Montana Integrated Carbon to Liquids (ICTL) Demonstration Program

Final Technical Report

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ABSTRACT

Integrated carbon-to-liquids technology (ICTL) incorporates three basic processes for the conversion of a wide range of feedstocks to distillate liquid fuels: (1) Direct Microcatalytic Coal Liquefaction (MCL) is coupled with biomass liquefaction via (2) Catalytic Hydrodeoxygenation and Isomerization (CHI) of fatty acid methyl esters (FAME) or trigylceride fatty acids (TGFA) to produce liquid fuels, with process derived (3) CO2 Capture and Utilization (CCU) via algae production and use in BioFertilizer for added terrestrial sequestration of CO2, or as a feedstock for MCL and/or CHI. This novel approach enables synthetic fuels production while simultaneously meeting EISA 2007 Section 526 targets, minimizing land use and water consumption, and providing cost competitive fuels at current day petroleum prices.

ICTL was demonstrated with Montana Crow sub-bituminous coal in MCL pilot scale operations at the Energy and Environmental Research Center at the University of North Dakota (EERC), with related pilot scale CHI studies conducted at the University of Pittsburgh Applied Research Center (PARC). Coal-Biomass to Liquid (CBTL) Fuel samples were evaluated at the US Air Force Research Labs (AFRL) in Dayton and greenhouse tests of algae based BioFertilizer conducted at Montana State University (MSU).

Econometric modeling studies were also conducted on the use of algae based BioFertilizer in a wheat-camelina crop rotation cycle. We find that the combined operation is not only able to help boost crop yields, but also to provide added crop yields and associated profits from TGFA (from crop production) for use an ICTL plant feedstock.

This program demonstrated the overall viability of ICTL in pilot scale operations. Related work on the Life Cycle Assessment (LCA) of a Montana project indicated that CCU could be employed very effectively to reduce the overall carbon footprint of the MCL/CHI process.

Plans are currently being made to conduct larger-scale process demonstration studies of the CHI process in combination with CCU to generate synthetic jet and diesel fuels from algae and algae fertilized crops. Site assessment and project prefeasibility studies are planned with a major EPC firm to determine the overall viability of ICTL technology commercialization with Crow coal resources in south central Montana.

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REPORT DETAILS

I. Executive Summary

ICTL is an efficient integrated process based upon Direct Coal Liquefaction (DCL)/Biomass Conversion via Catalytic Hydrodeoxygenation and Isomerization (CHI) to diesel and jet technology, coupled with Carbon Capture and Utilization (CCU) via conversion of process-derived CO_2 /waste water to produce algae-based BioFertilizer for terrestrial CO_2 sequestration and bio-oil as a feedstock for added fuels or chemicals production.

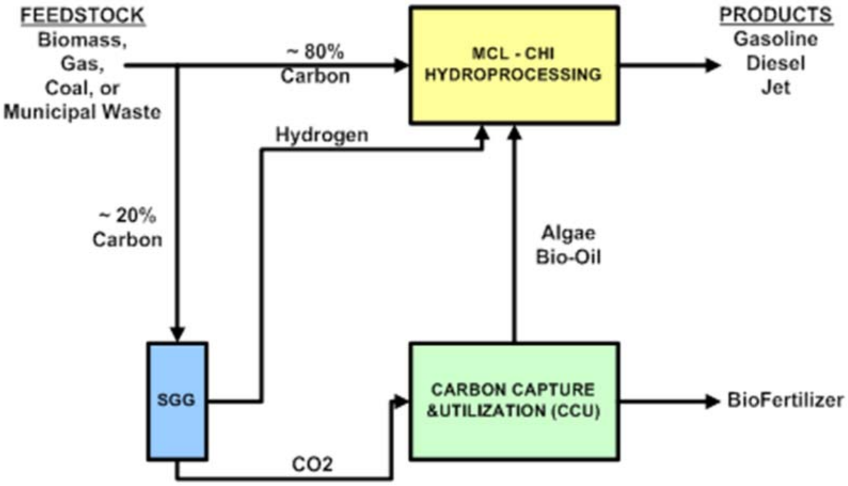


Figure I-1. Simplified ICTL Process Flow Scheme

ICTL technology was demonstrated with Montana Crow sub-bituminous coal in Microcatalytic Coal Liquefaction (MCL) pilot scale operations at the Energy and Environmental Research Center at the University of North Dakota (EERC). Pilot scale studies of Catalytic Hydrodeoxygenation and Isomerization (CHI) of bio-oil feeds were conducted at the University of Pittsburgh Applied Research Center (PARC), from which blended Coal-Biomass to Liquid (CBTL) fuel samples were evaluated at the US Air Force Research Labs (AFRL) in Dayton. Carbon Capture and Recycle was achieved via production of algae from CO_2 and greenhouse tests of algae derived BioFertilizer conducted at Montana State University (MSU). Hence, all the major technical objectives of this project were successfully completed.

This program provided proof of principle tests on all key steps of the ICTL flow scheme, and the results of these studies are providing a basis for taking this technology to the next phase of commercial development. Accelergy is conducting process screening and site assessment studies on Montana and other locations to advance these individual technologies.

ICTL conversion technology is configured to operate alone, or with other carbon based feedstocks such as natural gas as the primary source of hydrogen. This approach allows us to use coal as the primary feedstock for fuel production, while simultaneously mitigating CO_2 and generating added biomass for optional conversion to fuels.

The fully integrated ICTL flow scheme provides a combination of features and advantages that cannot be achieved with current or emerging indirect conversion alternatives. MCL pilot studies have shown that over 4 barrels of cleaner burning liquid fuel (up to 60% in the jet boiling range) can be produced per ton of carbon feed (from coal alone or coal plus biomass), almost twice the liquid yield possible from other indirect conversion technologies.

Process derived CO_2 is used to produce BioFertilizer which in normal use continues to capture CO_2 and nitrogen to produce stable carbon species in treated soil. In this manner, the algae BioFertilizer induces further capture of CO_2 via terrestrial sequestration leading to an overall capture ratio of CO_2 to algae carbon (LCA basis) of up to 150/1. Studies have shown that capture ratios of >10/1 are possible in 20-30 day soil treatment periods, while even higher ratios have been observed for net carbon capture in long-term multi-year desert soil stabilization studies.

Novel process integration also enables us to more effectively utilize by-product waste gas and wastewater streams from one section of the facility as feedstocks for another. This integrated design improves overall efficiency and eliminates a critical barrier to entry by reducing overall investment by up to 15-30%, as shown in recent scoping studies with partner EPC firms.

Life Cycle Assessment (LCA) studies showed that this approach can produce synthetic fuels form coal based feeds (optionally with natural gas as a source of hydrogen) to meet EISA 2007 Section 526 GHG requirements. Econometric studies showed that the CCU option provided lower cost than other carbon sequestration routes, and the algae BioFertilizer can provide economic advantages in a wheat-camelina crop production that incorporates the BioFertilizer as a one for one replacement of conventional ammonia based fertilizer.

Results from the current study are now being evaluated in collaboration with a global EPC engineering firm. Site assessment studies are being conducted on Montana and other North American locations where infrastructure, feedstock and agricultural land and water resources are sufficient to support commercial scale ICTL. It is anticipated that a prime location for further study will be identified in the coming months, and results from the current study will be utilized in a commercial project prefeasibility study.

II. MICROCATALYTIC COAL LIQUEFACTION (MCL)

a. Overview

MCL is an advanced Direct Coal Liquefaction technology supported by a very extensive operating data base covering a wide range of coal resources. The MCL development builds on the predecessor Exxon Donor Solvent (EDS) process and its extensive, large scale demonstration learnings (through 250 T/D).(1-7) The MCL process uses very low concentrations of dispersed catalyst that eliminates the need for a dedicated donor solvent recycle loop.

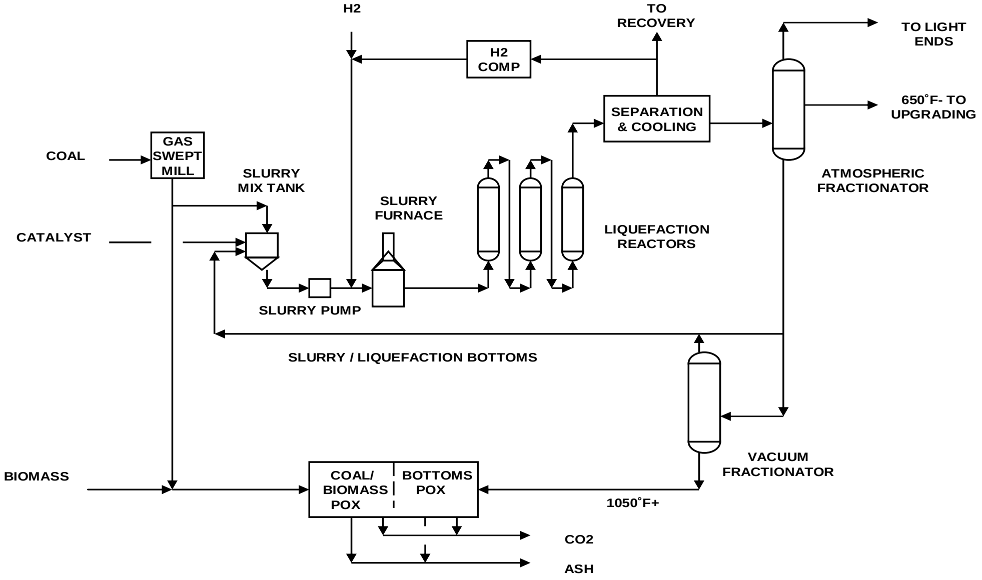


Figure II-1. Simplified MCL Process Flow Scheme

In a typical application, Figure I-1, dried and crushed coal is fed into mixing tank to form slurry by combination with the recycled bottoms, process-derived vacuum bottoms, and catalyst solution. The coal slurry and hydrogen are fed to liquefaction reactors operating at 427-454 deg. C (800-850 deg. F) and about 1.38-17.24 Mpa (200-2500 psig). The up flow tubular reactors contain essentially no internals thus ensuring good operability. The effluent from the last liquefaction reactor is separated into a gas stream and a liquid/solid stream. The depressurized liquid/solid stream is ultimately distilled into various boiling range products in an atmospheric fractionator followed by a vacuum fractionator. Finally, the raw products are upgraded in conventional Hydroprocessing facilities.

Hydrogen required for the liquefaction and Hydroprocessing is produced by partial oxidation of the vacuum fractionator bottoms and, if necessary supplemental coal. As part of this proposal, lipids-free algae or other biomass can be used as supplemental feedstock to the gasifiers. Moreover, in locations where natural gas is plentiful, hydrogen can be efficiently produced from steam reforming of methane.

The liquefaction portion of the MCL process represents about 25% of the total plant investment. The hydrogen generation, based on commercially demonstrated technologies, accounts for about 35% of the total. The balance of the investment (40%) involves adaptations of conventional refining technologies.

The unique features of the MCL process include:

- the use of micro-catalytic catalyst
- simplified process configuration) (no solvent recycle)
- large experimental data base
- feed coal flexibility
- ability to use natural gas derived hydrogen for increased carbon efficiency
- product flexibility
- comprehensive engineering technology development

The MCL process feed flexibility is evident in the wide range of coals from bituminous, sub-bituminous, and Lignitic coals that were processed in previous studies with units ranging in size from 75 lbs/day to 1 T/D. Selected coals were tested on the 250 T/D scale. Supplemental liquefaction feedstock e.g., biomass or algae can be fed to the process.

Unlike the Indirect Coal Liquefaction processes, MCL affords great flexibility to control the liquid product yields and their properties. Both the liquefaction and Hydroprocessing process conditions can be adjusted to drastically alter the MCL product distribution as shown below.

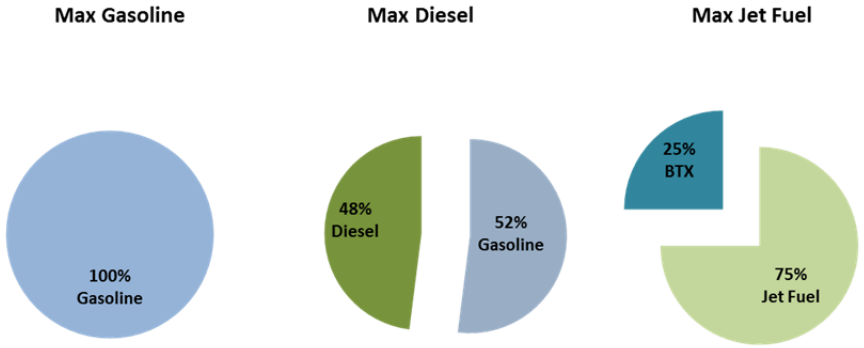


Figure II-2. Flexible Product Slate from MCL

In addition to the unprecedented feed and product flexibility, an MCL plant can also generate its own power or, in a limiting case, generate export power as well. Those considerations, combined with the flexibility to handle algae lipids in the upgrader and the residual algae in the gasifier offer unique opportunities to leverage the MCL technology in an integrated process that efficiently accomplishes the beneficial use of CO2.

Hydrogen required for the liquefaction and Hydroprocessing is produced by partial oxidation of the vacuum fractionator bottoms and, if necessary supplemental coal. As part of this proposal, lipids-free algae or other biomass can be used as supplemental feedstock to the gasifiers or to the MCL step or subsequent hydroprocessing steps for distillate upgrading.

b. MCL Experimental Program and Methods

Pilot scale studies were conducted on MCL at the EERC.(8) The results of these studies showed the overall viability of direct coal liquefaction (DCL) based operation to efficiently generate distillate range fuels.

The unit process basis included in the current flow through design provides the capability of operating under conditions of solvent and catalyst recycle with full product recovery for products from C5 thru 343 deg. C (650 deg.F) boiling range.

The DCL pilot facility at EERC is capable of producing middle distillate liquids suitable for upgrading to JP-8 at a production rate of 0.3 liters/hour based on a coal input rate of 2 pounds/hour, Figure II-3, 4 thru 11.

Preliminary drawings of the unit are based on a study from EERC and Accelergy with a simple multi plug flow reactor once -thru configuration. This enables us to evaluate different coal feedstocks in a straightforward manner for initial screening. Later, more commercial like operations will await construction of a larger scale demo unit that is being considered for Montana Billings area location.

Plans for a production run using MT sub-bituminous coal with unit performance criteria as noted below:

1. Once-through operations where about 45.4 liters (12 gallons) of feed is processed per day (about 15.1 liters (4 gallons)/8 hour shift).
2. Feed cases have a minimum hold-up of 7.6 liters (2 gallons), therefore each batch in the feed case and mix tank must be 6 gallons.
3. Distillation system will require 6 hours to process each product batch.
4. The third batch going through the unit will contain first recycle solvent.
5. A two-week run (14 days) will be required to produce 9.5 liters (2.5 gallons) of finished JP8 blendstock with 3 days required for heat-up and 2 days to cool down and secure the unit, leaving 9 days for coal-in operations.

6. In the batch mode, distillate derived from the coal has been declared “steady state” after three passes. 4 passes may be required to process the 7.6 liters (2-gallon) residual in the feed case and mix tank.

With the above operating assumptions, will estimate that 9.5 liters (2.5 gallons) of three pass plus JP8 blendstock material will be produced after about 80 hours of operation and it would require a minimum 37% service factor (>85% expected) during the coal-in operations.

The product from MCL operations was upgraded in a program under the direction of Accelergy at the University of Pittsburgh Applied Research Center (PARC) and products from that operation will be sent to the EERC for final blending with BTL liquids and certification at various DOD laboratories.

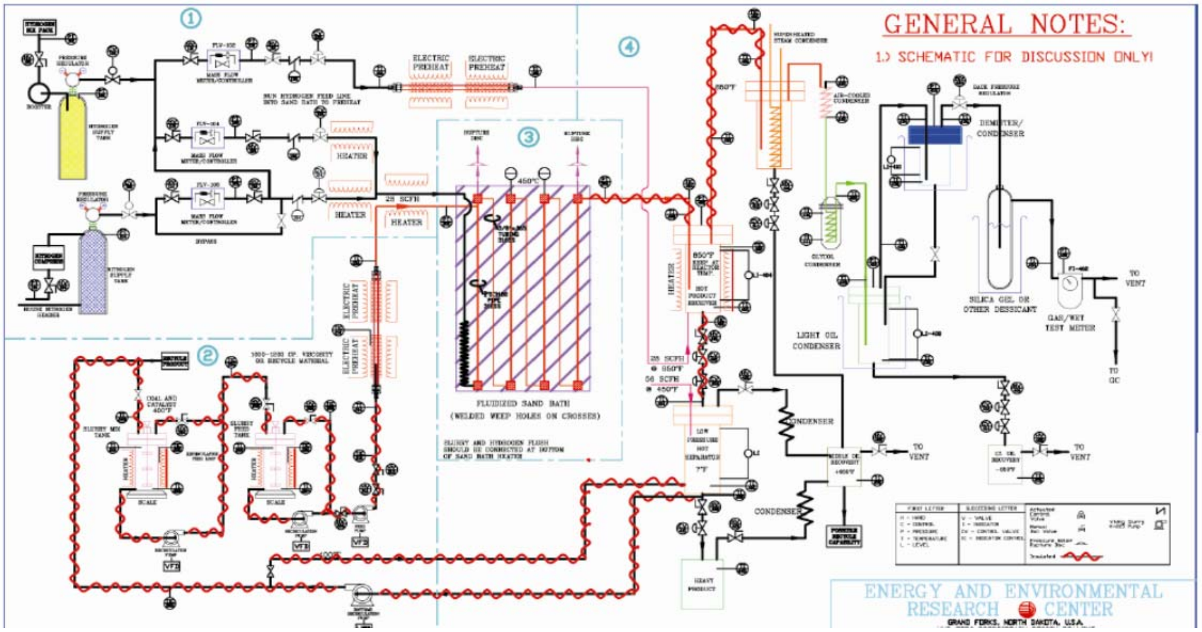


Figure II-3. Preliminary Drawing of Once Through MCL Pilot Unit for UND EERC.

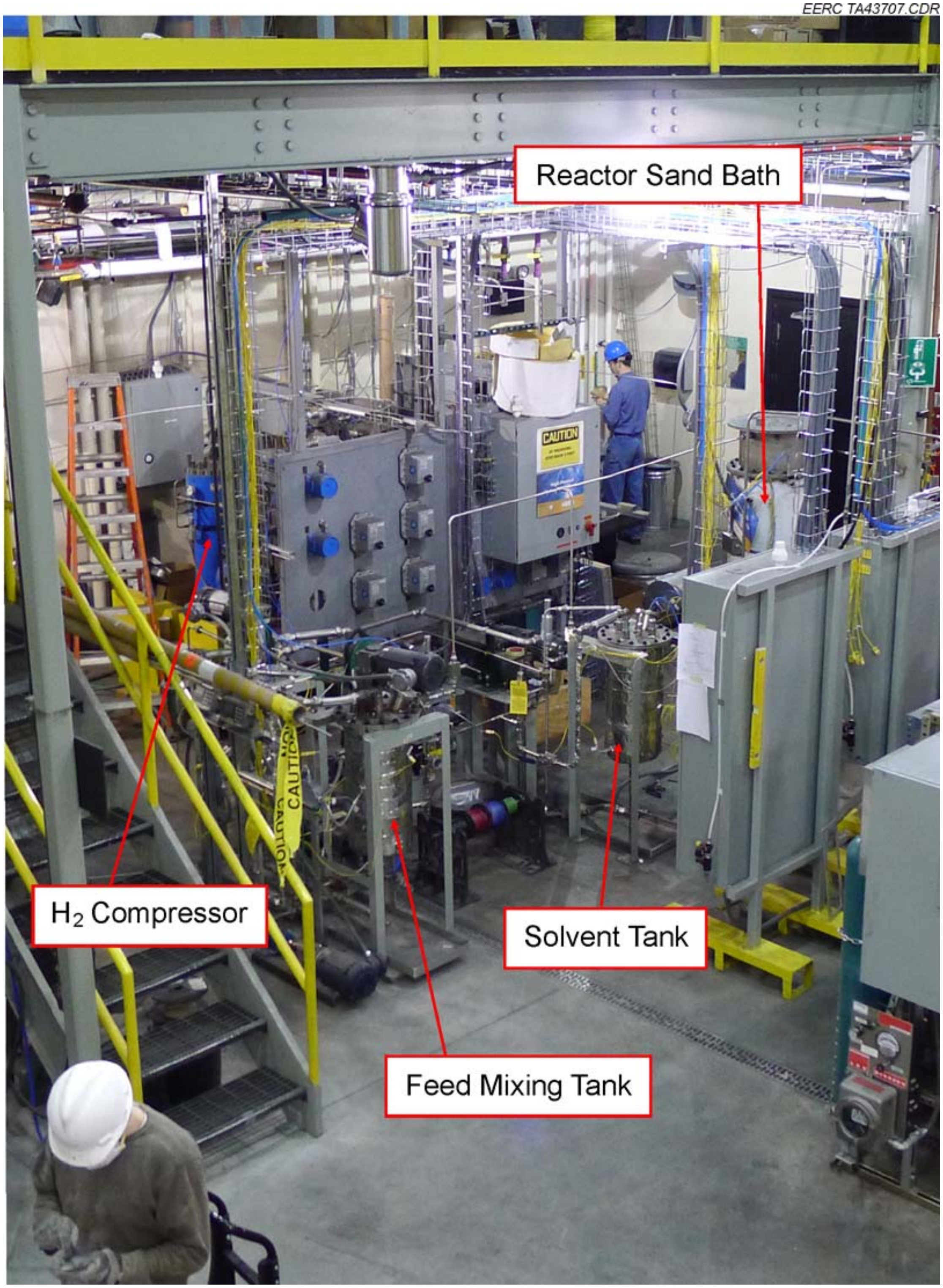


Figure II-4. MCL Pilot Plant First-floor View of DCL Reactor System.

EERC TA43708.CDR

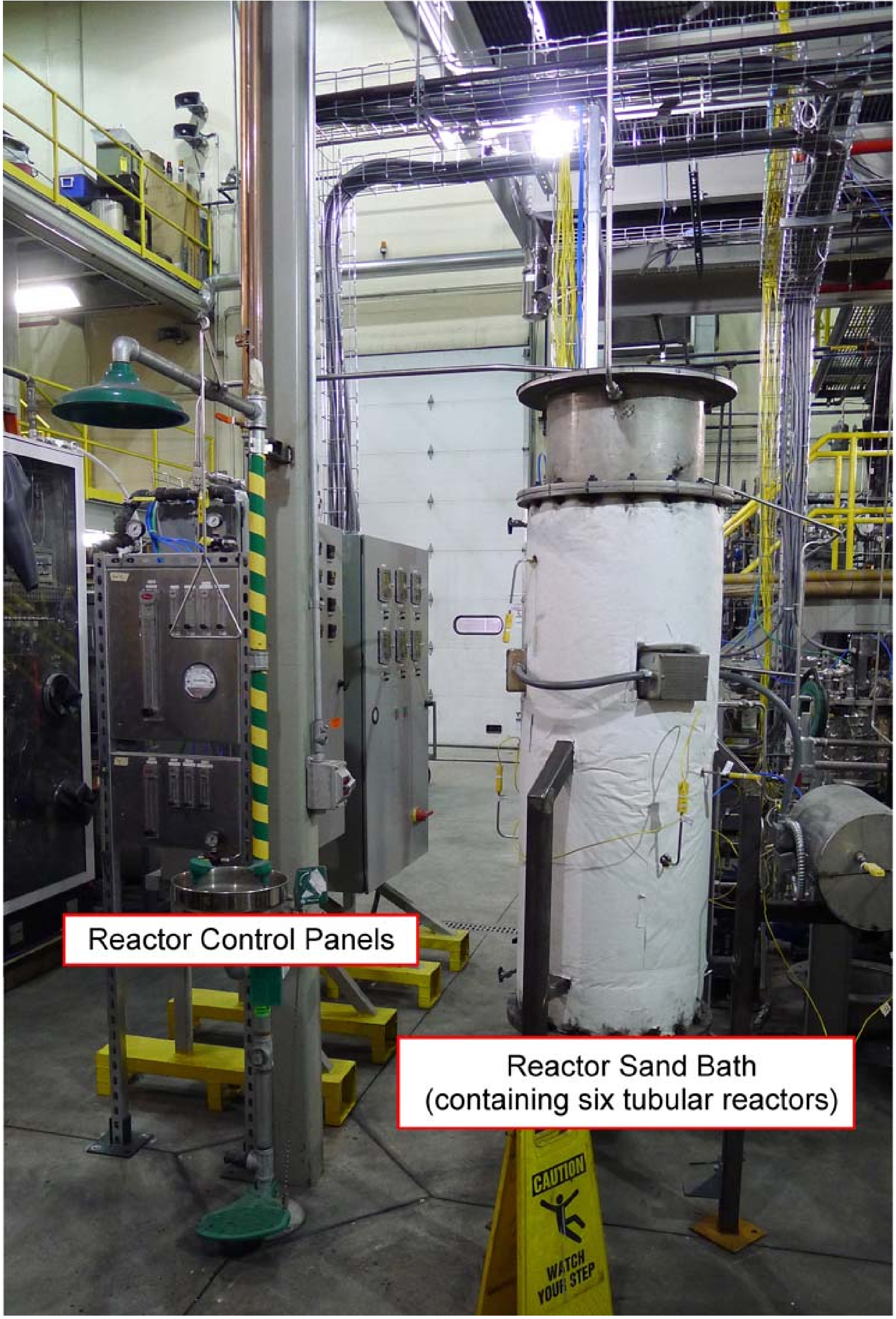


Figure II-5. MCL Pilot Plant Close-up of DCL Reactor Sand Bath.

EERC TA43709.CDR

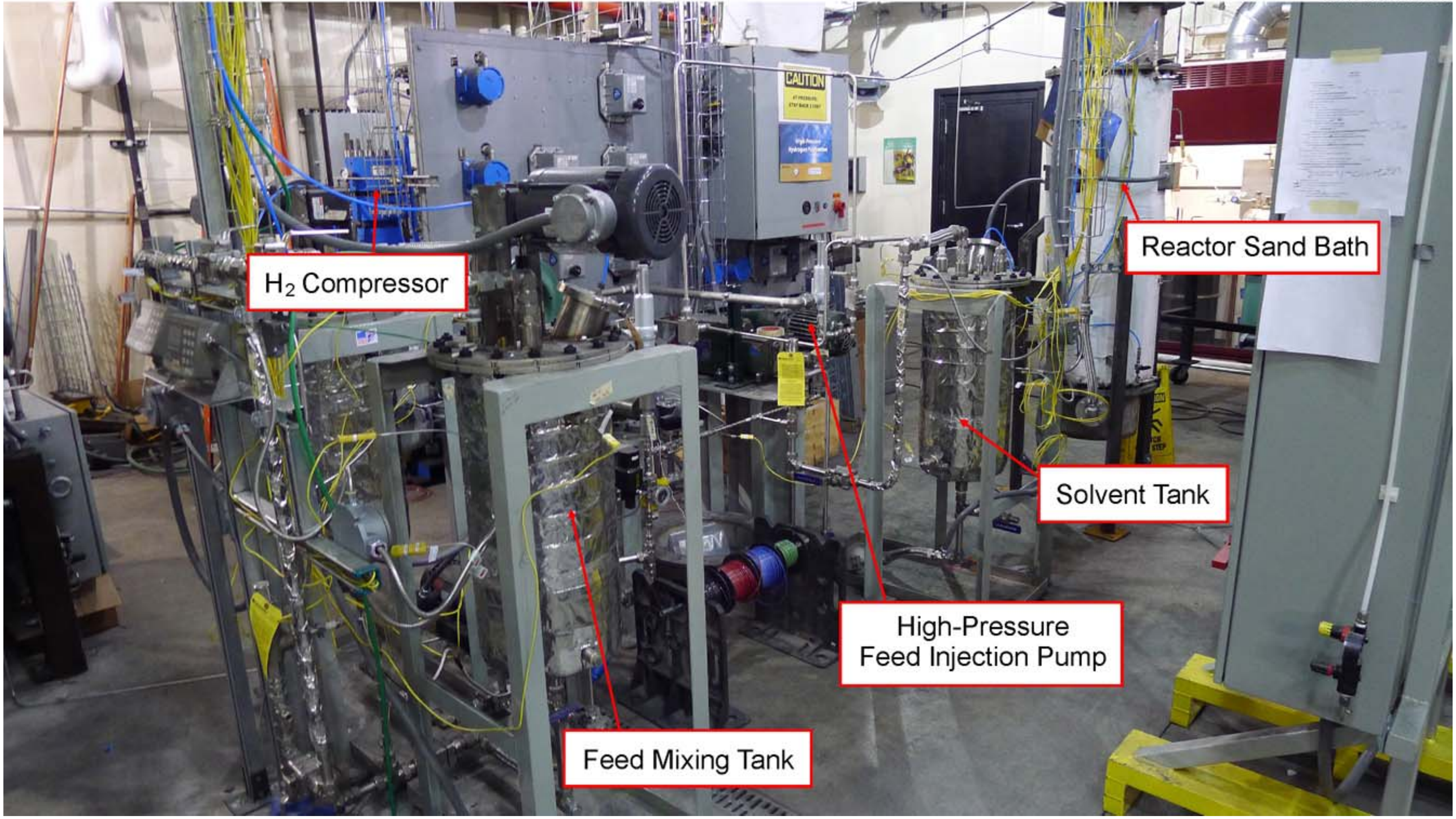


Figure II-6. MCL Pilot Plant Close-up of Pre-reactor Feed Preparation and Injection Systems.

Figure II-7. MCL Pilot Plant Hydrogen Compressor System.

EERC TA43705.CDR

Figure II-8. MCL Pilot Plant Nitrogen Compressor System.

EERC TA43710.CDR

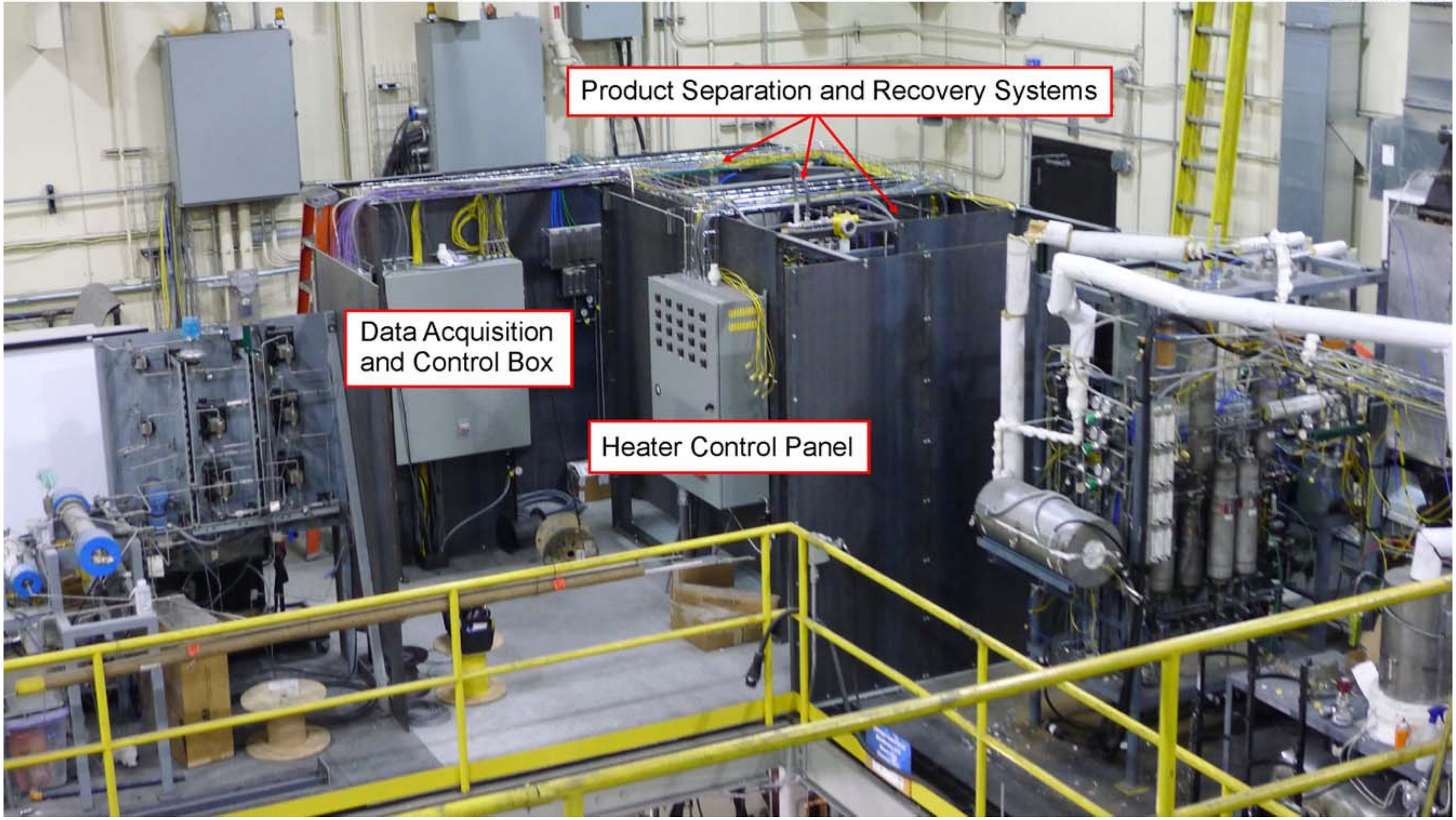


Figure II-9. Second-floor View of DCL Reactor System.

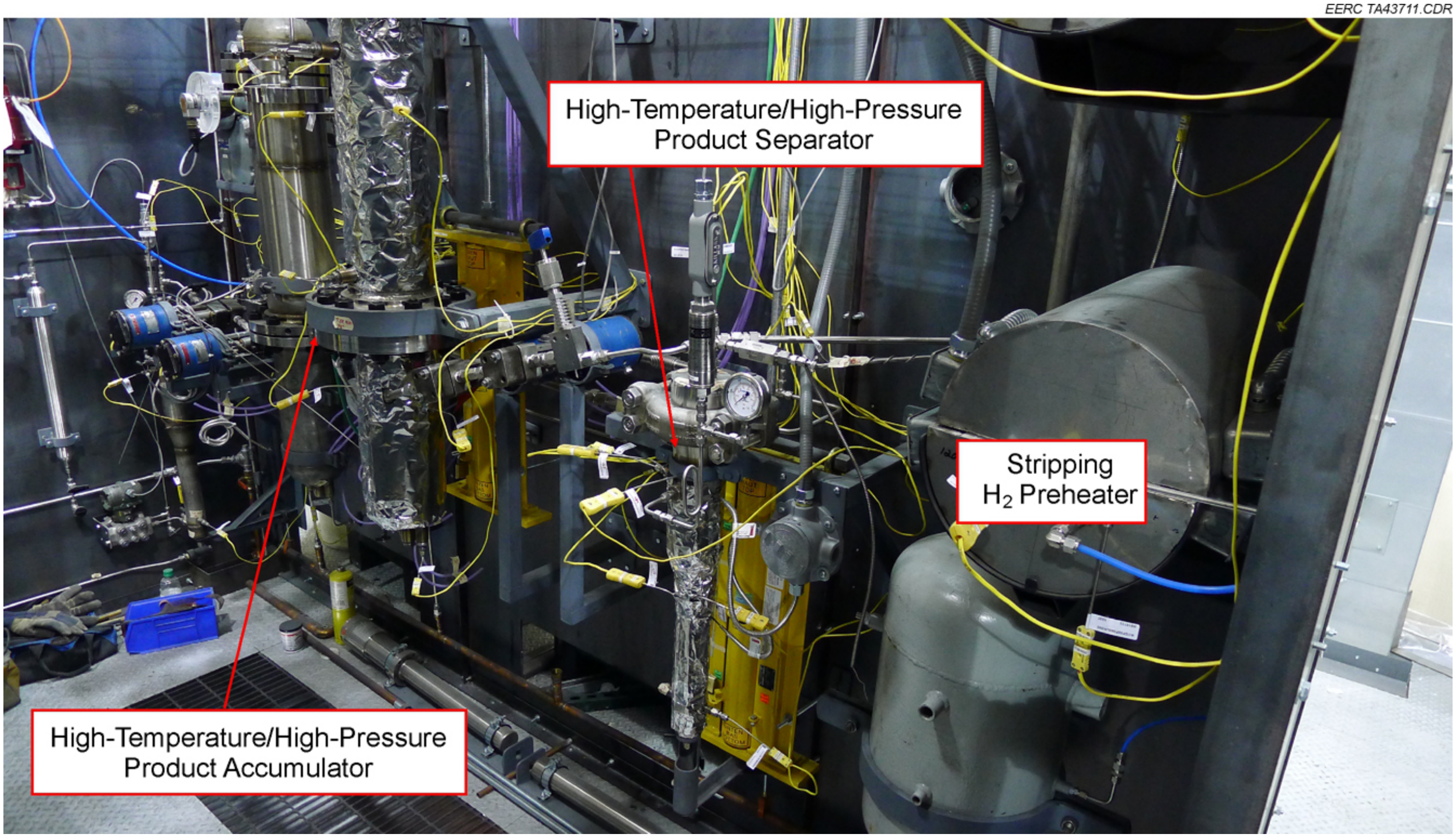


Figure II-10. Close-up of Product Separation and Accumulation Systems.

Figure II-11. Offline Distillation System at EERC

MCL Pilot Unit Duty Specification

The unit duty specification was defined for basic coal conversion and product generation capabilities and this is the basis for the initial configuration.

Capabilities for continuous feed and product recovery were selected over batch unit specifications – and continuous product fractionation and heavies recycle capabilities were incorporated to insure good steady-state operations.

Specifications were also set for design of a laboratory scale coal liquids upgrading system to allow small scale sample production of final hydroprocessed liquids for initial AFRL testing.

Stage 1 – MCL "Once-Through Operation": Preparation of VGO

The purpose of the once-through operation is to generate enough test coal-derived vacuum bottoms and VGO to start the liquefaction process; thereafter, the process is self-sustaining and generates bottoms and VGO on a continuous basis. After sufficient amounts of vacuum bottoms and VGO needed to initiate the liquefaction process are produced, further processing is conducted to produce test coal-derived raw middle distillate for upgrading to jet fuel or other fuel. Middle distillate upgrading will be conducted at Intertek PARC.

The volatile products were condensed to form a liquid using a series of condensers, and the remaining slurry was collected and transferred to a freezer for storage. The frozen slurry was pulverized and transferred to the mixing tank for recycle. The uncondensed gas as passed through a scrubber for removal of acid gases, and the remaining gas was sent to a flare. The condensed liquid was collected every 6 hours, transferred to a distillation unit located near the DCL system and batch distilled to give about 4.2 liters of VGO, 3 liters of naphtha, water and middle distillate. The VGO from distillation was recycled with previously obtained material to generate a test coal derived VGO for use in unit operations.

Stage 2 – MCL "Bottoms Recycle" Operation

After generating sufficient quantities of a Montana coal derived solvent VGO and vacuum bottoms, the liquefaction of pre-dried Montana Crow coal was conducted to generate a distillate fuel referred to as middle distillate for upgrading to synthetic fuel blendstocks.

For liquefaction processing of a test coal, coal and vacuum bottoms ground to ~100 mesh were mixed with VGO, and catalyst was transferred to the slurry tank. The overall process involved feeding slurry consisting of an approximate 1/1/1 mixture of dried coal (2 pounds), coal derived VGO (2 pounds), vacuum bottoms (2 pounds) and ppm quantities of catalyst per hour to the reactor. A constant pressure of 17.24 Mpa (2500 psig) was maintained through use of a pressure control valve and constant flow of hydrogen throughout the operation.

The bottoms recycle operation utilized the same procedures as described above. The vacuum bottoms and liquid products were collected every 6 hours. The liquid product was distilled to generate water, <149 deg. C (<300 deg.F) naphtha, 149-343 deg. C (300-650 deg. F) middle distillates, and >343 deg. C (650 deg. F) heavy oil (VGO).

We have also conducted preliminary tests at the Pittsburgh Applied Research Center (PARC) to begin unit and catalyst certification work and to be ready for testing of MT bituminous coal conversion studies using Crow coal.

The vacuum bottoms and VGO generated every 6 hours were mixed with freshly ground coal and catalyst and recycled until 3 gallons of middle distillate was produced. Samples that were sent to PARC in Pittsburgh were analyzed before upgrading – see Section XXYY below for further details on coal and biomass derived liquids production.

III. CATALYTIC HYDRODEOXYGENATION and ISOMERIZATION (CHI)

a. Overview

Previously conducted studies on bio-oil to JP-8 under contract by the Defense Advanced Research Projects Agency (DARPA) have been recently reported and serve as one of the key technology components for CHI in ICTL.(8) Activities conducted within that project led to the successful development of a unique technology pathway that economically converts renewable triacylglycerides (TAGs) including crop oils, algal oils, and animal fats to a liquid hydrocarbon stream that is further refined to produce a jet fuel identical in physical and chemical characteristics to petroleum-derived military and commercial jet fuel (JP-8 and Jet A1, respectively). In addition to jet fuel, other products include diesel fuel and a naphtha stream suitable for use in the production of a variety of chemicals. Additional hydroprocessing based technology for conversion of various vegetable based oils to JP-8 and diesel have been commercialized in Europe, and they too have been incorporated into the overall ICTL flow scheme as part of the CHI technology portfolio.

Unique from traditional transesterification - based biodiesel technologies to produce first generation biodiesel, CHI technology yields a hydrocarbon-only (oxygen-free) diesel fuel with cold flow, stability, and energy density characteristics similar to or more advantageous than those of petroleum diesel. Another advantage of CHI technology for renewable oil refining is the absence of trace metal and sulfur contaminants that are present in petroleum crude oils. The absence of sulfur eliminates the need for costly processing steps required to remove it from typical petroleum-derived fuels.

Although jet fuel was the primary focus of the DARPA effort, the hydrocarbon produced from TAG feedstock comprises the basic building blocks for a variety of fuels and petrochemical intermediates and products, and these were explored in the current study. Through the use of integrated unit operations including separations and thermo-catalytic reactions, products including naphtha, gasoline blendstocks, aromatics, olefins, and branched and cyclic paraffins can be produced.

Feedstock is an important factor in both the technical and economic viability of a commercial renewable oil refinery. Crop oils that have been tested and processed by the EERC into renewable hydrocarbon products include soybean oil, canola oil, cuphea oil, coconut oil, and waste grease. These feedstocks represent the range of what comprises typical TAG and were all processed similarly with similar performance results.

As illustrated in Figure III-1, the CHI pathway comprises:

1. Catalytic Hydrodeoxygenation (HDO) to convert TAG and/or FA feedstocks to normal paraffins ranging in carbon number from C3 (propane) to C24.
2. Polishing to remove trace quantities of residual water and/or unconverted FA's.
3. Catalytic Isomerization and Cracking to convert normal paraffins to an isoparaffin/paraffin mixture with significant content in the JP-8 carbon number range of C8–C16.
4. Distillation of the isoparaffin-rich mixture to yield a slate of products including a JP-8-grade synthetic paraffinic kerosene (SPK), diesel fuel, and naphtha/gasoline blendstock.

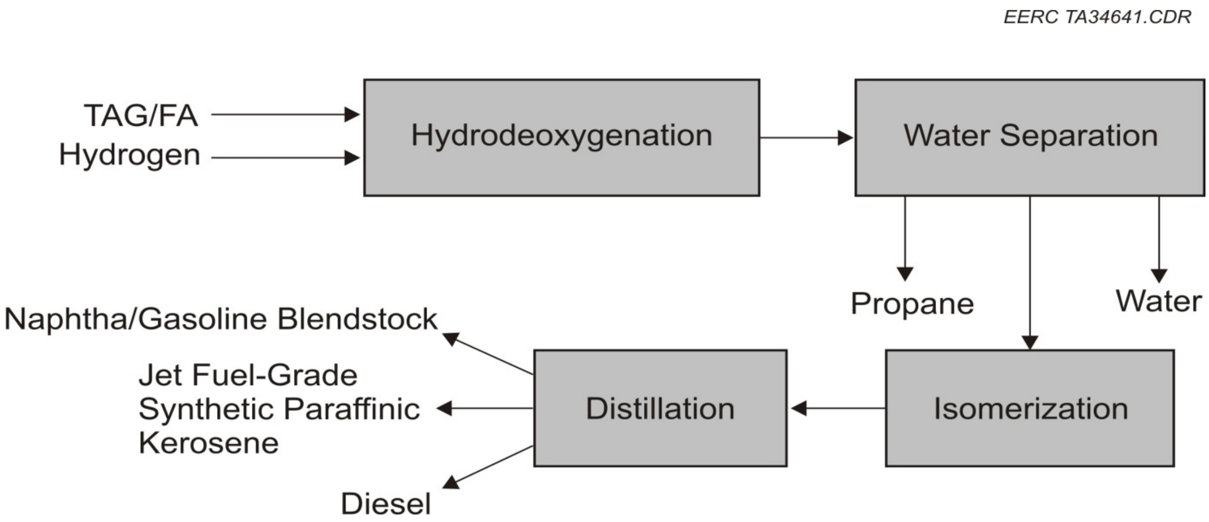


Figure III-1. Catalytic Hydrodeoxygenation and Isomerization Process (CHI)

b. CHI Experimental Methods and Program

Methodology for the current project is focused on two primary work areas:

1) Tailoring CHI technologies for optimum efficiency conversion of FAME (that is analogous to Montana type algae and camelina based feedstocks) to fuels and chemicals, with the primary objective of generating data and information needed to support development of a renewable ICTL refinery design.

2) Assessing the technical viability of an ICTL project based on feedstock availability and cost, energy input requirements, projected commercial-scale capital and operating costs.

Operational data generated during feedstock-specific process optimization activities will be used as the basis for development of a pilot-scale renewable ICTL refinery design. Product-specific activities are described below.

Jet Fuel Development*.* CHI jet fuel technologies can be optimally tailored for selected feedstock oils. Samples produced from FAME and TGFA based feeds will be blended with upgraded MCL distillates and submitted to the U.S. Air Force Research Laboratory (AFRL) at Wright–Patterson Air Force Base for evaluation based on fuel property requirements delineated in U.S. military jet fuel specifications MIL-DTL83133E and/or MIL-DTL 83133F.(9-13)

Diesel Fuel Sample Production**.** Diesel fuel samples will be produced from the same FAME and TGFA based bio-feedstocks with more traditional fatty acid profiles. Samples will be submitted to AFRL and/or another lab capable of performing full diesel fuel specification compliance testing.(14)

Naphtha Sample Production. Naphtha is a co-product of diesel and jet fuel production and comprises molecules with a carbon chain length ranging from about C4 to C8. Naphtha has applications as a feedstock for the production of gasoline, fertilizer, and olefins used in production of polymers and other chemical products.

The bio-feedstock is hydrotreated using a hydrotreating catalyst that is described in prior publications.(14-16) The hydrotreating catalyst includes one or more metals from Groups 6, 8, 9, and 10 of the periodic table of the elements. In some examples, the one or more metals can be selected from palladium (Pd), platinum (Pt), nickel (Ni), and combinations thereof, especially when fully saturated products are desired. (NiMo) catalyst including nickel and molybdenum, cobalt-molybdenum (CoMo) catalyst and other similar systems have been shown to be useful. The hydrotreating catalyst can include supported or unsupported metals. In various studies, the catalyst includes a support. In applications, the support includes alumina, silica, or a combination thereof. The catalyst can be a supported NiMo or CoMo catalyst. In embodiments, NiMo/Al_2O_3--SiO_2 or CoMo/Al_2O_3 catalyst is utilized.

General Operating Conditions for CHI

Reactor temperature parameters can vary between about 150.deg. C. and about 800.deg. C., or about 250.deg. C. to about 600.deg. C., or about 300.deg. C. to about 550.deg. C., or about 340.deg. C. to about 530.deg. C.

Reactor pressures can vary between about 0.79 Mpa (100 psig) to about 10.43 Mpa (1500 psig), or about 1.48 Mpa (200 psig) and about 5.22 Mpa (750 psig). In some embodiments, reactor pressures can vary between about 500 psig and about 7.0 Mpa (1000 psig), while in some embodiments, reactor pressures can vary between about 0.79 Mpa (100 psig) and about 3.5 Mpa (500 psig). Hydrogen flow rates can vary between about 70.8 liters (2.5 standard cubic feet) per liter and about 1,415 liters (50 standard cubic feet) per liter of TAG, FFAs, and C1-C5 FAEs, or about 424.8-566.3 liters (15-20 standard cubic feet) per liter. Liquid hourly space velocities (LHSV) can vary between about 0.1 reactor volumes/hr (e.g. hr^{-1}) and 8 hr^{-1}, about 0.5 hr^{-1} and about 4 hr^{-1}, or between about 0.8 hr^{-1} and about 1.2 hr^{-1} being most preferred.

A product including predominantly normal alkanes is produced via the hydrotreating step. In some embodiments, the product including predominantly normal alkanes can include aromatic hydrocarbons along with saturated hydrocarbons. The product including predominantly normal alkanes can overlap with the product described below including aromatic hydrocarbons along with saturated hydrocarbons to any degree.

Hydrotreating of the feedstock can be performed at modest temperatures and pressures (relative to other methods). The temperature is in the range of about 340.deg. to about 410.deg. C. Pressure is in the range of about 1.19 Mpa (150 psig) to about 1.48 Mpa (200 psig) with un-sulfided catalysts, and up to 10.43 Mpa (1500 psig) with sulfided catalysts. The temperature is about 400.deg. C., and the pressure is about 1.48 Mpa (200 psig) for unsulfided systems and up to 10.43 Mpa (1500 psig) for sulfided systems. Suitable pressures can include pressures that are below that typically employed in processes utilizing sulfided hydrotreating catalysts. In some embodiments, the hydrotreating of the feedstock can be performed at any suitable temperature and pressure, such as any temperature or pressure given in the present paragraph, or any temperature or pressure between the ranges given in the present paragraph and the ranges given in the section below for first products including saturated hydrocarbons and aromatic hydrocarbons.

IV. MCL AND CHI LIQUIDS PRODUCTION – RESULTS AND DISCUSSION

a. Fuels and Specialty Products from Coal/Bio-oil Conversion

Unlike FT-based CTL processes that require complete feedstock disassembly to a syngas followed by syngas reassembly into a fuel — both steps of which require high energy inputs/outputs — Accelergy's direct coal liquefaction MCL process leverages coal feed chemistry through partial feedstock disassembly to a liquid followed by liquid upgrading to a fuel. Both steps in Accelergy MCL involve significantly lower energy inputs/outputs than their FT process counterparts. A summary of analytical results for the MCL and HEFA products is provided in Tables IV-1-4 below.

The unique molecular composition of our fuels (with controlled isoparaffinic, cyclo-paraffinic and aromatics content) make them interesting candidates for fuel system applications where high energy density could be important, and for next generation aircraft engines where high thermal stability is an important feature.

Pilot scale samples of synthetic jet from Accelergy/EERC MCL/CHI pilot plant studies met Tier 1 certification requirements in tests performed at the US Air Force Research Labs. We plan to expand that program at EERC to produce larger quantities of JP-8/Jet A blendstocks for Tier 2-4 AFRL testing, and to examine different direct coal/biomass liquefaction routes and related fuel quality/composition effects.

It is clear from pilot scale studies that Accelergy's hybrid ICBTL routes for biomass and/or natural gas plus coal co-conversion are able to meet commercial specs for synthetic JP-8, Jet-A and related distillate fuels. Our goal is to continue that program to explore the full range of options for employing these materials for next generation jet propulsion platforms. Formal Cooperative Research and Development Programs are underway with the US DOD, EERC and others to develop a 100% fully synthetic jet fuel from coal and biomass – and efforts are underway to tailor make fuels in our EERC MCL pilot facilities and associated upgrading operations at the University of Pittsburgh Applied Research Center (PARC). This work is aimed at fuels for next generation propulsion systems where system thermal management, fuel stability and/or high fuel-energy-density requirements are important. Findings from these studies will be incorporated into the commercialization analysis of the proposed program.

The MCL coal derived mid-distillate produced at EERC was successfully upgraded at the University of Pittsburgh Applied Research Center (PARC), Figure IV-1. PARC operates a fully automated "P-87" Hydroprocessing (HP) pilot unit with several stages of product fractionation available together with a range of recycle treat-gas capabilities. Process data are retrievable hourly via an on-line web program. A schematic of the upgrading unit is shown below.

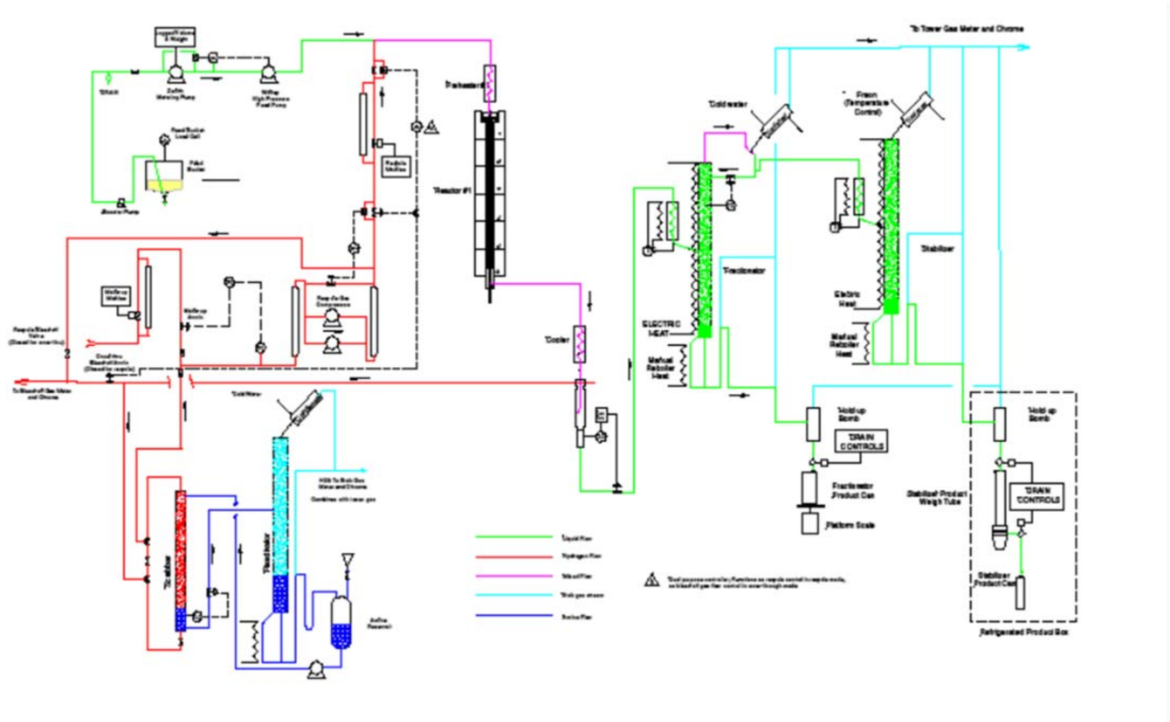
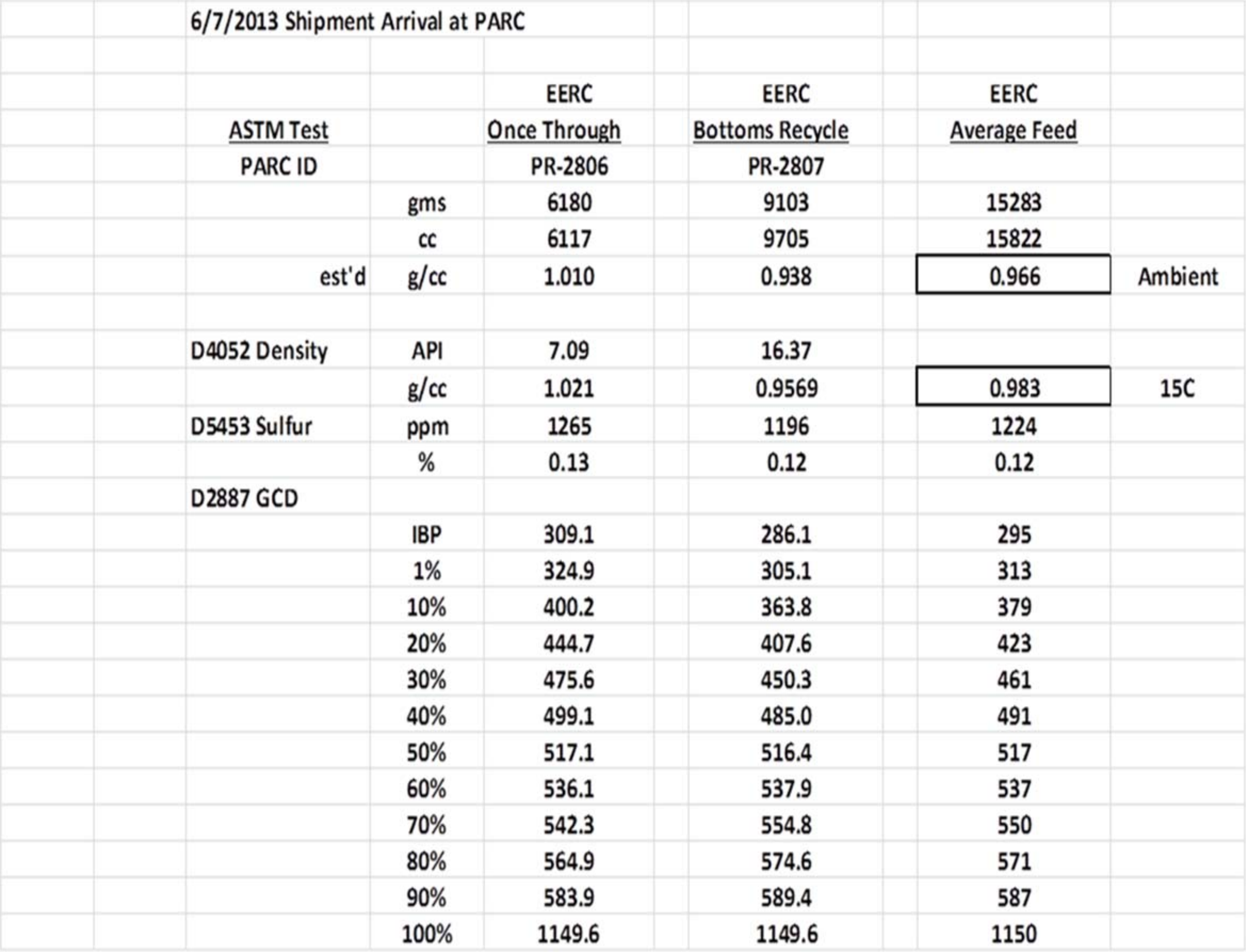


Figure IV-1. Simplified Flow Diagram of P87 CHI Pilot Plant.

Raw MCL product is comprised primarily of aromatics with <10% wt total paraffin and cycloparaffin (naphthene) content. Hydro-dearomatization (HDA) of this material leads to a product comprised primarily of cyclo- and acyclic- paraffins. Hydroprocessed Ester and Fatty Acid derived second generation bio-distillate, on the other hand, consists almost exclusively of normal and iso-paraffins which make idea blendstocks for jet or diesel fuels.

MCL product upgrading operations were conducted in a "once through" mode with direct recovery of distillate range products and a "bottoms recycle" mode where heavier products were recycled back to the Hydroprocessing operation for further upgrading, see Table IV-1. Composite samples were collected from the multi-day operating periods and evaluated for molecular composition and boiling range. Individual distillation cuts are being sent for ASTM D7566 and D975 testing.

Table IV-1. GCD Analysis of EERC DCL Distillate for PARC Upgrading



6/7/2013 Shipment Arrival at PARC

		EERC	EERC	EERC	
ASTM Test		Once Through	Bottoms Recycle	Average Feed	
PARC ID		PR-2806	PR-2807		
	gms	6180	9103	15283	
	cc	6117	9705	15822	
est'd	g/cc	1.010	0.938	0.966	Ambient
D4052 Density	API	7.09	16.37		
	g/cc	1.021	0.9569	0.983	15C
D5453 Sulfur	ppm	1265	1196	1224	
	%	0.13	0.12	0.12	
D2887 GCD					
	IBP	309.1	286.1	295	
	1%	324.9	305.1	313	
	10%	400.2	363.8	379	
	20%	444.7	407.6	423	
	30%	475.6	450.3	461	
	40%	499.1	485.0	491	
	50%	517.1	516.4	517	
	60%	536.1	537.9	537	
	70%	542.3	554.8	550	
	80%	564.9	574.6	571	
	90%	583.9	589.4	587	
	100%	1149.6	1149.6	1150	

Hydroprocessing of MCL distillate reduces overall heteroatom content as well as the total concentration of unsaturates and aromatics. In all cases, total aromatics were greatly reduced from the original raw MCL distillate sample and olefins reduced to about 3% vol. or lower. Sulfur levels were significantly reduced also to <2 ppmw or lower. Low levels of oxygenates were still detected in the final product and detailed characterization studies revealed the presence of highly hindered alcohols and ketones.

The unusual molecular composition of the various streams provides the opportunity to tailor make various formulated fuels with controlled levels of paraffins, cycloparaffins and aromatics. Moreover, it is possible to select specific aromatics for their fit for purpose performance thereby allowing the fuel producer to control overall lubricity, energy density, materials compatibility, and emissions properties, Figure IV-2 and Table IV-2.

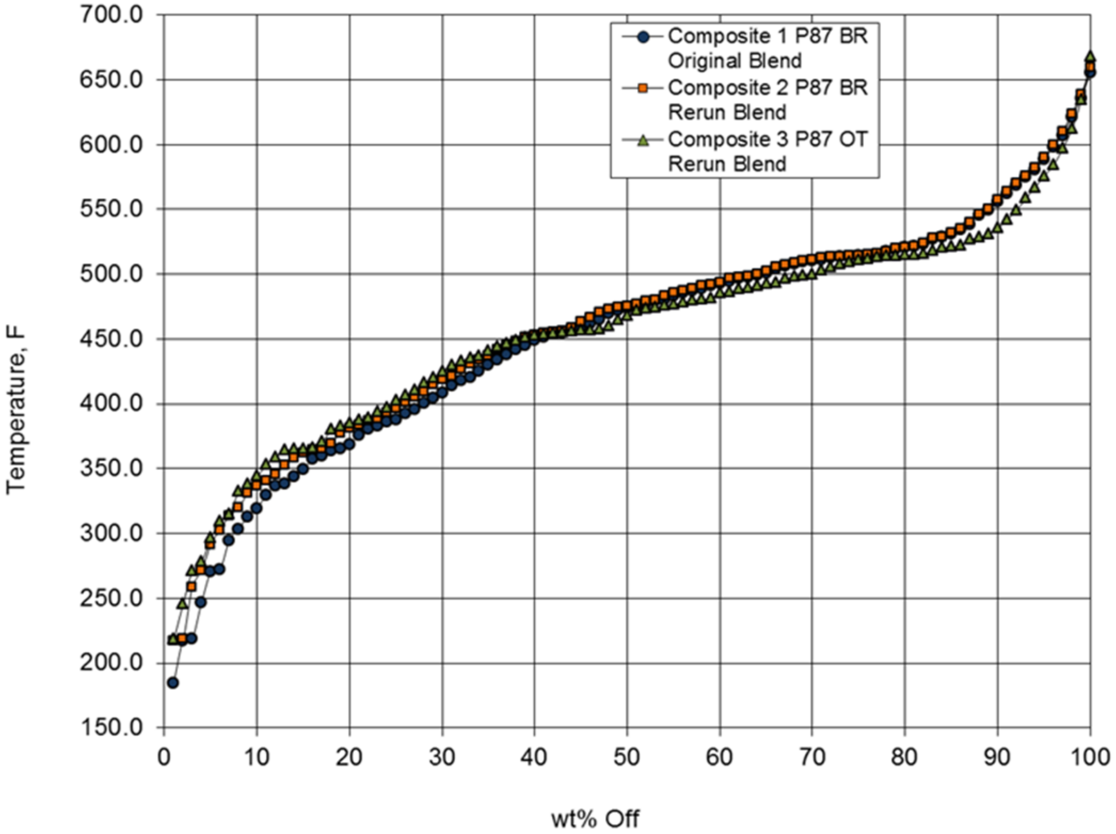


Figure IV-2. PARC Upgraded MCL Distillate Production Curves

Schobert's pioneering work(9) on coal based jet fuels provides significant guidance to our overall formulations program for next generation JP-8/JetA. They have reported on the basic structure function rules for highly stable JP-900 – a fuel which would offer significant advantage to emerging propulsion systems where high thermal and oxidative stability are important.

Schobert et al (9, 10, 13) reported:

Relative Stability of Hydrocarbon Components*. The relative stability of alkanes and cycloalkanes increases with increasing chain or side-chain length. Cycloalkanes are desirable components of advanced jet fuels, in terms of having higher thermal stability and density than n-alkanes of the same carbon number. The cis-isomer is typically more reactive than the* *transisomer, with the exception of cis-1,3-dimethylcyclohexane, which is more stable than its transisomer.*

The presence of a branch or branches appears to decrease the decomposition rate compared to normal alkanes.

Reactive Structure Index. *We developed a reactive structure index to correlate the molecular structures of saturated hydrocarbons with their reactivities using a linear group* method of physical organic structure function elements. The index is composed of several sub-indices determined from the structure, including carbon group indices, ring index and conformation index. We examined the effects on decomposition of ring structure, side-chain length, steric isomers, and branching. *Good correlations were obtained for two sets of saturated hydrocarbons.*

Quantitative Structure-Thermal Stability Relationships. *Quantitative structure-property relationships (QSPR) were applied to study the thermal stability of pure hydrocarbons typical of jet fuel components. A simple method of chemical structure description in terms of Benson groups was tested in searching for structure-property relationships for the hydrocarbons we tested experimentally. We also tested molecular connectivity as a structure-based approach to chemical structure-property relationship analysis.*

The quantitative structure-property relationship method proved to be a better predictor of degradation behavior for 13 compounds stressed for 4 hours at 450¡C than other approaches based only on topological descriptors. In addition, correlations based on comprehensive descriptors require a smaller number of parameters to achieve the same accuracy of prediction.

Pyrolysis of Binary Mixtures of n-Tetradecane and Hydrogen Donors*. Model compound reactions were carried out at 450°C in batch reactors. Tetralin appeared to be more effective than benzyl alcohol or n-butylcyclohexane in providing lower conversion of the n-tetradecane and leaving higher amounts of unconverted hydrogen donor.*

Thermal Decomposition of Norpar-13*. Norpar-13, a mixture of n-alkanes, was found to be a useful model for observing the effects of high-temperature stressing of jet fuels. Norpar was stable in the oxidative regime and increased the amount of pyrolytic deposition detected. The increased pyrolytic deposits made observing the mitigating effects of the additives easier than inan authentic jet fuel. Tetrahydroquinoline (THQ), benzyl alcohol, and tetralin all increased thethermal stability of Norpar-13 in a flow reactor. THQ was the most effective, consistent with batch reactor results, although an oxidative deposit formed with THQ addition.*

Norpar-13 was studied under supercritical conditions, both at 425°C in a glass tube reactor and at 450°C in conventional microautoclave batch reactors.

Cycloalkanes, xylene, toluene, and benzene were stable and did not contribute to the formation of solid deposits. Indan and C2 and C2-indans were very stable. Radicals formed from tetradecane and other alkanes can abstract hydrogen from these stable compounds to form reactive radicals. Deposit formation in jet fuel/tetradecane mixtures was proportional to the initial concentration of tetradecane, but the direct correlation between deposit mass and tetradecane conversion was poor.

Table IV-2. Analysis of Hydroprocessed Montana Coal-Derived MCL Distillate Products

Sample	**Composite**	**Composite**	**Composite**
ID	**1**	**2**	**3**
Reactor	**P87**	**P87**	**P87**
Source	**Bottoms Recycle Original**	**Bottoms Recycle Rerun**	**Once Through Rerun**
Wt gms.	**3997**	**2010**	**3061**
Vol. ~gal.	**1.23**	**0.62**	**0.95**
Specfic Graviity, g/cc	**0.8557**	**0.8557**	**0.8557**
Sulfur, ppm	**2.1**	**- -**	**- -**
FIA			
Aromatics, vol%	**<0.1**	**<0.1**	**1.5**
Olefins ,vol%	**2.9**	**3.1**	**2.5**
Saturates, vol%	**97.1**	**96.9**	**96.0**

The relative thermal stability of these materials frequently reflects the overall level of strain energy in the individual isomer – and efforts to control their presence via control over the CHI or HP processing conditions have been fairly successful at several major synthetic fuels programs.(13)

Schobert's quantification of structure function performance of paraffinic and cycloparaffinic streams with aromatics reveals a relatively straightforward stabilizing influence of the latter components on the overall blended fuel.

Product speciation studies reveal a range of normal, iso-, cyclo- paraffins together with trace levels of aromatics and oxygenates. Control over the degree of branching and the average chain length of branches has been shown to be an important aspect of overall oxidative and thermal stability of the products, Table IV-3 and IV-4.

Thermooxidative stability studies of blends of a straight-run Jet-A fuel (POSF-2827) and a paraffinic/cycloparaffinic solvent (Exxsol D-80) reported by Schobert et al(9) provide a solid basis for development of JP8+100 type fuels. Optimal blends were shown to be significantly more stable than either pure fuel or paraffin solvent. Surface fouling effects, attributed to reactions of natural antioxidants present in the fuel, can be isolated by controlling the exact composition of the aromatics present in the fuel. This aspect of future synthetic aviation fuel production is readily approached via ICTL where individual coal and biomass streams can be isolated for later separation and formulation into finished fuels.

The upgrading program consisted of two stages. Heteroatom removal and moderate aromatics hydrogenation are performed in the first stage, followed by additional hydrogenation in the second stage. For this program, the first stage product was essentially 100% saturated in the second stage, Tables IV-4 thru IV-6.

The upgrading progression is shown in the following table and figure. Raw distillate aromatics content was reduced by 100%, sulfur content was reduced from 1196 ppm to <100 ppm, and the density lowered from 0.957 to 0.859 g/cc. The distillation results show the expected boiling point shift of the higher boiling raw distillate into the jet range in the first stage, with little additional shift in the second stage, Figure IV-3.

Table IV-3. Hydrocarbon Type Analysis of Raw and Hydroprocessed Montana Coal-Derived Coal Liquids and CHI HEFA Liquids

Process	MCL	MCL-HP	MCL-HP	MCL-HP	CHI
Composition Wt% by MS	Raw Middle Distillate	Bottoms Recycle Original	Bottoms Recycle Rerun	Once Through Rerun	HEFA
n-Paraffins	3.29	6.45	7.32	4.50	16.21
i-Paraffins	3.76	4.75	6.60	5.90	83.14
Total Paraffins	6.65	11.20	13.92	10.40	99.35
1-R Naphthenes	3.8	15.81	13.15	7.97	0.35
2-R Naphthenes	0	32.98	33.54	32.34	0
3-R Naphthenes	0	36.38	34.13	46.29	0
4-R Naphthenes	0	0	0.87	0.82	0
Total Naphthenes	3.80	85.17	81.69	87.42	0.35
1-R Aromatics	36.41	0	0	0	0
2-R Aromatics	41.23	0	0	0	0
3-R Aromatics	11.90	0	0	0	0
4-R Aromatics	0	0	0	0	0
Total Aromatics		0	0	0	0
Oxygenates #	#	3.63	4.39	2.18	0
Total	100	100	100	100	100

 # NOTE: GC-MS and NMR reveal the presence of phenols, naphthenic alcohols, ketones, benzo-, dibenzo-furans and some sulfur and nitrogen containing compounds.

Table IV-4. Distillation Data for EERC Coal-Derived Fuels.

Process	**MCL**	**MCL-HP**	**MCL-HP**	**MCL-HP**	**CHI**
Sample Identification	**Raw Middle Distillate**	**Bottoms Recycle Original**	**Bottoms Recycle Return**	**Once Through Rerun**	**HEFA**
Wt% off at °C					
38 (100 °F)	0	0	0	0	0
66 (150 °F)	0	0	0	0	0
93 (200 °F)	0.02	0.42	0.18	0.13	0.42
121 (250 °F)	0.08	2.20	1.42	1.08	1.58
149 (300 °F)	0.78	6.20	5.04	4.74	12.88
177 (350 °F)	4.71	12.42	11.02	9.39	26.35
204 (400 °F)	11.60	22.15	20.76	19.83	38.73
232 (450 °F)	22.15	34.98	33.71	33.25	54.11
260 (500 °F)	38.94	56.75	56.22	62.36	64.59
288 (550 °F)	67.92	85.39	85.15	89.42	86.25
316 (600 °F)	89.86	93.03	92.80	95.02	100
343 (650 °F)	100	98.82	99.45	99.39	0
343+ (650+ °F)	0	1.18	0.55	0.61	0

Table IV-5. GCD Distillation Data for HEFA.

Wt% Sample Off - Temperature	HEFA
Wt% off at oC	
38 (100 oF)	0
66 (150 oF)	0
93 (200 oF)	0.42
121 (250 oF)	1.58
149 (300 oF)	12.88
177 (350 oF)	26.35
204 (400 oF)	38.73
232 (450 oF)	54.11
260 (500 oF)	64.59
288 (550 oF)	86.25
316 (600 oF)	100
343 (650 oF)	0
343+ (650+ oF)	0
Wt% off at °C	
149- (300°F-)	12.88
204- (400°F-)	38.73
232- (450°F-)	54.11
343+ (650°F+)	0

Table IV-6. Analysis of MCL Raw and Hydroprocessed Products.

Method	Raw Distillate	Stage 1 Product	Stage 2 Product
Gravity @16 deg. C (60 deg.F), g/cc	0.957	0.866	0.859
Sulfur, ppm	1196	12	<100ppm est.
Aromatics, FIA vol%	--	--	< 0.1%

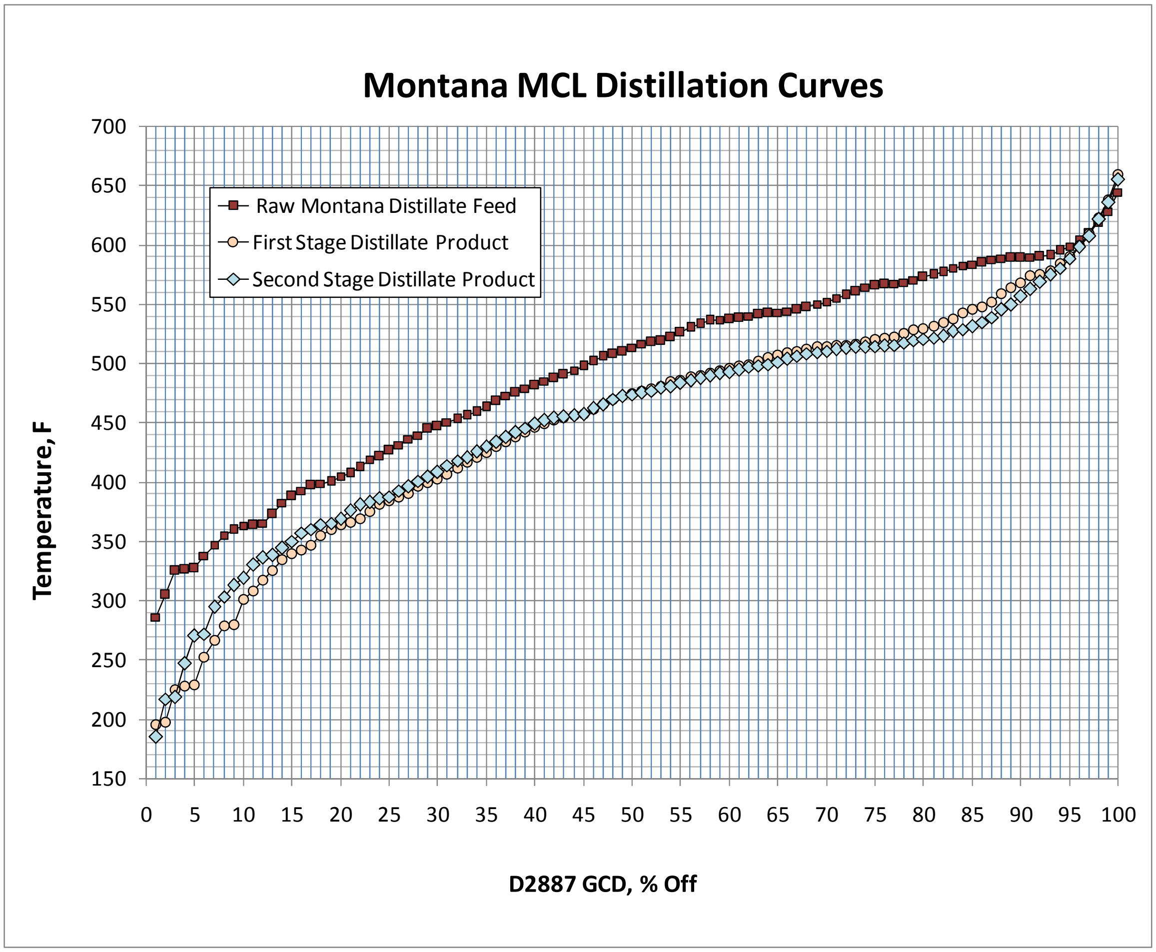


Figure IV-3. GCD Distillation Curve for Raw and MCL Hydroprocessed Liquids.

The total liquid product (TLP) was shipped to EERC for subsequent fractionation per ICTL program blending needs. EERC has provided samples for AFRL and some data from those studies is reported below.

Initial results of product upgrading at PARC were encouraging – but some problems with sample foaming were uncovered in our initial diesel product quality testing. These problems have been traced to use of specific types of vacuum grease in the distillation system – and provisions are being made to avoid this in future product separation work.

Samples of renewable jet fuels produced by CHI have been submitted to the Air Force Research Laboratory (AFRL) at Wright–Patterson Air Force Base for evaluation, and found to comply with key MIL-DTL-83133e-specified fuel property requirements including freeze point, flash point, physical density, and energy density.

b. Synthetic Jet Fuel from MCL and CHI

Summary:

Preparation of the Jet Fuel Sample

The jet fractions from isomerization and aromatization steps will analyzed by GC–MS to determine the hydrocarbon types. Based on the GC–MS data, the desired volumes of these jet fractions will be blended together to produce fuels that contains at least 8 vol% aromatic compounds.

Testing of the Jet Fuel Sample

The jet fuels produced above will be analyzed using a set of ASTM standard tests to evaluate the fuel properties. The proposed effort will be divided into two test phases. First, several bench-scale tests will be conducted to screen the fuel candidates to determine if they possess the minimum requirements of thermal stability, low temperature, and hydrocarbon range of conventional petroleum-based jet fuel. The purpose of these screening tests is to eliminate/disqualify low-quality ("bad") fuel candidates in a timely and cost-effective manner. Minimum quantities of fuel (~500 mL) are required to conduct these evaluations. The screening tests are listed below.

A. Thermal Stability (quartz crystal microbalance)
B. Freeze Point (phase tech automatic freeze point tester, ASTM D5972)
C. Distillation (ASTM D2887) 10 mL
D. Hydrocarbon Range (GC–MS) (ASTM D6379 and D2425)
E. Heat of Combustion (ASTM D4809)
F. Density, American Petroleum Institute Gravity (ASTM D4052)
G. Flash Point (ASTM D93)
H. Naphthalenes, % (ASTM D1840)
I. Aromatics and Olefins, % (ASTM D1319)
J. Mercaptan Sulfur, % (ASTM D3227)
K. Total Sulfur (ASTM D4294)
L. Hydrogen Content (ASTM D3343)

After having completed the in-house screening of the fuels produced at the EERC, the selected fuels will be submitted to the University of Dayton Research Institute (UDRI) and AFRL for Tier 1 testing, see Table IV-7. The fuels branch at the AFRL is a world-recognized research organization comprised of scientists and engineers with expertise in the analysis and evaluation of jet fuels. Under the current Defense Advanced Research Projects Agency Biofuels Program for the development of an affordable (bio-derived) alternative to petroleum-derived jet fuel, AFRL, in partnership with UDRI, proposes to conduct extensive and detailed analyses on biojet fuel candidates to assess their chemical and physical properties including thermal stability and low-temperature characteristics. Initial CHI process development activities were conducted using a small continuous-mode reactor system, and a larger continuous system was utilized for sample production. Reactor volumes for the small and larger systems are about 0.2 to 5.0 liters, respectively.

Table IV-7. Comparison of CHI JP-8 to JP-8 Average and JP-8 Specification.

Specification Test, units	EERC JP-8	JP-8 Average	JP-8 Spec.
Aromatics, vol%	**7.4**	**17.9**	**≤ 25.0**
Olefins, vol%	**1.2**	**0.8**	**≤ 5.0**
Specific Gravity	**0.786**	**0.803**	**0.775–0.840**
Flash Point, °C	**46**	**49**	**≥ 38**
Freeze Point, °C	**−49**	**−51.5**	**≤ −47**
Heat of Combustion, MJ/kg	**43.6**	**43.2**	**≥ 42.8**

A larger system is capable of operating in HDO and isomerization modes at maximum liquid throughputs of about 3 liters/hour and 1 liter/hour, respectively, and has been used to produce 25-gallon JP-8 samples that were delivered to AFRL for detailed specification compliance and turbine combustion performance and emissions testing.

A 500-ml MCL/CHI ICTL sample (ID: Coal-Biojet 3) from EERC/Accelergy was assigned an internal identification number 11-POSF-7681. The sample fuel underwent evaluations for use as a propulsion fuel for current aviation systems according to Tier I as outlined in the “Alternative and Experimental Jet Fuel and Jet Fuel Blend Stock Evaluation” protocol developed by Fuels and Energy Branch of AFRL. The fuel sample was evaluated in comparison to a representative propulsion fuel (POSF-4751) and a previous biofuel only blendstock from EERC (POSF-7492). A list of the fuel samples used in this study is shown in Table IV-8.

Table IV-8. List of Fuel Samples Used in this Study.

POSF No.	Manufacturer/ Source	Fuel Description
7681	EERC/Accelergy	Coal Biojet 3
7492	EERC	BJet2011
4751	WPAFB	JP-8

MIL-T-83133 Specification Evaluation

The biofuel sample (POSF-7681) was evaluated according to the current jet fuel specification for JP-8 specification properties, some of which are discussed below. Results from testing with POSF-7681, POSF-7492 and the representative JP-8 fuel (POSF-4751) are shown in Table IV-9, along with JP-8 specification limits.

Aromatics (D1319). POSF-7681 has lower aromatics (11 volume %) by the JP-8 specification method D1319, as compared to the JP-8 specification limit (maximum 25 volume %) and the representative JP-8 value (19 volume %); however, it has higher aromatics than POSF-7492 (7 volume %).

Heat of Combustion (D4809). The measured heat of combustion of POSF-7492 (43.1 MJ/kg) meets the specification requirement of 42.8 MJ/kg minimum, and is similar to the heats of combustion of POSF-7492 (43.2 MJ/kg) and the representative JP-8 fuel (43.3 MJ/kg).

Distillation (D86). The distillation temperatures of POSF-7681, like those of POSF-7492, meet the JP-8 specification limits, and are somewhat lower than those of POSF-4751.

Flash Point (D93). The flash point of POSF-7681 (44°C) meets the JP-8 specification minimum requirement of 38°C, is similar to the flash point of POSF-7492 (46°C), and below flash point of POSF-4751 (51 ºC).

Freeze Point (D5972). The freeze point of POSF-7681 (<-60°C) is comparable to the freeze of POSF-7492 (-62°C) as well. In addition, it meets the JP-8 specification maximum of -47°C, and is well below the freeze point of POSF-4751 (-50ºC).

Density (D4052). The density of POSF-7492 (0.809 kg/L) is the same as that of POSF-7492. It is within the JP-8 specification range of 0.775 to 0.840 kg/L, and slightly above density of POSF-4751 (0.804 kg/L).

Non-Specification Evaluation

Biofuel POSF-7681 was also evaluated with other non-specification analyses. The results of these analyses were compared to results obtained for the representative JP-8 fuel (POSF-4751) and the previous EERC biofuel (POSF-7492).

Hydrocarbon Type Analysis (D6379 & D2425). The biofuel (POSF-7681) contains a lower amount of aromatics by D6379 (10 volume %), as compared to 19 volume % in POSF-4751 (Table IV-10) and a higher amount of aromatics than biofuel POSF-7492 (6 volume %).

By method D2425, POSF-7681 contains 43 mass % paraffins, 46 mass % cyclo-paraffins, and 11.3 mass% aromatics; and POSF-7492 contains 39 mass % paraffins, 54 mass % cyclo-paraffins, and 6.9 mass% aromatics; whereas, the JP-8 fuel contains approximately 49% paraffins, 30% cyclo-paraffins, and 21 mass % aromatics (Table IV-11).

Hydrocarbon Type Analysis (GCxGC). By two-dimensional gas chromatography (GCxGC), POSF-7681 contains 44 mass % paraffins, 41 mass % cyclo-paraffins, and 14.2 mass% aromatics; while, the JP-8 fuel contains approximately 51% paraffins, 26% cyclo-paraffins, and 23 mass % aromatics (Table IV-12). The GCxGC hydrocarbon type results compare reasonably well with the D2425 results for the biofuel.

GC/n-Paraffins Analysis. When analyzed by gas chromatography-mass spectrometry (GC-MS), POSF-7681 contains a lower level of normal paraffins (8 weight %) as compared to 11 weight % in POSF-7492 and 19 weight % in POSF-4751 (TableIV-9, IV-13 and Figure IV-2).

Table IV-9. Results of Specification Testing.

Specification Test	**MIL-DTL-83133H Spec Requirement**	**7681 Coal Biojet 3**	**7492 BJet2011**	**4751 JP-8**
Aromatics, vol %	**≤25**	11.0	6.6	18.8
Olefins, vol %		0.5	0.6	0.8
Heat of Combustion (measured), MJ/Kg	**≥42.8**	43.1	43.2	43.3
Distillation:				
IBP, °C		151	153	159
10% recovered, °C	**≤205**	170	171	182
20% recovered, °C		177	178	189
50% recovered, °C		193	196	208
90% recovered, °C		230	235	244
EP, °C	**≤300**	259	260	265
Residue, % vol	**≤1.5**	1.0	1.3	1.3
Loss, % vol	**≤1.5**	0.8	0.4	0.8
Flash point, °C	**≥38**	44	46	51
Freeze Point, °C	**≤-47**	<-60	-62	-50
API Gravity @ 60°F	**37.0 - 51.0**	43.3	43.3	44.4
Density @ 15°C, kg/L	**0.775 - 0.840**	0.809	0.809	0.804

Chromatographic Comparison of Fuels. Gas chromatographic comparison of the biofuels to the representative JP-8 (Figure IV-4 and IV-5) further illustrates the similarities and differences between the fuels. The carbon distributions in the biofuels peak at a lower molecular weight (C_{10}) than in the JP-8. In addition, there is a predominance of cycloparaffins in the biofuels.

Polars by HPLC and SPE. POSF-7681was analyzed by High Pressure Liquid Chromatography (HPLC) for phenolic polar components of the type that can be present in JP-8 fuels (usually at <1000 mg/L). Semi-quantitative measurements were made by calibrating the HPLC with a mixture of phenolic compounds. POSF-7681 gave an HPLC response in the phenolic polars region that equated to 30 mg/L from the calibration, as well as a response in the mid-polars region. This is compared to 640 mg/L of phenolic polars in POSF-7492 and 160 mg/L of phenolic polars in POSF-4751 (Table IV-14).

In order to qualitatively examine the total polars content in the fuels, the biofuel was also solid-phase extracted (SPE) through a silica gel cartridge with methanol elution to separate the polar components from the non-polar components and concentrate them (20:1). The methanol extract was analyzed by GC-MS and found to contain a number of tentatively identified oxygenates, which were mainly cyclic alcohols and ketones.

Table IV-10. Aromatic Species Analysis by D6379 for Biofuel and JP-8 Fuel.

	7681 Coal Biojet 3	**7492 BJet2011**	**4751 JP-8**
D6379 (volume %)			
Mono-aromatics	9.5	6.2	17.5
Di-aromatics	0.6	<0.1	1.2
Total Aromatics	**10.1**	**6.2**	**18.7**
Total Saturates	**89.9**	**94.7**	**81.3**

Table IV-11. Hydrocarbon Type Analysis by D2425 for Biofuel and JP-8 Fuel.

	7681 Coal Biojet 3	**7492 BJet2011**	**4751 JP-8**
D2425 (mass %)			
Paraffins (normal + iso)	43	39	49
Cycloparaffins	46	54	30
Alkylbenzenes	8.7	5.4	13
Indans and Tetralins	1.6	1.5	5.8
Indenes and C_nH_{2n-10}	<0.3	<0.3	0.6

Naphthalene	0.7	<0.3	<0.3
Naphthalenes	<0.3	<0.3	1.0
Acenaphthenes	<0.3	<0.3	<0.3
Acenaphthylenes	<0.3	<0.3	<0.3
Tricyclic Aromatics	<0.3	<0.3	<0.3
Total	100	100	100

Table IV-12. Hydrocarbon Type Analysis by GCxGC for Biofuel and JP-8 Fuel.

COMPONENTS GCxGC (mass %)	**#7681 Coal- Biojet 3**	**#4751 JP-8**
n-Paraffins	9.2	18.8
iso-Paraffins	35.2	31.4
Monocycloparaffins	15.4	20.8
Dicycloparaffins	26.0	5.7
Alkylbenzenes	11.6	15.1
Indans and Tetralins	1.7	6.5
Naphthalene	0.9	0.1
Naphthalenes	<0.1	1.6
Total	100	100

Table IV-13. Weight Percent of Paraffins for Biofuel and JP-8 Fuel.

	#7681 Coal-Biojet 3	**#7492 BJet2011**	**#4751 JP-8**
n-Paraffins (weight %)			
n-Heptane	0.080	0.036	0.10
n-Octane	0.52	0.44	0.34
n-Nonane	1.17	1.79	1.21

n-Decane	2.29	2.53	3.48
n-Undecane	1.51	2.47	4.24
n-Dodecane	1.24	1.73	3.71
n-Tridecane	0.65	1.05	2.84
n-Tetradecane	0.32	0.46	1.79
n-Pentadecane	0.21	0.30	0.87
n-Hexadecane	0.049	0.068	0.27
n-Heptadecane	0.020	0.074	0.089
n-Octadecane	0.005	0.023	0.024
n-Nonadecane	<0.001	<0.001	0.008
Total n-Paraffins	**8.1**	**11.0**	**19.0**

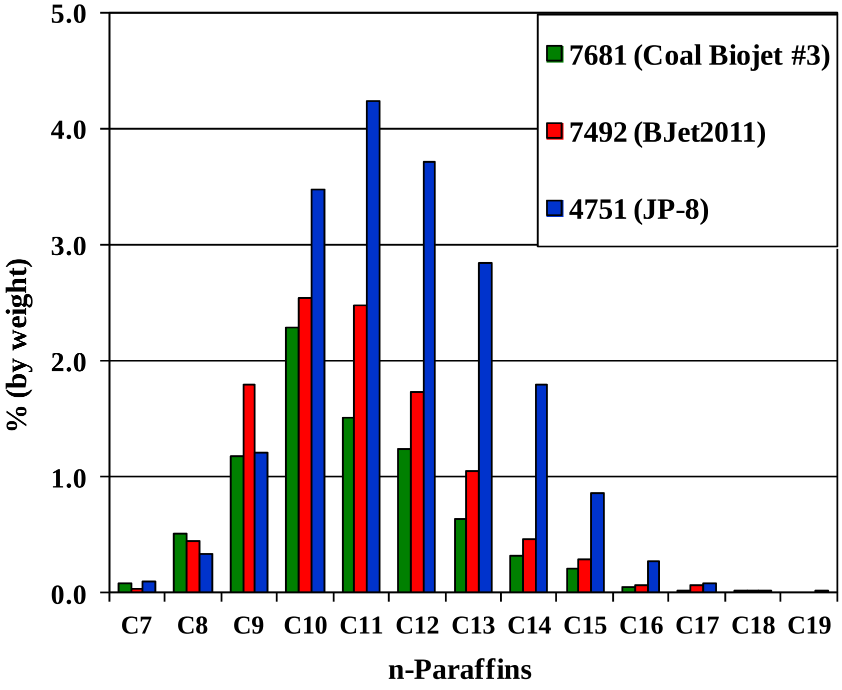
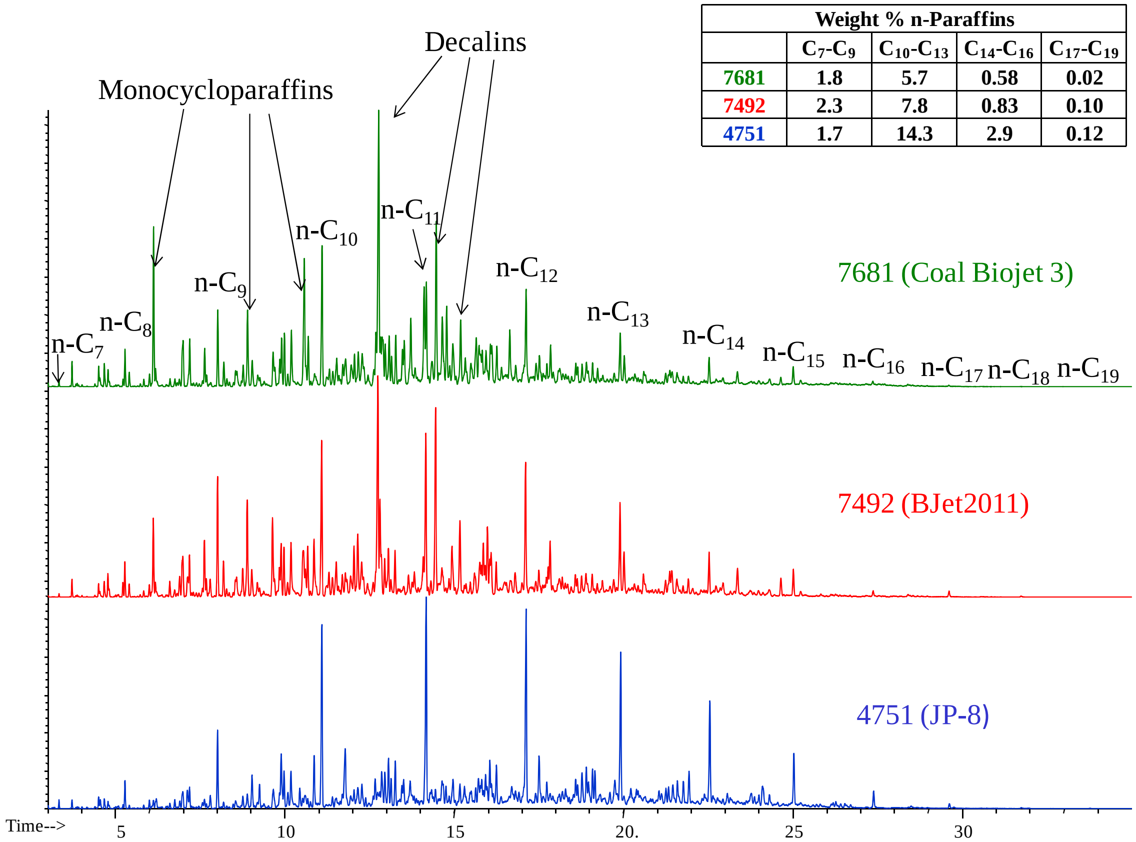


Figure IV-4. Weight Percent of n-Paraffins (C7-C19) for Biofuel and JP-8.



Weight % n-Paraffins				
	C_7-C_9	C_{10}-C_{13}	C_{14}-C_{16}	C_{17}-C_{19}
7681	1.8	5.7	0.58	0.02
7492	2.3	7.8	0.83	0.10
4751	1.7	14.3	2.9	0.12

Figure IV-5. Chromatograms of Biofuel and JP-8 Fuel.

Table IV-14. HPLC Phenolic Polars.

POSF No.	Fuel Description	Phenolic Polars by HPLC (mg/L)
7681	Coal Biojet 3	30
7492	BJet2011	640
4751	JP-8	160

Quartz Crystal Microbalance (QCM). Thermal stability characteristics of POSF-7681 were assessed using the QCM under typical experimental conditions (i.e., 140°C, air saturated fuel, 15 hours). QCM results for the fuels (see Table IV-15 and Figure IV-6) show that the biofuel produces a level of deposits (2.3 $\mu g/cm^2$) that is above that of POSF-7492 (1.4 $\mu g/cm^2$), below that of the representative JP-8 fuel (3.0 $\mu g/cm^2$), and within the average range of JP-8 fuels of 2 to 6 μg/cm2. With regards to oxygen consumption in the biofuel, the oxygen is consumed at a fairly rapid rate (within 3 hours), indicating that it contains no antioxidant.

Table IV-15. Data from QCM Thermal Stability Analysis.

POSF No.	Fuel Description	15 Hr Mass Accumulation ($\mu g/cm^2$)
7681	Coal-Biojet 3	2.3
7492	BJet2011	1.4
4751	JP-8	3.0

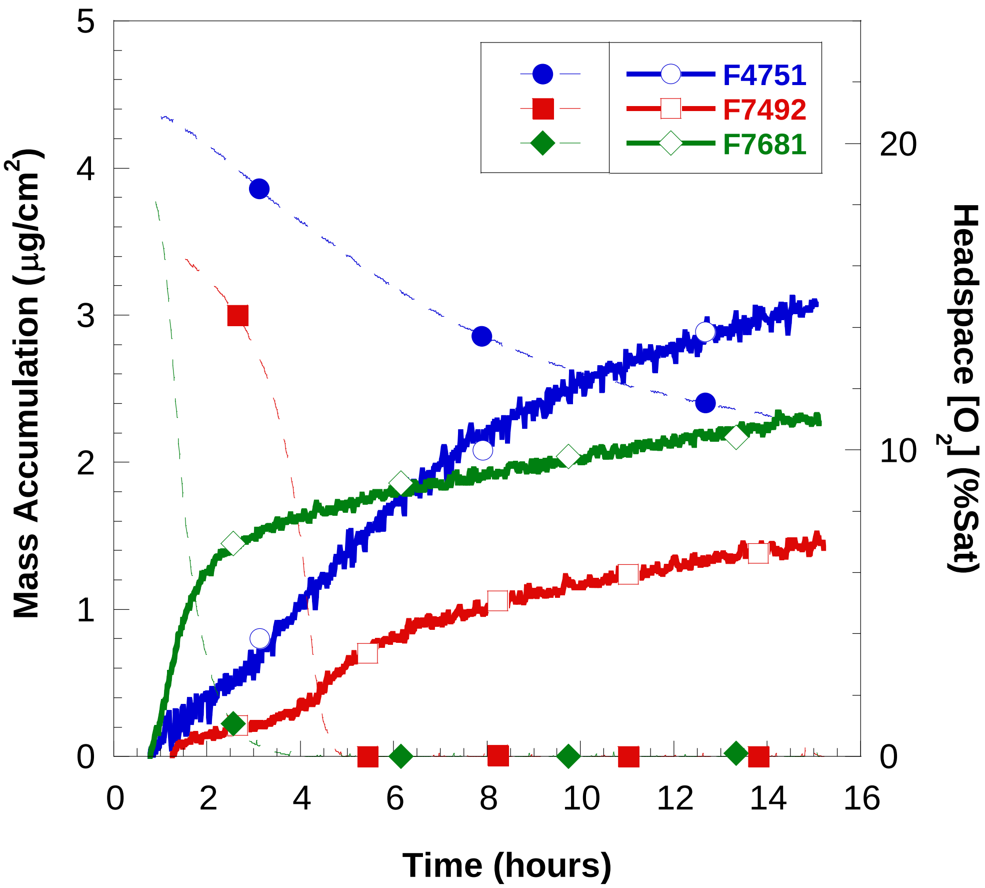


Figure IV-6. Mass Accumulation (solid curves, closed markers) and Headspace Oxygen Profiles (dashed curves, open markers) form QCM Analysis of Biofuel and JP-8 Fuel.

V. CO2 CARBON CAPTURE & UTILIZATION (CCU)

a. Overview

Algae can be economically produced(17,18) isolated in aqueous streams for use as a soil treatment material in order to increase the carbon content of the soil and for inducing photosynthesis to generate additional algae in the soil.(19,20) The algae can also be dried and combined with other additives such as organic binders, alkali containing residues from the petrochemical processing and/or catalytic conversion and the final mixture used as a natural biofertilizer. In this capacity, the material not only results in further growth of algae in the soil via photosynthesis and thereby increasing its natural carbon content, but also causes various forms of algae, including blue/green algae (i.e. cyanobacteria) to fix nitrogen, all of which promotes the growth of plant life in the treated soil and greatly reduces the GHG, and particularly the CO2, footprint of XTL (where X= C for coal, B for biomass, and G for natural gas) synthetic fuels production and coal based electric power generating processes. In this process, the naturally occurring complement of microorganisms, including cyanobacteria, occurring in the soil or type of soil to which the biofertilizer is to be applied is optimized and amplified in a closed PBR and the resulting material is dewatered and dried and treated with desirable additives; after which it is granulated, optionally coated with materials to optimize its spreading characteristics and distributed on the soil that is to be fertilized or restored.

In addition to the beneficial reduction of the GHG footprint of an XTL system, e.g. ICTL, by terrestrially sequestering the CO2 consumed by algae in the production fertilizer, the ICTL system has the additional advantageous characteristic that the algae applied to the soil, multiplies through photosynthesis, thereby extracting more CO2 from the atmosphere and fixing atmospheric nitrogen. This characteristic results in an increase in the net CO2 sequestered by a factor of 30 or more, and potentially as much 150 fold over the CO2 consumed during the production of algae in the ICTL process, and greatly enriches the fertility of soil.

The quality of the natural bio-fertilizer (as affected by the quality of the water and the purity of the CO2 and other nutrient streams provided to the PBR from other steps in the ICTL process can be controlled to generate food grade/FDA certified material for use in enhancing growth of various food crops; to an intermediate grade to serve as a soil amendment material for reclamation of arid soils to prevent or inhibit wind erosion via formation of a bio-active crust; or to lower purity material for use in reclamation of spent mine soils where the addition of a bio-reactive material inhibits leaching and erosion of contaminated soils to improve the quality of water drain off. An added biochar components (described below) can be applied to further control the overall hydrophylicity and hydrophobicity of the biofertilzer formulation to further control the water retention properties of the soil. By this mechanism, it is possible to tailor the biofertilizer formulations for optimal use in the production of specific crops.

The natural bio-fertilizer can also be used as a direct replacement for conventional ammonia based fertilizer, where it offsets large amounts of CO2 that would otherwise be generated in production of NH3 and the full range of ammonia based fertilizers. This also leads to other downstream benefits, such as a reduction in run off of NH3 based components that contaminate downstream waterways and cause unwanted blooms of algae and other aquatic plants.

BioFertilizer Formulations

BioFertilizer can be produced from a mixture comprised of cyanobacteria, biochar and/or inorganic residues from the biomass pyrolysis process, associated combustion processes, and the associated algae production system. Biofertilizer formulations comprised of different blends of the three process streams from the ICTL flow scheme, the cyanobacteria, biochar and the inorganic residues from the pyrolysis process exhibit superior performance to conventional soil treatment materials. It allows the elemental composition, the total nitrogen level, the total average surface area of the composition, the surface area of individual biochar components or mixtures thereof, the total alkali and composition of individual alkali components to be controlled in a way that is tailored to specific crops or end uses.

Greenhouse and Field Test Programs

The biofertilizer is designed, in addition to providing soil nitrogen and carbon, to behave as an erosion control agent. In most cases, the biofertilizer alone will achieve the desired results. Based on the flexibility of the biofertilizer, it can be used in conjunction with traditional erosion control methods such as fibrous mulches and tackifiers thus enhancing the efficacy of these traditional products. For instance, hard-rock mine tailings, waste and overburden characteristically become acidic ($pH<3$) through the oxidation of sulfur by bacteria. These acidic environments inhibit seed germination, and exceeds the lower pH limit of cyanobacteria ($pH<5$). However, we have shown that when a layer of mulch is applied to the surface, it serves as a chemical insulator that permits seed germination and the growth of the biofertilizer. The plant roots penetrate into the nitrogen-deficient acidic mine tailings and continue to grow when nitrogen is supplied by the biofertilizer.

The terrestrial cyanobacteria have evolved several adaptations that maintain membrane integrity and reduce photooxidation that permits their survival in harsh desert environments. The process of repeated dehydration and hydration of cyanobacteria is reviewed by Potts (1994). These terrestrial cyanobacteria withstand repeated cycles of hydration and dehydration in the natural environment. The cyanobacteria solve the problem of maintaining membrane integrity synthesizing membrane stabilizing proteins. In addition to membrane stability, the high solar input in arid terrestrial environments increases the rate of photooxidation with the production of highly reactive free radical species that can ultimately lead to cellular death. The solar input is reduced by the synthesis of a light absorbing compound called scytonemin. Scytonemin gives the characteristic black color of native crust communities, and this pigment works in the same way as suntan lotion. In addition, these cyanobacteria synthesize free radical scavengers, superoxide dismutase.

Field Deployment

A major advantage of the preservation process pertains to the flexibility of application. For instance, the dry algal powder can be applied by aircraft during the winter or wet seasons. Commercially available sprayers designed to disperse wettable powders, including backpack sprayers are the obvious choice. The reason for hydrating the biofertilizer is to improve soil adhesion to limit losses due to wind. In many situations, the biofertilizer alone will achieve the desired results of soil stabilization and fertilization. However, in cases where slope pitch requires traditional stabilization techniques such as using mulches and tackifiers, the biofertilizer will enhance the effectiveness of these products by contributing nitrogen and recruiting beneficial microorganisms.

b. Experimental Program and Methods

Preliminary Bioengineering Assessment/Modeling Study on Algae Production and Capture.

Optimizing growth rate and biomass productivity of *Anabaena cylindrica* strain B1611 in BG11-N medium was our primary focus during the second quarter of 2012. Based on our previous experiments showing rapid growth and non-biofilm growth habit, strain B1611 was selected for further experimentation from among eight nitrogen fixing cyanobacterial isolates obtained from the University of Texas culture collection. Parameters that affect growth, such as the temperature and composition of the nutrient medium, along with the effect of the gas delivery system were examined.(21 – 24 and references therein)

Temperature Effects on Growth in Photo-Bioreactors

The effect of temperature on growth of strain B1611 was evaluated at 25, 28, and 30°C in photo-bioreactor tubes containing 1.2 L of BG11 -N media. Air was injected into the bioreactors via capillary tubes at 400 mL/min. The lighting was set to a 14/10 hour light/dark cycle. The temperatures were regulated using heating elements in aquarium photo-bioreactor systems. Temperatures varied by ± 1°C over the duration of the experiments. The pH, optical density, cell density (visually counting cells) and biomass concentration of the cultures were measured daily. After measuring pH immediately after sampling, samples were sonicated prior to further measurements to increase culture suspension homogeneity. Figure 1 shows a plot of the cell densities over time for the three temperatures. The 25 and 28 °C cultures reached a similar cell densities and had similar average growth rates ($\mu \sim 0.0201 \pm 0.0026$ 1/hr). The cultures grown at 30 °C did not reach these cell densities and grew at a slower rate in comparison to the 25 and 28 °C treatments.

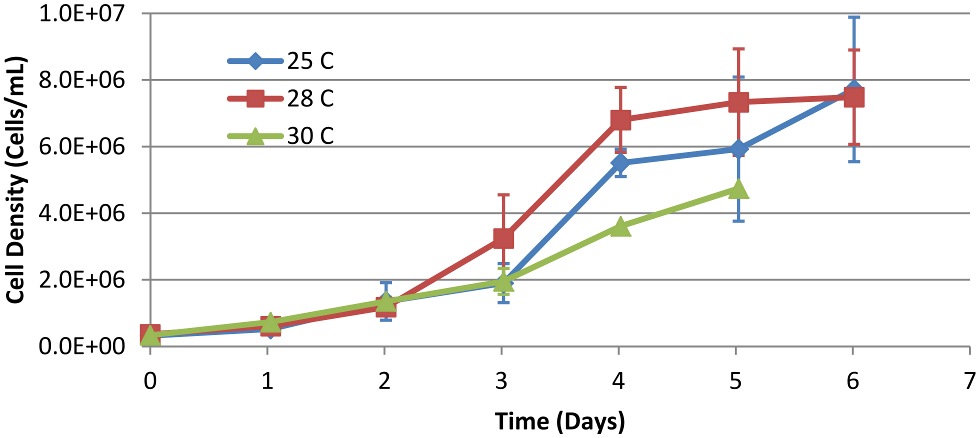


Figure V-1. Growth of *A. cylindrica* Strain B1611 as a function of temperature. Error bars represent standard deviations of three replicate photo-bioreactors.

The highest rate of biomass productivity was observed at 28 °C (0.039 ± 0.03 g/L·day). While all three temperatures generated about the same amount of biomass per liter, the 28 °C treatment had achieved 0.22 g/L nearly two days before the other two temperature treatments (Figure V-1).

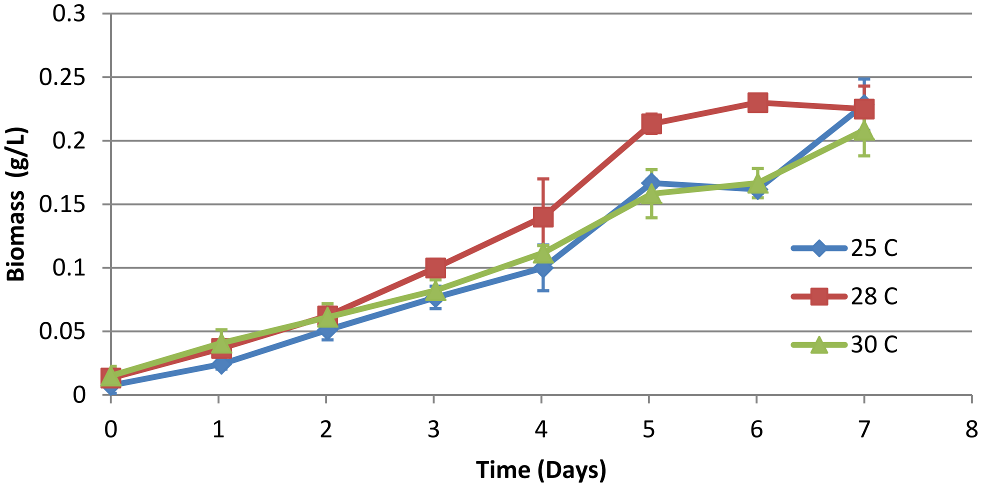


Figure V-2. Biomass of *A. cylindrica* strain B1611 as a function of temperature in photo-bioreactors. Error bars represent standard deviations of three replicates.

Limiting Nutrient Determination

Experiments were conducted to determine which nutrients were responsible for limiting the growth of strain B1611 in BG11-N medium. Previous experiments conducted during the first quarter of 2012 ruled out growth limitation due to any of the micronutrients (with the exception of Fe). Experimental treatments including increased concentrations of single nutrients as well as combinations of multiple nutrients were conducted in 250 mL baffled shaker flasks with gauze caps under a 14/10 hour light/dark cycle and shaken continuously at 120 rpm. Increasing the concentration of a single component did not have significant effects on biomass productivity. It was determined however, that increased concentrations of both Mg and EDTA were required for significantly enhanced biomass concentration. Increasing the concentration of Mg and EDTA to five times the standard concentration in BG11 medium increased the final biomass concentration from 0.280± 0.04 g/L to 0.767± 0.02 g/L. Figure V-3 shows the cell density of cultures grown in standard BG11-N media and in enhanced media containing five times the concentrations of Mg and EDTA. Although the final biomass concentration was significantly higher in the enhanced media, the maximum growth rate was actually slower. Optical density closely tracked with biomass and was significantly higher in the enhanced media (Figure V-4). Increased concentrations of Mg and EDTA in the medium did not result in clumping of cells or biofilm formation (Figure V-4).

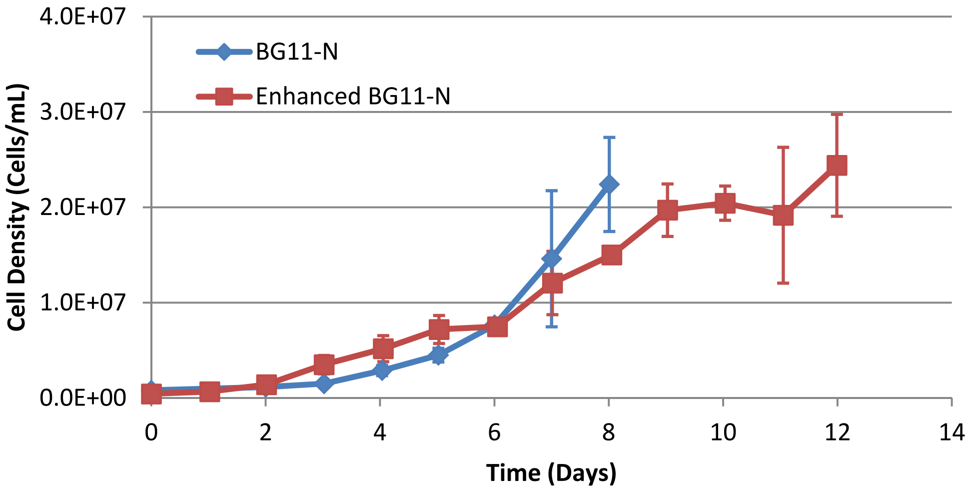


Figure V-3. Growth of *A. cylindrica* strain B1611 versus time in both the standard BG11-N media and with the enhanced media consisting of five times the standard concentration of magnesium and EDTA. Error bars represent standard deviations of triplicate flasks.

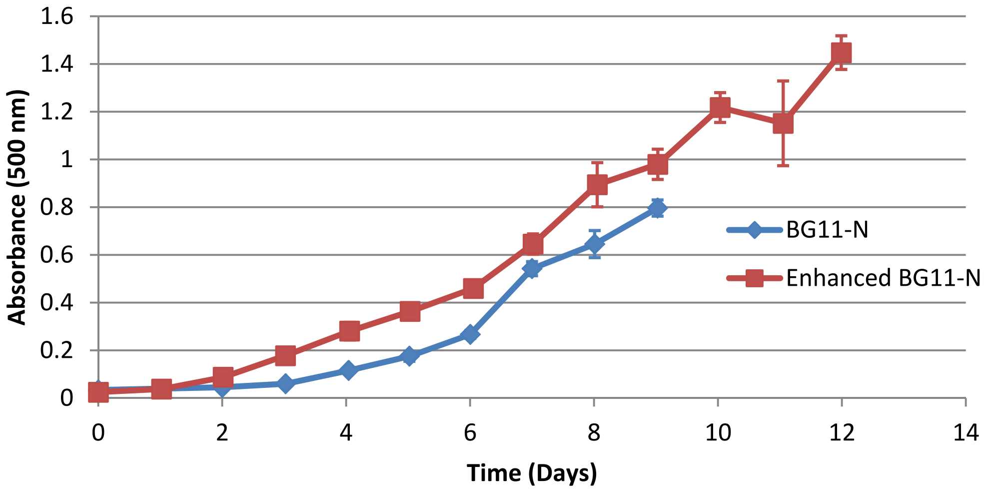


Figure V-4. Optical density of *A. cylindrica* strain B1611 versus time in both the BG11-N and enhanced BG11-N (5x Mg and EDTA concentrations). Error bars are standard deviations of triplicate flasks.

Figure V-5. Culture of *A. cylindrica* strain 1611 grown in the enhanced BG11-N media showing planktonic growth habit.

For comparison, the final biomass concentration for the five times Fe and EDTA treatment was 0.284± 0.01 g/L; while the five times Ca and EDTA treatment was 0.343± 0.04 g/L. Growth of strain B1611 (cell density versus time) with elevated concentrations of Mg, Fe and Ca are shown in Figure V-6. Further tests are needed to confirm these results.

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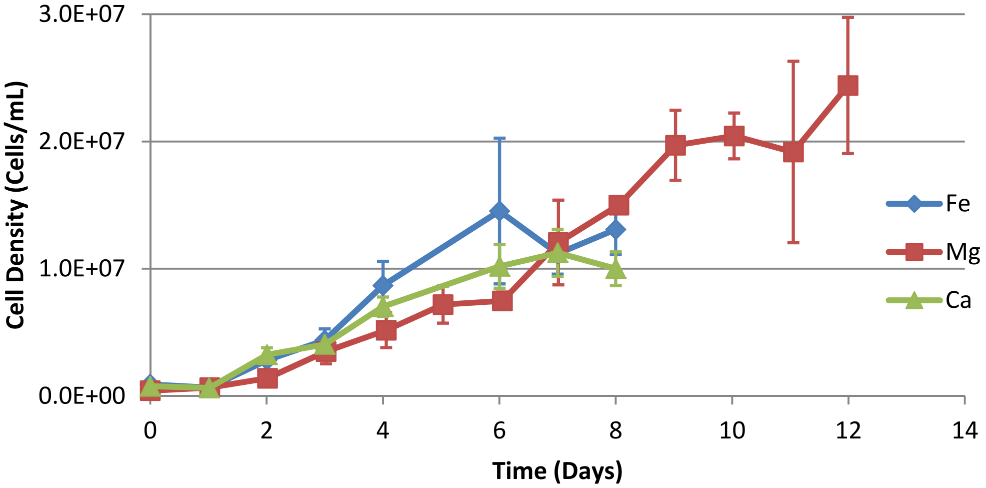


Figure V-6. Growth of *A. cylindrica* strain B1611 with five times the concentration of EDTA and five times the concentration of either iron, magnesium or calcium. Error bars are standard deviations of triplicate flasks.

Comparison of Growth in Flasks and Photo-Bioreactors

Strain B1611 was grown in 1.2 L photo-bioreactors using the enhanced BG11-N medium (five times the Mg and EDTA concentrations). Cultures were grown at 25 ^{o}C with 400 mL/min of air fed through a capillary tube and a 14/10 hour light/dark cycle. The results show that **growth** rates and maximum cell densities are lower in the photo-bioreactors relative to shaker flasks (Figure V-77). The decreased growth in photo-bioreactors may be attributed to differences in inoculation volumes used to start the experiments. Flasks received a higher percent inoculum than the bioreactors. Additional experiments to compare growth in these two systems are being conducted using controlled inoculation conditions.

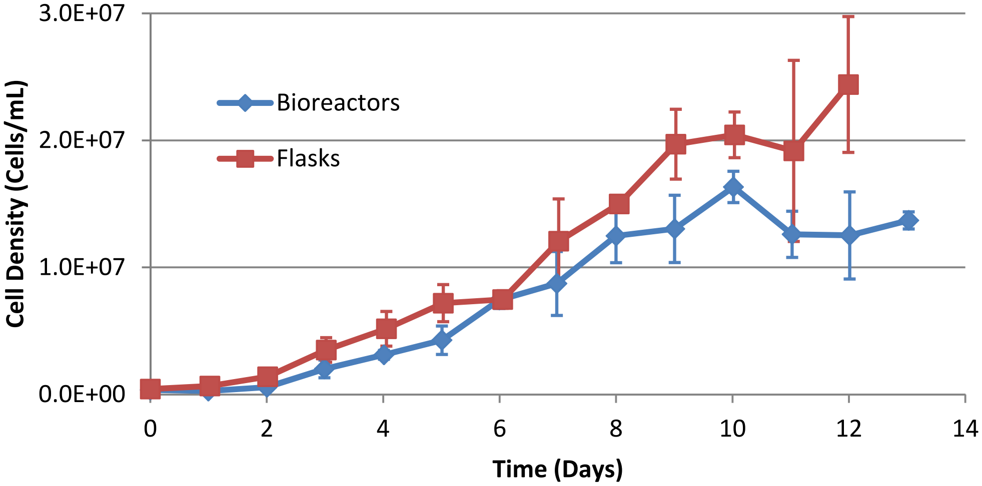


Figure V-7. Growth of *A. cylindrica* strain B1611 in 250 mL shaker flasks and 1.2 L photo-bioreactors. Error bars are standard deviations of triplicate flasks or photo-bioreactors.

Biomass measurements were taken daily during these photo-bioreactor experiments five times with enhanced BG11-N medium (Figure V-8). The final average biomass concentration was 0.592 ± 0.149 g/L.

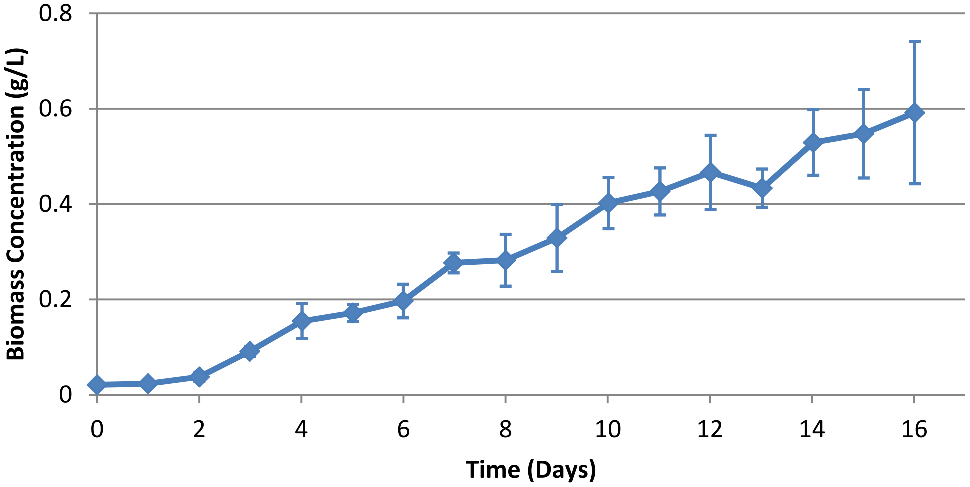


Figure V-8. Biomass concentration of *A. cylindrica* strain B1611 versus time grown in the enhanced BG11-N media in photo-bioreactors. Error bars are standard deviations for triplicate photo-bioreactors.

Growth in Raceway Pond

The enhanced .BG11-N medium was used to evaluate growth of strain B1611 in a 200 L raceway pond. The system reached a maximum cell density of 2.0 x 10^7cells/mL and the final biomass concentration was 0.53 g/L. As can be seen in **Figure V-9**, the culture became very dense after 7 d of growth. Additional experiments will be conducted to determine the minimum amount of Mg and EDTA that is required for optimal biomass production, Figure V-9.

Figure V-9. 200 L Raceway with *A .cylindrica* B1611 in the Enhanced BG11-N Media.

Effects of Air Flow Pattern on Growth

Two methods of delivering gas into the photo-bioreactors were used and the effects on growth of strain B1611 were evaluated. The delivery of air into the reactors affects several important parameters that impact growth including: shear stress on cells, access to light, mixing rate and gas diffusion rate.

Figure V-10. Photo-bioreactors receiving air via slug flow (left) and bubbly flow (right).

The first method was slug flow, which was created by using a small capillary tube inserted down into the reactor to release a steady stream of air at 400 mL/min. This creates large bubbles in the tube that promotes better axial mixing thus increasing the amount of light each cell receives.

The second method is bubble flow; in this scenario a small porous stone was attached to the bottom of the capillary tube to create many small bubbles throughout the entire cross sectional area of the reactor. A flow rate of 400 mL/min was also used. Bubble flow promotes greater gas diffusion due to the increase of gas to liquid interfaces but has less axial mixing. Figure V-10 shows the differences in the flow patterns created by these delivery systems.

The growth rate in the bubble flow reactors was significantly higher (0.0295 ± 0.003 1/hr) compared to the growth rate in slug flow reactors (0.0196 ± 0.002 1/hr). Conversely, slug flow reactors reached a higher maximum cell density (Figure V-11) and a greater biomass concentration, though not significantly different. Bubble flow produced an average biomass concentration of 0.23 g/L while slug flow was at 0.27 g/L. Bubble flow apparently provided better gas diffusion, which resulted in a delayed rise of pH (Figure V-12). These observations support the idea that gas delivery system design has significant implications for growth and biomass productivity. Consequently, testing of these systems will be included in future experiments.

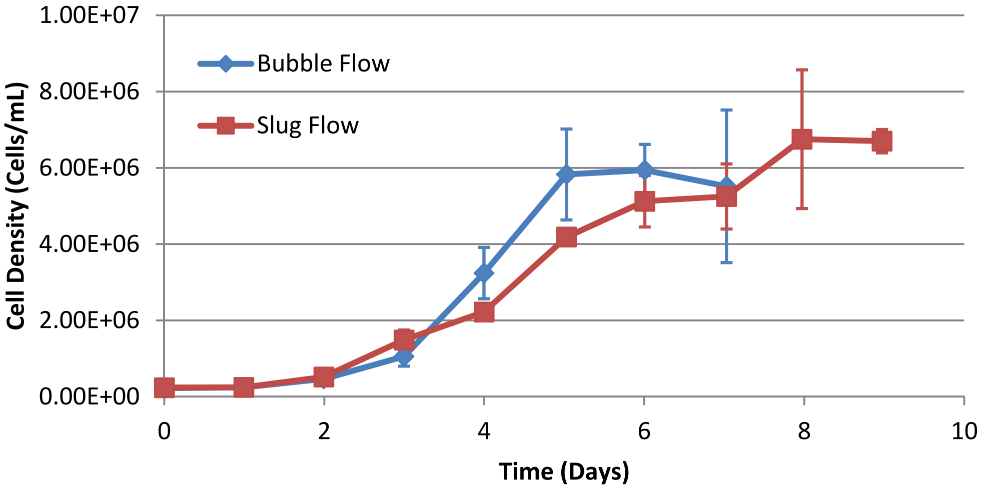


Figure V-11. Growth of *A. cylindrica* strain B1611 as a function of gas delivery system. Error bars are standard deviations of triplicate photo-bioreactors.

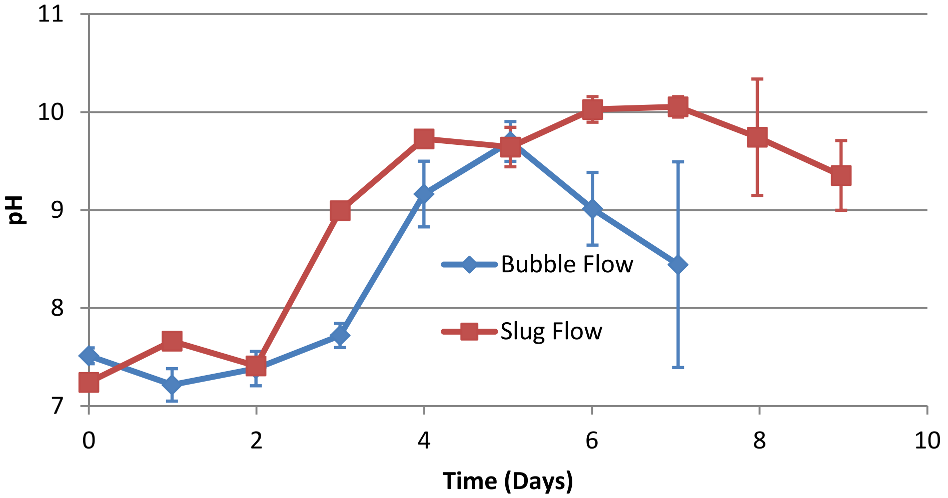


Figure V-12. The pH of *A. cylindrica* strain B1611 as a function of gas delivery system. Error bars are standard deviations of triplicate photo-bioreactors.

Optimal pH Determination

The effect of pH on growth of *A. cylindrica* strain B1611 was also examined. These experiments were conducted in 250 mL baffled shaker flasks with sterile gauze caps subjected to a 14/10 light/dark cycle and shaken at 120 rpm. Standard BG11-N media was used but buffers were used to control the pH. Strain B1611 grew best at pH 7.4 but showed only a slightly lower maximum cell density at pH 6.7 (Figure V-13).

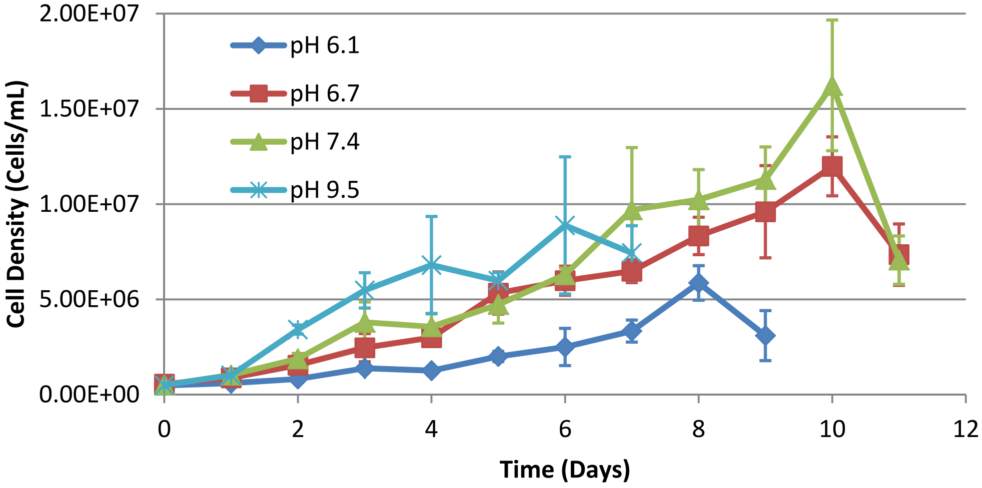


Figure V-13. Growth of *A. cylindrica* Strain B1611 at various pHs held constant with buffers. Error bars represent standard deviations of triplicate shaker flasks.

Future Work

Work on optimizing biomass productivity and growth rate of *A. Cylindrica* strain B1611 will be continued into the next quarter. Two important parameters that will be examined are light intensity and the light/dark cycle.

Furthermore, we will focus our efforts to isolate fast growing, high yield N-fixing cyanobacterial strains from regional field samples collected from the Crow Reservation. Additional scaled-up experiments in 75-100 L bag reactors and in the 200 L raceway pond (Phase IV)will be run using optimized growth conditions determined in shaker flask and photo-bioreactor experiments, particularly focused on effects of more direct pH control and to determine if the oscillations in N-fixing activity occur at these larger, more field relevant scales. The cellular biomass generated in the bag reactors and raceway will be centrifuged and lyophilized in preparation for future downstream experiments (Phase V). Future work will include determining the viability of the cyanobacterial biomass and the stability of its N-fixing capability as a function of storage time, temperature and dryness of the biomass as well as the ability of harvested cells to grow as biofilm on soil/sand. Expected outcomes from this NCE include enhanced biomass production for higher fertilizer yields *and* enhanced specific N-fixing activity. Additional outcomes include evaluation of storage time and conditions on the stability of the N-fixing activity (time, temperature and moisture content) and a screening of the ability of harvested cells to grow as biofilm on soil/sand.

c. Results and Discussion

Production and Use of Algae BioFertilizer to Grow Crops and/or Reclaim Spent Land

ICBTL algae can be cost effectively produced via an integrated scheme that utilizes nutrient (P, N, Group I and II metals) rich waste from DCL coupled with waste heat and relatively-clean process-derived CO_2 from the hydrogen production step. Algae can be used in aqueous suspensions for use as a soil treatment agent to directly increase the carbon content of the soil and to photosynthetically induce additional algae/micro-organism production in the soil. The algae BioFertilizer can also be dried with process waste heat and combined with other additives such as organic binders and alkali containing residues from the DCL process. The formulated BioFertilizer can be tailored for specific crops or soil conditions. In this capacity, the material not only induces further growth of carbon/nitrogen-fixing microorganisms in the soil via photosynthesis to increase its natural carbon content, but also promotes increased plant growth in the treated soil helping to further offset the net GHG-CO_2 footprint of the ICBTL process.

Life Cycle Analysis (LCA) of a conceptual Montana based ICBTL process and BioFertilizer has been used to evaluate greenhouse gas emissions, energy consumption, water use, and other environmental metrics. LCA studies include Montana specific ICBTL processing conditions/integration scenarios to quantify biomass productivity and soil carbon accumulation from field tests.

Use of BioFertilizer to treat spent mine land has successfully demonstrated the possibility of growing seed oil crops both as a soil reclamation pathway and to provide additional feedstock for the DCL process scheme. Accelergy studies with the Crow Nation and Montana State University have shown significant potential benefits of BioFertilizer for use in wheat-camelina crop rotation cycles.

The research conducted at Montana State University and supported by the Accelergy Corporation focused on the selection and characterization of nitrogen (N) -fixing cyanobacterial strains that could be used to scavenge waste CO_2 from the coal to liquid fuel conversion process (CTL) and provide an organic fertilizer product leading to a terrestrial pathway to carbon (C) sequestration.

Research conducted at Montana State University and supported by the Accelergy Corporation focused on the selection and characterization of nitrogen (N) -fixing cyanobacterial strains that could be used to scavenge waste CO_2 from the coal to liquid fuel conversion process (CTL) and provide an organic fertilizer product leading to a terrestrial pathway to carbon (C) sequestration.

The overarching goal of this effort is to develop an effective carbon capture and storage strategy that would significantly decrease the C footprint of CTL. In addition to removing CO_2 from the CTL waste stream, it is expected that the cyanobacterial biomass could be used as a soil fertilizer that would continue to grow and fix atmospheric CO_2 and N after application to soil. A certain fraction of the C in this biomass would ultimately be converted to recalcitrant soil humic materials for long-term C storage. The resultant elevation of soil organic matter levels would significantly improve long-term soil quality.

Previous reports have summarized our progress in all facets of Task 3, and recent work has culminated in small scale soil amendment studies summarized below.

In the final section of this report, we include our assessment on the benefits of using BioFertilizer as part of a wheat production protocol that includes camelina production with algae based BioFertilizer during the otherwise “fallow” year of the production cycle. As will be seen, the benefits of this to the farmer and to incremental production of biomass feedstock for added fuel production are quite significant. We are currently discussing this with the program team and plan to conduct small scale field tests in Crow farmland in early 2013.

Soil amendment studies.

Strain B1611 biomass was harvested from the 200 L raceway pond by centrifugation and stored at 4^{o}C or -20^{o}C for plant growth studies. Potting medium was prepared as a 25% soil/75% sand mix. The soil used for these experiments was the top 15 inches of a Vananda clay soil collected from the Crow Reservation. The Vananda soil is common across the Crow Reservation as well as south central Montana and is extensively used for crop production. The soil was ground and sieved (< 2 mm) and thoroughly mixed with 50 mesh quartz sand (0.05-0.3 mm). Six inch diameter pots were filled with 1800 g of the sand/soil mix and the pots were seeded with *Camelina sativa*, var. Suneson and wheat, var. Yellowstone. After nine days of growth, 3.0 g of moist strain B1611 biomass (0.51 g dry weight @ 8% N) representing an application rate of 20 lb N per acre (0.041 g N per pot) was added to pots seeded with camelina. Pots seeded with wheat were amended with 9.0 g of moist biomass (60 lb N per acre). Prior to soil application, the biomass had been refrigerated at 4^{o}C for six days. Control treatments included: 1) no amendment, 2) 20 lb N per acre as 34-0-0, a commercial ammonium nitrate fertilizer and 3) multiple applications of Hoagland’s liquid medium containing a full suite of macro and micronutrients. The first experiment conducted by our laboratory is currently in progress (Fig. V-14). Preliminary results clearly show the beneficial effects of biomass addition with amended soils supporting significantly greater growth compared to no amendment controls.

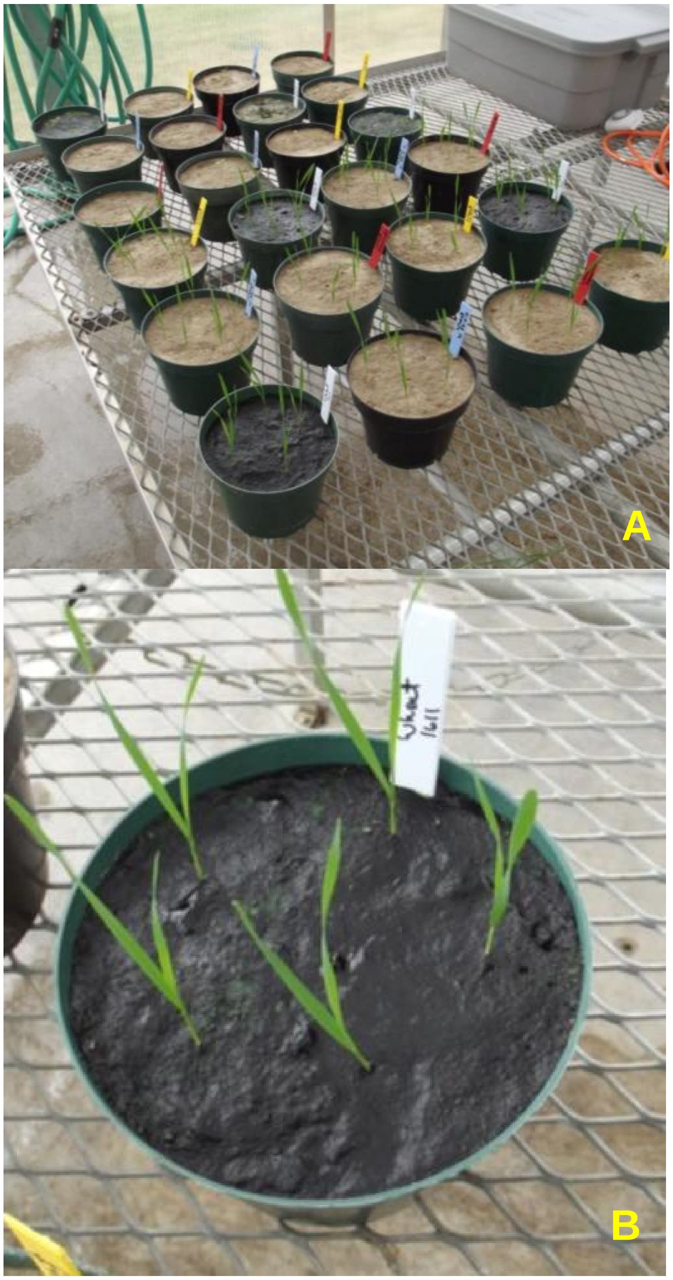


Figure V-14 **Effects of biomass addition with controls (A) and amended soils (B) supporting significantly greater growth.**

Figure V-15. Photos of pots seeded with wheat in each frame (left control) and (right subjected to four treatments including amendment with moist strain B1611biomass). Left and right frames show plants after 21 and 26 days, respectively.

Figure V-16. Photo shows growth of camelina after 26 d in pots amended with cyanobacterial biomass (right) and pots that did not receive any fertilizer amendment (left).

The soil amendment experiments are conducted in a greenhouse at the MSU Plant Growth Center. This space is temperature controlled (22 ± 1.5 ^{o}C) and uses both natural and artificial light, with automatic thermal/shade curtains implemented to obtain at least a 14 h light period. One of our 200 L raceway ponds is positioned next to our plant and soil experimental benches to facilitate direct cyanobacterial soil application in future experiments.

Future Studies

During the first phase of this project, we have made significant progress toward achieving our overall goal of isolating, selecting and characterizing N-fixing cyanobacterial strains that could be used to scavenge waste CO_2 and provide an organic fertilizer product. However, this work needs to be continued to understand key factors that are important for application of the technology at larger-scales in south central Montana.

Our plans for future investigations include:

- Continue isolation work to obtain additional pure cultures of algae and N-fixing cyanobacteria from samples obtained on the Crow Reservation. We will extend the media types used in these isolations and will include tap water as a base.
- Obtain additional samples and isolate phototrophs from poor quality waters in south central Montana, including CBM waste water impoundments.
- Continue screening experiments using strains obtained from south central Montana to select for the most promising cultures.
- Bioassays to test cultures for toxin production.
- Characterize growth of the most promising strains in photo-bioreactors as a function of light intensity and duration, temperature and CO_2 partial pressure.
- Scale-up the characterization experiments to 200 L raceway ponds.
- Continue greenhouse experiments using cyanobacterial biomass to enhance growth of camelina and wheat.
- Evaluate the effectiveness of biomass amendment as a function of cyanobacterial harvest, storage and application method.
- Evaluate the viability/growth/N-fixing activity of cyanobacteria after application to soil.
- Track C and N pathways in soil after application of cyanobacterial biomass.
- Evaluate longer term impacts of biomass addition on soil quality and health (plant productivity, soil organic matter content, soil organic matter composition, aggregate formation and stability).
- Conduct fertility studies at the field-scale in south central Montana including disturbed sites impacted by strip-mining of coal. The reclamation studies will be done in cooperation with the Montana Department of Environmental Quality who have expressed interest in assisting with this project.

The greenhouse-scale soil amendment studies will continue to be conducted at the Plant Growth Center on the MSU campus. Montana State University is a Land-Grant Institution and places considerable emphasis on applied plant and soil programs. The Plant Growth Center includes 8 Conviron growth rooms (96 square feet of bench top space with accurate control of temperature, light intensity and duration, and CO_2 partial pressure), 29 greenhouse rooms each with 288 square feet of bench space and 22 growth chambers ranging from 7 to 36 square feet. There are also macro and micro level containment labs and greenhouses available at the facility.

Future studies on cyanobacterial viability, growth and N-fixation after application to soil would be facilitated with use of the cutting-edge microscope labs and expertise available at the Center for Biofilm Engineering. The Center is a world-renown leader on investigating biofilms in the environment. Labs available at the Center include the Optical Microscopy Lab, which houses two Nikon Eclipse E-800 microscopes that are used for transmitted light and epi-fluorescent imaging of biofilms. The Confocal Microscopy Lab includes two brand-new (2011) Leica SP5 Confocal Scanning Laser Microscopes (CSLMs). The Image and Chemical Analysis Lab houses a state-of-the-art Zeiss field emission scanning electron microscope as well as other instrumentation (e.g., XPS, ToF-SIMS, Auger, XRD) for material analyses.

Studies on the fate of C in soil after addition of cyanobacterial biomass will be led by Dr. Rich Macur who has more than two decades of experience as a soil scientist, geochemist and geo-microbiologist. We plan to monitor fluxes of C after biomass application to soil; including inputs from photosynthesis, losses through volatilization as CO_2 or transformations into soil organic matter including recalcitrant humic materials (fulvic acid, humic acid and humin). These studies will be facilitated by the use of two Licor 8100A field units that can be multiplexed to monitor real-time CO_2 fluxes in multiple systems (e.g., multiple greenhouse pots, enclosed chambers in the field) and LECO total C and N analyzers. The effects on soil aggregate formation and stability as well as longer-term fertility will also be investigated.

This research explores an exciting new technology that has the potential to become a method of choice for capturing waste CO_2 from point sources and storing/sequestering that C in a form that benefits the environment. Our continued work in this area would expand on the knowledge we gained during the first phase of the project and would capitalize on our expertise in the fields of algae and soils as well as make use of relevant facilities and instrumentation available at MSU.

Montana Crow Algae BioFertilizer Testing – Technoeconmic Modeling

Our field test program is focusing on biomass production in Big Horn County and the sub-jurisdiction of the Crow Reservation, which makes up approximately 2.2 million acres of the 3.2 million acres in Big Horn County. According to the 2007 Census of Agriculture, there was 217,111 acres of harvested cropland within Big Horn County, the majority of which (173,368) was within the exterior boundaries of the Crow Reservation. As a general rule, if you can grow camelina you can grow wheat. However, camelina is seen as rotational crop- that can improve wheat yields in subsequent years. Farmers could choose to fallow their land (keep vacant and maintain with herbicide and pesticide) at a cost or grow an oil seed in order to maintain some revenue. Therefore the statistics collated in the table below show that there is an abundance of potential cropland available for both the pilot testing stage (10,000 acres) and scale-up to a 10 MGPY commercial production facility (65,000 acres).

From our research, below are some preliminary figures. The input numbers are taken from the Enterprise Budget System, as modeled in this article with input from Scott Johnson, President and CEO of Sustainable Oils:

Table V-1. Econometric Modeling of Wheat and Camelina with BioFertilizer.

Factor	**W. Wheat on Fallow**	**W. Wheat on Recrop**	**W. Wheat on Camelina**	**Camelina**	**Fallow**
Expected Yield (per acre)	40 Bu.	30 Bu.	34.5 Bu †	1000 lbs	0
Market Price	$7.00/ Bu.	$7.00/ Bu.	$7.00/ Bu.	0.13c/lb	0
Expected Revenue (per acre)	$280	$210	$241.50	$130	0
Expected Revenue w/Government Subsidies (per acre)	$308.00	$238.00	$269.50	$195.00	0
Total Operating Costs (per acre)	$151.30	$175.73	$175.73	$65	$58.44
Total Operating Costs w/half priced fertilizer (per acre)	$112.30	$121.73	$121.73	$56.75	
Returns over Operating Costs (per acre)	$128.70	$34.27	$68.54	$65.00	($58.44)
Returns over Operating Costs with Government Subsidies (per acre)	$156.70	$62.27	$96.54	$130.00	($58.44)
Returns over Operating Costs with Government Subsidies and Fertilizer Savings (per acre)	$195.70	$116.27	$147.77	$138.25	(58.44)

† Assumes 15% improved yield on W.Wheat on recrop

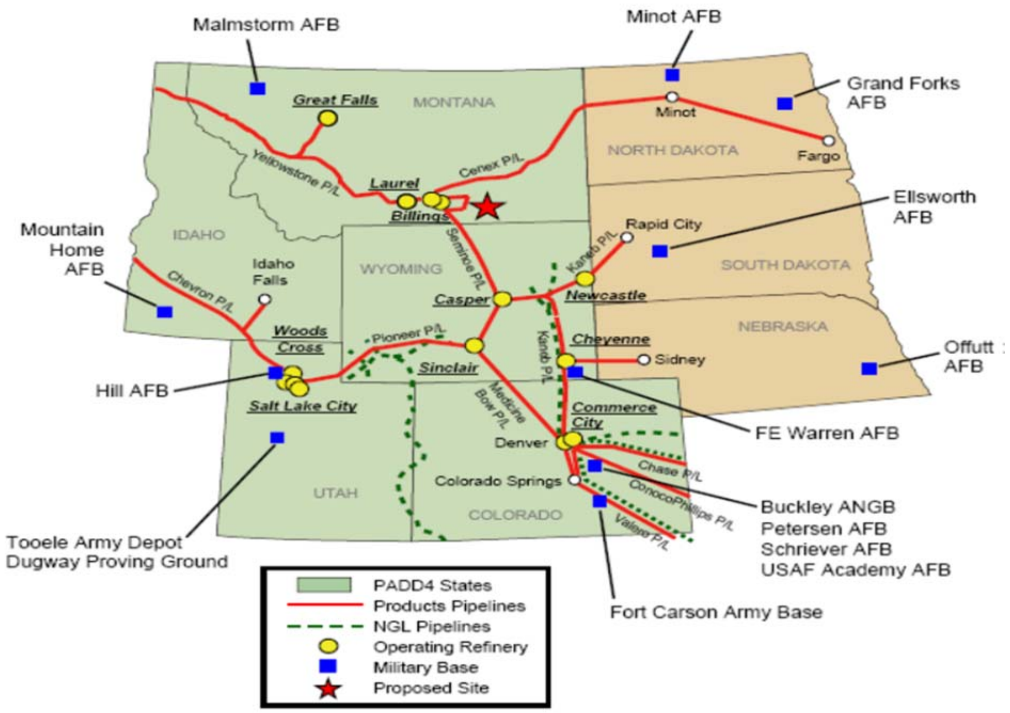
These numbers exclude ownership costs which amount to approximately $50 for each crop http://www.thebioenergysite.com/articles/460/economics-of-oilseeds-for-biofuels-in-montana, see Table V-1.

Therefore the current preferred rotation of two years Wheat and the third year fallow would net a farmer $312.00 per acre for the three year cycle inclusive of current government subsidies.

The Accelergy model, which assumes half-price fertilizer (TerraSync® BioFertilizer can be sold at 50% the equivalent price of ammonia based fertilizer on an equivalent "N" delivered basis) and 15% improved yield over a three year cycle of Wheat-Wheat-Camelina would net a farmer $402.22 per acre over a three year cycle.

The potential site for the Biorefinery associated with this scenario is well serviced by a network of pipeline and rail that connects the project to 11 military bases within the region. Further, the proposed site would be situated close to the Montana rail system which would allow quick and easy distribution to both the East and West. Both the rail and pipeline system run through the Crow Reservation. A map of the pipeline system is shown in Figure V-17.

Figure V-17. PADD 4 Pipeline System for Fuels Distribution to DOD Facilities.



A Montana based Biorefinery would benefit from the previous work completed by the Many Stars (http://www.manystarsctl.com/) project, in which Accelergy technology has been selected, including a comprehensive Environmental Assessment and the development of an Air Monitoring program plan as required by both the MT DEQ and Federal EPA.

Montana was recently included in the Biomass Crop Assistance Program by the USDA to encourage farmers to grow camelina for use in Biomass production. A grower can expect through this program to receive 1.4 times the crop rotation protocol value of the land to be used. According to Scott Johnson from Sustainable Oils- on average in Montana this equates to a subsidy of approximately $65, which coincides roughly with the input costs to a farmer who chooses to grow camelina. Similar incentives exist in Pennsylvania and Alaska.

Previously- the Montana state government has offered subsidies to help cover some of the seed costs of camelina through the Workforce Innovation in Regional Economic Development program and Senator Tester has helped to pass federal legislation that would develop a crop insurance program for pilot energy crops such as camelina (http://www.thebioenergysite.com/articles/460/economics-of-oilseeds-for-biofuels-in-montana).

Phototrophs for Carbon Capture from the MCL Coal Liquefaction Process

Soil Amendment Greenhouse Study

This research focused on the selection and characterization of nitrogen (N) -fixing cyanobacterial strains that could be used to scavenge waste CO_2 from the coal to liquid fuel conversion process (CTL) and provide an organic fertilizer product leading to a terrestrial pathway to carbon (C) sequestration. The work was conducted at Montana State University and Little Bighorn College in 2012-2013 under sponsorship of Accelergy Corporation and the American Indian Research and Education Initiative (AIREI).

The overarching goal of the project is to develop an effective carbon capture and storage strategy that would significantly decrease the C footprint of CTL. In addition to removing CO_2 from the CTL waste stream, it is expected that the cyanobacterial biomass could be used as a soil fertilizer that would continue to grow and fix atmospheric CO_2 and N after application to soil. A certain fraction of the C in this biomass would ultimately be converted to recalcitrant soil humic materials for long-term C storage. Furthermore, the resultant elevation of soil organic matter levels would significantly improve long-term soil quality. Results summarized below are from the “Soil Amendment Greenhouse Study” portion of the project .

Materials and Methods

Cyanobacterial biomass preparation. Strain 16 was grown in a 200 L raceway pond (Separation Engineering, Inc, Escondido, CA) at MSU under non-sterile conditions (Fig. V-9). BG11-N (http://www.sbs.utexas.edu/utex/mediaDetail.aspx?mediaID=180) media without thiosulfate was prepared using 200 L of non-sterile tap water. Losses of liquid volume due to evaporation during growth were replenished by adding tap water. The surface of the pond received an average of 60 µmoles m^{-2} s^{-1} of fluorescent light illumination at a 14/10 h light/dark cycle. Non-sterilized air was introduced into the system at a constant rate of 2.5 L/min through a counter current diffusion gas-liquid exchange column. The counter current flow pattern and packing in the gas-liquid exchange column enhances the transfer of CO_2 into solution. Temperature of the medium was maintained at 24 ± 1 ^{o}C using two aquarium heaters. To initiate the experiment, the raceway was inoculated with 4 L of strain 16 in the log growth phase (t_0 cell density ~10^5 cells/mL).

Strain B16 grew well in the raceway pond (Fig. V18b) and reached a maximum cell density of 2.5 x 10^7 cells per mL and a biomass of 0.67 g/L after 15 d. The biomass from the raceway pond was harvested by continuous centrifugation (Fig. V-18c) and stored at 4^{o} C prior to use in soil fertilizer amendment studies. The gravimetric water content of the cyanobacterial biomass after centrifugation was 0.83.

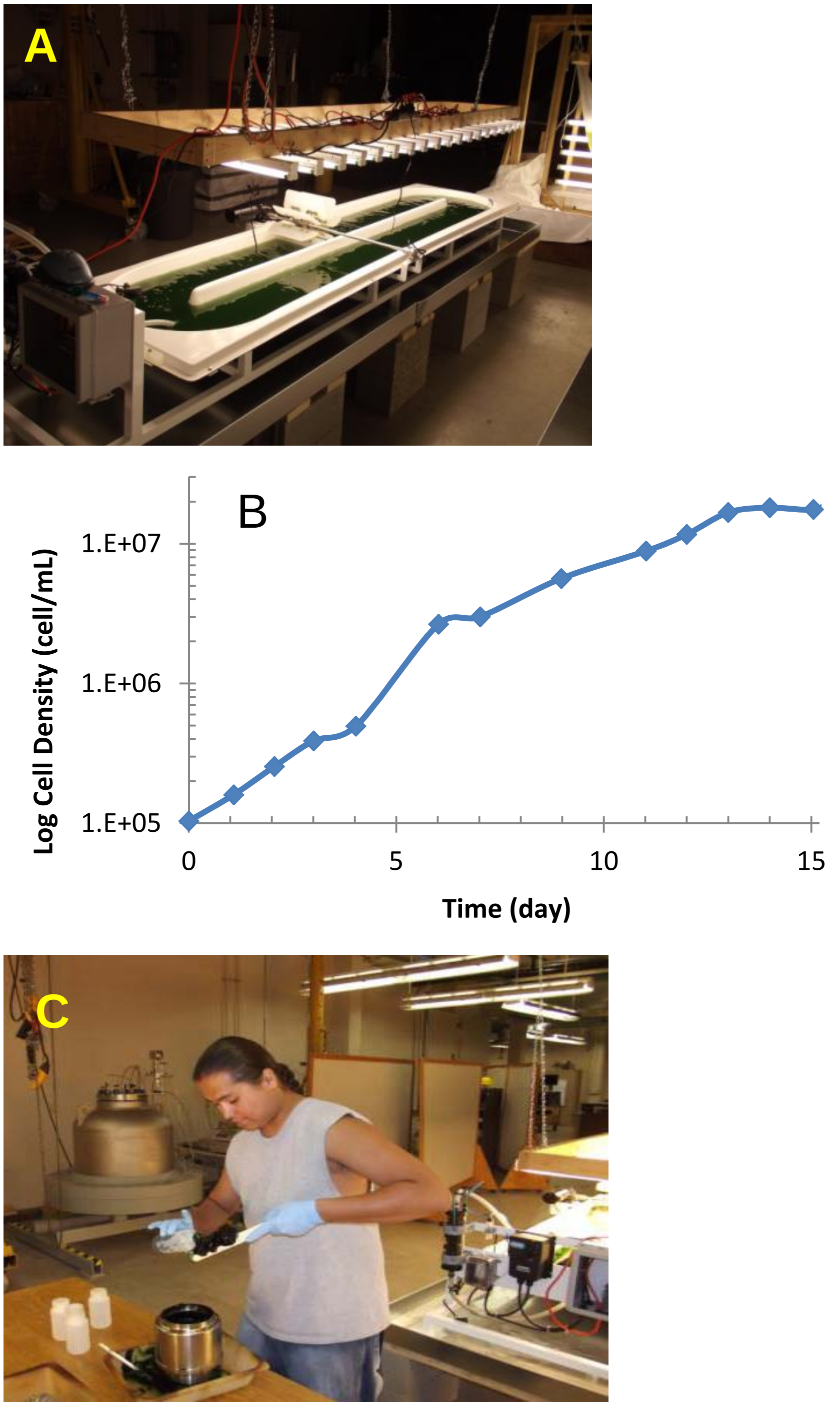


Figure V-18. *S*train 16 was grown in a 200 L raceway pond for 15 d in BG11-N media prepared from non-sterilized tap water (A). Growth (cell density, log scale) as a function of time in the raceway pond (B). Continuous centrifugation was used to harvest strain 16 biomass (C).

Soil Preparation. The top 15 inches of a Vananda Clay soil collected from the Crow Reservation in south-central Montana was used for growth experiments with wheat and camelina. The Vananda soil is common across the Crow Reservation as well as south central Montana and is extensively used for crop production. The soil was ground and sieved (< 2 mm) and thoroughly mixed with 50 mesh quartz sand (0.05-0.3 mm particle size; 25% soil:75% sand). Mixing with sand provided a non-compactable soil medium (important for working with a high clay soil) and insured nutrient poor conditions.

An additional experiment was conducted using an Amsterdam Silt Loam soil collected 18 miles west of Bozeman, Montana in the Gallatin Valley. This relatively fertile grassland soil contained about 2% organic matter.

Wheat and Camelina greenhouse study. Six inch diameter pots were filled with 1800 g of the Vananda soil/sand mix and the pots were seeded with wheat, var. Yellowstone and *Camelina sativa*, var. Suneson (Fig. V-19). The plant growth experiments were conducted in greenhouse space that was temperature controlled (22 ± 2 ^{o}C) and used both natural and artificial light, with automatic thermal/shade curtains implemented to obtain at least a 14 h light period. After seeding, the pots were watered with about 200 mL of tap water or Hoagland's nutrient medium every three to four days. For the wheat experiments, 9.0 g of moist strain 16 biomass (1.5 g dry weight @ 8% N) representing an application rate of 60 lb N per acre (0.126 g N per pot) was added as a slurry to pots after nine days of growth. This N application rate represents a low end rate for wheat grown in Montana (typical application rates are 100 – 200 lb N per acre) and was selected due to the short duration of these experiments (< 8 weeks) where wheat was harvested prior to the boot stage. Control treatments included: 1) no amendment, 2) 60 lb N per acre as 34-0-0, a commercial ammonium nitrate fertilizer and 3) 60 lb N per acre as Hoagland's liquid medium applied as 12 applications over 6 weeks. Hoagland's medium contains a full suite of macro and micronutrients. Each of the pots with wheat and treated with strain 16, ammonium nitrate or Hoagland's received 0.126 g of total N. However, it was expected that amendment with strain 16 would ultimately add more N since the cyanobacteria would continue to grown, fix N and further supplement the soil with N. Treatments were conducted in triplicate and the whole experiment was replicated.

The experimental conditions and treatments for camelina were identical to the wheat experiments with the exception that camelina was amended with 20 lb N per acre or 1/3 the application rate used for wheat. Camelina pots treated with strain 16 received 3.0 g of moist biomass. The N application rate for camelina represents a high end rate used in Montana for this short season oil seed crop that is adapted to grow in nutrient poor soils.

Carrot, Tomato, Kentucky bluegrass greenhouse study. And additional experiment was conducted using pots filled with 1800 g of 100% Amsterdam Silt Loam soil. Growth of World Vision variety carrots, Bonnie Best variety tomatoes and Scotts variety Kentucky bluegrass was evaluated. The 60 lb N per acre application rate was used in this experiment and the experimental treatments (35-0-0 treatment omitted) were as described above.

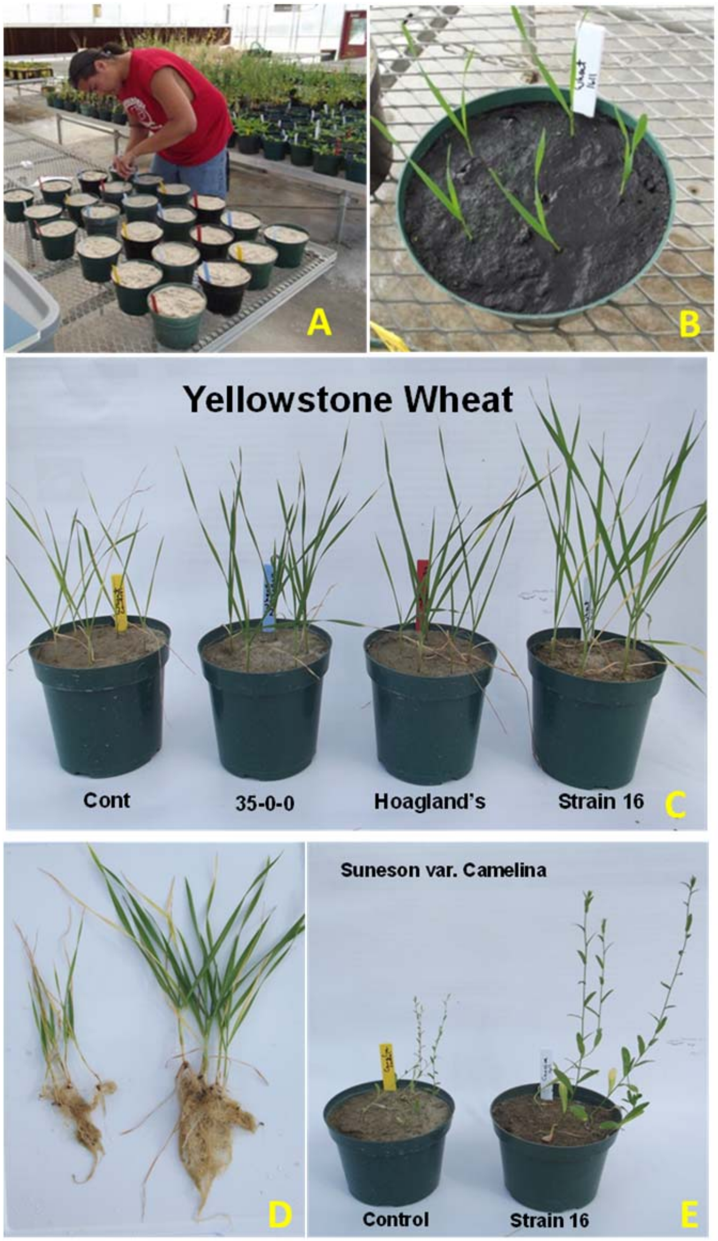


Figure V-19. Pots were seeded with wheat and camelina (A). Experimental treatment amended with moist strain 16 biomass (B; applied 9 d after seeding). Growth of wheat plants after 46 d (C,) in pots amended with N fertilizer (35-0-0), Hoagland's nutrient solution and cyanobacterial biomass Photo (D) – showing root system for control and Strain 16 treated plants. Photo (E) showing growth of camelina in soil that did not receive any fertilizer amendment (right) and soil amended with cyanobacterial biomass (left).

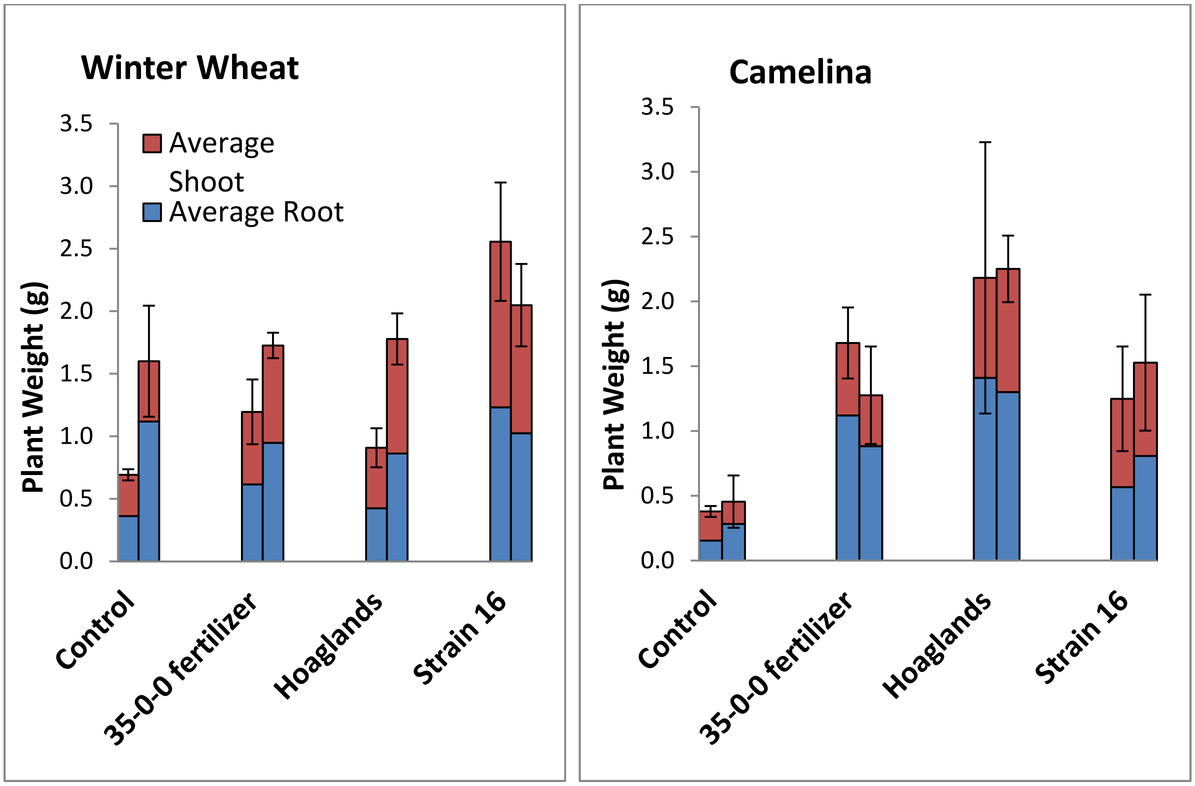


Figure V-20. Dry weights of roots and shoots of winter wheat and camelina amended with commercial N fertilizer (35-0-0), Hoagland's nutrient solution and cyanobacteria Strain 16 biomass. Plants were harvested after 46 and 55 days of growth (1st and 2nd experiments, respectively). Bars on the left side of each pair are results from the first experiment and bars on the right of each pair are results from the second experiment. Error bars are standard deviations of the average total plant dry weight in triplicate pots.

Results

Results from the greenhouse studies clearly show the positive effects of Strain 16 biomass addition on wheat and camelina growth (Fig. V-19). Winter wheat amended with Strain 16 outperformed all other treatments including the Hoagland's treatments, although the differences among treatments were not significant in the 2nd experiment. Hoagland's consists of a full suite of macro and micronutrients and the fact that the BioFertilizer outperformed the Hoagland's treatment for wheat points to its significant efficacy as a fertilizer. Camelina amended with strain 16 biomass did not perform as well in comparison to the commercial fertilizer treatment or Hoagland's, although application of strain 16 significantly enhanced growth in comparison to the control treatment. Experiments with carrots, tomato and

Kentucky bluegrass grown in Amsterdam soil also reveal the significant benefits of strain 16 application (Table V-2 and Figure V-21).

Consequently, these results support the use of strain 16 as a fertilizer amendment. The results also reveal that the degree of growth enhancement imparted by application of strain 16 is plant type dependent and possibly dose dependent.

Table V-2. Growth (dry weight) of carrots (tuber only), tomato (shoots only) and Kentucky bluegrass (shoots clipped 2.5 cm above soil surface) amended with Hoagland's nutrient medium and Strain 16 biomass. Carrots, tomato and Kentucky bluegrass (1st clipping) were harvested 80 d after planting.

	Carrots	*Tomato*	*Kentucky Bluegrass 1st clipping*	*Kentucky Bluegrass 2nd clipping*
		Dry weight (std dev) in grams		
Control	*2.58 (0.44)*	*3.36 (0.93)*	*1.11 (0.08)*	*0.97 (0.05)*
Hoagland's	*8.74 (1.29)*	*14.28 (1.47)*	*5.19 (0.49)*	*2.52 (0.15)*
Strain 16	*9.25 (0.40*	*13.29 (0.99)*	*5.01 (0.13)*	*3.09 (0.29)*

Figure V-21. Carrots and Kentucky bluegrass after 80 d of growth in pots amended with Hoagland's nutrient medium or moist Strain 16 biomass. Left – Control, Middle – Hoagland's, Right – Strain 16 Algae.

VI. STUDENT TRAINING AND INTERNSHIP PROGRAM

The program participants organized a student training and internship program to identify key undergraduate candidates who, if successful, would receive scholarships to participate in a work-study program on algae biofertilizer, energy service trade training and commercial driving and transport services. This effort was conducted with the full cooperation of Montana State University – Bozeman, Little Big Horn College and the University of North Dakota-EERC to identify candidates who are most appropriate for the openings.

An Application was developed for the *Cultivation and Characterization of Oil Producing Algae Internship* collaboration between MSU and LBHC, as a cornerstone program*.*

- Following an announcement run in the local daily newsletter, 73 total applications were received for the Work Readiness Scholarship program, with 53 determined to be complete. The Scholarship Committee developed the following Scoring System for applications:

    1. 10 points would be awarded for the personal essay
    2. 10 points for the letters of recommendation
    3. 3 points for their GPA
    4. 3 points for their overall ability to finish

- 15 students were selected in accordance with the internal selection process and admitted to the Algae Internship program. A total of 45 scholarships and Internships were granted over the life of the project.

- All students were given follow-up interviews to assist with potential job opportunities and to discuss the overall benefits of the class.

- For the overall effort, a total 38 out of the 45 students selected completed their programs.

This effort was acknowledged by DOE in a May 2012 newsletter, and the benefits of the program to students and program participants were highlighted as noted below:

Release Date: May 26, 2012

DOE-Supported Education and Training Programs Help Crow Tribe Promote Energy Independence and Education

Washington, DC —Two Department of Energy (DOE)-supported programs are helping the Crow Tribe in Montana produce energy with minimal environmental impact, educate future generations, and prepare its community for future jobs in energy fields.

At the heart of the Work Readiness Program and the Cultivation and Characterization of Oil Producing Algae Internship are 6-week intensive courses of study that teach real-world skills and provide opportunities for academic and industrial advancement in science, math, and energy.

The programs are supported in part by the Office of Fossil Energy's National Energy Technology Laboratory (NETL), as well as the Many Stars Project, Accelergy Inc., the University of North Dakota's Energy & Environmental Research Center, Little Big Horn College, and Montana State University. Ultimately, the two programs are helping the Crow Tribe take steps toward preserving local resources and jobs, and ultimately improving their reservation.

The Work Readiness Program teaches students classroom basics as well as specific job skills and how to apply these skills in a professional work setting. Students learn the basics of carpentry, welding, electrical work, rigging, reading blueprints, equipment operations, and safety standards. Students graduating from the program are well-positioned to help improve the quality of life within the reservation. For example, Fernando Long Soldier, a Crow Tribe member and program alumnus, is applying electrical skills learned in the program to infrastructure projects on the reservation, where he currently holds a supervisory position.

Amanda Not Afraid (front) and another student in the DOE-sponsored algae internship program work on cultivating and characterizing oil-producing algae.

Members of the sponsoring organizations serve as teachers and mentors for the Work Readiness Program, but qualified Crow Tribe members are also encouraged to become instructors and contribute to the learning process. Robert Stewart, a Crow Tribe member and core education instructor for the program, helped design practical hands-on experiences, including an assigned task of building a 16-foot flatbed trailer. "When the class was finished building the trailer, they were so proud of themselves that they had actually built it and it worked," said Stewart. "They were telling each other they are going to start building and selling their own trailers. That's what I wanted to hear!"

The Cultivation and Characterization of Oil Producing Algae Internship places students in a laboratory alongside established researchers to study local algae samples and evaluate their possible use in energy applications. The project focuses on Accelergy's integrated coal-to-liquid (ICTL) technology, which reforms local Montana bituminous coal and indigenous biomass feeds, like algae, into a liquid that is economical to transport and use as fuel. The student interns are involved in every aspect of the research. During last summer's program, students collected algae at two different pond sites outside of the reservation, built bioreactors to grow the algae, harvested the algae, and then freeze-dried their samples to check the algae for oil quantities that could be useful to the ICTL technology.

Crow Tribe member Amanda Not Afraid, who completed the algae internship, said her experiences taught her "to see all the opportunities that lie outside of the reservation and what skills it would take to succeed there." Since graduating from the program, Amanda has enrolled as a freshman at Little Big Horn College and is pursuing a degree in pre-medicine.

Acceptance into the two programs is competitive. Similar to applying for college, students are required to submit a packet of personal information, essays, and letters of recommendation which are reviewed by a board of four members. Of the 70 applicants in 2011, 45 were chosen and 38 graduated. The students who successfully completed the internship program are now in the workforce or attending one of the sponsoring institutions.

Because of the programs' success, DOE has awarded additional funding to the algae internship, and outside funding was granted to Work Readiness Program, ensuring that both will be available to a new wave of students in summer 2012.

VII. OVERALL CONCLUSIONS AND FUTURE DIRECTION

ICTL has been shown in laboratory studies to be a viable approach to the conversion of coal to distillate fuels with overall low GHG footprint and cost effective conversion due to the more efficient direct liquefaction technology coupled with carbon capture and utilization. This approach is based upon Direct Coal Liquefaction (DCL)/Biomass Conversion via Catalytic Hydrodeoxygenation and Isomerization (CHI) hydroprocessing technology coupled with Carbon Capture and Utilization (CCU) via conversion of process-derived CO_2 and waste water to produce algae-biomass based BioFertilizer for terrestrial CO_2 sequestration and bio-oil as a feedstock for added fuels or chemicals production.

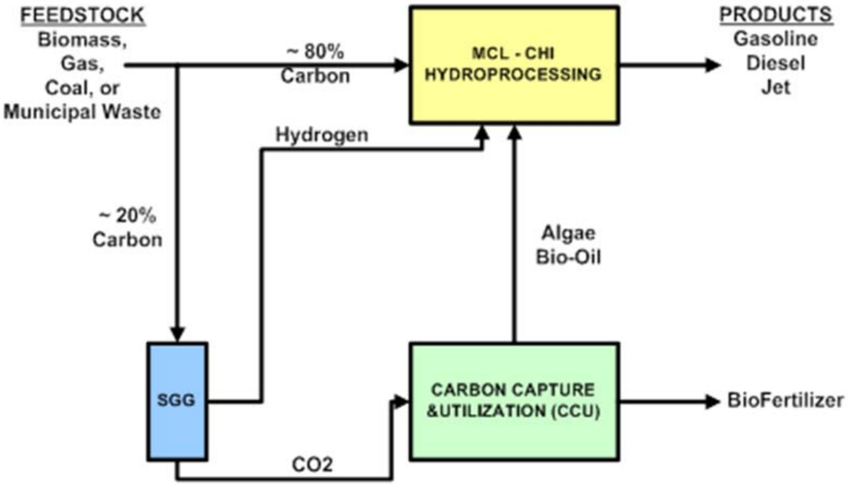


Figure I-1. Simplified ICTL Process Flow Scheme

ICTL technology was successfully demonstrated with Montana sub-bituminous coal in Microcatalytic Coal Liquefaction (MCL) pilot scale operations at the Energy and Environmental Research Center at the University of North Dakota (EERC). Products from that operation were isolated, characterized and tested at DOD AFRL labs in Dayton. These materials were very similar in composition to ones previously studied by Schobert et al – and they offer a potentially new and high performance pool of molecules for future synthetic jet fuel applications.

Pilot scale studies of Catalytic Hydrodeoxygenation and Isomerization (CHI) of bio-oil feeds were conducted at the University of Pittsburgh Applied Research Center (PARC). The ability to efficiently convert FAME, TAG, and FA feeds to a highly saturated normal and iso paraffinic distillate was demonstrated. Samples of those products were blended into Coal-Biomass to Liquid (CBTL) fuel samples and these were evaluated at the US Air Force Research Labs (AFRL) in Dayton. These materials make ideal blending components for the aromatic and highly cycloparaffinic blendstocks from MCL – in effect allowing the product of a fully synthetic jet fuel from the various molecular components.

Carbon Capture and Recycle was achieved via production of algae from CO2 and greenhouse tests of algae derived BioFertilizer conducted at Montana State University (MSU). The BioFertilizer was tested with various indigenous crops in Crow MT soil and shown to be an effective replacement for conventional ammonia and Hoagland's formulated chemical fertilizer. The ability to offset C emissions from production of conventional fertilizer and the ongoing terrestrial CO2 sequestration induced by BioFertilizer makes it a worthy candidate solution for GHG issues in synthetic fuels production. LCA studies have confirmed this concept and more larger scale studies are planned.

The MT ICTL Demonstration Program provided proof of principle tests on all key steps of the ICTL flow scheme, and the results of these studies are providing a basis for taking this technology to the next phase of commercial development. Accelergy is conducting process screening and site assessment studies on Montana and other locations to advance these individual technologies. The overall ICTL flow scheme offers thermal efficiencies from coal to liquids in excess of 70% on a high heating value basis. Water usage of <3 barrels per barrel of oil produced are possible and land use is less than 1/10th that it would be if the fuels were produced from a BTL (algae and seed crop) only route.

ICTL conversion technology is configured to operate alone, or with other carbon based feedstocks such as natural gas as the primary source of hydrogen. This approach allows us to use coal as the primary feedstock for fuel production, while simultaneously mitigating CO_2 and generating added biomass for optional conversion to fuels. The overall benefits of matching the aggregate feed C/H stoichiometry to C/H product stoichiometry are significant and help to not only reduce net GHG emissions but also to improve thermal efficiency.

The fully integrated ICTL flow scheme provides a combination of features and advantages that cannot be achieved with current or emerging indirect conversion alternatives. MCL pilot studies have shown that over 4 barrels of cleaner burning liquid fuel (up to 60% in the jet boiling range) can be produced per ton of carbon feed (from coal alone or coal plus biomass), almost twice the liquid yield possible from other indirect conversion technologies.

Process derived CO_2 is used to produce BioFertilizer which in normal use continues to capture CO_2 and nitrogen to produce stable carbon species in treated soil. In this manner, the algae BioFertilizer induces further capture of CO_2 via terrestrial sequestration leading to an overall capture ratio of CO_2 to algae carbon (LCA basis) of up to 150/1. Studies have shown that capture ratios of >10/1 are possible in 20-30 day soil treatment periods, while even higher ratios have been observed for net carbon capture in long-term multi-year desert soil stabilization studies.

Novel process integration also enables us to more effectively utilize by-product waste gas and wastewater streams from one section of the facility as feedstocks for another. This integrated design improves overall efficiency and eliminates a critical barrier to entry by reducing overall investment by up to 15-30%, as shown in recent scoping studies with partner EPC firms.

Life Cycle Assessment (LCA) studies showed that this approach can produce synthetic fuels form coal based feeds (optionally with natural gas as a source of hydrogen) to meet EISA 2007 Section 526 GHG requirements. Econometric studies showed that the CCU option provided lower cost than other carbon sequestration routes, and the algae BioFertilizer can provide economic advantages in a wheat-camelina crop production that incorporates the BioFertilizer as a one for one replacement of conventional ammonia based fertilizer.

Results from the current study are now being evaluated in collaboration with a global EPC firm. Accelergy and the Crow are now exploring various options for advancing ICTL to pioneer scale operations in Montana. Site assessment studies are being conducted on Montana and other North American locations where infrastructure, feedstock and agricultural land and water resources are sufficient to support commercial scale ICTL. It is anticipated that a prime location for further study will be identified in the coming months, and results from the current study will be utilized in a commercial project prefeasibility study.

VIII. LIST OF TABLES AND FIGURES

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FIGURE V-15. BIOMASS OF *A. CYLINDRICA* STRAIN B1611 AS A FUNCTION OF TEMPERATURE IN PHOTO-BIOREACTORS. ERROR BARS REPRESENT STANDARD DEVIATIONS OF THREE REPLICATES.

FIGURE V-16. GROWTH OF *A. CYLINDRICA* STRAIN B1611 VERSUS TIME IN BOTH THE STANDARD BG11-N MEDIA AND WITH THE ENHANCED MEDIA CONSISTING OF FIVE TIMES THE STANDARD CONCENTRATION OF MAGNESIUM AND EDTA. ERROR BARS REPRESENT STANDARD DEVIATIONS OF TRIPLICATE FLASKS.

FIGURE V-17. OPTICAL DENSITY OF *A. CYLINDRICA* STRAIN B1611 VERSUS TIME IN BOTH THE BG11-N AND ENHANCED BG11-N (5X MG AND EDTA CONCENTRATIONS). ERROR BARS ARE STANDARD DEVIATIONS OF TRIPLICATE FLASKS.

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FIGURE V-20. GROWTH OF *A. CYLINDRICA* STRAIN B1611 IN 250 ML SHAKER FLASKS AND 1.2 L PHOTO-BIOREACTORS. ERROR BARS ARE STANDARD DEVIATIONS OF TRIPLICATE FLASKS OR PHOTO-BIOREACTORS.

FIGURE V-21. BIOMASS CONCENTRATION OF *A. CYLINDRICA* STRAIN B1611 VERSUS TIME GROWN IN THE ENHANCED BG11-N MEDIA IN PHOTO-BIOREACTORS. ERROR BARS ARE STANDARD DEVIATIONS FOR TRIPLICATE PHOTO-BIOREACTORS.

FIGURE V-22. 200 L RACEWAY WITH *A .CYLINDRICA* B1611 IN THE ENHANCED BG11-N MEDIA.

FIGURE V-23. PHOTO-BIOREACTORS RECEIVING AIR VIA SLUG FLOW (LEFT) AND BUBBLY FLOW (RIGHT).

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FIGURE V-25. THE PH OF *A. CYLINDRICA* STRAIN B1611 AS A FUNCTION OF GAS DELIVERY SYSTEM. ERROR BARS ARE STANDARD DEVIATIONS OF TRIPLICATE PHOTO-BIOREACTORS.

FIGURE V-26. GROWTH OF *A. CYLINDRICA* STRAIN B1611 AT VARIOUS PHS HELD CONSTANT WITH BUFFERS. ERROR BARS REPRESENT STANDARD DEVIATIONS OF TRIPLICATE SHAKER FLASKS.

FIGURE V-14 EFFECTS OF BIOMASS ADDITION WITH CONTROLS (A) AND AMENDED SOILS (B) SUPPORTING SIGNIFICANTLY GREATER GROWTH.

FIGURE V-15. PHOTOS OF POTS SEEDED WITH WHEAT IN EACH FRAME (LEFT CONTROL) AND (RIGHT SUBJECTED TO FOUR TREATMENTS INCLUDING AMENDMENT WITH MOIST STRAIN B1611BIOMASS). LEFT AND RIGHT FRAMES SHOW PLANTS AFTER 21 AND 26 DAYS, RESPECTIVELY.

FIGURE V-16. PHOTO SHOWS GROWTH OF CAMELINA AFTER 26 D IN POTS AMENDED WITH CYANOBACTERIAL BIOMASS (RIGHT) AND POTS THAT DID NOT RECEIVE ANY FERTILIZER AMENDMENT (LEFT).

FIGURE V-17. PADD 4 PIPELINE SYSTEM FOR FUELS DISTRIBUTION TO DOD FACILITIES.

FIGURE V-18. *S*TRAIN 16 WAS GROWN IN A 200 L RACEWAY POND FOR 15 D IN BG11-N MEDIA PREPARED FROM NON-STERILIZED TAP WATER (A). GROWTH (CELL DENSITY, LOG SCALE) AS A FUNCTION OF TIME IN THE RACEWAY POND (B). CONTINUOUS CENTRIFUGATION WAS USED TO HARVEST STRAIN 16 BIOMASS (C).

FIGURE V-19. POTS WERE SEEDED WITH WHEAT AND CAMELINA (A). EXPERIMENTAL TREATMENT AMENDED WITH MOIST STRAIN 16 BIOMASS (B; APPLIED 9 D AFTER SEEDING). GROWTH OF WHEAT PLANTS AFTER 46 D (C,) IN POTS AMENDED WITH N FERTILIZER (35-0-0), HOAGLAND'S NUTRIENT SOLUTION AND CYANOBACTERIAL BIOMASS PHOTO (D) – SHOWING ROOT SYSTEM FOR CONTROL AND STRAIN 16 TREATED PLANTS. PHOTO (E) SHOWING GROWTH OF CAMELINA IN SOIL THAT DID NOT RECEIVE ANY FERTILIZER AMENDMENT (RIGHT) AND SOIL AMENDED WITH CYANOBACTERIAL BIOMASS (LEFT).

FIGURE V-20. DRY WEIGHTS OF ROOTS AND SHOOTS OF WINTER WHEAT AND CAMELINA AMENDED WITH COMMERCIAL N FERTILIZER (35-0-0), HOAGLAND'S NUTRIENT SOLUTION AND CYANOBACTERIA STRAIN 16 BIOMASS. PLANTS WERE HARVESTED AFTER 46 AND 55 DAYS OF GROWTH (1^{ST} AND 2^{ND} EXPERIMENTS, RESPECTIVELY). BARS ON THE LEFT SIDE OF EACH PAIR ARE RESULTS FROM THE FIRST EXPERIMENT AND BARS ON THE RIGHT OF EACH PAIR ARE RESULTS FROM THE SECOND EXPERIMENT. ERROR BARS ARE STANDARD DEVIATIONS OF THE AVERAGE TOTAL PLANT DRY WEIGHT IN TRIPLICATE POTS.

FIGURE V-21. CARROTS AND KENTUCKY BLUEGRASS AFTER 80 D OF GROWTH IN POTS AMENDED WITH HOAGLAND'S NUTRIENT MEDIUM OR MOIST STRAIN 16 BIOMASS. LEFT – CONTROL, MIDDLE – HOAGLAND'S, RIGHT – STRAIN 16 ALGAE.

TABLES:

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XI. LIST OF ACRONYMS AND ABBREVIATIONS

AAFI – Alternative Aviation Fuel Initiative
AFRL – Air Force Research Laboratory
CBTL – Coal-Biomass to Liquids
CCS – Carbon Capture and Sequestration
CCU – Carbon Capture and Utilization
CHI – Catalytic Hydrodeoxygenation and Isomerization
CRADA – Cooperative Research & Development Agreement
CTL – Coal to Liquids
DCL – Direct Coal Liquefaction
DDS – Duty Design Specification
DOD – Department of Defense
EDA – Exxon Donor Solvent
EISA – Energy Independence and Security Act of 2007
EPA – Environmental Protection Agency
EPC – Engineering, Procurement and Construction
FA – Fatty Acid
FAME – Fatty Acid Methyl Ester
FEED – Front End Engineering and Design
FT – Fischer Tropsch
GCD – Gas Chromatographic Distillation
HDO – Hydrodeoxygenation
HEFA – Hydroprocessed Ester and Fatty Acid
HP – Hydroprocessing
ICL – Indirect Coal Liquefaction
ICTL – Integrated Carbon to Liquids
KB – Thousands of Barrels
LCA – Life Cycle Analysis
MCL – Micro Catalytic Liquefaction
MDEA – N-methyl-diethanolamine
Mpa – Mega Pascal

XI. List of Acronyms and Abbreviations (cont.)

MSU – Montana State University

MTG – Methanol To Gasoline

SGG – Syngas Generation

SHG – Steam Hydrogasification

SMR – Steam Methane Reformer

SOPO – Statement of Program Objectives

SPK – Synthetic Paraffinic Kerosene

TAG – Triacyl-glyceride

TARDEC – Tank Automotive Research, Development and Engineering Center

TPD – Tons Per Day

UND – University of North Dakota

USAF – United States Air Force

VGO – Vacuum Gas Oil