil solvent combinations. These tests were all performed at a reaction time of 30 minutes. The data indicate that the best temperature to run reactions using either coal-derived solvent (Koppers or QRS) with BS-3 is 400°C for a 30-minute reaction time. Lower coal conversions were achieved at 385°C, while no significant increase in coal conversion was gained by running at 415°C. While no advantage in coal conversion was gained by operating at 415°C, an analysis of the liquid product's boiling point distribution also showed no benefit at the higher temperature.

Two series of experiments were also performed at a 30-minute reaction time replacing BS-3 with tetralin. The purpose of these tests was to evaluate the benefit of introducing a strong hydrogen donor solvent. Only a slight improvement in coal conversion was observed at 385°C. However, a greater increase in coal conversion was seen with tetralin at higher reaction temperatures (400°C and 415°C). This increased conversion can likely be attributed to the donation of additional hydrogen from the tetralin to free radicals, thus limiting coking of the coal and bio-oil mixture.

Figures 12 and 13 plot the percent coal conversion versus reaction temperature for each reaction time studied. Figure 12 compares tests performed using a solvent blend of Koppers and BS-3, while Figure 13 compares tests performed using a solvent blend of QRS and BS-3. These show that the coal-derived solvent from Quantex (QRS) performs better than the coal-derived solvent provided by Koppers. It also appears that a reaction time of 30 minutes is insufficient to achieve a maximum coal conversion at 385°C. While the shorter reaction time requires higher reaction temperatures, the coal conversion at longer reaction times (60 or 90 minutes) decreases at higher temperatures. This observation can possibly be attributed to repolymerization of the liquid products or thermal degrading of the bio-oil.

The best reaction condition appears to be when using tetralin with QRS (70.4 wt%), but the bio-solvent used thus far was getting decent results (~60-65 wt%). An additional bio-solvent (BS-19A) was tested in the microreactors at a solvent-to-coal ratio of 2:1 and higher. Although the coal conversions achieved with BS-19A were not as high as those observed with BS-3, the higher solvent-to-coal ratio did yield increased conversions. The higher solvent-to-coal ratio of 3:1 was also tested with tetralin (66.4 wt%). This test yielded similar increases in coal conversion to those using BS-19A.

The final series of tests performed in the microreactors was a determination of repeatability for this type of experiment. The repeatability was determined by performing an experiment in triplicate (PSU-13-1, PSU-13-2, and PSU-13-3) using the Koppers coal-derived solvent and BS-3 at a solvent-to-coal ratio of 2:1. The mean coal conversion for these three tests was 61.2 wt% with a repeatability of ± 0.6 wt%. This value can be used when comparing the coal conversion of a dissolution test with any other dissolution test.

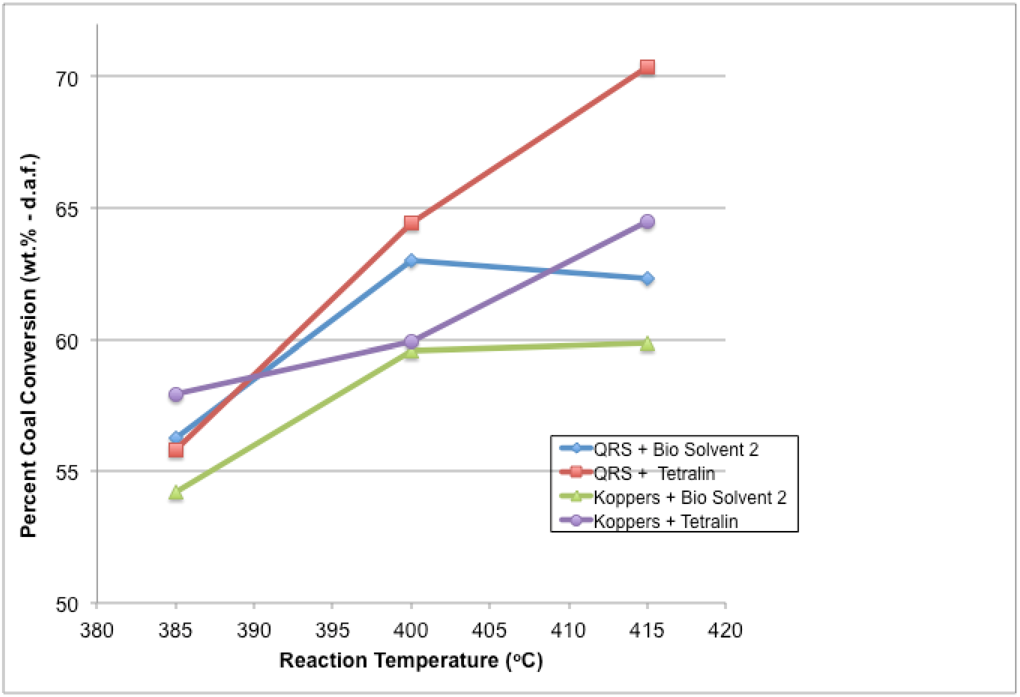


Figure 11. Percent coal conversion as a function of temperature for different coal-derived + bio-solvent combinations (solvent-to-coal ratio: 2:1, reaction time: 30 minutes).

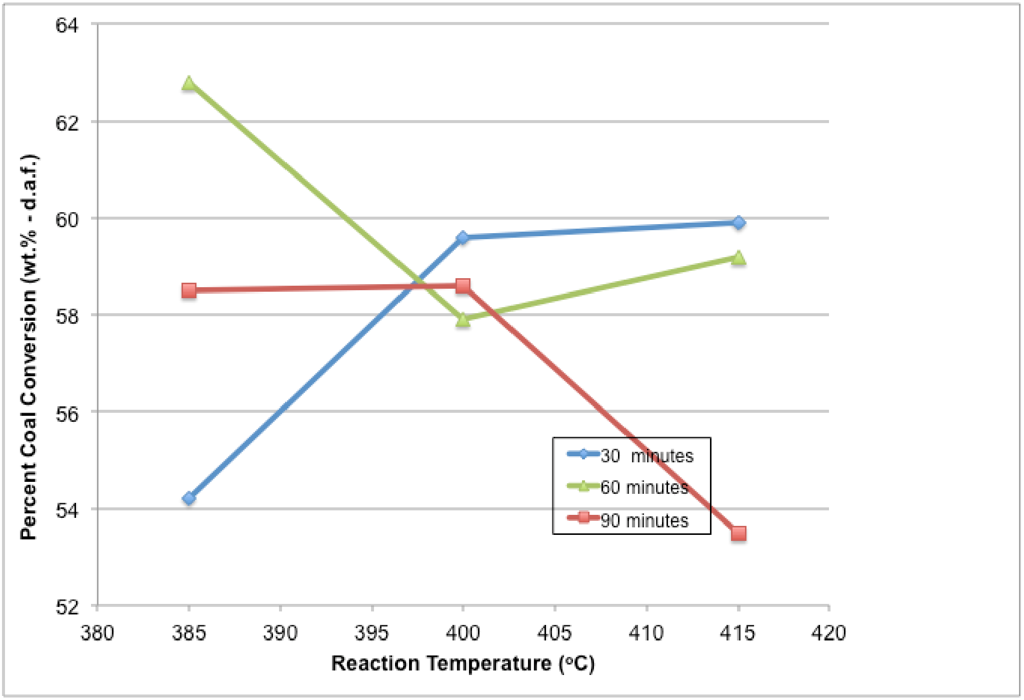


Figure 12. Reaction temperature versus reaction time for solvent blend of Koppers plus BS-3 reacted with Leer coal (solvent-to-coal ratio: 2:1).

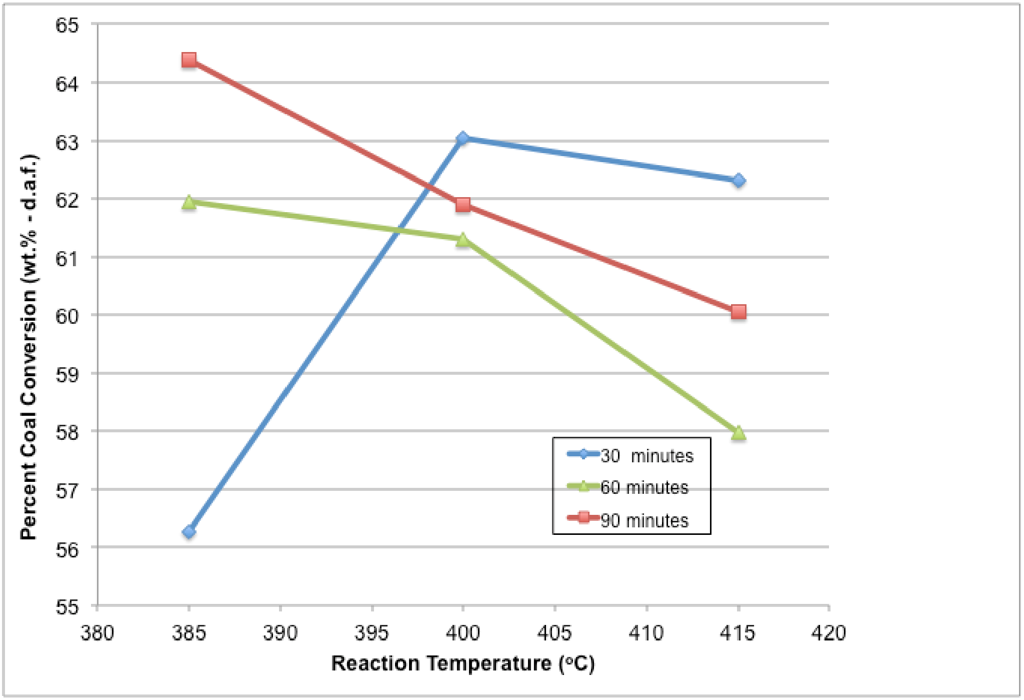


Figure 13. Reaction temperature versus reaction time for solvent blend of QRS plus BS-3 reacted with Leer coal (solvent-to-coal ratio: 2:1).

5.3 Bench-Scale Coal Liquefaction Testing at PSU

5.3.1 Test Equipment and Procedures.

A bench-scale coal dissolution system was constructed by PSU for this task. The system, shown in Figures 14 and 15, contains three one-liter continuously stirred tank reactors (CSTR(s)) operated in parallel to increase the processing volume. These larger reactors permit greater quantities of coal dissolution liquids to be produced for further analysis or upgrading. Each CSTR was equipped with a magnetic stirrer that had two impellers mounted on the internal shaft. The mixer’s speed was continuously monitored by a tachometer. The reactors were housed within an electrical heater that provided the energy to heat the reactor and coal/coal tar distillate/bio-oil slurry up to the reaction temperature. The internal reaction temperature was monitored throughout the test by a type-K thermocouple inserted into a thermowell located inside the reactor.

A test was performed in the large reactors by individually filling one of the CSTRs with approximately 800 grams of coal/coal tar distillate/bio-oil slurry. This is equivalent to roughly 750 mL in volume. The slurries were manually prepared and loaded into each CSTR. The reactors were then closed, the headspace purged with nitrogen, and the reactor pressurized with additional nitrogen up to 600 psig. The reactor was heated to the reaction temperature and held there for the required residence time. After the residence time had been reached, the dissolution products were drained into a product/settling tank through heated transfer lines (see Figure 15). Light ends were allowed to pass from the product tank, through a heat exchanger, and were collected in a separate condensate tank. Air loaded backpressure regulators were initially used to maintain pressure within each CSTR prior to venting to the atmosphere. The backpressure regulators were subsequently replaced by manual metering valves for much of the large reactor testing. The filter, shown in Figure 16, allows pressure filtration of the liquid products to remove unreacted coal and mineral matter greater than 10 µm in size. Product from either shakedown runs or actual tests performed at a solvent-to-coal ratio of 2:1 were too viscous to be filter. Therefore, the dissolution products were collected from the product and condensate tanks prior to filtration. Typically, a 15-gram sample was collected as the dissolution products flowed from the product tank. This sample was then filtered and extracted following the same procedure used in processing the microreactor samples.

Figure 14. One-liter CSTRs used at PSU.

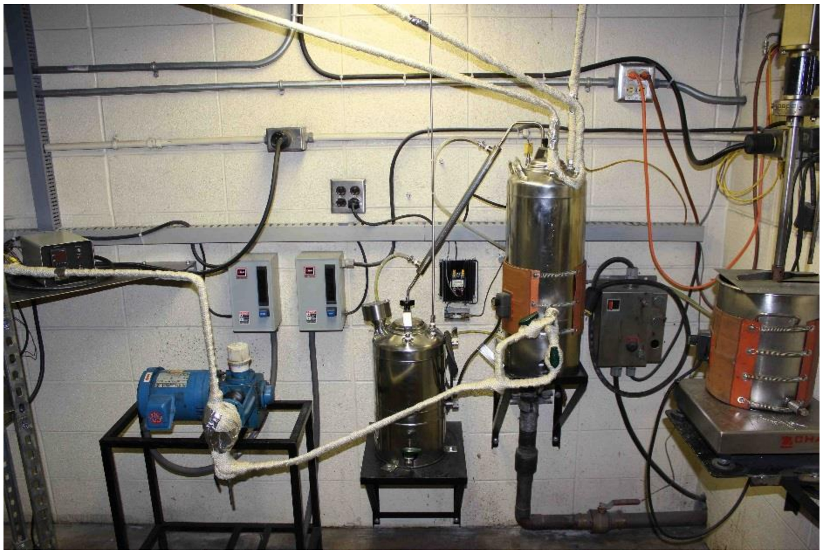


Figure 15. Product/settling and condensate tanks used at PSU.

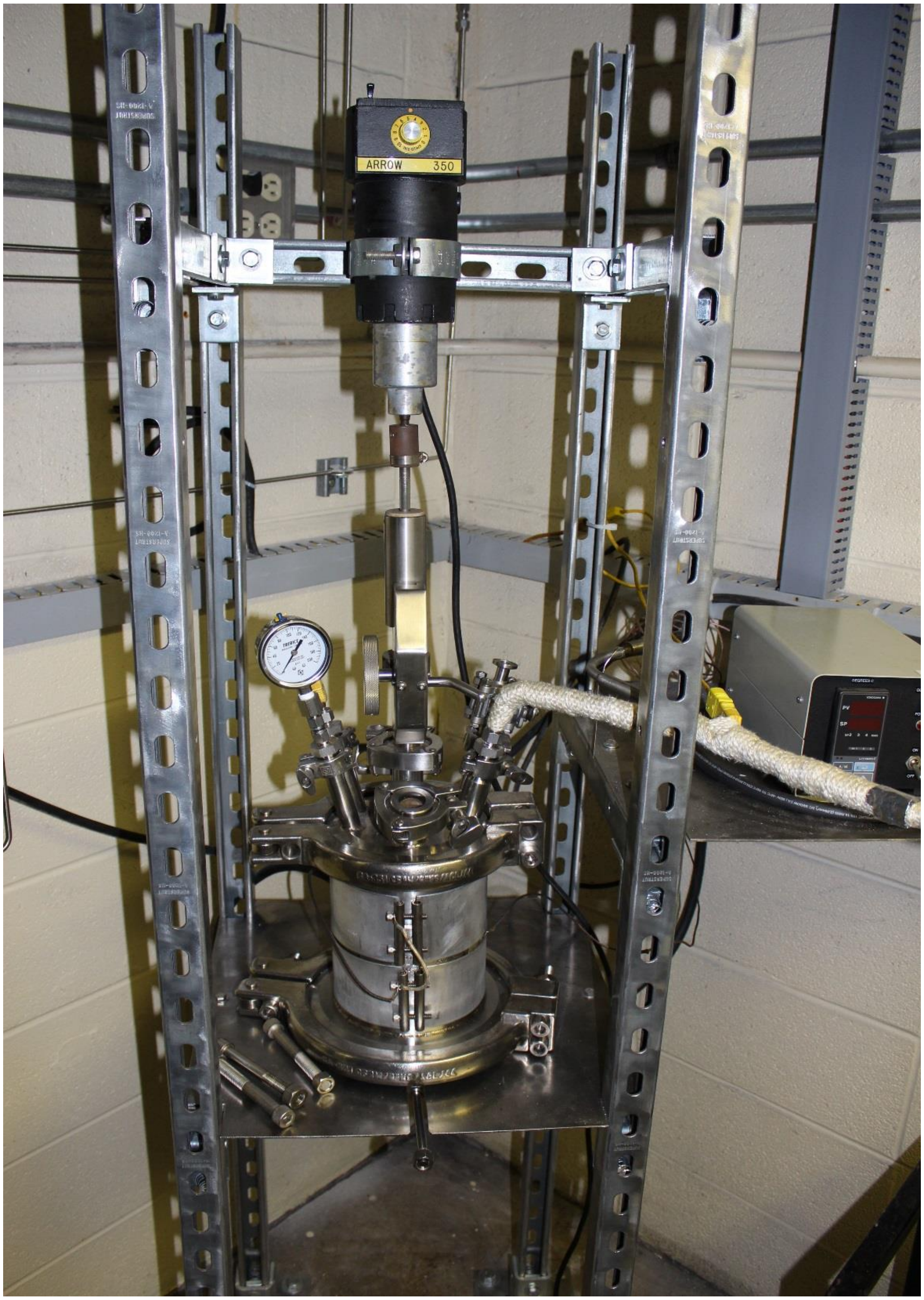


Figure 16. Pressure filter for the bench-scale coal liquefaction system at PSU.

5.3.2 Bench-Scale Test Results.

Several initial shakedown runs were performed in the CSTRs using the Ohio (Bramhi) coal, Koppers coal tar distillate, and BS-19A at the same weight percentages used in the microreactor testing. Performed at a reaction temperature of 410°C and a reaction time of 30 minutes, these tests produced a tarry product that had a consistency of a petroleum resid at room temperature. Attempts to reheat this material for filtering were not successful. We have learned that getting the material to flow in a uniform manner after allowing the reaction products to cool down does not work well, even when heating the material to 125-150°C. Three options for lowering the viscosity to permit filtering were discussed. They included: 1) increasing the solvent-to-coal ratio to 2.5:1, 2) mixing THF with the products in a 50:50 blend, 3) ship the product to Battelle for filtering. For time's sake, a decision was made to send the product from the first set of runs to Battelle for processing.

The next series of runs in the large reactor system were conducted using different bio-oil solvents. These tests are listed in Table 12. Not until test PSU-LR5 was a sample of the dissolution products processed and the coal conversion determined at PSU. Battelle also analyzed a portion of the dissolution product and we determined a significantly greater coal conversion (75-85 wt%). The reason for this difference is not apparent, but remains a point of interest.

Table 12. Dissolution Tests Performed in CSTRs (Bench-Scale Liquefaction Reactors)

					Weight % in Feed						
Test No.	Date	Coal	Coal-Derived Solvent	Bio-Solvent	Coal	Solvent	Bio-Solvent	Total Weight, g	Temperature, °C	Time, min.	Conversion, wt.%
PSU-LR1	7/10/15	Bramhi	Koppers	2	29	65	6	800.48	400	30	N.D.
PSU-LR2	7/10/15	Bramhi	Koppers	19A	29	54	17	800.38	400	30	N.D.
PSU-LR3	7/10/15	Bramhi	Koppers	23	29	65	6	800.59	400	30	N.D.
PSU-LR4	8/3/15	Bramhi	Koppers	19	29	65	6	800.51	400	30	N.D.
PSU-LR5	8/3/15	Bramhi	Koppers	25	29	65	6	800.71	400	30	46.8
PSU-LR6	8/4/15	Bramhi	Koppers	24	29	50	21	800.28	400	30	N.D.
PSU-LR7	8/24/15	Bramhi	Koppers	27A	29	54	17	799.81	400	15	44.8
PSU-LR8	8/24/15	Bramhi	Koppers	27A	29	54	17	800.03	400	0	40.9
PSU-LR9	9/1/15	Bramhi	Koppers	27A	29	54	17	800.00	400	30	45.5

5.3.3 Reaction Differences Between Microreactors and Bench-Scale Reactor

The purpose of microreactor testing was to evaluate the relative effects of different bio-solvents and operating conditions, such as reaction temperature and reaction time, and coal solubility. There are several operating differences between the microreactors and the larger CSTRs. First, the microreactors are agitated at approximately 200 cycles per minute, while internal impellers mix the CSTRs. It's assumed that the impellers provide better mixing of the slurry (and improved mixing may be better with higher solvent to coal ratios), but the importance of this difference hasn't been investigated. The second difference lies in the heating rate. It's predicted that the contents of the microreactors reach the reaction temperature in ~3 minutes after the reactor is plunged into the preheated sand bath. However, the heavy-walled CSTRs take approximately 75 minutes to reach the reaction temperature (400°C). These differences may make it difficult to directly compare results between reactor types. However, each type of reactor should provide a relative ranking for experiments performed in them.

Assuming that the extended time interval required for the CSTRs to reach the reaction temperature was allowing free radicals to repolymerize, yielding heavier products, an additional series of tests (PSU-LR7, PSU-LR8, and PSU-LR9) were performed using shorter reaction times of 0, 15, and 30 minutes. As shown in Table 3, these experiments indicate that a reaction time of 0 or 15 minutes is insufficient to maximize coal conversion. In fact, reaction times greater than 30 minutes may be required when performing reactions in the CSTRs.

5.3.4 Reaction Differences in PSU CSTRs and Battelle Batch Autoclave

There were also differences between CSTR reactor conditions at PSU and batch autoclave at Battelle. As discussed in Section 2.2, PSU tried reactions at lower residence times to see if PSU was reacting the materials took with the longer heat up times. However, PSU found that these experiments indicate that a reaction time of 0 or 15 minutes is insufficient to maximize coal conversion. In fact, reaction times greater than 30 minutes may be required when performing reactions in the CSTRs. Another issue is PSU operated reactors at lower pressures than Battelle; PSU used controllers to keep pressures at ~500 psig (as suggested by Battelle), while Battelle allowed the internal pressure to reach the maximum pressure, ~600-1200 psig. PSU also found that Battelle's batch autoclave has a faster heat up rate and an internal cooling loop, so heating and cooling could take place relatively quickly. PSU could not increase the heating rate, but PSU was able to remove the heater from the reactor at the end of the residence time and drop liquids out quickly in order to mimic Battelle's cooling profile. As discussed in the previous section, the differences may make it difficult to directly compare results between reactor types. However, each type of reactor should provide a relative ranking for experiments performed in them. Future work may require increased reaction pressures.

5.4 Down-Selection of Feedstocks and Operating Conditions for Continuous Coal Liquefaction Testing

The objective of this subtask was to document the rationale used in down-selection of the pre-pilot scale operating conditions for conversion of coal to jet fuel. The Program Plan outlines two series of pre-pilot runs. The first involves the preparation of Syncrude using the Quantex 1ton/day (1 TPD) coal liquefaction facility located in Morgantown, WV. The second run, to convert the syncrude to distillation fuels, will be conducted at the Intertek 1 BPD hydrotreating system. A discussion of the rationale for bio-solvent(s) and conditions used for the Quantex pre-pilot unit is provided below.

Battelle conducted over 100 batch liquefaction tests, PSU conducted over 30 microreactor semi-continuous tests, and Quantex conducted three continuous runs to gather the data needed to down-select the preferred set of operating conditions. As noted earlier, we set a minimum of 80% solubility as our acceptance criteria. Subsequently, we added viscosity, bio-solvent availability, bio-solvent usage and raw-material cost as additional discriminators.

5.4.1 Initial Liquefaction Testing.

Based on our work in the 1970s and 1980s, along with input from Quantex, we selected the initial range of operating conditions as follows:

- Temperature: 390 to 420°C
- Pressure: 400 to 500 psig (in some cases higher pressures were observed)
- Liquid to coal weight ratio: Initially at 2.0, and then increased to ~2.5 to accommodate the Quantex 1 TPD unit
- Residence time at temperature: 10 to 30 minutes.
- Bio-solvent: Soybean oil (SBO) was our baseline solvent.

We studied three coals: Leer, West Virginia bituminous coal from the lower Kittanning seam; Ohio bituminous coal from the middle Kittanning seam (coal supplied by the Bramhi Coal Company); and Black Thunder, Wyoming subbituminous coal supplied by Arch Coal Company. The majority of the work was focused on the Ohio coal.

In our testing we found that two types of bio-solvents were useful. One that could provide hydrogen to the coal matrix, such as a hydrogen-donor solvent, and one that could promote depolymerization. In order to maximize the donor-solvent capabilities, it was found that an optional pretreatment could, in some cases, be used to optimize performance. The process is shown schematically in Figure 17.

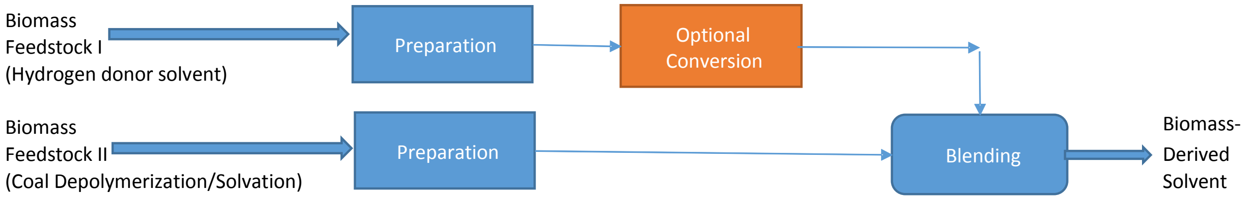


Figure 17. Production of a biomass-derived solvent for coal liquefaction

We conducted a series of tests, covering the range of liquefaction operating parameters. Some parametric testing was also conducted on high-priority bio-solvents. After review of the solubility data, we noticed that a test might produce a similar solubility, but the liquefied coal could appear dramatically different. Some products were a thick sludge and some were low-viscosity syrup-like liquids. Our experience indicated that lower viscosity product was superior, so viscosity determined at 50°C was added to our down-select criteria.

We initially tested a promising bio-solvent along with a depolymerization solvent. If successful, we progressively reduced the content of the depolymerization solvent and even dropped the bio-solvent-to-coal ratio to find the lowest, but still effective, bio-solvent-to-coal ratio.

The final criterion was bio-solvent availability and cost. In some cases we could purchase the bio-solvent from an established company, or we could easily convert a commercially available chemical. Cost was considered, but not in a rigorous manner. Some of the very best bio-solvents were also the most expensive. But, some relatively expensive bio-solvents could be used at relatively low proportions and still achieve good performance.

5.4.2 Initial Testing at Quantex.

We initially conducted three full-scale exploratory tests at the Quantex facility; one with Leer coal and two with Ohio coal. In these tests we fed -20 mesh Ohio (supplied by the Bramhi Coal Company), operated at approximately 400°C, 400 psig, and maintained a liquid to coal ratio of 1.9 to 2.0.

The coal was screw fed into a mixing pot that was co-fed with CTD (from a 250 gallon, room temperature tote), and bio-solvent (from a room temperature drum). The mixture was mixed in a special pump and then transferred to a preheater where most of the moisture was driven off. Next, the slurry was sent to a pump to bring the pressure up to the desired operating pressure. The coal was liquefied in two digesters. Excess pressure, caused by the vaporization of trapped water in the coal or the production of light hydrocarbons from thermal devolatilization, was purged to maintain the desired pressure. After liquefaction, the slurry was cooled to 100°C and then centrifuged to remove the bulk of the unreacted coal and residual mineral matter. The solids stream (the centrifuge “cake”) was sent to a drum. The centrate (liquid fraction from the centrifuge) was fed to a wiped-film evaporator (WFE) which served as a single-stage, vacuum-distillation column with a single cut point. Material boiled above or below this cut point. The below cut-point material exited the top of the WFE where it was cooled and stored in drums. The greater-than cut point material exited the bottom of the WFE and discharged directly to a drum.

Feed pump and feed line plugging was observed when using a 2:1 liquids to coal ratio. Coking in the two reactors (called digesters) was observed when operated at temperatures of 410°C. Plumbing modifications were instituted to reduce plugging. At Quantex's request, it was decided to operate the multi-ton run using a 2.5:1 liquids to coal ratio to further reduce the chance of plugging. The temperature used to control the digester temperature was the bulk fluid temperature (measured via a thermocouple inserted in a well extending into the digesters). If a layer of material built up on the digester walls, reducing heat transfer, the wall temperature was automatically raised to achieve the desired bulk temperature. Thus, it was possible to have a 410°C or even 420°C wall temperature, and that led to coking in the earlier runs. To overcome this, the temperature set point was lowered in future runs, as discussed in Section 6. This may result in reduced time at temperature. If in the longer-time tests it is found that the centrate viscosity is too high, we may need to reduce the feed rate, or raise the liquid level in the digesters, in order to increase residence time.

In the planned longer-time Quantex tests, we hoped to simulate commercial operation as closely as possible. One major difference between what we do in the lab and what we expect to do in a commercial plant relates to the use of CTD. In a commercial plant we would use CTD only for startup, using WFE bottoms instead of CTD. Tests in the batch autoclave where the equivalent of WFE bottoms was used to displace CTD resulted (in some cases) in comparable, or even superior solubility rates. So our plan is to start with a high proportion of CTD, but in subsequent runs to displace it with recycled CTD (RCTD) prepared from a mixture of WFE overhead and bottoms.

5.4.3 Top Biomass-Derived Solvents.

The top ten biomass derived solvents, along with their solubility of Ohio coal, viscosity, and availability are noted in Table 13.

Table 13. Top 10 Bio-Solvents

Ranking	Batch Run #	Biomass-Derived Solvent	Percent Soluble	Viscosity at 50°C, cP	Availability
1	123	BS-40D	92.1	639	Excellent[(b)]
2	103	BS-32	85.5	658	Good[(a)]
3	95	BS-27B	88.2	403	Excellent[(b)]
4	35	BS-12	88.3	94	Fair[(c)]
5	38	BS-15	86.2	9.2	Fair[(c)]
6	63	BS-23	85.2	1632	Fair[(c)]
7	40	BS-15	85.1	20	Fair[(c)]
8	69	BS-19	84.9	1047	Excellent[(b)]
9	43	BS-19	84.5	189.5	Excellent[(b)]
10	68	BS-23	83.8	1349	Fair[(c)]

(a) Can be easily modified using atmospheric pressure process and commercially available chemicals
(b) Can be purchased from a commercial supplier
(c) Must be synthesized at modest to severe conditions using commercially available chemicals

To accommodate the existing feeding system at the Quantex site, a 50:50 mixture of bio-solvent 27B and CTD was prepared at Battelle and then shipped to Quantex in four 55-gallon drums for Quantex Run #4. The contents of these drums, when heated to ~50°C, will have a viscosity of 3,650 cP (at 70°C, 359 cP, and at 90°C, 89 cP), so it can be fed in a manner similar to SBO that has been used in prior tests. Findings for BS-27B are noted in Table 14.

Table 14. Batch Autoclave Liquefaction for Bio-solvent 27 Using Carbon-Black Oil CTD

Rank	Biomass-Derived Solvent	Time, minutes	Temperature, °C	Solubility of Ohio Coal, wt %	Viscosity, Cp at 50°C
1	BS-27B	45	390	91.0	3,309
2	BS-27B	30	400	88.2	403

We chose BS-27B for the main test series at Quantex because of its excellent performance and excellent availability (it can be purchased from a commercial vendor). To support those tests, a series of parametric tests were conducted at two temperatures (390 and 400°C) and two residence times (10 and 30 minutes). Unfortunately, we had used up all of our high quality (Carbon Black Oil) CTD, and were forced to use an inferior “light” CTD. This resulted in an average drop in solubility of 15 to 17%. The parametric test results are shown in Table 15. As can be seen, at 390°C, even with longer reaction times, we obtained a difficult to filter product. Solubility was higher with the longer reaction time. In contrast at 400°C, even at 10 minutes reaction time, we produced an easy to filter product. At this higher temperature, solubilities were unchanged with longer reaction times.

Table 15. Parametric Study Results for BS-27 Using Light CTD at 29% BS/MF Coal

Run	Time, minutes	Temperature, °C	Solubility of Ohio Coal, wt %	Filtration Characteristics
91	30	390	73.8	Slow filtration; some heavy oil
92	10	390	65.3	Difficult filtration; heavy oil makes solid tacky
93	30	400	70.6	Fast filtration
94	10	400	70.7	Fast filtration

The down-selected operating conditions for the Quantex pre-pilot scale run are as follows:

1. Bio-solvent: 27B
2. Temperature: 375°C in digester 1 and 400°C in digester 2
3. Pressure: 400 psig
4. Liquid to coal weight ratio: 2.5 to 1
5. Bio-solvent to coal ratio: 24 lb/100 lb coal (mixed 50:50 with CTD)
6. Additional CTD to coal ratio: initially 677/300 lb coal; reduced progressively to 72/300 lb coal
7. Residence time at temperature: ~15 minutes in digester 1 and 15 minutest in digester 2, approximately 15 to 20 minutes at 400°C
8. WFE temperature set point: 160°C at 29 mm Hg vacuum (atmospheric-pressure temperature equivalent of 290°C); more about this parameter below.

The final parameter requirement was the WFE set point. Too high a set point (e.g., 500°C) and there will not be enough WFE bottoms available to displace the CTD. Too low a cut point (e.g., 200°C), and there will be inadequate production of liquids ready for hydrotreating, as well as producing an excess amount of recycle material.

5.4.4 Planned Quantex Run.

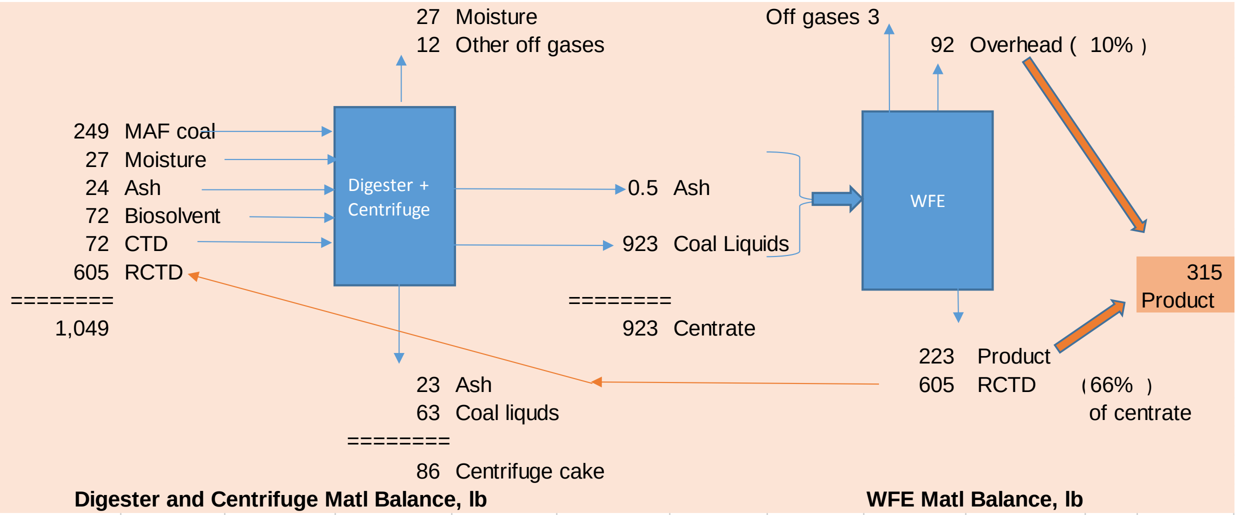
A typical Quantex batch size is 300 lb of as-received (AR) coal, enough for about 6 hours of operation. Quantex does not have a sufficient number of trained staff to run 24 hours a day, so operation between 3 and 6 hours (1 to 2 batches) a day was planned.

If we assume the coal has 8.7 wt% ash (dry basis), and the centrifuge will capture 98% of the ash/mineral matter, the coal solubility will be 87%, and the centrifuge cake ash level will be 36.9%, we can make a material balance. The assumptions are shown in Table 16 and the results are shown graphically in Figure 18.

Table 16. Quantex Run Assumptions

Assumptions							
	Mass					8.7	dry ash
		300	lb AR coal with	9%	Moisture	7.9%	AR ash
		72	lb biosolvent		24	lb biosolvent per 100 lb of AR coal	
1		605	lb internally generated recycle (RCTD)				
2	CTD	72		100%	of biosolvent		
3	Centrifuge cake has		36.9%	ash			
4	Ash captured in cake		98%	of that fed			
5	Losses to fuel gas		5%	based on MAF coal in			
6	WFE overhead	10%	of centrate goes to WFE overhead				
7	Liquid to coal ratio	2.50					

Items in blue cells represent assumptions. Non-bolded figures are calculated values.



IN	OUT	IN	OUT
1,049	1,049	923	923

Figure 18. Projected material balance around Digester/Centrifuge and WFE in the Quantex plant.

As noted in Figure 18 above, the process requires 605 lb/hr of RCTD. The relative split between the WFE overhead and bottoms is controlled by the selected set point temperature. The WFE is operated at a modestly-high vacuum 15-in. water (28 mm Hg) so that has been factored into the WFE set point operating parameter calculations. Based on batch single-stage distillation tests conducted under vacuum, we believe that set point such 320°F (160°C) at 15-in. water vacuum (28 mm Hg) is equivalent to 554°F (290°C) atmospheric pressure temperature and would meet these requirements.

In this configuration, all of the WFE overhead (92 lb) goes to the product stream. About 66% of the WFE bottoms (605 lb) are recycled as RCTD, leaving 223 lbs of bottoms to go to product. Total product per 300 lb coal lot is 315 lb or about 38 gallons.

6.0 PRE-PILOT-SCALE COAL LIQUEFACTION AND SYNCRUDE PRODUCTION

6.1 Introduction

Our team partner Quantex Energy was selected to produce large quantities of liquefied coal (Syncrude) in their pre-pilot plant scale coal liquefaction facility. To obtain information on scale up of the batch liquefaction tests conducted by Battelle and PSU, we elected to perform some tests to make enough material for syncrude upgrading in Subtask 1.04, described earlier in Section 5.4.

6.2 Description of the Quantex Pre-Pilot-Scale Coal Liquefaction Plant

A schematic of the Quantex liquefaction system is shown in Figure 19. A photograph of the system is shown in Figure 20.

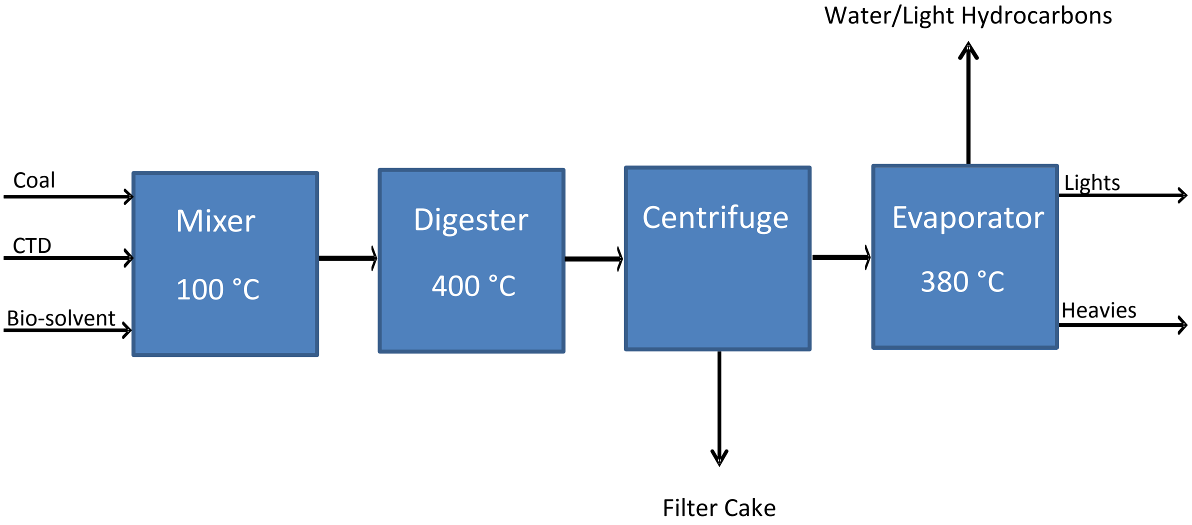


Figure 19. Process flow diagram for the 1 TPD Quantex facility

Figure 20. Photograph of the Quantex 1 TPD pre-pilot plant facility.

The five components that were used in the testing to date are noted below:

1. Coal preparation
2. Co-feeding of coal, bio-solvent, and coal tar distillate
3. Digestion
4. Solids removal by centrifugation
5. Thermal separation into a product fraction and a recycle CTD fraction.

Each step is shown in greater detail below.

6.2.1 Coal Preparation

Coal is obtained from the coal company in either 1-ton synthetic-fiber “Super Sacks” of in metal 55-gallon drums and transported to the Quantex site. In a special coal-grinding building, coal is conveyed up from the feed bin to a hammermill fitted with a metal screen. The mill produces coal with a size 90% smaller than 20 mesh (0.0331 inches, 0.841 mm); after it is ground it falls into 55-gallon drums. There is no drier including with the Quantex setup, but a small level of moisture removal is achieved during the handling and grinding process. Enough coal for the next day’s processing is typically ground and stored and be ready for liquefaction.

Representative samples of the Leer, West Virginal coal and Bramhi, Ohio coal were obtained and were analyzed for proximate and ultimate analysis along sulfur forms; results were presented earlier, in Section 5.1.1.

6.2.2 Preparation of the Battelle Bio-solvent and Coal Tar Distillate

The bio-solvents were prepared at Battelle using proprietary processes. Coal tar distillated (CTD) is a liquid obtained through pyrolysis of coal. It is distillation into different fractions before sale. Samples of three different CTD fractions were obtained from Koppers. Their relative effectiveness was evaluated in batch autoclave tests at Battelle and “carbon black oil” was determined to be the best.

6.2.3 Co-feeding of Coal, Bio-solvent, and Coal Tar Distillate

The pre-ground coal was screw-fed at a controlled rate of 100 lb/hr using a volumetric feeder. There it is mixed with CTD, from a 250-gal tote, and bio-solvent fed from a 55-gallon drum via a metering pump. There they were mixed using a special feed-mixing pump.

Depending on the set up of the feed-mixing pump, there can be limited or extensive grinding of the coal during its operation. Due to the grinding, the coal is preheated from ambient temperatures (80°F, 27°C) to over 150°F (66°C). The output of the mixing pump is sent to a slurry-preparation vessel. A pump at the bottom of the slurry-prep vessel sends the pre-heated coal/solvent/CTD mix to a valve that allows a portion to be sent back to the top of the slurry-prep vessel and a portion sent to the dewatering vessel. A similar mixing action is achieved as the coal temperature is raised about the boiling point of water and a portion of the water is removed. These gases are cooled and condensed and the liquids are sent to an oil/water separator. The gases are sent to a water scrubber for cleaning and removal of an organic mist.

After slurry prep and dewatering, the slurry is cooled and passed to a digester feed pump. Here the pressure is raised to the desired operating pressure.

6.2.4 Liquefaction of Coal

The output of the pressurization is sent to the first of two 10-gallon digesters. The digesters have level- control sensors so that when the volume exceeds 50%, a valve is automatically opened to allow a portion to be removed. A pump at the bottom of Digester 1 sends the fluid to a splitter. It allows a portion to be returned to the top of the first unit while the other portion is sent to Digester 2. The digesters do not have agitators, so this internal recirculation provides mixing. The output of Digester 2 output flows by pressure difference to a downstream heat exchanger/cooler. By adjustment of the level set points, different residence times can be achieved.

As the temperature of the coal and solvent mixture is increased any remaining water and a portion of the coal’s volatile matter are released. A pressure-control valve allows these gasses to be vented off while maintaining a constant pressure of 400 psig. These gases are sent to a condenser to knock out the organics and then to a holding tank. The gases are sent to the scrubber for cleaning.

6.2.5 Solids Removal by Centrifugation

The reacted coal is too hot to be dewatered directly. Therefore, the coal slurry is passed through two heat exchangers in series and then sent to a centrate feed and mix tank. From this agitated tank the liquefied coal can be held or sent to the centrifuge. In past runs, the material has been stored for several hours, and then centrifuged. The hope in this extended duration test is that the liquefied coal will spend a relatively short time in the feed tank before being de-ashed.

The solids from the centrifuge fall into a 55-gallon drum. The liquid stream, called the centrate, is sent to a centrate receiver. From there it can be held, pumped back to the centrifuge feed tank for reprocessing or sent on the wiped-film evaporator (WFE).

6.2.6 Thermal Separation into a Product Fraction and a Recycle CTD Fraction

The WFE is a tall, single column that allows the de-ashed, liquefied coal to be separated based on boiling point difference. The unit consists of a heated body and a rotor. The de-ashed, liquefied coal in pumped in above the heated zone and is evenly distributed over the unit's inner surface by the rotor. As the product spirals down the wall, the rotor blades generate highly turbulent flow to promote effective heating and rapid mass transfer. Volatile components are rapidly vaporized. Vapors flow co-currently with the de-volatilized liquid through the WFE and are condensed as our product and stored in a holding tank. The vapors off the tank are cooled to condense additional liquids – non-condensable gases are send to the scrubber for cleaning. The less volatile components are discharged at the WFE bottom directly into large tank and pumped, and pressure equalization, to a 55-gallon drum. A portion of these bottoms could be used as recycle coal tar distillate (RCTD). The unit is operated at vacuum to lower the fluid's boiling point and allow separation at a lower temperature. Its performance is similar to a single-stage vacuum distillation column without reflux.

The unit is run by selecting a single cut-point temperature. Everything that boils at a lower temperature passes up and is drawn off in the overhead stream, condensed and collected. Everything with a higher than cut-point boiling temperature flows out the bottom. This cut-point temperature is frequently reported as the atmospheric-pressure equivalent temperature. The actual temperature corresponding to this reported temperature depends on the vacuum available.

6.3 Shake-down Testing Conducted at Quantex (Quantex Run #1)

Since the Quantex system had not been operated for a while, several changes were made to the plant before shake-down testing began.

6.3.1 Description of First Run with Leer Coal Company, WV Coal.

In January 2015, a 30-gallon trial was carried out using the following:

- 10 gallons of Leer WV Lower Kittanning coal ground to -25 mesh
- 20 gallons of solvent
    - 14 gallons CTD.
    - 6 gallons soybean oil (SBO).

Several gallons were recovered from the WFE including pitch like material from the bottom, and a black fluid with a strong naphthenic odor from the overhead. The centrifuge tails were thick and had the brilliant sheen of coal tar. The trial was conducted primarily to evaluate the equipment and produce a few gallons of tails, pitch, and liquefied coal for evaluation. Because of the high ash content of the Leer coal, some operational problems, specifically poor ash separation in the centrifuge were anticipated.

During startup, problems with the software used to control the plant delayed operation. The problems were resolved, but the coal continued to recirculate through the colloidal mill in the feed preparation loop for hours (which allowed the coal to be ground and re-ground to a smaller and smaller size and the slurry had to be heated to temperatures greater than the planned 105°C level). The smaller-than planned coal particle size may have led to the clogging and plugging problems that were observed at several points in the system. It was concluded that the output would not be representative of the liquefaction of Leer coal so a complete material balance was not performed. While problems were noted, the equipment was operated long enough to make a first examination of the products that can be obtained by Leer coal liquefaction.

6.3.2 Repeat Run with Leer, WV Coal.

Modifications were made to the Quantex facility, including the use of fume hoods for removal of gas and vapors from the WFE. In addition, the Zenith pump that fed the primary digester was moved upstream in order to avoid gravity feeding from the slurry prep tank to the primary digester. The re-located pump allowed recirculation of liquids until there was demand at the reactor, in which case the 400 psig pump should be sufficient to deliver liquids through the line to the reactor.

As noted above, the colloid mill was used as a way to heat the slurry prior to its entry to the reactor. Operation in this manner allowed the coal to be ground to small particle sizes. This may be beneficiation from a reaction point of view but could also produce a more viscous slurry making it more difficult to pump. As the colloid mill is the primary way to add heat the inlet slurry it was retained – but the internal settings such that the teeth of the mill were adjusted to the largest possible gap, thus reducing the ability of the grinder to create an emulsion, while continuing to rely on the creation of shear as a means to heat the working fluid to desired temperature.

The Quantex team made several other improvements to the liquefaction system including installing cowls to permit takeoff of high temperature liquids from the WFE while containing the vapors. A protective epoxy floor coating was applied around the system to protect the cement floor.

A control run was carried out on 19 February 2015. It was operated without coal in order to ensure that the new pumped section was viable and leak free. The reactor was successfully loaded and unloaded at about 400°C. The system passed this test and was considered ready for trials with coal. However, as this was a major change, the planned Bramhi Ohio coal run was postponed, in order to evaluate the changes using the previously tested Leer coal.

The Leer coal test was initiated. Coal did not flow smoothly. The coarsely ground coal exiting the colloid mill plugged the line. In addition, other technical difficulties were encountered. As the slurry entered the digester, the fluid level sensor started to gyrate, bouncing from an indication of completely full to completely empty. This inability to accurately measure the fluid level may have been due to foaming inside the reactor, creating false liquid level signals.

The run was stopped. The sensor issue was later modified with the assistance of the manufacturer. In addition, because the last run had issues with a difficult-to-flow emulsion being formed, the Quantex team elected to return to the original protocol, which specified 75°C pre-heating of the slurry rather than 105°C. It was recognized, as a result, the heating would be insufficient to boil away moisture prior to the reactor. Moisture could instead be liberated and captured with overhead vent stream from the reactor loop. This was thought to be adequate for coal with moisture content of a few percent.

6.4 Run with Ohio Coal (Quantex Run # 2)

This test was conducted using soybean oil, in an attempt to establish a baseline to compare the Battelle process with. The Ohio (Bramhi) coal flowed more smoothly through the equipment, but it seemed to be more reactive upon entering the reactor, as the liquid level again showed wild gyrations. The varying liquid level can be due to the presence of boiling water. The system was stopped to make further adjustments to the liquid level control system. It was decided to run with WV coal to make sure the control problem was corrected, and then switch to Ohio coal. A sample of the WFE-overhead syncrude from this run was utilized for initial upgrading work at UDRI (see Section 7.4).

6.4.1 Work-up of Syncrude from Quantex Run # 2.

Quantex delivered a 5-gallon pail of the liquefied Ohio coal to Battelle. Inspection showed that the material in the top of the pail was free flowing and had a viscosity similar to vegetable oil while the material in the bottom of the pail was more viscous. This indicates, as also observed in lab-scale testing, that soybean oil does not react with coal, as it is incapable of hydrogen transfer.

The material in the 5-gallon pail was first mixed well and then 6 liters (L) were removed. Approximately 1 L was loaded into a pressure filter and filtered at room temperature. Over a series of tests, a total of 5,545 g was filtered. About 73 wt% of the material passed through the 20 micron filter paper. The once filtered material was re-filtered and 99.6% of this material passed through a 0.22 micron filter.

The filtered material was uniform with no separation in the top or bottom phases. Some physical properties were measured, see Table 17. They showed similar results regardless of whether the test sample was drawn from the top or bottom of the bottle.

6.5 Run with WV and Ohio Coal (Quantex Run # 3)

This test was conducted using Battelle-prepared BS-19A bio-solvent. To minimize digester level fluctuations, the plant setup was returned to a target slurry preheat temperature of 105oC in order to boil off moisture before it could enter the reactor loop. This was successful. The plant was operated one day with Leer coal. The following morning the tanks were drained and an Ohio coal test initiated. This run, designated Quantex Run #3, was successful as the Ohio coal was liquefied and de-ashed. The processed coal was then sent to the WFE. Some problems at the discharge end of the WFE were encountered preventing the production of a representative pitch product. However, the WFE overhead stream was recovered.

Process improvements allowed for processing most of the desired 203 kg run (69.4 kg coal; 96.0 kg CTD; 37.8 kg BS-19A). However, due to a digester wall being at 430°C the digester coked and plugged before processing the last 47.5 kg of mixture. The digester wall temperature will be held lower in future runs in order to avoid coking. The rest of the material was run through a centrifuge and then through the WFE, operating at 290°C atmospheric equivalent. The material through the WFE was found to be 10 wt% <290°C boiling and 90 wt%>290°C boiling. The Flow rates were estimated and materials sampled for analysis.

Table 17. Properties of Room-Temperature-Filtered Liquefied Coal from Quantex Run #2

Material	H_2O by Karl Fisher, Wt%	Density, g/mL	pH
Filtered material	0.10	1.073	6.52
Upper sample of filtered material	0.11	1.072	6.53
Bottom sample of filtered material	0.13	1.073	6.52

Discussions with Quantex indicated that there should be little if any insoluble material since the coal had been centrifuged and distilled (in the WFE). They suggested that we hot filter the material.

A sample of the liquefied Ohio coal from the 5-gallon pail, after good mixing, was withdrawn and hot filtered at 80 to 90°C in the same pressure filter. Under these conditions, the following was found:

- A total of 6,758 g was filtered; 99.5 wt% of the WFE material passed through 20-micron filter paper.
- Actual filtration time (after heating a liter of feed to temperature and preparing the apparatus) of each 1-L lot took less than 5 minutes.
- The once-filtered -20 micron material was re-filtered using a 0.22-micron paper. 98.6 wt% of the once-filtered material passed through the finer filter. The filtration of 1 L took 10 to 15 minutes.
- Overall, 98% of the raw WFE material was found to be smaller than 0.22 micron. It could be at higher temperatures, even more could be filtered.
- The filtrate the following day, at room temperature, was a sludge like material with liquid on top and a second semi-solid phase at the bottom. But, the measured densities of both phases were very similar, so the bottom phase was not actually a “heavy” phase. It compressed easily between your fingers, so it should be easy to pump.

Similar physical property data were collected for the hot-filtration series; see Table 18.

Table 18. Properties of Hot Filtered Liquefied Coal (Quantex Run #2)

Material	H_2O by Karl Fisher, wt%,	Density, g/mL	pH
Filtered material	**0.11**	**1.075**	**6.52**
Upper sample of filtered material	**0.10**	**1.076**	**6.55**
Bottom sample of filtered material	**0.12**	**1.076**	**6.55**

6.5.1 Work-up of Syncrude from Quantex Run #3.

A sample of the centrate before the WFE was taken and sent to UDRI for hydrotreatment. This centrate had the approximate distillation cuts, shown in Table 19, when distilled in the lab at Battelle.

Table 19. Material Sent to UDRI for Hydrotreatment Evaluation (Quantex Run #3)

Quantex Bio Solvent WFE Feed Distillation			
Boiling Point Range, °C	**g**	**wt%**	**Description**
<350	21.72	7.3	Light Yellow Semi-Solid
350-400	106.23	35.6	Orange/Brown Yellow Semi-Solid
400-450	45.94	15.4	Brown Semi-Solid
>450	124.43	41.7	Black Liquid
Total	298.32	100	

6.6 Quantex Run #4 with Ohio Coal

Quantex Run #4 was run with bio-solvent BS-27B. Because of processing issues, only 150 lbs coal was processed during this run. The process feed was:

- Coal: 150 lbs of ground, as received (AR) coal.
- CTD: 303 lbs of Koppers Carbon Black Oil CTD obtained from their Clairton, PA plant.
- Bio-solvent BS-27B: 36 lbs bio-solvent 27 premixed with 36 lbs of Koppers Carbon Black Oil CTD for a total feed of 72 lbs.

It was found that heating the slurry to temperatures greater than approximately 200°C caused the coal to swell, which led to extensive plugging. In order to reduce the likelihood of plugging, a slurry temperature of less than 150°C was used to process 150 lbs of coal. From the mixer, the slurry was and passed to a digester feed pump, where the pressure was increased to the operating pressure and pumped to the first of two 10-gallon digesters. The digesters have level- control sensors so that when the digester volume exceeded 50%, a valve automatically opened to allow a portion of the slurry to be removed. A pump at the bottom of Digester 1 allowed a portion of the slurry to be recirculated to the top of Digester 1 while the remaining portion was sent to Digester

2. The digesters did not have agitators, so the internal recirculation provided mixing. Digester 2 output was pumped to a downstream heat exchanger/cooler.

The digester operating conditions for Quantex Run #4 were as follows:

- Temperature:
  - Digester 1: 375°C
  - Digester 2: 400-450°C (there was a thermocouple issue leading to over-heating)
- Pressure: 390 psig
- Residence time: 35 minutes
- Liquid to coal ratio: 2.5:1 (weight basis)

Coking likely took place in one of the digesters, due to a failed thermocouple, which led to the digester operating above 410°C. At temperatures above 410°C, coking occurred in bench scale tests, so it is probable that coking also occurred at the pre-pilot scale when the bulk fluid temperature increased above 410°C. The failed thermocouple was fixed in order to ensure the digester temperatures were maintained within the operating range for future runs.

The material exiting the digester was fed to the centrifuge feed tank and maintained at a temperature of about 140°C. Next, the material was run through the centrifuge (at about 110°C). Roughly 123 lbs solids from the centrifuge formed a filter cake and fell into a 55-gallon drum (approximately 50% solids). The liquid stream, called the centrate, was sent the wiped-film evaporator (WFE) feed tank, then pumped to the WFE. The WFE is a tall, single column that allows the de-ashed, liquefied coal to be separated based on boiling point differences. The WFE consists of a heated body and a rotor. The de-ashed, liquefied coal was pumped in above the heated zone and was evenly distributed over the unit's inner surface by the rotor. As the product ran down the wall, the rotor blades generated turbulent flow to promote effective heating and rapid mass transfer. Volatile components in the feed were rapidly vaporized. Vapors flowed co-currently with the de-volatilized liquid through the WFE and were condensed as our product and stored in a holding tank. Vapors off the tank were cooled to condense additional liquids, while non-condensable gases were sent to the scrubber for cleaning. The less volatile components were discharged at the WFE bottom directly into a 55-gallon drum. The unit was operated at a vacuum pressure of about 21 mm Hg and a temperature of 230°C giving an atmospheric equivalent distillation temperature of 380°C. The distillate was labeled "lights" and the WFE bottom was labeled "heavies".

In Quantex Run #4, approximately 70% of the moisture- and ash-free (MAF) coal fed was solubilized producing about 184 lbs of lights, and 201 lbs of heavies, while the unsolubilized coal and some liquids formed 123 lbs of centrifuge filter cake. These materials were produced from 150 lbs of Ohio Bramhi coal, 303 lbs of Koppers Carbon Black Oil CTD, and 36 lbs of bio-solvent BS 27B. Materials produced during Run #4 were sent to Battelle for further analysis and verification.

A mass balance was conducted on Quantex Run #4 as shown in Figure 21 and Table 20.

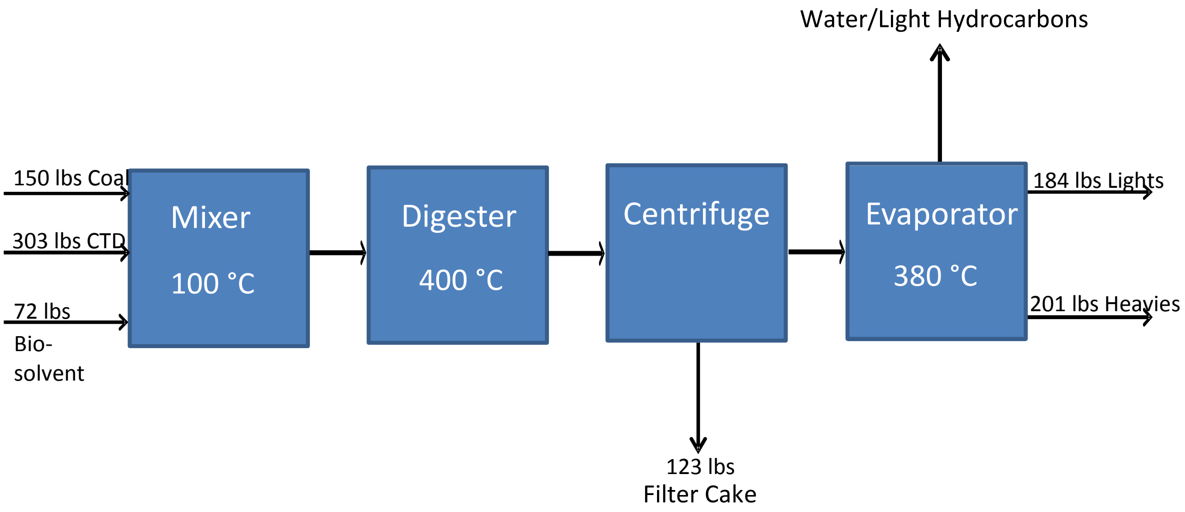


Figure 21. Quantex Test #4 process conditions, inputs, and outputs.

Table 20. Quantex Run #4 Overall Material Balance

Parameter	IN, lbs	OUT, lbs
Coal (Ohio Bramhi)	150	
CTD (Koppers Carbon Black Oil)	303	
Bio-solvent BS 27B	72	
Water/Light Hydrocarbons		Unknown
Filter Cake		123
Lights		184
Heavies		201
Total	525	508

Total out/in provides a 97% mass balance for Run #4 at Quantex. Contributions to the 4% mass lost likely came from a small amount of coking on the digesters, residual material left in the system, leaks, and water/light hydrocarbons vented during the evaporation process. Overall, the 97% mass balance provides excellent closure for the entire Run #4.

6.7 Quantex Run #5

Quantex Run #5 was run with bio-solvent BS-32. The operating conditions for Quantex Run #5 were as follows:

- Material
    - Coal: 160 lbs of ground, as received (AR) coal.
    - Koppers Carbon Black Oil CTD: 368 lbs CTD obtained from their Clairton, PA plant.
    - Bio-solvent BS-32: 64 lbs.
- Temperature:
    - Digester 1: 401°C
    - Digester 2: 404°C
- Pressure: 370 psig
- Residence time: 30-34 minutes
- Liquid to coal ratio: 2.7:1 (weight basis)

The following were the products:

- WFE Light: 228 lbs
- WFE Heavy: 206 lbs
- Filter Cake: 131 lbs

Based on the above, the MAF coal solubility is estimated to be 80%. A mass balance was conducted on Quantex Run #5, as shown in Figure 22 and Table 21.

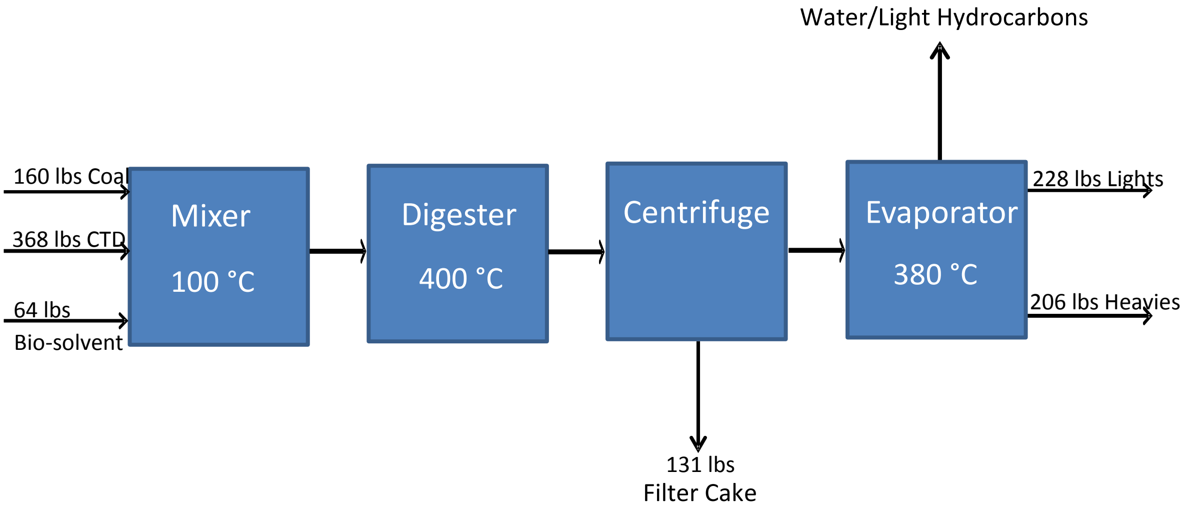


Figure 22. Quantex Test #5 process conditions, inputs, and outputs.

Table 21. Quantex Test #5 Overall Material Balance

Parameter	IN, lbs	OUT, lbs
Coal (Ohio Bramhi)	160	
CTD (Koppers Carbon Black Oil)	368	
Bio-solvent BS 32	64	
Water/Light Hydrocarbons		Unknown
Filter Cake		131
Lights		228
Heavies		206
Total	592	565

Total out/in provides a 95% mass balance for Run #5 at Quantex. Contributions to the 5% mass lost likely came from a small amount of coking on the digesters, residual material left in the system, leaks, and water/light hydrocarbons vented during the evaporation process. Overall, the 95% mass balance provides excellent closure for the entire Run #5.

6.7.1 Discussion on Results from Quantex Runs #4 and #5.

Both Quantex Runs #4 and #5 successfully produced enough material for hydrotreatment/hydrogenation to jet fuel. The Battelle bio-solvents performed well, but minor adjustments are necessary to improve performance. Further optimization is needed for tests using BS-27, due to the coking and plugging issues observed in Run #4. We found that BS-27 would benefit from the addition of a second bio-solvent in order to maintain a slurry that doesn’t swell and plug lines. This is supported by the work in Quantex Run #3 with bio-solvent BS-19A, which has similar structure to BS-27. In addition, maintaining lower slurry temperatures also inhibits early coal swelling. Run #5 with BS-32 ran fairly smoothly and also benefitted from the addition of a second bio-solvent to prevent coal swelling in the slurry stage. When recycling WFE heavies to replace Koppers CTD, it was found that adjustments in the level of BS-32 are needed. Very heavy oil was produced when the WFE heavies were recycled due to hydrogen-starving the system, resulting in only partially liquefied coal. Initially, we used heavies to replace 50% of the CTD without adjusting the bio-solvent, which led to plugging of the centrifuge lines. In order to reduce plugging, the level of bio-solvent or recycled WFE heavies must be adjusted. However, sufficient syncrude quantities have been produced from both runs to allow testing in Task 3 (pre-pilot hydrotreatment/hydrogenation). The syncrude for Quantex Run #5 was actually used in Intertek Run #1 test.

6.8 Run with Ohio Coal (Quantex Run #6A)

This test was conducted using Battelle-prepared BS-40D bio-solvent and the previously-tested Ohio coal from Bramhi Coal Company. To minimize potential issues in the slurry step, the slurry preheater temperature was held below 150ºC. On the first day, we consistently had plugging of Digester 1 recirculation pump. This was due to the slurry not reaching a sufficient temperature and pretreatment time before reaching the gear pump. A decision was made to reverse the recirculation in Digester 1 so that the mixture would gain more pretreatment time at temperature before reaching the gear pump. These changes were successful and were implemented on day two. The slurry temperature on day two ended up reaching 71°C due to manual feeding of the system. The plant was then operated for one day with the Ohio/Bramhi coal. The product was then centrifuged and 15 gallons of centrate were transferred to a drum. The leftover centrate was then sent to the wiped film evaporator (WFE) to fractionate the centrate boiling below 380°C. The WFE ran for one pass to obtain a light (<380°C boiling point) and heavy (>380°C) product.

The improvements allowed for processing of a 234 kg run (66.18 kg coal; 119.36 kg CTD; 31.91 kg BS-19A; 16.55 kg SBO). Fluctuations were noted in the digester temperatures but both indicated a range of 400-415°C. The centrate through the WFE was found to be about 40 wt% light and 60 wt% heavy product. The flowrates were estimated and materials sampled for analysis. The mass balance for this run was about 97.0 wt%; about 18.68 kg were last in piping tanks.

6.9 Run with Ohio Coal (Quantex Run #6B)

This test was conducted using Battelle-prepared BS-40D bio-solvent and recycle solvent from Quantex Run #6A to better simulate commercial-scale operation under steady-state recycle of some solvent. To minimize potential issues in the slurry pretreatment step, the slurry preheater temperature was held below 150ºC. We used the same flow scheme as Run #6A. The plant was operated for a half-day with Ohio/Bramhi coal. The product was then centrifuged and all centrate was transferred to drums for testing at Intertek (Task 2.02.01). This approximately half-day run allowed for processing of 217.1 kg of feed (54.27 kg coal; 68.39 kg CTD; 27.14 kg BS-19A; 67.43 kg Recycle). Fluctuations were noted in the digester temperatures but both indicated a range of 400°C-415°C. This process produced 132.27 kg of centrate, which was placed into drums. The Flow rates were estimated and materials sampled for analysis. The mass balance for this run was about 97.6%. The syncrude from Quantex Run #6B was used for upgrading testing in Intertek Run #2.

6.9.1 Product Analyses

The liquid samples from runs 6A and 6B were submitted for ultimate analysis and can be seen in Table 22. The samples were also submitted for viscosity analysis.

Table 22. Ultimate Analyses of Syncrude for Quantex Runs #6A and #6B

Sample	Ash wt%	Carbon wt%	Hydrogen wt%	Nitrogen wt%	Oxygen wt%	Sulfur wt%
Quantex 6A Light	<0.05	89.02	6.34	<0.5	2.65	0.46
Quantex 6A Heavy	<0.07	88.25	6.74	<0.5	3.82	0.43
Quantex 6B Centrate	<0.07	87.53	6.77	<0.5	4.00	0.40

We experienced difficulty in obtaining a representative sample of the centrifuge tails from both runs. This difficulty is due to various layering that takes place when starting and finishing the run through the centrifuge. It was decided that the best option for sampling was to drive a 1 inch pipe through the deepest part of the mixture. The liquid/solid mixture was then worked up by solvent rinsing and drying. The solid was submitted for ultimate analysis. The fraction of solids in the centrifuge tails for Runs #6A and #6B were 38.9 wt% and 42.1 wt%, respectively.

7.0 LAB-SCALE CATALYST TESTING FOR SYNCRUDE HYDROTREATING/HYDROGENATION

7.1 Introduction and Objective

The conversion of liquefied coal (coal converted from a solid to a liquid using bio-derived solvents) into a form suitable as a blending stock for jet turbine fuel requires three broad processes. First, the heteroatom species must be removed; primarily components containing nitrogen, oxygen, and sulfur. Second, the largely polynuclear aromatic structure of the coal derived components must be reduced (hydrogenated/hydrocracked) to predominantly paraffinic components, though some single and two-ring aromatics are permitted within the fuel specification. Third, the boiling range of the final product should be within the fuel specification. The first two processes, heteroatom removal and reduction, are typically accomplished via heterogeneous catalysis. The third may also be accomplished through heterogeneous catalysis, though fractionation may also be used.

The primary objectives of this subtask were to identify commercially available candidate catalysts for heteroatom removal and hydrogenation and the nominal processing conditions.

7.2 Catalytic Upgrading Background

For the upgrading of syncrude from the Battelle CTL process, a two-stage process was conceptualized. The two stages, shown graphically in Figure 23, are designated as Stage-1 and Stage-2, where Stage-1 would perform mainly heteroatom removal and Stage-2 would perform hydrogenation and hydrocracking reactions. A review of the literature shows that the most common commercially available catalysts for heteroatom removal are sulfided forms of CoMo and NiMo [5-11]. Catalysts for hydrogenation and hydrocracking (reduction) are bi-functional catalysts such as PtPd, sulfided NiMo deposed on acidic support such as zeolite Y and alumina [5-8]. Generally, PtPd is preferred, though this catalyst is more expensive than sulfided NiMo and is very sensitive to residual heteroatoms in the feed, principally N and S. NiMo is less expensive and can be sulfided, providing good performance in the presence of heteroatom species.

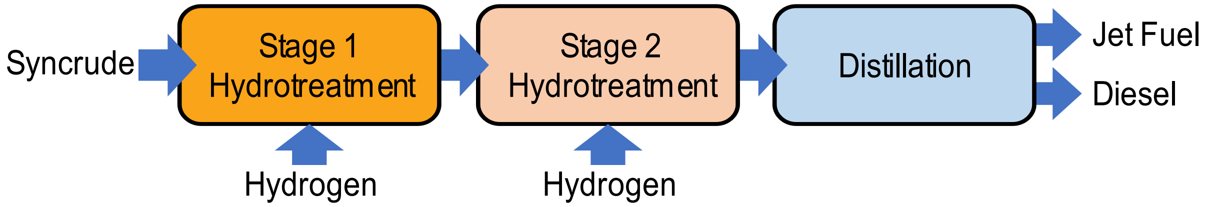


Figure 23. Two-stage hydrotreatment/hydrogenation of CTL syncrude.

Literature Review of Catalysts for CTL Syncrude Upgrading. Battelle team member PSU performed a literature review of catalysts for upgrading of coal-derived syncrudes. The review and the associated references are provided in Appendix A.

7.3 Jet Fuel and Diesel Specifications

The primary focus of this project was to produce jet fuel from coal. However, one can also produce diesel if desired. The specification for various distillate products of interest are discussed below.

The specification for conventionally produced (i.e., petroleum-based) jet fuel is ASTM D1655 – 11a. The requirements are presented in Table 23 [12]. Analysis indicates there is no stated ash or nitrogen limit in D1655. A discussion of each is provided below.

- Ash: No limit stated in D1655. However, there are practical limits. The limit for diesel fuel is 0.01 wt. % ash; so the practical limit for jet fuel is approximately the same.
- Nitrogen: D1655 states “Conventionally refined jet fuel contains trace levels of materials that are not hydrocarbons, including oxygenates, organosulfur, and nitrogenous compounds.”
- Sulfur:
    - Sulfur, mercaptan, 0.003 mass % max by D3227
    - Sulfur, total 0.30 mass % max by D1266, D2622, D4294, or D5453.
- Aromatics:
    - Aromatics, 25 volume % max by D1319; or 26.5 volume % max of by D6379.
    - Naphthalene (a $C_{10}H_8$, double cyclic aromatic hydrocarbon), 3 volume percent max.
    - Further breakdown of the types and amount of allowable aromatics are not listed. However they are indirectly restricted due to limitations on smoke point. The aromatic content and type affect combustion characteristics and smoke-forming tendencies.
    - In general, paraffin hydrocarbons offer the most desirable combustion cleanliness characteristics for jet fuels. Naphthalenes are the next most desirable hydrocarbons for this use. Although olefins generally have good combustion characteristics, their poor gum stability usually limits their use in aircraft turbine fuels to about 1% or less. Aromatics generally have the least desirable combustion characteristics for aircraft turbine fuel. In aircraft turbines they tend to burn with a smoky flame and release a greater proportion of their chemical energy as undesirable thermal radiation than the other hydrocarbons. Naphthalenes or bicyclic aromatics produce more soot, smoke, and thermal radiation than monocyclic aromatics and are, therefore, the least desirable hydrocarbon class for aircraft jet fuel use. All of the following measurements are influenced by the hydrocarbon composition of the fuel and, therefore, pertain to combustion quality: smoke point, percent naphthalenes, and percent aromatics.

Table 23. ASTM D1655 Standard Specification for Aviation Turbine Fuels

Property and Method	Limits	Typical Jet A-1
Net Heat of Combustion, MJ/kg, ASTM D4529	42.8 min (a)	43.09
Density, kg/m^3, ASTM D4052	775 - 840	814.8
Aromatics, % by volume, ASTM D1319	25 max (b)	18.3
Total Sulfur, % by mass (ppm), ASTM D5453	0.3 (3000)	0.019
Smoke Point, mm, ASTM D1322	18.0 min	22
Freezing Point, °C, ASTM D5972	- 40 max	-53.2
Flash Point, °C, ASTM D5006	38 min	54
Kinematic Viscosity @ -20°C, cSt, ASTM D445	8.0 max	4.65
Electrical Conductivity, pS/m, ASTM D2624	50-600	146 @ 25.5ºC
Thermal Stability JFTOT @ 260°C ASTM D3241		
Tube Deposit, ASTM D3241	3 max	< 1
Filter Pressure Drop, mm Hg, ASTM D3241	25 max	0.7
Distillation Temperature, °C, ASTM D86		
Initial Boiling Point (IBP)	report	173.8
10%	205 max	185.8
50%	report	206
90%	report	241.9
Final Boiling Point (FBP)	300 max	259.8
Residue, % by volume	1.5 max	1.2
Loss, % by volume	1.5 max	0.3
Acid Number, mg KOH/g, ASTM D3242	0.1 max	0.007
Existent Gum, mg/100 mL, ASTM D381	7 max	< 1
Aniline Point, °C, ASTM D611A	report	55.6
Visual, ASTM D4176P1	Clear & Bright	Pass @ 24.0ºC
Naphthalene, % volume, ASTM D1840	3 max	1.89

(a) min: minimum; max: maximum

There is also a specification for synthetically produced jet fuel, D7566-11a. The D7566 has different Annexes for different synthetic fuel; see Figure 23. However, there is no Annex for jet fuel from coal via direct liquefaction.

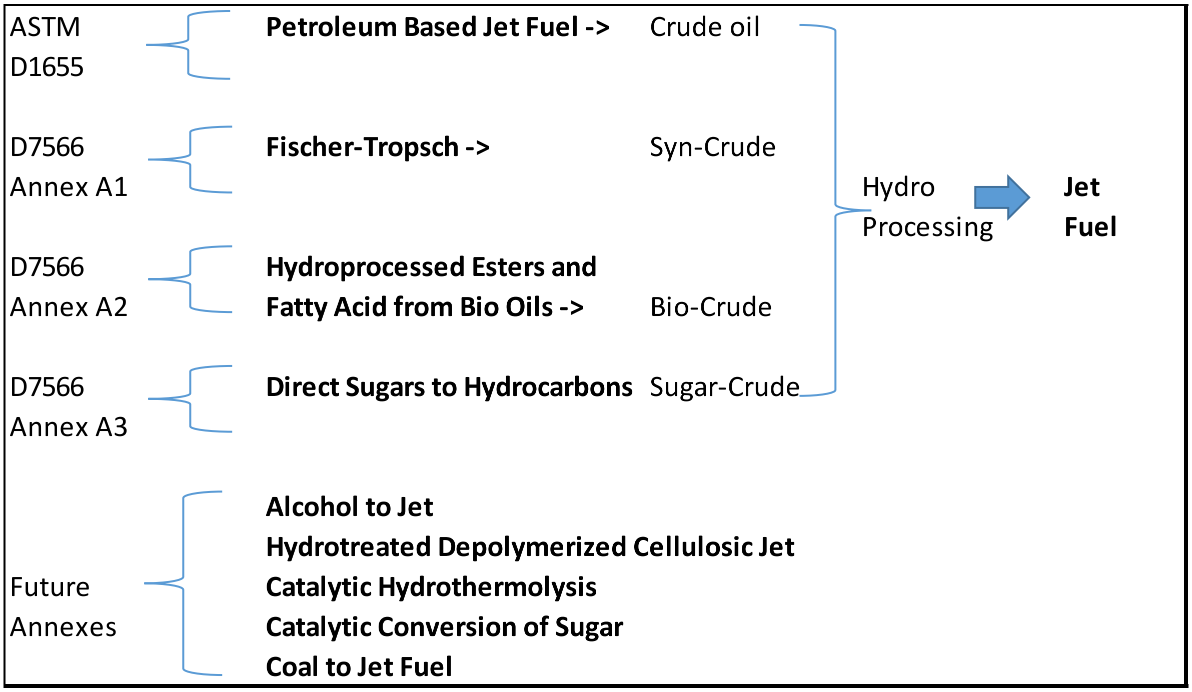


Figure 23. Annexes for synthetic aviation fuels.
(From: https://www1.eere.energy.gov/bioenergy/pdfs/10_brown_roundtable.pdf)

Annex A1 is for Fischer-Tropsch (FT) synthetic paraffinic kerosene (SPK) fuel, Annex A2 is for Hydrotreated Esters of Fatty Acids (HEFA) SPK, and Annex A-3 is for the recently approved Direct Sugar to Hydrocarbons process to make Synthesized Iso-Paraffins (SIP). Annex A1 and A2 fuels must be blended with at least 50% petroleum jet fuel; Annex A3 fuel must be blended with at least 90% petroleum jet fuel.

It would be reasonable to expect the direct-coal-liquefaction jet fuel would require its own annex; it would definitely not fall under Annex A1 for FT fuels (even though A1 covers coal gasification to make syngas which is converted by FT technology into jet fuel). The annexes contain, in some cases, limits different than those specified in D1655. For example, for SPK and SIP, which contain only aliphatic hydrocarbons, the upper limits on the amount of aromatics is 0.5%; this is in contrast to D1655 where the limit is 25 volume % aromatics.

There are no stated ash limits, but there are limits on nitrogen, sulfur, and aromatics in D7566-11a. Details are provided below.

- Ash: No limit stated in D7566, however the practical limit is 0.01 wt. % established for diesel fuel.
- Nitrogen: In D7566 for all three annexes the nitrogen limit is 2 ppm; from: http://mycommittees.api.org/rasa/jfm/Shared%20Documents/Resource%20Materials/ASTM%20on%20Bio-Derived%20Fuels%20-%20D02.J0%20(10-02)%20item%205.pdf - see section 2.2.1.2.1 “Table A1.2 of ASTM D7566.”
- Sulfur: In D7566 for all three annexes, the limit is 0.0015 mass percent (15 ppm) – the same as ultra-low sulfur diesel.

- Aromatics limits are set for SPK and SIP (paraffinic compounds): In D7566 for all three annexes, the limit is 0.5 %. It would be reasonable to expect that for direct CTL jet fuel, a higher aromatics content would be permitted up to at least the D1655 maximum of 25 volume %.

Diesel Requirements. The specification for conventionally produced (i.e., petroleum-based) diesel fuel is established in ASTM. The specification covers seven grades, but the following two are the likely targets for the Battelle CTL process:

- Grade No. 1-D S15: A special-purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 15 ppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S15 fuel.
- Grade No. 2-D S15: A general purpose, middle distillate fuel for use in diesel engine applications requiring a fuel with 15 ppm sulfur (maximum). It is especially suitable for use in applications with conditions of varying speed and load. S15 grades were not in the previous grade system and are commonly referred to as “Ultra-Low Sulfur” grades or ULSD. This is the more likely the target grade for the Battelle CTL process.

7.4 Experimental Approach for Syncrude Upgrading

The overall approach was to identify and obtain small quantities (100 to 1000 mL) of commercially available catalysts and to screen their performance using model or actual syncrudes using a set of small trickle-bed reactors operating under nominal processing conditions. From this screening process one or more promising candidates were to be selected for more detailed evaluation.

The first task was to adjust and calibrate the reactor systems for these type of reaction “Syncrude Upgrade to jet fuel”. UDRI has several reactor systems that were used for this project. All of these reactor systems are very similar in their overall construction and flow path. A general schematic is shown in Figure 24, and a photograph of reactor #2 is shown in Figure 25. (Note that the reactors may be fitted with different inlet gases and product tanks depending on the specific configuration.) Each system includes separate gas and liquid feeds with heated transfer lines, a heated catalyst reactor with a moveable axial thermocouple, heated product collection tanks, and a gaseous vent that can be monitored with various online and offline analyzers.

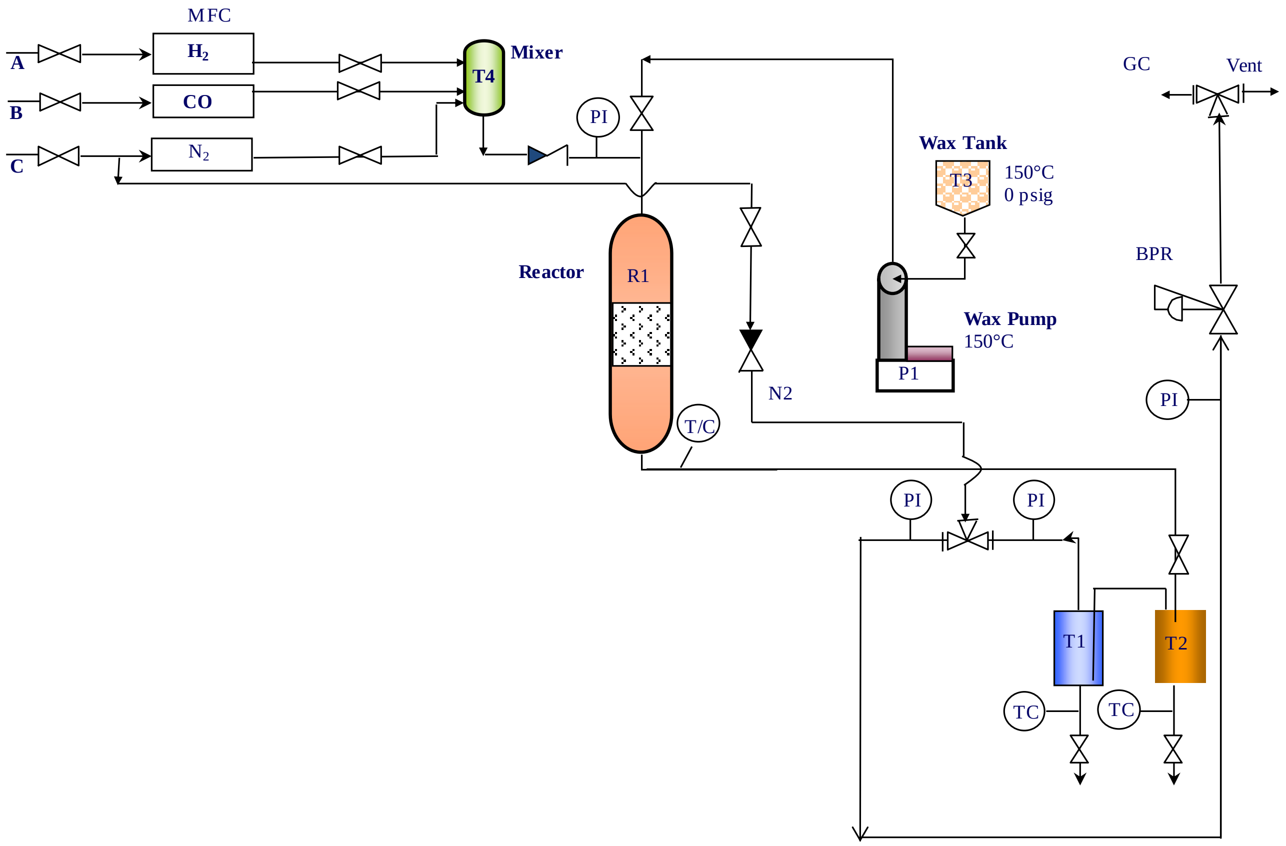


Figure 24. General schematic of the trickle-bed catalyst reactors at UDRI.

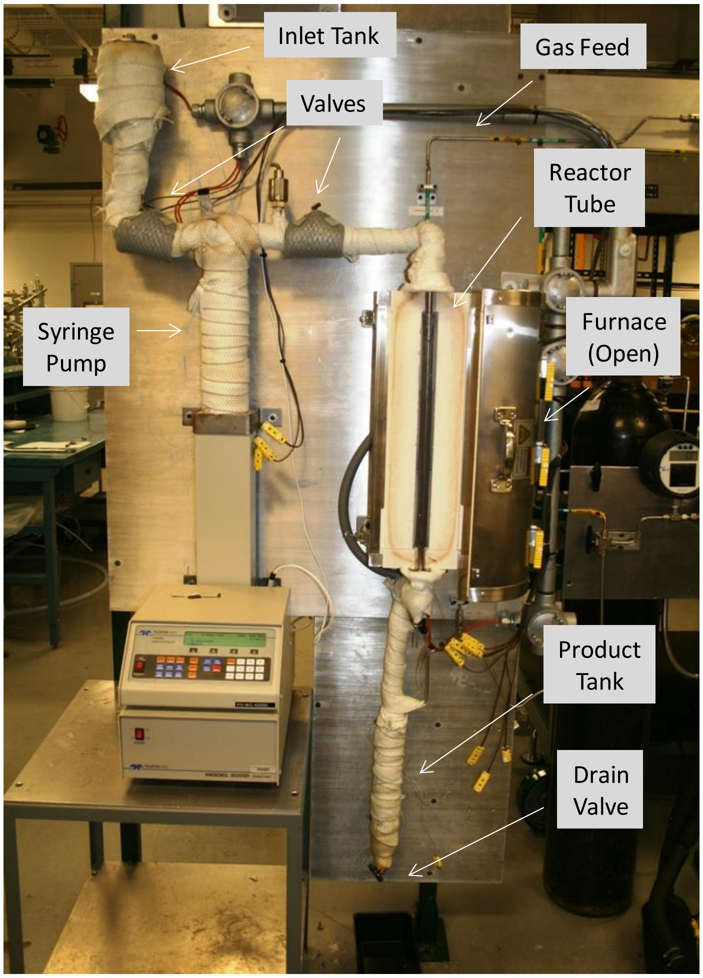


Figure 25. Photograph of Reactor #2 configured for heteroatom removal.

Each reactor is a ½” diameter by 24” long 316 stainless steel tube vertically oriented inside a 3-zone furnace (Applied Testing Systems Inc.). The temperature of the 6” central heating zone can be controlled independently through thermocouples that are spot welded to the exterior of the reactor tube at the center of each heated zone and the temperature of the center zone can be monitored by a moveable thermocouple located within a well extending through the center of the reactor tube. The length of the tube within the furnace is covered with a split cylindrical brass tube of 1/8” thickness to assist in evenly distributing the heating loads. Reactor pressure is controlled by a back- pressure regulator downstream of the product receiver. Gases are supplied from regulated cylinders which were also used to pressurize the system. Gas flow rates were precisely controlled with 5850i Brooks mass flow controllers. Liquid feeds can be heated to avoid crystallization in a one liter feed tank and charged into a heated ISCO-500D syringe pump. The liquid and gas feeds combine at the top of the fixed-bed column and mix while flowing through approximately 4” of 54 mesh silicon carbide before contacting the catalyst-containing portion of the bed. Catalysts can be used as the as-received extrudates, crushed and sieved extrudates, or, more commonly, the crushed extrudates diluted with inert, high-conductivity material, such as silicon carbide. (Diluting the catalyst provides superior temperature control in the presence of strongly exo- or endothermic reactions and reduces channeling through the bed.) The lower section of the reactor is similar to the inlet section with a volume of 54 mesh silicon carbide resting on a plug of quartz wool on a 20 μm sintered stainless steel filter at the exit of the reactor tube.

If sulfiding and/or activation procedures are provided by the manufacturer, these procedures are used. In the manufacturer's SOPs are not provided then procedures developed in-house are used. For example, base metal catalysts are activated after the reactor has been prepared and mounted in the reactor furnace. This is usually conducted at 450°C with hydrogen flowing at an equivalent gas hourly space velocity (GHSV) of 13.7/hr at 100 psi for 4 hours. Catalysts that require sulfiding are treated after they are loaded into the reactor tube, but before the tube is installed in the reactor furnace. Briefly, the reactor is mounted in a horizontal furnace, supplied with a flowing mixture of hydrogen and hydrogen sulfide at atmospheric pressure, and heated gradually over 2 hours to 350°C, held for 6 hours, cooled to room temperature, and then capped for transfer to the reactor furnace.

For each test run the reactors are typically operated with a LHSV of 1/hr based on the dry mass of the catalyst. Hydrogen is supplied at a molar ratio of 10:1 based on the known or estimated mean molecular weight of the liquid feed. To measure H_2 consumption N_2 (%volume ~2%) can used as internal reference gas. The sulfided reactors and the base metal reactors are typically operated with 800 psi of hydrogen. The sulfided reactors are conditioned at the initial temperature for the test sequence with flowing liquid feed for 1.5 hours. The product collected during this period is then drained from the product tank, and a test volume collected for 1.5 hours. This sample is then drained from the tank and stored for analysis. The temperature is then set for the next test point and the reactor allowed to run until the reactor temperature is steady, typically about 1.5 hours. The product tank is then drained, and the process repeated until the test sequence is completed. The reactor temperature is normally increased from the starting temperature to the final temperature in predetermined steps. However, in some cases the temperature may be decreased from some upper starting temperature to a lower ending temperature. To measure the hydrogen consumption the reactor effluent rates are recorded and averaged, then the effluent gas is analyzed using the online 3000 Micro GC (Inficon).

Reviewing the available reactors, Reactors #2 and #6 were selected for the heteroatom removal since these systems have been used previously with sulfided catalysts. Reactor #1 was selected for the upgrading of the product from the heteroatom removal as this system has been previously used as a hydrotreating reactor and has not been operated with sulfided catalysts.

To quantify the performance of the Stage-1 reactor, the conversion of selected heteroatom components was measured using gas chromatography–mass spectrometry (GC-MS). Furthermore, selected samples were submitted for quantitative elemental analysis. Briefly, the analysis was used to measure the relative concentration of carbazole (N), dibenzothiophene (O), and dibenzofuran (S) between the product and feed. This analysis was relatively quick and could be performed in-house and served as a general-purpose screen tool. The quantitative analysis of selected elements (C, H, N, O, and S) was conducted by an analytical services laboratory

(Galbraith Laboratories, Inc., Knoxville, TN) which gave more comprehensive results for the heteroatom conversion, but was more costly in terms of time and resources.

The performance of the Stage-2 reactor was quantified using GCxGC to conduct a hydrocarbon type analysis of the reactor feed and product. This analysis quantifies the major hydrocarbon classes in the sample by type such as the number of aromatic rings, cyclic or linear and branched alkyl aromatics, and cyclic, linear, or branched paraffins. Of particular interest for this program is the conversion of polynuclear aromatic hydrocarbons to single-ring aromatic hydrocarbons and paraffins (linear, branched, and cyclic). From this analysis, the degree of HDA could be determined as well as measuring the concentration of various aromatic components in the product. The latter is of interest as jet fuel specifications allow up to 25% single-ringed aromatics and 3% di-aromatics (alkyl naphthalenes).

7.5 Materials.

The feedstocks used in this program consisted of model fluids composed in-house at UDRI and actual syncrudes provided by Battelle. The model fluids consisted of Aromatic-200 (Exxon Mobile), a complex petroleum distillate of C12–C15 aromatics in the form of alkylnaphthalenes. This was used either as-received or blended with selected heteroatom components. Based on a review of the literature on petroleum refining and the production of ultra-low sulfur diesel fuel, dibenzothiophene (DBT) and carbazole (see Figure 26) were selected as model sulfur and nitrogen containing species, respectively. These were blended with the Aromatic-200 to give a total sulfur content of 1% mole/mole and a nitrogen content of 0.01% mole/mole. After blending, the Aromatic-200 was designated Aromatic-200SN. Note that the molecular structures of these model compounds are very similar to dibenzofuran, which was later used as a marker species for the presence of oxygenates in the actual syncrudes, but not used in the model feedstocks.

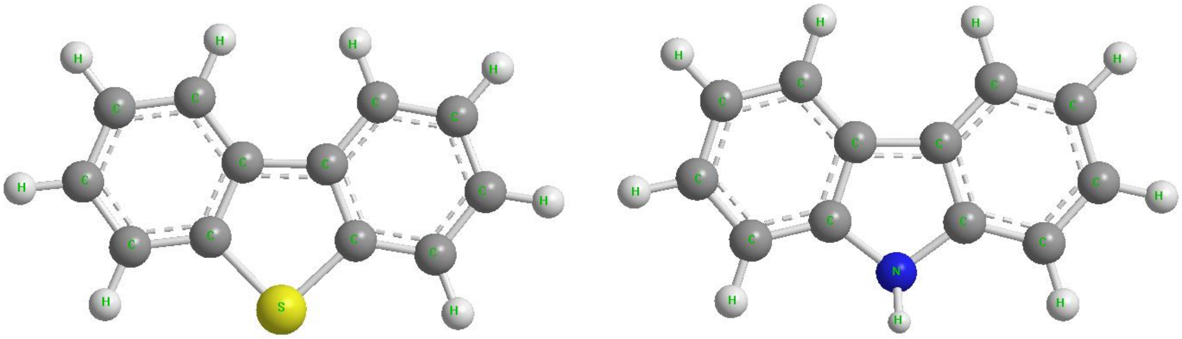


Figure 26. Molecular structures of dibenzothiophene (left) and carbazole (right).

The actual syncrudes were initially made available in relatively small volumes and were the products of an evolving process. In total, 6 syncrudes were delivered in two broad versions. The first two syncrudes (SC-1 and 2) were from an early development production batch (Quantex Run #2). These were very viscous and had a significant solid or gel phase that required sonication and/or mild heating (80-90°C) to homogenize. The syncrudes WFE SC-1 through 3 are from the same syncrude batch but filtered on different days as needed; these were from a more refined production process (Quantex Run #3; feed to the wiped film evaporator – WFE). WFE SC-4 is distillation fraction of WFE (Quantex Run #3) below 450°C. These were less viscous than the first set, though they also included a second phase that required sonication and/or mild heating (50-80°C) to homogenize.

GC-MS analysis of the syncrudes showed that their overall composition was very similar. All of the syncrudes were very complex mixtures of polynuclear aromatic hydrocarbons (PAHs) spanning from about naphthalene (2 rings) to benzopyrene (5 rings) with an average density of 1.102 g/mL. Figure 27 includes the GC-MS analysis of the Aromatic-200SN showing that this model feed consists primarily of alkyl naphthalenes plus the added dibenzothiophene and carbazole (average density 0.982 g/mL). The elemental analysis and density of the syncrudes are summarized in Table 24. It shows that there was some variability in the heteroatom content of the various syncrudes, though the density was fairly consistent. Taking 10ppm as a nominal target for the final concentration of N, O, and S, suggested that an average heteroatom removal efficiency on the order of 99.9% was required.

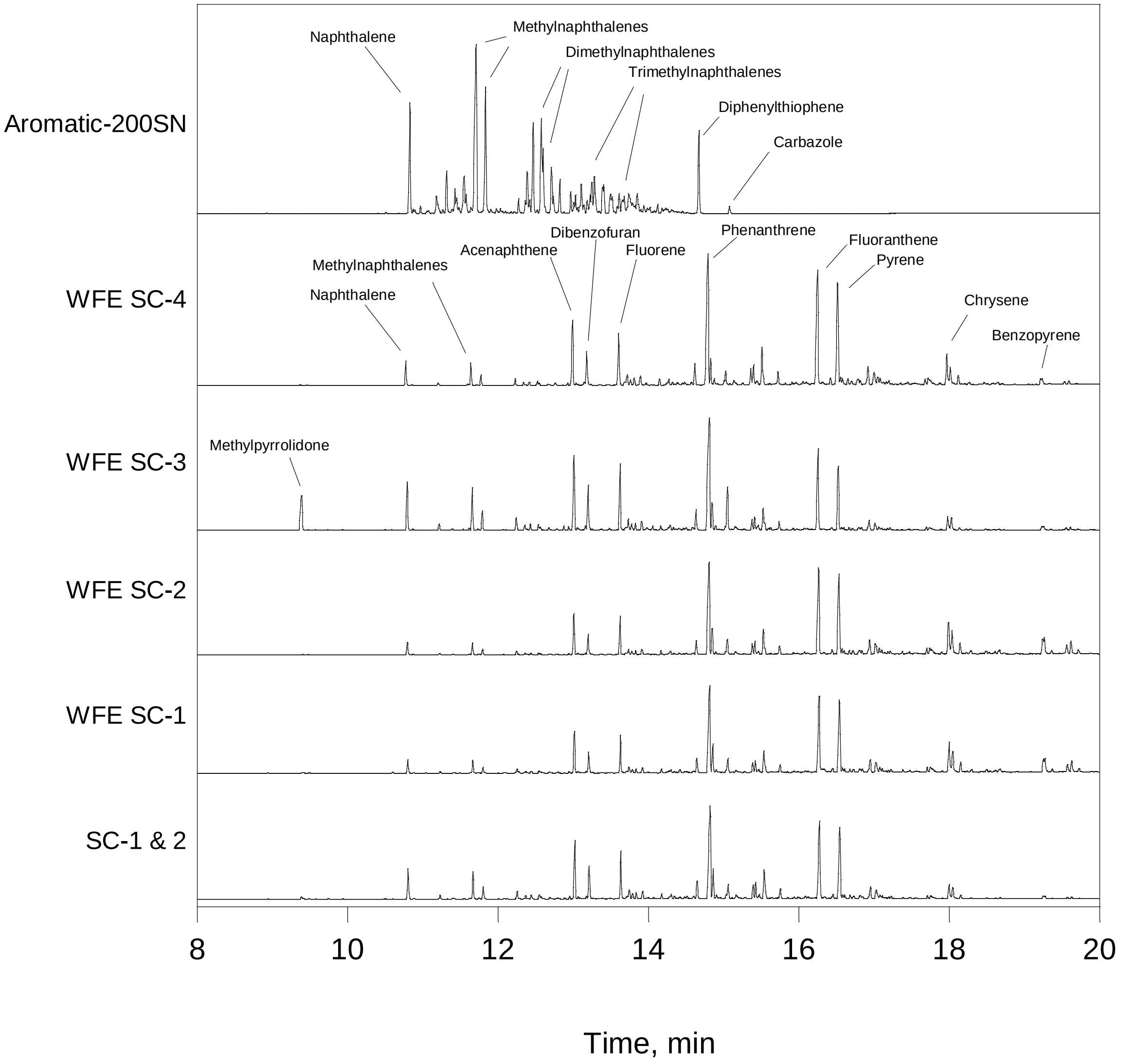


Figure 27. GC-MS analysis of the various syncrudes and the model feed.

Table 24. Syncrudes

Syncrude	C wt%	H wt%	N wt%	O wt%	S ppm	Density g/mL	H/C mole ratio
SC-1 & 2	90.32	6.13	0.85	2.11	5950	1.09	0.814
WFE SC-1	87.52	7.36	1.05	4.13	4250	1.1	1.009
WFE SC-2	87.6	7.23	1.03	3.81	4880	1.1	0.990
WFE SC-3	85.34	6.95	2.02	3.36	2790	1.09	0.977
average WFE SC1-3	86.82	7.18	1.37	3.77	3973	1.10	0.992
WFE SC-4	90.32	6.17	1.43	1.86	5520	1.13	0.820

The catalysts used in this subtask were commercial and developmental catalysts. We are required by non-disclosure agreement (NDA) to not disclose the identity of these catalysts. A list of the catalysts tested is provided in Table 25.

Table 25. Catalysts Tested for Upgrading of CTL Syncrudes.

Type	Catalyst	Stage
S-CoMo	A	1
	B	1
S-NiMo	C	1
	D	1
	E	1
	F	1
	G	1
	H	1
	I	1
S-NiW	J	2
Pt	K	2

7.6 Results and Discussion.

The Stage-1 catalyst evaluation was conducted in four broad phases largely driven by the availability of syncrude and catalysts. The first phase was conducted using the model Aromatic-200SN feed with catalysts available in-house. This verified the operation of the reactors, calibration of the system and established the initial operating conditions for subsequent analyses. The second phase used the first samples of syncrude. These were processed through Stage-1 and provided information on the operating conditions and challenges associated with these feeds and analysis. The third phase focused on screening the remaining Stage-1 catalysts using a standardized set of conditions based on the initial work with the first syncrude material. In the fourth phase the most promising candidate was selected for more detailed evaluation and to produce a finished Stage-1 product for upgrading in Stage-2.

7.6.1 Stage-1, Series 1 - Aromatic-200SN Model Feed.

For this initial test sequence the reactor was prepared and catalyst sulfided as described above using the as-received extrudates that were crushed, sieved 32/60 mesh, weighed (approximately 2.6 g, 3.5 mL), diluted 1:1 with 54 mesh SiC, loaded into the reactor tube, sulfided, and then transferred to the reactor assembly. The catalyst was initially conditioned using the neat Aromatic-200, and then with the Aromatic 200SN. Tests were conducted from 300°C to 400°C at 5°C intervals using a LHSV of 1/hr (nominally 5.2-5.5 L/min) and 800 psi hydrogen flowing at a molar feed ratio of 10:1 (nominally 46-49 mL/min at STP) assuming a mean molecular weight for the feed of 252.54 g/mol. At each temperature, a sample of the product liquid was analyzed by GC-MS. The conversion of DBT and carbazole was measured using the peak areas from the extracted ion chromatograms taking the 184 m/e and 167 m/e mass fragments as being characteristic of DBT and carbazole, respectively. The sulfur and nitrogen concentration was estimated from the measured conversion and the known starting concentrations of DBT and carbazole and assuming that no other organic sulfur or nitrogen compounds were produced as products.

The initial tests were performed using catalyst A (CoMo) and the Aromatic-200SN feed. The overall conversion and heteroatom results are summarized in Figure 28. These results show that the concentration of DBT steadily declined as the temperature increased from 300°C to 400°C, while the carbazole passed through a minimum at approximately 350°C. Conversion of the Aromatic-200 to naphthalenes and tetrahydronaphthalenes was also observed. Small amounts of alkyl benzenes and decalin are also present in the product.

As the tests with Catalyst-1 were concluding the commercial catalysts became available for testing. Catalyst "C" was selected for the first series of tests using the Aromatic-200SN feed as there was interest in comparing this NiMo catalyst with the CoMo catalyst used previously. Catalyst "D" was also selected for evaluation at the manufacturer's literature indicated that this catalyst may show an activity lower than Catalyst "C".

The results for the catalysts 'C" and "D" are summarized in Figures 29 and 30, respectively. These show that the performance of these two catalysts is indeed very similar to each other. Both showed excellent activity towards the conversion of carbazole, reducing it to below the detection limit of the GC-MS by approximately 320°C. They also showed good activity towards the conversion of DBT up to about 350°C, after which the activity slightly declined. Both of these catalysts showed a much higher activity towards the reduction of carbazole as compared to catalyst "A", while they showed a similar level of activity towards the conversion of DBT throughout most of the temperature range used here.

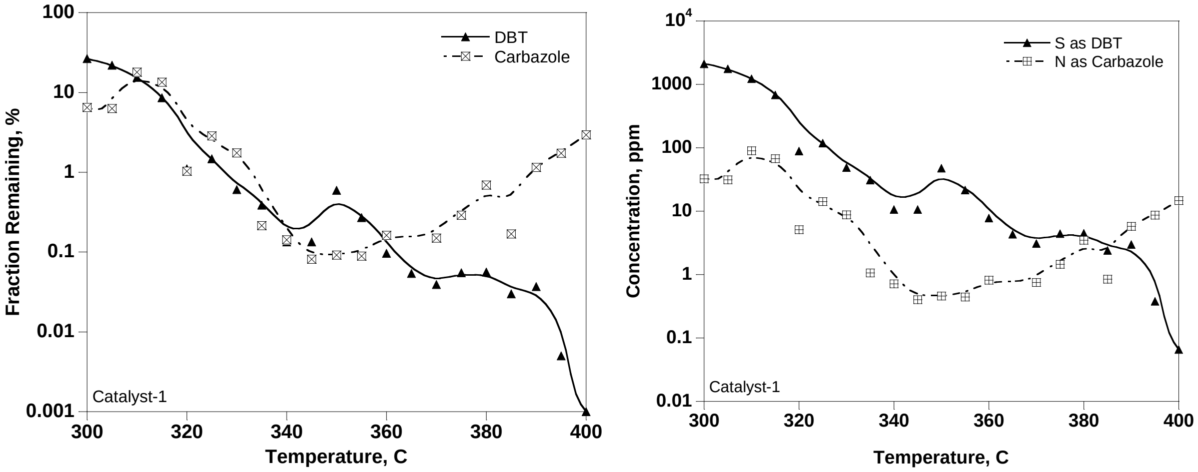


Figure 28. Summary of the results for Aromatic-200SN using catalyst "A" (CoMo) from 300-400°C with 800 psi hydrogen and a LHSV of 1/hr.

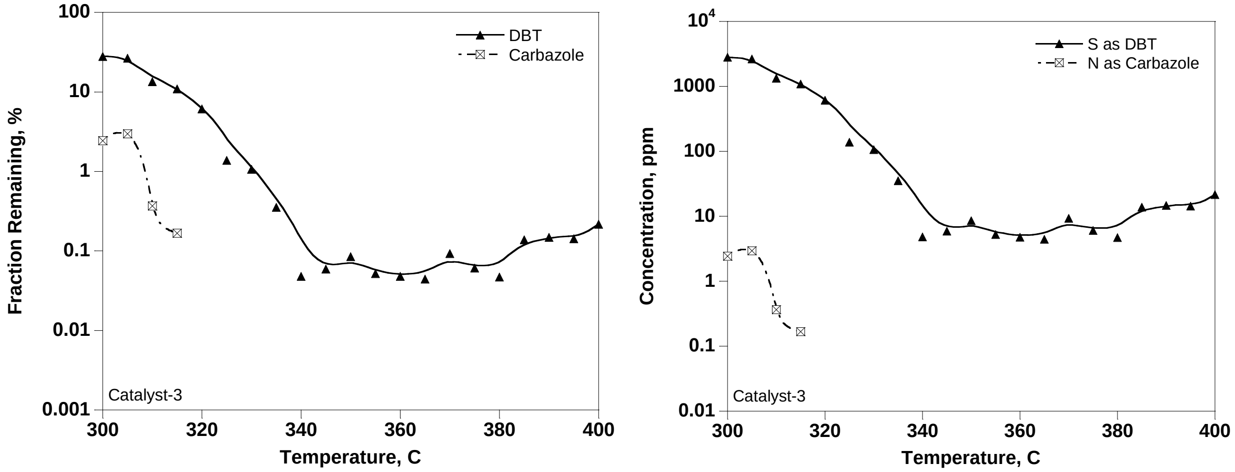


Figure 29. Summary of the results for Aromatic-200SN using catalyst "C" (NiMo) from 300-400°C with 800 psi hydrogen and a LHSV of 1/hr.

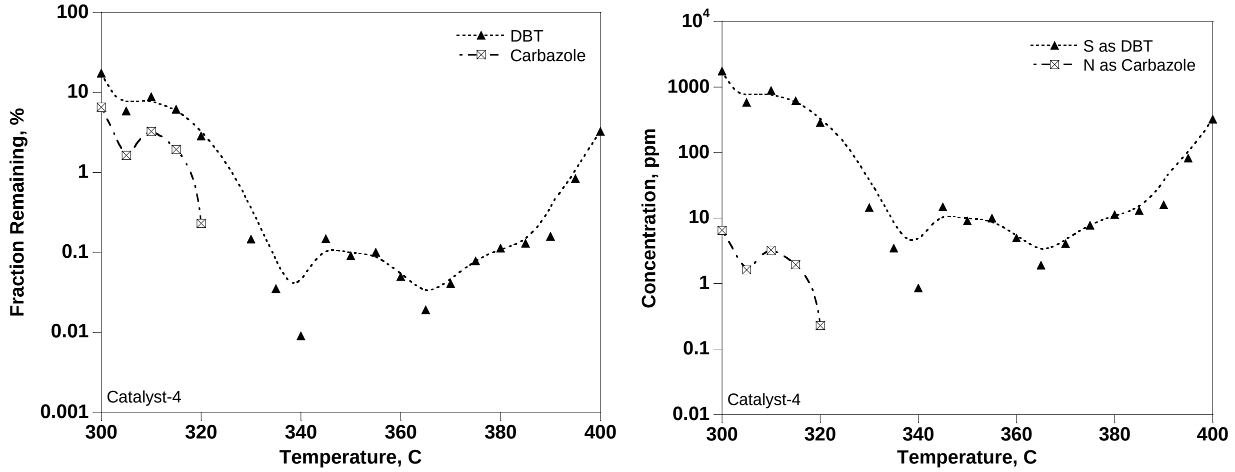


Figure 30. Summary of the results for Aromatic-200SN-2 using catalyst "D" (NiMo) from 300-400°C with 800 psi hydrogen and a LHSV of 1/hr.

The overall results from all three of the catalysts described above are summarized in Figure 31 This illustrates that the performance of the sulfided CoMo and sulfided NiMo catalysts was very similar in their ability to reduce the concentration of dibenzothiophene present in the model feed and an optimal temperature range of approximately 340°C to 370°C. The NiMo catalysts showed higher performance in the removal of N with the concentration dropping below the detection limit of approximately 0.1 ppm by 320°C. In contrast, the concentration of N from the CoMo catalyst remained above the detection limit across the temperature range used here, though the performance passed through a maximum at approximately 350°C with less than 1 ppm N remaining in the liquid product.

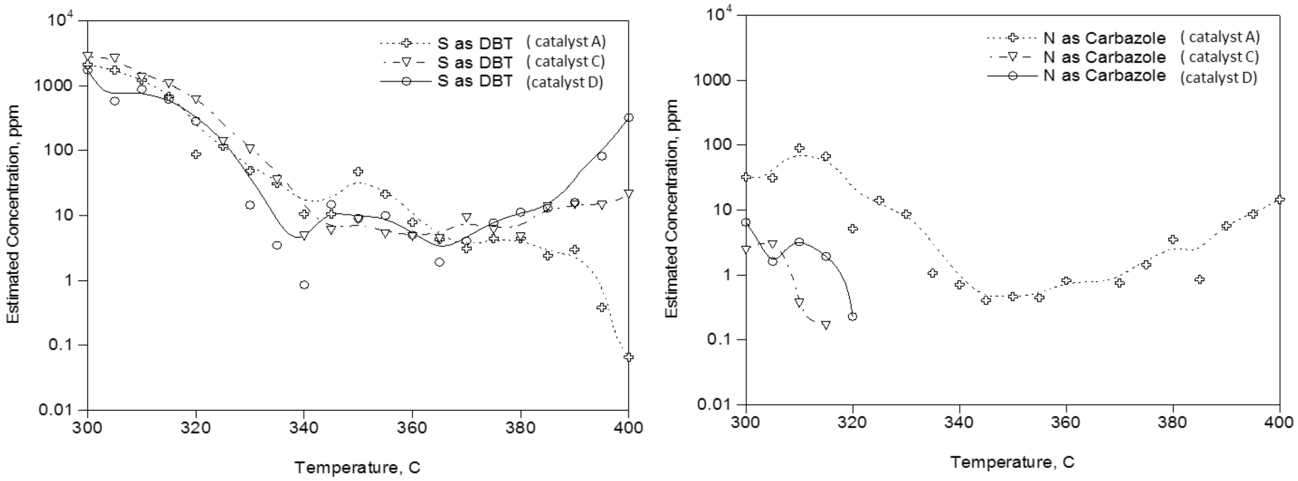


Figure 31. Comparison of the overall results for S (left) and N (right) from the CoMo (Catalyst A) and NiMo (C and D) catalysts.

7.6.2 Stage-1, Series-2 - Syncrudes SC-1 & 2 and WFE SC

Series-2 included the initial tests using the early syncrudes SC-1 and -2 and WFE SC-1. These syncrudes were produced using the baseline solvent, i.e., soybean oil. The SC-1 and -2 were small volumes of a very similar syncrude that had a coarse solid phase at room temperature that required sonication and/or mild heating (80-90°C) to homogenize. In the initial Phase the catalysts were crushed, sieved, and diluted 1:1 with SiC before being sulfided. The goal of dilution of catalyst with SiC is to better control exothermic reaction and prevent hotspots. The runs included an initial conditioning period of 150 hours under a nominal startup condition; typically 360°C with 700 psi of hydrogen and a LHSV of 0.3/hr. After this initial conditioning period the reactor performance was evaluated at various temperatures and pressures at a fixed LHSV. The primary measure of reactor performance was the analysis of the N, O, S marker components (carbazole, dibenzofuran, and dibenzothiophene) as described above as well as the product density and appearance. Selected samples were submitted for elemental analysis (N, O, S). Series-2 ended with the migration to a simpler standardized test sequence using the as-received catalysts without dilution, a LHSV of 0.15/hr, a fixed temperature (380°C) and pressure (950psi), and a fixed run time of 100 hours.

The product from the Series-2, Stage-1 reactors was typically very dark and often contained what appeared to be very fine particulate that slowly settled. The product could be clear when the catalyst was relatively new or when the temperature and pressure were increased. However, the quality of the product as indicated by the GC-MS or elemental analysis did not seem to correlate with the visual appearance of the product.

The GC-MS analysis of the Phase-2, Stage-1 reactor products for WFE SC-1 feed shown in Figure 32 illustrate that there were essentially no differences in the principal organic constituents in the reactor products, though the relative concentrations of the individual components did show some variability. These results also show that the reactor feed was almost universally partially hydrogenated. Specifically, while the feed was composed almost entirely of PAHs, the reactor products show varying degrees of ring saturation. However, there is little evidence for ring opening. It is also interesting to note the presence of dibenzofuran in all of the reactor products, illustrating the limited conversion of this specific heteroatom component. Similarly, pyrene was noted as one of the few PAHs present in both the feed and product, suggesting that this component is exceptionally resistant to hydrogenation.

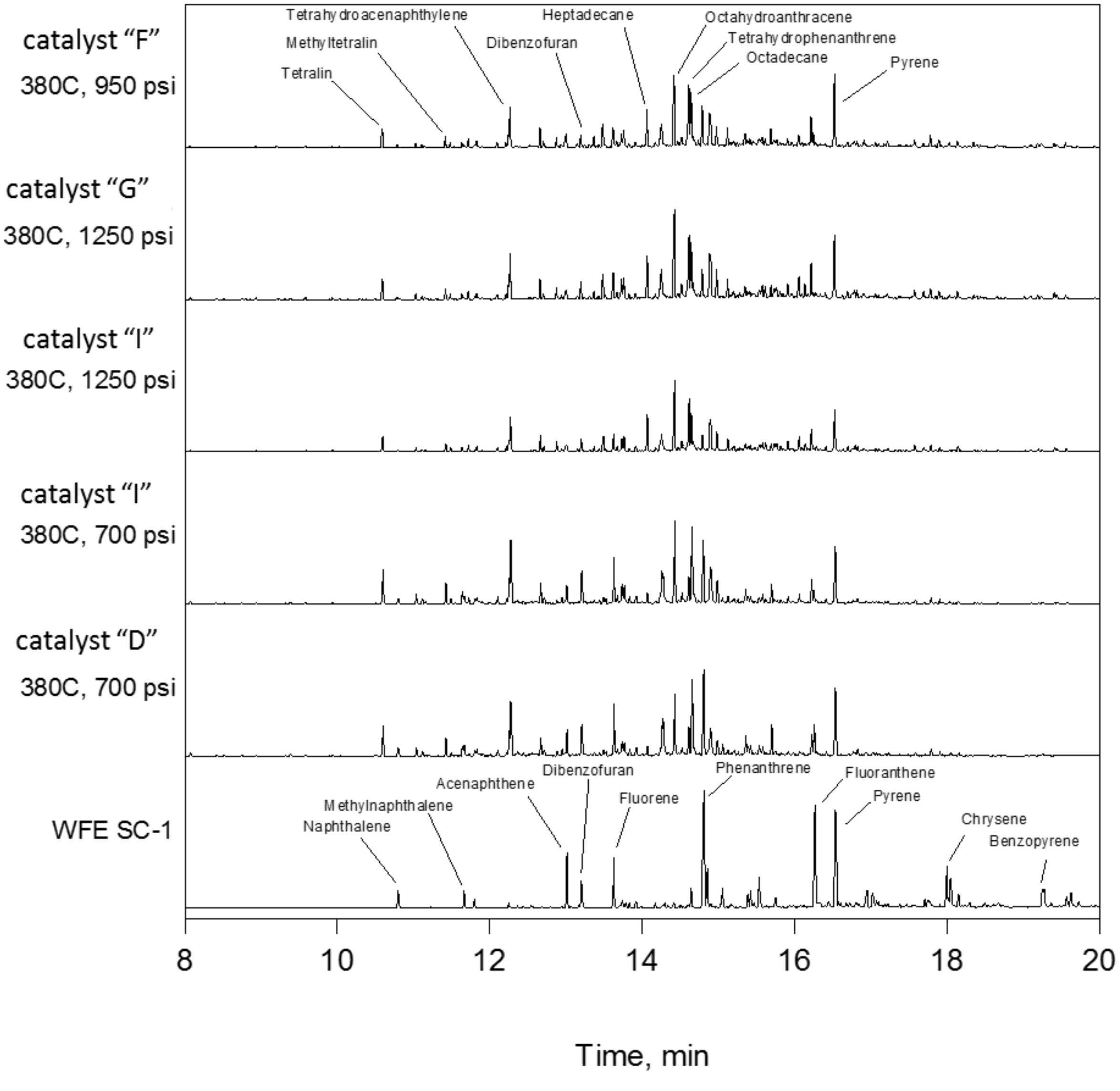


Figure 32. GC-MS analysis of selected products and the WFE SC-1 feed.

The overall results summarized in Table 26 suggest that the most promising candidates from the Phase-2 evaluation were the "I" and "F" catalysts based largely on the GC-MS analysis of the marker components for nitrogen (carbazole) and sulfur (dibenzothiophene) as well as the elemental analysis for sulfur. Only modest reduction in the marker component for oxygen (dibenzofuran) was noted from any of the catalysts. This is consistent with literature that suggests that dibenzofuran is exceptionally stable. The decrease in the density of the product relative to the feed indicates a modest degree of hydrogenation consistent with the GC-MS analysis described above. Note that in the absence of significant ring-opening the lightest product that can be produced from these syncrudes is decalin with a density of 0.895 g/mL.

Table 26. Summary of Stage-1, Series-2 Results

							Product Elemental Analysis						GC-MS Analysis		
Catalyst[a]	Feed	Temp.	Pressure	LHSV	Density, g/mL		Remaining, ppm			Conversion, %[b]			Conversion, %		
					Feed	Prod.	N	O	S	N	O	S	Carb (N)	DBF (O)	DBT (S)
Catalyst D	SC-1	360-400	800	0.3	1.09	1.03	<5000	<5000	133	>41.2	>76.3	97.8	4.8	16.4	98.7
Catalyst I	SC-2	360-380	700-950	0.3	1.09	1.02	7400	6400	359	12.9	69.7	94.0	78.3	8.4	98.1
Catalyst I	WFE SC-1	380	950	0.3	1.10	0.98	<5000	<5000	167	>51.8	>87.4	96.3	95.1	32.5	98.2
Catalyst G	WFE SC-2	380-400	950-1250	0.3	1.10	0.97	<5000	<5000	286	>30.6	>86.9	94.1	89.6	29.2	98.3
Catalyst F	WFE SC-2	380	950	0.15	1.10	0.99	<5000	<5000	242	>30.6	>86.9	95.0	96.5	43.0	96.7

(a) All of these catalysts were NiMo
(b) Conversion % represents removal on a wt% basis

7.6.3 Stage-1, Series-3 - Syncrudes WFE SC-2, 3, and 4

Series 2 showed that relatively aggressive conditions of temperature and pressure would be needed to successfully remove the heteroatom components from the coal-derived syncrudes. It was also desirable to standardize the exposure conditions to make the results more comparable. For these reasons, the exposure conditions were fixed at 380°C and 1250 psi. Furthermore, the Series 3 catalysts were loaded as-received (extrudates) and without dilution. This doubled the amount of catalyst in the reactor, and by leaving the flow rates of feed and hydrogen unchanged the LHSV dropped from 0.3/hr to 0.15/hr without decreasing the production rate of Stage-1 product. It was observed that the hydrotreatment of syncrude is not excessively exothermic and therefore the catalyst can be used catalyst without SiC dilution

Photographs of selected Series-3 products are shown in Figures 33 and 34. The GC-MS total ion chromatograms of selected products are shown in Figure 35. The overall results from the Phase-3 evaluation are summarized in Table 27.

The photographs shown in Figures 33 and 34 illustrate that the product from the Series-3, Stage-1 reactors were relatively clear, though some contained what appeared to be very fine particulate that slowly settled. The fine material could also agglomerate with the water phase, making it somewhat difficult to separate.

Figure 33. Selected products from the processing of the WFE SC-3 syncrude over the "E" NiMo catalyst at 380°C and 1250 psi with a LHSV of 0.15/hr.

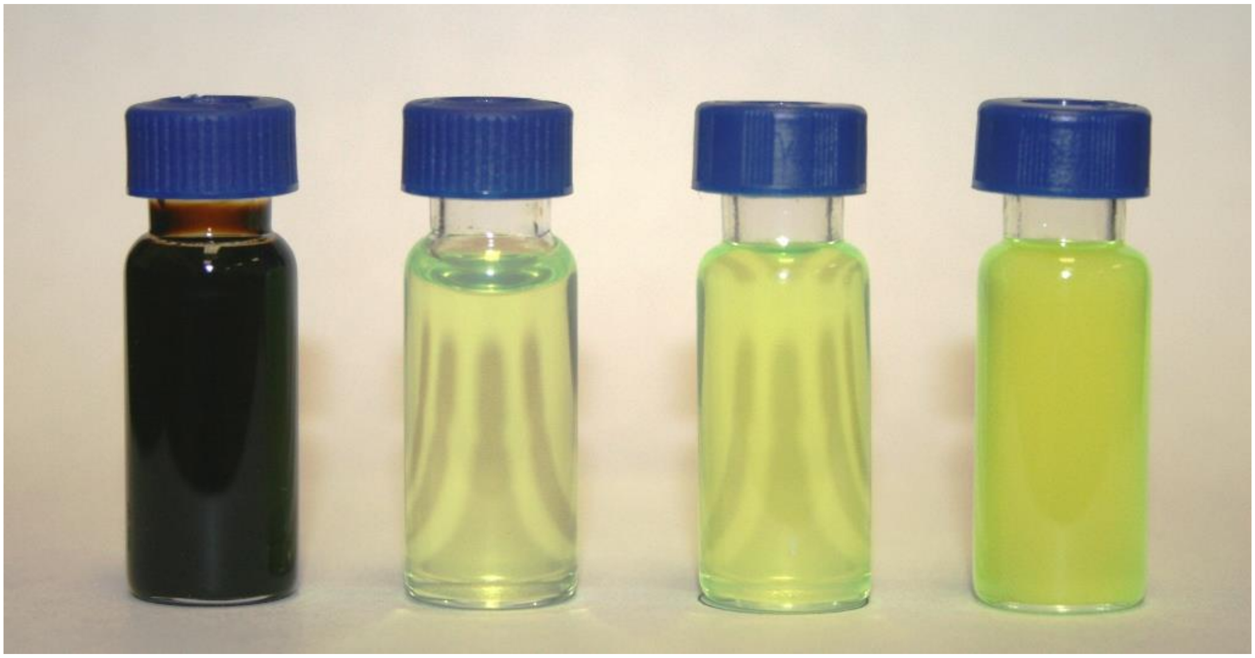


Figure 34. Selected products from the processing of the WFE SC-3 syncrude over the "H" NiMo catalyst at 380°C and 1250 psi with a LHSV of 0.15/hr.

The GC-MS analysis of the Series-3, Stage-1 reactor products shown in Figure 38 illustrate that there were essentially no differences in the principal organic constituents in the reactor products after 100 hours of operation with the syncrude, though the relative concentrations of the individual components did show some variability. These results also show that the reactor feed was almost universally partially hydrogenated. Specifically, while the feed was composed almost entirely of PAHs, the reactor products show varying degrees of ring saturation. However, there is little evidence for ring opening after the first few hours of operation with the syncrudes. It is also interesting to note the presence of dibenzofuran in all of the reactor products, illustrating the limited conversion of this specific heteroatom component. Similarly, pyrene was noted as one of the few PAHs present in both the feed and product, suggesting that this component is exceptionally resistant to hydrogenation.

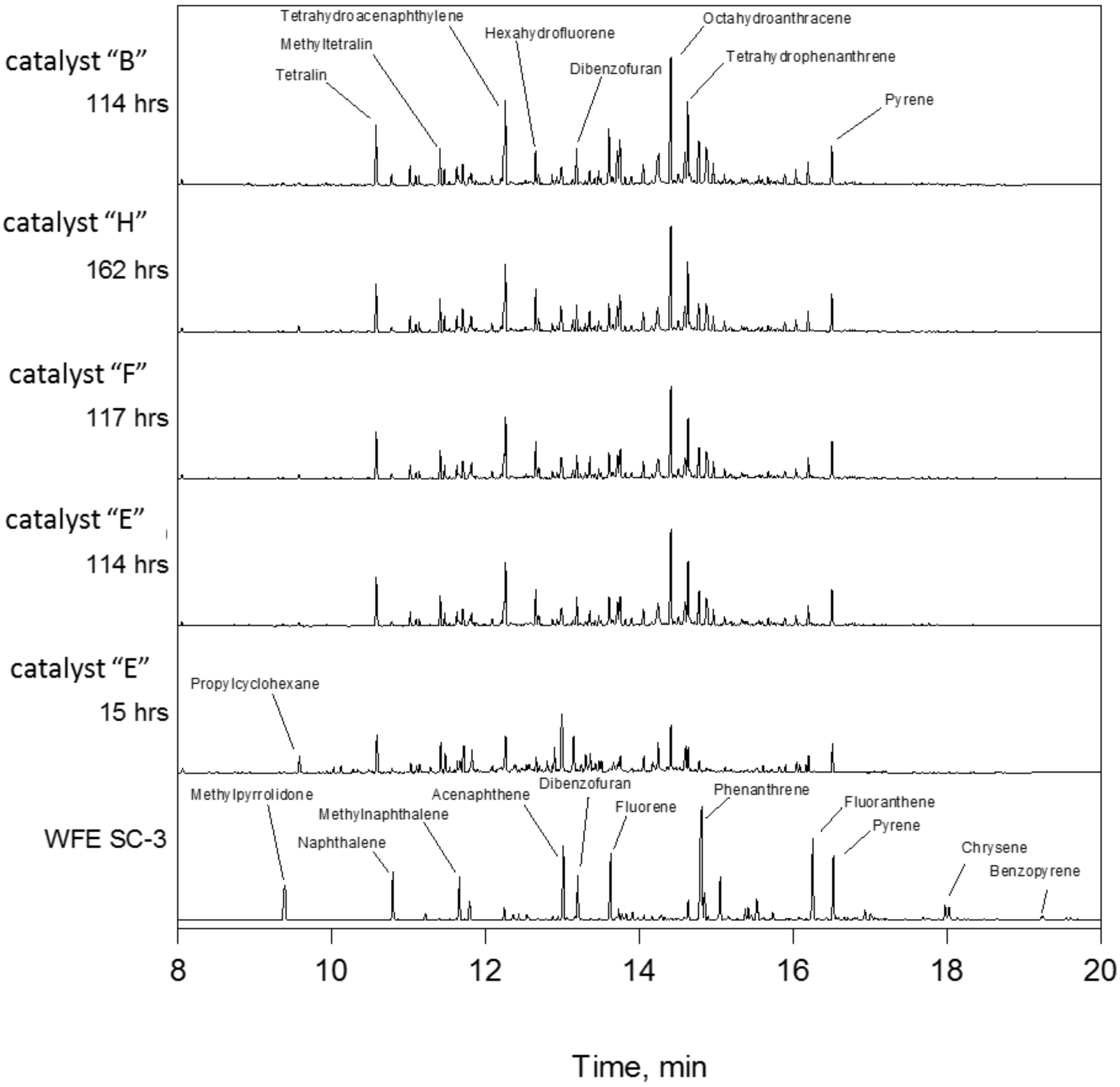


Figure 35. GC-MS analysis of selected products and the WFE SC-3 feed.

The overall results summarized in Table 27 suggest that the most promising candidates from the Series-3 evaluation were the "E" and "H" catalysts. These showed the best reduction in heteroatom content based on the elemental analysis. The GC-MS analysis of the marker components also showed excellent reduction in nitrogen (carbazole) and sulfur (dibenzothiophene). Only modest reduction in the marker component for oxygen (dibenzofuran) was noted from any of the catalysts after 100 hours of operation with the syncrudes. This is consistent with literature that suggests that dibenzofuran is exceptionally stable. The decrease in the density of the product relative to the feed indicates a modest degree of hydrogenation consistent with the GC-MS analysis described above. Note that the greatest reduction in the product density was also found with the "E" and "H" catalysts. Note that in the absence of significant ring-opening the lightest product that can be produced from these syncrudes in decalin with a density of 0.895 g/mL.

Table 27. Summary of Stage-1, Series-3 Results

			Product Elemental Analysis						GC-MS Analysis		
Catalyst	**Density, g/mL**		**Remaining, ppm**			**Conversion, %**			**Conversion, %**		
	Feed	**Prod.**	**N**	**O**	**S**	**N**	**O**	**S**	**Carb (N)**	**DBF (O)**	**DBT (S)**
"E" (15 hrs)	1.09	0.942	6100	<5000	100	69.8	>85.1	96.4	>99.0	92.6	98.4
"E" (110 hrs)	1.09	0.942	7100	7400	93	64.9	78.0	96.7	>99.0	33.8	98.4
"F"	1.09	0.952	10200	<5000	132	49.5	>85.1	95.3	98.6	53.8	98.2
"H"	1.09	0.945	7300	<5000	83	63.9	>85.1	97.0	>99.0	56.8	98.2
"B" (CoMo)*	1.09	0.969	8200	5100	191	59.4	84.8	93.2	95.0	41.4	98.4

*Note that the "B" was the only CoMo catalyst evaluated in Series 3.

Note that the products from Series-3 were much lighter in color and clean compared to those from Series-2. The key reason for this is that Series-2 syncrude was made using soybean oil, which did not turn out to be a hydrogen donor, so the resulting syncrude was very heavy. On the other hand, Series-3 syncrude was made using a bio-solvent from the Battelle. CTL process.

7.6.4 Stage-1, Series-4 - Production of Stage-1 Product.

Based on the evaluations described above, the "H" sulfided NiMo catalyst was selected to produce Stage1 product for upgrading in Stage-2. To maximize the heteroatom removal from the Stage-1 process the approach was modified by conducting it in two steps referred to as Stage-1a and Stage-1b. The Stage-1a reactor was operated as described above. However, the elemental analysis of the reactor product as shown in Table 27 suggests that significant amounts of N remain in the product and the level of S is not low enough to permit the use of a noble metal catalyst in Stage-2. Therefore, the product from the Stage-1a reactor was sparged with nitrogen and washed twice with water to remove residual NH_3 and H_2S. (Sparging was conducted with nitrogen for 1 hour. Washing was with 1:1 HPLS water with gentle swirling and decanting in a separatory funnel.) This washed product was then processed through a Stage-1b reactor to complete the heteroatom removal. The catalysts and processing conditions for both reactors were the same; “H” NiMo catalyst at 380°C, 1250 psi, and with a LHSV of 0.15/hr. The syncrude used as the feed to the Stage-1a reactor was WFE SC-4.

Photographs of selected Stage-1a products are shown in Figure 36. This illustrates that the Stage-1a product is quire dark. These contrast with the product from the earlier evaluation of this catalyst using the WFE SC-3 syncrude (see Figure 34) which were relatively clear. As was previously observed, apparently small changes in the feed can make significant changes in the appearance of the product. Photographs of the Stage-1a and Stage-1b products given in Figure 37 shows that the Stage-1b process gives a relatively clear product.

Figure 36. Selected products from the processing of the WFE SC-4 syncrude over the”H” NiMo catalyst at 380°C and 1250 psi with a LHSV of 0.15/hr (Stage-1a).

Figure 37. The original WFE SC-4 feed and the final Stage-1a and Stage-1b products after they have been sparged and washed.

Recall that the primary purpose of the two-step Stage-1 process is to remove products such as NH_3 and H_2S that could reduce the activity of the catalyst downstream of the initial reaction zone while at the same time preserving the fuel value of the product stream. To monitor the effect of the nitrogen sparge and water wash on the removal of ionic species, the pH of the reactor products was measured as-produced from the reactor, after the nitrogen sparge, and after the water wash. These results, summarized in Table 28, show that the sparge and wash effectively reduced the pH from basic (>9) to near-neutral (~7).

Table 28. pH of the Stage-1a and 1b Reactor Products

Sample	Condition	pH
Stage-1a Product	Source	9.82*
	Sparged	8.83
	Wash #1	7.84
	Wash #2	7.20
Stage-1b Product	Source	9.10
	Sparged	7.60
	Wash #1	6.82
	Wash #2	6.90

*Estimated

Analysis of the products by GC-MS (see Figure 38) shows that the process of sparging and washing does not have a significant effect on the principal organic components of the product, so the fuel value of the product stream is preserved. This analysis also shows that the Stage-1b process reduces the high molecular weight fraction to a small degree and increases the hydrogenation of the process stream. The extent of hydrogenation was quantified by conducting a hydrocarbon type analysis using comprehensive two-dimensional gas chromatography (GCxGC) as summarized in Table 29. This shows that the overall aromatic content after Stage-1a was approximately 60%, and after Stage-1b 42%. Recalling that the feed is essentially 100% aromatics in the form of PAHs, this data suggests that the that the HDA after Stage-1 was on the order of 40% and after Stage-1b it was on the order of 58%. Furthermore, the GC-MS analysis given in Figure 38 shows that the bulk of the product is heavier than decalin, indicating that the fuel value of the feed is preserved and that the hydrocarbon components of the process stream are well suited for upgrading in Stage-2. Finally, the density of the Stage-1a (0.97) and Stage-1b (0.93) products summarized in Table 30 shows that a reasonable degree of hydrogenation is occurring in the Stage-1 reactors and that the product stream is well suited for upgrading. The H/C ratio increases from 0.89 (feed) to 1.42 (Stage-1, Pass1) and 1.53 (Stage-1, Pass 2)

The choice of the catalyst to be used in Stage-2 will depend on the heteroatom content of the process stream leaving Stage-1. The preferred catalyst in Stage-2 would be a noble metal material such as Pt or Pt/Pd. However, if the heteroatom content of the process stream is not appropriate for a noble metal catalyst, then a hydrogenation catalyst such as a sulfided NiW may be necessary. The elemental analysis of the Stage-1 reactor products summarized in Table 29 and the GC-MS analysis of the heteroatom marker components suggest that the two-step Stage-1 process can indeed produce a product low enough in N and S to permit a noble metal catalyst to be considered for Stage-2.

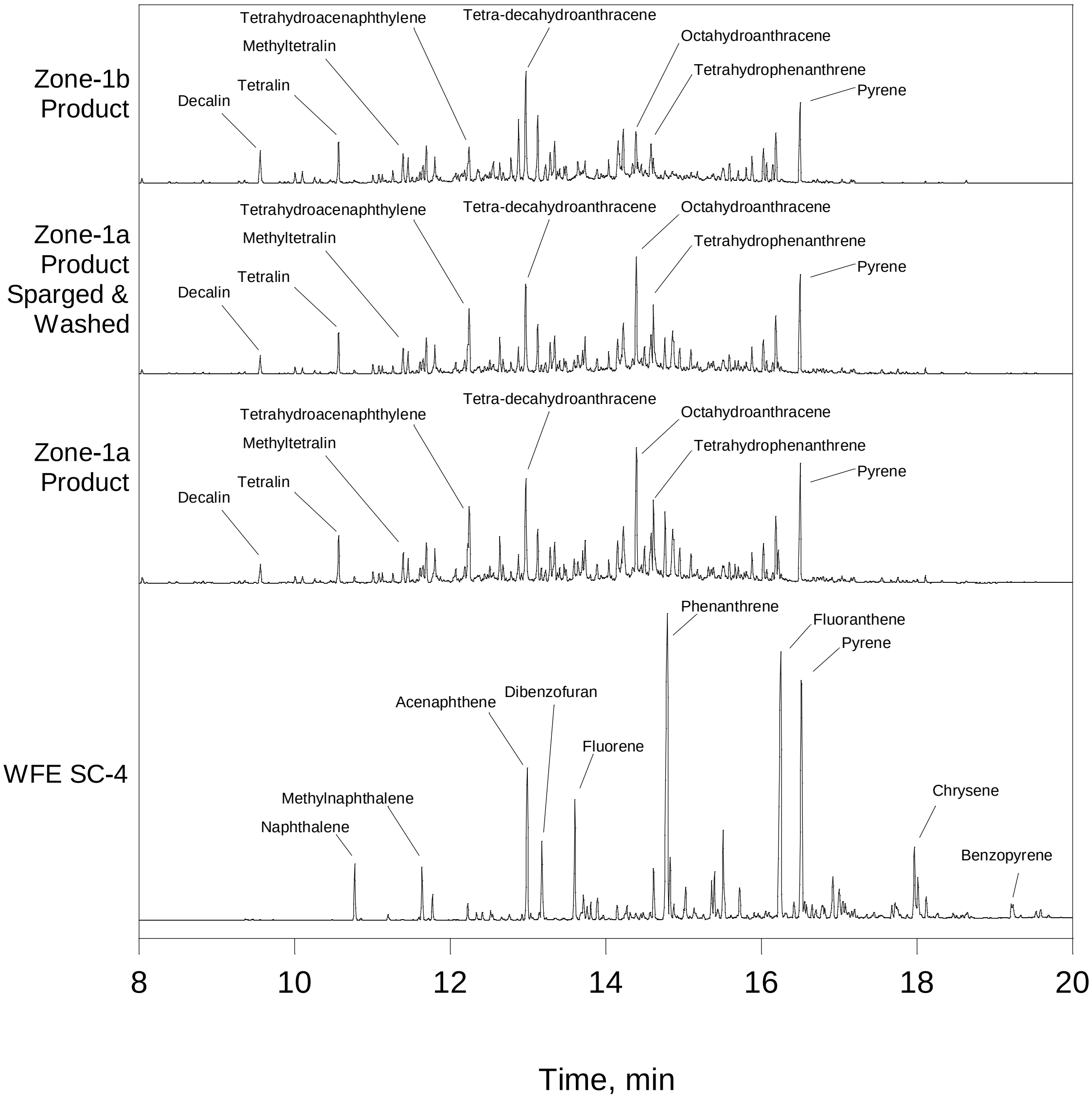


Figure 38. GC-MS analysis of the WFE SC-4 feed and the Stage-1a and Stage-1b products.

Table 29. Stage-1a & 1b GCxGC Hydrocarbon Type Analysis

Class	Sub-class	Stage-1a Product	Stage-1b Product
Aromatics	Alkylbenzenes	0.94	1.61
	Diaromatics (Biphenyls, Naphthalenes, etc.)	4.73	2.17
	Cycloaromatics (Indans, Tetralins,etc.)	10.40	10.63
	Multi-ring Cycloaromatics (CnH$_2$n-10)	19.77	12.81
	Other Multi-ring Cycloaromatics	13.22	8.52
	Other Multi-ring Aromatics	11.09	6.31
	Total Aromatics	**60.15**	**42.05**
Paraffins	iso-Paraffins	2.31	3.69
	n-Paraffins	2.83	2.88
	Total n, iso-Paraffins	**5.14**	**6.57**
Cycloparaffins	Monocycloparaffins	2.89	3.71
	Dicycloparaffins	6.59	11.92
	Tricycloparaffins	16.75	26.35
	Other Cloparaffins	8.08	9.21
	Total Cycloparaffins	34.31	51.20

Table 30. Summary of Stage-1, Phase-3 Results

Condition	Density g/cm3	Composition wt%					H/C mole ratio
		C	H	N	O	S	
WFE 4	1.13	90.32	6.17	1.43	1.86	0.552	0.82
Post zone 1 pass 1 (N2 purge and water wash)	0.968	88.95	10.48	0.0074	<0.5	0.0114	1.41
Post zone 1 pass 2 (N2 purge and water wash)	0.93	88.41	11.29	0.0021	0.5	0.0017	1.53
% heteroatom remover (wt%) after zone 1 pass 1 only				99.48	>74	97.93	
% heteroatom remover (wt%) in pass 2 only				71.62	>74	85.09	
% heteroatom remover (wt%) in pass 1 and 2				99.85	>73	99.69	

Characterization of Feed and Product with 1HNMR. The syncrude and products from Stage-1 were characterized with 1HNMR. Figure 39 is 1HNMR profile for SC-1 (blue) and product from Stage-1 (red) on “D” catalyst at 1250 psi, 380°C, hydrogen/syncrude weight ratio = 3000 and LHSV 0.3. There are two regions: aromatic and aliphatic. The hydrotreatment causes shift of aromatic to aliphatic. The aliphatic/aromatic ratio based on hydrogen is 0.41 in the feed (blue) and 2.5 in the product 1(red). Further treatment of product 1 with “J” catalyst under same conditions increases the ratio to 5.4 (green). Figure 40 is 1HNMR of WFE SC-2 and product over catalyst “J” catalyst under the same conditions. Same phenomena are observed: hydrogenation of aromatic and the aliphatic/aromatic ratio increases from 0.49 to 4.1. Figure 41 is 1HNMR from the hydrotreatment of WFE-4 over “H” catalyst at 1250 psi, 380°C, hydrogen/syncrude weight ratio = 3000 and LHSV 0.15 on two passes as described in Phase 4, Stage-1a. After Stage-1b the aliphatic/aromatic ratio increases considerably from 0.35 to 11.2 showing that changing the reaction condition and specifically LHSV improved considerably the hydrogenation of aromatics.

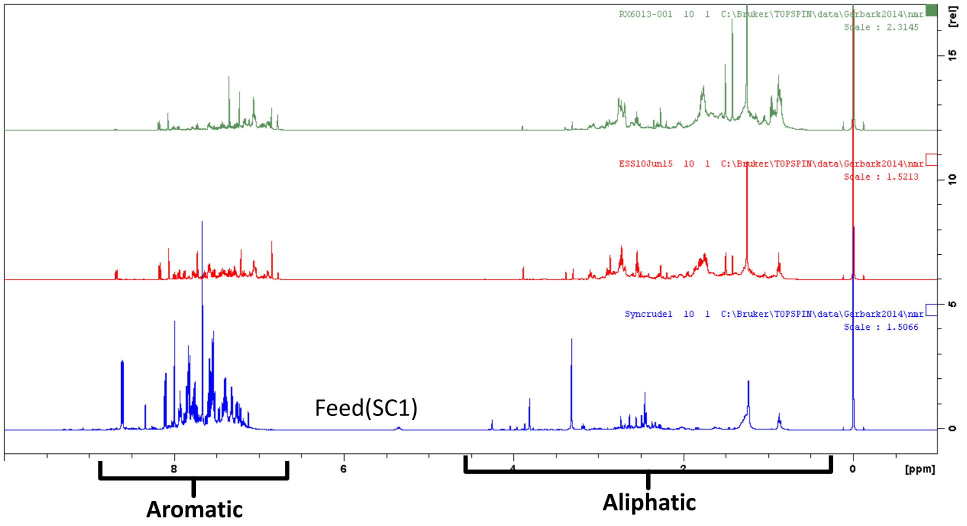


Figure 39. 1HNMR of SC-1 (blue) and product 1 over "D" catalyst at 1250 psi, LHSV: 0.3 and H/syncrude ratio 3000, and temperature of 380°C (red). Product 2 is processing of the product 1 under the same conditions with "J" catalyst (green).

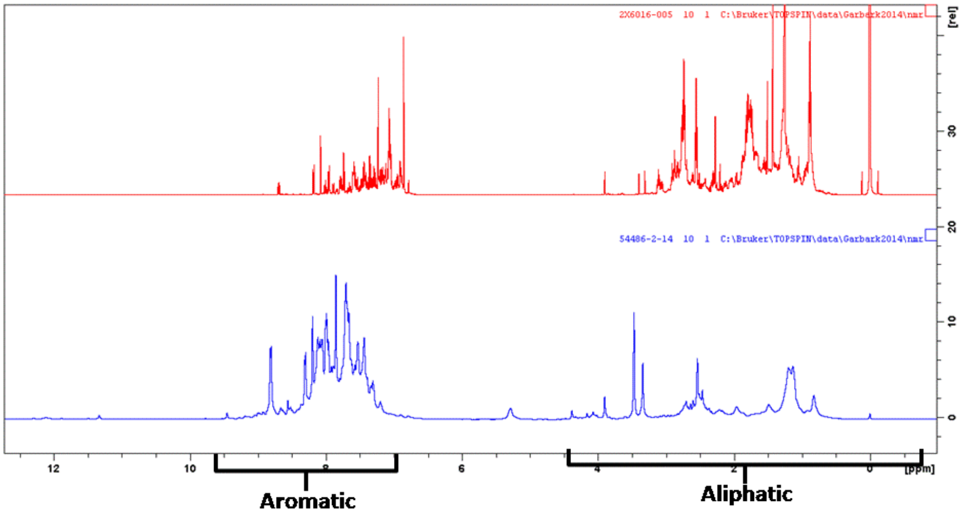


Figure 40. 1HNMR of WFE-2 (blue) and product over "H" at 1250 psi, LHSV: 0.3 and H/syncrude ratio 3000, and temperature of 380°C (red).

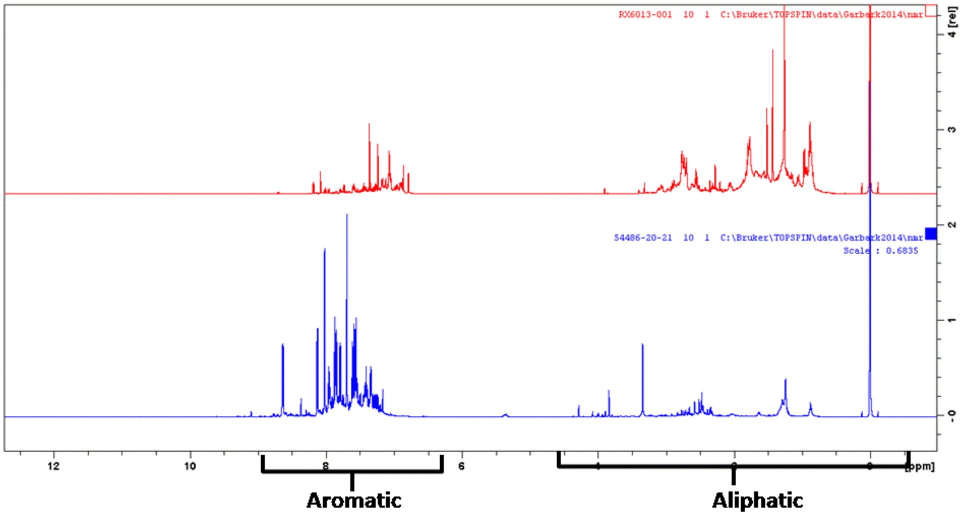


Figure 41. 1HNMR of WFE4 (blue) and product over "H" at 1250 psi, LHSV: 0.1.5 and H/syncrude ratio 3000, and temperature of 380°C second pass (red).

7.6.5 Stage-2 Results

As described above, the function of the Stage-1 reactors is to remove the N, O, and S using a robust, sulfided catalyst to condition the feed for upgrading in Stage-2. This upgrading consists of converting the process stream into a mixture of hydrocarbons suitable for blending with conventional jet turbine fuels at levels up to 50% coal-derived fuel. The general requirements for this product includes that it be within the carbon number range of jet fuel (approximately C8 to C18) and be composed of at least 75% paraffins and no more than 25% aromatics, of which no more that 3% of the aromatics can be di-aromatics (naphthalenes). An overall analysis of the WFE SC-4 feed, the final Stage-1b product, and an example jet turbine fuel (JP-8) shown in Figures 42 and 43 along with the hydrocarbon type analysis summarized in Table 22 shows that the conversion of the coal-derived syncrude to a suitable blending stock has been partially completed during the heteroatom removal in Stage-1. Specifically, the hydrocarbon type analysis summarized in Table 22 shows that the aromatic content has been reduced from approximately 100% in the syncrude feed to 42% in the final Stage-1 product. Furthermore, the carbon distribution summarized in Figure 42 shows that the mass fraction of the syncrude heavier than the jet turbine range was reduced from 61% to 24%. This shows that a modest degree of hydrogenation and cracking is needed in Stage-2, therefore it is desirable to process the heavy fraction above the jet fuel range to bring the composition of the process stream to within the program goals.

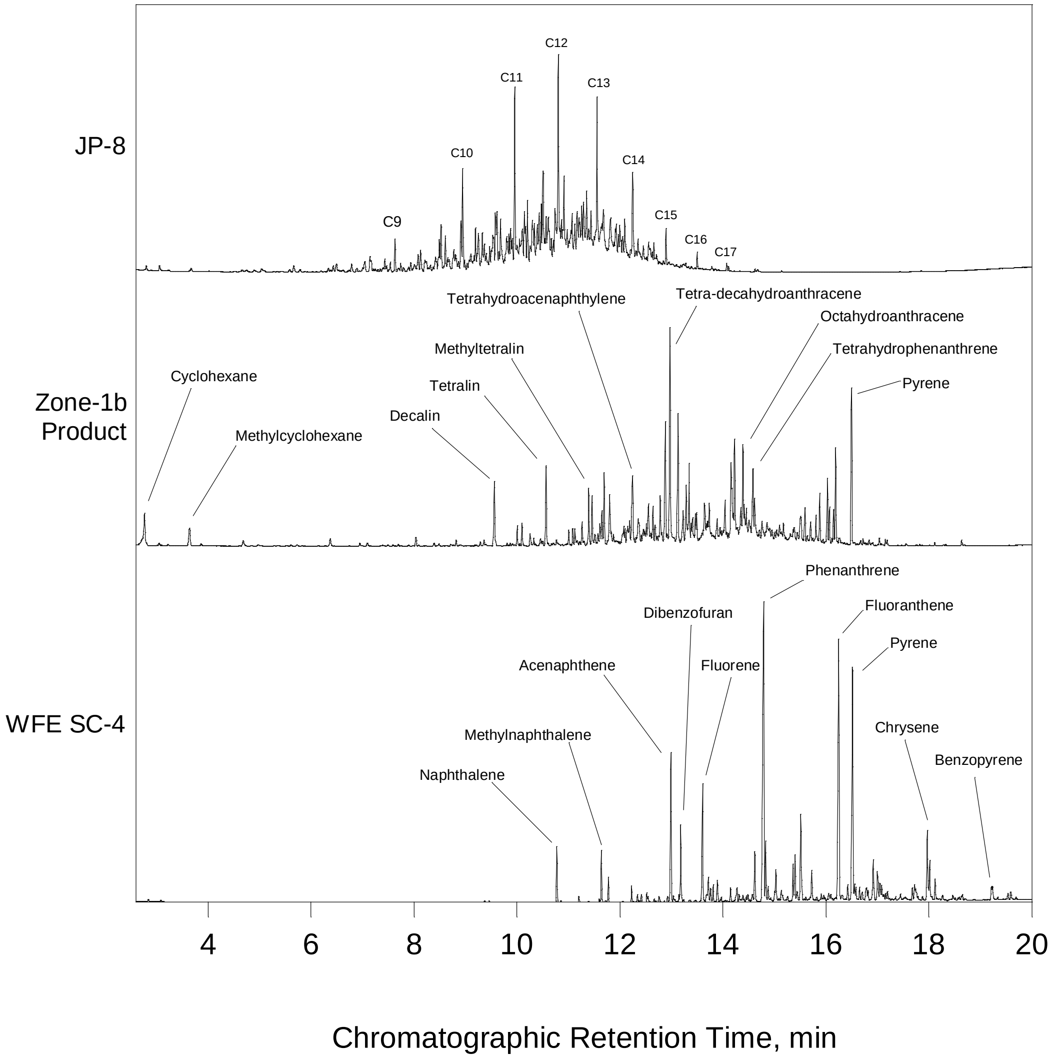
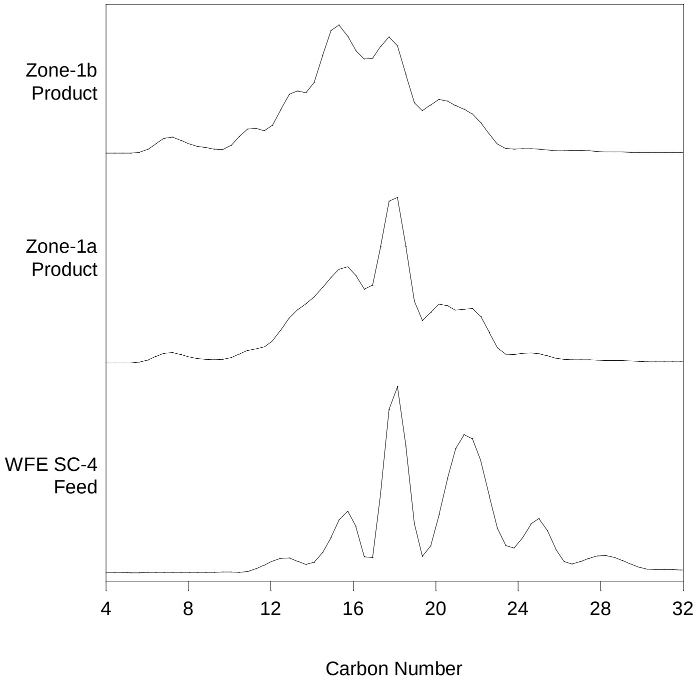


Figure 42. GC-MS analysis of the WFE SC-4, Stage-1b product, and an example jet turbine fuel (JP-8).



Carbon #	WFE SC-4	Zone 1a	Zone 1b
<C4	0.00	0.00	0.00
C4	0.00	0.00	0.01
C5	0.00	0.01	0.02
C6	0.00	0.27	0.39
C7	0.02	1.17	1.82
Total <C8	0.03	1.44	2.24
C8	0.02	0.69	1.10
C9	0.01	0.38	0.56
C10	0.04	0.55	0.77
C11	0.18	1.49	2.88
C12	1.22	2.31	2.94
C13	1.59	5.43	7.02
C14	1.00	7.32	7.55
C15	4.47	10.00	14.43
C16	6.18	10.46	12.18
C17	2.43	9.37	11.03
C18	21.68	19.63	12.98
Total C8-C18	38.82	67.63	73.45
C19	4.83	6.52	5.52
C20	5.07	6.50	6.00
C21	14.36	6.04	5.43
C22	14.17	5.89	4.02
C23	5.04	1.69	1.05
C24	3.23	1.04	0.50
C25	6.17	1.05	0.46
C26	1.89	0.48	0.28
C27	1.25	0.38	0.34
C28	1.93	0.29	0.16
C29	1.46	0.26	0.12
C30	0.50	0.14	0.09
C31	0.32	0.12	0.08
C32	0.31	0.12	0.08
>C32	0.63	0.40	0.17
Total >C18	61.15	30.93	24.32

Figure 43. Carbon distribution of the WFE SC-4 feed, Stage-1a and Stage-1b.

7.6.5.1 Stage-2 Testing with Model Compunds

For Stage-2 noble metal and sulfided catalysts can be used. The initial evaluation of the Nobel metal “K” catalyst was done with Aromatic-200 model as feed at 300-400°C, LHSV of 1/hr, 400 psi hydrogen, and a H:feed ratio of 10:1 mol/mol. Sulfided “J” catalyst was also evaluated with same model feed 300-380°C, 0.3 LHSV , 950 psi hydrogen, and a H:feed ratio of 3000:1 v/v. The overall results of these analyses are summarized in the GC-MS data shown in Figures 44 and 45 for the ”K” and “J”, respectively, and the hydrocarbon type analysis summarized in Table 31. Briefly, it was found that the “K” catalyst was very efficient at hydrogenating the model feed, but showed little cracking. In contrast, the “J” showed a very high degree of cracking to the point that at temperature above 320°C only light, largely incondensable products were produced. As shown in Figure 44, even at 320°C the product showed a very high degree of cracking with a modest degree of hydrogenation. Therefore, 300°C was chosen as the basis for comparing these two catalysts. As shown in Table 31, the “K” catalyst gave a very high degree of hydrogenation with an HDA of 96% as compared with 40% for “J”. This suggests that “K” would be preferred as a hydrogenation catalyst whereas “J” may serve as a cracking catalyst. Therefore, a combination of these two may be effective in processing the Stage-1 product as a combination of hydrogenation and cracking is indicated.

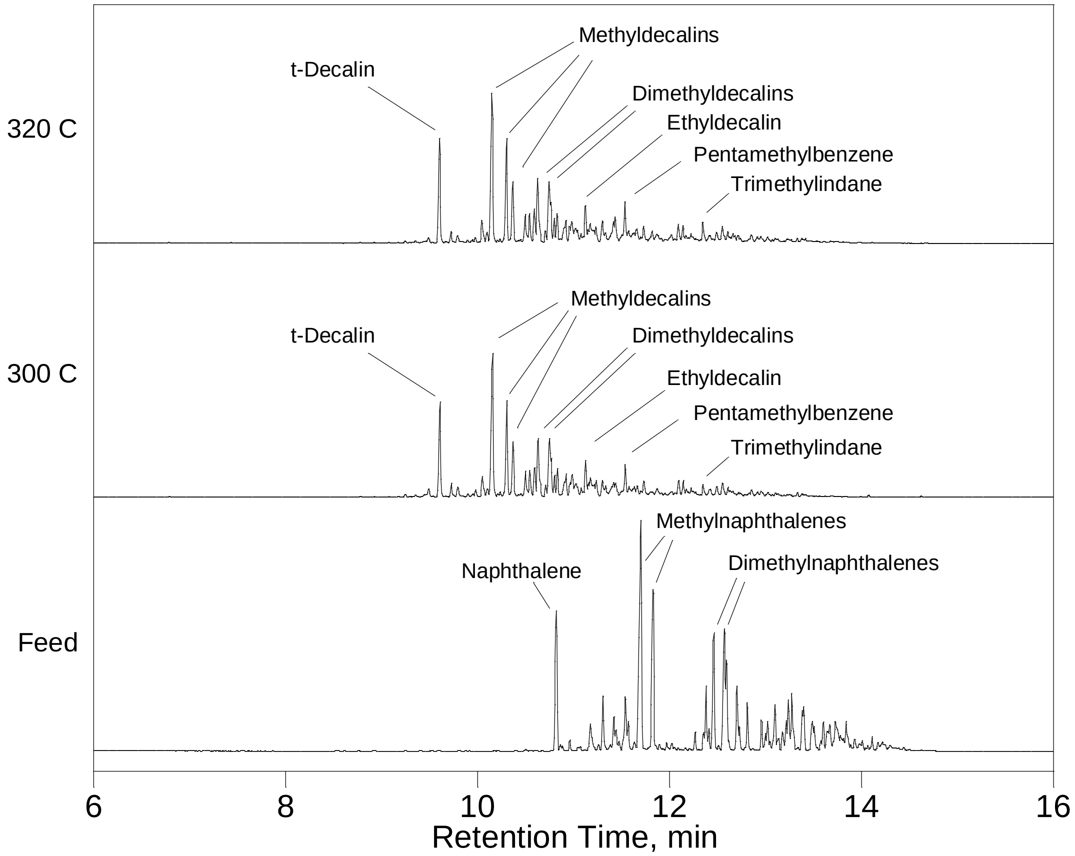


Figure 44. GC-MS analysis of the Aromatic-200 model feed and the Stage-2 products using the “K” catalyst.

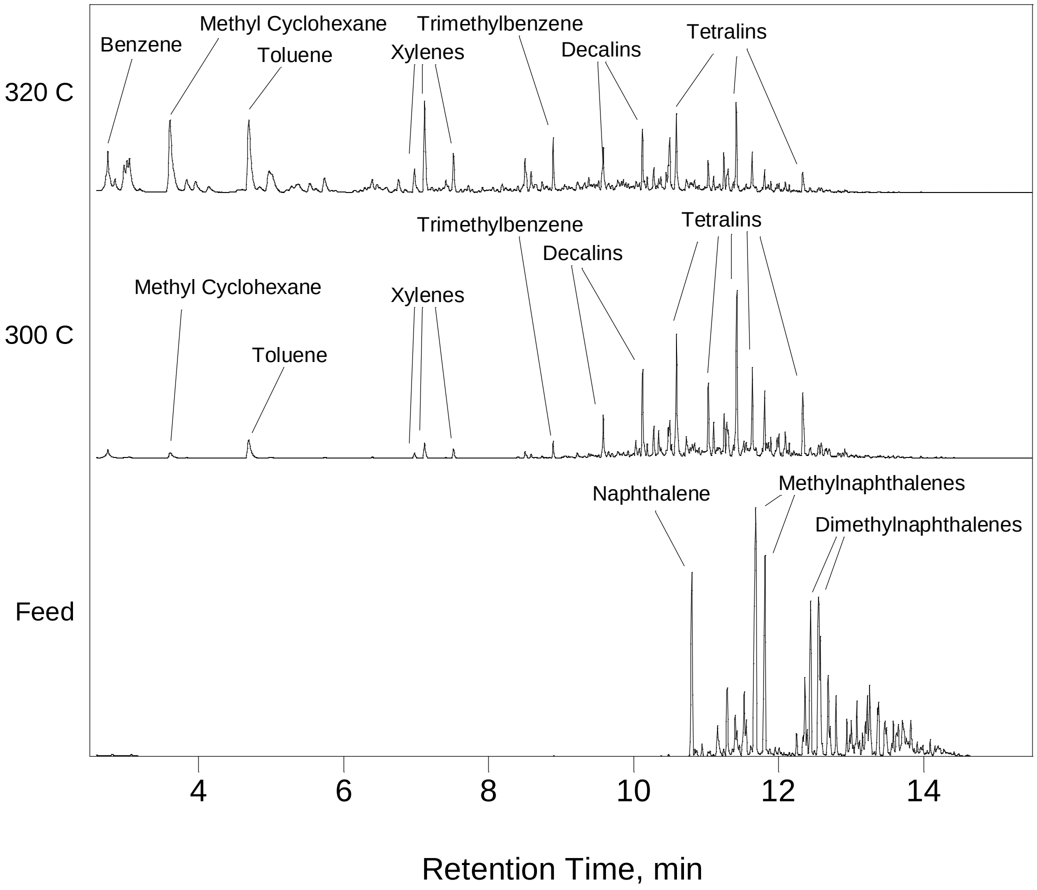


Figure 45. GC-MS analysis of the Aromatic-200 model feed and the Stage-2 products using the sulfided "J" catalyst.

Table 31. Model Feed Stage-2 Hydrocarbon Type Analysis at 300°C

Class	Sub-class	Feed	K catalyst 1/hr	J catalyst 0.3/hr
			400psi	900psi
Aromatics	Alkylbenzenes	6.00	0.98	23.48
	Diaromatics	83.91	2.86	3.81
	Cycloaromatics	10.09	0.17	32.32
	Total Aromatics	**100.00**	**4.01**	**59.61**
Paraffins	iso-Paraffins	<0.01	0.57	1.48
	n-Paraffins	<0.01	0.24	1.00
	Total n, iso-Paraffins	<0.01	5.66	2.48
Cycloparaffins	Monocycloparaffins	<0.01	86.94	13.27
	Dicycloparaffins	<0.01	2.59	24.63
	Total Cycloparaffins	<0.01	95.19	37.90
HDA, %		n.a.	96%	40%

7.6.5.2 Initial Stage-2 Testing with Stage-1 Product

The first attempt to upgrade a Stage-1 product was made using the WFE SC-2 syncrude processed through a Stage-1 reactor and the "I" NiMo catalyst. Briefly, all of the product from this reactor was combined to form a composite Stage-1 product. This product was used without any additional cleaning steps described above. This gave a Stage-2 feed with 7400 ppm N and 359 ppm S. The Stage-2 reactor configured with the sulfided "J" catalyst and operated the at 380°C with a LHSV of 0.3/hr, 1250 psi hydrogen, and a H feed ratio of 3000:1 v/v. Figure 46 shows a photograph of the Stage-2 feed and product and the overall results are summarized in the GC-MS data shown in Figure 47 and the hydrocarbon type analysis summarized in Table 32. Briefly, it was found that the "J" catalyst gave a product that was clear and lightly colored. The GC-MS analysis shows that the product was a very complex, partially hydrogenated mixture. The hydrocarbon type analysis also shows a modest degree of hydrogenation with an HDA (based on the Stage-2 reactor feed and product) of 21%.

Figure 46. Photograph of the Stage-1 product (Stage-2 feed) and the Stage-2 product using the sulfided "J" catalyst at 380°C with a LHSV of 0.3/hr, 1250 psi hydrogen, and a H:feed ratio of 3000:1 v/v.

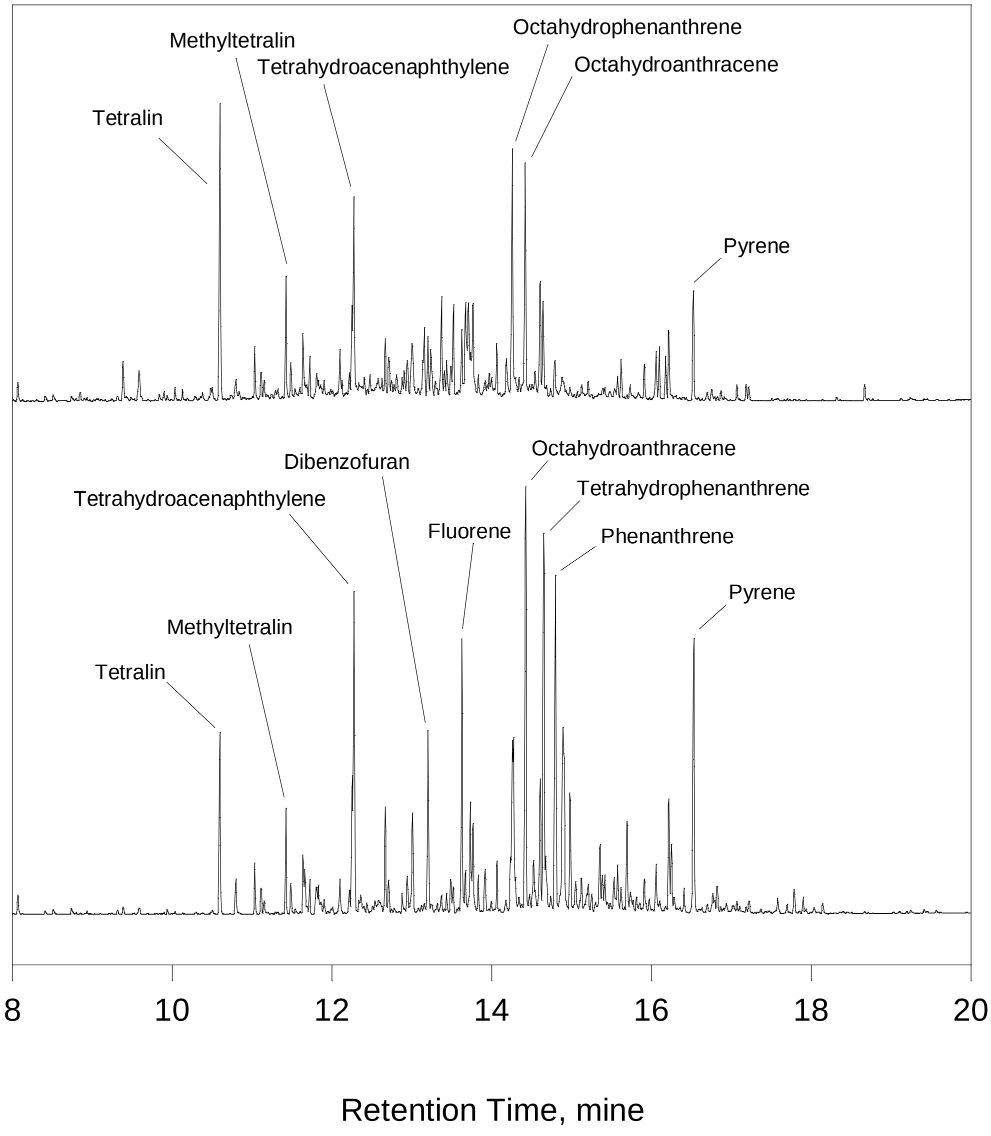


Figure 47. The composite product from the SC-2/catalyst “I” (bottom) that was used as the feed to the Stage-2 reactor using the sulfided “J” catalyst at 380°C with a LHSV of 0.3/hr, 1250 psi hydrogen, and a H:feed ratio of 3000:1 v/v and the product from the Stage-2 reactor (top) at 380°C, 1250 psi hydrogen and 0.3/hr LHSV.

Table 32. Stage-2 Hydrocarbon Type Analysis at 300°C, 1250 psi and 0.3/hr with a "J" Catalyst

Class	Sub-class	Feed	Product
Aromatics	Alkylbenzenes	1.41	3.63
	Diaromatics (Biphenyls, Naphthalenes, etc.)	7.60	6.56
	Cycloaromatics (Indans, Tetralins,etc.)	11.31	21.53
	Multi-ring Cycloaromatics (CnH_2n-10)	26.57	24.32
	Other Multi-ring Cycloaromatics	22.73	7.25
	Total Aromatics	86.73	68.83
Paraffins	iso-Paraffins	1.25	7.10
	n-Paraffins	3.42	3.43
	Total n, iso-Paraffins	4.67	10.53
Cycloparaffins	Monocycloparaffins	2.82	5.59
	Dicycloparaffins	2.38	8.37
	Tricycloparaffins	1.45	5.91
	Total Cycloparaffins	6.65	19.88
HDA, %		n.a.	21%*

*Based on the Zone-2 feed.

The second attempt to upgrade a Stage-1 product was made using the WFE SC-1 syncrude processed through a Stage-1 reactor and the "I" NiMo catalyst. Briefly, all of the products from this reactor was combined to form a composite Stage-1 product. This product was then sparged with nitrogen for 1 hour, but it was not washed with water as was later adopted for the Stage-1 product. This gave a Stage-2 feed with <5000 ppm N and 167 ppm S. The Stage-2 reactor was configured with the "K" catalyst and was operated the at 300-360°C with a LHSV of 0.3/hr, 950 psi hydrogen, and a H:feed ratio of 3000:1 v/v. Figure 48 shows a photograph of the Zone-2 feed and product and the overall results are summarized in the GC-MS data shown in Figure 49 and the hydrocarbon type analysis summarized in Table 33. Briefly, it was found that the "K" catalyst gave a product that was surprisingly dark. However, as noted previously, the visual appearance often does not correlate with the product quality. The GC-MS analysis shows that the product was a very complex, partially hydrogenated mixture. The hydrocarbon type analysis also shows a modest degree of hydrogenation with an HDA (based on the Stage-2 reactor feed and product) of 22% was observed at 300°C, though this increased to 45% at 360°C. Recall that the refined Stage-1 product described above had an aromatic content of 42%. Reducing this to 25% to meet the goal for a blending stock would require an HDA on the order of 40%, which compares well with the HDA measured for the "K" catalyst. This suggests that a noble metal catalyst should be capable of upgrading the refined Stage-1 product to a suitable blending stock, though some cracking may be needed to reduce the carbon distribution to within the jet-fuel range.

Figure 48. Photograph of the Stage-1 product (Stage-2 feed) and the Stage-2 product using the "K" catalyst at 300-360°C with a LHSV of 0.3/hr, 950 psi hydrogen, and a H:feed ratio of 3000:1 v/v.

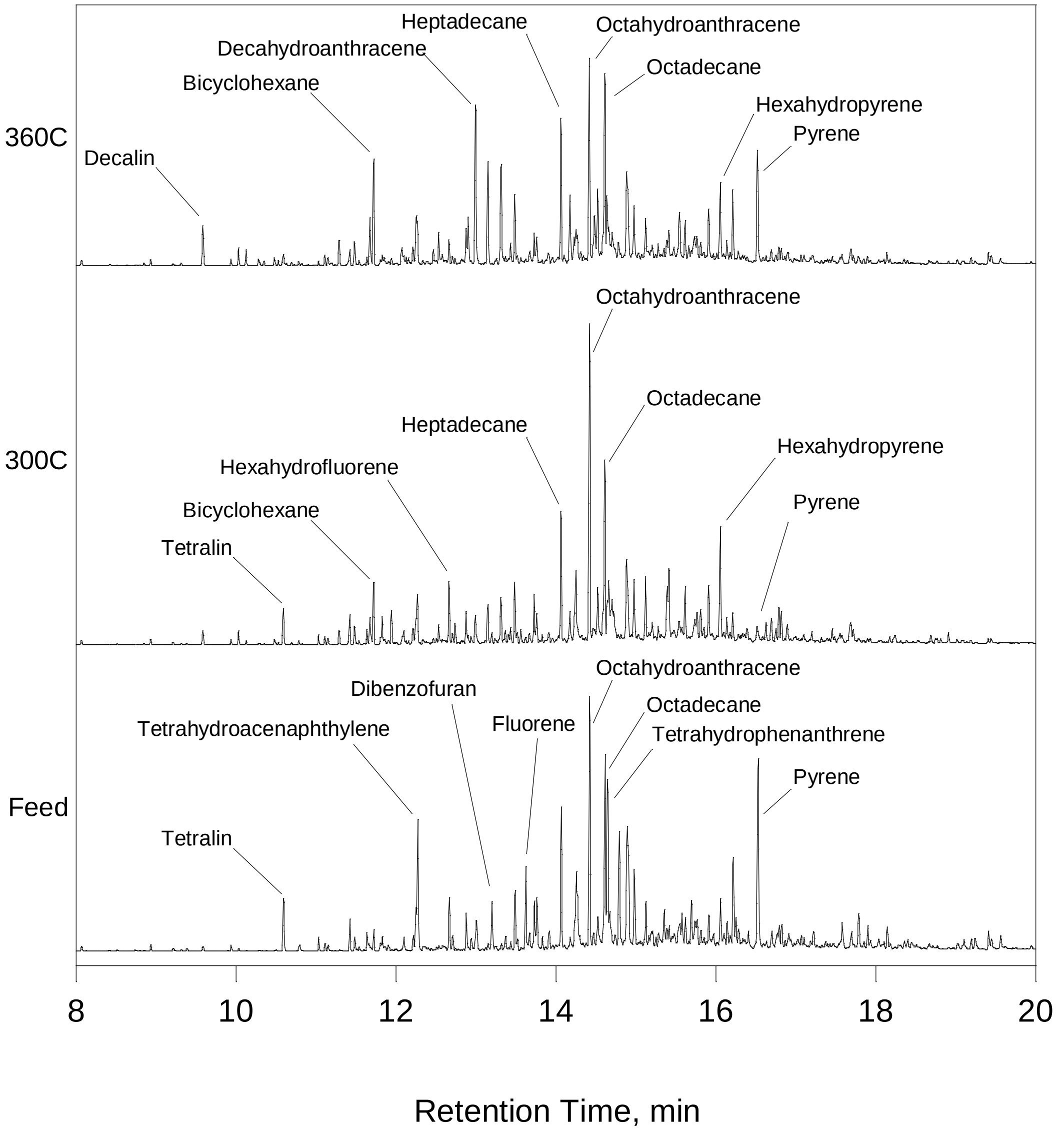


Figure 49. The composite product from the WFE SC-1/ "I" catalyst (bottom) that was used as the feed to the Stage-2 reactor using "K" catalyst at 300-360°C with a LHSV of 0.3/hr, 950 psi hydrogen, and a H:feed ratio of 3000:1 v/v and the product from the Stage-2 reactor at 300°C (middle) and 360°C (top).

Table 33. Stage-2 Hydrocarbon Type Analysis at 950psi and 0.3/hr with "K" Catalyst

Class	Sub-class	Feed	Product	Product
			300°C	360°C
Aromatics	Alkylbenzenes	1.22	1.10	0.81
	Diaromatics (Biphenyls, Naphthalenes, etc.)	7.12	1.42	1.45
	Cycloaromatics (Indans, Tetralins,etc.)	6.15	6.23	3.82
	Multi-ring Cycloaromatics (C_nH_{2n-10})	20.82	22.96	12.97
	Other Multi-ring Cycloaromatics	18.66	19.65	12.85
	Other Multi-ring Aromatics	18.51	5.21	7.65
	Total Aromatics	72.48	56.56	39.55
Paraffins	iso-Paraffins	1.36	3.57	2.19
	n-Paraffins	13.07	12.26	12.87
	Total n, iso-Paraffins	14.43	15.84	15.06
Cycloparaffins	Monocycloparaffins	3.81	4.07	5.10
	Dicycloparaffins	2.60	5.53	10.00
	Tricycloparaffins	3.75	10.57	21.28
	Other Cloparaffins	1.62	6.88	8.77
	Total Cycloparaffins	11.79	27.05	45.15
HDA, %		n.a.	22%*	45%*

*Based on the Zone-2 feed.

7.6.5.3 Hydrocracking of Stage-1 Product from Intertek Run #1 Over Proprietary Bi-functional Catalyst

One L of Stage-1 product from Intertek Run #1 (hydrotreated syncrude) was sent to UDRI for further treatment at 1250 psi, LHSV = 0.3 hr^{-1}, Hydrogen to liquid volume ratio = 1000. The test was performed at two temperatures (320ºC and 340ºC) over a proprietary, NiW, bi-functional catalyst, obtained by Battelle. The temperature was increased from 320°C to 340°C at 48.4 hours TOS. The sample taken at 9.4 hrs was clear and lightly colored with some sediment. The sample taken at 19.0 hrs was clear and somewhat darker, with significantly more sediment. The samples taken from 27.0 to 65.6 hrs were clear, without any significant sediment. The samples taken at 70.9 and 77.2 hrs appeared dark and possibly cloudy. Some light, non-condensable product was noted in all of samples.

The volumetric product yield was between 90 wt% and 97 wt%, the balance being light hydrocarbons. Effectively, the online GC analysis (not described in this report) showed formation of C1 through C6 products. The density dropped significantly from 0.95 g/cm^3 to a value below 0.86 g/cm^3, but it increased with TOS. Increasing the temperature from 320ºC to 340°C dropped the density from 0.85 g/cm^3 to 0.82 g/cm^3, but again started increasing with TOS. Two explanations are possible:

1. Since the run was performed for less than 80 hrs (TOS), the catalyst surface structure may still have been adjusting to the reaction conditions and it did not reach steady state.

2. There was progressive carbon deposition on the catalyst and it continued to deactivate.

However, we cannot draw a final conclusion unless we run the catalyst for an extended period (more than 500 hrs).

The GCxGC class fraction analysis (see Table 34) shows that hydrocracking of Stage-1 product significantly reduced the amount of total aromatic from 33 wt% to 15 wt%, which is in the range of commercial jet fuel. The tri- and multi-cycloparaffins were converted to mono- and di-cycloparaffins, which indicated that the catalyst was active in cleavage of the C-C bond.

Table 34. GCxGC Analysis Summary for Lab-scale Hydrocracking of Stage-1 Product from Intertek Run #1

Class	Sub-class	Feed	-002	-003	-004	-005	-007	-009
			320°C	320°C	320°C	320°C	340°C	340°C
Aromatics	Alkylbenzenes	1.35	2.64	2.97	2.87	2.71	4.15	4.12
	Diaromatics (Biphenyls, Naphthalenes, etc.)	1.49	0.05	0.06	0.08	0.21	0.18	0.24
	Cycloaromatics (Indans, Tetralins,etc.)	5.55	2.27	2.72	3.20	3.76	4.00	5.29
	Multi-ring Cycloaromatics (CnH$_2$n-10)	10.55	0.99	1.28	1.56	1.79	1.55	1.90
	Other Multi-ring Cycloaromatics	8.19	1.04	1.37	1.74	1.93	1.51	1.76
	Other Multi-ring Aromatics	5.99	0.57	0.66	0.78	0.86	1.18	1.45
	Total Aromatics	33.12	7.56	9.05	10.23	11.27	12.58	14.77
Paraffins	iso-Paraffins	0.47	9.97	7.81	5.88	5.03	11.32	7.48
	n-Paraffins	2.05	3.28	3.19	3.08	2.97	3.16	2.85
	Total n, iso-Paraffins	2.52	13.25	11.00	8.95	8.00	14.48	10.33
Cycloparaffins	Monocycloparaffins	1.98	32.63	27.54	23.35	18.66	32.11	24.84
	Dicycloparaffins	12.92	30.96	33.07	35.15	35.39	26.14	31.57
	Tricycloparaffins	35.15	11.08	13.62	15.77	19.04	10.50	13.39
	Other Multi-ring Cycloparaffins	13.33	4.24	5.34	6.09	7.15	3.90	4.76
	Total Cycloparaffins	63.38	78.92	79.57	80.37	80.23	72.66	74.56
Other	Dibenzofuran	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Cyclic oxygenates-258	0.56	0.16	0.22	0.26	0.30	0.18	0.22
	Unknown products-244	0.30	0.09	0.12	0.14	0.16	0.08	0.10
	Unknown products-274	0.10	0.03	0.03	0.04	0.04	0.03	0.03
	Total Other	0.97	0.27	0.38	0.45	0.50	0.29	0.34

7.7 Catalysts Selection for Pre-Pilot Testing

Based on the results of laboratory-scale catalyst screening, the following catalysts are recommended for pre-pilot testing:

- Stage 1. Catalyst “I” (NiMo) is recommended in a two-pass configuration. After Pass 1, the NH_3 and H_2S are separated from the liquid and the liquid is then re-treated in Pass 2.
- Stage 2. It is recommended that both a noble-metal catalyst similar to Catalyst “K’ and a bi-functional catalyst similar to Catalyst “J” be tested. The first one is a better hydrogeneration catalyst, so a very low total aromatic content can be achieved, while the second one is a better cracking catalyst, which leads to a higher aromatic content.

8.0 PRE-PILOT SCALE: SYNCRUDE HYDROTREATMENT AND HYDROGENATION TO JET FUEL/DIESEL

8.1 Objectives

The objectives of this effort were as follows:

- Demonstrate that syncrude from the Battelle CTL process can be upgraded to jet fuel and diesel by hydrotreatment/hydrogenation and distillation, at pre-pilot scale
- Characterize the upgraded product before and after distilling into various fuel cuts
- Prepare a jet fuel fraction and a diesel fraction for detailed analysis by UDRI and others.

8.2 Syncrude Preparation

Battelle selected two syncrudes that where produced from Quantex Run #5 and #6B for conducting two tests at Intertek for upgrading these to distillate products. The details of the liquefaction tests were described in Section 6.0. The ultimate analyses of these two feedstocks are provided in Table 35. The key difference between the two is that the bio-solvent for Syncrude 6B had a higher H/C ratio and its density was lower.

Table 35. Ultimate Analysis of Syncrudes Used for Intertek Run #1 (Syncrude 5) and Intertek Run #2 (Syncrude 6B)

Property	Syncrude 5	Syncrude 6B
C (wt%)	91	89.01
H (wt%)	6.3	7.33
H/C atomic ratio	0.83	1.00
O (wt%)	1.5	2.13
N (ppm)	4760	5700
S(ppm)	5800	5300
Ash (wt%)	<0.08	<0.08
Water (wt%)	<0.2	<0.2
Density (g/cm^3)	1.13	1.05

8.3 Standard Operating Procedures for Handling and Hydrotreatment of Syncrude

Before shipment of syncrude to Intertek for hydrotreatment, a Standard Operating Procedures (SOPs) critical to the safe hydrogenation operations was discussed with Intertek personnel. Some of the SOPs discussed include Safety, Chemical Hygiene, Spill Response, Fire Safety, First Aid, Lockout/Tagout, PPE, Work Place Air Monitoring, and Emergency Shutdown Procedures. In addition, controls to mitigate potential syncrude hydrogenation safety hazards were identified and added to the Test Plan and Environmental Health and Safety Plan.

8.4 Description of Pre-Pilot-Scale Reactors

Hydrotreatment operations were conducted at Intertek in two pilot plant units: P63 and P67. Each unit is composed of two trickle-bed reactors assembled in series. Figure 50 is photo of the P63 which is similar to P67. Each trickle reactor can hold up to 2.5 L of catalyst and it is composed of 6 heating and quenching zones. The temperature of the reactors is monitored at different zones with several thermocouples (TC). Figure 51 shows the catalyst loading and TC locations for Reactor #1 and Reactor #2.

Figure 50. Intertek's continuous syncrude hydrotreatment system P63 unit.

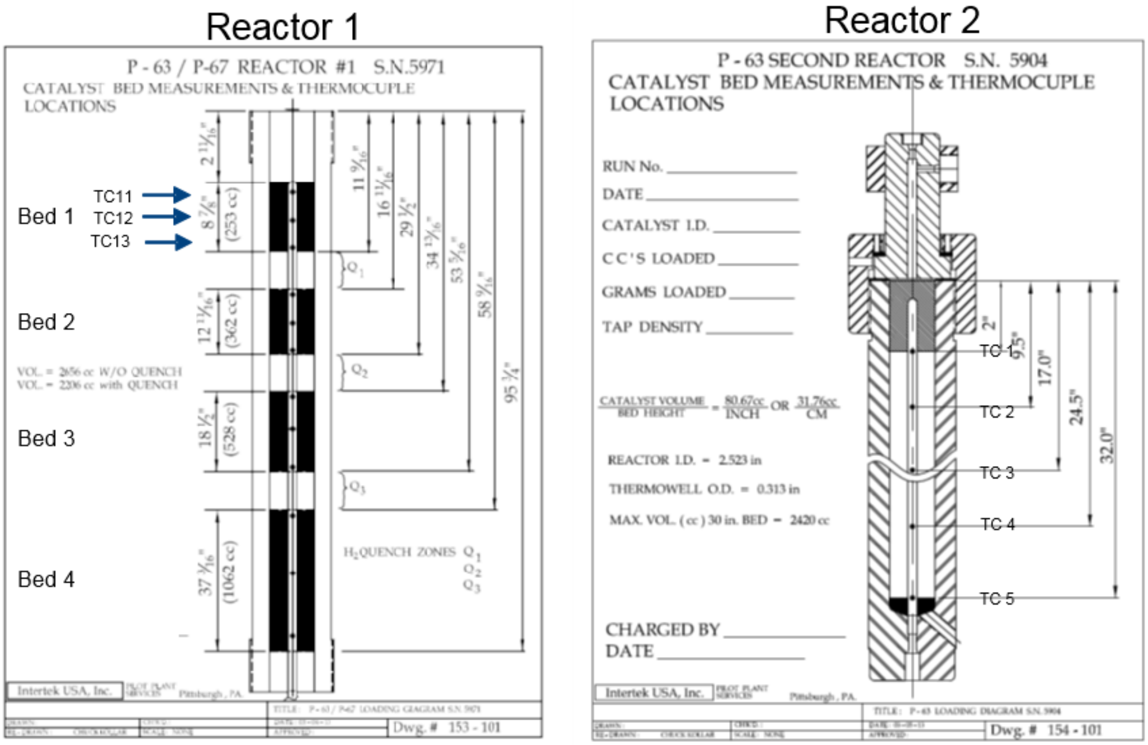


Figure 51. Thermocouples (TCs) location and reactor loading. In Reactor #1 there are 4 catalyst beds each with 3 TCs. Reactor#2 has one catalyst bed with 5 TC.

8.5 Pretreatment of Syncrude 5

Battelle shipped 162 kg of syncrude 5 to Intertek. The syncrude was filtered via 1- micron filter at 65°C to remove any residual material left from its preparation at Quantex. The filtered syncrude was loaded into a Fractioneer distillation unit, but the unit plugged and was not able to achieve the desired 500°C cut point. The bottoms material from the Fractioneer unit was therefore transferred to a smaller, single-stage Sarnia unit to achieve the desired 500°C cut point. Distillate from the Sarnia and the Fractioneer were combined and filtered at 65°C and 0.5 micron. About 136 kg of distillate was recovered after filtration and was then hydrotreated.

8.6 Hydrotreatment of Syncrude 5 (Intertek Run #1)

As discussed in Section 7.0, the upgrading was performed in two stages: hydrotreatment, followed by hydrogenation. The details for each stage are provided below.

8.6.1 Stage-1 Reaction (Run #1)

During the first stage, heteroatoms, specifically sulfur, nitrogen and oxygen, are removed by hydrodesulfurization (HDS), hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN). These reactions take place over a sulfided catalyst at a temperature of 380^{o}C, Liquid Hour Space Velocity (LHSV) of 0.15 hr^{-1}, a pressure of 1300psi and a hydrogen/syncrude volume ratio of 1000. Table 36 provides the reaction conditions used. Figure 52 displays the temperature profile of the reactors during four TOS (time on stream) periods during hydrotreatment. It can be divided into four sections with respect to time on stream.

- 0< TOS<100hrs: Initiation step where the catalyst was not at steady state and the temperature profile was not uniform due to the high activity of fresh catalyst and the exothermic hydrogenation reaction.
- 100<TOS<130hrs: The catalyst was at steady state. The temperatures were uniform throughout the reactors.
- 130<TOS<160hrs: An external problem due to a malfunction in the hydrogen compressor forced a shut down. The operator decreased the temperature to protect the catalyst and resumed the reaction after fixing the compressor.
- 160 <TOS<230hrs: The system was restarted and the remaining feed was processed.
- 230<TOS<300 Select material was reprocessed to ensure adequate sulfur and nitrogen removal.

Table 36. Reaction Conditions for Stage-1 (Same Catalyst in Reactors #1 & #2)

	Reactor 1	Reactor 2	Total
Reactor volume (L)	2.5	2.5	
Catalyst (L)	2.4	2.2	4.60
LHSV (hr^{-1})	0.29	0.31	0.15
H2/Liquid (V/V)	1000	1000	1000
Syncrude density (g/ml)	1.12	1.12	1.13
H2/Liquid (scf/bbl)	5608	5608	5608
Liquid (L/h)	0.69	0.69	0.69
Liquid (kg/h)	0.77	0.77	0.78
Liquid (g/min)	12.88	12.88	13.00
Liquid (ml/min)	11.50	11.50	11.50
H2 (L/h)	690	690	690
H2 (L/min)	11.5	11.5	11.5
H2 (g/h)	28.72	28.72	28.72
Pressure (psi)	1300	1300	1300
Total amount of feed (gallon)			40
Total amount of feed (L)			151
Time On Stream (hr)			219
Reactor Tempearture (oC)	380	380	380

The analysis of Stage-1 product showed a substantial (>99.9%) removal of S and N, with the product values being 2 ppm and 7 ppm, respectively.

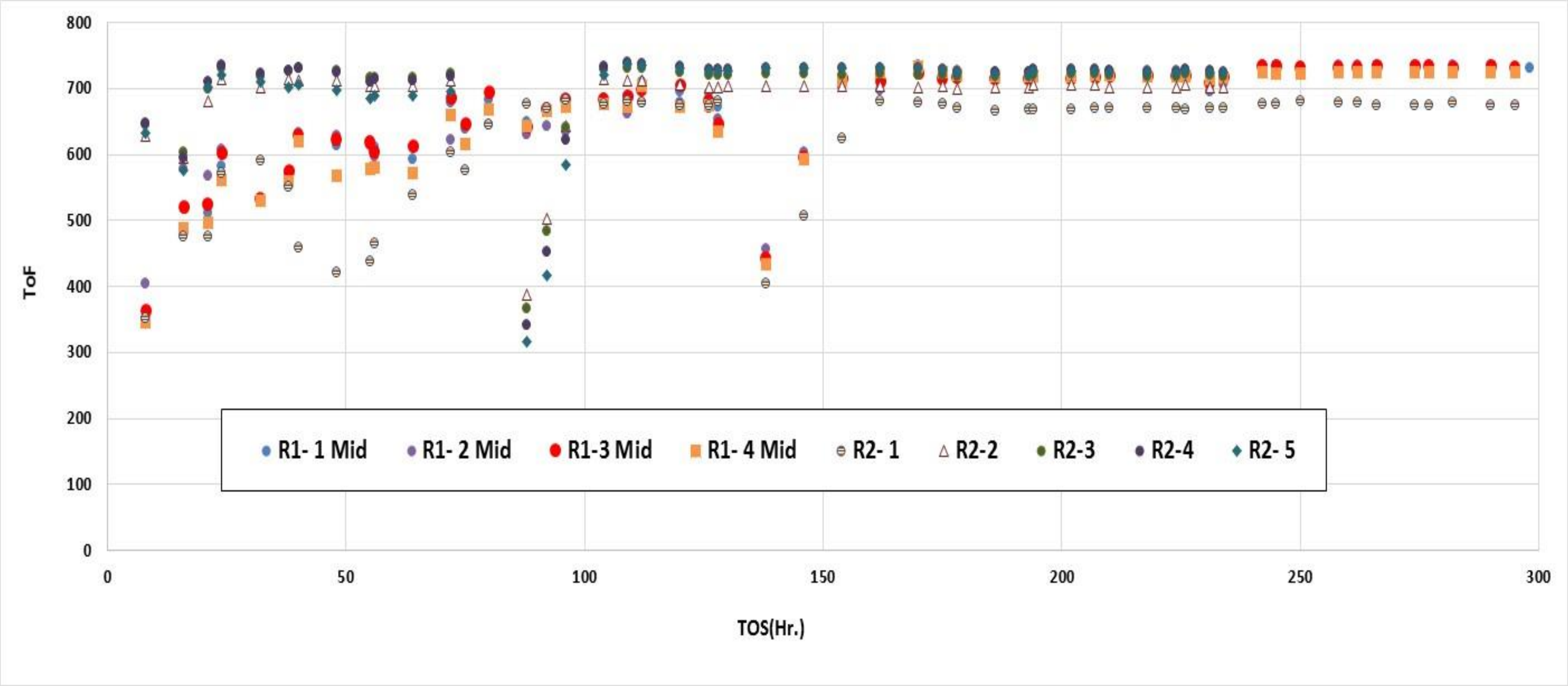


Figure 52. Reactor #1 (R1) and Reactor #2 (R2) temperature profile.

8.6.2. Stage 2 Reaction (Run #1)

The goals of this Stage-2 (hydrogenation) reaction was to reduce the concentration of aromatics present in syncrude from approximately 100 wt% to less than 20 wt% and to reduce the density from ~0.98 g/cm^3 to less than 0.90 g/cm^3. This reaction was carried out in unit P63, using a proprietary noble-metal catalyst. This catalyst was tested earlier this year at UDRI with syncrude and with model compounds, as discussed in Section 7.6.5. It has a good hydrogenation activity at temperatures between 200ºC and 360°C. Therefore, we conducted the reaction at low temperatures (240°C) and at a relatively high Liquid Hourly Space Velocity (LHSV) of 0.6 hr^{-1}, as compared to hydrotreatment reaction LHSV of 0.15 hr^{-1}at a pressure of 1300 psi and a hydrogen/syncrude volume ratio of 1,000. Around 32 gallons of syncrude was processed over 2.2 L catalyst volume, filled in Reactor #1 of the P63 unit while bypassing Reactor #2. Table 37 summarizes of reaction conditions. The temperature profile of Reactor #1 is displayed in Figure 53. The target temperature was 240°C, but given the exothermicity of the reaction and short time on stream (TOS) of 90 hrs., the temperature varied between 220°C and 260°C.

Table 37. Reaction Conditions for Stage 2 (Hydrogenation of Hydrotreated Syncrude)

	Reactor #1
Reactor volume	2.5
Catalyst Pt-Pd	2.205
LHSV (hr^{-1})	0.60
H_2/Liquid (V/V)	1000
Syncrude density (g/ml)	0.97
H_2/Liquid (scf/bbl)	5608
Liquid (L/hr)	1.32
Liquid (Kg/h)	1.28
Liquid (g/min)	21.39
Liquid (ml/min)	22.05
H_2 (L/h)	1323
H_2 (ml/min)	22.05
H_2 (g/h)	55.07
Pressure (psi)	1300
Total amount of feed (gallon)	32
Total amount of feed (L)	119
Time On Stream (hr)	90
Reactor Temperature (°C)	220

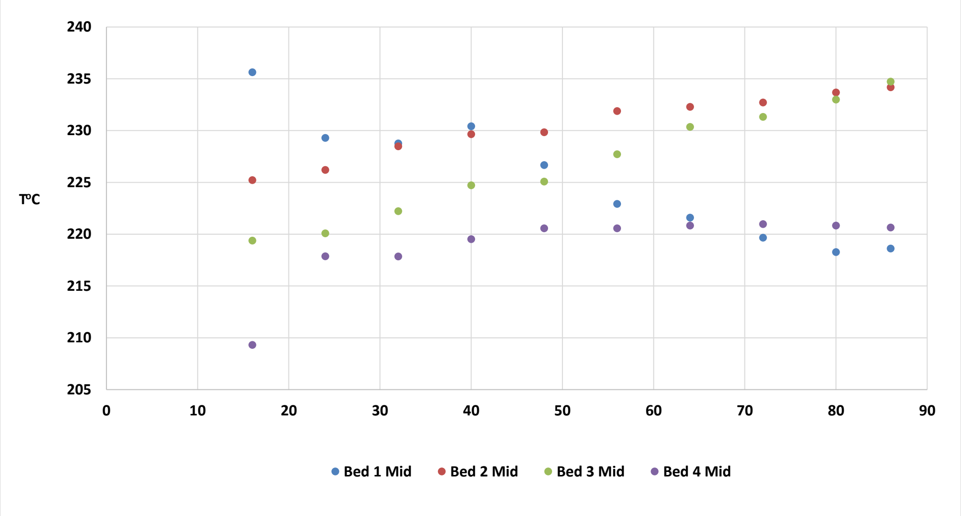
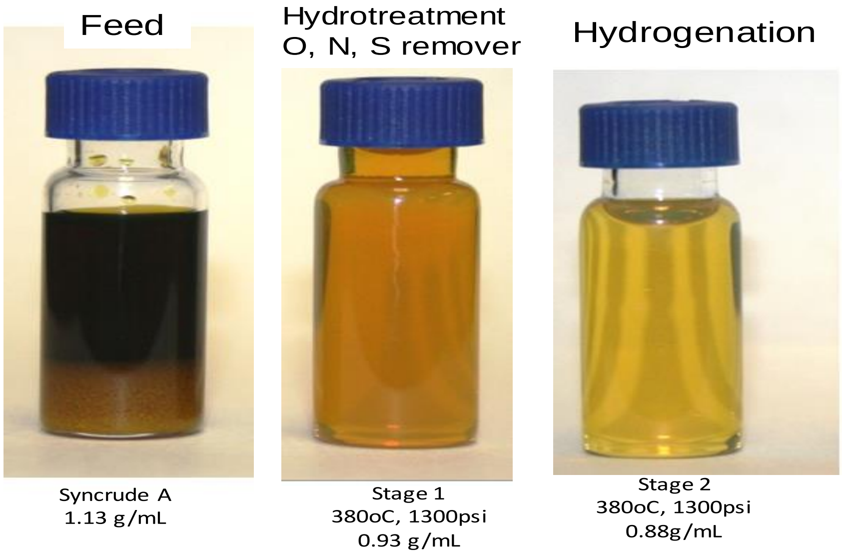


Figure 53. Temperature profile of Reactor #1 (P63 unit) during hydrogenation of hydrotreated syncrude produced in syncrude 5.

8.7. Analysis of Feed, Stage-1 and Stage-2 Products from Intertek Run #1

8.7.1 Feed and Product

Figure 54 shows photos of feed and products from the two stages of upgrading. The hydrotreatment converted a heavy crude to refined liquids. The final product was a yellow, transparent liquid, while the feed was composed of mostly heavy, aromatic compounds.



Feed
Syncrude A
1.13 g/mL

Hydrotreatment
O, N, S remover
Stage 1
380oC, 1300psi
0.93 g/mL

Hydrogenation
Stage 2
380oC, 1300psi
0.88g/mL

Figure 54. Photos of feed and products from Stage-1 and Stage-2 for Run #1.

8.7.2 Ultimate Analysis of Stage-1 and Stage-2 Products

The elemental analyses of the feed and products from Stage-1 (hydrotreatment) and Stage-2 (hydrogenation) are shown in Table 38.

Table 38. Elemental Characteristic of Feed, Stage-1 and Stage-2 Products

	Feed	Stage 1	Stage 2
C (Wt. %)	91.0	88.6	87.6
H (Wt. %)	6.3	11.1	12.2
H/C atomic ratio	0.83	1.5	1.7
O (Wt. %)	1.5	<0.5	<0.5
N (ppm)	4760	7	1
S(ppm)	5800	2	1
Ash (Wt. %)	<0.08	<0.08	<0.05
Water (Wt. %)	<0.14	<0.1	<0.1
Density (g/cm^3)	1.13	0.98	0.93

The analyses show the following:

- The H/C atomic ratio increased from 0.83 (feed) to 1.5 (Stage-1) and 1.7 (Stage-2). Both catalysts thus have good hydrogenation activity.
- The ash content of the feed to the reactor was <0.08 wt, compared to 0.14 wt% in Syncrude 5. This indicates that our pretreatment of feed by distillation and filtration removed most of the ash that can plug and/or poison the catalyst.
- The hydrotreatment catalyst (Stage 1) dropped the S and N from 5,800 ppm and 4,760 ppm, respectively, to less than 2 ppm and 7 ppm, respectively. The oxygen concentration dropped below detection limit for the instrument (Thermo Finnigan Flash EA).
- The density dropped from 1.13 g/cm^3 to .97 g/cm^3 in Stage-1 and to 0.93 g/cm^3 in Stage-2, which indicates that both catalysts have moderate hydrocracking activity.

8.7.3 HPLC Analysis of Stage-2 Product (Run #1)

The level of hydrogenation of aromatics in Stage-2 was determined by HPLC. As shown in Figure 55, the aromatics content dropped by 96%. The active-metal catalyst used in Stage-2 is known to be superactive; it completely hydrogenated the double bounds in the aromatics present after Stage-1 reaction.

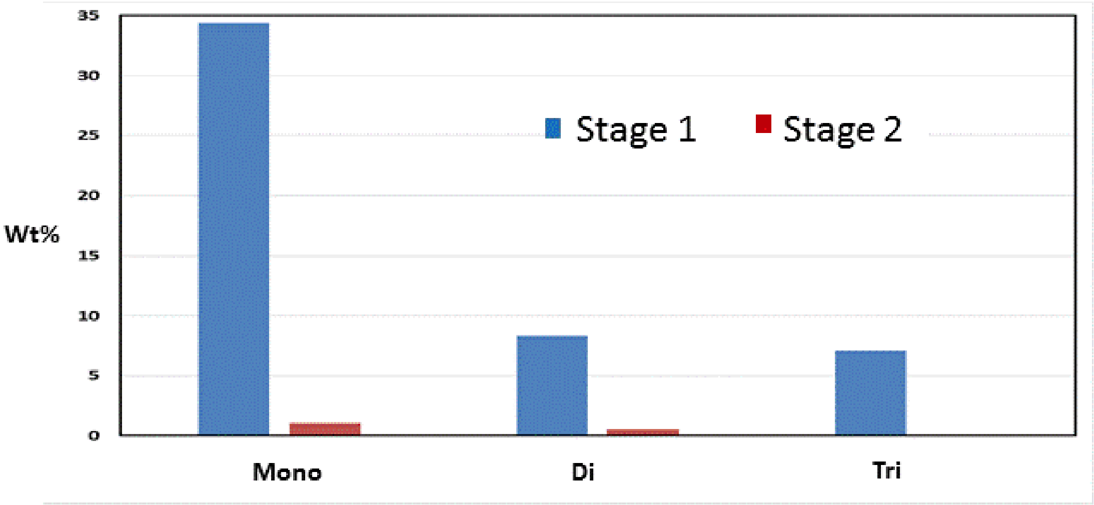


Figure 55. Concentration of mono, di, and tri aromatics in Stage-1 and Stage-2 products as determined by HPLC.

8.7.4 Simulated Distillation of Feed, Stage-1 and-2 Products (Run #1)

Figure 56 shows the simulated distillation of feed as well as Stage-1 and Stage-2 products. It shows that the hydrotreatment in Stage-1 dropped the boiling point significantly. This result is explained by the cleavage of C- heteroatom bonds. In Stage-2, there is only the hydrogenation of double bonds which explains the only slight change in the simulated distillation curve.

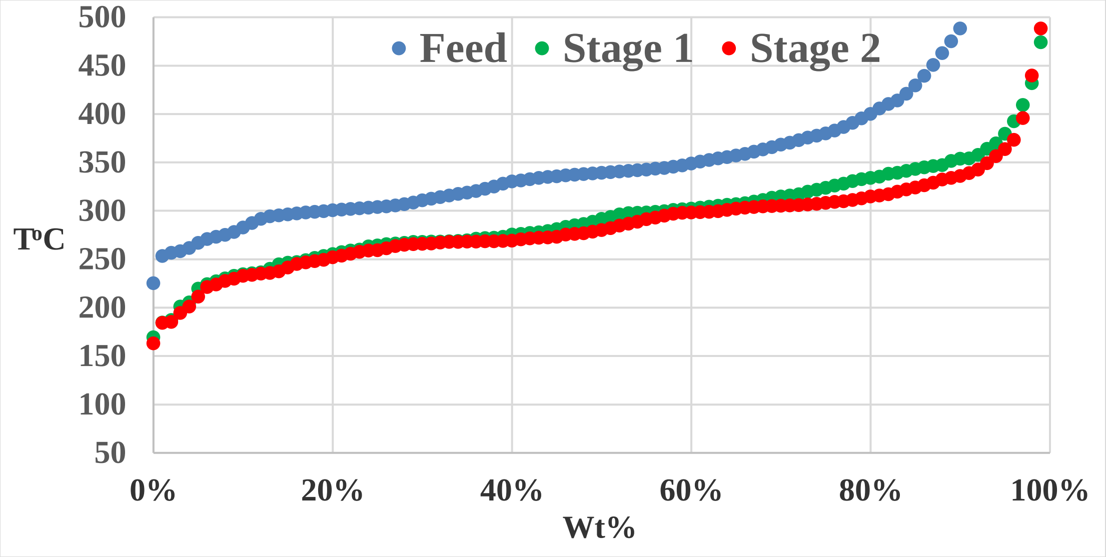


Figure 56. Simulated distillation of feed (syncrude), Stage-1 (hydrotreated syncrude) and Stage-2 (hydrogenated Stage-1 product) for Run #1.

8.7.5 Comparison of Batch and Pre-Pilot Results

The results of laboratory testing were compared with the results from pre-pilot testing, with respect to sulfur and nitrogen removal. As shown in Figure 57, for any given LHSV value, the sulfur and nitrogen removal was better in pre-pilot testing. This is likely because the longer catalyst-bed height in the pre-pilot test improved the gas-solid contact.

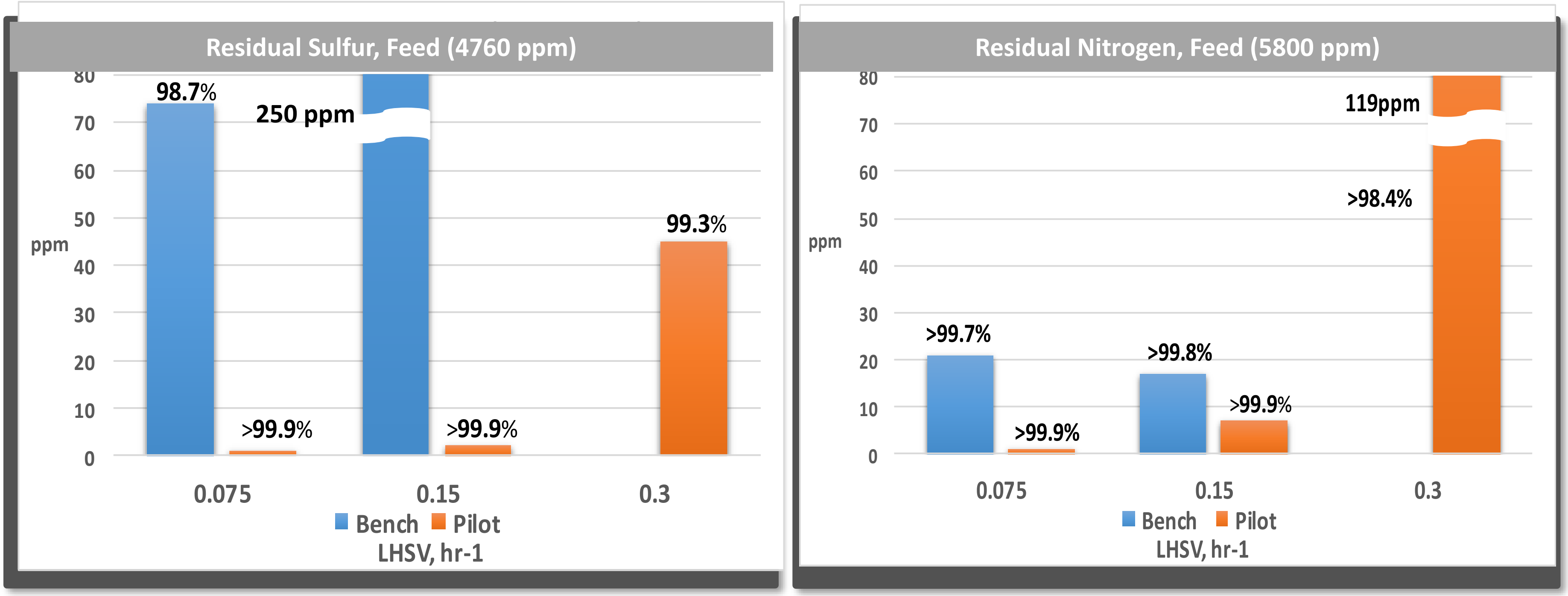


Figure 57. Residual “S” and “N” at different LHSV in lab & pilot scale reactors.

8.8 Fractionation of the Stage-2 Product (Run #1)

Around 32 gallons of distillate was produced by hydrogenation of hydrotreated syncrude. It was then divided into three portions:

- Portion #1: 8 gallons was distillated at Intertek to produce two distillate fractions: a fraction boiling below 337°C (called diesel fraction) and a fraction boiling above 337°C.
- Portion #2: 8 gallons was distillated at Intertek to produce two fractions: a fraction boiling below 295ºC (called jet-fuel fraction) and a fraction boiling above 295ºC.
- Portion #3: 16 gallons was left without distillation for further study, if necessary.

The yields for each distillation cut are shown in Table 39. As shown, 93.3 wt% of Stage-2 product was in the diesel range and 59.3 wt% was in the jet-fuel range. The loss in the distillation process was negligible.

Table 39. Distillation of Stage-2-Product (Intertek Run #1)

	Fraction <337ºC	Fraction >337ºC	Loss
Portion #1	93.3	6.8	0.0
Portion #2	59.3	38.3	2.4

8.9 Hydrotreatment of Syncrude 6B (Intertek Run #2)

A total of 92.3 kg of Syncrude 6B was hydrotreated in the P67 pre-pilot reactor, for Intertek Run #2. The unit details and operating procedures were reported in section 8.3. The first reactor was loaded with a sulfided catalyst and second reactor was loaded with a proprietary, bi-functional hydrocracking catalyst. During hydrotreatment, NH_3 is produced, which may negatively impact the performance of hydrocracking catalyst. Therefore, the upgrading was performed in two stages with intermediate N_2 purge at atmospheric pressure to minimize the amount of NH_3 and H_2S, as described below. In Stage-1, heteroatom removal was achieved using Reactor #1 while Reactor #2 was in bypass mode (under hydrogen atmosphere at room temperature), as indicated in Figure 58A. The reaction conditions are reported in Table 40. The Stage-2 operation was performed using two reactors: Reactor #1 to further reduce the heteroatoms, followed by hydrocracking in Reactor #2 (Figure 58B). The general reaction conditions are reported in Table 41.

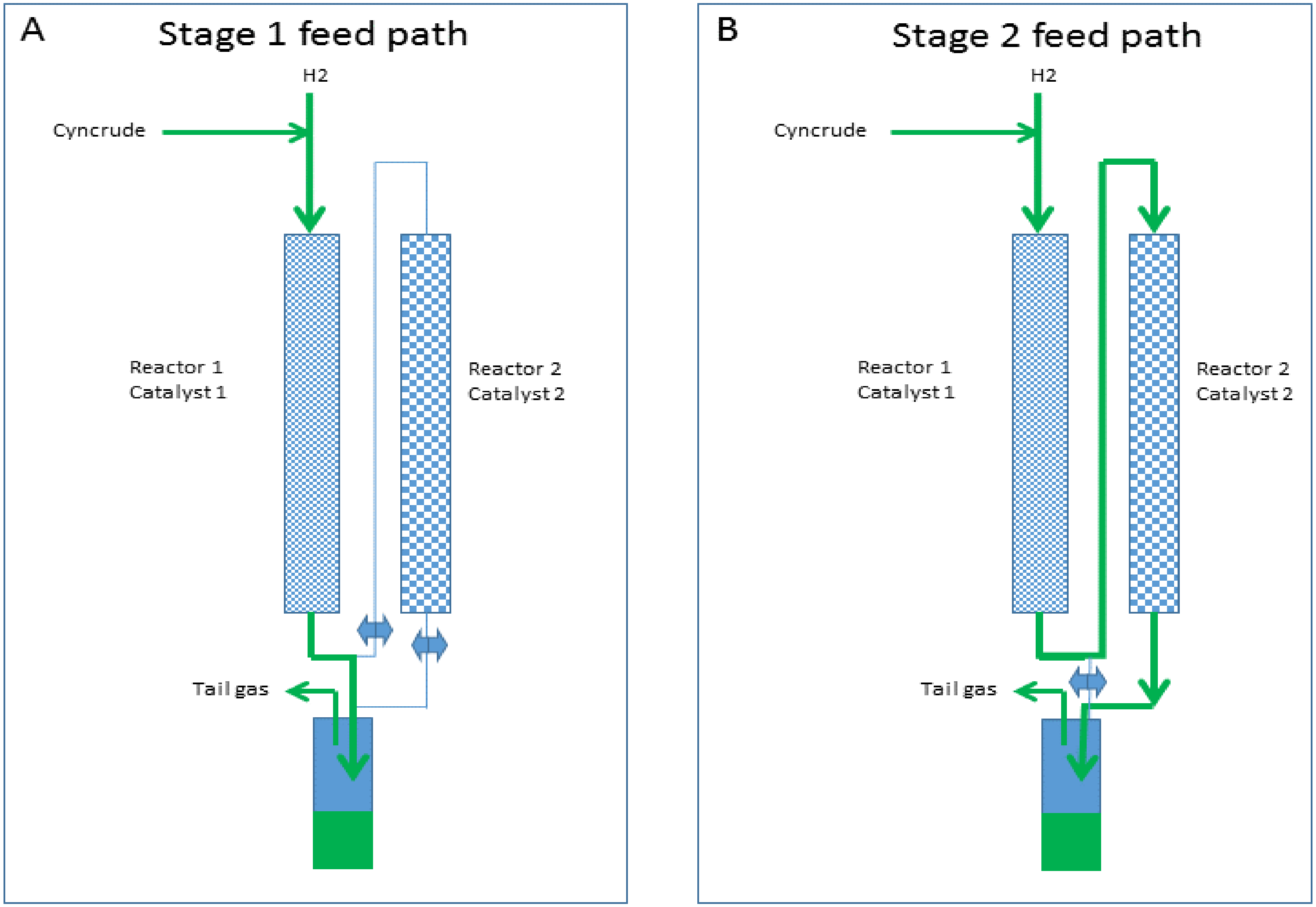


Figure 58. Run #2 feed path for Stage-1 (hydrotreatment) and Stage-2 (hydrocracking).

Table 40. Stage-1 General Reaction Conditions (Reactor #2 in Bypass Mode) for Run #2

	Reactor #1
Reactor volume (l)	2.5
Hydrotreatment catalyst (l)	2.4
Hydrocracking catalyst (l)	0
LHSV (hr^{-1})	0.25
H_2/Liquid (V/V)	1000
Liquid feed density (g/cm^3)	1.12
Liquid (l/h)	0.6
liquid density	1.12
Liquid (kg/h)	0.672
H_2 (l/h)	600
H_2 (g/h)	49.95
Pressure (psi)	1300
Temperature (°C)	380

Table 41. Stage-2 General Reaction Conditions for Run #2

	Reactor #1	Reactor #2
Reactor volume (l)	2.5	2.5
Hydrotreatment catalyst (l)	2.4	0
Hydrocracking catalyst (l)	0	1.5
LHSV (hr^{-1})	0.25	0.4
H_2/Liquid (V/V)	1000	1000
Liquid feed density (g/cm^3)	1	1
Liquid (l/h)	0.6	0.6
Liquid density	1	1
Liquid (kg/h)	0.67	0.67
H_2 (l/h)	600	600
H_2 (g/h)	50	50
Pressure (psi)	1300	1300
Temperature (°C)	380	320

The Stage-1 reaction was carried out in Reactor #1 during the first 112 hrs. The temperature profile can be divided in two sections: first 30 hrs. heat up period and the period between 30 and 180 hrs where the reactor reached the target temperature (380°C). The syncrude was injected at temperature around 150°C. At a total on-stream time (TOS) between 40 and 48 hrs, a hydrogen leak occurred in the lab, which required shut down of the system and resumption of the reaction after controlling the leak. Therefore, the initial, off-spec material was reprocessed. The temperature profile is shown in Figure 59.

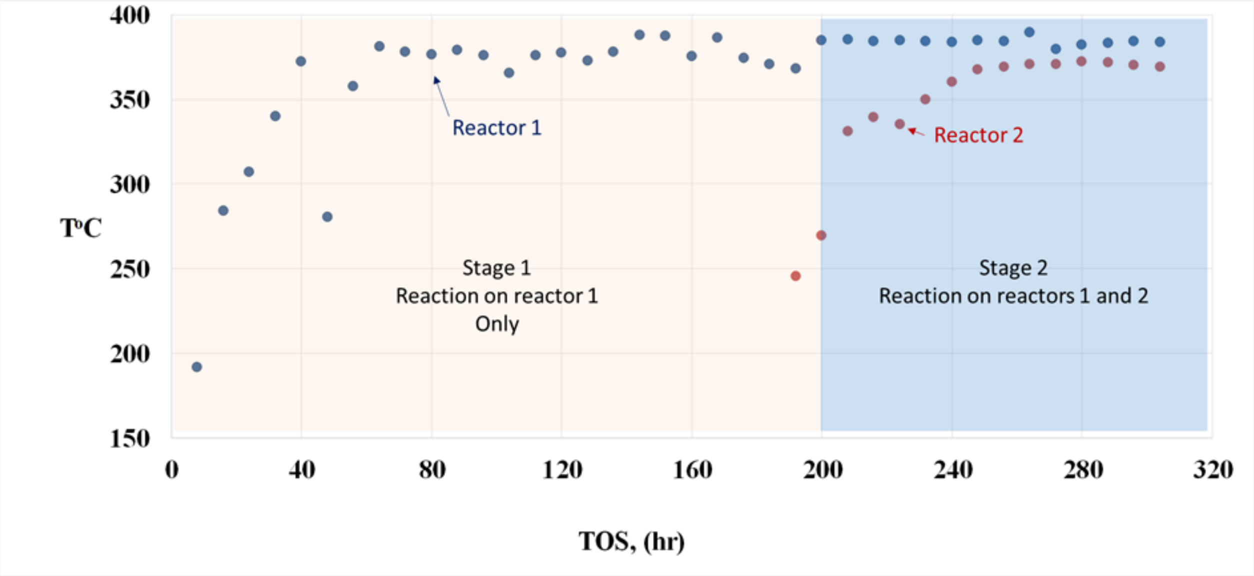


Figure 59. Temperature profile for Stage-1 and Stage-2 of Run #2.

The liquid from Stage-1 was processed in Reactor #1 (380°C) and Reactor #2 (320°C) at TOS between 180 hrs. and 300 hrs. (blue zone in Figure 11). The target temperature for Stage-2 was 320°C. However, given the limited amount of feed and the high space velocity (0.4 hr^{-1}) we were not able to adjust the temperature, so we decided to run it at a slightly higher temperature (360°C).

8.10 Analysis of Syncrude and Distillate Products for Run #2

Table 42 summarizes the ultimate analysis of the feed and products from Stages-1 and -2. As shown, the H/C mole ratio increased by 50% in Stage-1 and by an additional 20% in Stage-2. Both sulfur and nitrogen dropped by more than 98% in Stage-1 and by more than 90% of the remaining portion in Stage-2. The density decreased by 8% in Stage-1 and by an additional 8% in Stage-2. The liquid wt% in Table 42 represents the mass recovery from the process.

Table 42. Ultimate Analysis of Feed (Syncrude), Stage-1 Product, and Stage-2 Product

Property	Syncrude	Stage-1 Product	Stage-2 Product
C (wt%)	89	88.7	86.3
H (wt%)	7.3	11.2	12
H/C mole ratio	1.0	1.5	1.7
O (wt%)	2.1	0.5	0.5
N (ppm	5700	119	3.6
S (ppm)	5300	45	5.66
Water (wt%)	<0.2	<0.2	<0.2
Density (g/cm^3)	1.05	0.97	0.89
Liquid yield (wt%)	100	93	97
Carbon balance (wt%)	100	82	78

Table 43 shows the aromatic contents of the syncrude, Stage-1 product, and Stage-2 product. The di-, tri-, and total aromatic concentration decreased with upgrading in Stage-1 and Stage-2. The tri-aromatics and di-aromatic were converted to mono-aromatics. A large portion of the total aromatics was converted to cycloparaffins.

Table 44 summarizes the GCxGC-MS of Stage-1 and Stage-2 products. The Stage-2 catalyst dropped aromatics concentration by at least 60%, increased the cycloparaffins by 100%, and reduced the paraffins by 14%. It looks like the hydrocracking catalyst has good activity in reducing double bonds but limited activity for the cleavage of C-C bonds.

Table 43. Aromatic Composition of Feed (Syncrude) and Stage-1 and Stage-2 Products for Run #1

Compound	Unit	Syncrude	Stage-1 Product	Stage-2 Product
Mono-aromatics	wt%	1.7	54.6	24.6
Di-aromatics	wt%	14.8	10.7	3.6
Tri-aromatics	wt%	67.3	8.4	1.85
Total aromatics	wt%	83.8	73.7	30

Figure 60 provides the Simulated-Distillation curves of feed, Stage-1 product, and Stage-2 product. The amount of jet fuel (fraction below 300ºC) in the feed is 20%, but increases to 50% and to 70% after Stage-1 and Stage-2, respectively.

Table 44. GCxGC-MS for Stage-1 Product and Stage-2 Product (wt%) for Run #1

Class	Sub-class	Stage-1 Product	Stage-2 Product
Aromatics	Alkylbenzenes	0.37	1.61
	Diaromatics (Biphenyls, Naphthalenes, etc.)	3.08	0.47
	Cycloaromatics (Indans, Tetralins,etc.)	7.03	7.63
	Multi-ring Cycloaromatics (C_nH_{2n-10})	20.26	4.89
	Other Multi-ring Cycloaromatics	16.65	3.24
	Other Multi-ring Aromatics	8.83	2.24
	Total Aromatics	**56.22**	**20.09**
Paraffins	iso-Paraffins	0.33	1.05
	n-Paraffins	9.5	10.22
	Total n, iso-Paraffins	**9.83**	**11.27**
Cycloparaffins	Monocycloparaffins	2.97	7.59
	Dicycloparaffins	6.25	25.51
	Tricycloparaffins	15.21	25.17
	Other Multi-ring Cycloparaffins	8.89	9.92
	Total Cycloparaffins	**33.31**	**68.2**
Unknown products		0.47	0.44

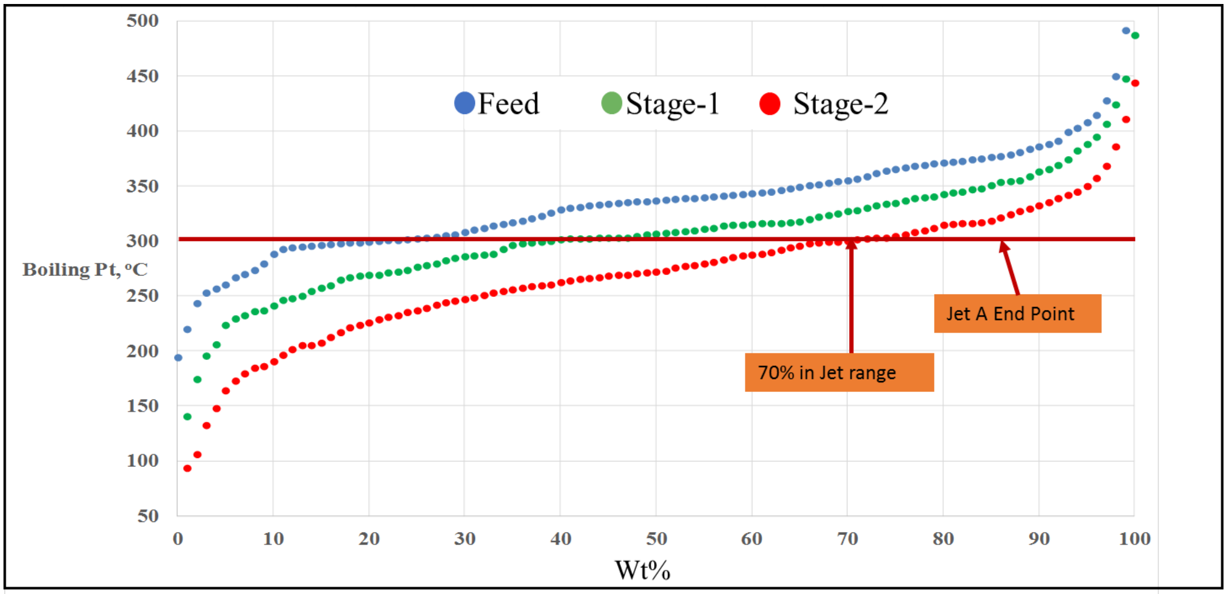


Figure 60. Simulated distillation curves for feed, Stage-1, and Stage-2 for Run #2.

8.11 Fractionation of the Distillate from Run #2

A total of 27.3 kg of Stage-2 product was batch distilled to obtain cuts representative of jet fuel products. The material was first cut at 205°C at atmospheric pressure to prevent loss of the light fraction. Afterwards we dropped the temperature to 100°C and then the unit was brought down to 100 mm Hg absolute pressure. Then, 1-liter volume cuts were taken until the overhead vapor temperature reached 217°C at 100 mm Hg, which is equivalent to 295°C at atmospheric pressure. A total of 14 (1-liter) cuts were taken in this way. Table 45 summarizes the performed cuts. Figure 61 is a photo of jet fuel fraction and the still pot liquid fraction (residue) with boiling point above 295°C.

To prepare a jet-fuel fraction that meets flash point specifications, we removed by distillation the light fraction that has boiling point below 160°C. This light fraction corresponds to 4.5 percent volume of the liquid product. A synthetic jet fuel blend was thus prepared using 65% volume from the upper boiling range from cut #1 along with 100% each from cut #2 through cut #7. A detailed characterization of this “neat” jet-fuel product along with a blend with a commercially-used jet fuel is provided in Section 9.1.

The synthetic diesel fraction was prepared by removing the 35% volume from the lower-boiling range from cut #1 along with 100% each of all other cuts. A detailed characterization of this “neat” diesel product is provided in Sec 9.2.

Table 45. Distillation of Stage-2 Product (Jet Fuel Fraction Cut below 295°C)

Cut #	Cut temperature °C atm equivalent	Amount of material L	Density g/cm^3
Feed (product stage)		30.21	0.902
cut1	205	3.89	0.843
cut2	213	1.02	0.887
cut3	228	0.98	0.892
cut4	240	1	0.892
cut5	244	1.2	0.897
cut6	252	0.94	0.901
cut7	258	1	0.904
cut8	264	0.95	0.906
cut9	269	1.04	0.908
cut10	272	0.95	0.908
cut11	279	1.06	0.908
cut12	283	0.97	0.908
cut13	286	1	0.905
cut14	291	0.96	0.903
cut15	295	1.11	0.902
Still pot	>295	9.75	0.927
Total		27.84	

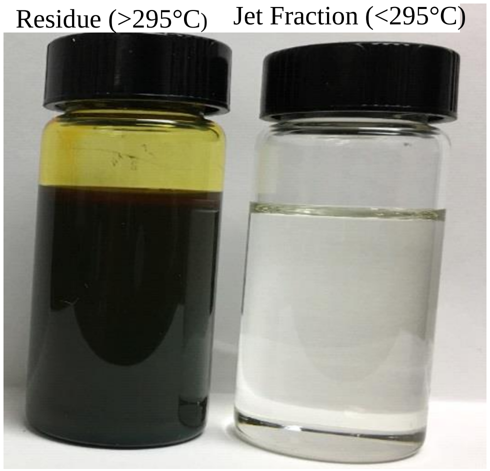


Figure 61. Photo of jet fuel fraction and still pot (residue) fraction for Run #2.

8.12 Comparison of Distillates from Runs #1 and #2

Due to differences in the syncrude properties as well as due to differences in the Stage-2 catalysts, the two upgrading runs produced distillates that had significantly different properties. The results for jet fuel fractions for Run #1 and Run #2 are shown in Table 46. As shown, the jet fuel produced in Run #2 has better properties than jet fuel produced in Run #1: lower freezing point; lower viscosity; lower pressure drop cross the filler; and slightly lower density. It has significantly higher aromatic and n-paraffin content with a concurrent reduction in tri-cycloparaffinic composition. Based on the GCxGC analysis (Table 47), it appears that there is less severe hydrogenation of the Stage-2 product. Although the total aromatic content of Run #2 jet fuel (~17%) is similar to conventional jet fuels, there is an appreciable quantity of 2- and 3-ring aromatic compounds, which is higher than in typical aviation fuels. The distillation step for the Run #2 jet fuel resulted in an improved distillation profile and carbon number distribution as compared to the Run #1 jet fuel sample (Figure 62 and Table 48). The higher concentration of lower molecular weight compounds (e.g., < C9) in Run #2 helped reduce the flash point to 38.9°C from 61.1°C in Run #1.

Table 46. Selected Jet Fuel Specification Tests Performed for Jet Fuel Fractions from Run #1 and Run #2

Analysis	Unit	Jet A	Jet Fuel (Run #1)	Jet Fuel (Run #2)
D56 Flash Point	°C	>38	61.1	38.9
D2386 Freeze Point	°C	<-40	-11.0	-32.0
D445 Kinematic Viscosity at 40°C	cSt		3.110	2.219
D445 Kinematic Viscosity at -20°C	cSt	<8		10.120
D2622 XRF Sulfur	ppm	<3000	< 50.0	< 50.0
D1319 FIA				
Aromatics	vol. %	<25	4.0%	18.3%
Olefins	vol. %		6.9%	5.6%
Saturates	vol. %		89.1%	76.1%
D3241 Filter Pressure Drop				
Test Temperature	°C		260	260
Max Pressure Drop Across Filter	mm Hg	<25	4.0	1.0
D3242 Acidity	mg KOH/g	<0.1	0.079	0.044
Specific Gravity	g/cm3	0.775 to 0.840	0.8920	0.8879
D4629 Chemiluminescence Nitrogen	ppm	<2	2.0	< 1.0
D5291 Instrumental C and H	total (wt. %)	>99.5%	99.120%	99.530%
Carbon	wt. %		86.22%	86.97%
Hydrogen	wt. %		12.90%	12.56%
D6304A Karl Fisher Water	ppm	<75	34	63
D7359 OPC CIC: F, Cl, and S	ppm (each element)	<1	< 1.0	< 1.0
D7111 Metals (Cr, Fe, Pb, Mo Ni)	ppm (each element)	<0.1		< 1.00

Table 47. GCxGC Run #1 vs. Run #2 Product (Stage-2 Product)

Class	Sub-class	Run #1	Run #2
Aromatics	Alkylbenzenes	1.73	2.79
	Diaromatics	0.01	0.42
	Cycloaromatics	0.26	10.19
	(C_nH_{2n-10}) Aromatics	0.15	3.72
	Other Multi-ring Cycloaromatics	0.01	0.03
	Other Multi-ring Aromatics	0.01	0.10
	Total Aromatics	**2.15**	**17.25**
Paraffins	Iso-Paraffins	0.29	1.05
	n-Paraffins	1.11	6.17
	Total n, iso-Paraffins	**1.40**	**7.22**
Cycloparaffins	Monocycloparaffins	3.96	9.63
	Dicycloparaffins	31.08	34.45
	Tricycloparaffins	57.07	28.19
	Other Cycloparaffins	4.33	3.27
	Total Cycloparaffins	**96.44**	**75.54**

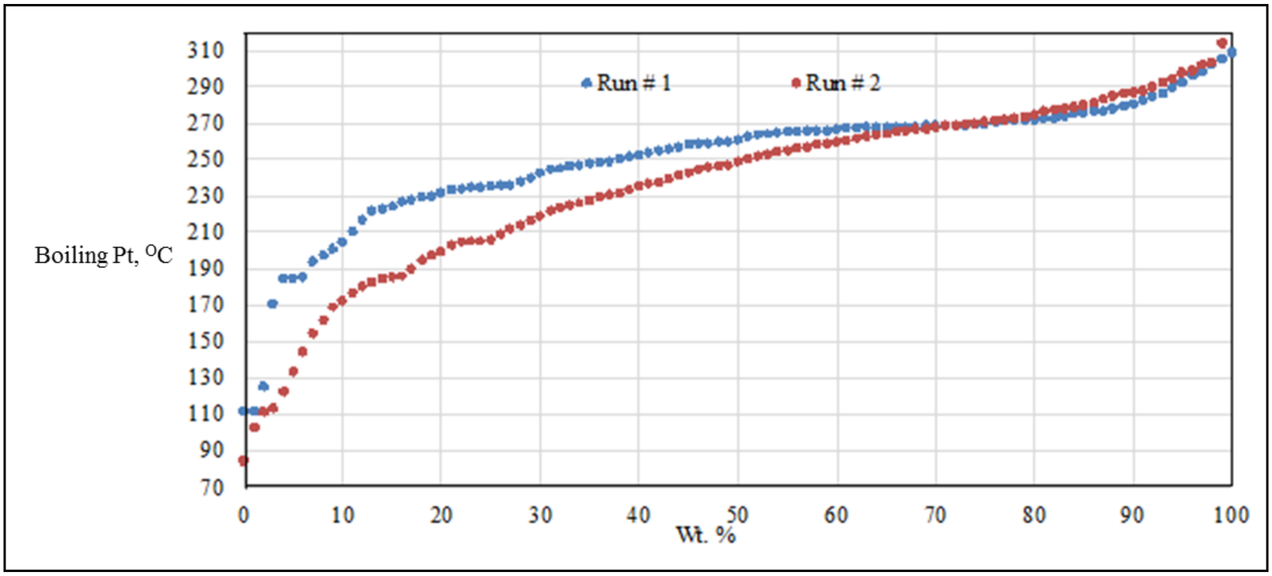


Figure 62. Simulated distillation of jet fuel fraction (≤295°C) for Run #1 and Run #2.

Table 48. Jet Fuel Carbon Distribution for Run #1 and Run #2 (wt%)

Carbon No	Run #1	Run #2
C6	0.03	0.60
C7	1.76	2.22
C8	0.32	2.30
C9	0.63	3.48
C10	4.66	10.84
C11	3.35	6.90
C12	16.14	12.66
C13	15.47	14.90
C14	42.66	25.95
C15	8.25	9.48
C16	6.21	7.93
C17	0.40	2.19
C18	0.03	0.54
C19	<0.01	<0.01
C20	<0.01	<0.01
C21+	<0.01	<0.01

A comparison of diesel fractions from Runs #1 and #2 is provided in Table 49. A more detail analysis of the diesel product from Run #2, which was significantly better than from Run #1, is provided in Section 9.2.

Table 49. Comparison of Diesel Cuts from Run #1 and Run #2 Compared to ASTM 975 Specifications

Specification	Method	Unit	ASTM D975 S15	Diesel Run #1 <337°C	Diesel Run #2 >160°C
Flash Point	D93	°C	>52 (for No. 2D)	91.1	80.5
Water and Sediment	D2709	% volume	≤0.05	<0.005	0.05
Kinematic Viscosity at 40 °C	D445	mm^2/S	1.9 to 4.1 (No. 2D)	4.63	3.74
Distillation Temperature at 90% volume (T90)	D86	°C	282 to 338	337	340.5
Ash	D482	% mass	<0.01	< 0.001	<0.001
Sulfur	D2622	ppm (mass)	15	1	3.5
Copper strip corrosion rating	D130	rating number	<3	1a	1a
Cetane No., engine test	D613		>40		42.5
Derived cetane No., IQT	D6890			28.2	
Aromatics	D1319	% volume	<35	2.6	18.4
Carbon residual	D542	% mass	<0.35 (No. 2D)	0.1	1.07
Lubricity at 60 °C	D6079	µm	<520	397	260
Conductivity	D2624	pS/m	>25		<1.0

9.0 CHARACTERIZATION OF DISTILLATE – PRODUCT FRACTIONS AS JET FUEL OR DIESEL

The distillate product from Intertek Run #2 was fractionated into a jet-fuel cut as well as to a diesel cut. The jet-fuel cut was analyzed extensively because jet fuel was the primary focus of this project. However, standard specification testing also was done to analyze the diesel fraction.

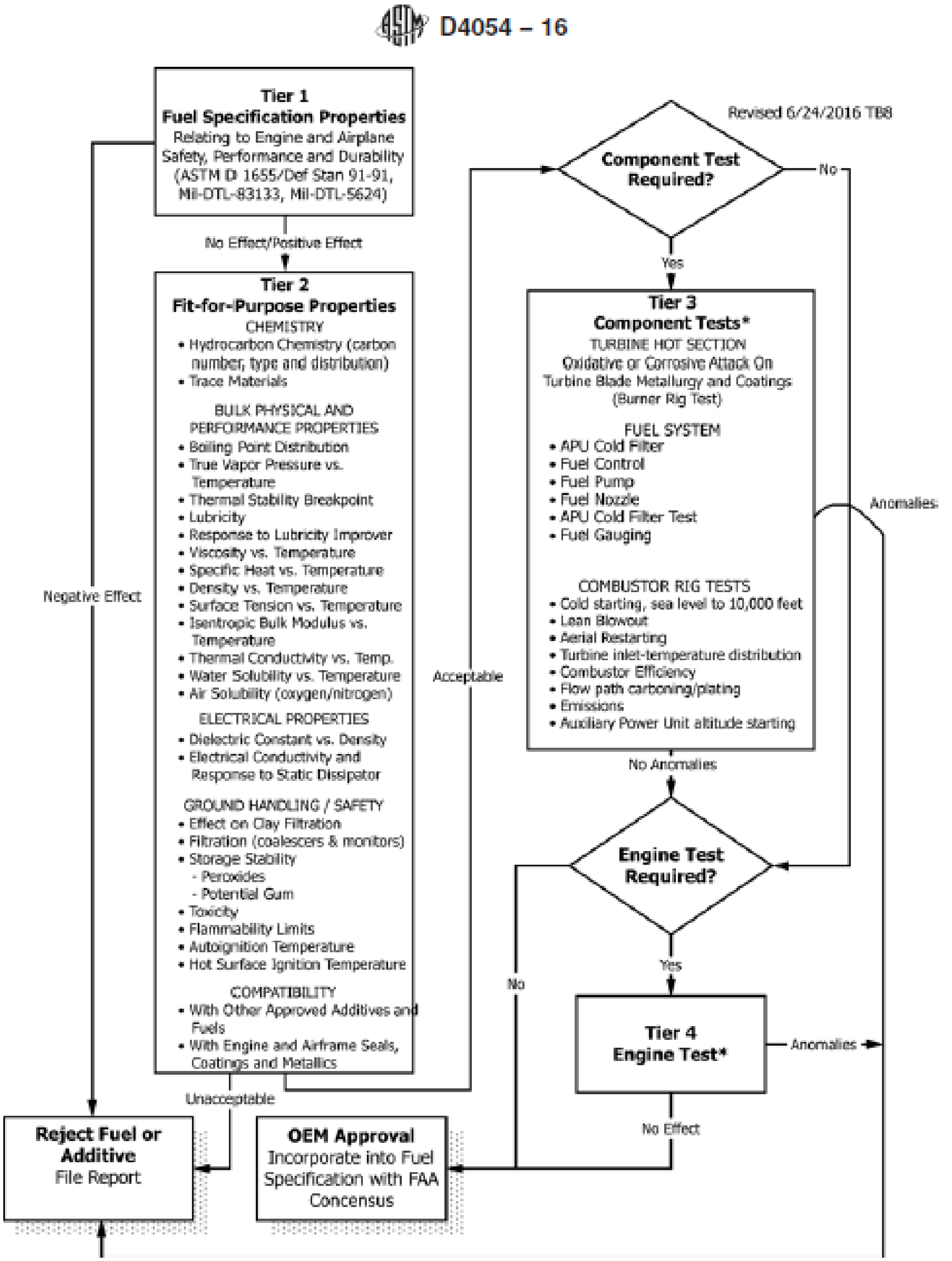
9.1 Evaluation of Battelle-CTL-Derived Neat Synthetic Fuel and Synthetic Fuel Blend for Use in Aviation Applications

9.1.1 Introduction

In recent years, significant efforts have been made to develop, evaluate and certify synthetic (e.g., non-petroleum derived) jet fuels for use in commercial and military aircraft. Initial focus was related to the approval of synthetic formulations which could be blended with conventional fuels for use. These efforts resulted in the certification and approval of several types of synthetic fuels as blending feedstocks in commercial and military aviation fuels. Commercial Jet A (ASTM D7566) and military JP-8 (MIL-DTL-83133J) fuel specifications detail requirements for both the currently approved synthetic blending feedstocks and the resulting fuel blends [13-14]. The properties of the synthetic fuel blends must conform to those required for typical petroleum-derived fuels. In addition, each synthetic blending feedstock has specific property requirements included in appendices of the fuel specifications. These latter requirements provide confidence that the fuel blend will conform to all operational and safety needs of current aircraft fuel systems and engines and insure process quality control during production.

Guidance on recommended protocols and methodologies for the evaluation and certification of synthetic aviation fuels and fuel additives was formalized and documented in ASTM D4054-09 and MIL-HDBK-510A. These protocols were developed to facilitate the approval process in a time- and cost-effective manner. The overall process is divided into ‘Tiers’; the proposed test program from ASTM D4054 is shown in Figure 63 [15]. Initial tiers focus on evaluation of chemical and physical properties of the fuel candidate to determine potential suitability prior to larger-scale turbine hot section and component/system-level testing. Fuel specification testing (referred to as Tier 1) is initially performed to determine conformity of the synthetic fuel candidate to physical property specification requirements. Upon determination of acceptable property conformance, more detailed testing (referred to as Tier 2) is performed to evaluate select “Fit-for-Purpose” (FFP) properties. FFP refers to a property required for safe operation which is not directly controlled by the respective fuel specification; a petroleum-derived fuel which meets all fuel specification requirements will inherently satisfy all FFP property needs. The FFP evaluations include several temperature-dependent properties (e.g., density, specific heat, thermal conductivity). Evaluation of all fuel specification and FFP properties outlined in ASTM D4054 and MIL-HDBK-510 requires several gallons of the neat synthetic fuel and blending feedstock [16].

Battelle produced a synthetic aviation fuel candidate from its CTL process based on the use of biomass-derived solvents. The ‘final’ synthetic jet fuel produced by Battelle was provided to the UDRI for preliminary evaluation of the suitability for use as either a neat ‘drop-in’ jet fuel or synthetic bending component. The evaluation approach was based on guidance in the aforementioned certification protocols; however, it was not possible to complete all required fuel specification and FFP property evaluations for the neat synthetic fuel and blend due to insufficient total available volume. Therefore, fuel specification and select FFP properties were evaluated to provide a quantitative basis for preliminary evaluation of the potential suitability of the submitted synthetic fuel for use in aircraft systems. The following sections discuss the analyses and results performed on the neat synthetic fuel and fuel blend.



* Testing must be performed at P&W, GE, Rolls Royce, Snecma, Honeywell, or in other locations per OEM agreement due to proprietary concerns and test methods

NOTE 1—Additive testing to be performed at 4× the concentration being requested for approval except for filtration.

Figure 63. Proposed test program for qualification and approval of new aviation turbine fuels and fuel additives (Ref: ASTM D4054-16).

9.1.2 Evaluation of Neat Synthetic Fuel Formulation

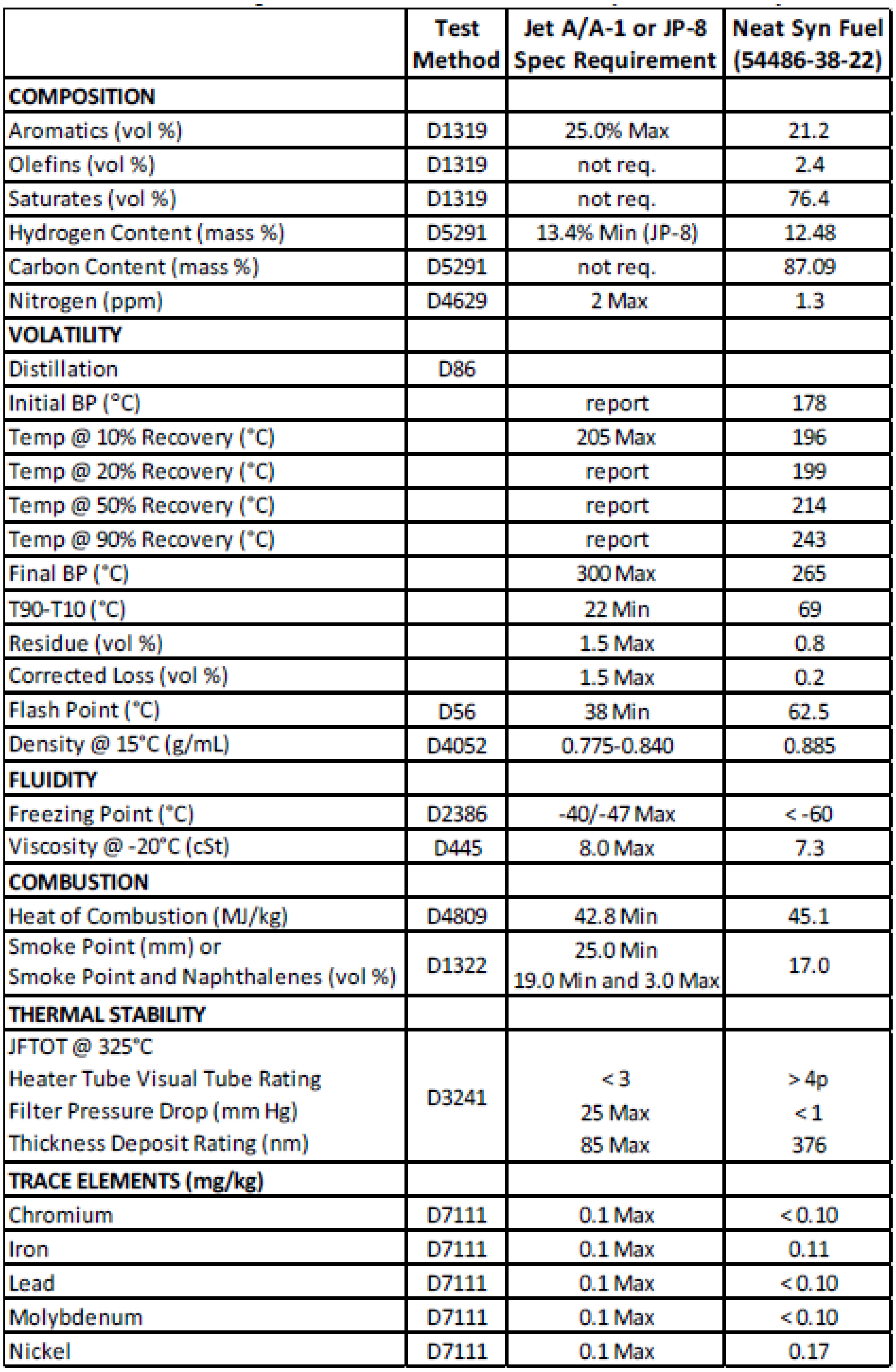
The ‘final’ neat synthetic fuel in the DOE program was produced at Intertek Laboratories in a pilot scale unit using Battelle catalysts and processing conditions and was given the internal designation **“54486-38-22”.** It was the composite of distillation fractions of cut #1 (65% heavy fraction) trhough cut #7 (see Table 45). The synthetic fuel was analyzed for selected specification (and additional elemental analysis) properties using ASTM test methods by Intertek and analyzed for Hydrocarbon-type (HC-type) composition and carbon number distribution by UDRI. HC-type and carbon number analyses were performed using Two-Dimensional Gas Chromatography (GCxGC) with simultaneous Mass Spectrometry (MS) for species identification and Flame Ionization Detection (FID) for quantitation.

The specific ASTM tests performed were selected to provide guidance regarding suitability of the neat synthetic fuel as a direct ‘drop-in’ aviation fuel (i.e., blending with petroleum-derived fuel not necessary). The results from these ASTM tests are shown in Table 50. The HC-type composition is shown in Table 51 and the carbon number distribution is shown in Table 52. The analyses of the neat synthetic fuel indicated that it was not feasible to use this formulation directly as a ‘drop-in’ synthetic fuel; several properties did not conform to the required Jet A/A-1 and JP-8 property requirements. Specifically, the density (0.885 g/mL) was greater than the maximum specification requirement for aviation fuels (0.840 g/mL), the smoke point (17 mm) did not satisfy the sooting requirement (25 mm), and the hydrogen content (12.48% by mass) was below the military fuel requirement (13.4%).

With respect to other properties, the low temperature viscosity (7.3 cSt) was near the specification requirement (8.0 cSt), but the fuel had an acceptable measured freeze point (< -60°C). Nitrogen and trace elemental analyses showed the fuel had minimal residual inorganics from the production and upgrading processes employed; additional sulfur and nitrogen analyses were performed using non-ASTM test methods (reported in Section 4.2.2/Table 9) and indicated very low heteroatomic content in the synthetic fuel. These results are notable based on the elemental composition of the feedstocks used to produce this synthetic fuel. The distillation profile was similar to conventional aviation fuels; with a T90-T10 of 69.2°C. This range is significantly higher than the current synthetic fuel blending feedstock minimum limit of 22°C, which was implemented to insure a blending feedstock would not result in a significant discontinuity in the fuel distillation profile. The flash point was higher than typical Jet A/A-1 fuels due to the lower concentration of low molecular weight species. However, as discussed in Section 8.11, this can be brought down closer to typical Jet A/A-1 fuel values by not removing some of the <160°C fraction.

The thermal-oxidative stability of the neat synthetic fuel was evaluated via testing with the Jet Fuel Thermal Oxidation Tester (JFTOT) with a test temperature of 325°C. This test condition is very aggressive and has been used for evaluation of previously approved synthetic aviation fuel blending feedstocks; a satisfactory result is an indication that the synthetic fuel should not detrimentally affect the thermal stability characteristics of the fuel blend (per ASTM D7566). The coal-derived synthetic fuel did not pass the JFTOT requirements under this test condition (details regarding potential causes for this behavior will be discussed in Section 9.1.3.1.5). However, this result does not preclude the possible use of this synthetic fuel as a blending feedstock as the specification test temperature for a synthetic fuel blend is 260°C.

Table 50. Select Jet Fuel Specification and Elemental Analyses for Neat Synthetic Fuel



	Test Method	Jet A/A-1 or JP-8 Spec Requirement	Neat Syn Fuel (54486-38-22)
COMPOSITION			
Aromatics (vol %)	D1319	25.0% Max	21.2
Olefins (vol %)	D1319	not req.	2.4
Saturates (vol %)	D1319	not req.	76.4
Hydrogen Content (mass %)	D5291	13.4% Min (JP-8)	12.48
Carbon Content (mass %)	D5291	not req.	87.09
Nitrogen (ppm)	D4629	2 Max	1.3
VOLATILITY			
Distillation	D86		
Initial BP (°C)		report	178
Temp @ 10% Recovery (°C)		205 Max	196
Temp @ 20% Recovery (°C)		report	199
Temp @ 50% Recovery (°C)		report	214
Temp @ 90% Recovery (°C)		report	243
Final BP (°C)		300 Max	265
T90-T10 (°C)		22 Min	69
Residue (vol %)		1.5 Max	0.8
Corrected Loss (vol %)		1.5 Max	0.2
Flash Point (°C)	D56	38 Min	62.5
Density @ 15°C (g/mL)	D4052	0.775-0.840	0.885
FLUIDITY			
Freezing Point (°C)	D2386	-40/-47 Max	< -60
Viscosity @ -20°C (cSt)	D445	8.0 Max	7.3
COMBUSTION			
Heat of Combustion (MJ/kg)	D4809	42.8 Min	45.1
Smoke Point (mm) or Smoke Point and Naphthalenes (vol %)	D1322	25.0 Min 19.0 Min and 3.0 Max	17.0
THERMAL STABILITY			
JFTOT @ 325°C Heater Tube Visual Tube Rating Filter Pressure Drop (mm Hg) Thickness Deposit Rating (nm)	D3241	 < 3 25 Max 85 Max	 > 4p < 1 376
TRACE ELEMENTS (mg/kg)			
Chromium	D7111	0.1 Max	< 0.10
Iron	D7111	0.1 Max	0.11
Lead	D7111	0.1 Max	< 0.10
Molybdenum	D7111	0.1 Max	< 0.10
Nickel	D7111	0.1 Max	0.17

Table 51. Hydrocarbon Type Analysis of Neat Synthetic Fuel by GCxGC (Intertek Run #2)

Compound Class	Weight %
Aromatics	
Total Alkylbenzenes	2.73
Total Diaromatics	0.25
Total Cycloaromatics	14.22
Total (CnH2n-10) Aromatics	0.89
Total Other Multi-ring Aromatics	0.03
Total Aromatics	18.13
Paraffins	
Total iso-Paraffins	0.70
Total n-Paraffins	2.22
Cycloparaffins	
Total Monocycloparaffins	12.49
Total Dicycloparaffins	51.13
Total Tricycloparaffins	15.20
Total Other Cycloparaffins	0.13
Total Cycloparaffins	78.95

Table 52. Carbon Number Distribution of Neat Synthetic Fuel (Intertek Run #2)

Carbon Number	Weight %
C6	<0.01
C7	0.0
C8	0.2
C9	6.0
C10	24.0
C11	15.7
C12	23.1
C13	18.0
C14	11.4
C15	1.2
C16	0.3
C17	0.03
C18+	0.04

The HC-type analysis shown in Table 51 indicted the fuel had a total concentration of aromatics (~18.1% by mass) similar to typical aviation fuels; however, there was a higher quantity of 2- and 3-ring cycloaromatics (i.e., partially hydrogenated) than in typical aviation fuels. Petroleum-derived aviation fuels typical contain appreciable concentrations of iso- (~30-40%) and n-paraffin (~20-25%); however, the neat synthetic fuel had very low concentrations of branched and linear paraffins (approximately 0.7 and 2.2%, respectively). The synthetic fuel was primarily comprised of cycloparaffins (79% by mass), with a very high concentration of di- and tri-cycloparaffins (51.1% and 15.2%, respectively). Petroleum-derived aviation fuels typically contain ~30% cycloparaffins, which are primarily monocycloparaffins. The larger molecular weight cycloparaffins in the synthetic fuel were most likely produced directly from the coal feedstock via fragmentation and hydrogenation of the high molecular weight coal moieties. Likewise, the cycloaromatics in the neat synthetic fuel were produced via incomplete hydrogenation of the upgraded feedstocks. The high concentrations of the di-/tri-cycloparaffins and cycloaromatics are the primary cause for the high fuel density and most likely the reduced smoke point value (e.g., increased sooting tendency).

9.1.2.1 Estimation of Blending Ratio for Synthetic Fuel

Based on properties and compositional analysis of the neat synthetic fuel, it was determined that the viable approach for use in aviation applications was as a blending feedstock with petroleum-derived aviation fuel. Therefore, determination of optimal and maximum blending ratios is necessary to allow detailed evaluation of the resulting specification and selected FFP properties of the synthetic fuel blend. The target blend ratio must be specified such that the synthetic fuel blend conforms to all specification requirements identified for commercial (ASTM D7566/D1655) and military (MIL-DTL-83133J) aviation fuels. The maximum allowable blend concentration is dependent on the specific chemistry and properties of the synthetic fuel. For example, Synthetic Paraffinic Kerosenes (SPKs) derived from either Fischer-Tropsch (FT) Synthesis or Hydoprocessed Esters and Fatty Acids (HEFAs), which are primarily comprised of iso- and n-paraffins, can be blended at concentrations up to 50% by volume provided all specification requirements are satisfied. Depending on the properties of the fuel to which these are blended, the density or aromatic content (or both) of the refined fuel may limit the amount of SPK that can be added to the final blend to less than 50% (per D7566). On the contrary, iso-paraffinic compounds produced via oligomerization of iso-butanol (termer Alcohol-to-Jet Synthetic Paraffinic Kerosene [ATJ-SPK]) can only be blended to a maximum concentration of 30% by volume for use.

Based on the specification and compositional properties shown in Tables 1 and 2, the high density of the neat synthetic fuel (0.885 g/mL) is the primary property limiting the maximum blending ratio for application. Specifically, the synthetic fuel blend must have a final density ≤ 0.840 g/mL for use. Improved thermal stability and smoke point are also expected upon blending (due to dilution). The density (@ +15°C) of typical aviation fuels range from approximately 0.780 to 0.830 g/mL, with an average of approximately 0.803 g/mL. The resulting density of a synthetic and petroleum-derived aviation fuel blend is expected to be linear with the volumetric blending ratio as the fluids are expected to behave as ideal fluids; this has previously been shown during blending of FT-derived SPK with aviation fuels [17]. Calculations were performed to investigate the effect of blending ratio and petroleum-derived fuel density on the resulting synthetic fuel blend density. Figure 64 shows the estimated density values of the fuel blend as a function of blending ratio with aviation fuels with densities of 0.780, 0.803 and 0.830 g/mL, respectively. As shown, the primary limiting factor occurs when the petroleum-derived fuel has a high density (e.g., maximum blend percentage of ~18% by volume when petroleum fuel has a density of 0.830 g/mL). However, fuels with lower density values (which comprise the majority of aviation fuels) allow higher blend percentages with the neat synthetic fuel. Based on the density trends shown in Figure 2, the recommendation was made to evaluate the corresponding specification and FFP properties for a 20% blend by volume of the synthetic fuel with an ‘average’ (or ‘nominal’) jet fuel. This provides guidance on the expected performance when using the synthetic fuel as blending feedstock and will most likely mitigate potential issues related to the concentration of certain compound classes which are higher than typically present in aviation fuels (e.g., di-/tri-cycloparaffins).

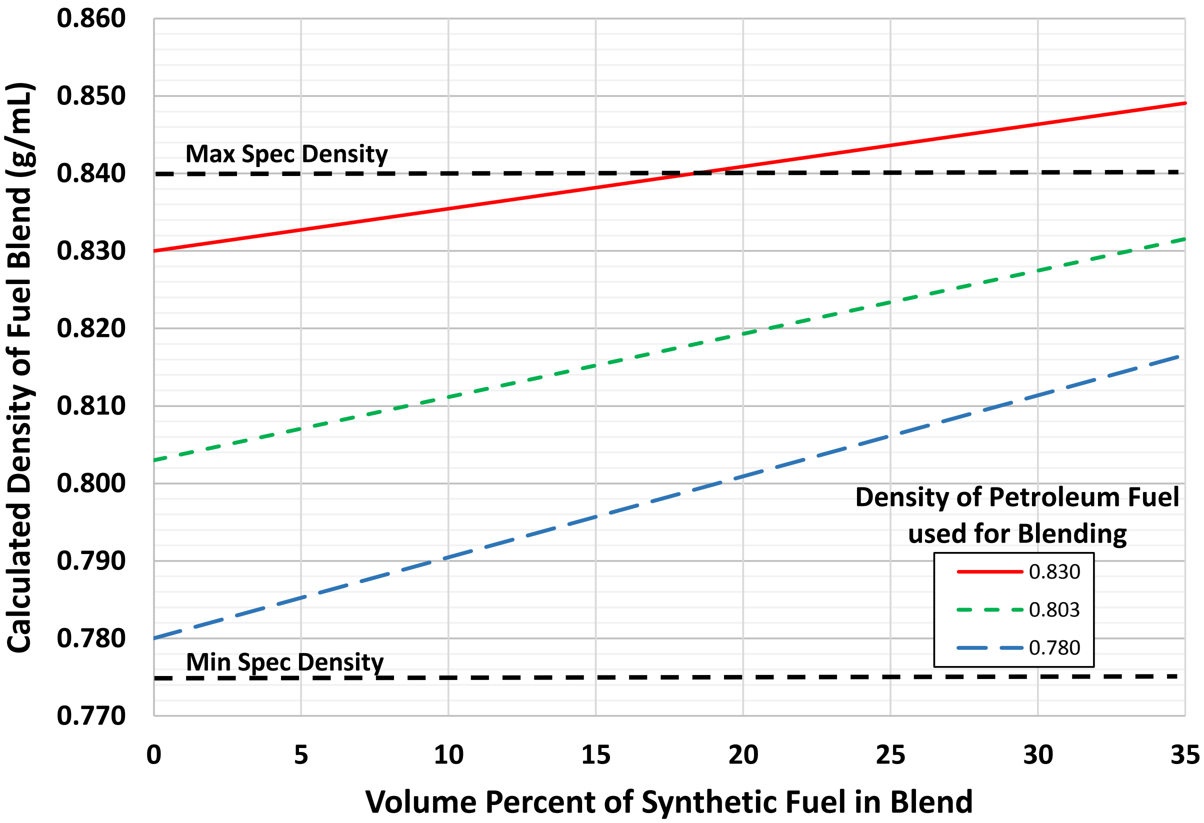


Figure 64. Effect of volumetric blending ratio and corresponding density of petroleum-derived fuel on calculated density for synthetic fuel blend.

9.1.3 Evaluation of Synthetic Fuel Blend

Evaluation of the specification and selected Fit-For-Purpose properties of a 20% blend by volume of the synthetic fuel with a petroleum-derived aviation fuel was performed to provide preliminary guidance regarding the potential suitability for use in aviation applications. Subsequent testing and evaluation as outlined in ASTM D4054 and MIL-HDBK-510 is necessary to provide sufficient data to determine suitability for pursuing certification and approval of the synthetic fuel as a blending feedstock. Blending was performed using a Jet A fuel provided by the Fuels & Energy Branch of the Air Force Research Laboratory. This specific Jet A (with internal identification POSF 10325) has been termed an ‘average’ (or ‘nominal’) jet fuel as the specification properties are very close to historical averages for aviation fuels. This specific Jet A has been used as the ‘average’ fuel in the Federal Aviation Administration (FAA) National Jet Fuel Combustion Program (NJFCP). Results obtained for the synthetic fuel blend will be compared to those for the neat Jet A and are discussed in the following sections.

Due to the limited quantity of batch **54486-38-22**, Battelle prepared a “second batch” of neat synthetic fuel from the same process streams; this batch of neat synthetic fuel was given the internal designation “**54486-39-16**”. The composition of **54486-39-16** was compared to the initial batch **(54486-38-22)** to determine suitability for testing. HC-type composition and carbon number distribution analyses (shown in Section 4.1) indicated the compositions of the two batches were sufficiently similar to proceed with blend preparation and preliminary evaluation for this program.

Battelle had a limited overall volume of the neat synthetic fuel **54486-39-16** available for blend preparation and testing, which precluded completion of all recommended Tier 1 and 2 testing and evaluations in this effort. Therefore, the decision was made to evaluate all fuel property specification requirements; specific FFP evaluations were selected which would provide detailed insight regarding the suitability of the blend for use. The 20% blend by volume of the neat synthetic fuel **(54486-39-16)** with the ‘nominal’ jet fuel (POSF 10325) was given the internal designation **“54486-39-26”**. Results from these tests and pertinent discussion are included in the following sections.

9.1.3.1 Chemical Composition and Specification Properties

The chemical composition and aviation fuel ASTM specification fuel properties were evaluated for the 20% by volume synthetic fuel blend. HC-type analysis obtained using GCxGC analysis and ASTM D2425/6379 are shown in Tables 53 and 54 (a more detailed summary of HC-type analysis is included in appendix of report), carbon number distributions are shown in Table 55, and ASTM specification properties are presented in Table 56. Results for the Jet A used for blending and the neat synthetic fuel(s) are included for comparison.

Table 53. Comparison of Hydrocarbon Type Analyses of Fuels by GCxGC

	Weight %			
Compound Class	**Neat Syn Fuel (54486-38-22)**	**Neat Syn Fuel (54486-39-16)**	**Jet A (POSF 10325)**	**20% SynBlend (54486-39-26)**
Aromatics				
Total Alkylbenzenes	2.73	4.21	12.83	11.01
Total Diaromatics	0.25	0.28	2.27	1.90
Total Cycloaromatics	14.22	14.28	3.42	5.48
Total (CnH2n-10) Aromatics	0.89	1.00	<0.01	0.25
Total Other Multi-ring Aromatics	0.03	0.07	<0.01	0.01
Total Aromatics	18.13	19.84	18.52	18.66
Paraffins				
Total iso-Paraffins	0.70	0.60	29.02	22.57
Total n-Paraffins	2.22	2.18	19.43	15.68
Cycloparaffins				
Total Monocycloparaffins	12.49	11.45	25.48	22.18
Total Dicycloparaffins	51.13	51.40	7.42	17.25
Total Tricycloparaffins	15.20	14.46	0.16	3.63
Total Other Cycloparaffins	0.13	0.13	<0.01	0.05
Total Cycloparaffins	78.95	77.45	33.06	43.11

Table 54. Comparison of Hydrocarbon Type Analyses of Fuels via ASTM D2425/D6379

Compound Class	Neat Syn Fuel (54486-39-16)	Jet A (POSF 10325)	20% SynBlend (54486-39-26)
D2425 (mass %)			
Paraffins (normal + iso)	2	48	42
Cycloparaffins (non-condensed)	22	25	22
Dicycloparaffins (condensed)	29	7	12
Triycloparaffins (condensed)	24	2	6
Alkylbenzenes	6.4	12.1	11.0
Indans and Tetralins	15.9	3.2	5.4
Indenes and C_nH_{2n-10}	<0.2	0.4	0.3
Naphthalene	<0.2	0.2	<0.2
Naphthalenes	<0.2	2.0	1.4
Acenaphthenes	<0.2	0.2	<0.2
Acenaphthylenes	<0.2	<0.2	<0.2
Tricyclic Aromatics	<0.2	<0.2	<0.2
Total	100	100	100
D6379 (mass %)			
Mono-aromatics	22.4	15.6	16.7
Di-aromatics	0.4	2.3	1.8
Total Aromatics	**22.8**	**17.9**	**18.5**
Total Saturates	**77.2**	**82.1**	**81.5**
D6379 (vol. %)			
Mono-aromatics	19.6	14.2	15.1
Di-aromatics	0.3	1.8	1.5
Total Aromatics	**19.9**	**16.0**	**16.6**
Total Saturates	**80.1**	**84.0**	**83.4**

Table 55. Carbon Number Distributions of Fuels

Carbon Number	Neat Syn Fuel (54486-38-22)	Neat Syn Fuel (54486-39-16)	Jet A (POSF 10325)	20% SynBlend (54486-39-26)
C6	<0.01	<0.01	0.14	0.12
C7	0.03	0.03	0.64	0.53
C8	0.23	0.18	2.79	2.26
C9	6.05	5.08	8.44	7.76
C10	23.96	21.67	16.11	17.42
C11	15.66	14.54	20.72	19.32
C12	23.12	24.61	18.45	19.75
C13	18.00	19.58	14.14	15.12
C14	11.39	12.52	10.57	11.30
C15	1.21	1.32	4.98	3.98
C16	0.28	0.33	1.97	1.62
C17	0.03	0.03	0.76	0.58
C18+	0.04	0.08	0.29	0.24

Table 56. Jet Fuel Specification Test Results of Fuels

	Test Method	Jet A/A-1 or JP-8 Spec Requirement	Neat Syn Fuel (54486-38-22)	Jet A (POSF 10325)**	20% SynBlend (54486-39-26)
COMPOSITION					
Acid Number (mg KOH/g)	D3242	0.10 Max	< 0.10*	0.005	0.008
Aromatics (vol %)	D1319	25.0% Max	21.2	17.0	15.6/18.0***
Olefins (vol %)	D1319	not req.	2.4	--	1.8
Saturates (vol %)	D1319	not req.	76.4	--	82.6
Hydrogen Content (mass %)	D5291	13.4% Min (JP-8)	12.48	13.9 (by D7171)	13.5 (by D7171)
Carbon Content (mass %)	D5291	not req.	87.09	--	--
Sulfur Content (mass %)	D5453	0.30% Max	--	0.04	0.0297
Mercaptan Sulfur (mass %)	D3227	0.003% Max	--	0.000	0.0010
VOLATILITY					
Distillation	D86				
Initial BP (°C)		report	178	159	160
Temp @ 10% Recovery (°C)		205 Max	196	177	180
Temp @ 20% Recovery (°C)		report	199	185	188
Temp @ 50% Recovery (°C)		report	214	205	208
Temp @ 90% Recovery (°C)		report	243	245	246
Final BP (°C)		300	265	271	271
T90-T10 (°C)		22 Min	47	68	66
Residue (vol %)		1.5 Max	0.8	1.2	0.8
Corrected Loss (vol %)		1.5 Max	0.2	0.5	0.9
Flash Point (°C)	D56	38 Min	62.5	48.0	47.5
Density @ 15°C (g/mL)	D4052	0.775-0.840	0.885	0.804	0.820
FLUIDITY					
Freezing Point (°C)	D2386	-40/-47 Max	< -60	-51	-52
Viscosity @ -20°C (cSt)	D445	8.0 Max	7.3	4.4	4.9
Viscosity @ -40°C (cSt)	D445	12.0 Max	--	9.1	10.3
COMBUSTION					
Heat of Combustion (MJ/kg)	D4809	42.8 Min	45.1	43.1	43.1
Smoke Point and Naphthalenes (vol %)	D1322 D1840	18.0 Min (19.0 JP-8) 3.0 Max	17.0	23.0 1.5	20.9 1.2
THERMAL STABILITY					
JFTOT @ 260°C	D3241		@ 325°C		
Heater Tube Visual Tube Rating		< 3	> 4p	1	<1
Filter Pressure Drop (mm Hg)		25 Max	< 1 mm Hg	0 mm Hg	14 mm Hg
Thickness Deposit Rating (nm)		85 Max	376 nm		
CONTAMINANTS/CORROSION/WEAR					
Existent Gun (mg/100 mL)	D381	7 Max	2*	<1	< 1
MSEP (Rating)	D3948	85 Min	--	97	93
Lubricity-Wear Scar Diameter (mm)	D5001	0.85 Max	--	0.59	0.64
Conductivivty (pS/m)	D2624	report	--	0	0
Copper Corrosion @ 100C/2 hr	D130	1b Max	--	1a	1b

*Properties measured with neat synthetic fuel 54486-39-16

**Data for Jet A (POSF 10325) obtained from Tim Edwards (AFRL/RQTF)

***Repeat measurements of aromatic content performed by different laboratories

9.1.3.1.1 Composition

Blending of the neat synthetic fuel at 20% by volume with petroleum-derived Jet A resulted in an overall chemical composition similar to typical aviation fuels, with the exception of the cycloaromatic and di-/tri-cycloparaffins content. The concentration of these latter compound classes is higher than typically observed in aviation fuels. This result was expected based on the coal feedstock used for production of the synthetic blend feedstock. Differences were observed between hydrocarbon type analyses performed on the neat synthetic fuel and blend using GCxGC and ASTM D2425/D6379. However, there was good agreement between the techniques for the ‘nominal’ Jet A fuel. The differences most likely occur since the ASTM techniques were developed for petroleum-derived aviation fuel; therefore, the GCxGC results provide improved accuracy of the overall fuel composition. A comparison of the carbon number distribution data from Table 55 is shown in Figure 65. The synthetic fuel had a carbon number distribution slightly narrower than typical aviation fuels, but with an acceptable range of molecular weights. The higher concentration of C10-C14 compounds in the synthetic fuel and blend is due to high concentrations of multi-ring cycloparaffins and cycloaromatics (e.g., decalin, tetralin, dodecahydro-acenaphthylene, perhydrophenalene). The impact of increased concentrations of these higher molecular weight cycloaromatics and cycloparaffins will be more apparent when comparing combustion and FFP characteristics of the synthetic fuel blend. If necessary, subsequent processing could be performed to reduce the concentration of these compound classes in the neat synthetic fuel via either further distillation or hydrocracking.

The compositional characteristics determined by ASTM specification testing shown in Table 56 indicated the synthetic fuel blend conformed to the primary compositional properties required for aviation fuels containing synthesized hydrocarbons. More specifically, the acid number, total and mercaptan sulfur and hydrogen content all met current specification requirements for synthetic fuel blends. The total aromatic content for the synthetic fuel blend (15.6%) was lower than expected based on the composition of the neat synthetic fuel and Jet A; a repeat analysis via ASTM D1319 resulted in a total of 18% aromatics by volume. These quantified aromatic values are within the measurement uncertainty of the ASTM technique employed.

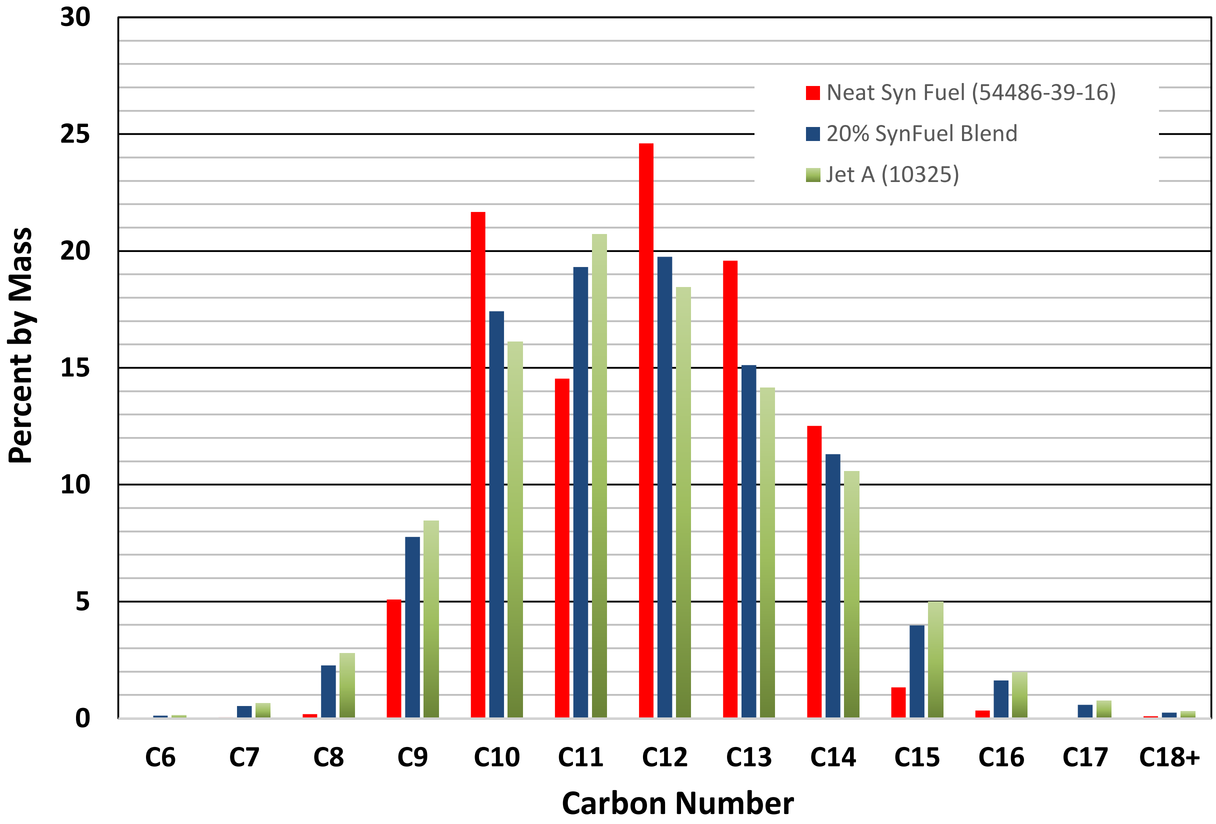


Figure 65. Comparison of carbon number distribution for neat synthetic fuel, Jet A, and 20% by volume synthetic fuel blend.

9.1.3.1.2 Volatility

The volatility characteristics of the synthetic fuel blend satisfied all current fuel specifications and were similar to a 'nominal' aviation fuel. Although the flash point of the neat synthetic fuel (62.5°C) was near the high end of typical Jet A fuels, the synthetic blend had a flash point similar to the Jet A used for blending. This behavior is a result of the flash point being primarily dependent on the most volatile components in the fuel. The distillation profile of the blend was very similar to the nominal Jet A, which is a favorable characteristic during application. The distillation profiles for the synthetic blend and 'nominal' Jet A are shown in Figure 66. Included are distillation profiles for two additional jet fuels, a JP-8 (POSF 10264) and JP-5 (POSF 10289), which have also been used in the FAA NJFCP. The JP-8 has been termed a 'best case' jet fuel (e.g., low viscosity, aromatics and flash point with high H-content) while the JP-5 is a 'worst case' jet fuel (e.g., high viscosity and flash point with low H-content). As shown in Figure 4, the volatility profile of the synthetic fuel blend is within the bounds of the two reference fuels. The blend density (0.820 g/mL) was within the specification limits and is identical to the value calculated based on the blending ratio of the two fuels. A favorable characteristic of the synthetic aviation fuel produced in this program is that blending will increase the density relative to the neat petroleum-derived fuel.

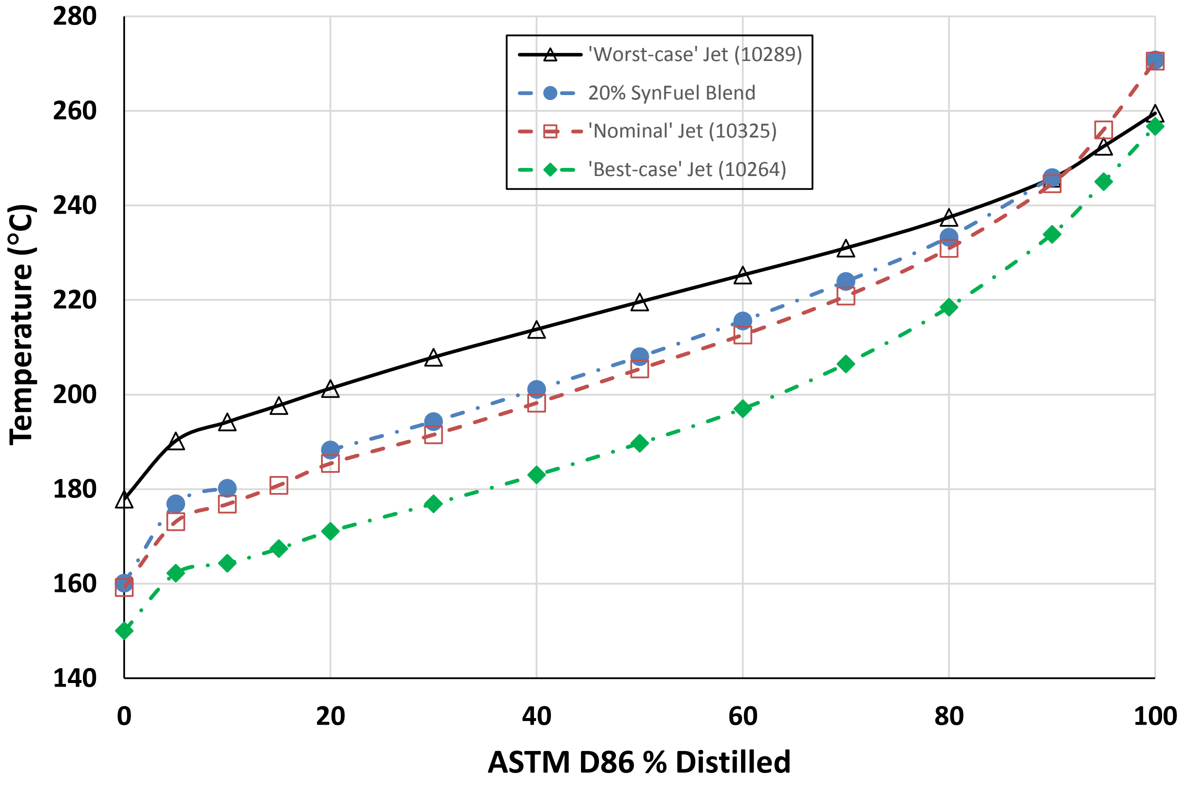


Figure 66. Distillation (D86) profiles for 20% by volume synthetic fuel blend and 'Nominal', 'Worst', and 'Best-Case' jet fuels from FAA NJFCP program. 'Nominal' jet fuel used for blend preparation; value in parentheses corresponds to AFRL/RQTF identification number.

9.1.3.1.3 Fluidity

The fluidity characteristics of the synthetic fuel blend satisfied the aviation fuel specification requirements for fuel freeze point and low temperature viscosity (at -20 and -40°C). The freeze point behavior was expected due to the low value for the neat synthetic fuel. Blending of the synthetic fuel with the Jet A only slightly increased the viscosity relative to the neat petroleum-derived fuel (from 4.4 to 4.9 cSt at -20°C and 9.1 to 10.3 cSt at -40°C). This is a favorable result as the resulting viscosity was within specification requirement. The low temperature viscosity characteristics of the synthetic fuel blend will be further discussed below (See Section 9.1.3.2.1).

9.1.3.1.4 Combustion

The primary combustion characteristics in the aviation fuel specification requirement pertain to the energy content (i.e., Heat of Combustion) and sooting propensity. The synthetic fuel blend heat of combustion (43.1 MJ/kg) satisfied the specification requirement, as expected based on the high energy content for the neat synthetic fuel (45.1 MJ/kg). As discussed in Section 3.0, the high concentrations of high molecular weight cycloparaffins and cycloaromatics were most likely the cause for the low smoke point of the neat synthetic fuel (17 mm). However, blending with the petroleum-derived fuel resulted in an improvement to the smoke point (20.9 mm). This increased value with the corresponding concentration of naphthalenes (1.2% by volume) satisfy the fuel specification requirement. Further evaluation of the impact of the higher molecular weight cyclic compounds on combustion performance/stability and sooting propensity, as recommended in the ASTM D4054 and MIL-HDBK-510A processes, may be necessary to insure suitability of the fuel for use.

9.1.3.1.5 Thermal Stability

The thermal-oxidative stability of aviation fuels is evaluated using the JFTOT; the specification requirement for a synthetic fuel blend is a passing rating at 260°C. The synthetic fuel blend passed the JFTOT specification at this test temperature with a Visual Tube Rating (VTR) of < 1 and Filter pressure drop of 14 mm Hg. The VTR result demonstrated negligible tube deposition during stressing. However, the filter pressure drop of the blend was higher than observed for the neat Jet A. As discussed in Section 9.1.2, the neat synthetic fuel did not obtain a passing rating at 325°C, which is the test condition previously used for qualifying synthetic fuel blending feedstocks. However, passing at 325°C may not be necessary for eventual certification and use as the specific requirements for a synthetic fuel blending feedstock are determined based on the feedstock and production processes employed. Further evaluation, including determination of the JFTOT breakpoint (highest test temperature at which there is a passing result), is necessary to provide improved insight into the overall thermal stability characteristics of this fuel. Potential causes for the observed behavior for the neat synthetic fuel and the blend may be related to the presence of high molecular weight polar compounds (e.g., oxygenated multi-ring cycloparaffins and cycloaromatics). Further evaluation of fuel blend thermal-oxidative stability characteristics was performed using a Quartz Crystal Microbalance, and will be discussed in Section 9.1.3.2.3.

9.1.3.1.6 Contaminants/Corrosion/Wear

Several aviation fuel specification tests are performed to verify the fuel has acceptable compatibility and performance characteristics with minimal contamination. The synthetic fuel blend passed the existent gum, microseparator (MSEP; measure of impact on water coalescing/removal performance) and copper corrosion requirements. As expected, the blend had zero conductivity due to the low heteroatomic composition. If the conductivity of the blend would need to be increased, this can be addressed via use of static dissipater additive. The lubricity of the fuel blend (wear scar of 0.64 mm) is below the maximum allowable value of 0.85 mm.

9.1.3.2 Fit-For-Purpose Properties

The synthetic fuel blend met all current specification requirements for an aviation fuel which contains synthesized hydrocarbons. However, further evaluation of the performance and compatibility of the synthetic fuel blend beyond those characteristics evaluated by the specification properties is necessary to determine suitability for implementation and use on aviation platforms. These are referred to as “Fit-for-Purpose” (FFP) properties. FFP properties refer to a property required for safe operation which are not directly controlled by the respective fuel specification; a petroleum-derived fuel which meets the fuel specification will inherently satisfy all FFP property requirements. ASTM D4054 and MIL-HDBK-510 provide guidance on pertinent FFP tests to be performed when evaluating synthetic fuels and additive for use in aviation applications. Specific areas of recommended tests include those shown in Figure 1. Additional recommended testing may arise depending on results from the specification and compositional property results. FFP properties do not have well defined limits; rather the effect of the proposed fuel or additive on the corresponding FFP property must fall within the scope of experience of the engine and airframe manufacturers. The results from the FFP testing provide the basis for the FAA, DOD and aircraft engine/airframe OEMs to evaluate the potential suitability of the proposed fuel/additive for use and determine if further testing and evaluation is warranted. Completion of all recommended FFP tests requires several gallons the synthetic fuel blend for completion.

There was insufficient total volume of the synthetic fuel blend to complete all recommended FFP tests. Therefore, specific FFP tests were selected based on the available volume and composition/specification test results which would provide guidance regarding the potential suitability of the synthetic fuel blend for use in aviation applications. The selected FFP property tests performed in this effort are shown in Table 57. Subsequent evaluation of other FFP characteristics as outlined in the recommended approval guidelines must be completed to provide the basis for determination if the synthetic fuel blend is suitable for further evaluation and use. The following section discuss results from the specific FFP testing performed in this effort.

Table 57. Selected Fit-For-Purpose Property Testing Performed on Synthetic Fuel Blend

FFP Property
Low Temperature Viscosity
Analysis of Polars and S/N content
Thermal-Oxidative Stability via Quartz Crystal Microbalance
Ignition Quality Test (Derived Cetane Number)
Initial Material Compatibility (Seal Swell)

9.1.3.2.1 Low Temperature Viscosity

The synthetic fuel blend satisfied the specification requirements for viscosity at -20 and -40°C; however, additional guidance regarding the corresponding fluid behavior within the low temperature regime is beneficial. Therefore, the low temperature dynamic viscosity characteristics of the neat Jet A and synthetic fuel blend were measured from -20 to < -56°C using a Brookfield Scanning Viscometer with a cooling rate of -5°C/hr. The dynamic viscosity is converted to kinematic by normalizing to the corresponding temperature-dependent density. Results from these measurements are shown in Figure 67. Both the Jet A and synthetic fuel blend exhibit characteristics consistent with typical aviation fuels; the viscosity increases with decreasing temperature until there is a rapid increase near the phase transition (e.g., crystallization) temperature. For aviation fuels, this is typically due to crystallization of long chain n-paraffins in the fuel. The addition of the synthetic fuel suppressed this transition by approximately 2°C. The addition of the synthetic fuel slightly increased (~1-2 cSt) the kinematic viscosity relative to the baseline Jet A; however, this increase is minor and not expected to result in a significant performance impact.

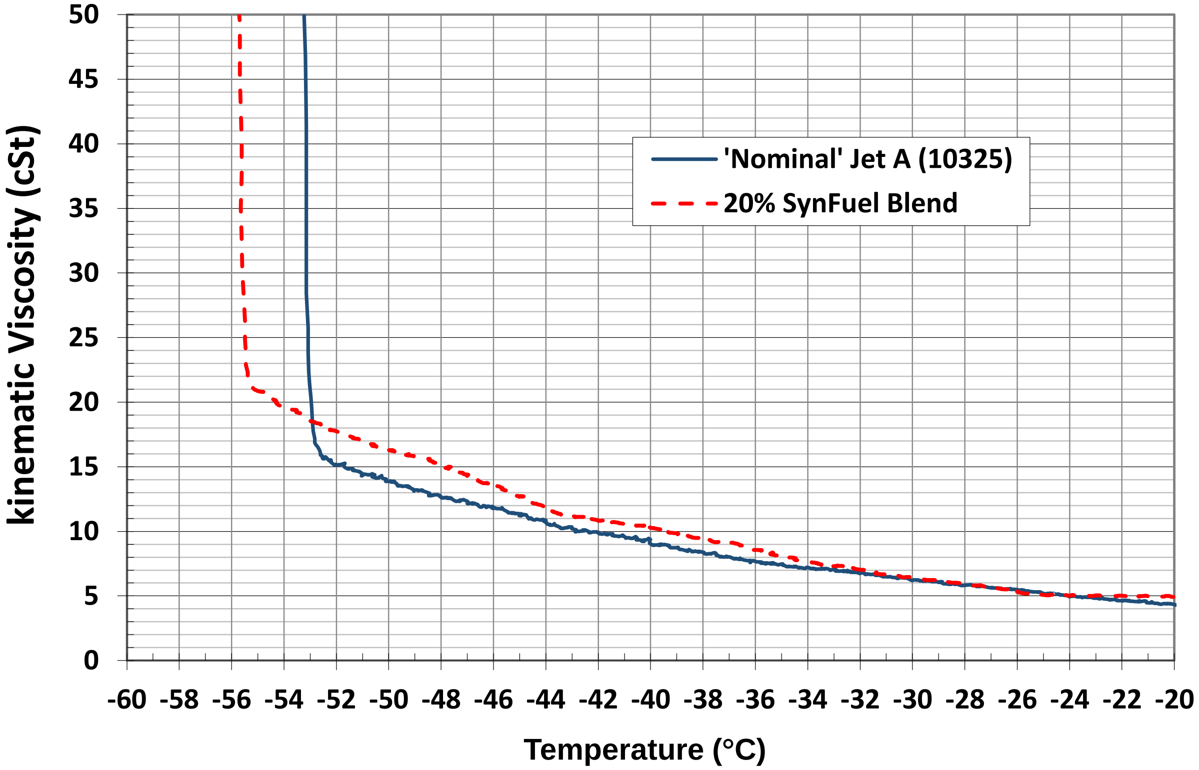


Figure 67. Low temperature kinematic viscosity measurements of Jet A and synthetic fuel blend.

9.1.3.2.2 Analysis of Polars and S/N Content

Analysis of the heteroatomic and polar composition was performed to provide insight into the quantitative levels of these classes of species in the synthetic fuel blend. Heteroatomic and polar species are known to affect thermal-oxidative stability of aviation fuels and can impact material and storage compatibility. The sulfur and nitrogen content (total and polar) of the neat synthetic fuel, Jet A and neat synthetic blend were quantified using Gas Chromatography with Sulfur and Nitrogen Chemiluminescence Detection; results are shown in Table 58. The neat synthetic fuel had very low sulfur/nitrogen content, demonstrating that the processes and catalysts used in the fuel production were effective at removing the heteroatomic species.

The polar composition of the fuels was investigated via extraction using silica gel solid phase extraction. Retained polar compounds were eluted with methanol and analyzed using GCxGC-FID/MS to quantify the respective classes of polar compounds in the fuels; results are shown in Table 59. The Jet A fuel had ‘typical’ levels of polar compounds, primarily phenols and lower molecular weight compounds. Although the neat synthetic fuel had a similar total polar content, the respective species were of higher molecular weight (primarily 2-ring). The presence of these types of species is due to the composition of the neat synthetic fuel (e.g., tetralone related to high concentration of tetralin). The oxygenated species are either residual in the fuel following synthesis or formed via oxidation during storage. The presence of these types of species may impact the thermal-oxidative stability and seal swell propensity during application (discussed below). The polar content of the synthetic fuel blend was a result of blending of the neat synthetic and Jet A fuels.

Table 58. Total and Polar Sulfur/Nitrogen Content of Fuels using Gas Chromatography with Chemiluminescence Detection

Compound	Neat Syn Fuel (54486-39-16)	Jet A (POSF 10325)	20% SynBlend (54486-39-26)
Total Sulfur (ppm)	3	399	312
Polar Sulfur (ppm)	1	8	11
Total Nitrogen (ppm)	<1	3	3
Polar Nitrogen (ppm)	<1	3	3
Methyl-dihydro-dithiazine (ppm)	<0.2	0.6	<0.2

Table 59. Polar Content of Fuels Determined using Solid Phase Extraction and Two-Dimensional Gas Chromatography

Polars (mg/L)	Neat Syn Fuel (54486-39-16)	Jet A (POSF 10325)	20% SynBlend (54486-39-26)
Phenols	16	155	128
Anilines	<5	<5	<5
Indoles	<10	<5	<5
Quinolines	<5	9	8
Tetrahydroquinolines[1]	<5	<5	<5
Pyridines[2]	<5	<5	<5
Carbazoles	<5	<5	<5
Ketones	19	60	59
Cycloketones[3]	8	19	18
Alcohols & Esters[4]	6	27	26
Aldehydes	<5	9	8
Ethers[5]	<5	<5	<5
Phthalates[3]	<5	<5	<5
Phenyl-ethanones[6]	6	<5	<5
Benzaldehydes[6]	33	<5	8
Tetrahydronaphthalenols & Methyl-indanols[6]	87	<5	19
Tetralones &Indanones[6]	184	<5	39
Decalones[3]	5	<5	<5
Other[3]	83	97	100
Total	**447**	**377**	**415**

[1]quantified as quinolines, [2]quantified as anilines, [3]quantified as ketones

[4]quantified as alcohols, [5]quantified as aldehydes, [6]quantified as phenols

9.1.3.2.3 Thermal-Oxidative Stability via Quartz Crystal Microbalance

The thermal-oxidative characteristics of the neat synthetic fuel and blend were previously analyzed via JFTOT testing. The synthetic fuel blend passed the specification criteria at a test temperature of 260°C; however, the neat synthetic fuel failed at an elevated test temperature of 325°C. Improved insight into potential causes for these results would be useful regarding the suitability of the synthetic fuel for use in aviation applications. Therefore, the thermal-oxidative stability of the synthetic fuel blend was further evaluated using a Quartz Crystal Microbalance (QCM). QCM analysis has primarily been used to provide insight regarding oxidation and deposition tendencies of jet fuels due to differences in trace chemical composition (e.g., heteroatomic species and dissolved metals content).

The thermal-oxidative stability characteristics of the Jet A and synthetic fuel blend were assessed using the QCM operated under typical experimental conditions (i.e., 140°C, air saturated fuel, 15 hours). These experimental conditions are sufficient to identify inherent differences in oxidation rate and level of deposit accumulation of aviation fuels. Results from this testing are shown in Figure 68. The Jet A fuel is a slow oxidizer; deposit accumulation occurs as oxidized fuel species are produced and undergo further molecular growth reactions. The oxidation and deposition characteristics of the synthetic fuel blend were qualitatively similar to the Jet A fuel; however, the rate of oxidation and level of deposition were increased relative to the petroleum-derived fuel. Typical aviation turbine fuels produce about 1 to 6 $\mu g/cm^2$ of deposition under these test conditions; the synthetic fuel blend is near the high end of this range.

The impact of the addition of the synthetic fuel on the corresponding thermal-oxidative stability characteristics may be related to the polar composition and the primary species formed during oxidation of the synthetic fuel. As discussed in Sections 4.1 and 4.2.2, the synthetic fuel had a higher concentration of 2 and 3-ring cycloparaffins and cycloaromatics (and higher molecular weight polar compounds) than typically observed in aviation fuels. These species may be more prone to molecular growth via oligomerization reactions during oxidative stressing; similar behavior had been observed during a previous study investigating the impact of aromatic addition to SPK fuels [18]. Pretreatment of the synthetic fuel prior to blending (e.g., extraction of polars via silica or clay filtration) and addition of an antioxidant could possibly improve the corresponding thermal stability behavior. Although the neat synthetic fuel may be inherently more prone to deposit formation than a typical aviation fuel, the corresponding behavior is within ranges of typical aviation fuels when blended at reasonable concentrations (i.e., ≤ 20% by volume). Further evaluation of the thermal stability characteristics, such as JFTOT breakpoint or flowing system testing, would provide improved insight regarding the impact of the synthetic fuel during use. This could assist in determining if processing modifications or post-production treatments, such as filtration or addition of antioxidant, could further improve the thermal stability characteristics of the synthetic fuel blend.

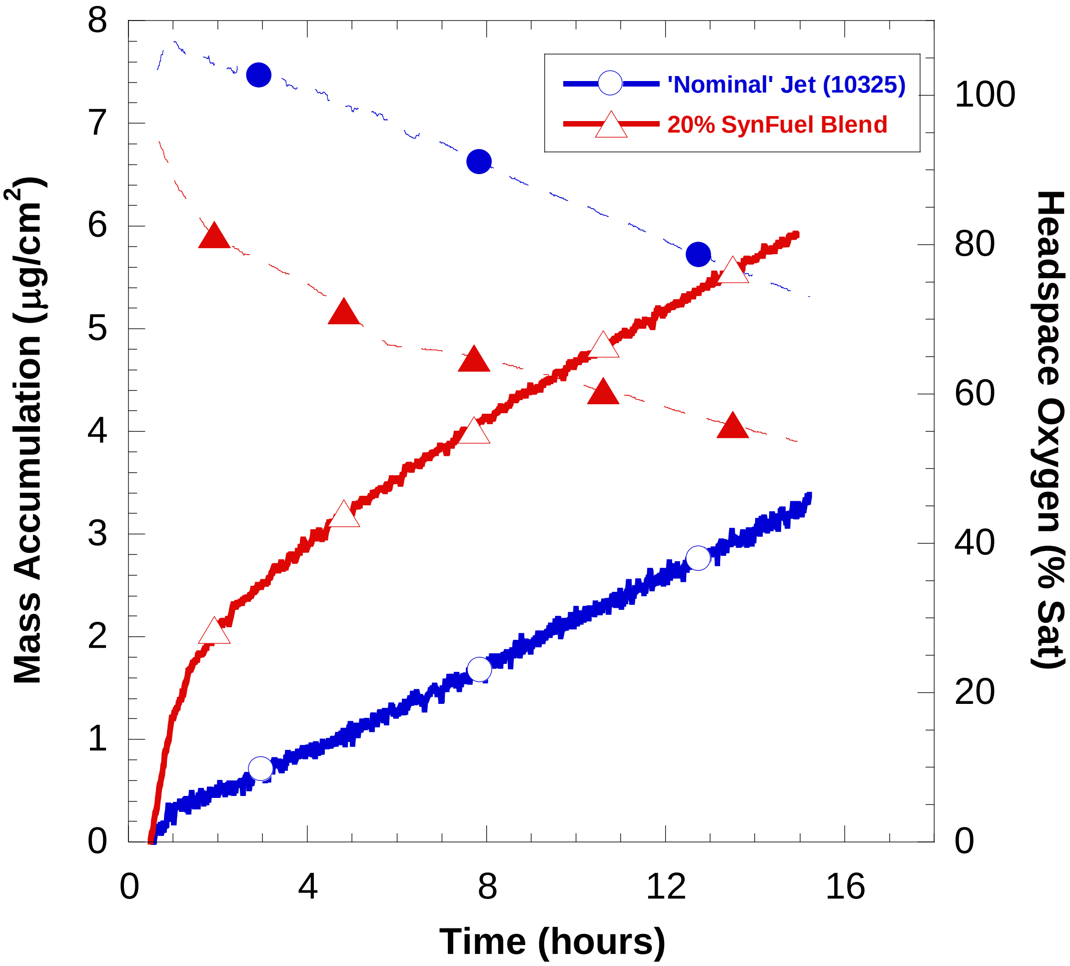


Figure 68. Deposition (solid lines) and oxidation (dashed lines) profiles for thermal stressing of fuels using quartz crystal microbalance at 140°C.

9.1.3.2.4 Ignition Quality Test (Derived Cetane Number)

The Derived Cetane Number (DCN) of a fuel is primarily relevant to use in diesel engines. DCN is a measure of the combustion speed during compression needed for ignition. This is an important property for use of military aviation fuels in ground support systems and vehicles. The DCN can be measured using an Ignition Quality Tester (IQT) per ASTM D6890. An acceptable DCN range of 40-65 has been recommended during qualification of synthetic aviation fuels (per MIL-HDBK-510A). The Jet A (POSF 10325) used in the blend formulation had a measured DCN of 48.3, while the synthetic fuel blend had a measured value of 45.5. The synthetic fuel blend value is within the recommended range for DCN and would be expected to perform satisfactorily during use.

9.1.3.2.5 Initial Material Compatibility (Seal Swell)

Compatibility of candidate synthetic fuels and additives with fuel system materials is critical to insure suitability for use without adverse effects. Materials of interest include metallic/non-metallic components and elastomers. The commercial and military fuel certification processes describe recommended approaches for evaluating the physical properties of materials following extended exposure to the test fuel. This includes aging the materials in the test fluids for extended durations and comparing the impacts to those observed with ‘typical’ petroleum-derived fuels. Compatibility testing for all fuel system materials requires very large volumes of fuel for completion. However, initial material compatibility evaluations can be performed via investigation of seal swell characteristics of elastomers. Elastomer seal swell has been shown to be critical during the certification of synthetic fuel blends to insure there is sufficient swell to prevent leakage in aircraft fuel systems. Therefore, the volume swell characteristics of selected O-rings exposed to the synthetic fuel blend were evaluated and results were compared to a historical reference data sets for normal volume swell behavior in aviation turbine fuels. This testing has previously been used to provide detailed information regarding material compatibility of potential synthetic fuel formulations while requiring very small fuel volumes for testing.

The volume swell of the synthetic fuel blend was evaluated using three different types of elastomers which are the most prevalent fuel wetted o-ring materials in conventional aircraft. Specifically, nitrile rubber (Identification Number N0602), fluorosilicone (L1120), and fluorocarbon (V0747) O-rings manufactured by Parker Hannifin were used in this evaluation. The plasticizer was removed from samples of the N0602 nitrile rubber using acetone solvent extraction and designated N0602e. For each analysis, two size -001 O-rings were cut in half with one section from each O-ring being used for this analysis. Volume swell characteristics were measured by performing optical dilatometry at room temperature. UDRI has used optical dilatometry for evaluating the impact of synthetic fuels on the seal swell of various elastomeric materials, including the initial evaluation of synthetic SPK fuel blends during certification for use in B-52 and C-17 aircraft. This technique requires a very small volume of fuel for evaluation and significantly shorter test durations than conventional ASTM soak tests. Briefly, two samples were placed in a reservoir with 5 mL of the test fuel. Starting at 1 minute after being immersed in the fuel, the samples were digitally photographed every 20 seconds for the next 3 minutes. At 5 minutes total elapsed time, the samples were photographed every 30 minutes for the next 40 hours. After the aging period was completed, the cross-sectional area was extracted from the digital images and taken as a characteristic dimension proportional to the volume. The results reported below are the average values obtained from the two samples. At the completion of the aging period, the absorbed fuel was extracted and the composition was analyzed by GC-MS. By comparing the GC-MS analysis of the fuel absorbed by the O-ring with that of the neat fuel, the relative solubility of the major classes of fuel components were summarized in terms of their respective polymer-fuel partition coefficients (Kpf). The major class fractions were taken as the normal-, and *iso*-alkanes, normal- and *iso*-alkyl benzenes, naphthalene, and alkyl naphthalenes. These were isolated from the GC-MS total ion chromatograms using ions 57 (*n*,*i*-alkanes), 105 (principally the C_3 substituted alkyl benzenes), 128 (naphthalene), and 141 (C_1 and C_2

substituted naphthalenes). Furthermore, cycloalkanes and tetrahydronaphthalene (tetralin) were analyzed using ions 83 and 104, respectively.

The basis for comparison was the average values and 90% prediction intervals for the volume swell and partition coefficients obtained from 12 reference JP-8s with aromatic contents from 10.9% to 23.6% by volume (v/v) (prior studies have shown that the volume swell behavior of JP-8 is similar to Jet-A). It should be noted that the prediction interval is a statistical estimate for the range of values that would be exhibited by 90% of all individual JP-8s, and therefore reflects the estimated range of behavior for 'normal' JP-8s with 10-25% aromatics. The results summarized in Table 60 and Figure 69 show that the volume swell behavior of the synthetic fuel blend and the Jet A used for blend preparation were well within the normal range typically observed for JP-8 for the nitrile rubber and fluorosilicone materials. The volume swell of the fluorocarbon was somewhat lower than average, likely due to the lack of Fuel System Icing Inhibitor additive (Di-Ethylene Glycol Monomethyl Ether) which is required in military aviation fuels. However, the absolute difference is very small and does not indicate a potential issue with either the Jet A or synthetic fuel blend.

The overall absorption of fuel by the sample O-rings is summarized in Table 61 and Figure 70. These results show that the average solubility of all major class fractions examined are within the range typically observed for JP-8s. Note that the solubility of the cycloalkanes in the test fuels with nitrile rubber is about 10% higher than exhibited by linear and branched alkanes, which is consistent with prior work. The solubility of tetralin, a significant component of the synthetic fuel, was modestly higher than the C_3 alkyl benzenes, but lower than the alkyl naphthalenes. This suggests that the presence of the synthetic fuel components slightly elevates the overall solubility in the elastomer which increased the volume swell character of this fuel blend as compared to the neat Jet A.

Overall, the volume swell character of the synthetic fuel blend is within the range typically observed for aviation turbine fuel and should therefore be compatible with the O-ring materials studied. Further evaluation of the compatibility characteristics of the synthetic fuel with other fuel system and engine materials may be warranted.

Table 60. Summary of Volume Swell of Selected O-rings Aged in the Test Fuels and the Average Values for JP-8

Material ID	Material	JP-8 90% Prediction Interval			Jet A		Synthetic Blend	
		LL %v/v	Mean %v/v	UL %v/v	Mean %v/v	90% CI %v/v	Mean %v/v	90% CI %v/v
N0602e*	Nitrile Rubber	16.38	21.43	26.54	20.05	1.15	22.54	0.37
N0602	Nitrile Rubber	3.39	6.92	10.52	7.14	0.13	8.02	0.42
L1120	Fluorosilicone	5.01	5.95	6.92	5.63	0.21	5.94	0.19
V0747	Fluorocarbon	0.19	0.44	0.69	0.11	0.06	0.27	0.26

*Plasticizer pre-extracted
LL: Lower Limit; UL: Upper Limit; CI: Confidence Interval.

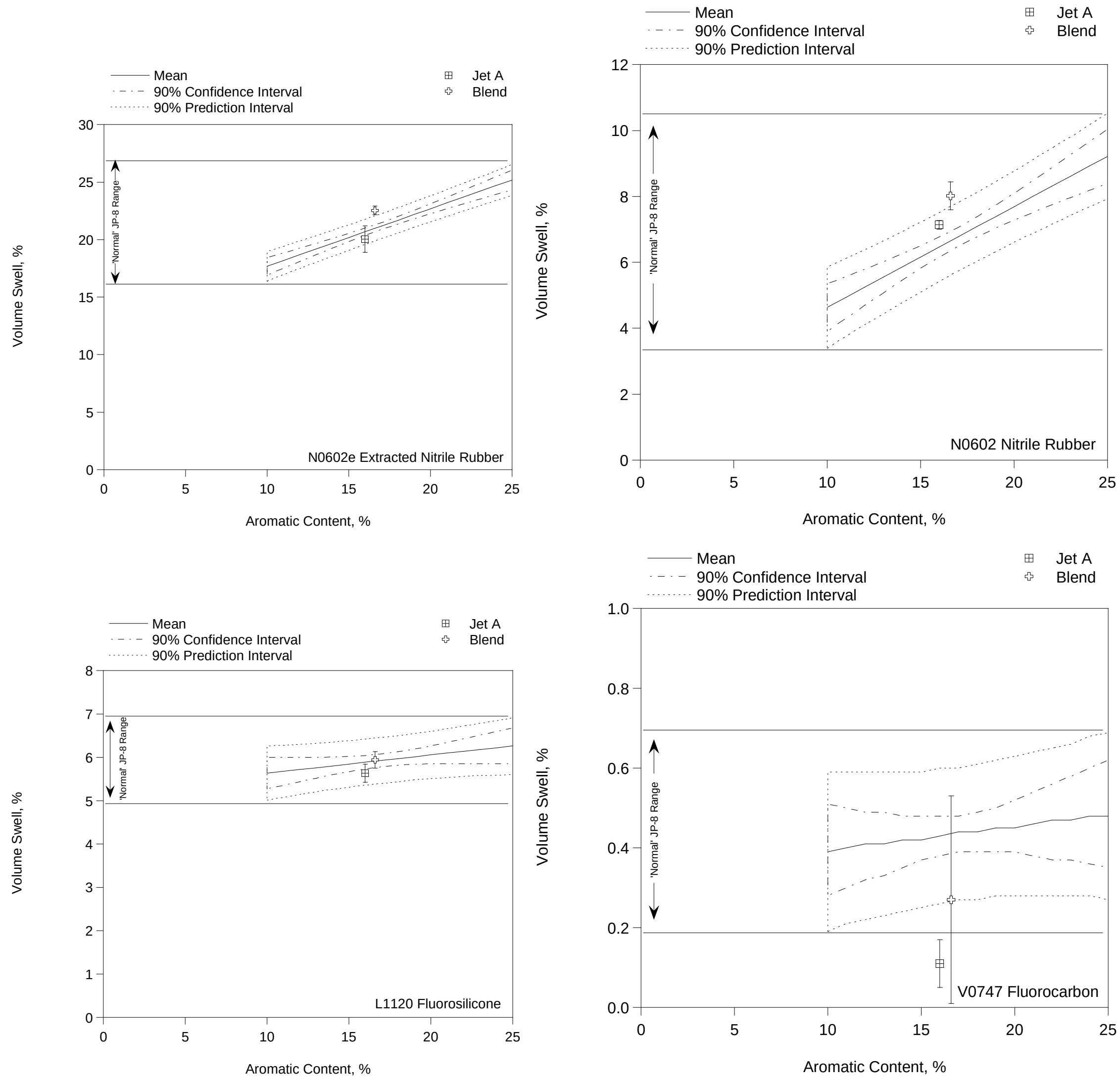


Figure 69. Volume swell and 90% confidence intervals of selected O-ring materials in the synthetic fuel blend and neat Jet A compared with the 90% prediction regions for JP-8.

Table 61. Average Polymer-Fuel Partition Coefficients (Kpf) of Major Fuel Class Fractions in Selected O-Rings Aged in the Synthetic Fuel Blend and Neat Jet A Compared to Average Values for JP-8

Material	Class	JP-8 90% Prediction Interval			Jet A	Fuel
	Fraction	LL	Mean	UL		Blend
N0602 & N0602e	Overall	0.170	0.224	0.280	0.203	0.205
	n,i-Alkanes	0.102	0.135	0.170	0.111	0.112
	Cyclo-alkanes	n.a.	n.a.	n.a.	0.137	0.140
	C3 Alkyl Benzenes	0.344	0.420	0.499	0.403	0.379
	Tetrahydronaphthalene	n.a.	n.a.	n.a.	0.505	0.507
	Naphthalene	0.854	1.099	1.343	1.093	1.002
	Naphthalenes	0.744	0.869	0.994	0.796	0.726
L1120	Overall	0.052	0.074	0.097	0.058	0.046
	n,i-Alkanes	0.047	0.063	0.080	0.046	0.038
	Cyclo-alkanes	n.a.	n.a.	n.a.	0.050	0.042
	C3 Alkyl Benzenes	0.087	0.121	0.156	0.103	0.084
	Tetrahydronaphthalene	n.a.	n.a.	n.a.	0.110	0.092
	Naphthalene	0.155	0.207	0.259	0.195	0.153
	Naphthalenes	0.113	0.152	0.191	0.124	0.092
V0747	Overall	0.001	0.009	0.016	0.007	0.004
	n,i-Alkanes	0.001	0.004	0.008	0.003	0.002
	Cyclo-alkanes	n.a.	n.a.	n.a.	0.002	0.001
	C3 Alkyl Benzenes	0.006	0.031	0.055	0.019	0.014
	Tetrahydronaphthalene	n.a.	n.a.	n.a.	0.018	0.016
	Naphthalene	0.000	0.076	0.172	0.052	0.040
	Naphthalenes	0.000	0.052	0.106	0.025	0.019

Index	Assignment
9-17	C9-C17 Normal Alkanes
A	Xylenes
B	Trimethylbenzene
C	Decalin
D	Tetrahydronaphthalene
E	Methyltetrahydronaphthalene
F	Methylnaphthalenes
G	Dimethylnaphthalenes

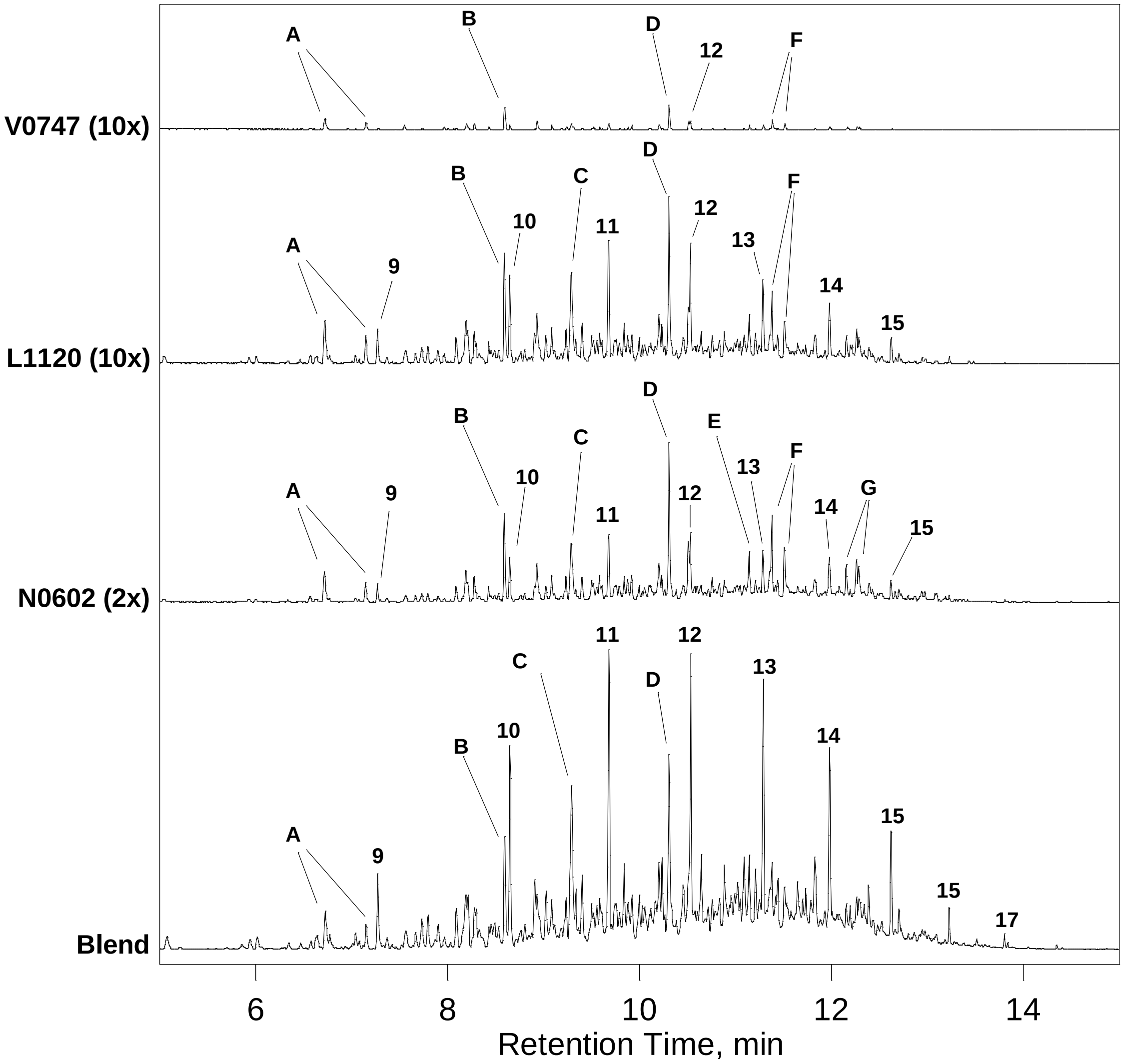


Figure 70. Example GC-MS chromatograms of similar volumes (approximately 1 L) of synthetic fuel blend and fuel components absorbed by elastomers (see Table 11 for Parker Identification Number). Primary compounds are identified. chromatograms scaled for comparison. Note: Peak assignments tentative based on NIST mass spectral library.

9.1.4 Summary of Jet Fuel Characterization

Testing and analyses were performed to provide preliminary guidance regarding the potential suitability for using a synthetic fuel produced from coal and biomass-derived feedstocks in aviation applications. The approach followed recommended protocols for evaluation and certification of synthetic fuels for commercial and military applications and included evaluation of fuel specification and limited Fit-For-Purpose (FFP) properties of the neat synthetic fuel and a blend with petroleum-derived aviation fuel. It was determined the neat synthetic fuel could not be used as a direct ‘drop-in’ aviation fuel as several properties did not conform to required commercial and military fuel specification requirements. However, it was determined the potential exists for using the synthetic fuel as a blending feedstock with petroleum-derived fuels.

A 20% by volume blend of the synthetic fuel was prepared with a ‘nominal’ Jet A fuel and evaluated for potential suitability for use. Efforts included characterizing the chemical composition of the fuel blend, performing ASTM fuel property specification testing, and evaluating select FFP properties (due to limited available volume of the synthetic fuel blend). The composition of the fuel blend was similar to typical aviation fuels, with a slight increase in higher molecular weight cycloparaffins and cycloaromatics. The fuel blend satisfied all physical property requirements in current commercial and military aviation fuel specifications. Limited FFP testing demonstrated that the fuel blend had operational characteristics consistent with typical aviation fuels. Overall, the results indicate the potential exists for using the synthetic fuel as a synthetic blending feedstock for aviation applications. However, evaluation of other FFP properties identified in aviation fuel certification processes must be performed to provide improved guidance regarding suitability for use. These results would allow determination of subsequent required testing (e.g., Turbine Hot Section, Component-Level, Engine Testing) for the synthetic fuel blend to ultimately be consider for OEM and FAA approval.

9.2 Characterization of Battelle-CTL-Derived Neat Synthetic Fuel for Use as a Diesel Fuel

The distillate from Intertek Run #2 was fractionated into a synthetic diesel fuel. A portion of the gasoline-boiling portion of the distillate was removed to increase its flash point above 52°C. This report summarizes the evaluation of the Battelle synthetic fuel for diesel engine applications. This evaluation focused on testing the specification properties, as well as limited fit-for-purpose (FFP) properties, of the Battelle synthetic diesel fuel. The tests were performed on the unblended synthetic liquid; no conventional petroleum diesel was present.

9.2.1 Relevant Diesel Fuel Specifications

The ASTM standard specification for D975 S15 diesel fuel was chosen as the basis for comparison. This diesel fuel is a general-purpose, middle distillate fuel for use in diesel engine applications requiring a fuel with a maximum of 15 ppm sulfur. It is especially suitable for use in applications with conditions of varying speed and load.

9.2.2 Adjustment of Fuel Volatility

Because the presence of light hydrocarbon can affect other requirements such as flash point, we decided to remove by distillation the light fraction that has boiling point below 160 °C. This light fraction corresponds to 4.5 percent volume of the liquid product. Figure 71 is the profile of simulated distillation of total product by ASTM method D2887 and distillation profile (by ASTM method D86) of the product after removing the fraction with boiling point below 160°C.

9.2.3 Analysis of Battelle CTL Synthetic Fuel

According to ASTM D975 S15 specification for No. 2 diesel fuel, twelve requirements must be met for an acceptable diesel fuel. Table 62 reports the results of analysis performed on the Battelle synthetic fuel and compares these results with the ASTM D975 S15 requirements.

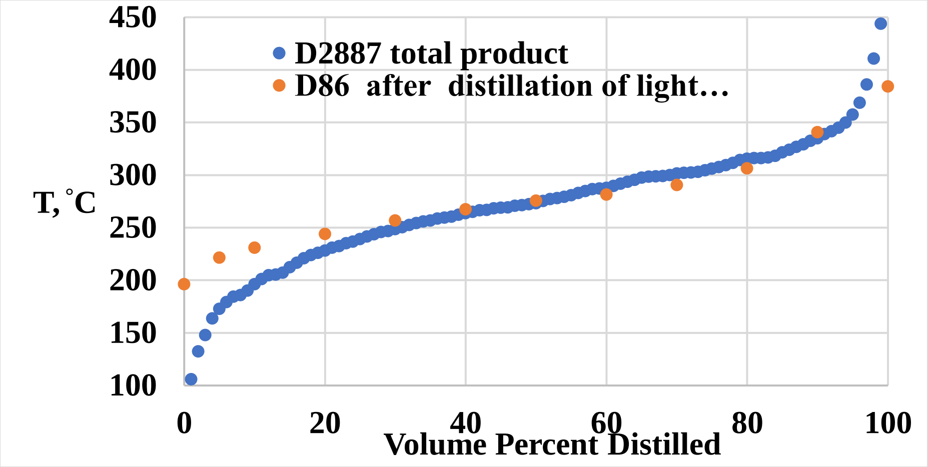


Figure 71. Profile of simulated distillation of total product (D2887 total product) and distillation of product after removing the fraction with boiling point below 160°C (D86 after distillation of light fraction).

Table 62. Comparison of Battelle Synthetic Diesel with ASTM Standard Specification for Diesel Fuel D975 S15

Specification	Method	Unit	ASTM D975 S15	Synthetic Diesel
Flash Point	D93	°C	>52 (for No. 2D)	80.5
Water and Sediment	D2709	% volume	≤0.05	0.05
Kinematic Viscosity at 40 °C	D445	mm^2/S	1.9 to 4.1 (No. 2D)	3.736
Distillation Temperature at 90% volume (T90)	D86	°C	282 to 338	340.5
Ash	D482	% mass	<0.01	<0.001
Sulfur	D2622	ppm (mass)	15	3.5
Copper strip corrosion rating	D130	rating number	<3	1a
Cetane No., engine test	D613		>40	
Derived cetane No., IQT	D6890			42.5
Aromatics	D1319	% volume	<35	18.4
Carbon residual	D542	% mass	<0.35 (No. 2D)	1.07
Lubricity at 60 °C	D6079	µm	<520	260
Conductivity	D2624	pS/m	>25	<1

9.2.4 Discussion

The synthetic fuel meets all the ASTM D975 requirements except for conductivity, carbon residual, and T90.

9.2.4.1 Conductivity

The conductivity of Battelle synthetic is below the D975 requirement of 25 pS/m. However, the conductivity can easily be increased though use of a conductivity additive.

9.2.4.2 Carbon Residual

The D975 requirement for carbon residue is 0.35 mass percent max according to ASTM D524. The ASTM D524 test method covers the determination of the amount of carbon residue left after evaporation and pyrolysis of an oil and it is intended to provide some indication of relative coke-forming propensity. The carbon residue of the Battelle synthetic fuel is 1.07 wt.% and therefore it does not meet the expectation. It is possible that further filtration of the Battelle Syncrude with a 0.2µm filter and/or blending with commercial diesel can drop the residual carbon to less than 0.35%.

9.2.4.3 Maximum T90 Temperature

The D975 requires the 90 percent volume recovered temperature (T90) to be 282-338°C. The T90 temperature for the Battelle synthetic fuel is 340.5 °C. which is 2.5 °C higher than the range allowed. A simple adjustment of the diesel by blending of commercial fuel or additional hydrocracking is projected to resolve this problem.

Alternatively, the carbon residual and T90 temperature requirements can be met by removing a heavy fraction from the fuel. For another similar synthetic fuel, we demonstrated that removing the fraction with boiling point above 337 °C eliminated the T90 temperature issue and also reduced the residual carbon concentration to 0.1 weight percent.

9.2.5 Additional Discussion of Battelle Synthetic Diesel Fuel Properties

In addition to the above requirements, several other analyses were performed.

9.2.5.1 Density

The density of the Battelle synthetic fuel is 0.890 kg/L. This relatively high density is a plus. Customers who normally buy fuel by volume (such as in gallons) will get more energy for their money. See also heat of combustion comment, below.

9.2.5.2 Heat of Combustion

The heat of combustion of the Battelle synthetic fuel is 44.9 MJ/kg. This relatively high heat of combustion is also a plus. Customers who buy fuel by weight will get more energy.

9.2.5.3 Molecular Structure Information Derived from GCxGC-MS

The GCxGC-MS data (see Table 63) show the synthetic fuel is comprised primarily of cycloparaffins (69.1%) and aromatics (19.4%). The concentrations of di-/tricycloparaffins of 50.7 wt. % are significantly higher than observed in typical diesel fuel 27 wt. % [C.A. Baldrich]. It is likely that the relatively high concentrations of di and tri-cycloparaffins are responsible for both the high fuel density and the high carbon residual. The concentration of di-/tri-cycloparaffins can be adjusted either by selective solvent extraction, by blending with commercial fuel or by selective hydrocracking of di-/tri-cycloparaffins.

Table 63. Hydrocarbon Type Analysis of Synthetic Fuel by GC x GC – MS

Compound class	Weight %
Aromatics	
Total Alkylbenzenes	1.15
Total Diaromatics	0.47
Total Cycloaromatics	7.33
Total (C_nH_{2n-10}) Aromatics	4.96
Total Other Multi-ring Cycloaromatics	5.48
Total Aromatics	19.40
Paraffins	
Total iso-Paraffins	1.05
Total n-Paraffins	10.22
Cycloparaffins	
Total Monocycloparaffins	7.59
Total Dicycloparaffins	25.44
Total Tricycloparaffins	25.35
Total Other Cycloparaffins	10.72
Total Cycloparaffins	69.10

9.2.5.4 Carbon-Hydrogen Mole Ratio

The carbon-hydrogen mole ratio of a petroleum diesel is usually about 1.8. For example, the base fuel used in the Diesel Emission Control Sulfur Effects program, which was intended to be representative of diesel fuels used in the U.S., had a carbon-hydrogen ratio of 1.85. The ASTM D5291 shows lower H/C mole ratio of 1.71 for Battelle synthetic fuel. This probably related to high concentration of di-/tri-cycloparaffins.

9.2.6 Summary of Diesel-Fuel Characterization

Battelle has successfully demonstrated that using a novel biomass-derived hydrogen donor under relatively mild process conditions, a high proportion of the mass of coal (more than 85 percent) can be made into a synthetic diesel fuel that has the potential to meet all ASTM specifications.

10.0 CTL PLANT DESIGN AND ECONOMIC ANALYSIS

10.1 Introduction

Based on data on solvent refining of coal published by Longanbach and Chauhan of Battelle in late 1970s [1], and confirmed by Battelle project team member Quantex, coal can be dissolved quickly (<10 minutes) at mild conditions (~400°C and 500 psi) with addition of only 0.3–0.5% hydrogen, by weight of coal, which increases the H/C molar ratio from about 0.80 to 0.86. In over 140 experiments at Battelle, it was proven that solvents can be engineered to alter the nature and quantities of the cyclic/aromatic species with desired hydrogen-donor properties. Based on the low hydrogen-addition requirements, it was demonstrated that as little as 10% of H-donor bio-solvent based on weight of coal is sufficient without requiring any gaseous H_2.

The selected bio-solvent is important. Depending on the specific bio-solvent, the viscosity and conversion of coal can be affected. A chosen bio-solvent mixure was selected by Battelle. The selection is identified as a proprietary mixture and is called BS-41A hereafter. It has the following properties:

- The system allows solubilization of >85% of the moisture- and ash-free (MAF) composition of coal in less than 10 minutes at 400°C (>90% has been observed with this particular material and reaction systems for the plant were designed to give >90%).
- All components of the mixture are available, having both large (>100 MMT/yr available production in the US) and being available for purchase on the open market.
- The mixture can be economically used in a syncrude production process.

Coal, biomaterials, coal tar distillate, and recycled distilled syncrude product are mixed together. The product is a material that is solvated coal, undissolved coal and coal ash as solids, and a heavy-oil product. The recipe which was used in the engineering evaluation is shown in Table 64 below.

Table 64. Laboratory Formulation Used as Basis for Design

Reaction #	Materials	Coal Ash %	Coal % Water	Coal grams	Coal Solvent grams	Bio-Solvent grams	Total Mass grams	Solvent to Coal Ratio	Solvent to MF Coal
140	Bituminous, CTD 02/16, BS-41A	7.69	9.28	88.34	241	27.38	356.72	3.0	3.3

The products from the reaction are a gas and a solid/liquid mixture. Residual coal (MAF basis) was found to be in the 5-15 percent range (85-95% conversion). In the shorter runs, conversion was not reduced significantly, but gas production (probably decaroboxylation of the solvents) was reduced.

The heavy-oil product and solids are separated to remove solids. Liquid recovery from this run was 89% of the total mass fed. Gas produced was estimated at 2-3% of the total material fed after compensating for water. The reactor produces gases which are primarily H_2, CH_4, H_2S, CO, and CO_2. The gas contained less than 2 percent of hydrocarbon vapors.

Six pilot runs were made at Quantex to produce materials for use. The liquid from the final run, #6B, produced material which was closest to the products from laboratory reactions. The Quantex 6B product was made with limited recycle, so the material was heavier in start-up coal tar distillate (CTD) than expected from a final product. Hence, density is higher and C/H ratio is lower. That product has been used for characterization, hydrotreating, and distillation to final fuel products. These products have been blended to produce a fuel which can be blended with Jet A or used as a diesel product. Because the reactors were not optimized for these runs lower conversions than measured in the laboratory were achieved. Because material balances for the Quantex runs were not able to be closed adequately (for example, gaseous products were not collected, so could not be analyzed or quantified), the laboratory runs were used for the modeling results rather than the Quantex runs. The Quantex evaporators were also found to be unable to give a 500°C cut for the final product, which was the then-desired end point.

Intertek was contracted with and conducted re-evaporation, hydrotreating, and final distillation (see Section 8). The testing at Intertek provided feasibility that the <500°C material which is produced can be successfully hydrotreated and used as a blending stock for Jet-A or used as diesel fuel.

Process and economic modeling is based on Quantex Run #6B, Intertek Phase 2, as represented by small-scale run numbers 139 and 140 for syncrude production. The hydrotreating modeling is not done rigorously; it was scaled from a prior bio-based hydrotreating model and was done only to the extent necessary to produce energy and hydrogen estimates for the hydrotreater. Hydrogen production was done similarly from DOE references ([19], [20]). Block modeling was done for the overall material balance of the hydrotreater.

10.2 Process Flow Diagram

A block diagram of the process is shown in Figure 72. The nine components of the process are listed below. The direct process train elements (100, 300-600, and H100-H102) have been tested. The processes that are support blocks have not been tested (e.g., tank storage, process heater, scrubber) in the pilot testing. All syncrude and hydrotreater blocks are discussed below.

The reacted solids are sent from hydrocyclones to a centrifuge for further heavy oil recovery. The liquids are sent to a multi-effect evaporator and are separated into a heavy oil and a syncrude. These will be referred to by these names in the rest of this report.

The syncrude fraction can be varied somewhat base on desired products. If optimized to fuel, the top cut would be split at about 500°C. If, however, the bottom cut was desired for production of polyol, the cut would be made at about 380°C. This represents about 7.1% less oil recovered (Table 45, extrapolated).

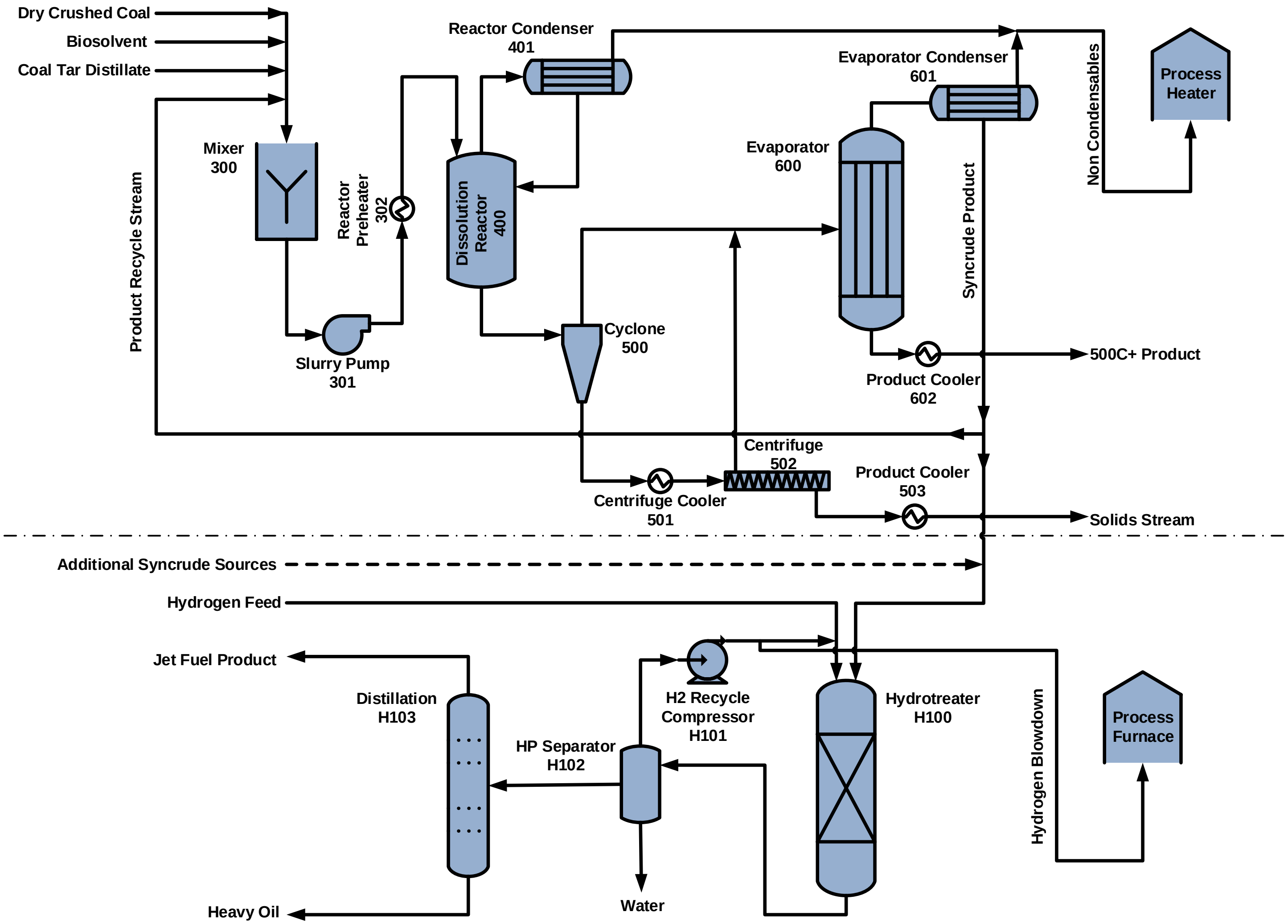


Figure 72. Simplified flow diagram for the Battelle CTL process

The process is discussed in greater detail below. The paragraphs are numbered to represent the figure and the list of processes above. Drawings for Systems 100-700 are provided in Appendix B.

100. Coal receipt and preparation. Coal is received, piled, ground, and dried to about 2% moisture and ground to -8 mesh. Water from drying is condensed and further used as cooling water.

200. Process Tank Farm. B41A components are received and placed in heated tanks. Coal tar distillate (initial feed or makeup) is received and placed in heated tanks.

300. Mixing of coal, bio-solvent, and coal tar distillate. Recycle material, the components of BS-41A, makeup CTD, and dry crushed coal are mixed. The slurry is preheated to a maximum of 150°C to remove any additional free water. The heated material is then fed to the digester.

400. Digestion. The feed material is processed at 400°C. The coal is digested at about 28.6 Bar and residence time of 10-30 minutes. The slurry is partially depressurized and the lights are condensed from the digester exhaust. The exhaust gases (sulfur-containing gases, methane, CO_2, and hydrogen are the principal constituents) are vented to the process furnace. Modeling was conducted to determine the size and number of reactors in process step 400 using the 10-minute and 30-minute residence time results. Batch reaction results were converted to continuous, stirred tank reactor (CSTR) assuming a first-order reaction rate. A series of four 3-reactor trains were defined to allow for three operating at a time and an extra train installed for maintenance to assure 90% operability.

500. Solid/liquid Separation. The hot, partially depressurized slurry is mixed with the evaporator heavy liquids and passed through two stages of hydrocyclones to remove the majority of solvent and light materials. The hydrocyclone system is operated with counter-current flow of >500°C product to recover most of the light material from the solids stream. A centrifuge is used to remove additional liquid from the cake. The liquid is passed to a fractionator and the solids are sent off-site for use.

600. Thermal separation. A vacuum evaporator is used to remove the low cut material. The highly volatile material is removed through the vacuum pump and also is fed to the process heater; lighter syncrude stream (ranges from 380 -500°C atmospheric boiling point [ABP]) is removed from the fractionator overhead, and a 500°C+ oil stream is removed from the bottoms of the evaporator. The digester exhaust is combined with syncrude evaporator lights from the vacuum pump and sent to the fired heater. The liquid light evaporator fraction is a syncrude. The heavy fraction is a separate product. The solids from the centrifuge and hydrocyclones will have all of the ash and unconverted coal as well as being rich

in heavy-oil.

700. Product liquids are stored in tanks for shipment.

800. Utilities. The waste gas (non-condensables from the evaporator vacuum pump exhaust plus the digester gases) are burned in a heat-recovery furnace. In this analysis it is assumed they all are burned at an atmospheric-pressure furnace. Options such as O_2 combustion at higher pressure were not evaluated. This furnace is used to provide all of the process heat energy during normal operating periods. The digester gas is supplemented by natural gas during start-up and other outages. The furnace will be fitted with a limestone scrubber to remove SO_2 from the product gases. Hot oil (modeled preference) or molten salt is circulated through the heater. A cooling tower will be required to cool most process streams. Air cooling is used in selected areas where the high temperatures might cause equipment stress if water were used. Electrical and other miscellaneous utilities (e.g. compressed gas for instruments) are provided.

Hydrotreater. The syncrude is hydrotreated in a trickle-bed, fixed bed hydrotreater with hydrogen and naphtha is taken off in the hydrotreater off-gas. The hydrotreated product can then be used as a diesel stream. Alternately, Jet-A boiling-range material can be distilled off and the remainder used as a heavy oil (diesel, other fuel purposes are what is envisioned in the cost evaluation section later). Off-gases (H_2, NH_3, H_2S, H_2O, CO_2, lights) are treated by PSA or Selexol-type process to recover H_2. The off-gases are incinerated for energy recovery.

Hydrotreating, hydrocracking, and distillation are expected to be conducted either in a refinery or as a larger-scale process where the products from several liquefaction sites are put together. It is also entirely feasible to run liquefaction at a scale similar to the Fischer-Tropsch units that are currently used to make synthetic paraffinic distillates such as synthetic paraffinic kerosene (SPK).

The elements of the hydrotreater system are as follows:

H100. Reaction. Crude is fed with hydrogen through a mixed-fluid reactor. In the early part of the reactor, oxygen, sulfur, and nitrogen are converted into vapor, H_2O, gaseous H_2S, and NH_3.

H101. Reforming and Compression. Hydrogen is reformed (preference) or received and is compressed to operating conditions.

H102. Gas/liquid separation. A high-pressure separator is used to separate the liquid and gas. The liquid flows to the distillation process. The gas is treated to remove sulfur, nitrogen, and water, and is mostly recycled. A bleed stream will be used to provide some economic benefit for process heating.

H103. Product distillation. The liquid products are distilled in a combination of atmospheric and vacuum distillation processes.

> H200. Product and receiving storage. Distilled products are held for shipment. The material would be received from the CTL "syncrude" process.
>
> H300. Utilities. Water treatment, cooling water treatment, waste water, are all provided for the hydrotreatment process.

Process steps H100-H103 were tested at laboratory/pre-pilot scale and reported in prior sections of this report. The other process steps are virtually identical to synthetic petroleum distillates (SPDs) being produced and are standard steps used in many other chemical processes so they were not tested in the laboratory-scale testing.

10.3 Coal Liquefaction Process Modeling

10.3.1 Coal Liquefaction Balance

To size equipment and utilities for the coal liquefaction process, a mass and energy balance was constructed using ChemCAD process modeling software. This allows for a flexible and consistent mass and energy balance that can be used to explore process configurations, estimate utility requirements, and provide preliminary sizing parameters for process equipment. The model in this case was largely based upon laboratory and pilot scale testing and analytical results to calculate product yields and understand thermodynamic behavior.

For this project, the feed rate of coal was assumed to be 1,000 MT per day (MT/day), and the model includes systems to dry the coal, digest the coal, remove residual solids, and evaporation to split the fuel product into two boiling-point fractions. At this scale, the hydrotreatment size is about 4,000 barrels (bbl) per day (BPD) for the lighter fraction. The scales of 2,000 MT/day coal (8,000 BPD fuel) and 8,000 MT/day coal with 32,000 BPD fuel are also evaluated to give the economics on a larger coal and regional hydrotreatment system. This scale was used to demonstrate that the process is economical at a smaller scale than the 17,000-19,000 MT/day of indirect liquefaction plants with less than 50,000 BPD production.

The water cooling system, heating loop, a scrubber for sulfur oxides (SOx), and preliminary work for CO_2 capture were also modeled.

A reformer model done for DOE/NETL by Molburg, et al [24] to evaluate H_2 generation costs was used. Their baseline model, adjusted for size and using a 3/1 steam/NG ratio, was used as the reformer for the Battelle CTL cases. The reformer was scaled to 2011 costs using Ref [21] data.

At 90% on-line/year, 90% coal conversion, Table 65 shows the annual flows of syncrude inputs, hydrotreating inputs, and waste products.

Table 65. Syncrude Material Balance for 1,000 MT/Day Coal, 90% Conversion, 90% On-Stream

Item	Quantity	Units
Coal	328,500	MT/yr
Bio-solvent	118,259	MT/yr
Koppers Coal Tar Distillate	32,850	MT/yr
Water	25,363	MT/yr
Limestone	7,745	MT/yr
Digester Gas and Evaporator Vapor used for process heat	38,773	MT/yr
Elect Energy Usage	47,867	MWH/yr
Natural Gas Energy Usage	77,606,000	MJoules/yr
Fuel use locomotive, endloader, dump truck 43.5 gal/hr, daylight [22]	4,530	bbl /yr
Waste Disposal	25,363	MT/yr
CO_2 Emissions (Flared Digester Gas, Natural Gas, and Liquid Fuel Use)	227,690	MT/yr

The process operates on these process inputs and produces waste products and the following estimated quantities of products and byproduct materials as shown in Table 66. The background on selection of yields, gases, etc., are provided in the ChemCAD modeling section.

Table 66. Syncrude and Products at 1,000 MT/Day Coal, 380°C Split, 90% On-Stream

Item	Quantity	Units	Coal Ratios
Centrifuge Solids (45% liquid organic content)	107,602	MT/yr	0.4327 MT/MT coal
Heavy Oil from Evaporator	71,862	MT/yr	0.219 MT/MT coal
Syncrude quantity, 1.05 SG	1,394,836(a)	bbl /yr	4.25 bbl/MT coal

(a) At 500°C, production of syncrude could be as high as 1,501,000 bbl/yr (4.57 bbl/MT)

10.3.2 Hydrotreating and Hydrotreating Balance

The hydrotreater balance is performed based upon data obtained from operations at the pilot scale and design data for a similar hydrotreater plus reformer. These operations yielded a hydrotreater carbon balance of 87 percent; the other 13 percent is assumed to be contained in the emissions and includes sulfur as H_2S, nitrogen as NH_3 and oxygen as H_2O. Reformer product and CO_2 yields are treated in Tables 67 and 68.

The hydrogen/carbon balance is based on taking the total H/C in the syncrude from 1.22 to a ratio of 1.86 which is typical of Jet-A products (our Jet products are slightly lower in H_2 at 1.7 – 1.8 for Jet A distillate, so this H/C gives conservative H_2 usage). Burning the hydrotreater tail gas plus natural gas is used for energy to operate the process. Removal of heteroatoms plus hydrogenation will require 2.712 scf/ bbl minimum; hydrogen requirements for the hydrotreating assume 120% of this value as fresh H_2. Because Intertek uses single-pass hydrogen in their hydrotreater and because we used a 1.05 H/C crude (from Quantex Run #6B) at Intertek, this ratio could not be verified at the pre-pilot level.

Using the syncrude balance data discussed above gives the input data in Table 67. An efficiency of 70% of theoretical is assumed for converting natural gas to H_2 in the reformer. This is consistent with references [19] and [20].

Table 67. Hydrotreater Material Balance at 4,000 BPD and 90% On-Stream

Item	Quantity	Units
Hydrogen	10,588	MT/yr
Water	60,210	MT/yr
Limestone	4,178	MT/yr
Catalyst Replacement/Rejuven	193	MT/yr
Labor, Hours 28 people scaled	56,000	hrs/yr
Eng & Sup, Hours (5 people)	10,000	hrs/yr
Waste Disposal	14,371	MT/yr
CO_2 Emissions	153,819	MT/yr
Elect Energy Usage	91,196	MWH/yr
Natural Gas for Shift and Heating	31,785	MT/yr
Reformer /Hydrotreater Tailgas Credit for Shift and Heating	26,943,132	MJ/yr
Switch Engine Fueling	1,512	bbl/yr

The products from the hydrotreater are listed in Table 68.

Table 68. Hydrotreater Products

Item	Quantity	Units
Ammonium Sulfate (10% in 90% water)	2,570	MTyr
Fuel yield (jet plus diesel)	55,521,700	gal/yr

The fuel yield is about 4.02 bbl/MT coal. The fuel split appears to be about 10% naphtha used as fuel, 60% jet, and 30% diesel from the hydrotreating of the syncrude. The weight yield of syncrude into hydrotreated and saleable product is estimated at 80.3%.

10.3.3 Options for the Heavy-Oil Product

Several applications are possible for the heavy-oil product. The economic approaches in order of preference are:

- Use as a feed for a high-value specialty product. A coal-to-polyol process is used here. Other uses are coker-feeds for high-value carbon coal tar distillate, as heavy fuel oil.

- Use as a high-value product such as an organic binder (binder pitch) for which both the solid by-product and the heavy-oil fraction can be used.
- Use as a direct fuel.
- Upgrade as a motor fuel, or as fuel oil.

The options used in the cost models were that of direct sale as a binder material and producing a specialty chemical from a significant fraction coming from a 1,000 tonne/day coal plant. In the former application, the world market is so large that sale was not expected to modify the world market. However, in the specialty chemical market, there is good growth but the current world capacity would be in the range of 6 million MT/year. Using all of the heavy oil from one plant would produce about 166,000 MT/year. Based on the considerations of flooding the market and depressing the price, the estimate uses about 3% of the total world market for production regardless of scale for the process. This application is proprietary and is not described in the following ChemCAD modeling section.

10.3.4 ChemCAD Modeling

10.3.4.1 Assumptions

The mass and energy balance generated in ChemCAD is based on a number of assumptions that were derived from laboratory testing and engineering judgement. These assumptions are outlined in the following based on whether they applied to the whole process or were specific to the liquefaction step or scrubbing step. Where appropriate, references are cited to support the assumptions.

10.3.4.1.1 Overall Assumptions

In order to estimate vapor liquid equilibria throughout the process, an appropriate thermodynamic model must be selected. For this model, Peng Robinson was selected as it is commonly applied for general hydrocarbon species at moderate to high pressures. Additional global assumptions are listed in Table 69. Pump efficiencies are taken to be 60%, while compressor efficiencies are taken to be 50%. Cooling water is assumed to be available at 30°C, and is limited to a heat exchanger outlet temperature of 40°C to prevent excessive scaling. In all heat exchangers, the minimum approach temperature is taken to be 10°C, although not all exchangers necessarily assume this aggressive of an approach. Liquid stream pressure drops through exchangers are taken to be on the order of 0.35 bar (~5 psi).

Table 69. Overall Assumptions Made in the ChemCAD Process Model

Overall Process Assumptions	
Vapor Liquid Equilibrium Model	Peng Robinson
Pump Efficiencies	60%
Blower/Compressor Efficiencies	50%
Cooling Water Inlet Temperature/Max Outlet Temperature	30°C/40°C
Minimum Heat Exchanger Approach Temperature	10°C
Liquid Stream Heat Exchanger Pressure Drops	0.35 bar (~5psi)

4.2.2.1.2 Coal Liquefaction Assumptions

Key mass balance assumptions for the coal liquefaction operation are provided in Table 70, and are based upon laboratory and pilot testing results. The coal tar distillate and bio-solvent feeds as a mass fraction of dry coal feed are about 10% and 40%, respectively. The centrifuge cake is taken to be 50% solids. Baseline coal conversion is assumed to be 90% of the organic component, although this conversion is changed in the model based upon the content and composition of the proprietary bio-solvent. Non-condensable gases from the reactor are taken to be about 7% by weight of the dry feed coal, and the recycle rates are adjusted to provide 3 mass units of liquid per mass unit of dry coal feed.

Table 70. Mass Balance Assumptions Made in the Coal Liquefaction Process

Coal Liquefaction Mass Balance Assumptions	Model
Coal Tar Distillate Makeup as Mass Percent of Dry Coal Feed	10%
Bio-solvent Feed as Mass Percent of Dry Coal Feed	40%
Centrifuge Cake Solids Content by Mass	50%
Baseline Conversion of Coal Organics	90%
Noncondensable Gas Generation as Mass Percent of Dry Coal Feed	7%
Mass Ratio of Liquid Recycle to Dry Coal Feed	3:1

A few assumptions in the coal liquefaction step had to be made regarding the composition and properties of certain streams. For coal tar distillate, a number of surrogate compounds were selected, and their mass ratios assumed based on GC-MS data in literature sources[29]. The selected model compounds and their relative mass concentration in coal tar distillate is presented in Table 71. The organic portion of coal was modeled in ChemCAD as ovalene, which structure is shown in Figure 73 and was a user-added compound in ChemCAD built by Joback functional groups. The coal ash was modeled as silicon dioxide only, and the feed coal was taken to be 5% moisture, 9.5% ash, and the balance organic material. A distillation curve for the liquefaction product was created in laboratory testing and is shown Table 72. The final liquefaction product in the ChemCAD model was adjusted to match this distillation curve based upon model component boiling points.

To understand the heat of reaction for coal liquefaction, a number of surrogate compound reactions were run within the model. The first two reactions account for the processes of dehydrogenation and decarboxylation within the bio-solvent. The actual depolymerization of the coal was assumed to be cleavage of a phenolic ether. In this case, the reaction was simplified to cleavage of diphenyl ether into phenol and benzene. In this manner, the overall liquefaction reaction was estimated to be slightly endothermic, which is consistent with other depolymerization reactions. The evaporator was operated to obtain two products with a cut at approximately 500°C (later revised downward to 380°C) to allow for polyol processing. The 500°C (380°C+) product was assumed to be usable as a heat transfer fluid to provide heat in the process; heating the reactors, influent, and used to dry the incoming coal. This assumption will need validation, as the material will need to be recycled approximately 12 times through a fired heater without substantial degradation.

Table 71. Model Compounds and Relative Mass Concentrations of Each Used to Represent Coal Tar Distillate

Model Compound	Relative Mass Concentration in Coal Tar Distillate
3-Methylphenol	14.8%
Methyl Ethyl Phenol	14.8%
1-Tridecene	4.9%
N-Tetradecane	9.1%
Tetramethyl Benzene	2.3%
Ethyl Naphthalene	17.0%
Methyl Naphthalene	17.0%
Phenyl Naphthalene	17.0%
Biphenyl	1.5%
Cyclohexylbenzene	1.6%

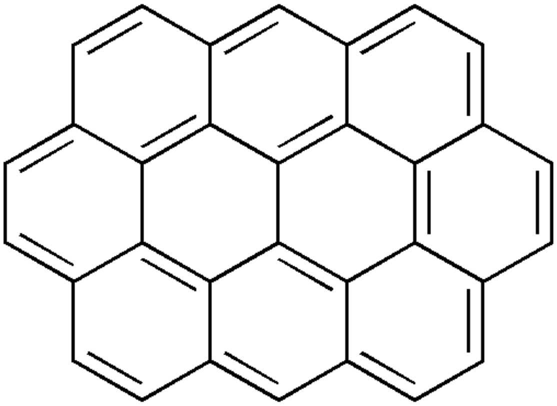


Figure 73: Structure of the ovalene molecule, which was used to represent the organic portion of coal in the ChemCAD model.

Table 72. Distillation Curve of Coal Liquefaction Product

Distillation Fraction	Lab Results Weight Percent of Liquefaction Product	Model Matched Weight Percent of Liquefaction Product
< 350°C	24.7%	24.7%
350 - 400°C	24.1%	24.1%
400 - 450°C	15.0%	15.0%
450 - 500°C	14.7%	14.7%
500°C +	21.5%	21.5%

10.3.4.1.3 SOx Scrubbing Assumptions

The SOx scrubber in this model was assumed to be a limestone forced oxidation (LSFO) scrubber, and key mass balance parameters are shown in Table 73. The liquid to gas ratio was assumed to be 70 gallons per actual cubic foot of scrubbed gas effluent, and the oxygen required for sulfite oxidation was taken to be 3:1 O:SO_2 removed. The entrance and exit temperatures were important for energy balances as well as the water balance to account for water vapor leaving the scrubber. SOx was estimated based on the analysis of gases from laboratory testing. Removal was taken to be 95%. Methane combustion was assumed to be 99.5% since emissions of greenhouse gases are tracked in this project. The excess limestone is assumed to be 1.05, and the gypsum cake moisture is taken to be 50%. This moisture does not account for the waters of hydration for gypsum, and in the model 'gypsum' is taken to be $CaSO_4 \bullet 2H_2O$. It was assumed that the air sparge for oxidation would require 15 psi, and the pressure drop of the lime slurry going up the column and through the nozzles was 60 psi.

Table 73. Key SOx Scrubbing Mass Balance Assumptions Used in the ChemCAD Model

SO_x Scrubbing Mass Balance Assumptions	
Liquid to Gas Ratio	70 gallons/actual cubic foot [23]
Oxygen Requirement for Sulfite Oxidation, O:SO_2	3:1 [24]
Entrance Temperature	150°C [24]
Exit Temperature	54°C [24]
SO_x Removal	95% [24]
Methane Combustion Efficiency	99.5%
Limestone Stoichiometric Excess	1.05 [24]
Gypsum Cake Moisture Content	50%

The non-condensable gas composition was measured in the lab by an HP online GC and by GC-MS. The gas entering the Gibbs reactor has the measured composition shown in Table 74.

Table 74. Non-Condensable Gas Composition used in the SOx Scrubber Model

Component	Mole Fraction
Hydrogen	0.23
Carbon Dioxide	0.13
Methane	0.3
Propane	0.05
Ethane	0.11
Carbon Monoxide	0.07
Ethylene	0.01
Propylene	0.01
N-Butane	0.01
I-Pentane	0.002
N-Pentane	0.005
N-Hexane	0.01
Hydrogen Sulfide	0.06
Higher Heating Value	34,480 kJ/kg
Lower Heating Value	31,350 kJ/kg

10.3.4.1.2 CO_2 Scrubbing Assumptions

Key CO_2 scrubbing mass balance assumptions are shown below in Table 75. A monoethanol amine (MEA) scrubbing solution at 30% by weight in water is assumed for carbon capture, and the target is capture of 85% or more of the CO_2 generated. The amine regeneration column is limited to a reboiler temperature of 125°C, and aggressive heat integration is used for cooling and heating of the MEA within the recycle loop. The captured CO_2 is compressed to 2,200 psig, and the compression ratio in each compressor stage is limited to prevent compressor stage outlet temperatures above 250°C. One key assumption in the carbon capture modeling is that there are no heat stable salts formed, which would require an MEA reclaimer that uses caustic and temperature to recover MEA from the salts.

Table 75. CO_2 Scrubbing Model Mass Balance Assumptions

CO_2 Scrubbing Mass Balance Assumptions	
Monoethanol Amine Solution Concentration	30 wt%
Amine Regeneration Reboiler Temperature	125°C
Maximum Compressor Outlet Temperature	250°C
CO_2 Compressor Target Outlet Pressure	2,200 psig
Target CO_2 Capture Efficiency	> 85%

10.3.4.1.3 Hydrotreatment Assumptions

Key assumptions in the simplified hydrotreatment model are shown in Table 76. Hydrogen consumption was calculated based upon C/H analysis of the liquid before and after hydrotreatment, while yields of methane, H_2S, methane, and C2-C6 hydrocarbons were taken from analyses during the hydrotreatment runs. The reaction temperatures and pressures were similarly taken from the hydrotreatment runs. Hydrogen recovery through the pressure swing adsorber for hydrogen purification was assumed to be 80%, with the balance of the hydrogen and contaminants recovered in a blowdown stream used for fuel gas.

Table 76. Simplified Hydrotreatment Model Mass Balance Assumptions

Hydrotreatment Mass Balance Assumptions	
Hydrogen Consumption	2,725 SCF/bbl
Mass yield of H_2S	0.09%
Mass yield of Methane	0.09%
Mass yield of C2-C6	0.76%
Stage 1 Reaction Temperature	380°C
Stage 2 Reaction Temperature	240°C
Minimum Hydrogen Pressure	1300 psig
Pressure Swing Adsorption (PSA) Hydrogen Recovery	80%

10.3.4.2 Model Narrative

10.3.4.2.1 Base Case

Figure 74 shows a part of the ChemCAD flowsheet that covers the feed portion of the process. Moist, crushed coal is fed in stream 1, where it is then heated in HX 42 by 500°C+ product. Evaporated water is removed as stream 35 from a flash drum. The dry coal is mixed with coal tar distillate from stream 2 and bio-solvent in stream 4, before being mixed with recycle material in mixer number 36. This combined stream is pumped to 405 psig for feed to the reactors by pump 18. Figure 75 shows the reactor portion of the flowsheet. The combined feed enters heat exchanger 10, where it is heated to 400°C by heated 500°C+ product. This then enters Reactor #3, which is a stoichiometric reactor used to model dehydrogenation of the bio-solvent. This enters a feed-forward controller which provides inputs to a separate heat of reaction calculation. The next reactor is a stoichiometric reactor to model decarboxylation of the bio-solvent, and the feed forward controller 20 controls the coal conversion rate based upon the current state of the bio-solvent. Reactor #4 is the digester, where ovalene in the simulated coal is converted into hydrocarbon pseudocomponents with specific boiling points to match the distillation curve of the liquefaction product. This distillation curve matching is done in an external excel spreadsheet and fed into the stoichiometric reactor by data map functionality.

Controllers 17 and 23 feed forward heat duties to heat exchangers 11 and 24 to model the heat of reaction. The dehydrogenation and decarboxylation reactors are run isothermally, and the heat duty required to maintain constant temperature is fed into the heat exchangers. A separate model reaction of diphenyl ether converting to phenol and benzene is used to predict the heat of reaction of coal depolymerization. The overall heat of reaction is endothermic, and heat exchanger 25 adds heat from 500°C+ product to maintain reactor temperature at 400°C. Flash drum 5 removes any vapors from the reactor headspace at 405 psig and 400°C. This vapor is partially condensed with cooled 500°C+ product, with condensate reheated in heat exchanger 90 and returned to the reactor. A second condenser cools the vapor to 50°C, and this condensate is sent to the evaporator. Non-condensable gas is removed from the process and used as fuel in the fired heater.

Liquid from the reactors is let down in pressure through valve 9 before entering a flash drum (Figure 76). A train of hydrocyclones is then used to wash and concentrate the solids material by washing the solids with evaporator bottoms product. The flash liquid is mixed with solids product from the second-stage hydrocyclone in order to recover light material. The washed liquid and solids are then pumped to a second-stage hydrocyclone, where they are washed with evaporator heavy product (>500°C). The solids proceed to the centrifuge, while the liquid proceeds to the first-stage hydrocyclone. The solids are cooled to 75°C with water in heat exchanger 26. In this separation/washing scheme, light material is reduced in the centrifuge solids, making them better for binder applications. As a benefit, the product syncrude is also increased.

The hydrocyclone solids are then centrifuged. Solids leave the centrifuge at about 50% solids, and the centrate is mixed with the liquid from the hydrocyclone second stage. At divider 38, a recycle stream is removed to be taken back to the front of the process. The balance of material is mixed with light condensate from the reactor, lights from flash drum 64, and lights from the recycle stream. This is then fed through a valve to an evaporator operating at roughly 5.85 psia. Heat exchanger 30 preheats the feed at a 15°C approach temperature, and the evaporator operates at 370°C. After the preheater, the distillate is cooled with water in exchanger 31. Uncondensed vapors and gases are sent to the syncrude process furnace.

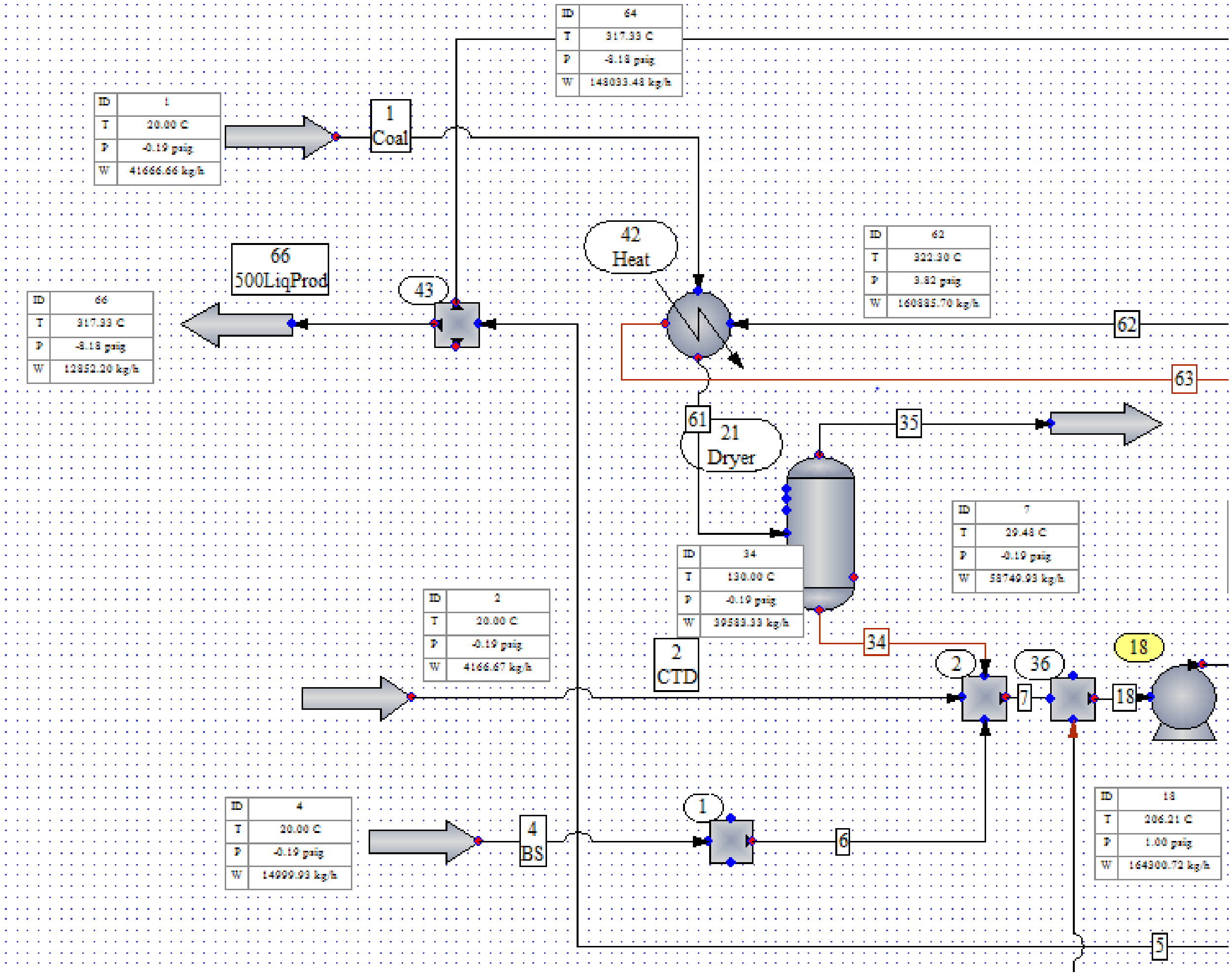


Figure 74. ChemCAD flowsheet for the feed portion of the coal liquefaction process.

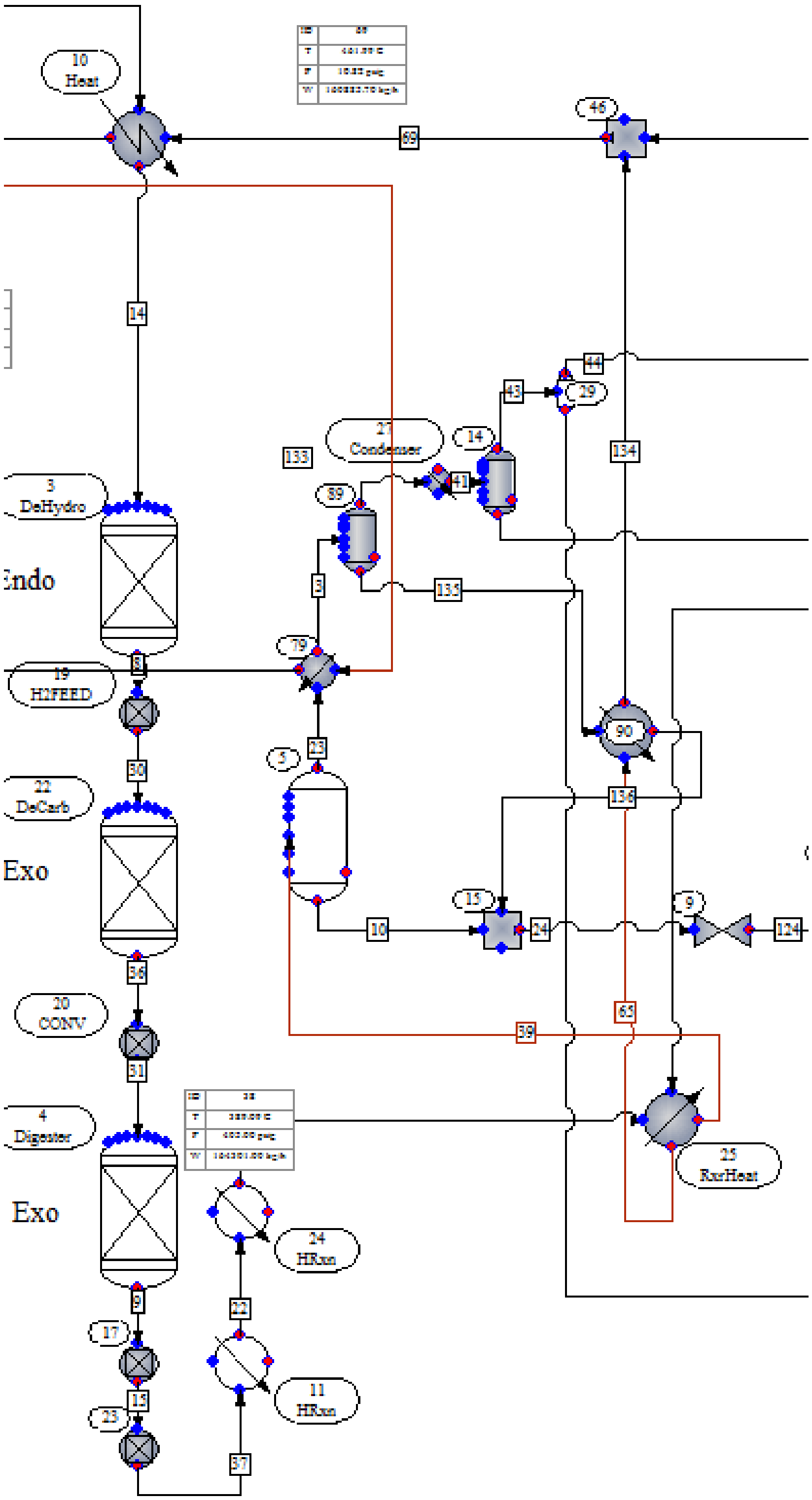


Figure 75. Flowsheet for the liquefaction reactor portion of the coal liquefaction process.

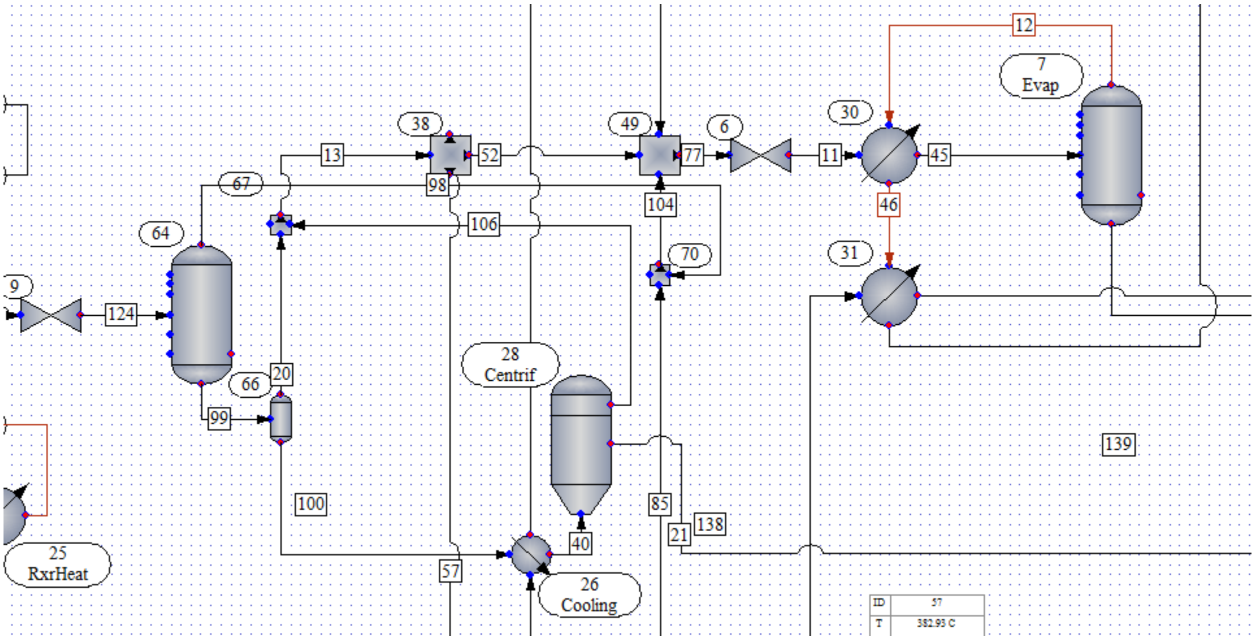


Figure 76. Solids handling and evaporator portion of the coal liquefaction flowsheet.

Figure 77 provides the flowsheets for the product handling. Distillate oil from the evaporator is in stream 47, and enters a knockout pot. Lights from here are removed by the evaporator vacuum pump, and later used as fuel in the fired heater. Bottoms of the knockout pot are the crude fuel product, and are pumped out of the process. A portion of this stream is recycled back to the front of the process. The heavy oil from the evaporator enters feed forward controller 44, which controls how much of the 500°C+ product is removed from the heating loop. Pump 34 then delivers the heavy product to the fired heater process. Solids are cooled with water in heat exchanger 13, then removed from the process.

500°C+ liquid from the process is fed into the heating process (Figure 78), where it is mixed with recycle heating fluid, then pumped into fired heater 12. This heater is run on non-condensable gas from the process, with natural gas makeup as required. It heats the heavy oil to 475°C, and the heavy oil is used to heat the reactors, preheat the feed, and dry the feed coal. As mentioned previously, the product is used as both a washing and a heat-transfer oil so it is recycled approximately 12 times before it is removed from the system.

The recycle system, not pictured, mixes the two recycle streams and flashes them, with lights returning to the evaporator. It is then pumped to the front of the process. The cooling water system is not shown, and cools the water to 30°C in a cooling tower before pumping it to the required heat exchangers.

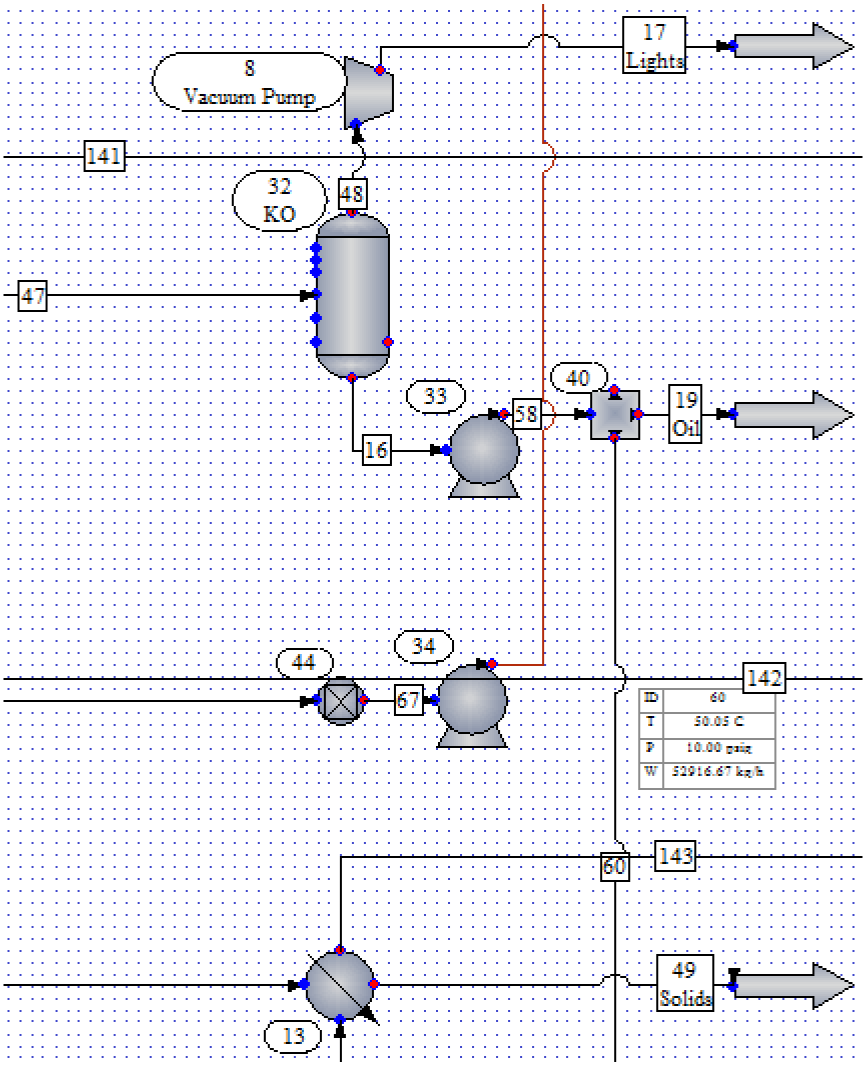


Figure 77. Products flowsheet from the coal liquefaction process.

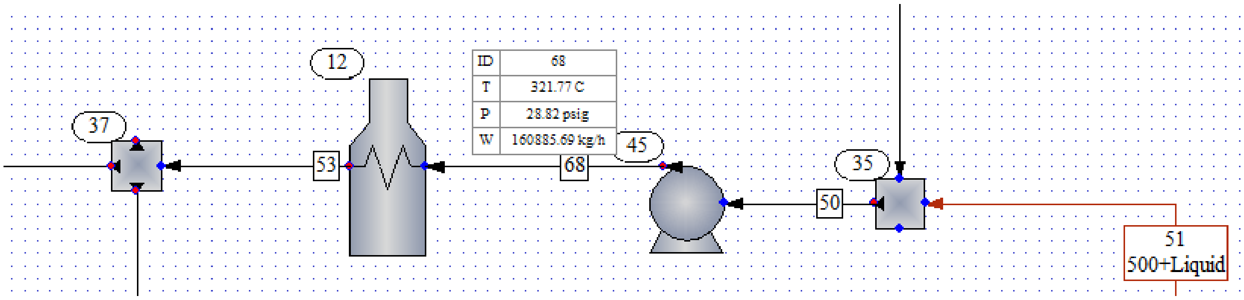


Figure 78. Fired heater flowsheet from the coal liquefaction process.

The SOx scrubbing system is shown in Figure 79. Feeds to the process include non-condensable gas, combustion air, natural gas, and air for the limestone forced oxidation scrubber. The rate of non-condensable gas feed is equivalent to that produced from the reactors and evaporator in the process, and the composition is as shown Table 70 the assumptions section. Component separator 60 on the NC gas stream bypasses 0.005 mole percent of the methane to enforce the 99.5% methane conversion assumption. Reactor #61 is a Gibbs reactor that simulates the fired heater in the process. Air is added in excess to provide an exit temperature of about 900°C, and the Gibbs reactor automatically calculates the formation of SOx gases in the combustion reaction. Heat exchanger 65 represents the demands of the coal liquefaction process, and air cooler 48 reduces the temperature to about 140°C. Feed forward controller 50 controls the amount of limestone added to the scrubber and controller 63 the amount of air added for sulfite oxidation, both based upon the levels of SOx in the stream. Air for sulfite oxidation is fed in stream 91 and compressed to 15 psig in compressor 62.

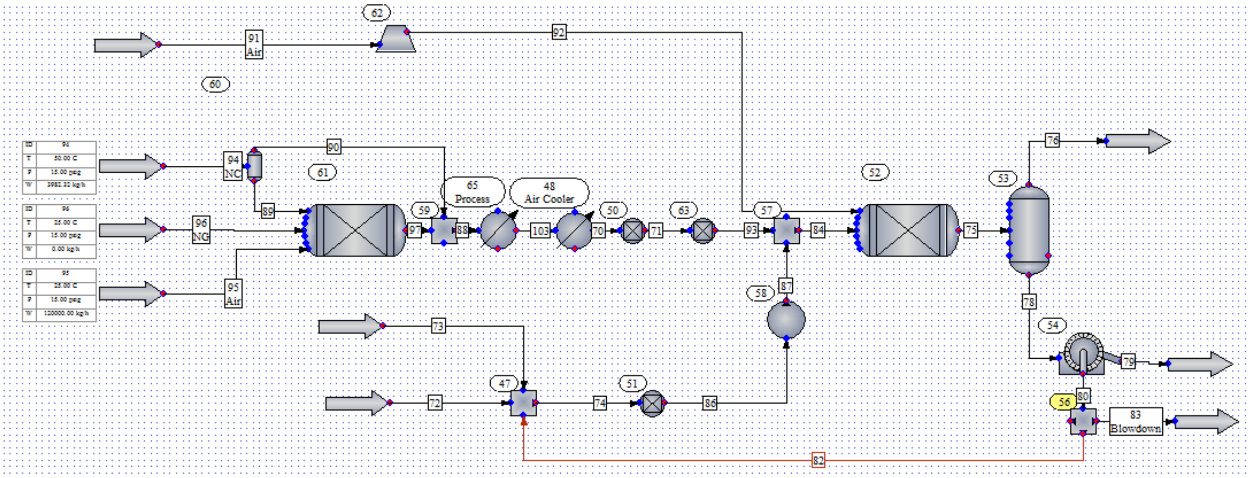


Figure 79. SOx scrubbing flowsheet from the ChemCAD model.

The scrubber is modeled by Reactor #52, which is a stoichiometric reactor performing three reactions at set conversions. The reactions are shown below:

$$SO_2 + CaCO_3 + 0.5H_2O = CaSO_3{\bullet}0.5H_2O + CO_2$$
$$SO_3 + CaCO_3 + 2H_2O = CaSO_4{\bullet}2H_2O + CO_2$$
$$CaSO_3{\bullet}0.5H_2O + 0.5O_2 + 1.5H_2O = CaSO_4{\bullet}2H_2O$$

This is absorption of SO_2 and SO_3 by conversion to calcium sulfite and calcium sulfate, respectively, and then oxidation of calcium sulfite to calcium sulfate. Note that this reaction leads to liberation of CO_2. Leaving this reactor, the stream is then flashed at 54°C, with liquid going to a filter to remove the precipitate gypsum. Filtrate enters a divider that provides a blowdown stream if needed. The recycle is then mixed with makeup water and limestone, and controller 51 maintains water levels in the recycle. Pump 58 pumps the liquid up the column and through the nozzles.

10.3.4.2.2 Other Cases

Several other process flow schematics were also tested. One notable case was changing the recycle stream to be composed entirely of syncrude product, rather than split 50:50 between product and centrate liquid. This case could have impacts on product quality that are not described by the ChemCAD model, but energy consumption is increased slightly due to increased flow through the evaporator. A second case is shown in Figure 80, and involved flowing through the evaporator and centrifuge in parallel rather than in series. Here, the top stream from the cyclone goes to the evaporator, and bottoms from the evaporator are mixed with bottoms from the cyclone. This mixed stream is flashed, with lights recycled to the evaporator, and the balance being cooled and fed to the centrifuge. This layout was intended to improve energy efficiency, as the centrifuge feed for the selected centrifuge needs to be at low temperatures to avoid seal damage. Additionally, the total flow rate into the evaporator is reduced, lowering energy and capital demands. However, there are tradeoffs in reduced syncrude product recovery, and light components entering the hot oil system.

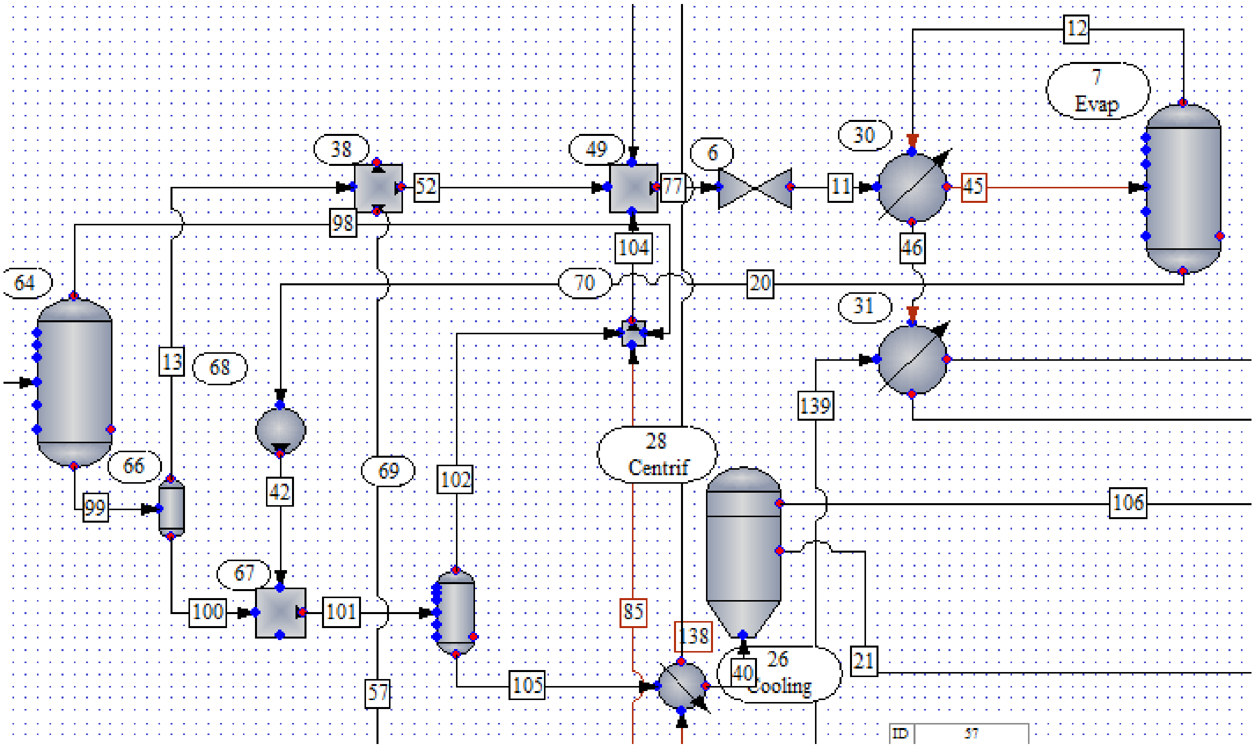


Figure 80. Flowsheet describing the case of the centrifuge and evaporator running in parallel rather than in series.

10.3.4.2.3 Amine Scrubbing

Figure 81 provides the ChemCAD flowsheet for the amine scrubbing process model. The fired heater is represented by Gibbs Reactor #61, which combusts non-condensable gas and natural gas to provide heat to the process. The heat demand from the process is accounted for in heat exchanger 65. There is still significant energy in this stream, so it is used to heat loaded MEA going into the regenerator, before being cooled in heat exchanger 66. This cools the flue gas prior to entering the scrubber. Component separator 63 removes trace compounds in the gas stream that interfered with convergence of the scrubbing column, and is not a part of the actual process. Flash drum 67 removes water from the cooled flue gas before the gas enters scrubber column 68. Flue gas flows counter flow to the MEA solution, which absorbs the CO_2. Cleaned flue gas exits in stream 99 with about 85% of the CO_2 removed.

The loaded MEA from the scrubber is pumped through a first heat exchanger that recovers heat from the regenerated MEA. The second heat exchanger uses the flue gas to heat the stream to about 118°C before entering the regenerator. In the regenerator, CO_2 is released from the MEA by heating. A condenser recovers volatile MEA and water, and refluxes it to the column. The released CO_2 is fed to a compressor. Regenerated MEA is pumped through a heat recovery exchanger, and mixed with some of the condensed MEA from the overhead condenser. Feed forward controller 73 maintains the mass of MEA within the recirculation loop, accounting for any MEA loss through volatilization or carryout. The stream is then mixed with makeup MEA and water. Water content in the recirculation loop is controlled by feedback controller 54, which feeds water in stream 98 to maintain solution concentrations. This stream is then pumped back to the scrubber column.

Figure 82 shows the CO_2 compression portion of the ChemCAD flowsheet. CO_2 from the regenerator is compressed to 2,200 psig in four stages. There is interstage cooling and a knockout pot for each stage to remove water. The compression ratio in each stage is adjusted to keep the compressor stage exit pressure below 250°C.

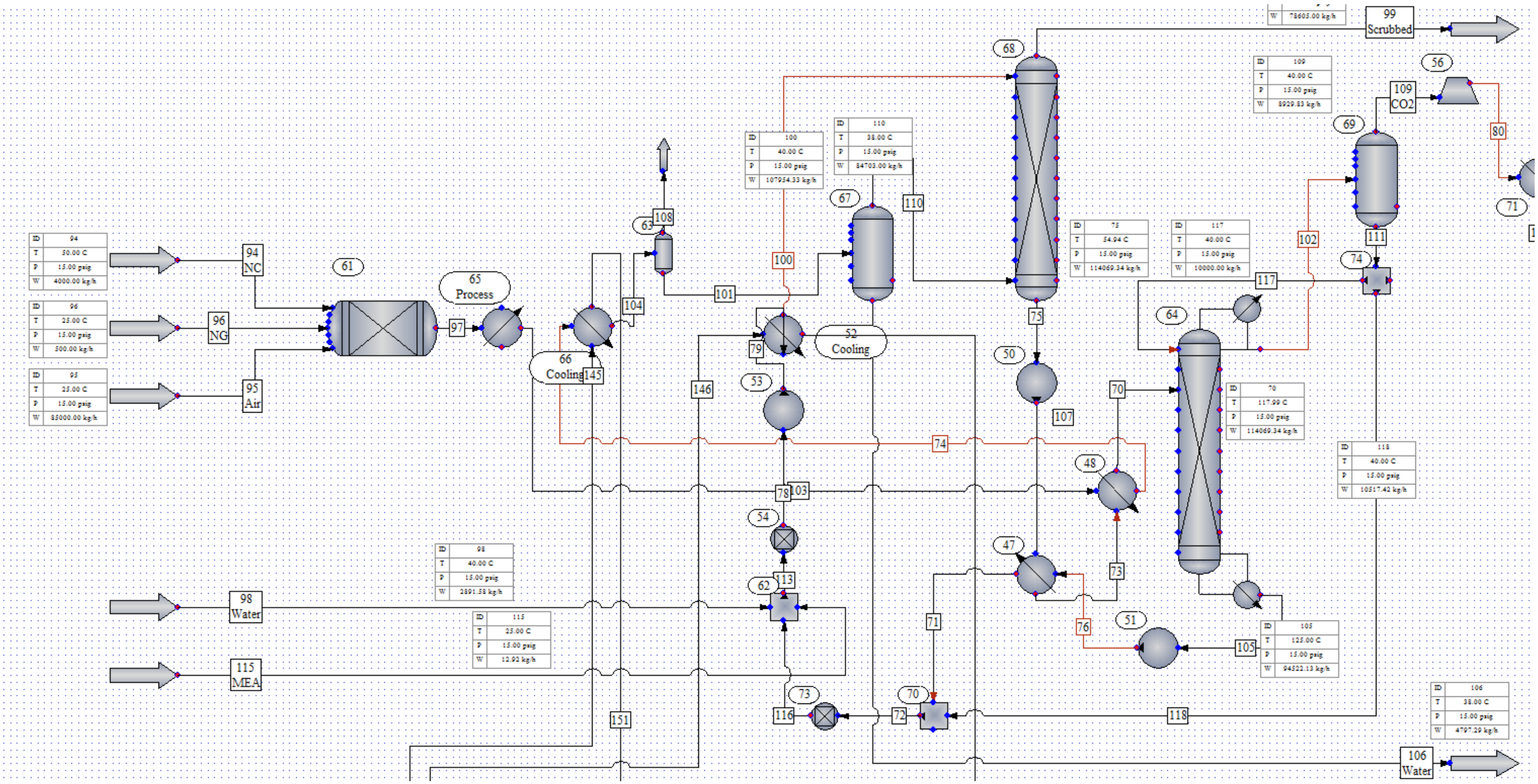


Figure 81. Amine scrubbing and regeneration flowsheet from ChemCAD.

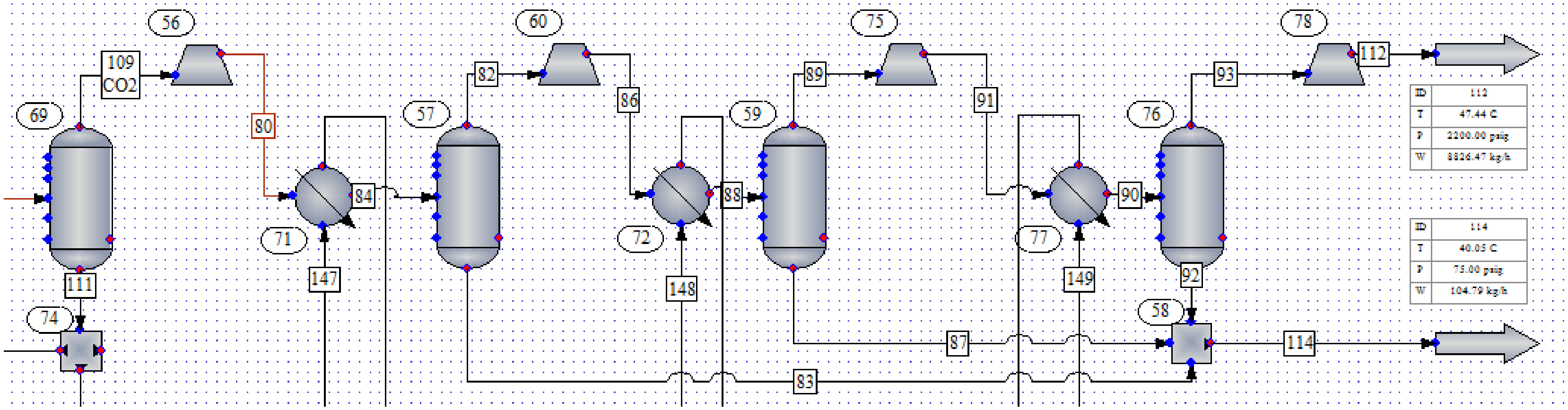


Figure 82. CO_2 compression flowsheet from ChemCAD.

10.3.4.2.4 Hydrotreating

Figure 83 below shows the ChemCAD flowsheet from the simplified hydrotreatment model. Stream 105 is feed hydrogen to replace what is consumed in the reaction along with lost in the pressure swing adsorption blowdown stream. The hydrogen mass feed is controlled by controller 82, which maintains 10,000 kg/hr of hydrogen in the recycle to ensure high hydrogen partial pressures. The feed hydrogen is compressed to 1,300 psig in compressor 73 before being mixed with recycle hydrogen and compressed to 1,500 psig in the recycle compressor number 74. Syncrude is fed in stream 101 then pumped to 1,500 psig in pump 71. For this simplified model, the syncrude is represented by cyclohexylbenzene, along with oxygen, nitrogen, and sulfur added per the syncrude's compositional analysis. In the first hydrotreatment reactor, sulfur is converted to H_2S, oxygen to water, and nitrogen to ammonia. This stream is cooled to 240°C, then the second reactor converts the cyclohexylbenzene to a pseudocomponent boiling at 450°C, methane, and n-pentane to represent the light hydrocarbons generated in the process. This stream is cooled to 50°C in flash 72, then split in divider 77. A portion of the gas is recycled directly, while a portion enters component separator 76 which models a pressure swing adsorption system recovering 80% of the incoming hydrogen. The blowdown from the pressure swing adsorption system is fed to a Gibbs reactor along with air to combust it for process heat.

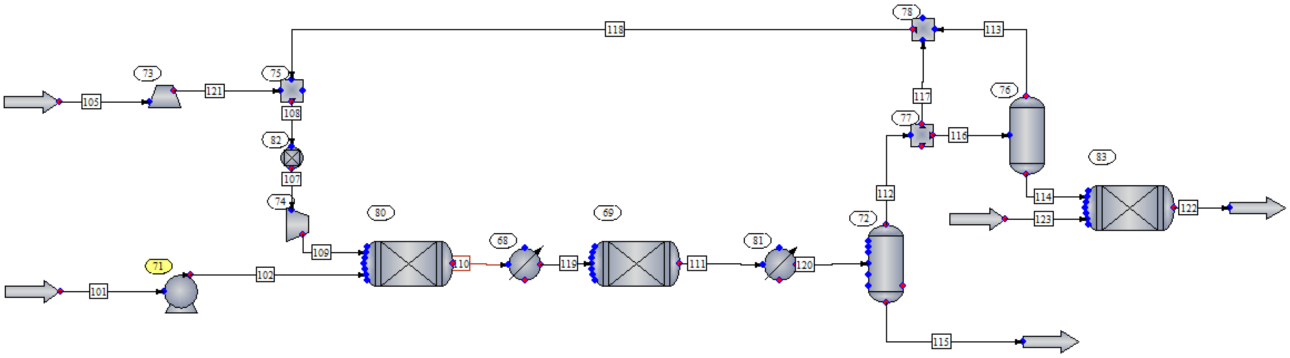


Figure 83. ChemCAD flowsheet of the simplified hydrotreatment model.

10.3.5 ChemCAD Modeling Results

The primary outputs from the ChemCAD model are mass and energy balances that allow for estimations of the cost of manufacture for the fuel products. The mass balance covers all material inputs and outputs for the coal liquefaction and SOx scrubbing portions. The energy balance covers the heating and cooling inputs, as well as electrical inputs for pumps and compressors. It is important to note that electrical demands for centrifuges, filters, mixers, conveyors, etc. are not included in the model. Additionally, the SOx scrubbing and coal liquefaction models are independent models, primarily due to the complexity of matching the GC-MS data in the non-condensable gas through the digestion reactor stoichiometry. Accordingly, the scale of each process is very close, but they do not match exactly.

10.3.5.1 *Liquefaction Reactor Heat and Mass Balances*

Heating, cooling, and electrical requirements for the liquefaction process are shown in Table 77. Heating is primarily required for drying the coal, preheating the reactor charge, and running the evaporator. Cooling is required in the reactor condensers, and the cool the reactor effluent and product streams. Electricity is required to run feed and process pumps, including the vacuum pump for the evaporator. This electricity demand does not include any equipment for coal prep, nor conveyors, and excludes the centrifuge electricity demand.

Table 77: Heating, Cooling, and Electrical Demands for the Coal Liquefaction Process

Description	Value
Heating, MJ/hr (adsorbed)	67,920
Cooling, MJ/hr	-76,236
Electricity, kW (pumps and compressors)	744

Table 78 shows the process inputs and outlets for the coal liquefaction process. The primary feed is coal, with a coal tar distillate makeup stream and bio-solvent stream. These streams are processed, yielding a moisture stream from drying the coal, a non-condensable stream from the digester, solids stream from the centrifuge, lights stream from the evaporator, and an oil product and 500°C+ product stream. The overall mass balance closes to within 200 kg/hr, or 0.4% of the feed rate.

Table 78. Input and Outlet Mass Flow Rates for the Coal Liquefaction Process

Description	Mass Rate, kg/hr
INPUTS	
Coal Feed	41,667
Coal Tar Distillate Feed	4,167
Bio-solvent Feed	15,000
OUTLETS	
Non-Condensable Gas Rate	3,023
Solids Rate	13,648
Syncrude Product Rate	31,787
Evaporator Lights Rate	1,010
500°C+ Product Rate	9,115
Water Vapor Rate	2,083

10.3.5.2 *SOx Scrubber Heat and Mass Balances*

Table 79 provides the heating, cooling and electrical requirements for the SOx scrubbing process. The process requires no heat addition, as the fired heat effluent is the feed stream to this process. This stream is cooled prior to the spray tower. Electricity is required to run the recirculation pump(s) and the air compressor for forced oxidation. Note that this electricity demand does not include limestone milling, conveyors, and mixing, and excludes the gypsum solids separation process.

Table 79. Heating, Cooling, and Electrical Demands for the SO_x Scrubbing Process

Description	Value
Heating, MJ/hr	0
Cooling, MJ/hr	-52,257
Net Heating and Cooling, MJ/hr	-52,257
Electricity, kW	147

Inputs and outlets for the SOx scrubber operation are provided in Table 80 below. Fuel gas is a mixture of the non-condensable gas from the digester and the lights produced from the evaporator. Natural gas is included in the table, as it would be needed for process startup and potentially to make up any deficiencies in the fuel gas rate or heating value. Combustion air is used in the fired heater, while the forced oxidation air is used in the scrubber to convert sulfites into sulfates. Water is makeup for evaporative losses and losses with the gypsum cake, and limestone is the active scrubbing compound. The process outlets are solely the scrubbed gas and the gypsum cake. The mass balance for the SOx scrubbing process closes to within 5 kg/hr, or 0.004% of the total feed rate.

Table 80. Input and Outlet Mass Flow Rates for the SOx Scrubber Process

Description	Mass Rate, kg/hr
INPUTS	
Fuel Gas	3,982
Natural Gas	0
Combustion Air	120,000
Forced Oxidation Air	1,658
Water	1,985
Limestone	982
OUTLETS	
Scrubbed Gas	125,392
Gypsum Cake	3,217

10.3.5.3 CO_2 Scrubber Heat and Mass Balances

The amine scrubbing model was built for consideration early in the modeling task, and was ultimately not included in the final model, design, or costing for syncrude processing. Accordingly, the inputs are slightly different than the SOx scrubber or base case model. Table 81 provides the energy requirements for the CO_2 scrubbing. Heating is necessary for the MEA regenerator reboiler. Cooling is required for the flue gas entering the process, cooling the recirculating MEA, and interstage cooling at the CO_2 compressors. Electricity demand is primarily for CO_2 compression from atmospheric to transport pressure.

Table 81. Energy Requirements for the CO_2 Scrubber Portion of the ChemCAD Model

Description	Value
Heating, MJ/hr	45,642
Cooling, MJ/hr	-88,871
Net Heating and Cooling, MJ/hr	-43,229
Electricity, kW	1,357

Inputs and outputs for the CO_2 scrubbing operation are provided in Table 82 below. The model associated with this CO_2 scrubber did not include as in-depth heat integration as the base case model, and so the fuel gas was augmented with natural gas. Water and MEA are required to make up for the losses in the scrubber column. The scrubbed gas still contains about 1,300 kg/hr of CO_2, but the remaining 8,800 kg/hr is captured and compressed, potentially for subsurface injection or enhanced oil recovery projects. There is also a significant amount of condensed water recovered from the process. The mass balance for the CO_2 scrubber closes to 71 kg/hr, or within 0.08% of the input mass.

Table 82. Mass Balance for the CO_2 Scrubber Portion of the ChemCAD Model

Description	Mass Rate, kg/hr
INPUTS	
Fuel Gas	4,000
Natural Gas	500
Combustion Air	85,000
Water	2,891
Monoethanol Amine	13
OUTLETS	
Scrubbed Gas	78,605
CO_2 Emitted	1,336
Condensed Water	4,902
Compressed CO_2	8,826

10.3.5.4 Hydrotreater Heat and Mass Balances

The hydrotreater model was built only for a rough understanding of the heat and mass balances, and was not used in design or costing. The energy demands for the hydrotreater are shown in Table 83 Heating is required entering the first stage of hydrotreatment to bring the syncrude and hydrogen to 380°C. The cooling is required between stages and also in the product cooler. Electricity demand is primarily from the hydrogen feed compressor, but also from the feed pump and recycle compressor. Energy requirements from the pressure swing adsorber are not estimated in this model, but should be comparatively low due to the relatively small feed stream, and the feed pressure should be more than sufficient for adsorption of the contaminants. Only a small amount of heat can be realized from combustion of the PSA blowdown gas, and it would need to be augmented with natural gas or some other fuel. It is important to note that heat of reaction in the hydrotreatment reactors was not modeled in this exercise, and may reduce the heating requirements for the process.

Table 83. Energy Requirements for the Hydrotreater Portion of the ChemCAD Model.

Description	Value
Heating, MJ/hr	25,370
Cooling, MJ/hr	-75,370
Net Heating and Cooling, MJ/hr	-50,000
Electricity, kW	8,467
Heat from Combustion of PSA Blowdown Stream, MJ/hr	3,075

Inputs and outputs for the hydrotreatment model are provided in Table 84. Roughly 1,200 kg/hr of hydrogen is used to upgrade the syncrude and maintain high hydrogen partial pressures. The syncrude feed is the same mass as exits the base case model, and combustion air is selected arbitrarily to keep the combustion reactor temperature below 900°C. The mass balance closes to within 62 kg, or 0.2% of the feed mass.

Table 84: Mass Balance for the CO_2 Scrubber Portion of the ChemCAD Model.

Description	Mass Rate, kg/hr
INPUTS	
Hydrogen	1,196
Syncrude	27,906
Combustion Air	3,000
OUTLETS	
Upgraded Syncrude	28,975
Burner Tail Gas	3,065

10.4 CTL Process Design and Equipment Sizing

The process design is adapted from the CTL ChemCAD model using 47 MT/hr of coal as its basis and is used for the process conceptual development and equipment sizing. Flow rates from the ChemCAD model were used to estimate the throughput needed for each unit operation. Pumps and heat exchange surfaces were sized mostly from the values provided by the ChemCAD model. Tanks were sized for process inlet and outlet storage using maximum flow rates in the process and estimated duration of storage. The details are provided in Appendix B.

10.5 Capital Costs Estimation

Per the DOE requirements, the cost estimate is stated in June 2011 dollars. Various indexes are available to factor costs based on time. The Chemical Engineering Plant Cost Index (CEPCI) [21] (extracted) has been used to factor the capital costs obtained to June 2011 dollars. This index is more aligned to chemical equipment costs than a Marshall and Swift index or an RSMeans index. Indices used in this evaluation are shown in Table 85.

Table 85. Chemical Engineering Plant Cost Index

Published in Chemical Engineering Magazine (various issues)	
Time Frame	**CEPCI®**
1998	389.5
1999	390.6
2000	394.1
2001	395.4
2001	394.3
2002	395.6
2003	402
2004	444.2
2005	468.2
2006	499.6
2007	525.4
2008	575.4
2009	521.9
2010	550.8
2011	585.7
2012	584.6
2013	567.3
2014	576.1
2015	556.8
2016	540.9

The data in Appendices B and C were used to generate capital costs for the total process. Capital costs were estimated at 1,000 MT/day (MTPD) and 4,000 BPD hydrotreater/reformer. Table 86 shows the breakdown of the total installed costs at the 1,000 TPD Syncrude, a 70 TPD Polyol Plant, and a 4,000 BPD Hydrotreater.

Table 86. Total Installed Cost for Syncrude, Polyol, and Hydrotreater at Likely Commercial Scale

Capital Costs		1,000 TPD Coal Syncrude	70 TPD Polyol	4,000 BPD Hydrotreater
Bare Equipment Costs, 2011		$41,152,967	$7,311,348	$13,005,790
2011 Installed Costs		$117,109,399	$16,354,242	$49,060,000
Misc. Power Plant Equipment		3,122,917	$734,197	$1,300,579
Piping and Ducting		$9,368,752	$2,202,592	$3,901,737
Service Facilities		$10,930,211	$2,569,690	$4,552,026
Total Installed Process Cost (June 2011)		$117,109,399	$21,860,721	$49,060,000
Owner's Costs				
2008 Costs		$21,749,544	$4,059,971	
2009 Costs		$33,439,923	$ 6,242,205	
2010 Costs		$34,275,922	$6,398,260	$19,145,366
2011 Costs		$23,421,880	$4,372,144	$29,436,000
Instantaneous Capital Cost (Sum of Above)		$112,887,268	$21,072,580	$48,581,366
Contingency at 00%		$	$	$12,145,341
Rounded Instantaneous Capital Cost with Contingency		$112,887,000	$21,073,000	$61,205,341
Engineering and Supervision @ 25%		$28,221,750	$5,268,250	$3,249,007
Total Engineered Costs		$141,108,750	$26,341,250	$64,454,348
6 Months All Labor		$2,638,590	$1,890,000	$1,710,000
1 Month Maintenance Materials		$195,182	$109,304	$81,767
1 Month Non-fuel Consumables		$5,628,031	$6,069,560	$4,701,623
1 Month Waste Disposal		$65,958	$168	$65,958
25% of 1 Months Fuel Cost at 100% CF		$62,334	$64,151	$85,497
2% of TPC		$2,822,175	$421,452	$971,627
Total		$152,521,020	$34,895,883	$83,487,440
Inventory Capital				
60 day supply of fuel and consumables at 100% CF		$12,244,210	$2,379,466	$12,009,432
0.5% of TPC (spare parts)		$705,544	$105,363	$245,300
Total		$165,470,773	$37,380,712	$95,742,172
Equipment Shipping Cost	20%	$22,577,454	$4,214,516	$2,575,781
Initial Cost for Catalyst and Chemicals		$2,602,168	$2,379,466	$1,018,322
Land		$3,000,000	$300,000	$3,000,000
Other Owner's Costs	3%	$10,330,530	$2,449,662	$5,942,353
Financing Costs	7%	$25,029,156	$3,992,984	$4,740,871
Total As-Constructed Costs		$214,239,921	$50,717,339	$113,019,500
TASC Multiplier	5%	105%	105%	105%
Total As-Spent Cost (TASC)		$224,952,000	$53,253,000	$118,670,000
Grand Total TASC				**$396,875,000**

The TASC costs without polyol inclusion are given in Table 87.

Table 87. TASC for Two Process Size Options Without Polyol

Process Description	TASC Syncrude Plant, millions	TASC Syncrude Plus Hydrotreatment, millions
1,000 tone/day coal with fuel and heavy oil production	$225.0	$343.6
Four 2,000 tonne/day coal with fuel and heavy oil production	$1,382.8	$1,813.6

The TASC including the polyol plant costs are shown in Table 88. These costs will be for a plant that produces fuel, polyol, and reduced quantities of heavy oil.

The costs at this scale were not easily compared to other costs by DOE primarily due to comparing the small-scale of production here to much larger DOE plants. To provide a summary of the costs that would be comparable to larger plants used to make Fischer-Tropsch fuels (Reference [25] is about 50,000 BPD), the costs were scaled for better economic comparability. To scale the results, the coal plant costs were scaled from 1,000 MTPD to 2,000 MTPD and assumed that 4 plants would feed one hydrotreater (scaled from 4,000 daily bbl to 32,000 daily bbl). The capital costs were scaled using a 0.62 scale factor. Figure 84 shows the effect on $/daily barrel capital cost for scaling. The costs were scaled at the Total Installed Cost level and then developed to Total As-Spent Costs because some factors are linear (e.g. raw materials use, electrical energy) which are contained in the Total As-Spent Cost as working capital costs.

These costs (8,000 MTPD coal and 32,000 BPD product) are used below and are those primarily discussed in the rest of this report.

Table 88. TASC for Two Process Size Options With Polyol

Process Description	TASC Syncrude/Polyol Plant, millions	TASC Syncrude/Polyol Plus Hydrotreatment, millions
1,000 Tonne/day coal with fuel, polyol, and heavy oil production	$278.2	$396.9
Four 2,000 Tonne/day plants with fuel, polyol, and heavy oil production	$1,436.1	$1,866.9

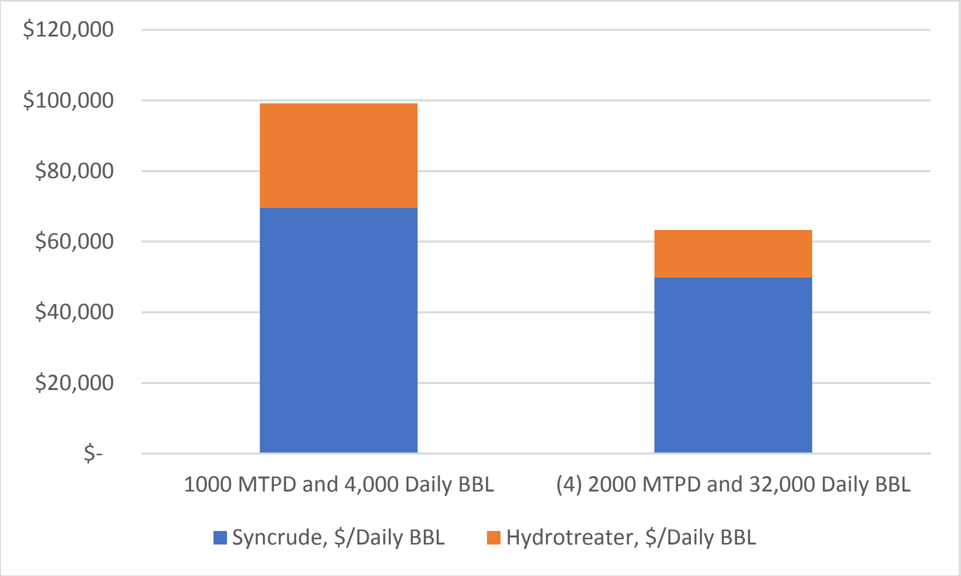


Figure 84. Effect of increasing scale of plant on TASC per daily bbl.

A Greenfield cost estimate is used as the likely maximum capital cost in all cases. It is more likely that a location on or nearby to a mine would be preferred which would reduce shipping and receiving facilities, potentially electrical and water infrastructure and more likely grading and other utilities as well. If a Brownfield were available (for example, a utility boiler facility or other coal plant) direct cost items such as coal grinding and drying, rail spurs, etc. may be already available and coal could be handled through these facilities. Site cost items such as a level area, transformers for power, water and wastewater treatment, and electrical substation, may also be available. On this basis, a Brownfield cost might be reduced by 10-20 percent considering only such facilities as the common ones, but would be reduced even more if the whole coal yard (about 5 percent of the installed cost) and combustion facilities were able to be used. This type of site would even more favorably affect economics, such as was done with F-T piloting at the Wabash facility. In an existing plant, many other decisions, such as using the solid stream for a boiler fuel, might also affect economics. To determine the impact of these items, an actual site-specific design and estimate would be required.

10.6 Operating Cost Estimation

The ChemCAD modeling and capital cost estimates above were also used to determine syncrude operating costs. The ChemCAD models were used to define flow rates of materials and products. The values in the model, which included factors such as coal, bio-solvent, and CTD flow rates, recycle rates, byproduct flow rates, syncrude flow rates, equipment sizing, and energy requirements all came from the ChemCAD flow sheet which had appropriate heat and mass balances. Limestone requirements for SO_2 scrubbing and waste products were determined as discussed. CO_2 scrubbing and compression energy were also modeled using ChemCAD. Yields, percent solids from centrifugation, and the yield by boiling point were all determined from the laboratory studies.

Hydrotreatment values were determined by calculating from the previously-discussed ChemCAD results using minimum hydrogen requirements, using prior ChemCAD modeling experience to determine hydrogen blow-down requirements, experience to determine energy requirements for hydrogen compression, hydrogen and liquid circulation, and prior experience to evaluate the hydrogen requirements and off-gases from the overall material balance. Rather than purchase H_2 on the gas market, a package reformer cost was added to the hydrotreater estimate. The cost was derived from a DOE report for hydrogen generation as an alternate fuel [20].

While the composition of coal was used as measured from the laboratory samples, the cost of equivalent coal was calculated using DOE references which showed market costs for fuels by region and sector. Base prices were taken from Ohio data. Ranges are given in Table 89. The September 2011 EIA documentation was used [26]. Chemical costs for non-fuel components were obtained using www.icis.com data [27].

Table 89. Baseline Input Costs and Values Used for the Cost Model

Material / Item	Baseline Cost	Unit	Range (for Monte Carlo)
Coal	$54.57	MT	$49.50 - $55.00
Bio-solvent	$272.14	MT	$245 - $272
Koppers Solvent	$530.54	MT	$477 - $530
Heavy Product Sale Price	$477.48	MT	90% Koppers CTD
Centrifuge Product Sale Price	$217.32	MT	$25 - $250
Diesel Fuel	$475.96	MT	
Ammonia As Ammonium Sulfate	$20.99	MT	
Limestone	$77.11	MT	$63 - $70
Catalyst Cost	$800	MT	$720 - $800
CO_2 emissions	$0	MT	$54 - $60
Compressed CO_2		MT	
Water/Wastewater Treat	$2.64	MT	$1.32 - $2.64
Waste Disposal	$55.08	MT	
NG Costs	$0.082	MJ	$0.0068 - $0.0075
Electricity	$60.00	MWh	$54 - $60
Process Labor	$45.00	hr laborer	
Eng Labor	$90.00	hr engr/super	
Capital Charges	18	Percent	16.2% - 18%

Operating costs for the baseline system are provided in Table 90. Product values for the syncrude and for distillate products such as diesel and jet fuel were determined from the above EIA reference. For syncrude, a derating factor comparing Hardesty and WTI was developed in conjunction with Quantex and applied to the average crude price from the EIA reference to get the price expected for the CTL syncrude product. For the jet and diesel, a 13% reduction in selling price was applied to EIA data to account for taxes because EIA data include taxes. The 2011 price before tax was $3.09 for diesel and $3.10 for jet fuel [28]. A comparison of baseline cost for the CTL plant vs crude-derived products are listed in Table 89. The table contains the projected syncrude and hydrotreated product prices for both 1,000 MTPD/4,000 daily bbl and for four 2,000 MTPD plants and a 32,000 daily bbl hydrotreater. In both cases, polyol is not included.

Table 90. Product Prices Determined from Modeling, June 2011 Data(a-d)

Equivalent Syncrude Break-even Price, June 2011 Dollars w/o Contingency				
Capital Cost Factor	**18% CCF**		**12.0% CCF**	
Coal Throughput Basis	**1000 MTPD**	**2000 MTPD**	**1000 MTPD**	**2000 MTPD**
	Syncrude Only, $/bbl			
With RIN Credit	$31.52	$24.05	$21.97	$16.71
W/O RIN Credit	$45.63	$38.17	$36.08	$30.83
Equivalent Fuel (Diesel or Jet) Break-even Price, June 2011 Dollars				
	Syncrude + Hydrotreatment, $/gal			
	4,000 BPD	**32,000 BPD**	**4,000 BPD**	**32,000 BPD**
With RIN Credit	$1.63	$1.42	$1.27	$1.13
W/O RIN Credit	$1.96	$1.76	$1.60	$1.46

(a) EIA 2011 average crude price: $68.11/bbl
(b) EIA 2011 average fuel price less 13% taxes: $2.68/gal
(c) 18% derated crude price: $55.85/bbl
(d) RIN credit: $0.75/gal at 100% bio-content

The heavy oil and centrifuge cake that are produced are like other materials which have been treated as “binder” materials by Quantex. The values for these products which are used were provided by Battelle’s Quantex partner. Battelle included a 10% derating of that price into these factors [29]. Note that the values used for the hydrocarbon content are lower than the sale price for equivalent residual or bunker oil in the EIA data ($1.98 for our product vs $2.47 for residual oil in June 2011 [28]. The >500°C product is lower in ash and metals than residual oil and should go for a premium cost over resid. Because resid is not considered to be the final market, this cost basis was not used. Both of these materials could also potentially be used for gasification or petroleum feedstock purposes or possibly sold as a bunker or heavy material, all at a lesser value than they are worth as a binder or other feedstocks. Particularly for the >500°C liquid fraction, the solids are actually equivalent to most motor fuels, so delayed coking to recover lighter products and use of the carbon for a product like graphite or carbon fibers might be a reasonable use for this material. This was briefly evaluated but no interest could be obtained from Exxon in providing a quotation for a coker due to the small size.

DOE NETL had suggested in the October 2016 review that gasification of the centrifuge solid stream be considered and that hydrogen be produced in that manner. To evaluate this option, Battelle evaluated a "non-capital" economic value proposition to see what the operating costs might be, and to also see what the capital which might be available would be. A DOE Report described the comparison as well and is in general agreement with this rough calculation [20]. Assuming that a steam-blown gasifier would be used, that the steam/solid would be operated at 1.2/1 ratio to assure fluidization, and gasification efficiency is 60%, a cost of \$3.94/kg of H_2 was calculated for steam plus solid product. A similar cost for H_2 reformed from natural gas shows a cost of about \$2.21/kg H_2. Typical costs for a gasifier plus all of the shift and membrane or PSA equipment being the same for a reformer and a gasifier would make capital costs for the equivalent amount of hydrogen substantially higher than a reformer. Hence, unless this product has a fair market value of half or less its assumed value, the gasification approach should not be considered unless other factors, like an existing gasifier already exists which could be used to gasify this material.

On the basis of total cost, a reformer was chosen. Reformer costs were scaled for this project from capital and operating costs [20]. Scaling was done from 2009 to 2011 costs and to the flow of H_2 for this project using a 0.62 factor on the capital cost. The capital for reforming was added into the hydrotreater total budgetary cost. Operating costs for natural gas for reforming, catalyst, maintenance, and operating labor are also included in the hydrotreater operating costs.

Maintenance was assumed to be done by on-staff personnel and maintenance cost for materials was determined using 6 % of cost of equipment in addition to the on-line spares in the estimates. As mentioned previously, equipment spares were put in place in the syncrude plant where high-frequency repairs were expected as described in the capital equipment costing section previously. These included in the reactor area, in the pressure let-down valve area, in the cooling water circulation area, in the solids separation area, and in the evaporation area as the five prevalent areas in the Syncrude production. In the hydrotreater, an in-line spare reactor would be expected as would spare rotating equipment (pumps and compressors). Fired heaters were not spared for either case.

A labor estimate of 52 craft and 5 technical/supervisory persons were determined to be the appropriate number of staff for the 1,000 MT/day syncrude plant. This staffing level was scaled linearly for the 2,000 MT/day unit to 104 craft and 10 technical/supervisory persons. An integrated 70 MT/day polyol plant was assumed to require 32 craft and 5 technical/supervisory staff.

A separate 4,000 BPD hydrotreater would be staffed with 28 craft and 5 technical/supervisory staff. This staff was also scaled linearly for the 32,000 BPD hydrotreater to 224 craft and 40 technical/supervisory staff. It is likely that the larger plants could be staffed with lower numbers of staff, but this linear scaling assumption was used for conservatism. This derives a potential labor force for this project of approximately 1,000 persons for the larger facilities (8,000 MTPD/32,000 BPD fuel/70 TPD polyol).

The base case cost demonstrates that the syncrude could be sold for less than the cost of heavy crude without RIN credits even at 1,000 tonne/day of coal flow. The fuel from hydrotreating also could be sold for less than the then-current market cost of fuel at the 4,000 BPD size. If a 30% contingency were added to the calculated syncrude and fuel cost, syncrude would be more expensive than then-current heavy crude at 1,000 MTPD but less at 2,000 MTPD (still without RIN credit).

RINs were not promulgated in the U.S. until 2010 (Renewable Fuel Standards 2) but the concept, which allows a credit for biologically-derived carbon content is useful. With the RIN credit included, the value of the total proposition of direct liquefaction with a non-recovered bio-solvent will produce a valuable crude. The fuel produced, when inflated with a 30% contingency, would cost more at 4,000 BPD than then-current fuel price, but would cost less at 32,000 BPD than then-current fuel. The RIN credit would again make both scales of production economical.

The operating costs for including polyol production in the baseline plant were also considered. The advantage of polyol production is that a chemical product is produced from the heavy oil that can sell for a premium value. Polyol is valued for foam production. The costs below in Table 91assume that polyol will sell for about $0.90/lb. This “upcharge”, when taking into account all production costs and 12% capital cost, would yield additional revenue of $8.8 million. At 18% capital cost, it still would yield $5.5 million when compared with sale of heavy oil at the anticipated price.

Table 91. Product Prices Determined from Modeling, June 2011 Data Including Polyol(a-d)

Equivalent Crude Oil Break-even Price, June 2011 Dollars w/o Contingency				
Capital Cost Factor	**18% CCF**		**12.0% CCF**	
Coal Throughput Basis	**1000 MTPD**	**2000 MTPD**	**1000 MTPD**	**2000 MTPD**
	Syncrude Only, $/bbl			
With RIN Credit	$26.60	$22.09	$15.64	$13.55
W/O RIN Credit	$41.71	$36.21	$29.76	$27.67
Equivalent Fuel (Diesel or Jet) Break-even Price, June 2011 Dollars				
	Syncrude + Hydrotreatment, $/gal			
	4,000 BPD	**32,000 BPD**	**4,000 BPD**	**32,000 BPD**
With RIN Credit	$1.53	$1.32	$1.11	$0.97
W/O RIN Credit	$1.86	$1.66	$1.44	$1.30

(a) EIA 2011 average crude price: $68.11/bbl
(b) EIA 2011 average fuel price less 13% taxes: $2.68/gal
(c) 18% derated crude price: $55.85/bbl
(d) RIN credit: $0.75/gal at 100% bio-content

10.7 Sensitivity Analysis for Costs

Cost sensitivity was run for varying cases of costs for the syncrude and the syncrude plus reformer cases discussed above. Sensitivity cases are provided in Appendix F. Cases evaluated included capital cost, electricity cost and carbon dioxide penalty, compression of CO_2, and variability of byproduct value. A Monte-Carlo simulation of 10,000 iterations using Crystal Ball® was conducted on various process variables.

The standard capital cost factor was directed from Attachment 2 from the contract. By Battelle PM direction, capital was baselined at 12% and varied to 18% for costs. Costs were evaluated at 12% and 18% for the 1,000 MTPD/4,000 BPD and the 2,000 MTPD/32,000 BPD syncrude/polyol plus hydrotreatment cases.

Compression of CO_2 was not considered at the CTL site and was evaluated only briefly at the hydrotreater site. The amount of CO_2 produced from syncrude production is 73,000 MT/year for all syncrude sources at 1,000 MT/day (total coal conversion to CO_2 would be about 1 million MT/year).

The cost avoidance for CO_2 using compression is about $64/MT based on references [30]. In the syncrude production process, a much higher per-MT cost is expected due to the much-smaller production of gas. This lower production of CO_2 is because we are producing about 1% of the coal flow in equivalent CO_2 and because both 1,000 MT/hr of coal are much less than the coal flow to this size pulverized coal facility equivalent production.

Compression of CO_2 was considered as a sensitivity factor for the hydrotreater site, because the amount of CO_2 produced is much larger than from liquefaction site, both because of hydrotreater operational energy and hydrogen which is made at the reformer plant at the hydrotreater site.

The reformer plant has two streams that are rich in CO_2, one from the reformer tailgas itself and the other from the fired heater source. The tailgas is the only economical gas to compress; a cost avoidance of $47/MT for compression of the compressed gas plus several dollars/ton for shipping vs. a $60/MT emission charge are nearly equivalent and would give a net zero cost avoidance for compressed CO_2 . The carbon dioxide from the reformer tailgas is about 40% of the total CO_2 produced in the hydrotreater.

The syncrude reactor tailgas could potentially be a pressure source, but if it were then either oxygen would have to be supplied or feed air pressurized. This obviates the benefit of this gas unless it is steam shifted. The syncrude reactor bleed gas will have some H_2 in it which could be recovered for hydrotreatment, but will mostly be CO_2 and water. The gas is also mixed with the vacuum pump tailgas which is at atmospheric pressure. The mixed tail-gas is used as fuel rather than any other use. Similarly, the hydrotreater tailgas will have mostly hydrogen, hydrogen sulfide and ammonia in it. Hydrogen recovery has already been done to the extent feasible; on this basis, it is also used as a fuel gas. SO_2 scrubbing with limestone was done on both streams after combustion. To recover a combustion stream at a pressure other than atmospheric, air will either need to be compressed or an oxygen plant will be required for combustion air. With these drawbacks it is likely that the only CO_2 that might be compressed from the hydrotreater plant would be about 38,000 MT/year of the 146,000 MT/year of CO_2 produced from the 4,000 BPD hydrotreater. This small quantity could not justify a pipeline, so it is more likely to be transported by rail than by pipeline (estimated 4 cars/day) which would add to the cost for CO_2 recovery and further reduce the savings. However, this would be highly pure CO_2 and may represent a higher-value product.

If there is also the possibility that the CO_2 could be sold rather than disposed of, then economics should be revaluated. When it can be sold, the scenario changes in that a product value would be recovered for the CO_2 sold. For our purposes, a market value of

\$150/MT is assumed with a compression cost of \$64/MT. [20] By selling compressed CO_2 at this price, the cost of fuel is reduced by \$0.11 and \$0.12 at the two scales of hydrotreater operation assuming a \$64/MT compression cost for the CO_2 (typical for reformer exhaust gas after shift and H_2 recovery; reports on CO_2 by DOE indicate that the cost of compressing CO_2 from atmospheric gas is on the order of \$75/MT based on the 2010 report previously cited.)

Other variables were also considered for hydrotreatment. The Crystal Ball® analysis for fuel sales cost is also evaluated here. Figure 85 shows the variation across the total suite of variables for both the syncrude and the fuel product. The analysis was generated using 20,000 Monte Carlo iterations and 10% variations in raw material and energy costs. Table 89 (previously presented) contains the variations on inputs which were used for Crystal Ball. Both the 1,000 MTPD/4,000 BPD and the 8,000 MTPD/32,000 BPD cases were evaluated in Crystal Ball.

As stated above, a uniform 10%variation in inputs was used for the Crystal Ball analysis. The sensitivity results are shown in Figure 85. These results show that the same variables affect both the syncrude and the fuel break-even price. CO_2 emissions is much more important for fuel because of the need to make H_2 to produce the fuel. Natural gas is similarly important to fuel production because of the need to make H_2 but is not a major variable in the cost of syncrude or fuel. Otherwise, the variables are quite similar in magnitude for syncrude and fuel.

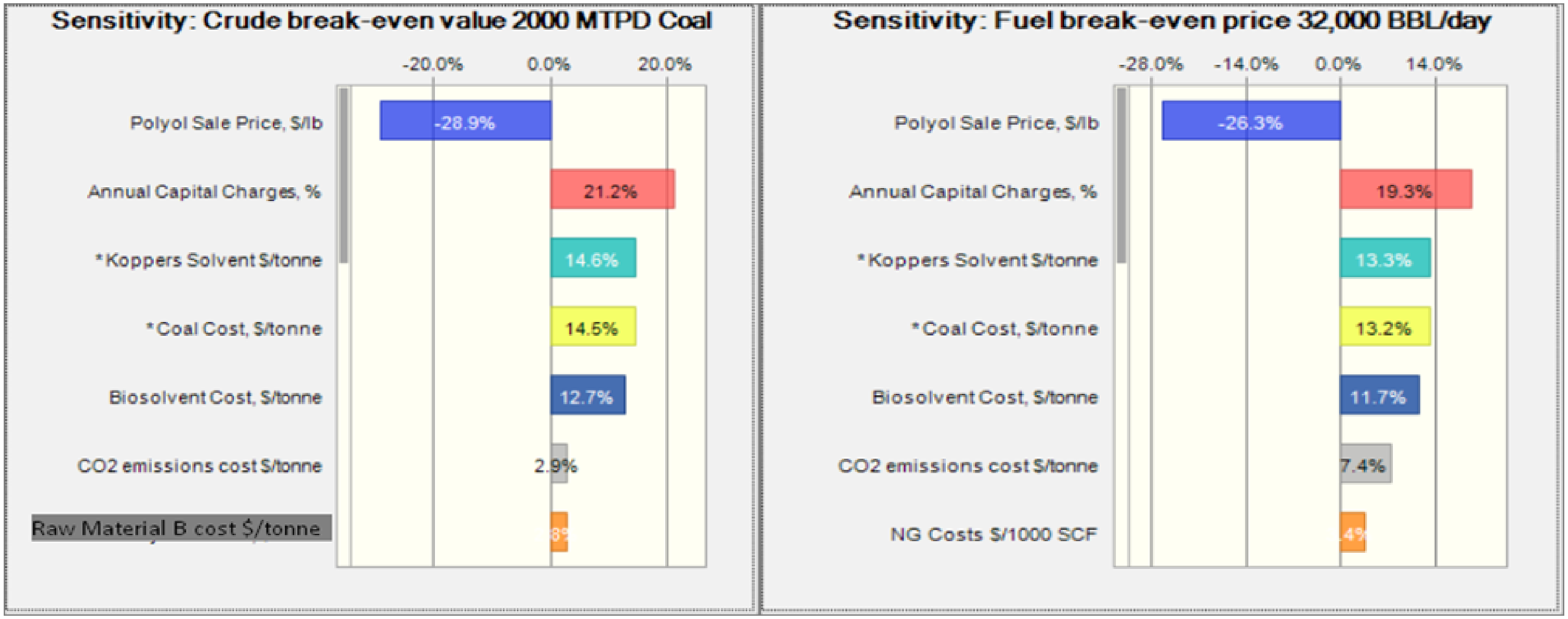


Figure 85. Sensitivity of primary variables on crude and fuel break-even price (8,000 MTPD/32,000 BPD case).

Because the syncrude is highly dependent on CO_2 emissions, so will be the hydrotreated product. It is important to the value of this project that the polyol be salable at more than $0.70/lb, which is break-even. The estimated of current market price for the equivalent product is $1.00. A 10% polyol variation produces a 29% variation in crude price and a 26% variation in fuel price.

Also important are capital charges (21% and 19% for crude and fuel) and CO_2 penalties. Koppers solvent cost, coal cost, and bio-solvent cost all have a >1 ratio of effect to change in price.

10.8 Costs for Battelle CTL vs. FT Indirect CTL

Table 92 provides a summary comparison for CTL fuel costs ($/bbl) and the effect of capital charges. A 50% increase in capital charges will make a $13.00 (21%) increase in the break-even selling price of fuel without RIN credits, and a 28% increase in the break-even selling price for RIN-credited fuel. A 12% rate is representative of well-established, long-term technology. An 18% rate represents a more risky, shorter-horizon project. Either gives a better cost than other alternatives.

Table 92. Distillate Selling Price for Battelle's CTL Process

	12% CCF	18% CCF
Selling Price without RIN Credit, $/bbl	61	74
Selling Price with RIN Credit, $/bbl	47	60

Table 93 compares CTL operating at a 12% capital cost factor vs Gasification/FT operating at the same capital factor. This shows that the CTL project would be less costly (about 36% of a gasification/FT indirect liquefaction plant cost) and is also more economical at a smaller scale (about 65% of the plant product quantity). This demonstrates the ability of a CTL plant to produce fuel much more economically than an FT plant with indirect liquefaction.

Table 93. 2011 Capital and Operating Costs (at 12% CCF, no RIN credits)

	Battelle Direct CTL	Gasification/FT Indirect CTL
Coal, MT/day	8,000 (4 CTL plants)	19,050
Bio-Solvent Blend, MT/day	3,680 (4 CTL plants	Not Applicable
Distillate Product, bbl/day	32,000	49,990
Capital Cost[(a)], $Millions	1,436 (4 CTL plants)	7,550
Unit Capital Cost, $Thousands/daily bbl)	45	151
Selling Cost, $/bbl Distillate	61	95 (estimated by authors)
Selling Cost, $/bbl Synthetic Crude	31	Not Applicable

(a) Capital cost for CTL is used here, not previously used TASC.

11.0 GREENHOUSE GAS (GHG) EMISSIONS ANALYSIS

Emissions estimates were developed for the syncrude part of the process and the hydrogenation and distillation part of the process using ChemCAD runs for both the syncrude and hydrotreater, and the referenced Reformer report. Emissions estimates were developed without GHG control.

To demonstrate that GHG release can be limited to levels comparable to or lower than petroleum-based jet fuel, the approach of Life Cycle Assessment (LCA) [31] was applied on a commercial plant design proposed in this task. The GHG lifecycle emissions from the direct CTL jet fuel process is being assessed and compared to that for the production of petroleum-based jet fuels. The GHG accounting methodology developed is believed to be consistent with industry guidelines for performing LCA's developed in ISO 14040 [31]. The study uses applicable and publicly-available LCA evaluations contained in GREET [32]. OSU has developed a subset of this for the proprietary bio-solvent so that comparison of results with those from previous studies can be made. The boundary of the unique assessment is well-to-pump. Existing pump-to-wheels will be used so that raw material extraction through fuel use can be addressed for the fuel portion. The GHG assessment of the other products has been considered but is not addressed herein.

This effort was subcontracted to Dr. Bhavik R. Bakshi, a Professor in the Systems Analysis Department of The Ohio State University who specializes in GHG estimation work. Dr. Bakshi, supported by a graduate student, Mr. Kyuha Lee, prepared a GHG evaluation based upon data provided by the Battelle team. This work uses the GREET software as much as possible, and supplement it with data from other life cycle inventory sources. The overall model is developed in openLCA software [33].

The following data summarize the syncrude and fuel portion of the process as analyzed:

- Syncrude oil product from the liquefaction process, 220,095 MT/yr, employing 1,000 MT/day of coal and done at 1,000MT/day
- Jet fuel product from the hydrotreating process, 186,043 MT/yr
- Syncrude oil product from the conventional process, 220,095 MT/yr
- Jet fuel product from the conventional process, 186,043 MT/yr.

As mentioned earlier, there are by-products produced from this process also.
A network diagram for the process used for the GHG analysis is shown in Figure 86. Inputs to the GHG syncrude model are shown in Table 94. Outputs from the GHG syncrude model are shown in Table 95. The source for factors and their total quantities of impact are shown for a Well to Pump (WTP) analysis. References to data sources are shown in the Reference column. These data all assume that CO_2 is not recovered for the synthetic crude portion of the process. To evaluate the emissions accurately for the hydrotreater if compression is assumed for the shift-gas CO_2, the footprint for MEA was required. Because it could not be found in the GREET data base, a footprint was constructed. That footprint is shown in Table 96 and Table 97. Data for input and outputs for the hydrotreatment of the syncrude portion are provided in Table 98.

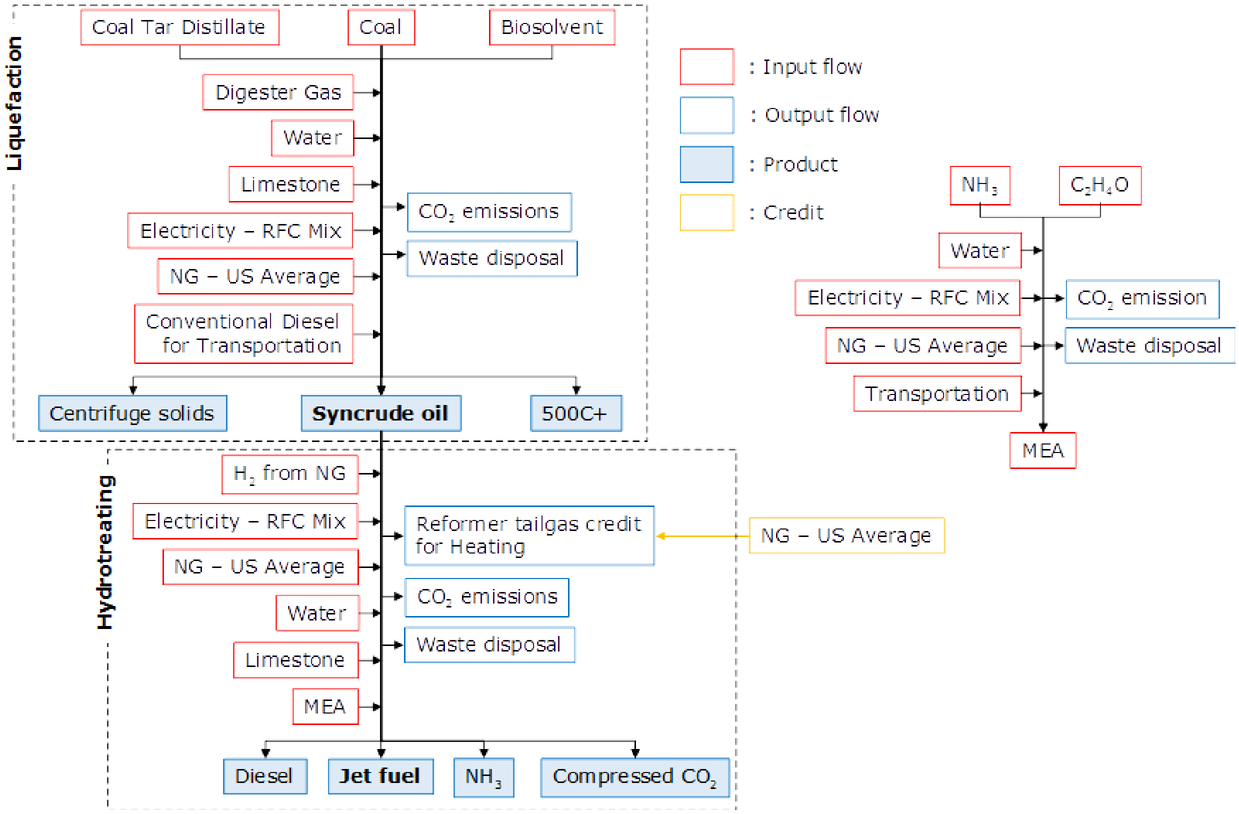


Figure 86. Block diagram for GHG analysis.

Table 94. Inputs from the GHG Syncrude Evaluation

Flow		Amount	Unit	Note	Reference for quantity	Life cycle inventory (LCI) data	LCI data source	CO_2 Emissions (WTP)	Unit
Input - Resource	Coal	328500	MT/yr	Mined Bituminous	Coal to Syncrude Economics	Bituminous Coal Mining and Cleaning	GREET 2016	18.82	g/kg
Input - Resource	Bio-solvent	118259	MT/yr	Battelle BS-41B	Coal to Syncrude Economics	-	Battelle	0.33	kg/kg
Input - Resource	Coal Tar Distillate	32850	MT/yr		Coal to Syncrude Economics	Residual Oil (Petroleum) from Crude Oil	GREET 2016	0.41	kg/kg
Input - Resource	Digester Gas	23561	MT/yr		Coal to Syncrude Economics	Animal Waste Anaerobic Digestion to Natural Gas as an Intermediate Fuel	GREET 2016	1.89	kg/kg
Input - Resource	Water	25363	MT/yr		Coal to Syncrude Economics	N/A			kg/kg
Input - Resource	MEA	8.76E-05	MT/yr		Coal to Syncrude Economics	-			
Input - Resource	Limestone	7745	MT/yr		Coal to Syncrude Economics	Limestone Mining	GREET 2016	2.09	g/kg
Input - Utility	Electricity	37843	MWh/yr		Coal to Syncrude Economics	Electricity Distributed - RFC Mix	GREET 2016	0.59	kg/kWh
Input - Utility	Natural Gas	1521	MT/yr		Coal to Syncrude Economics	NA NG from Shale and Regular Recovery	GREET 2016	0.22	kg/kg
Input - Transport	Fuel use locomotive, endloader, dump truck 43.5 gal/hr, daylight	635	MT/yr		Coal to Syncrude Economics	Conventional Diesel from Crude Oil for US Refineries	GREET 2016	0.58	kg/kg

Table 95. Outputs from the GHG Syncrude Evaluation

Flow		Amount	Unit	Note	Reference for quantity	Life cycle inventory (LCI) data	LCI data source	CO_2 Emissions (WTP)	Unit
Output - Main product	**Syncrude Oil**	**220095**	**MT/yr**	**<500C Product, 4012 BPD**	**Flow Assumptions**	**-**			
Output- By-product	500C+ Heavy Oil	101327	MT/yr	similar with Pet Coke	Coal to Syncrude Economics	-			
Output - By-product	Centrifuge Solids	108823	MT/yr	will be used as binding materials	Coal to Syncrude Economics	-			
Output - Waste	Digester gas	23652	MT/yr	72 MT/day	Flow Assumptions	N/A			
Output - Waste	Water	16425	MT/yr	50 MT/day	Flow Assumptions	N/A			
Output - Waste	Limestone	7884	MT/yr	24 MT/day	Flow Assumptions	N/A			
Output - Waste	Scrubber sludge	25363	MT/yr	77 MT/day	Flow Assumptions	N/A			
Output - Emission	CO_2 emissions	72294	MT/yr	from combustion	Coal to Syncrude Economics	N/A			

Table 96. Estimation of MEA GHG Input Footprint

Flow		Amount	Unit	Note	Reference for quantity	Life cycle inventory	LCI data source	CO_2 Emissions (WTP)	Unit
Input	Water	8.20E-04	m^3		ecoinvent v2.2	N/A			
	Water, cooling	0.024	m^3		ecoinvent v2.2	N/A			
	Ammonia	0.788	kg		ecoinvent v2.2	Ammonia Production	GREET 2016	2.43	kg/kg
	Electricity	0.333	kWh		ecoinvent v2.2	Electricity Distributed - RFC Mix	GREET 2016	0.59	kg/kWh
	Natural gas	0.041031818	kg		ecoinvent v2.2	NA NG from Shale and Regular Recovery	GREET 2016	0.22	kg/kg
	Transport, train, diesel powered	0.963	t.km		ecoinvent v2.2	Freight Rails: Conventional Diesel (WTW)	GREET 2016	17.03	g/t/km
	Transport, combination truck, diesel powered	0.16	t.km		ecoinvent v2.2	HD Truck: Combinationa Short-Haul - CIDI BD20 (WTW)	GREET 2016	44.93	g/t/km
	Ethylene oxide	0.7344	kg		ecoinvent v2.2	Ethylene Oxide Production	GREET 2016	2.5	kg/kg

Table 97. Estimation of MEA GHG Output Footprint

Flow		Amount	Unit	Note	Reference for quantity	Life cycle inventory	LCI data source	CO_2 Emissions (WTP)	Unit
Output	**MEA**	**1**	**kg**		ecoinvent v2.2	**-**			
	Heat, waste	1.2	MJ	air	ecoinvent v2.2	N/A			
	CO_2	0.0265	kg	air	ecoinvent v2.2	N/A			
	Ethylene oxide	0.00163	kg	air	ecoinvent v2.2	N/A			
	Ammonia	0.00158	kg	air	ecoinvent v2.2	N/A			
	BOD5, Biological Oxygen Demand	0.0213	kg	water/river	ecoinvent v2.2	N/A			
	COD, Chemical Oxygen Demand	0.0213	kg	water/river	ecoinvent v2.2	N/A			
	DOC, Dissolved Organic Carbon	0.00802	kg	water/river	ecoinvent v2.2	N/A			
	TOC, Total Organic Carbon	0.00802	kg	water/river	ecoinvent v2.2	N/A			
	Ethylene oxide	0.00147	kg	water/river	ecoinvent v2.2	N/A			
	Ammonium, ion	0.00304	kg	water/river	ecoinvent v2.2	N/A			
	Nitrate	0.00697	kg	water/river	ecoinvent v2.2	N/A			

Table 98. Input and Output GHG Estimates for Hydroreating of Syncrude

Flow		**Amount**	**Unit**	**Note**	**Reference for quantity**	**Life cycle inventory**	**LCI data source**	**CO_2 Emissions (WTP)**	**Unit**
Input - Resource	Syncrude oil	220095	MT/yr	<500C Product, 1,317,826 bbl/yr	Syncrude to Fuel Economics	-			
Input - Resource	Hydrogen	10003	MT/yr		Syncrude to Fuel Economics	G.H_2 Produced from NA NG (H_2A model) with CO_2 sequestration	GREET 2016	2.06	kg/kg
Input - Resource	Water	81633	MT/yr		Syncrude to Fuel Economics	N/A			kg/kg
Input - Resource	Limestone	3947	MT/yr		Syncrude to Fuel Economics	Limestone Mining	GREET 2016	2.09	g/kg
Input - Utility	Electricity	91196	MWh/yr		Syncrude to Fuel Economics	Electricity Distributed - RFC Mix	GREET 2016	0.59	kg/kWh
Input - Utility	NG for Shift and Heating	30286	MT/yr		Syncrude to Fuel Economics	NA NG from Shale and Regular Recovery	GREET 2016	0.22	kg/kg
Output - Product	Jet Fuel	186043.46	MT/yr	4,240.70 BPD, ρ =133.55 kg/bbl	Hydrotreater Energy Balance	-			
Output - By-product	Switch Engine Fueling	211.58	MT/yr	Diesel	Syncrude to Fuel Economics	-			
Output - By-product	Ammonia	2570	MT/yr	from coal and limestone scrubbing	Syncrude to Fuel Economics	-			
Output - By-product	Compressed CO_2	37000	MT/yr	from steam reforming, as a product	Syncrude to Fuel Economics	-			
Output - Credit	Reformer tailgas credit for Shift and Heating	26943132	MJ/yr	576.82796 MT/yr of NG	Syncrude to Fuel Economics	NA NG from Shale and Regular Recovery	GREET 2016	0.22	kg/kg
Output - Waste	Waste disposal	13578	MT/yr		Syncrude to Fuel Economics	N/A			
Output - Emission	CO_2 emissions	109036	MT/yr	from combustion	Syncrude to Fuel Economics	N/A			

The emissions burden of the proposed liquefaction process was divided into three products, synthetic crude oil, >500°C heavy oil, and centrifuge solids by a mass-based partitioning. The life cycle CO_2 emissions were 97,401, 44,841, and 48,159 MT CO_2/yr, respectively.

Figure 87 shows that the liquefaction process was the highest contributor to the emissions, followed by digester gas and bio-solvent. In case of the hydrotreating process, the life cycle CO_2 emissions of jet fuel, switch engine fueling, ammonia, and compressed CO_2, were 219,974, 250, 3039, and 43,748 MT CO_2/yr, respectively. As shown in Figure 88, the hydrotreating process was the most dominant contributor. It should be noted that the shift-CO_2 is not shown here. It is a water product (37,000 MT/yr).

The life cycle CO_2 emissions of conventional alternatives to synthetic crude oil and jet fuel were obtained from corresponding GREET models. The CO_2 emissions of synthetic crude oil, based on bitumen from oil sands as a conventional process were 224,497 MT CO_2/yr, which are significantly higher than those from the liquefaction/hydrotreating process. The uncontrolled CO_2 emissions of F-T jet fuel from coal were 852,079 MT CO_2/yr, which are higher than those from the hydrotreating process.

The CO_2 emissions of conventional jet fuel from crude oil and FT jet fuel from natural gas were lower than those from the hydrotreating process, showing 74,417 and 208,369 MT CO_2/yr, respectively.

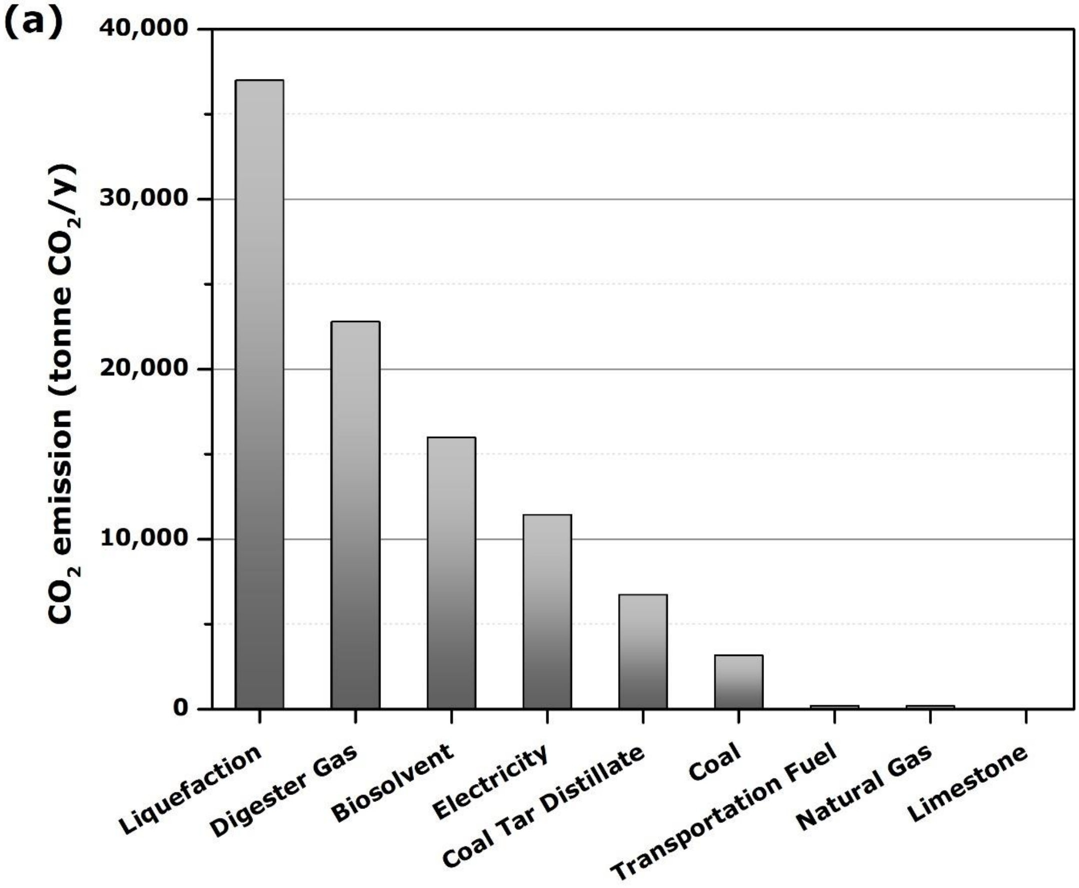


Figure 87. Syncrude relative emissions estimates.

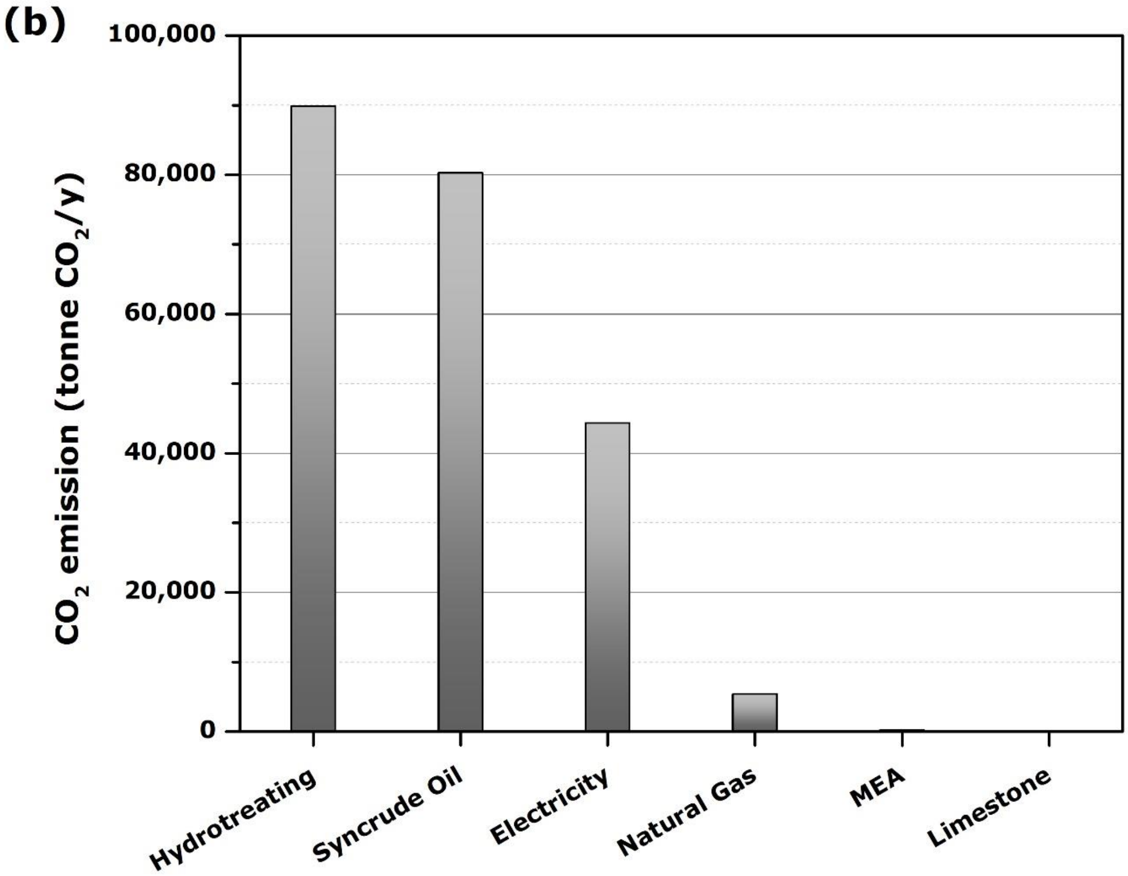


Figure 88. Syncrude plus hydrotreating estimates of CO_2 generation.

Figure 89 shows the life cycle CO_2 emissions of products when different allocation methods were employed. The results of the displacement method show higher emissions that those of other partitioning methods. However, actual emissions of the displacement method may be lower because credits from some byproducts were not included in the analysis by the displacement method. In case of the partitioning method based on exergy, the CO_2 emissions of synthetic crude oil from the liquefaction process were not calculated since the chemical composition of by-products, which are >500°C heavy oil and centrifuge solids, is unknown, and therefore, exergy values of those by-products are hard to calculate. Regardless of which allocation method was selected, the CO_2 emissions of synthetic crude oil from the liquefaction process were much lower than those from the conventional process. That is, about 43.7% reduction of the CO_2 emissions is expected to produce synthetic crude oil by employing the proposed liquefaction process. Also, regardless of the allocation methods, the CO_2 emissions of jet fuel from the hydrotreating process were higher than those of conventional jet fuel from crude oil and crude oil, but 68.6% lower than those of F-T jet fuel from coal.

A mass basis was used for this analysis as previously described. Figure 89 shows that other choices could have a significant effect on emissions allocated to the fuel product.

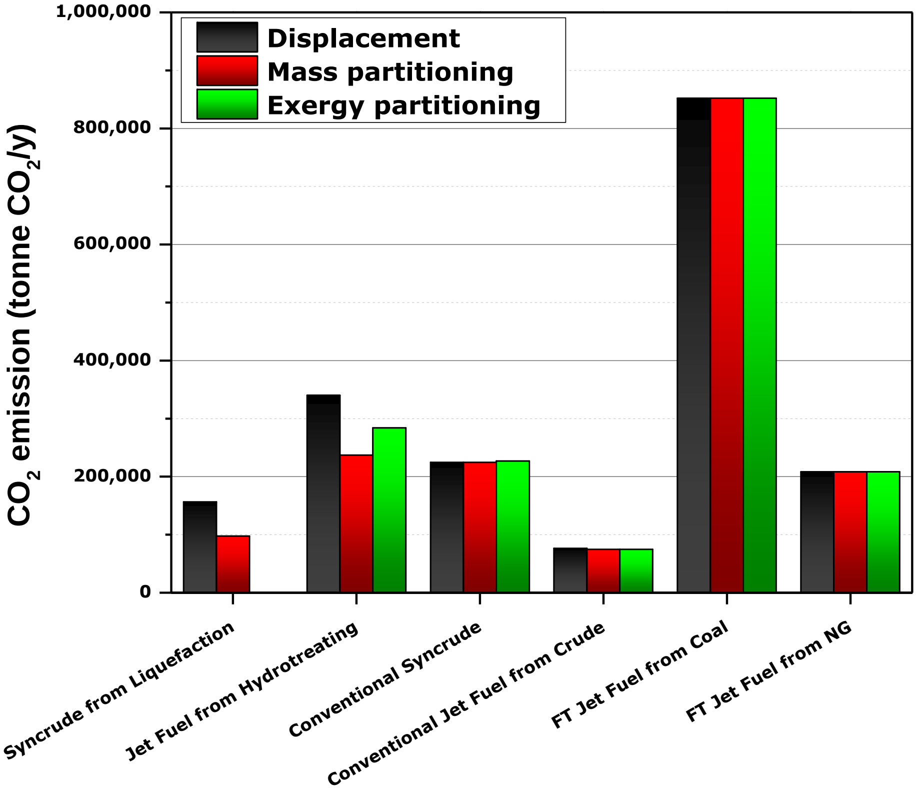


Figure 89. Comparison of WTP GHG Footprints with Synthetic Crude, Petroleum and FT.

Table 99 shows the comparison of uncontrolled emissions from well-to-pump (WTP) and well-to-wheels (WTW) for the Battelle CTL process and coal gasification/FT process. As shown, the WTP emissions for the FT process are 2.75 times higher than for the Battelle CTL process. This is partly because the CTL has ~40% bio-content while the gasification/FT (and NG/FT) have none. On this basis, the pump-to-wheels (PTW) emissions for the Battelle CTL process are 40% less than either of these products on a MT-to-MT comparison; about 1.3 MT CO_2/MT product. To be comparable, both FT processes would have to emit less than 0.6 MT CO_2/MT product. This would represent 60% CO_2 control on the NG to fuel indirect process and greater than 90% on the coal indirect liquefaction. The uncontrolled emissions are slightly lower (3.56 vs. 3.79 MT CO_2/MT product) with those from conventional petroleum-to-jet fuel processes. Further, the 40% bio-content of CTL jet fuel from the Battelle process would help meet Section 526 of EISA 2007 goals without any CCS. If CCS were added to the highly-pure reformer shift-gas outlet, this could represent a further GHG emissions reduction of 0.2 MT CO_2/MT product from the Battelle CTL process, adding to its benefit.

Table 99. Greenhouse Gas (GHG) Emissions (Petroleum Well-to-Wheels (WTW) Baseline: 3.79MT CO_2/MT Fuel)

GHG Emissions, Life-Cycle Basis	Battelle Direct CTL	Gasification/FT Indirect CTL
Coal-to-Syncrude, MT CO_2/MT Product	0.44	Not Applicable
Coal-to-Distillate, MT CO_2/MT Product	1.66	5.58
Coal-to-Fuel Combustion	3.56	7.77

12.0 PRODUCTS DEVELOPED

A number of products were developed under this project, as discussed below.

12.1 Technologies Developed

In addition to advancing the Battelle CTL technology to TRL 5, the following technologies were created (patent application filed) [34]:

- Conversion of heavy-oil byproduct to a high-value carbon product
- Conversion of non-coal carbonaceous feedstocks to fuels and/or high-value carbon products.

12.2 Publications

The following papers were presented at international coal conferences:

- Chauhan, Satya P., "Direct Coal-to-Liquids (CTL) For Jet Fuel Using Biomass-Derived Solvents", presented at the 2015 International Pittsburgh Coal Conference, held in Pittsburgh, PA, October 5-8, 2015.
- Chauhan, Satya P., "Scale-Up of Battelle's Direct Coal-to-Liquids (CTL) Process For Jet Fuel Using Biomass-Derived Solvents", presented at the 2016 International Pittsburgh Coal Conference, held in Cape Town, South Africa, August 8-12, 2016.
- Chauhan, Satya P., "Direct Coal-to-Liquids (CTL) For Jet Fuel and Diesel Using Biomass-Derived Solvents", presented at the World CTX2017 Conference, held in Beijing, China, March 27-29, 2017.
- Chauhan, Satya P., "Direct Coal-to-Liquids (CTL) For Jet Fuel and Diesel Using Biomass-Derived Solvents", presented at the 2017 International Pittsburgh Coal Conference, held in Pittsburgh, PA, October 5-8, 2017.

12.3 Post-Graduate Education Supported

This grant supported two Ph.D. students and two postdoctoral associates at three different universities: (a) Pennsylvania State University; (b) University of Dayton; and (c) the Ohio State University.

12.4 Technology Transfer

Several potential licensees around the world were identified. Also, the Battelle CTL process was nominated for an R&D 100 Award, since it became available for licensing in 2016/2017.

13.0 CONCLUSIONS

The following conclusions can be drawn from this project:

- Two bituminous and one subbituminous coals were successfully converted to syncrude to provide for the desired ≥80% coal solubility using one of many identified biomass-derived solvents without the use of H_2 or catalyst. The typical coal conversion was over 85% on a moisture- and ash-free (MAF) basis.
- A total of 12 novel bio-solvents were identified that met the key liquefaction performance goals of the project, namely high coal solubility and low syncrude viscosity, both being indicative of excellent hydrogen transfer. The majority of these bio-solvents were superior than tetralin, which is the most researched and, until now, regarded the most effective hydrogen-donor solvent. The preferred bio-solvents are an order-of-magnitude lower in cost compared to tetralin.
- The coal liquefaction process was scaled up to 1 TPD, which represents TRL 5 targeted for this project. The pre-pilot-scale test results show a good correlation with laboratory-scale testing at Battelle. The pre-pilot test data was adequate to develop a conceptual, commercial-scale liquefaction-plant design.
- A 2-stage catalytic hydrotreatment/hydrogenation for upgrading the Battelle-CTL syncrude to jet and diesel was developed and demonstrated at pre-pilot scale. The Stage-1 catalyst removed more than 99.9% of nitrogen and sulfur removed and reduced oxygen below detection limit. In Stage-2, the hydrotreated syncrude was hydrocracked and further hydrogenated to obtain a distillate with high (60-70%) selectivity for jet-fuel boiling range. Nearly 100% of the distillate was in the diesel fuel range.
- A detailed characterization of the synthetic jet fuel from the Battelle CTL process indicated that:
    - up to about 30% of it could potentially be used for blending with a commercial jet fuel
    - a 20% synthetic, 80% commercial fuel blend was tested to demonstrate it met all standard fuel specifications for Jet A/A-1 fuels.
    - the synthetic diesel will likely not require any blending with a commercial diesel fuel.
- A conceptual plant design and an economic analysis following DOE/NETL methodology showed that the process is competitive for both syncrude and jet fuel (or diesel) applications at crude oil prices of less than $48/bbl. The selling price of jet fuel or diesel at the CTL plant is estimated to be $61/bbl or $1.46/gallon, compared to $95/bbl ($2.26/gal) for an indirect CTL plant using FT technology.
- The use of biomass-derived solvents in the Battelle CTL process brings about major process simplification, such as mild operating conditions and elimination of the need for gaseous hydrogen during liquefaction. As a result, the Battelle CTL process is economical at a much smaller scale for coal liquefaction (1000-2000 TPD) compared to

FT-based plants. The resulting capital cost for a 32,000 BPD jet fuel/diesel plant 36% for the Battelle CTL process compared to that for FT based processes.

- A greenhouse gas (GHG) emissions analysis shows that the life-cycle GHG emissions for coal-mine-to-fuel combustion are 3.56 MT CO_2/MT fuel, which is lower than the 3.79 MT CO_2/MT fuel for petroleum based well-to-wheels (WTW) for jet fuel.
- The WTW emissions for the uncontrolled FT process is 7.77 MT CO_2/MT fuel for FT based CTL, which is 2.2 times higher than for the Battelle CTL process.

This report demonstrates that the Battelle CTL meets the most important goal of this project, i.e., meeting the goal of Section 526 of EISA of 2007, for producing alternative jet fuel/diesel that has GHG emissions no worse than for petroleum-based fuels at a lower cost. The key reasons for this achievement for Battelle CTL process are (a) the ~40% reduction in hydrogen requirement for upgrading coal to jet fuel and (b) having a 40% bio-content in the fuel products. The complete elimination of the carbon capture and storage (CCS) requirements in the Battelle CTL process is a major achievement of this process since indirect CTL requires ~90% carbon capture for coal-to-jet fuel to have GHG emissions no worse than for petroleum-based jet fuel.

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- Professor Caroline B. Clifford served as a PI for PSU's bench-scale liquefaction efforts. Ron Wineck (a Ph.D. student), Dr. Xiaoxing Wang (a postdoctoral associate), and Sharon Miller made important contributions.
- Dr. Matthew DeWitt served as a PI for UDRI's effort on catalyst testing and jet-fuel characterization. Dr. John J. Graham and Linda Shafer performed much of the testing and analysis.
- Dr. Tim Edwards of Air Force Research Lab guided the jet-fuel characterization efforts by UDRI and also provided a commercially-used jet fuel for blending with synthetic fuel for the Battelle CTL process.
- Ed Koppola and Sanjay Nana carried out efforts at ARA.
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- Professor Bhavik Bakshi and Kyuha Lee (a Ph.D. student) of OSU carried out the GHG analysis.

Last, but not least, the authors greatly appreciate the efforts of the following Battelle research leaders, all of whom are now retired: (a) Dr. Herman Benecke; (b) Nick Conkle; (c) Russell K. Smith; and (d) Marty Zilka.

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LIST OF ACRONYMS AND ABBREVIATIONS

ABP	Atmospheric Boiling Point
ACS	American Chemical Society
AIChE	American Institute of Chemical Engineers
AR	As received
ARA	Advanced Research Associates
Bbl	barrel, 42 U.S. gallons
BPD	Barrel per day
CBTL	Coal-biomass to liquid
CCS	Carbon Capture and Storage
CH	Catalytic Hydrothermolysis
CSTR	Bench-Scale Liquefaction Reactors
CTD	Coal Tar Distillate
CTL	Coal-to-Liquids
DBT	Dibenzothiophene
DCL	Direct Coal Liquefaction
DMF	Dimethylformamide
DOE	Department of Energy
EDS	Exxon Donor Solvent
FeS	Troilite
FSI	Free Swelling Index
FT	Fischer Tropsch
GC-MS	Gas Chromatography–Mass Spectrometry
GCxGC	Comprehensive Two-dimensional Gas Chromatography
GHG	Greenhouse Gas
GHSV	Gas Hourly Space Velocity
HCR	Hydrocracking
HDA	Hydrodearomatization
HDM	Hydrodemetallization
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
HDT	Hydrotreating
LHSV	Liquid Hourly Space Velocity
MAF	Moisture- and Ash-Free
MF	Moisture-Free
MT	Metric ton (tonne)
MTPD	Metric ton (tonne) per day
N	Nitrogen
NDA	Non-disclosure Agreement
Ni	Nickel
NiO	Nickel oxide
NiW	Nickel-Tungsten
NMR	Nuclear Magnetic Resonance

O	Oxygen
ODSA	Ohio Development Services Agency
PAH	Polynuclear Aromatic Hydrocarbons
Pd	Palladium
PI	Principal Investigator
PMP	Project Management Plan
PSU	Pennsylvania State University
Pt	Platinum
PTW	Pump-to-Wheels
RCTD	Recycle Coal Tar Distillate
S	Sulfur
SBO	Soybean Oil
SiC	Silicon carbide
SIP	Synthesized Iso-Paraffins
SPK	Synthetic Paraffinic Kerosene
STP	Standard Temperature and Pressure
TEA	Techno-economic Analysis
THF	Tetrahydrofuran
TPD	Ton per day
TRL	Technology readiness level
UDRI	University of Dayton Research Institute
USAF	United States Air Force
W	Tungsten
WFE	Wiped Film Evaporator
WTW	Well-to-Wheels
WTP	Well-to-Pump
WV	West Virginia
WVU	West Virginia University

APPENDIX A

LITERATURE REVIEW OF CATALYSTS FOR UPGRADING COAL-DERICED SYNCRUDE

Liquid fuels can be produced from coal through direct coal liquefaction (DCL) processes at 450-500 °C under 15-30 MPa hydrogen in a suitable solvent with appropriate catalysts. [1-5] In many processes, the solvent used can facilitate the heat and mass transfer during chemical reactions, and function as a hydrogen donor by shuttling hydrogen from the gas phase to the coal. Catalysts were often used to increase the rates of the desirable reactions such as the cracking, hydrogenation, and oxygen/nitrogen/sulfur removal reactions. Direct coal liquefaction was developed as a commercial process in Germany based on research pioneered by Friedrich Bergius in the 1910s (so-called the Bergius process). Table A-1 summarizes the DCL processed developed in different countries [2-5] and the operating parameters and experimental results of four major DCL processes are shown in Table A-2. [2-6]

Catalysts were employed in almost all of the DCL processes developed. Iron-based catalysts, such as pyrite (FeS_2), troilite (FeS), pyrrhotite (Fe1-xS), iron oxide, iron sulfate, iron hydroxide and other iron resources, have been studied extensively due to their low costs and environmental tolerance. It is widely accepted that pyrrhotite is the most active form for iron sulfide catalysts. The iron-based catalysts could promote coal pyrolysis by markedly reducing the pyrolysis activation energy [7]. The major role of an iron-based catalyst in DCL is to promote the formation of activated hydrogen atoms and accelerate the secondary distribution of hydrogen atoms in the whole reaction system [8]. It was widely recognized that a highly dispersed catalyst can be superior to a supported catalyst, because the dispersed catalyst has an intimate contact with the surface of coal particles, which facilitates the activation and transfer of hydrogen to the coal-derived fragments and reactive sites. Accordingly, finer particles and a higher dispersion of the catalyst species would lead to a higher catalytic activity [8-11].

In addition to the Fe-based catalysts discussed above, Mo, Co and Ru were also tested as the catalysts for DCL. The results also implied that there were synergistic effects between the Ni and Mo catalysts [12-13] on promoting coal conversion and oil yield. Another type of novel catalysts for DCL is SO_4^{2-}/MxOy solid acid, such as SO_4^{2-}/Fe_2O_3 and SO_4^{2-}/ZrO_2 [14-15]. The solid acid could be a bi-functional catalyst for pyrolysis and hydrogenation. The use of SO_4^{2-}/ZrO_2 catalyst in the DCL of Shenhua coal at 400 °C and 4.0 MPa H_2 resulted in a coal conversion and (gas + oil) yield, up to 76.3% and 62.5%, respectively, much higher than those obtained with FeS or (FeS + S) catalyst under the same conditions.

Table A-1. Summary of major DCL processes developed around the world [2-5].

Country	Process	Reactor	Catalyst	Cap.(t/d)	Time
USA	SRC-I	Coal slurry dissolver	–	6	1974
	SRC-II	Coal slurry dissolver	–	50/25	1974 – 1981
	EDS	Entrained-bed	Ni/Mo	250	1979 – 1983
	H-Coal	Fluidized-bed	Co-Mo/Al_2O_3	600	1979 – 1982
	CTSL	Fluidized-bed	Ni/Mo	2	1985 – 1992
	HTI	Suspended-bed	GelCat^{TM}	3	1990s
Germany	IGOR	Fixed-bed	Co-Mo/Al_2O_3	200	1981 – 1987
	PYROSOL	Counter-current	–	6	1977 – 1988
Japan	BCL	Fixed-bed	Co-Mo/Al_2O_3	50	1986 – 1990
	NEDOL	Fluidized-bed	Nature pyrite/ Co-Mo/Al_2O_3	150	1996 – 1998
USSR	LSE	Stirred tank-type, fluidized-bed	–	2.5	1983 – 1995
UK	CT-5	–	Mo	7	1986 – 1990
China	Shenhua	Suspended-bed	Fe-based	7,000	Start-up 2008

Table A-2. The operating parameters and experiment results of some major DCL processes [2-6].

Process	HTI	IGOR	NEDOL	Shenhua
Coal	Shenhua	Xianfeng lignite	Shenhua	Shenhua
Temp. (°C)	440-450	470	465	455
Pressure (MPa)	17	30	18	19
Space Velocity (t/m^3/h)	0.24	0.60	0.36	0.70
Conversion (%, daf coal)	93.5	97.5	89.7	91.7
C_4+ oils (%, daf coal)	67.2	58.6	52.8	61.4
Residues (%, daf coal)	13.4	11.7	28.1	14.7
H_2 consumption (%, daf coal)	8.7	11.2	6.1	5.5

Catalytic hydrotreating (HDT) plays an essential role in the DCL processes for the conversion of heavy feedstocks and for improving the quality of oil products. Hydrotreating refers to a variety of catalytic hydrogenation processes, which saturate unsaturated hydrocarbons and remove S, N, O and metals from different petroleum streams in a refinery. Hydrotreatment usually implies only small changes in overall molecular structure but hydrocracking (HCR) reactions often occur simultaneously and may in fact be desired. Depending on the nature of the feed and the amount and type of the different heteroatoms (i.e., different reactivities compounds), specific hydrotreating processes have been developed. The reactions occurring during hydrotreating are hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), hydrodearomatization (HDA), hydrodemetallization (HDM), and hydrodeasphaltenization (HDAs). For a long time, the most important hydrotreating reaction has been the removal of sulfur from various fuel fractions. Consequently, hydrotreating catalysts are also commonly referred to as hydrodesulfurization (HDS) catalysts. Typical hydrodesulfurization catalysts consist of molybdenum supported on an alumina carrier with either cobalt or nickel added as promoters for improving the catalytic activity.

The most common combinations of active elements in hydrotreating catalysts are the CoMo, NiMo and NiW families [16] such as Criterion NiMo SynCat-37, Grace NiMo AT-505 catalysts. The concentration by weight of the metals is usually 1-4% for Co and Ni, 8-16% for Mo and 12-25% for W. Typical support materials are alumina, silica-alumina, silica, zeolites, kieselguhur, and magnesia, with surface areas in the 100-300 m^2/g range. CoMo catalysts are excellent HDS catalysts but are somewhat less active for HDN and hydrogenation of aromatics. As a result, the CoMo catalysts give relatively low hydrogen consumption. NiMo catalysts, on the other hand, are very good HDN and hydrogenation catalysts but give rise to higher hydrogen consumption. Consequently, NiMo catalysts are often preferred for treating unsaturated feeds. An increase in the selectivity of heteroatom removal vs. hydrogenation can be achieved for alumina-supported catalysts by addition of P [9-14]. Of the three combinations mentioned above, the NiW catalysts have the highest activity for aromatic hydrogenation at low hydrogen sulfide partial pressures [23-25] and are also active for HCR, but their use has been limited due to the higher cost.

In hydrotreating, reaction rates are often influenced by diffusion in the catalyst pores. Thus, the choice of catalyst particle size and shape, as well as the geometry of the pore system, is important [16]. This is especially true in the treatment of heavier feeds, where the reactions may be limited by diffusion of reactants and products in and out the pore system. The diffusion restrictions will in general become more severe during operation due to the deposition of metals and coke at the pore entrances. Therefore, for real application, there is a tendency to use small catalyst particles with relatively large pores and shapes, which expose appreciable external surface area [26-27]. For a given equivalent diameter, these shapes, especially rings, have the advantage of minimizing the pressure drop across the reactor [27]. Song's Research Group at PSU has also explored novel dispersed (unsupported) sulfide catalysts for deep desulfurization of more refractory sulfur compounds in middle distillate fuels. High metal loaded NiMo and CoMo/MCM-41 catalyst show high HDS activity of 4,6-DMDBT at 300 and 325°C. Specifically, NiMo/MCM-41 has higher HDS activity than other catalysts and even higher than commercial NiMo catalyst (Cr424), which contains 14wt% MoO3 and 3wt% NiO on alumina before sulfidation.

Metal phosphides are a novel catalyst group for deep hydrotreating and have received much attention due to their high activity for HDS and HDN [28-36]. Transition metal phosphide catalysts have been studied in hydrogenation reactions [37-40] but research focusing on hydrotreating has been carried out only recently. There has been heightened interest in new supports for HDS catalysts in recent years, due to the need to improve catalytic activity, and the availability of new materials of high surface area with new properties. The alteration of catalytic activity by the support may arise as a result of changes in dispersion and morphology of the active component and possible metal–support interactions. Supported Ni phosphide catalysts were also tested by Song's Group at the same conditions as the NiMo and CoMo catalysts were. Ni_2P/MCM-41 had higher activity than the other phosphide catalysts and Ni_2P/Al_2O_3 had a very high HYD/DDS ratio, while CeO_2 supported Ni phosphide had a lower ratio [35].

It should be pointed out that the coal-derived liquids, especially through the process developed in this project using bio-oil as the H-donor solvent, may have relatively high concentrations of oxygen-containing molecules which may include ethers, furans, carboxylic acids and phenols [41]. Conventional metal sulfide catalysts [42-46] and noble-metal catalysts were employed for hydrodeoxygenation (HDO) processes of bio-oil [47-48]. The metal sulfide catalysts are cheaper than noble metal catalysts, and they have good hydrogenation activity. However, because of the low sulfur content of bio-oil, an additional sulfiding agent is needed to maintain the hydrogenation activity of the metal sulfide catalysts or the hydrogenation performance of the metal sulfide catalysts will degrade due to the graduate loss of sulfide. In addition, these typical hydrodesulfurization catalysts such as $NiMoS/Al_2O_3$ and $CoMoS/Al_2O_3$ were found to quickly deactivate by coke deposition in HDO reactions because of the acidity of the reactant [49]. To the contrary, transition metal phosphides supported on neutral silica could be a promising class of new hydroprocessing catalysts [50-51] for HDO reactions.

In a summary, for a specific hydrotreating application with given feed and product specifications, the choice of catalyst is seldom only related to catalyst activity. Many other features are important, such as catalyst life, activity toward side reactions, and pressure drop build-up. Ease of activation, regeneration and price should also be considered. Furthermore, for certain applications, the optimum solution may be to use different types of catalyst in the same reactors. Catalyst selection thus generally requires a detailed study of the specific situation. In addition, the process may require the use of mixed or multiple beds of catalysts.

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APPENDIX B

CTL PROCESS DESIGN AND EQUIPMENT SIZING

APPENDIX C

CAPITAL COSTS ESTIMATION DETAILS

APPENDIX B: CTL Process Design and Equipment Sizing

The process design is adapted from the CTL Chemcad model using 47 tonnes/hr of coal as its basis and is used for the process conceptual development and equipment sizing. Flow rates from the ChemCAD model were used to estimate the throughput needed for each unit operation. Pumps and heat exchange surfaces were sized mostly from the values provided by the ChemCAD model. Tanks were sized for process inlet and outlet storage using maximum flow rates in the process and estimated duration of storage.

All Figures referenced below are inserted at the end of Appendix B.

Area 100 – Tank Farm

Figure B-1 shows Area 100, the raw material tank farm. Quotes were obtained for all equipment in the raw material tank farm area. The storage tanks were quoted as field erected with the erection cost included. Foundations were to be completed by others. The suction heaters were selected based on flow and condensing steam on the tubes. If we use a thermal oil for heating, these could be undersized. Conversely, the thermal oil could be used to generate steam for the suction heaters. Pumps were sized based on the material balance and a nominal head of 60 ft of fluid. Rail car unloading stations could be dedicated to a raw material or multi-use. There was no need for spare equipment in this area.

Area 200 – Coal Prep

The coal preparation system is shown in Figure B-2. The plant is assumed to be located near a coal mine, with the coal being delivered to the plant property fence line. The coal handling is sized for 100 tons per hour to allow for some down time in the coal yard for maintenance, break time, and refueling the loader without interrupting the reactor flow. The continuous usage is 47 tonness per hour. The distribution conveyor was sized based on 150 m of length for a conveyor to the coal pile. The pile collection conveyor was also assumed to be 150 m in length. A coal elevator would be used to lift the coal up to the storage silos, using buckets and running at 53 m per minute. Three raw coal storage silos are based on three days of inventory, with each silo holding 1200 tons of coal. A crusher feed conveyor is will feed the Impact Dryer System and is sized for a length of 61 m.

The Impact Dryer System was quoted by the Williams Patented Crusher and Pulverizer Company. The system consists of a feed system, crusher and classifier, cyclone separator, baghouse main circulating fan, heater with burner and an exhaust fan. Ground coal product is estimated to contain about 1% moisture with about 99% passing through a 40 mesh screen. This is a finer size than the 8 mesh coal used in the lab scale testing.

The crushed coal will be transported to two finished coal storage bins, each holding 1200 tons, using a 76 m belt conveyor with walkway. Two 30 m long crushed coal conveyor will feed the mix tank feed bins located above the mix tanks. The crushed coal will discharge from the feed bin through a rotary valve, onto a controlled flow feed bin conveyor. This crushed coal will then drop onto the coal distribution conveyor and be diverted to the mix tanks when making a batch of slurry to feed the reactors.

Conveyor costs were obtained from the Matches website (http://www.matche.com). Costs are in 2014 dollars, and are based on a 1 m wide conveyor running at 150 m per minute. Coal storage bin costs were also obtained from the Matches website.

Spare conveyors were not added to the capital costs. It is assumed that there would be spare parts purchased for needed repairs or replacements, such as motors, pulleys, bearings, and belts. The impact crusher would also have spare parts that would be expected to be stored on site, such as motor, bags, crusher bits, bearings.

Area 300 – Coal Slurry Mix Tanks

Figure B-3 shows the coal slurry mix tanks system. Four 38,750 l mix tanks will be required for the reactor feed system. They are batch filled will hold about 20 minutes of slurry each. It is assumed that the coal can be mixed with the coal tar distillate in 20 minutes. The four stages for the mix tanks will be:

1. Fill with liquid (20 min)
2. Start agitator, add powdered coal (20 min)
3. Mix (20 min)
4. Feed reactors (20 min)

The slurry will be mixed with the yellow grease, brown grease and tall oil in the suction line of the reactor feed pumps. Each reactor feed pump will pull from a common suction line to a reactor train. Feed to the reactor will be measured and controlled by the speed of the reactor feed pump. The reactor feed will be heated to the reaction temperature with reactor train feed heat exchanger, using a thermal fluid. It is assumed that we will be able to use the 500+ product from the reaction as the thermal fluid for the high temperature requirements.

Quotes were obtained for the mix tank, the slurry pump and the heat exchanger. The agitator was estimated using the matches website based on preliminary horsepower requirement. The reactor feed heat exchanger pump cost was also estimated using the matches website.

Installed spare parts include a feed mix tank with agitator, a reactor feed pump, reactor train feed heat exchanger, and its thermal fluid circulating pump.

Area 400 – Reactors

Figure B-4 and Figure B-5 show the reactor system process flow diagram. Overall single stage yield for 30 minutes in both pilot and laboratory was determined to be >85 percent, with values of >90 percent routinely obtained with the solvent combinations defined. A series of 3 trains of 4 CSTRs, each 100,000 L volume, was evaluated for operations. Based on first order kinetics, the reactors would give enough volume to react to about 93% based on an 85% single-stage yield. On this basis, an overall coal yield of 90% was taken as a reasonable value. Even though reaction times as low as 10 minutes were demonstrated in the laboratory with greater than 85% conversion, an average of 30 minutes of residence time was used for the reactor train. Two trains were sufficient for operation; a third train was used in costing to allow the process to achieve 90% on-stream time.

The reactor flow rate is 181,670 liters per hour. For a 30 minute residence time, the required reactor volume is 90835 liters. Using three reactor trains consisting of 4 reactors each, the required liquid reactor volume is 7570 liters each. The nominal reactor volume is 10,000 liters to allow for sufficient free board. Reactors are to be operated at 400 C and 405 psig. The first reactor will be operated at a higher pressure sufficient to overcome the pressure drop which allows for the flow to cascade from the first to the fourth reactor. Reactor pressure will ultimately be controlled by the valve on the slurry discharge line The reactors are connected by a pipe which Is split to feed both the top and bottom of the reactor. This allow the solids to be introduced to the bottom of the reactor and also allows the non-condensable gassed generated to pass from one reactor the next.

The fourth reactor in each reactor train will have a partial condenser, reflux vessel, reflux pump, reflux heater with a thermal fluid circulating pump, and a final condenser. The partial condenser will cool the vent stream using thermal fluid exiting the feed heater. The condensed fluid will then be heated and returned to the fourth reactor.

Further process development may indicate that condensate should be returned to the first reactor, if the components are to be incorporated into the reaction products and need more residence time. The slightly higher pressure in the first reactor may keep the reflux in the liquid phase longer to allow for the reactions to proceed.

The reactor products contain about 4.5% solids consisting of principally coal ash, unreacted coal solids, and silica. The product will flow from the reactors through a partial cooler to reduce the chance of vapor flashing through the pressure reducing valve. This high pressure letdown from 400 psig to about 150 psig is expected to wear and will need to be rebuilt periodically. An installed spare with isolation valving is estimated.

Quotes were obtained for the reactors, the partial condenser, and the reflux heater, product cooler, and reflux pump. The reflux tank cost was ratioed off of the reactor cost using the volume raised to the 0.6 power. The estimated final condenser surface area was within 10% of the partial condenser surface area, so the same cost was used for both. The agitator was estimated using the matches website based on preliminary horsepower requirement. The reactor jacket pump cost was also estimated using the matches website.

Installed spare equipment includes an additional pump for each pump in the reactor area, and two reactors with agitators.

Area 500 – Hydrocyclone and Centrifuge

A combined hydrocyclone/centrifuge system was chosen for the process. Figure B-6 shows the hydrocyclone process flow diagram. Figure B-7 shows the centrifuge process flow diagram. The reduced pressure product from the reactors will flow to the high pressure separator tank, allowing any flashed vapor to separate, before flowing to the hydrocyclone. The hydrocyclone will separate the solids in the product while still maintaining the high temperature of the product. The design is based on 90% of the solids contained in 25% of the total hydrocyclone flow in the hydrocyclone bottoms product. Quoted performance based on an assumed particle distribution is much better that the design and may simplify the process. The reported performance would need to be proved at the pilot plant level. The hydrocyclone lights will feed the first stage of the evaporator.

Evaporator bottoms from each train will be mixed with the hydrocyclone bottoms from each train in a common centrifuge feed tank. This heavy solids product will be pumped with a slurry pump through a cooler and through a centrifuge. The centrifuge centrate will be the 500+ product while the centrifuge bottoms will be the heavy solids product.

If the hydrocyclone proves to be as efficient as quoted, the hydrocyclone bottoms may be the heavy solids product directly. This would contain some portion of the product oil, as it was not driven off before the solids separation.

If the 500+ liquid can be sold with the 3% solids, the centrifuge may be eliminated. If not, the centrifuge may be required for just the 500+ fluid, reducing the size of the centrifuge from 53 m3/hr to 8 m3/hr.

Quotes were obtained for the high pressure separator tank, the hydrocyclone, centrifuge feed tank and the centrifuge feed pump. The centrifuge feed cooler was ratioed from a previous quote. The agitator was estimated using the matches website based on preliminary horsepower requirement. The centrate pump cost was also estimated using the matches website.

Installed spare equipment for this area include a complete hydrocyclone train and a redundant centrifuge system.

Area 600 – Evaporator

Figure B-8 shows the system used to separate the <500°C product for fuel processing from the >500°C product. The evaporator system is based on a triple effect evaporator, using vapor from two stages as the heating medium for two following stages. The selection of three evaporators will need to be proven and optimized in a further design effort. Latent heats at each pressure and temperature, along with any boiling point rise will need to be determined in further research.

Each effect is sized at 7570 liters which allow about 50% of the volume for vapor separation. Each effect will require an external heat exchanger and circulating pump, as a jacket would not provide sufficient heat to accomplish the evaporation load.

Quotes were obtained for the vessels and the vacuum pump. Heat exchangers surface areas were determined using a conservative overall heat transfer coefficient. The heat exchangers were estimated using the matches website based on surface area and pressure. The pump costs were also estimated using the matches website.

Installed spare equipment for this area include a second pump for each instance where a pump is required and a spare vacuum pump.

Area 700 – Product Tank Farm

The product tank farm (Figure B-9) is sized to accommodate seven days of production. The product oil is assumed to not need a suction heater to pump to the rail car loading station. Four rail loading stations are included in the estimate. Four 182 m3/hr load out pumps will be manifolded to the 15 – 380,000 liter product oil storage tanks. The 500+ liquid product will require a suction heater and local pump for each of the 4 - 380,000 liter storage tanks. The heavy solids product will also require a suction heater and local pump for each of the 4 380,000 liter storage tanks. The pump out rate for these two fluids will be dependent on the suction heaters' ability to reach a sufficient pumping temperature. The maximum size suction heater offered by the vendor was selected. Recycle from the loading station to the tanks should be provided to prevent slurry settling and maintain an acceptable pumping temperature.

Quotes were obtained for the storage tanks, suction heaters, slurry pumps, and the load out station. 500+ liquid product pump costs were estimated using the matches.com website.

Area 800 - Process Utilities

A process furnace, scrubber, stack, and support equipment were defined and costed to provide energy to the syncrude process. A hot oil circulation and storage system was defined. The data from the ChemCAD flowsheet on process flows was used to size the items for cost.

A cooling tower and circulation system was incorporated to provide process cooling that was not provided by the air coolers. Air compression would likely be required for instrumentation operation and some other miscellaneous uses. A separate air compressor is not costed in direct equipment but would be provided through the service facilities allocations used.

Process Concerns and Potential Alternates

Thermal fluid

The process temperature requirement of 400°C is above is at the maximum use temperature of commercially available thermal fluids. The simulation uses a thermal fluid of 475°C to allow for a temperature difference to transfer the heat to the reactants. We are assuming that our 500+ product could be used as the thermal fluid for the reactors. There are cooling needs in the process that are suited to using a cooler thermal fluid, operating between 38°C and 60°C. The simulation indicates that the 500+ fluid would have a high viscosity at the cooling temperatures. Further evaluation of the reactor heating system should be addressed in the future. Thermal cooling could be by using air cooled fintubes directly, or using an evaporative cooler, which may reduce energy integration. The heating duty could be accomplished with an eutectic nitrate salt circulating system.

Centrifuge and hydrocyclone

A hydrocyclone was selected in the design to allow for solids separation without cooling to the centrifuge maximum temperature of 100°C. This allowed for the bulk of the fluid to pass to the evaporator with requiring the heat duty to bring it up to the evaporation temperature. The disadvantage is that the heavy solids product will have some product oil remaining in it, unless the heavy solids is stripped in a further processing step.

The evaporator bottoms will also carry a small amount of solids, and could be passed through a centrifuge or filter to separate the solids from the 500+ liquid or combined with the heavy solids product and sent to the centrifuge.

Start Up and Shutdown Requirements

The start-up and shutdown requirements have not been examined fully and may require additional tanks to hold flush out liquids and partially reacted fluids. Flush out with other materials, such as CTD, may also require additional material purchase which is not reflected in tankage. Tankage may not be required, and this flush may be able to be handled directly with 1-2 rail cars of material.

Area H – Hydrotreater

Because the goal of this study was to evaluate the cost of fuel and carbon emissions from this process, a hydrotreater area was defined. A detailed design was not performed; instead, verbal quotes on a similar hydrotreater (4500 bbl/day) and a natural gas reformer were defined for this process. As mentioned below, a gasifier for the solid waste was also briefly considered, and may make sense if there is not a market for the material. At this time, Quantex is evaluating the market for the material and has recommended a price for that material.

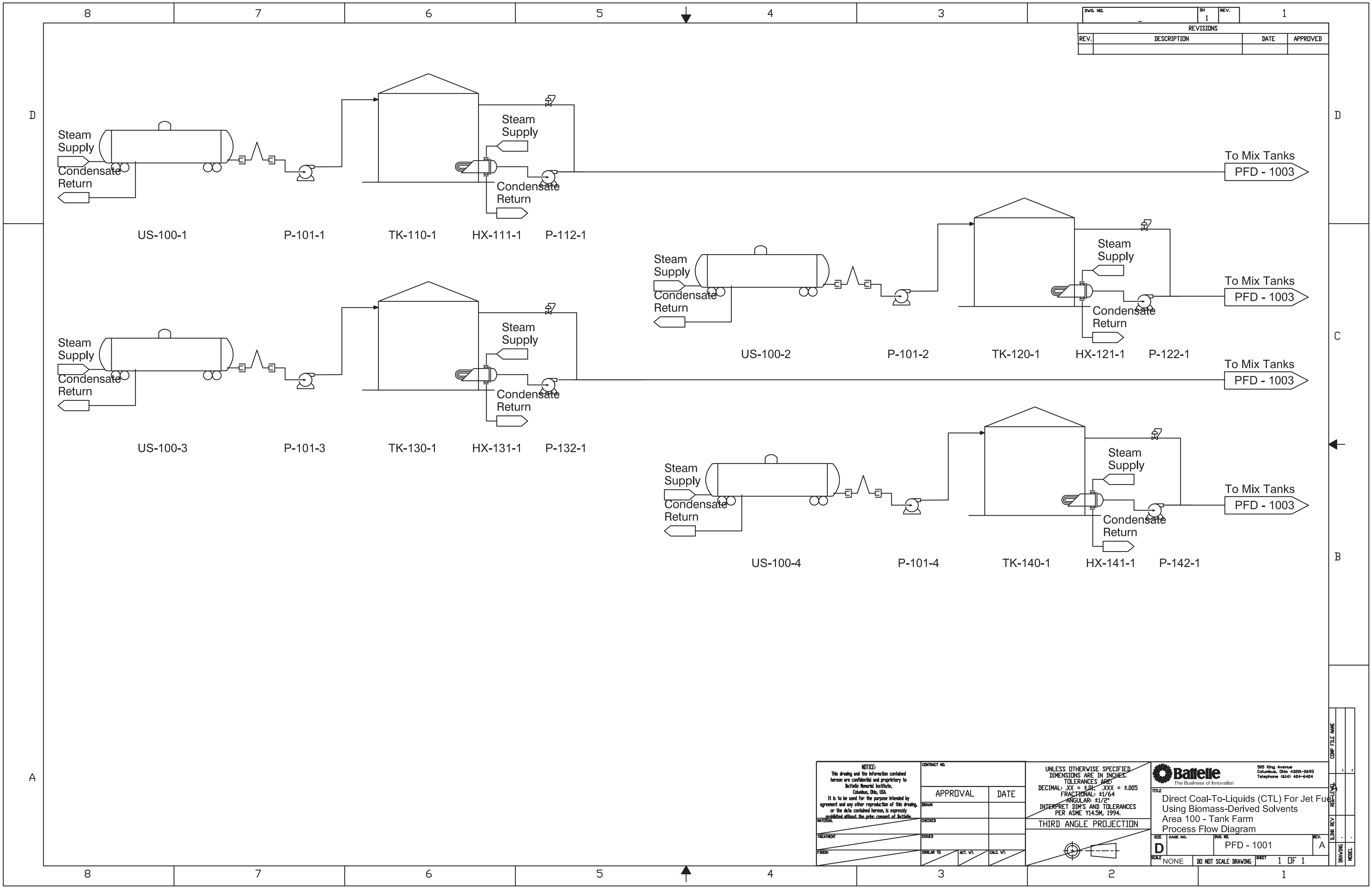

Figure B-1. Raw Material Tank Farm Process Flow Diagram

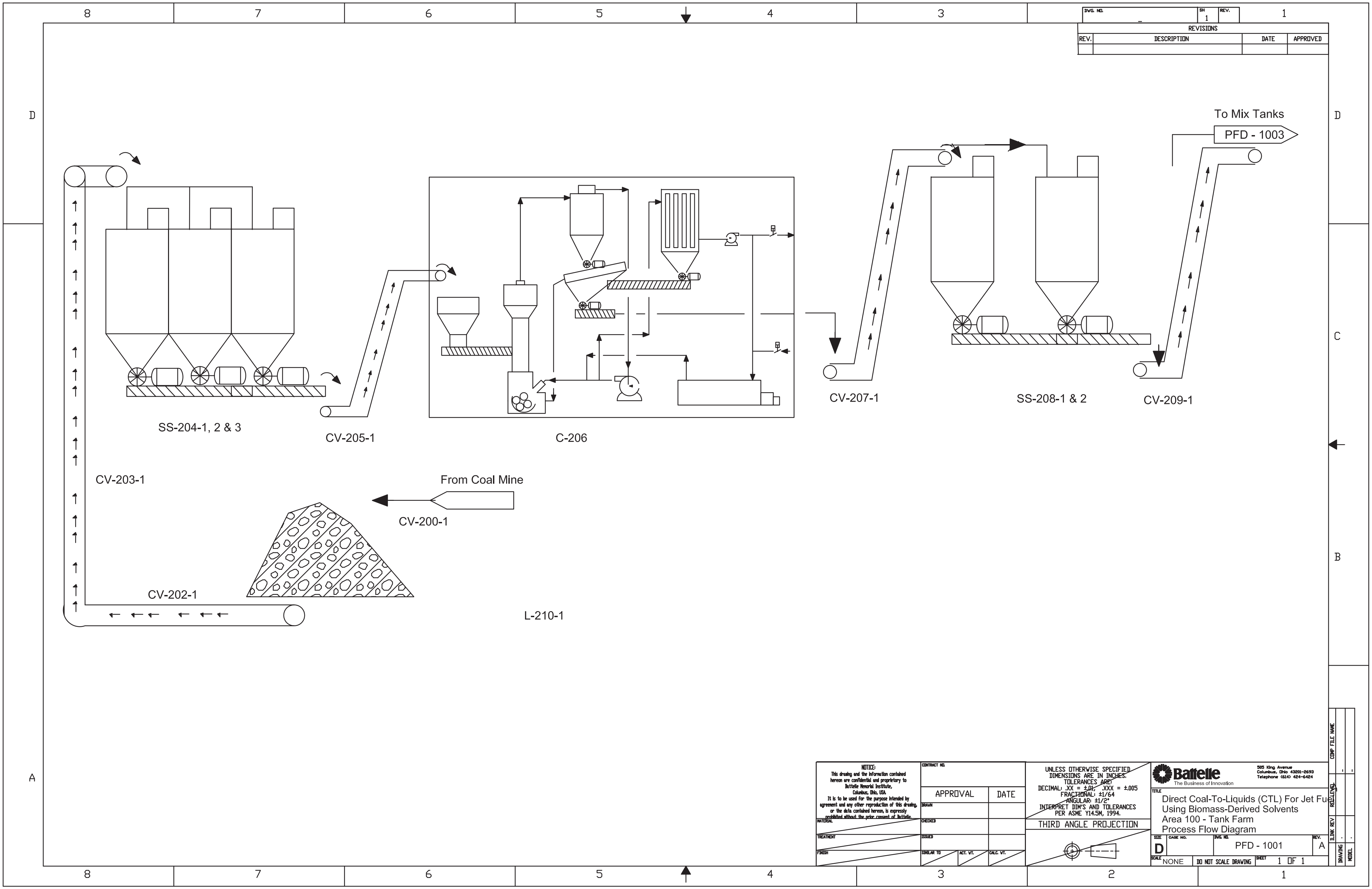

Figure B-2. Coal Preparation Process Flow Diagram

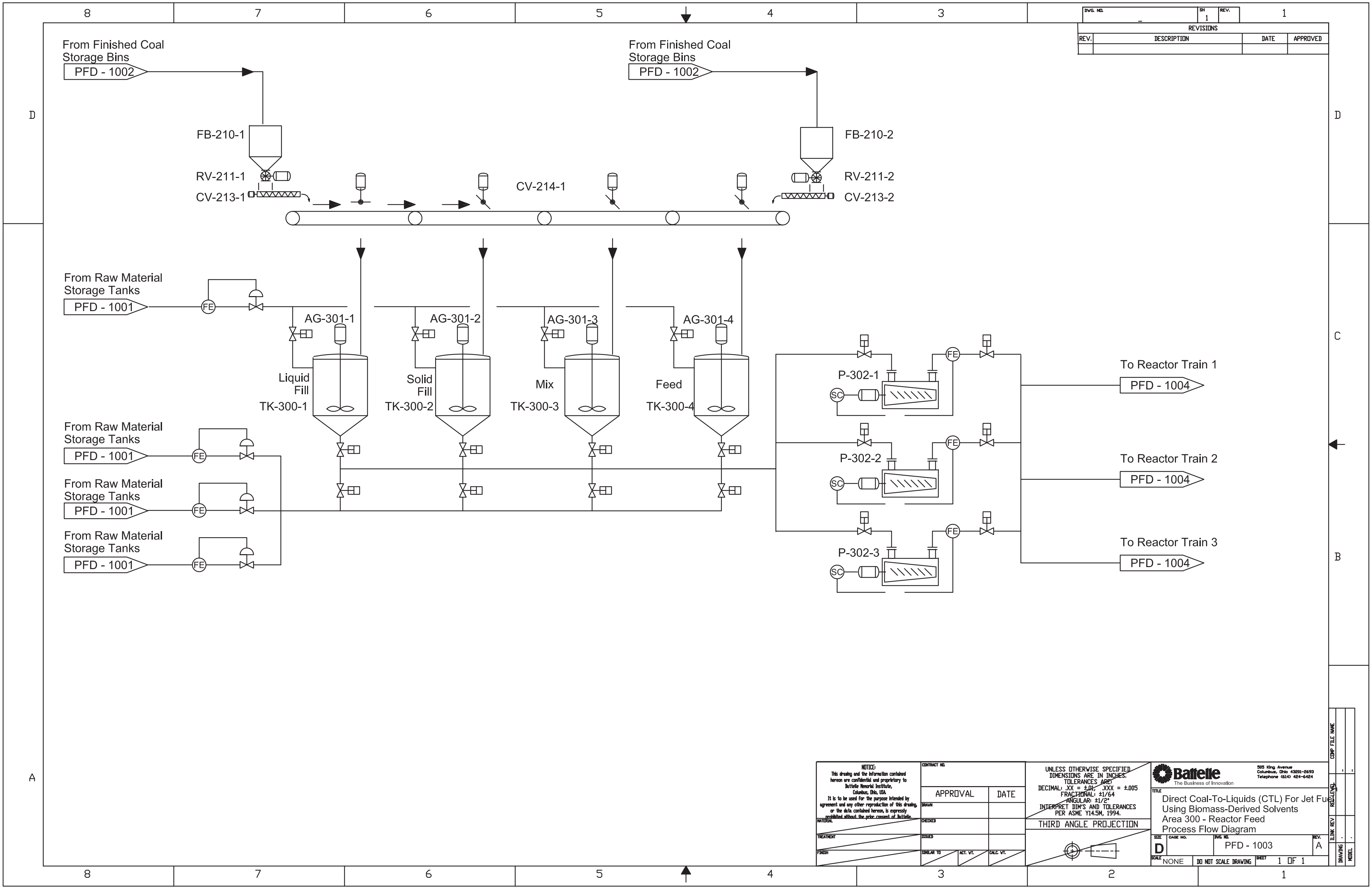

Figure B-3. Coal Slurry Mix Tanks Process Flow System

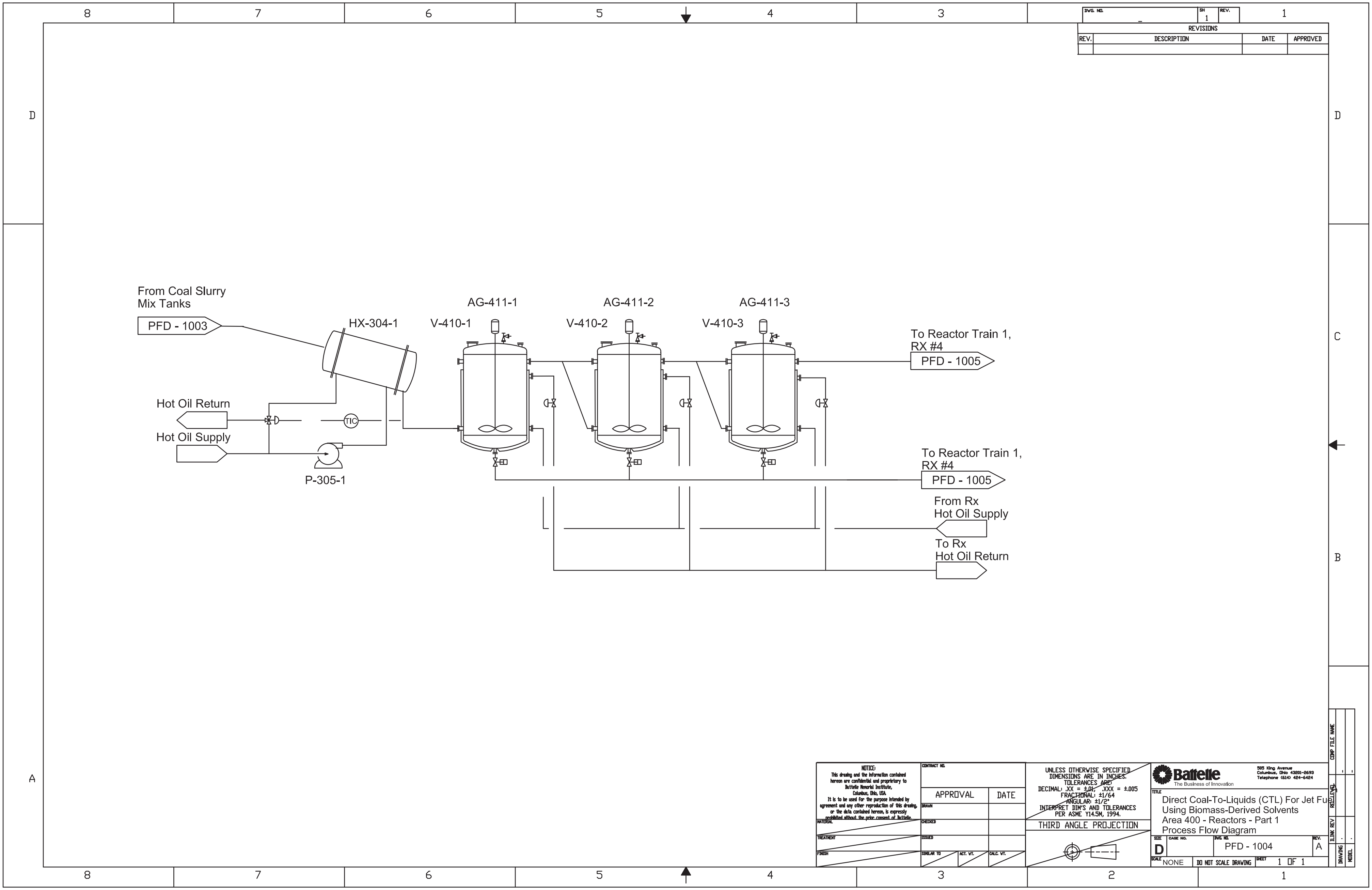

Figure B-4. Reactor Process Flow Diagram – Part 1

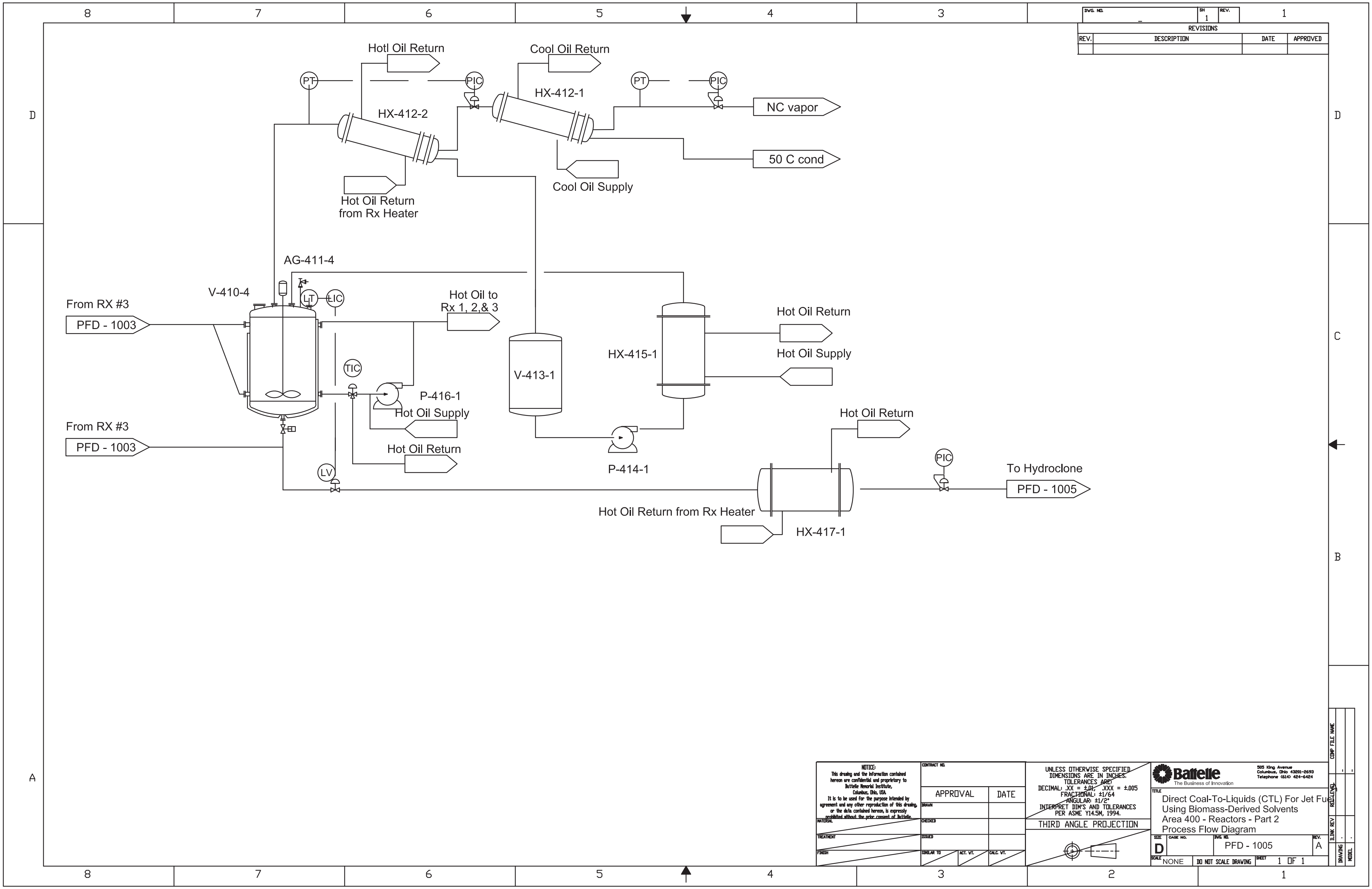

Figure B-5. Reactor Process Flow Diagram – Part 2

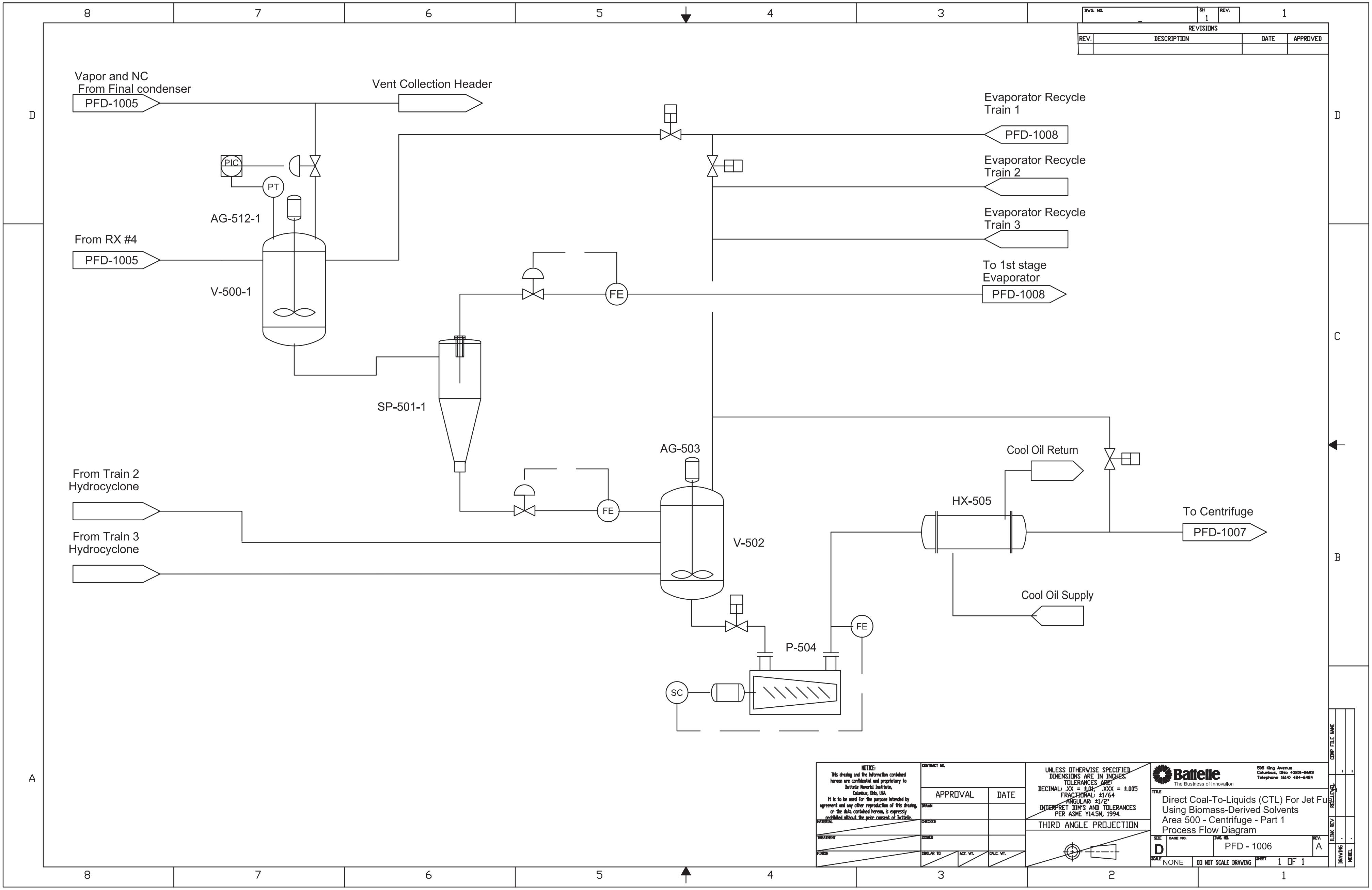

Figure B-6. Hydrocyclone Process Flow Diagram

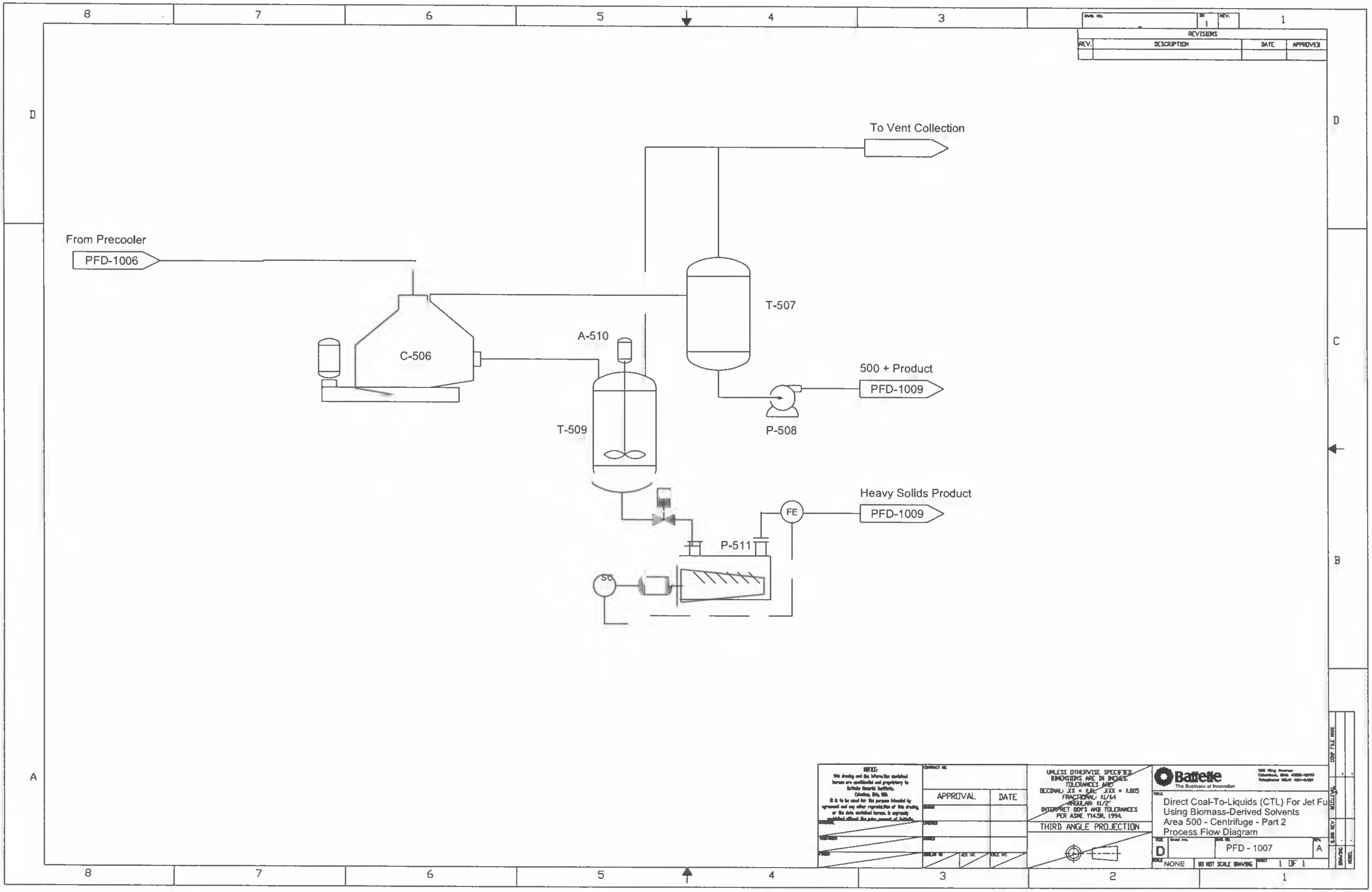

Figure B-7 Centrifuge Process Flow Diagram

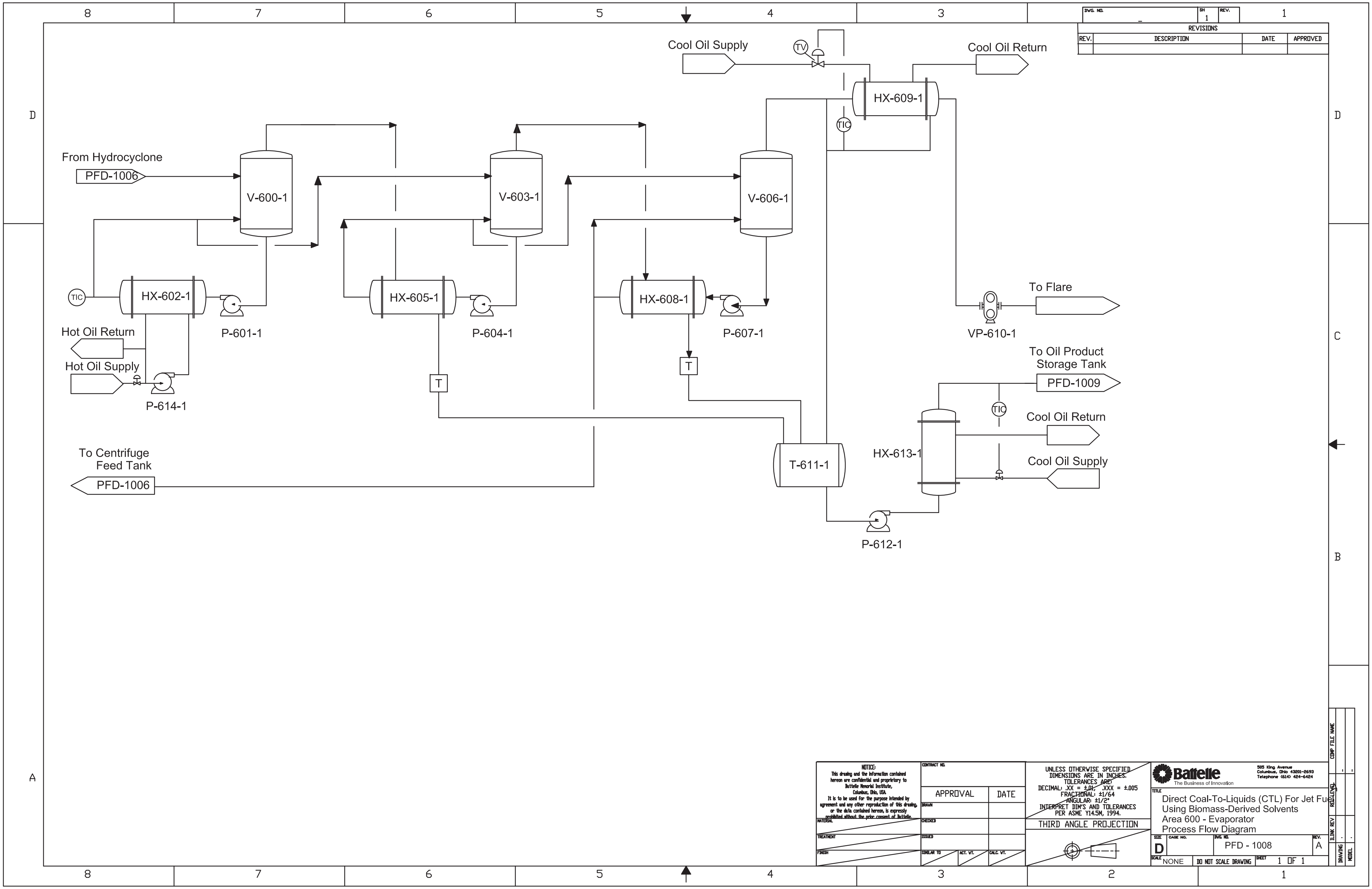

Figure B-8. Evaporator Process Flow Diagram

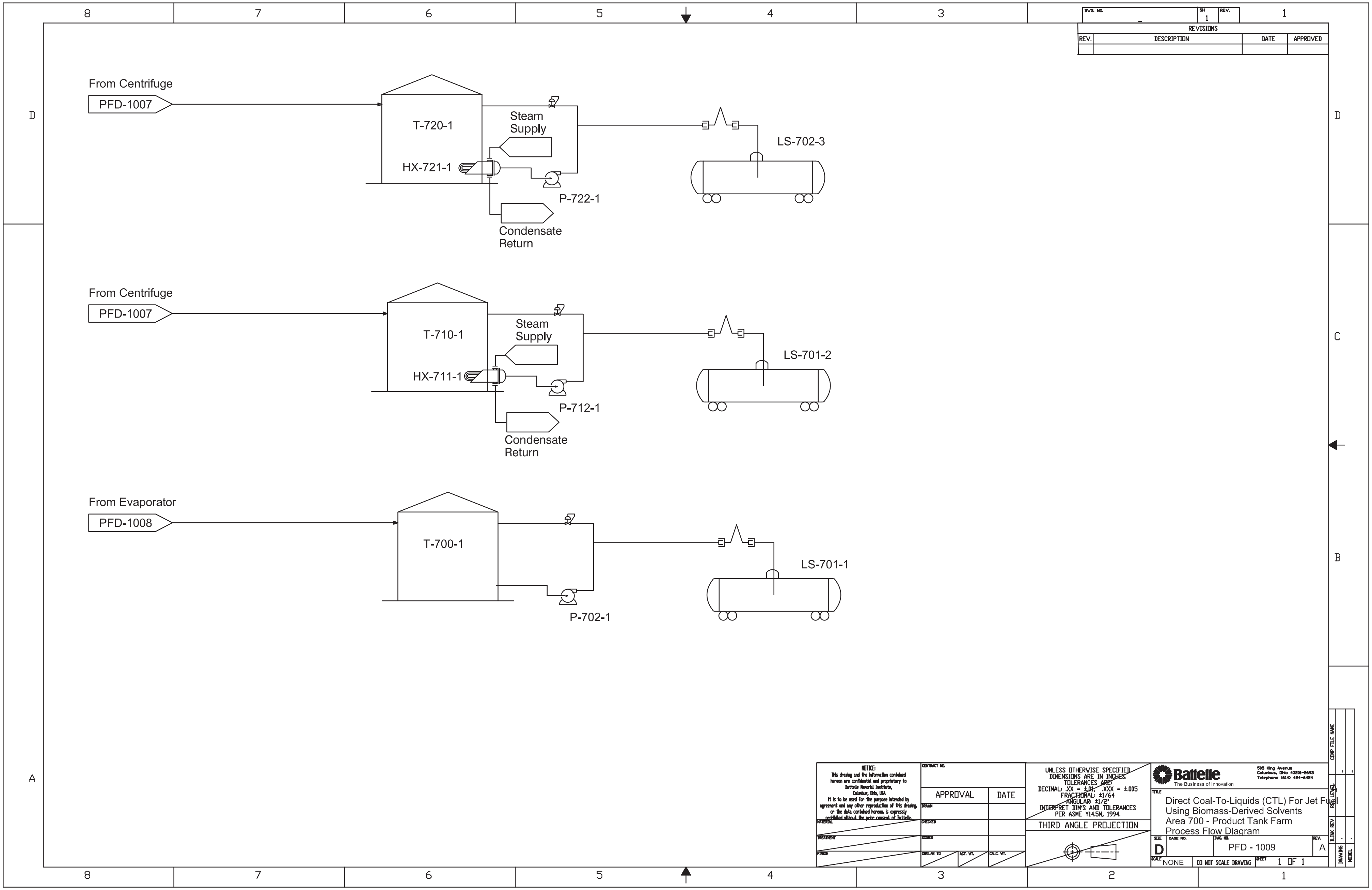

Figure B-9. Product Tank Farm Process Flow Diagram

APPENDIX C: Capital Costs Estimation Details

Per the RFP, the cost estimate is stated in June 2011 dollars. Various indexes are available to factor costs based on time. The Chemical Engineering Plant Cost Index (CEPCI) has been used to factor the capital costs obtained to June 2011 dollars. This index is more aligned to chemical equipment costs than a Marshall and Swift index or an RSMeans index. Indices used in this evaluation are shown in Table C-1.

Table C-1. Chemical Engineering Plant Cost Index.

Published in Chemical Engineering Magazine (various issues)	
Time Frame	**CEPCI®**
1998	389.5
1999	390.6
2000	394.1
2001	395.4
2001	394.3
2002	395.6
2003	402
2004	444.2
2005	468.2
2006	499.6
2007	525.4
2008	575.4
2009	521.9
2010	550.8
2011	585.7
2012	584.6
2013	567.3
2014	576.1
2015	556.8
2016	540.9

The Chemical Engineering Plant Cost Index (CEPCI) was used to take the current costs from quotes and factor it to June 2011 cost by using the ratio.

Equipment cost x (June 2011 CEPCI/May 2016 CEPCI) = June 2011 cost

Equipment cost x (588.9/543.5) = June 2011 cost

Example: Reactor cost, 60" I.D. x 192" LG. Vessel, 450 PSIG @ 932° F, w/ jacket = $194,100

$194,100 x (588.9/543.3) = $210,314

The Matches website estimates equipment costs in 2014 dollars. Equipment that was estimated using the Matches website uses the July 2014 CEPCI to yield a June 2011 equipment cost.

Equipment cost x (June 2011 CEPCI/July 2014 CEPCI) = June 2011 cost

Equipment cost x (588.9/576.1) = June 2011 cost

Example: Reactor Train #1 Jacket Pump, 400 gpm, 60 ft TDH, 10 hp, 6” discharge, steel = $16,200

$16,200 x (588.9/576.1) = $16,560

This study estimate is based on generating the equipment cost and using specific factors based on historical plant cost to predict the total installed cost of the equipment. A study estimate of this type should be within the range of 30% of the final cost of the plant. Factors have been developed for different types of plants, based on the primary state of the chemicals used, such as solids, liquids, gases and slurries. Material and labor factors for foundations, structural steel, buildings, insulation, Instruments, electrical, piping, painting, and other miscellaneous expenses are applied to the capital equipment cost to estimate the total installed cost of the equipment.

Table C-2. Distributive Factors for Bulk Materials

Cost Category	**Cost Type**	**Solids Handling Processes <400 °F**	**Liquid and Slurry Systems**		**Gas Handling Processes <400 °F**		**Gas Handling Processes >400 °F**	
			< 150 psig	>150 psig	< 150 psig	>150 psig	< 150 psig	>150 psig
		(%)	(%)	(%)	(%)	(%)	(%)	(%)
Foundations	*Material*	4	5	6	5	6	6	5
	Labor	133	133	133	133	133	133	133
Structural Steel	*Material*	4	4	5	5	5	5	6
	Labor	50	50	50	50	50	50	50
Buildings	*Material*	2	3	3	3	3	3	4
	Labor	100	100	100	100	100	100	100
Insulation	*Material*	---	1	3	1	1	2	3
	Labor	---	150	150	150	150	150	150
Instruments	*Material*	6	6	7	6	7	7	7
	Labor	10	40	40	40	40	75	40
Electrical	*Material*	9	8	9	8	9	6	9
	Labor	75	75	75	75	75	40	75
Piping	*Material*	5	30	35	45	40	40	40
	Labor	50	50	50	50	50	50	50
Painting	*Material*	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Labor	300	300	300	300	300	300	300
Miscellaneous	*Material*	3	4	5	3	4	4	5
	Labor	80	80	80	80	80	80	80

Note: DOE 1998, Extracted and Combined

Example of determining the total installed cost of the reactor from the escalated equipment cost is shown below.

Table C-3. Example of Determining the Total Installed Cost of the Reactor from the Escalated Equipment

Example :	**Reactor capital cost**				**=**	**$210,314**
Distributive Factors for Bulk Materials - Liquid and Slurry Systems						
Pressure		>150 psig				
		(%)				
Foundations	*Material*	6	x	$210,314	=	$12,619
	Labor	133	x	$12,619	=	$16,783
Structural Steel	*Material*	5	x	$210,314	=	$10,516
	Labor	50	x	$10,516	=	$5,258
Buildings	*Material*	3	x	$210,314	=	$6,309
	Labor	100	x	$6,309	=	$6,309
Insulation	*Material*	3	x	$210,314	=	$6,309
	Labor	150	x	$6,309	=	$9,464
Instruments	*Material*	7	x	$210,314	=	$14,722
	Labor	40	x	$14,722	=	$5,889
Electrical	*Material*	9	x	$210,314	=	$18,928
	Labor	75	x	$18,928	=	$14,196
Piping	*Material*	35	x	$210,314	=	$73,610
	Labor	50	x	$73,610	=	$36,805
Painting	*Material*	0.5	x	$210,314	=	$1,052
	Labor	300	x	$1,052	=	$3,155
Miscellaneous	*Material*	5	x	$210,314	=	$10,516
	Labor	80	x	$10,516	=	$8,413
		Total installed cost			=	$471,166

Another factor applied to the capital costs are the labor factors for setting equipment. For this study, most labor factors for setting equipment were 20%, with a 30% factor used for the coal crusher system as the only exception. Pump costs were also factored by 20% for setting.

Table C-4. Distributive Labor Factors for Setting Equipment

Equipment Type	Factor	Equipment Type	Factor
	(%)		(%)
Absorber	20	Hammermill	25
Ammonia Still	20	Heater	20
Ball Mill	30	Heat Exchanger	20
Briquetting machine	25	Lime Leg	15
Centrifuge	20	Methanator (catalytic)	30
Clarifier	15	Mixer	20
Coke Cutter	15	Precipitator	25
Coke Drum	15	Regenerator (packed)	20
Condenser	20	Retort	30
Conditioner	20	Rotoclone	25
Cooler	20	Screen	20
Crusher	30	Scrubber (water)	15
Cyclone	20	Settler	15
Decanter	15	Shift converter	25
Distillation column	30	Splitter	15
Evaporator	20	Storage Tank	20
Filter	15	Stripper	20
Fractionator	25	Tank	20
Furnace	30	Vaporizer	20
Gasifier	30		

The following is an example of applying the Distributive Labor Factors for Setting Equipment on the reactor cost in June 2011 dollars.

Reactor capital cost = $210,314

Distributive Labor Factors for Setting a Tank = 20%

Reactor setting in place cost = $210,314 x 20% = $42,063

Table C-5 summarizes both the Syncrude and Hydrotreater costs for a 1,000 MTPD syncrude/4,000 BPD hydrotreater system. The costs are provided in FY 2011 (June) dollars.

Process equipment was sized using ChemCAD results and quotes were requested. Where quotes were available, those were used for equipment costs. Where quotes were not received, estimates were obtained from the www.matches.com webpage. Where neither were available, other literature sources, and finally verbal quotes were relied upon.

Factors were applied to the total equipment installed cost for miscellaneous electrical (10% bare equipment), piping and ducting (30% bare equipment), and service facilities (35% bare equipment). With these factors added, the cost for the syncrude process is $109,472,000 and the cost for hydrotreatment at 4500 barrels/day is $40,420,000 (rounded totals, June 2011 costs).

Table C-5. Summary Equipment Costs for Syncrude and Hydrotreater Systems

Area 100 - Tank Farm Excludes Installed Tanks	$1,762,712
Area 100 - Tank Farm Installation w/o Tanks	$1,811,186
Area 100 Cost of Installed Storage Tanks	$2,860,526
Area 100 Foundations for Installed Storage Tanks	$333,251
Area 100 - Setting Equipment	$208,702
Area 200 - Coal Preparation Capital Cost	$5,254,389
Area 200 - Coal Preparation Installation Cost	$2,972,408
Area 200 - Setting Equipment	$1,213,408
Area 300 - Reactor Feed Capital Cost	$3,219,758
Area 300 - Reactor Feed Installation Cost	$3,308,301
Area 300 - Setting Equipment	$643,952
Area 400 - Reactor Train Capital Cost	$7,003,189
Area 400 - Reactor Train Installation Cost	$8,686,055
Area 400 - Setting Equipment	$1,400,638
Area 500 - Centrifuge Capital Cost >150 psig	$767,541
Area 500 - Centrifuge Installation Cost >150 psig	$951,981
Area 500 - Centrifuge Capital Cost <150 psig	$4,168,243
Area 500 - Centrifuge Installation Cost <150 psig	$4,282,870
Area 500 - Setting Equipment	$833,649
Area 600 - Evaporator Capital Cost	$3,670,931
Area 600 - Evaporator Installation Cost	$3,771,882
Area 600 - Setting Equipment	$734,186

While this is the estimated capital cost, it is not the final costs for financing this project. To these capital costs the normal project and owner's costs were added; these factors are shown in Table C-6

Table C-6. Project and Owner's Costs

Engineering and Supervision
Equipment Shipping Cost
6 Months All Labor
1 Month Maintenance Materials
1 Month Non-fuel Consumables
1 Month Waste Disposal
25% of 1 Months Fuel Cost at 100% CF
2% of TPC
Inventory Capital
60 day supply of fuel and consumables at 100% CF
0.5% of TPC (spare parts)
Initial Cost for Catalyst and Chemicals
Land
Other Owner's Costs
Financing Costs
Total Overnight Costs (TOC)
TASC Multiplier

The TASC is used to apply the capital cost factor in the operating costs. Note that it also has operating cost factors included in categories such as All Labor, Non-fuel Consumables, Waste Disposal, Fuel Costs, and Consumables. Therefore, the capital cost will affect the operating cost which will affect the capital cost. To allow iteration of these costs, two spreadsheet books were used; one for capital costing, and one for operating economics, so that iteration could be controlled easily.

The hydrotreater cost was estimated at 4,500 bbl/day. This size was determined based upon availability of a verbal estimate for this size unit for a similar material. The cost was developed and was taken back from 2015 costs to 2011 costs. The hydrotreater was then scaled using the 0.62 exponential factor to 4,000 bbl/day. Normally, hydrotreaters are much larger and are probably closer to 40,000 bbl/day in most modern refineries which means that the capital becomes less of a factor in the operating cost. The hydrotreater size in the F-T example cost data appears to be is about this 40,000 bbl size. For this reason, the hydrotreater estimate developed was also scaled to 36,000 bbl/day to represent eight 1,000 tonne/day coal plants or four 2,000 tonne/day plants as feed to the hydrotreater.

It was assumed that the syncrude plant would require 4 years of construction (2008-2011) and the construction would proceed along a 20/50/80/100 percent completion schedule for the years of construction. Interest costs at 7% were assessed for the installed cost to convert it to a project cost. For the hydrotreater, a 2-year 40/100 schedule (2010-2011) was planned with the same 7% interest rate assessed.

Applying all of these factors and appropriate percentages, similar to those used for F-T plant capitalization (Shah, 2014) gives the following estimates of installed equipment cost and TASC. Note that the CO_2 and the electrical costs are both spelled out in the tables, because these are the primary fluctuating parameters in the cases evaluated, and operating costs affect the TASC through the working capital costs.

Table C-7. Estimated Installed Equipment Cost

Area 100 - Tank Farm							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
US-100-1	Rail Car Unloading Station #1	Steam station, 4" suction, Top access, Bottom unloading, Flow metering	221257	1.084	204200	20	44251
US-100-2	Rail Car Unloading Station #2		221257	1.084	204200	20	44251
US-100-3	Rail Car Unloading Station #3		221257	1.084	204200	20	44251
US-100-4	Rail Car Unloading Station #4		221257	1.084	204200	20	44251
P-101-1	CTD Unloading Pump #1	800 gpm, 100 ft TDH					
P-102-1	YG Unloading Pump #1	800 gpm, 100 ft TDH					
P-103-1	BG Unloading Pump #1	800 gpm, 100 ft TDH					
P-104-1	Tall Oil Unloading Pump #1	800 gpm, 100 ft TDH					
P-105-1-A&B	Condensate Return Station #1						
P-105-2-A&B	Condensate Return Station #2						
	eyewash station		4069	1.084	3755		
		CTD Storage basis - 7 day supply = 189115 gal					

Table C-7. Estimated Installed Equipment Cost (continued)

Area 100 - Tank Farm							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
TK-110-1	CTD Storage Tank #1	100000 gal 32 ft dia x 16 ft ss, carbon steel, SG = 0.931	357566	1.084	330000		
TK-110-2	CTD Storage Tank #2	100000 gal	357566	1.084	330000		
HX-111-1	CTD Storage Tank #1 Suction Heater	Model S-610	9752	1.084	9000	20	1950
HX-111-2	CTD Storage Tank #2 Suction Heater	Model S-610	9752	1.084	9000	20	1950
P-112-1	CTD Supply Pump #1	25 gpm. 60 ft TDH Gould Model 3196 1x1.5-8 STi Ductile iron with 316SS impeller 3.0 hp/182T 1800 rpm	7378	1.084	6809	20	1476
P-112-2	CTD Supply Pump #2	25 gpm. 60 ft TDH	7378	1.084	6809	20	1476
		Yellow Grease Storage basis - 7 day supply = 186732 gal					
TK-120-1	Yellow Grease Storage Tank #1	100000 gal, SG = 0.892	357566	1.084	330000		

Table C-7. Estimated Installed Equipment Cost (continued)

Area 100 - Tank Farm							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
TK-120-2	Yellow Grease Storage Tank #2	100000 gal	357566	1.084	330000		
HX-121-1	YG Storage Tank #1 Suction Heater	Model S-610	9752	1.084	9000	20	1950
HX-121-2	YG Storage Tank #2 Suction Heater	Model S-610	9752	1.084	9000	20	1950
P-122-1	YG Supply Pump #1	25 gpm. 60 ft TDH Gould Model 3196 1x1.5-8 STi Ductile iron with 316SS impeller 3.0 hp/182T 1800 rpm	7378	1.084	6809	20	1476
P-122-2	YG Supply Pump #2	25 gpm. 60 ft TDH	7378	1.084	6809	20	1476
		Brown Grease Storage basis - 7 day supply = 187251 gal					
TK-130-1	Brown Grease Storage Tank #1	100000 gal, SG = 0.889	357566	1.084	330000		
TK-130-2	Brown Grease Storage Tank #2	100000 gal	357566	1.084	330000		

Table C-7. Estimated Installed Equipment Cost (continued)

Area 100 - Tank Farm							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
HX-131-1	BG Storage Tank #1 Suction Heater	Model S-610	9752	1.084	9000	20	1950
HX-131-2	BG Storage Tank #2 Suction Heater	Model S-610	9752	1.084	9000	20	1950
P-132-1	BG Supply Pump #1	25 gpm. 60 ft TDH Gould Model 3196 1x1.5-8 STi Ductile iron with 316SS impeller 3.0 hp/182T 1800 rpm	7378	1.084	6809	20	1476
P-132-2	BG Supply Pump #2	25 gpm. 60 ft TDH	7378	1.084	6809	20	1476
		Tall Oil Storage basis - 7 day supply = 319831 gal					
TK-140-1	Tall Oil Storage Tank #1	100000 gal SG = 1.069	357566	1.084	330000		
TK-140-2	Tall Oil Storage Tank #2	100000 gal	357566	1.084	330000		
TK-140-3	Tall Oil Storage Tank #3	100000 gal	357566	1.084	330000		
TK-140-4	Tall Oil Storage Tank #4	100000 gal	357566	1.084	330000		

Table C-7. Estimated Installed Equipment Cost (continued)

Area 100 - Tank Farm							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
HX-141-1	Tall Oil Storage Tank #1 Suction Heater	Model S-1010	10619	1.084	9800	20	2124
HX-141-2	Tall Oil Storage Tank #2 Suction Heater	Model S-1010	10619	1.084	9800	20	2124
HX-141-3	Tall Oil Storage Tank #3 Suction Heater	Model S-1010	10619	1.084	9800	20	2124
HX-141-4	Tall Oil Storage Tank #4 Suction Heater	Model S-1010	10619	1.084	9800	20	2124
P-142-1	Tall Oil Supply Pump #1	50 gpm. 60 ft TDH Gould Model 3196 1x1.5-6 STi Ductile iron with 316SS impeller 5.0 hp/184T 3600 rpm	6615	1.084	6105	20	1323
P-142-2	Tall Oil Supply Pump #2	50 gpm. 60 ft TDH	6615	1.084	6105	20	1323

Table C-7. Estimated Installed Equipment Cost (continued)

Area 200 - Coal Preparation							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
CV-200-1	Coal Distribution Conveyor	100 tph, 36", 500 fpm	340603	1.022	333200	20	68121
CV-202-1	Coal Pile Collection Conveyor	100 tph, 36", 500 fpm	340603	1.022	333200	20	68121
CV-203-1	Coal Elevator	100 tph, 175 fpm 24"x14"x7" buckets	37311	1.022	36500	20	7462
SS-204-1	Raw Coal Storage Silo	1 day inventory = 1200 tons	357163	1.022	349400	20	71433
	Bin Vent Filter		20649	1.022	20200	20	4130
SS-204-2	Raw Coal Storage Silo	1 day inventory = 1200 tons	357163	1.022	349400	20	71433
	Bin Vent Filter		20649	1.022	20200	20	4130
SS-204-3	Raw Coal Storage Silo	1 day inventory = 1200 tons	357163	1.022	349400	20	71433
	Bin Vent Filter		20649	1.022	20200	20	4130
CV-205-1	Crusher feed conveyor	100 tph, 36", 500 fpm	220901	1.022	216100	20	44180
Williams Impact Dryer System	47 tonnes per hour						
F-206-1	Feeder	Williams 5100 Impact Dryer Mill with Spinner Separator	1625299	1.084	1500000	30	487590
C-206-2	Crusher	600 HP mill motor					
F-206-3	Main Mill Fan	75 HP spinner separator motor and VFAC Drive					

Table C-7. Estimated Installed Equipment Cost (continued)

Area 200 - Coal Preparation							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
S-206-4	Turbine Separator	Main Fan with motor					
CC-206-5	Cyclone Collector	Exhaust Fan with motor					
DC-206-6	Dust Collector	Primary Dust Collector for 4:1 Air to Cloth Ratio					
CV-206-7	Fines Conveyor	Cyclone Collector					
F-206-8	Exhaust Fan	Air Heater 10 MMBTU/hr					
B-206-9	Burner	Feeder with motor and VFAC Drive					
		PLC Controller					
BL-207-1	Crushed Coal Conveyor	100 tph, 36", 500 fpm	206079	1.022	201600	20	41216
SS-208-1	Finished Coal Storage Bin w/ Filter	one day storage = 1200 tons	357163	1.022	349400	20	71433
	Bin Vent Filter		20649	1.022	20200	20	4130
SS-208-2	Finished Coal Storage Bin w/ Filter	one day storage = 1200 tons	357163	1.022	349400	20	71433
	Bin Vent Filter		20649	1.022	20200	20	4130
BL-209-1	Crushed Coal Conveyor	100 tph, 36", 500 fpm	97929	1.022	95800	20	19586
BL-209-2	Crushed Coal Conveyor	100 tph, 36", 500 fpm	97929	1.022	95800	20	19586
FB-210-1	Mix Tank Feed Bin w/ Filter	20 tons	68489	1.022	67000	20	13698

Table C-7. Estimated Installed Equipment Cost (continued)

Area 200 - Coal Preparation							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
	Bin Vent Filter		20649	1.022	20200	20	4130
FB-210-2	Mix Tank Feed Bin w/ Filter	20 tons	68489	1.022	67000	20	13698
	Bin Vent Filter		20649	1.022	20200	20	4130
RV-211-1	Feed Bin Rotary Valve	ACS ROTARY AIRLOCK Model CI 26 x 26, 9.0 C.F.R. 7.5 HP drive assembly including TEXP enclosure Final drive RPM is 15 - 100 tph	29445	1.084	27,175	20	5889
RV-211-2	Feed Bin Rotary Valve	100 tph	29445	1.084	27,175	20	5889
CV-212-1	Feed Bin Conveyor	100 tph	28315	1.022	27700	20	5663
CV-213-2	Feed Bin Conveyor	100 tph	28315	1.022	27700	20	5663
CV-214-1	Coal Distribution Conveyor	100 tph	104880	1.022	102600	20	20976

Table C-7. Estimated Installed Equipment Cost (continued)

Area 300 - Reactor Feed							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
TK-300-1	Feed Mix Tank #1	10,000 Gallon Rubber Lined Mix Tank w/ Flat Top & Slight Cone, 200 F, Carbon steel, 114" dia x 240" ss Cleaned & Lined w/ 3/16" HNBR - Hydrogenated Nitrile	106728	1.084	98500	20	21346
TK-300-2	Feed Mix Tank #2		106728	1.084	98500	20	21346
TK-300-3	Feed Mix Tank #3		106728	1.084	98500	20	21346
TK-300-4	Feed Mix Tank #4		106728	1.084	98500	20	21346
AG-301-1	Feed Mix Tank #1 Agitator		27804	1.022	27200	20	5561
AG-301-2	Feed Mix Tank #2 Agitator		27804	1.022	27200	20	5561
AG-301-3	Feed Mix Tank #3 Agitator		27804	1.022	27200	20	5561
AG-301-4	Feed Mix Tank #4 Agitator		27804	1.022	27200	20	5561
P-302-1	Reactor Feed Pump #1	Moyno model 6K175G1 CDQ 3AAA 500 psig, 250 gpm, 150 Hp, 300 rpm	92100	1.084	85000	20	18420
P-302-2	Reactor Feed Pump #2		92100	1.084	85000	20	18420

Table C-7. Estimated Installed Equipment Cost (continued)

Area 300 - Reactor Feed							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
P-302-3	Reactor Feed Pump #3		92100	1.084	85000	20	18420
HX-303-1	Reactor Train #1 Feed Preheater	Not used					
HX-303-2	Reactor Train #2 Feed Preheater	Not used					
HX-303-3	Reactor Train #3 Feed Preheater	Not used					
HX-304-1	Reactor Train #1 Feed Heat Exchanger	Estimate Q = 36162000 btu/hr U=61.68 btu/hr-ft2-F LMdT = 204.3 F Ft=0.65 A = 12000 ft2	812216	1.084	749600	20	162443
HX-304-2	Reactor Train #2 Feed Heat Exchanger		433413	1.084	400000	20	86683
HX-304-3	Reactor Train #3 Feed Heat Exchanger		433413	1.084	400000	20	86683
P-305-1	RX Feed Heat Exchanger Pump	350 gpm, 60 ft TDH, 10 HP	16560	1.022	16200	20	3312
P-305-2	RX Feed Heat Exchanger Pump		16560	1.022	16200	20	3312
P-305-3	RX Feed Heat Exchanger Pump		16560	1.022	16200	20	3312
installed spare equipment							

Table C-7. Estimated Installed Equipment Cost (continued)

Area 300 - Reactor Feed							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
TK-300-	Feed Mix Tank		106728	1.084	98500	20	21346
AG-301	Feed Mix Tank Agitator		27804	1.022	27200	20	5561
P-302	Reactor Feed Pump		92100	1.084	85000	20	18420
HX-304	Reactor Train Feed Heat Exchanger		433413	1.084	400000	20	86683
P-305	RX Feed Heat Exchanger Pump		16560	1.022	16200	20	3312

Table C-7. Estimated Installed Equipment Cost (continued)

Area 400 - Reactor Train							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
V-410-1	Reactor Train #1 - RX #1	2500 gal 60" I.D. x 192" LG. PRESSURE VESSELS VESSEL DESIGN = 450 PSIG @ 932° F. MATERIAL = SA-387 GR. 22 CL. 2 (PLATE); SA-182 F22 CL. 3 (FORGINGS) NOZZLES = (1) 12" 600#; (2) 6" 600#; (1) 2" 600#; (4) 1" 600# SUPPORT = SKIRT W/CHAIR & BASE RINGS 68" I.D. VESSEL JACKETS JACKET DESIGN = 100 PSIG @ 932° F. MATERIAL = SA-387 GR. 22 CL. 2 (PLATE); SA-182 F22 CL. 3 (FORGINGS)	210314	1.084	194100	20	42063
V-410-2	Reactor Train #1 - RX #2	2500 gal	210314	1.084	194100	20	42063
V-410-3	Reactor Train #1 - RX #3	2500 gal	210314	1.084	194100	20	42063
V-410-4	Reactor Train #1 - RX #4	2500 gal	210314	1.084	194100	20	42063
AG-411-1	Reactor Train #1 - RX #1 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397

Table C-7. Estimated Installed Equipment Cost (continued)

Area 400 - Reactor Train							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
AG-411-2	Reactor Train #1 - RX #2 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
AG-411-3	Reactor Train #1 - RX #3 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
AG-411-4	Reactor Train #1 - RX #4 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
HX-412-1	Reactor Train #1 - RX #4 Partial Condenser	2626 ft2	333295	1.084	307600	20	66659
HX-412-2	Reactor Train #1 - RX #4 Final Condenser	2405 ft2 estimate	333295	1.084	307600	20	66659
V-413-1	Reactor Train #1 - RX #4 Reflux Vessel	500 gal	80073	1.084	73899.8459	20	16015
P-414-1	Reactor Train #1 - RX #4 Reflux Pump	30 gpm, 60 ft TDH, 600 psi flange, 1.5 hp	9446	1.084	8718	20	1889
HX-415-1	Reactor Train #1 - RX #4 Reflux Heater	2270 ft2	261673	1.084	241500	20	52335
P-416-1	Reactor Train #1 Jacket Pump	400 gpm, 60 ft TDH, 10 hp	16560	1.022	16200	20	3312

Table C-7. Estimated Installed Equipment Cost (continued)

Area 400 - Reactor Train							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
HX-417-1	Reactor Train #1 Product Cooler	Duty + 810100 btu/hr product out at 650 F, thermal fluid in at 572 F A = 805 ft2	166647	1.084	153800	20	33329
V-420-1	Reactor Train #2 - RX #1	2500 gal	210314	1.084	194100	20	42063
V-420-2	Reactor Train #2 - RX #2	2500 gal	210314	1.084	194100	20	42063
V-420-3	Reactor Train #2 - RX #3	2500 gal	210314	1.084	194100	20	42063
V-420-4	Reactor Train #2 - RX #4	2500 gal	210314	1.084	194100	20	42063
AG-421-1	Reactor Train #2 - RX #1 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
AG-421-2	Reactor Train #2 - RX #2 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
AG-421-3	Reactor Train #2 - RX #3 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
AG-421-4	Reactor Train #2 - RX #4 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
HX-422-1	Reactor Train #2 - RX #4 Partial Condenser	2626 ft2	333295	1.084	307600	20	66659

Table C-7. Estimated Installed Equipment Cost (continued)

Area 400 - Reactor Train							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
HX-422-2	Reactor Train #2 - RX #4 Final Condenser	2405 ft2 estimate	333295	1.084	307600	20	66659
V-423-1	Reactor Train #2 - RX #4 Reflux Vessel	500 gal	80073	1.084	73899.8459	20	16015
P-424-1	Reactor Train #2 - RX #4 Reflux Pump	30 gpm, 60 ft TDH, 600 psi flange, 1.5 hp	9446	1.084	8718	20	1889
HX-425-1	Reactor Train #2 - RX #4 Reflux Heater	2270 ft2	261673	1.084	241500	20	52335
P-426-1	Reactor Train #2 Jacket Pump	400 gpm, 60 ft TDH, 10 hp	16560	1.022	16200	20	3312
HX-427-1	Reactor Train #2 Product Cooler	Duty + 810100 btu/hr product out at 650 F, thermal fluid in at 572 F A = 805 ft2	166647	1.084	153800	20	33329
V-430-1	Reactor Train #3 - RX #1	2500 gal	210314	1.084	194100	20	42063
V-430-2	Reactor Train #3 - RX #2	2500 gal	210314	1.084	194100	20	42063
V-430-3	Reactor Train #3 - RX #3	2500 gal	210314	1.084	194100	20	42063
V-430-4	Reactor Train #3 - RX #4	2500 gal	210314	1.084	194100	20	42063
AG-431-1	Reactor Train #3 - RX #1 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397

Table C-7. Estimated Installed Equipment Cost (continued)

Area 400 - Reactor Train							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
AG-431-2	Reactor Train #3 - RX #2 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
AG-431-3	Reactor Train #3 - RX #3 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
AG-431-4	Reactor Train #3 - RX #4 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
HX-432-1	Reactor Train #3 - RX #4 Partial Condenser	2626 ft2	333295	1.084	307600	20	66659
HX-432-2	Reactor Train #3 - RX #4 Final Condenser	2405 ft2 estimate	333295	1.084	307600	20	66659
V-433-1	Reactor Train #3 - RX #4 Reflux Vessel	500 gal	80073	1.084	73899.8459	20	16015
P-434-1	Reactor Train #3 - RX #4 Reflux Pump	30 gpm, 60 ft TDH, 600 psi flange, 1.5 hp	9446	1.084	8718	20	1889
HX-435-1	Reactor Train #3 - RX #4 Reflux Heater	2270 ft2	261673	1.084	241500	20	52335
P-436-1	Reactor Train #3 Jacket Pump	400 gpm, 60 ft TDH, 10 hp	16560	1.022	16200	20	3312

Table C-7. Estimated Installed Equipment Cost (continued)

Area 400 - Reactor Train							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
HX-437-1	Reactor Train #3 Product Cooler	Duty + 810100 btu/hr product out at 650 F, thermal fluid in at 572 F A = 805 ft2	166647	1.084	153800	20	33329
installed spare equipment							
V-410	Reactor Train #1 - RX #3	2500 gal	210314	1.084	194100	20	42063
V-410	Reactor Train #1 - RX #4	2500 gal	210314	1.084	194100	20	42063
AG-411	Reactor Train #1 - RX #1 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
AG-411	Reactor Train #1 - RX #2 Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
P-414-1 - B	Reactor Train #1 - RX #4 Reflux Pump	30 gpm, 60 ft TDH, 600 psi flange, 1.5 hp	9446	1.084	8718	20	1889
P-416-1 - B	Reactor Train #1 Jacket Pump	400 gpm, 60 ft TDH, 10 hp	16560	1.022	16200	20	3312
P-424-1 - B	Reactor Train #2 - RX #4 Reflux Pump	30 gpm, 60 ft TDH, 600 psi flange, 1.5 hp	9446	1.084	8718	20	1889
P-426-1 - B	Reactor Train #2 Jacket Pump	400 gpm, 60 ft TDH, 10 hp	16560	1.022	16200	20	3312
P-434-1 - B	Reactor Train #3 - RX #4 Reflux Pump	30 gpm, 60 ft TDH, 600 psi flange, 1.5 hp	9446	1.084	8718	20	1889
P-436-1 -B	Reactor Train #3 Jacket Pump	400 gpm, 60 ft TDH, 10 hp	16560	1.022	16200	20	3312

Table C-7. Estimated Installed Equipment Cost (continued)

Area 500 - Centrifuge							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
V-500-1	Train 1 High Pressure Separator Tank	1000 gal	15711	1.084	14500	20	3142
SP-501-1	Train 1 Hydrocyclone	250 gpm	127777	1.022	125000	20	25555
V-500-2	Train 2 High Pressure Separator Tank	1000 gal	15711	1.084	14500	20	3142
SP-501-2	Train 2 Hydrocyclone	250 gpm	127777	1.022	125000	20	25555
V-500-3	Train 3 High Pressure Separator Tank	1000 gal	15711	1.084	14500	20	3142
SP-501-3	Train 3 Hydrocyclone	250 gpm	127777	1.022	125000	20	25555
AG-512-1	Train 1 High Pressure Separator Tank Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
AG-512-2	Train 2 High Pressure Separator Tank Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
AG-512-3	Train 3 High Pressure Separator Tank Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
V-502	Centrifuge Feed Tank	2000 gal	23296	1.084	21500	20	4659
A-503	Centrifuge Feed Tank Agitator	Turbine top entering, 25 Hp, carbon steel, 10 atm	19524	1.022	19100	20	3905

Table C-7. Estimated Installed Equipment Cost (continued)

Area 500 - Centrifuge							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
installed spare equipment							
V-500-1	Train 1 High Pressure Separator Tank	1000 gal	15711	1.084	14500	20	3142
SP-501-1	Train 1 Hydrocyclone	250 gpm	127777	1.022	125000	20	25555
AG-512-1	Train 1 High Pressure Separator Tank Agitator	Top entering turbine, 30 Hp, Carbon Steel, 40 atm	26987	1.022	26400	20	5397
V-502	Centrifuge Feed Tank	2000 gal	23296	1.084	21500	20	4659
A-503	Centrifuge Feed Tank Agitator	Turbine top entering, 25 Hp, carbon steel, 10 atm	19524	1.022	19100	20	3905
P-504	Centrifuge Feed Pump	235 gpm	21671	1.084	20000	20	4334
HX-505	Centrifuge Feed Cooler	6728 ft2	650120	1.084	600000	20	130024
C-506	Centrifuge	275 gpm feed at 50 C, , 5366 lb solid/hr , 49% solids discharge, discharge to atmosphere. MISX520 centrifuge recommended 200 kW	1354416	1.084	1250000	20	270883
T-507	Centrate Collection Tank	500 gal	12461	1.084	11500	20	2492

Table C-7. Estimated Installed Equipment Cost (continued)

Area 500 - Centrifuge							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
P-508	Centrate Pump	35 gpm	7871	1.022	7700	20	1574
T-509	Heavy Solids Collection Tank	500 gal	12461	1.084	11500	20	2492
A-510	Heavy Solids Collection Tank Agitator	Turbine top entering, 15 Hp, carbon steel, atm	15027	1.022	14700	20	3005
P-511	Heavy Solids Pump	70 gpm	10096	1.084	9318	20	2019
installed spare equipment							
P-504	Centrifuge Feed Pump	235 gpm	21671	1.084	20000	20	4334
HX-505	Centrifuge Feed Cooler	6728 ft2	650120	1.084	600000	20	130024
C-506	Centrifuge	275 gpm feed at 50 C, , 5366 lb solid/hr , 49% solids discharge, discharge to atmosphere. MISX520 centrifuge recommended 200 kW	1354416	1.084	1250000	20	270883
T-507	Centrate Collection Tank	500 gal	12461	1.084	11500	20	2492
P-508	Centrate Pump	35 gpm	7871	1.022	7700	20	1574
T-509	Heavy Solids Collection Tank	500 gal	12461	1.084	11500	20	2492
A-510	Heavy Solids Collection Tank Agitator	Turbine top entering, 15 Hp, carbon steel, atm	15027	1.022	14700	20	3005
P-511	Heavy Solids Pump	70 gpm	10096	1.084	9318	20	2019

Table C-7. Estimated Installed Equipment Cost (continued)

Area 600 - Evaporator Capital Cost							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
V-600-1	Train 1 Effect #1	2000 gal	23296	1.084	21500	20	4659
P-601-1	Train 1 Effect #1 Circulation Pump	400 gpm, 60 ft TDH, 650 F 300 psig casing pressure	16560	1.022	16200	20	3312
HX-602-1	Train 1 Effect #1 Heat Exchanger	900 ft2	41911	1.022	41000	20	8382
V-603-1	Train 1 Effect #2	2000 gal	23296	1.084	21500	20	4659
P-604-1	Train 1 Effect #2 Circulation Pump	400 gpm, 100 ft TDH, 625 F	16560	1.022	16200	20	3312
HX-605-1	Train 1 Effect #2 Heat Exchanger	3600 ft2	107537	1.022	105200	20	21507
V-606-1	Train 1 Effect #3	2000 gal	23296	1.084	21500	20	4659
P-607-1	Train 1 Effect #3 Circulation Pump	400 gpm 100 ft TDH, 610 F	16560	1.022	16200	20	3312
HX-608-1	Train 1 Effect #3 Heat Exchanger	3600 ft2	107537	1.022	105200	20	21507
HX-609-1	Condenser	6520 ft2	160999	1.022	157500	20	32200
VP-610-1	Vacuum Pump	4154 cfm	398135	1.084	367442	20	79627
T-611-1	Condensate Oil Collection Tank	1000 gal	15711	1.084	14500	20	3142
P-612-1	Condensate Oil Pump	140 gpm, 100 TDH, 450 F	8791	1.022	8600	20	1758

Table C-7. Estimated Installed Equipment Cost (continued)

Area 600 - Evaporator Capital Cost							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
HX-613-1	Condensate Oil Cooler	1231 ft2	51826	1.022	50700	20	10365
P-614-1	Train 1 Effect #1 Heat Exchanger Thermal Fluid Pump	250 gpm, 60 ft TDH, 840 F	10222	1.022	10000	20	2044
V-620-1	Train 2 Effect #1	2000 gal	23296	1.084	21500	20	4659
P-621-1	Train 2 Effect #1 Circulation Pump	400 gpm	16560	1.022	16200	20	3312
HX-622-1	Train 2 Effect #1 Heat Exchanger	900 ft2	41911	1.022	41000	20	8382
V-623-1	Train 2 Effect #2	2000 gal	23296	1.084	21500	20	4659
P-624-1	Train 2 Effect #2 Circulation Pump	400 gpm	16560	1.022	16200	20	3312
HX-625-1	Train 2 Effect #2 Heat Exchanger	3600 ft2	107537	1.022	105200	20	21507
V-626-1	Train 2 Effect #3	2000 gal	23296	1.084	21500	20	4659
P-627-1	Train 2 Effect #3 Circulation Pump	400 gpm	16560	1.022	16200	20	3312
HX-628-1	Train 2 Effect #3 Heat Exchanger	3600 ft2	107537	1.022	105200	20	21507
HX-629-1	Condenser	6520 ft2	160999	1.022	157500	20	32200

Table C-7. Estimated Installed Equipment Cost (continued)

Area 600 - Evaporator Capital Cost							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
VP-630-1	Vacuum Pump	4154 cfm	398135	1.084	367442	20	79627
T-631-1	Condensate Oil Collection Tank	1000 gal	15711	1.084	14500	20	3142
P-632-1	Condensate Oil Pump	140 gpm	8791	1.022	8600	20	1758
HX-633-1	Condensate Oil Cooler	1231 ft2	51826	1.022	50700	20	10365
P-634-1	Train 2 Effect #1 Heat Exchanger Thermal Fluid Pump	250 gpm	10222	1.022	10000	20	2044
V-640-1	Train 3 Effect #1	2000 gal	23296	1.084	21500	20	4659
P-641-1	Train 3 Effect #1 Circulation Pump	400 gpm, 60 ft tdh	16560	1.022	16200	20	3312
HX-642-1	Train 3 Effect #1 Heat Exchanger	900 ft2	41911	1.022	41000	20	8382
V-643-1	Train 3 Effect #2	2000 gal	23296	1.084	21500	20	4659
P-644-1	Train 3 Effect #2 Circulation Pump	400 gpm, 60 ft tdh	16560	1.022	16200	20	3312
HX-645-1	Train 3 Effect #2 Heat Exchanger	3600 ft2	107537	1.022	105200	20	21507
V-646-1	Train 3 Effect #3	2000 gal	23296	1.084	21500	20	4659

Table C-7. Estimated Installed Equipment Cost (continued)

Area 600 - Evaporator Capital Cost							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
P-647-1	Train 3 Effect #3 Circulation Pump	400 gpm, 60 ft tdh	16560	1.022	16200	20	3312
HX-648-1	Train 3 Effect #3 Heat Exchanger	3600 ft2	107537	1.022	105200	20	21507
HX-649-1	Condenser	6520 ft2	160999	1.022	157500	20	32200
VP-650-1	Vacuum Pump	4154 cfm, 0.7 psia, 350 hp motor, 270 duty hp, 300 gpm cooling water	398135	1.084	367442	20	79627
T-651-1	Condensate Oil Collection Tank	1000 gal	15711	1.084	14500	20	3142
P-652-1	Condensate Oil Pump	140 gpm, 100 ft tdh	8791	1.022	8600	20	1758
HX-653-1	Condensate Oil Cooler	1231 ft2	51826	1.022	50700	20	10365
P-654-1	Train 3 Effect #1 Heat Exchanger Thermal Fluid Pump	250 gpm, 60 ft tdh	10222	1.022	10000	20	2044
installed spare equipment							
P-601-1	Train 1 Effect #1 Circulation Pump	400 gpm, 60 ft TDH, 650 F 300 psig casing pressure	16560	1.022	16200	20	3312
P-604-1	Train 1 Effect #2 Circulation Pump	400 gpm, 100 ft TDH, 625 F	16560	1.022	16200	20	3312
P-607-1	Train 1 Effect #3 Circulation Pump	400 gpm 100 ft TDH, 610 F	16560	1.022	16200	20	3312

Table C-7. Estimated Installed Equipment Cost (continued)

Area 600 - Evaporator Capital Cost							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
VP-610-1	Vacuum Pump	4154 cfm	398135	1.084	367442	20	79627
P-612-1	Condensate Oil Pump	140 gpm, 100 TDH, 450 F	8791	1.022	8600	20	1758
P-614-1	Train 1 Effect #1 Heat Exchanger Thermal Fluid Pump	250 gpm, 60 ft TDH, 840 F	10222	1.022	10000	20	2044
P-621-1	Train 2 Effect #1 Circulation Pump	400 gpm, 60 ft tdh	16560	1.022	16200	20	3312
P-624-1	Train 2 Effect #2 Circulation Pump	400 gpm, 60 ft tdh	16560	1.022	16200	20	3312
P-627-1	Train 2 Effect #3 Circulation Pump	400 gpm, 60 ft tdh	16560	1.022	16200	20	3312
P-632-1	Condensate Oil Pump	140 gpm, 100 ft tdh	8791	1.022	8600	20	1758
P-634-1	Train 2 Effect #1 Heat Exchanger Thermal Fluid Pump	250 gpm, 60 ft tdh	10222	1.022	10000	20	2044
P-641-1	Train 3 Effect #1 Circulation Pump	400 gpm, 60 ft tdh	16560	1.022	16200	20	3312
P-644-1	Train 3 Effect #2 Circulation Pump	400 gpm, 60 ft tdh	16560	1.022	16200	20	3312
P-647-1	Train 3 Effect #3 Circulation Pump	400 gpm, 60 ft tdh	16560	1.022	16200	20	3312

Table C-7. Estimated Installed Equipment Cost (continued)

Area 600 - Evaporator Capital Cost

Equipment number	Description	Specification	June 2011 Cost	CEPCI Factor	Capital Cost	Setting Equipment Factor	Setting Equipment Cost
P-652-1	Condensate Oil Pump	140 gpm, 100 ft tdh	8791	1.022	8600	20	1758
P-654-1	Train 3 Effect #1 Heat Exchanger Thermal Fluid Pump	250 gpm, 60 ft tdh	10222	1.022	10000	20	2044

Area 700 - Product Tank Farm

Equipment number	Description	Specification	June 2011 Cost	CEPCI Factor	Capital Cost	Setting Equipment Factor	Setting Equipment Cost
	Product Oil 7 day storage = 1,495,348 gal						
T-700-1	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-2	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-3	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-4	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-5	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-6	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-7	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-8	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-9	Product Oil Storage Tank	100000 gal	357566	1.084	330000		

Table C-7. Estimated Installed Equipment Cost (continued)

Area 700 - Product Tank Farm							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
T-700-10	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-11	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-12	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-13	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-14	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
T-700-15	Product Oil Storage Tank	100000 gal	357566	1.084	330000		
LS-701-1	Rail Car Loading Station #1	Steam station, 4" suction, Top access, Bottom unloading, Flow metering	221257	1.084	204200	20	44251
LS-701-2	Rail Car Loading Station #2		221257	1.084	204200	20	44251
LS-701-3	Rail Car Loading Station #3		221257	1.084	204200	20	44251
LS-701-4	Rail Car Loading Station #4		221257	1.084	204200	20	44251
P-702-1	Product Oil Load Out Pump	800 gpm Included in Loading station					
P-702-2	Product Oil Load Out Pump	800 gpm Included in Loading station					

Table C-7. Estimated Installed Equipment Cost (continued)

Area 700 - Product Tank Farm							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
P-702-3	Product Oil Load Out Pump	800 gpm Included in Loading station					
P-702-4	Product Oil Load Out Pump	800 gpm Included in Loading station					
	500+ Liquid 7 day storage = 333,101 gal						
T-710-1	500+ Liquid Storage Tank	100000 gal	357566	1.084	330000		
T-710-2	500+ Liquid Storage Tank	100000 gal	357566	1.084	330000		
T-710-3	500+ Liquid Storage Tank	100000 gal	357566	1.084	330000		
T-710-4	500+ Liquid Storage Tank	100000 gal	357566	1.084	330000		
HX-711-1	500+ Liquid Suction Heater	Manning and Lewis suction heater model S-1224	38682	1.084	35700	20	7736
HX-711-2	500+ Liquid Suction Heater	Manning and Lewis suction heater model S-1224	38682	1.084	35700	20	7736
HX-711-3	500+ Liquid Suction Heater	Manning and Lewis suction heater model S-1224	38682	1.084	35700	20	7736
HX-711-4	500+ Liquid Suction Heater	Manning and Lewis suction heater model S-1224	38682	1.084	35700	20	7736
P-712-1	500+ Liquid Load Out Pump	300 gpm	13289	1.022	13000	20	2658

Table C-7. Estimated Installed Equipment Cost (continued)

Area 700 - Product Tank Farm							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
P-712-2	500+ Liquid Load Out Pump	300 gpm	13289	1.022	13000	20	2658
P-712-3	500+ Liquid Load Out Pump	300 gpm	13289	1.022	13000	20	2658
P-712-4	500+ Liquid Load Out Pump	300 gpm	13289	1.022	13000	20	2658
	Heavy Solids7 day storage = 337,029 gal						
T-720-1	Heavy Solids Storage Tank	100000 gal	357566	1.084	330000		
T-720-2	Heavy Solids Storage Tank	100000 gal	357566	1.084	330000		
T-720-3	Heavy Solids Storage Tank	100000 gal	357566	1.084	330000		
T-720-4	Heavy Solids Storage Tank	100000 gal	357566	1.084	330000		
HX-721-1	Heavy Solids Suction Heater	Manning and Lewis suction heater model S-1224	38682	1.084	35700	20	7736
HX-721-2	Heavy Solids Suction Heater	Manning and Lewis suction heater model S-1224	38682	1.084	35700	20	7736
HX-721-3	Heavy Solids Suction Heater	Manning and Lewis suction heater model S-1224	38682	1.084	35700	20	7736
HX-721-4	Heavy Solids Suction Heater	Manning and Lewis suction heater model S-1224	38682	1.084	35700	20	7736

Table C-7. Estimated Installed Equipment Cost (continued)

Area 700 - Product Tank Farm							
Equipment number	**Description**	**Specification**	**June 2011 Cost**	**CEPCI Factor**	**Capital Cost**	**Setting Equipment Factor**	**Setting Equipment Cost**
P-722-1	Heavy Solids Load Out Pump	250 gpm	21671	1.084	20000	20	4334
P-722-2	Heavy Solids Load Out Pump	250 gpm	21671	1.084	20000	20	4334
P-722-3	Heavy Solids Load Out Pump	250 gpm	21671	1.084	20000	20	4334
P-722-4	Heavy Solids Load Out Pump	250 gpm	21671	1.084	20000	20	4334