Recovery Act: Demonstration of a Pilot Integrated Biorefinery for the Efficient, Direct Conversion of Biomass to Diesel Fuel

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Disclaimer:

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Executive Summary

The Renewable Energy Institute International, in collaboration with Greyrock Energy (formally called Pacific Renewable Fuels) and Red Lion Bio-Energy (RLB) has successfully demonstrated operations of a 25 ton per day (tpd) nameplate capacity, pilot, pre-commercial-scale integrated biorefinery (IBR) plant for the direct production of premium, "drop-in", synthetic fuels from agriculture and forest waste feedstocks using next-generation thermochemical and catalytic conversion technologies (Schuetzle and Tamblyn et. al, 2011a, 2011b, 2013, 2014). The IBR plant was built and tested at the Energy Center, which is located in the University of Toledo Medical Campus in Toledo, Ohio. The schedule for this IBR project is illustrated in Figure E1.

	2010	2011	2012	2013	2014
Budget Period 1 (BP1)	▬				
Preliminary Engineering	▬				
Permitting	▬				
Budget Period 2 (BP2)	▬				
Final Engineering	▬				
Procurement		▬			
Construction		▬			
Operations			▬▬		
Reporting	▬▬▬▬▬▬▬▬▬▬				
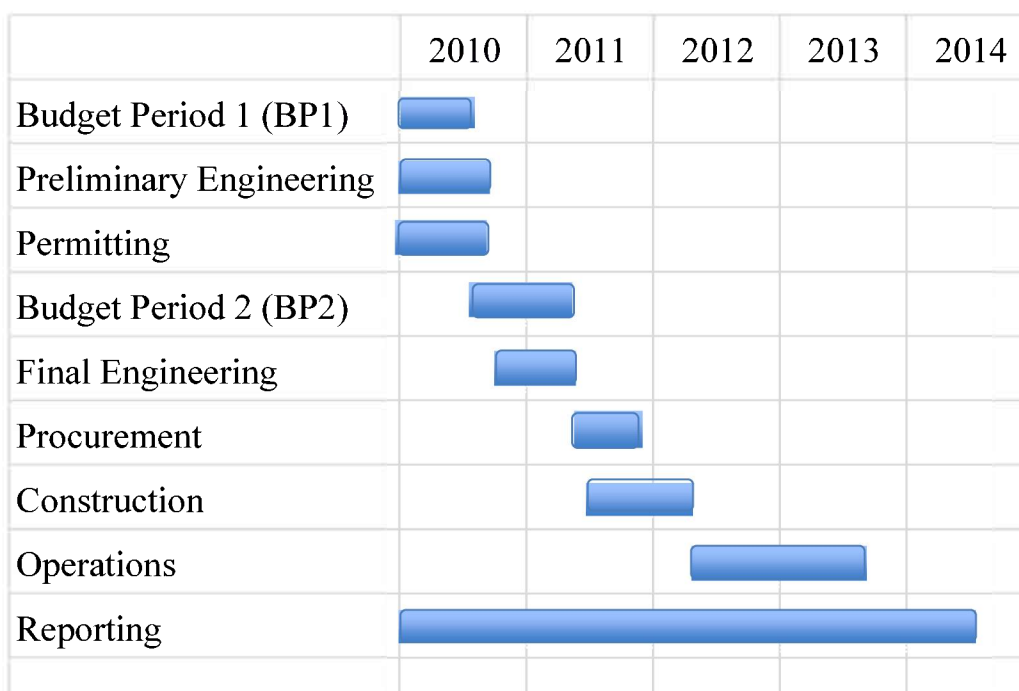
Figure E1: IBR Project Schedule

This IBR plant is based upon unique technologies developed by RLB and Greyrock. It has been demonstrated that this integrated technology is able to efficiently convert nearly any type of biomass into "drop-in" liquid fuels. Wood and rice hulls were chosen as the primary feedstocks for extensive testing and validation of this IBR technology. A distinctive advantage is that this process can accept ground biomass up to 2.0"- 2.5" in size and water content up to 35 weight %.

The IBR plant is comprised of two major processes, the RLB Thermochemical Conversion process (TCC) and the Greyrock Liquid Fuel Production (LFP) process (Figure E2).

Thermochemical Conversion (TCC)   **Liquid Fuel Production (LFP)**
Biomass Pyrolysis & Steam Reforming   Direct Fuel Production
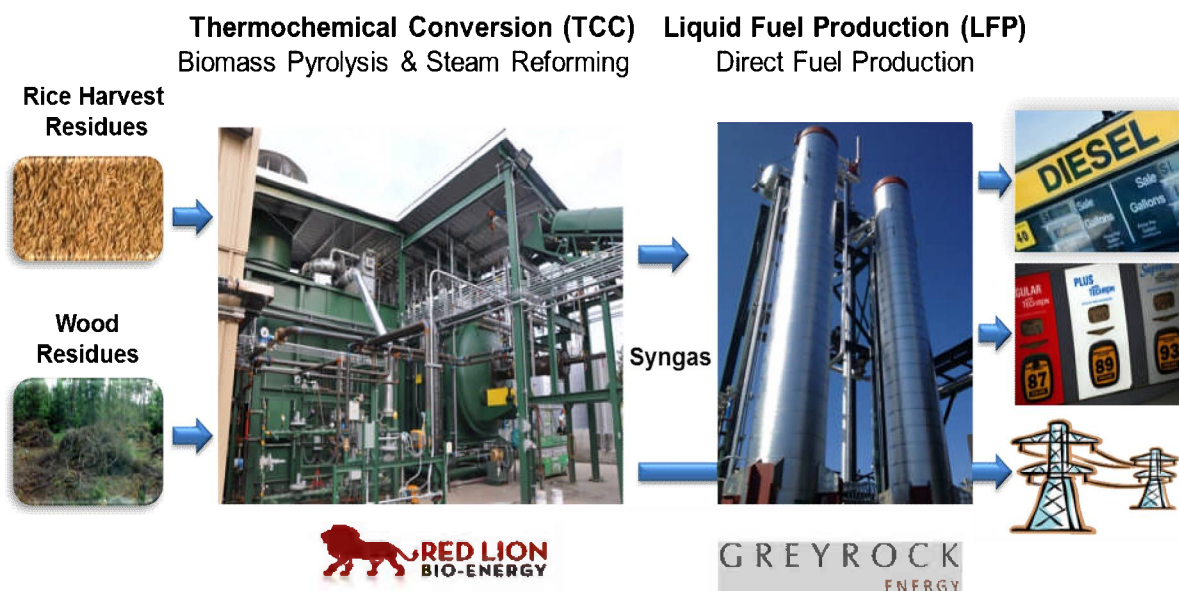
Figure E2: Main IBR Plant Processes

The TCC process converts the biomass into high purity syngas using slow (10-20 min.) pyrolysis under steam reforming conditions at 1,480-1,530 °F, followed by a fast (3-12 sec.) steam reforming process at 1,790-1,815 °F. The syngas composition, produced from the wood and rice hulls, was comprised of an average of 46 volume % hydrogen (H_2) and 23 volume % carbon monoxide (CO), with the remainder of the syngas comprised of methane (12 volume %) and CO_2 (19 volume %).

The H_2 and CO was directly converted to "drop-in" synthetic diesel and reformulated gasoline blendstock fuels using "designer" catalysts employed in the LFP process. This new generation of catalysts directly produces these fuels by means of free radical processes that differ from that of the chemical processes typically employed using Fischer-Tropsch (F-T) catalysts. The by-product gases (consisting primarily of C_1-C_4 hydrocarbons), produced from the LFP process, are used as fuels for the TCC burners and for the generation of electricity using a gen-set or gas turbine. As a result, once the plant becomes operational, no external power or natural gas is needed. As illustrated in Figure E2, some of the syngas from the TCC system can be added to the by-product gases to produce additional power which can be used by a co-located facility and/or exported to the grid.

It was established that this IBR technology has several benefits over other thermochemical processes. These benefits include:

- Feedstock carbon was efficiently converted to syngas with the proper stoichiometric H_2/CO ratio of ~2.0/1.0 for the efficient conversion to fuel.

- Tar production was reduced by 100-1,000 times (compared to traditional gasification processes as described by Rabou, 2009), which significantly reduced syngas purification processing requirements. It was determined that this reduction in tars was primarily due to the thermochemical conversion carried out under reducing conditions (no oxygen or air), and at the optimum steam to feedstock carbon ratios, temperatures, and reaction times. The overall tar concentrations, excluding benzene and toluene, in the raw, unpurified syngas ranged from 260-296 ppmv. The syngas purification system effectively removed these tars from the syngas (> 99% for naphthalene and 100% for heavier tars).

- Premium synthetic fuels were produced directly with minimal production of wax ($\leq$ 1.0 weight % of the fuel products at the optimum catalyst operating conditions), compared to competing F-T approaches, which produce wax as the primary product for which the production of fuels from the wax requires costly, refinery type conversion processes.

The IBR plant was designed using modular unit operations so that these modules could be economically built by a number of preferred U.S. contractors at their manufacturing locations and moved to the plant site by truck. This modular design and assembly approach significantly reduced capital costs and plant assembly time. Plant construction was carried out during the third quarter of 2011 and completed under budget and on time during the first quarter of 2012 during winter conditions in Toledo, OH.

Table E1 summarizes the IBR plant biomass testing and validation that was conducted between May 9, 2012 and September 21, 2013. The plant was run for a couple of months to check and calibrate all unit operations, instrumentation, control procedures, and data acquisition systems (runs #1-4) (Table E1).

The next four runs were carried out to optimize and validate the integrated plant operation (runs #5-8) as needed to maximize fuel production. This objective was successfully achieved by carrying out comprehensive chemical and physical measurements on each unit operation and for the entire integrated plant. The data generated from these tests were used in chemical models to determine the optimum plant operating conditions.

Once the optimum plant operating conditions were determined, another eight runs (#9-#16 from 12/2012 to 8/2013) were undertaken to validate these optimum operating conditions and to monitor the performance of each unit operations and the total integrated plant process. The final run (#17), the Independent Engineer's (IE) Performance Test, was carried out during September of 2013.

During this 16-month test period under very cold and hot climatic conditions, the plant was operated under integrated conditions for a total of 992 hours on wood and rice hulls (not including plant warm up, shut down, and calibration, which typically took from 48-60 hours per run. The TCC system was operated alone for an additional 178 hours.

Several standard reference materials were used for calibration of the total integrated system before biomass runs. These reference materials included mixtures of methane & CO_2, methanol & CO_2, and glycerol & CO_2 mixtures, that were run for a total of 220 hours under integrated operating conditions.

Table E1: Summary of IBR Plant Testing and Validation

Test Period (Run Numbers)	Test Objectives	Plant Operation Periods (hrs.)		
		Total Integrated		TCC Only
		Biomass	Standards	
5-7/2012 (#1-4)	Checkout & Calibration	198	0	60
8-11/2012 (#5-8)	Optimization & Validation	322	55	57
12/2012 – 8/2013 (#9-16)	Validation & Performance	374	141	69
9/2013 (#17)	Independent Engineer's Test	98	24	0
Total		992	220	178

It was found that the % carbon conversion for feedstock to syngas and feedstock to fuels averaged 85 +/- 3% and 40 +/- 2%, respectively over the test period. The fuel production averaged 58 +/- 4 gallons/1,000 lbs. of carbon input for the rice hulls and 57 +/- 3 gallons/1,000 lbs. of carbon input for the wood feedstocks when the plant was operated under the optimum conditions and the correct number of recycle loops to convert approximately 90% of the CO to fuel. As predicted, the fuel productivity in terms of gallons/dry ash free ton (daft) and gallons/1,000 lbs. of carbon input were nearly the same. These fuel production rates were achieved without recycling of the minor side products (e.g. tailgas, wax and water) to produce additional syngas.

Gas phase feedstocks, consisting of methane/CO_2 and methanol/CO_2 mixtures, were introduced into the plant for calibration purposes and for comparing fuel production results (in gallons diesel/1,000 lbs. carbon input) with the biomass feedstocks. The percent carbon conversion for the methanol/CO_2 mixtures averaged 80% at the optimal plant operating temperatures. These mixtures were easy to introduce into the plant and they produced very clean syngas which exceeded the purity specifications for the efficient, catalytic production of fuel.

In comparison to the gas-phase feedstocks, the biomass feedstocks were more difficult to introduce and they produced syngas contaminants, which necessitated removal before fuels could be effectively produced. The RLB technology was very efficient in reducing all contaminants to very low levels in the syngas, except for benzene. Benzene was produced from the pyrolysis of the biomass feedstocks, which are comprised of complex aromatic structures. Since the gas-

phase feedstocks do not contain aromatic components, no benzene was generated from the gas-phase feedstocks.

The benzene had no detrimental effect on the fuel production catalyst and was collected as a constituent in the reformulated gasoline blendstock (RGB) fuel. The benzene was easily removed from the RGB during the final fuel distillation step and it will be marketed separately as a high value commodity chemical from the commercial scale plants.

The plant was operated also as a hybrid system in which various gas-phase mixtures of methanol, CO_2, and rice hulls were co-introduced in varying proportions. It was found that the fuel production rates as a function of carbon input were constant, averaging 56 ± 2 gallons/1,000 lbs. carbon input for these gas-phase/solid phase mixtures. Since the conversion efficiency of the methane/CO_2 mixture to syngas was 80% compared to the 85% for the wood feedstock, the adjusted fuel production was 57 gallons/1,000 lbs. of carbon input, which was nearly the same as that for the fuel productivity from wood.

During the 16 months of operation, the entire plant was operated seventeen times from non-operating to operating conditions. Typically, such cycling creates stresses and possible non-functionality or partially functioning systems in refinery and chemical production plants. However, the fuel production system, which incorporates the "designer" catalyst and catalytic reactors, showed a slight improvement in fuel productivity over the 16-month test period even though there were several periods during which the catalyst poisons produced from biomass, hydrogen sulfide and ammonia, spiked for short periods to low ppm levels during several tests. Although these levels were 100 times higher than the safe levels established for the catalyst, the relatively constant fuel productivity during the 16 months of operation confirms Greyrock's predicted catalyst lifetime of three years or more. A comparison of fuel productivity measured during 2012 and during the Independent Engineer's (IE's) test during September 8-20, 2013 demonstrated that fuel productivity increased to some extent over this 10-month period (53.0 gallons/1,000 lbs. of carbon to 56.6 gallons/1,000 lbs. of carbon for the wood feedstock). These differences may have been the result of the plant running under slightly optimized conditions during the 2013 runs compared to the 2012 runs. In any case, this data demonstrates that the catalyst productivity remained relatively constant over this time period.

All IBR plant systems have proven to be robust except for the feedstock introduction and ash removal processes in the TCC system. As a result, more robust feedstock introduction and ash removal processes have been re-designed for incorporation into future systems. Some minor failures occurred in the TCC system during the 16 month test period including: 1). A break in the welded interface between the drive shaft and the rotating drum inside Unit Process 2; 2). Stress cracks in the hot syngas transfer pipes and; and 3). Plugging of the hot syngas heat exchanger tubes. As a result, RLB has re-designed these components to insure their long-term durability. In contrast, no system failures occurred in the Greyrock liquid fuel production (LFP) system.

The fuel produced from the solid biomass and gas phase feedstocks were virtually identical in chemical composition and physical properties, when the LFP was run at H_2/ CO ratios of 2.0-2.2 to 1.0. The fuel consisted of two drop-in fuel products, a synthetic diesel fuel (syndiesel) and reformulated gasoline blendstock (RGB). The yields of synthetic diesel fuel and RGB averaged

72.0 volume % and 22.7 volume % of the total fuel produced, respectively. The remaining 5.3 volume % was benzene (a high-value commodity chemical). Benzene was only produced when biomass feedstocks were used.

Since comprehensive, quantitative chemical measurements were made on each unit operation, it was possible to carry out a detailed carbon mass balance for the plant. It was found that greater than 96% of the carbon input into the plant could be accounted for by the primary fuel products, co-products (primary biochar), air emissions (primarily CO_2) and water effluents (primarily containing $C_1 - C_5$ alcohols).

Comprehensive engine dynamometer tests, carried out using a 500 horsepower 2014 diesel engine, demonstrated that 20 volume % blends of the synthetic diesel fuel with petroleum derived ultra-low sulfur diesel fuels reduced tailpipe emissions even though this engine employs advanced emission control technologies. This blend reduced CO_2 emissions by 1.0% and methane emissions by 9.2%, which will help reduce greenhouse gas emissions since the comparative impact of methane on climate change is over 20 times greater than CO_2 over a 100-year period (EPA, 2014). In addition, this blend improved fuel lubricity from 520 to 404 using the ASTM D6079 HFRR test (see Section XV for further details on the HFRR test), which will reduce engine wear, improve long-term engine durability, and decrease repair costs.

As based upon the composition of this synthetic diesel fuel and published diesel engine performance and emissions tests, it is forecast that the synthetic diesel fuel will reduce emissions from "in-use" diesels by up to 50%, and more than 50% for off-road diesels typically used for farming, mining, power generation, rail transportation, and maritime shipping (Lloyd, 2011).

A commercial scale plant has been designed that can convert 240 daft of biomass/day to 4.40 million gallons/year of fuel in the northern Central Valley of California. The current capital cost of the BTL plant is $40.4 million with an operations and maintenance (O&M) cost of $4.21 million/year (excluding feedstock cost). It was determined that the installed capital cost (Capex) of the plant for the first full year of operation is $9.18/gallon with a projected internal rate of return (IRR) of 10.6%. This IRR is based upon an average fuel production cost of $2.37/gallon GGE (Gasoline Gallon Equivalent), and a wholesale market value of the synthetic diesel of $3.08/gallon and reformulated gasoline blendstock of $2.65/gallon, respectively. These economics were based upon the 2014 U.S. average for oil at about $90/barrel with average 2014 retail diesel and gasoline fuel costs of $4.15 and $3.70, respectively. This IRR does not include renewable fuel incentives. If renewable fuel standard credits are included in the plant economics, the IRR increases to 21.0%. However, these potential credits are not included in the TEA since their long-term viability is not known. This commercial plant is expected to produce "drop-in" fuels with a feedstock carbon to fuel carbon production efficiency of 39.7%; a feedstock carbon to fuel and biochar carbon production efficiency of 53%, and an energy efficiency of 53.9%.

During the first quarter of 2015, the U.S. average cost for a barrel of oil has dropped to about $50, with corresponding average U.S. retail diesel and gasoline fuel costs of $3.10 and $2.20, respectively. As a result, the IRR for the 2014 BTL plant design has dropped to - 0.2%. Therefore additional work will be carried out during 2015 to reduce the capital and O&M costs

of this 240 daft/day plant to $34.4 million and $3.79 million/year, respectively. In addition, the 2014 commercial IBR plant design is being upgraded to increase fuel production by the end of 2015. These improvements and other enhancements are expected to increase the IRR to 11.6% (without incentives).

The data generated in this study was used to carry out a collaborative life-cycle assessment (LCA) with the National Renewable Energy Laboratory and Argonne National Laboratory to determine the reduction in greenhouse gases that would be generated by the deployment of the commercial-scale BTL technology. As based upon the Argonne National Laboratory GREET "well to wheels" model, it was determined that the greenhouse gas (GHG) emissions would be reduced by 157% for the BTL plant, compared to diesel fuel produced from petroleum.

I. Introduction

A. Background

This DOE Integrated Biorefinery (IBR) project was formally initiated during January 2010 with the primary objective to upgrade an existing thermochemical conversion (TCC) system and build a new liquid fuel production (LFP) system that directly converts biomass into diesel fuel at a larger capacity and at a higher conversion efficiency than has been previously demonstrated. Construction of the 25 ton per day nameplate capacity IBR plant in Toledo, OH was completed on schedule and on budget (Figures IA.1 to IA.8) in April 2012 and plant performance and validation tests were initiated on May 9, 2012. Seventeen test campaigns were carried out from May 9, 2012 to September 20, 2013 in which the integrated IBR plant was operated for a total of 992 hours.

Figure IA.1 is a process flow diagram for the IBR plant, which shows the primary unit operations and Figures 1A.2 to 1A.9 are photographs of the completed plant, the unit operations, and the central control system.

Solid
Feedstocks

Gas & Liquid
Feedstocks

Syngas

Unit 1 – Feedstock
Introduction

Unit 2 – Solids
Steam Reforming

Unit 3 – Gases
Steam Reforming

Unit 4a – Syngas
Purification

Syngas

Unit 4b – Syngas
Polishing

Unit 5 –
Compression

Unit 6 – Catalytic
Conversion

Unit 7 – Product
Separation

Unit 8 – Fuel
Storage
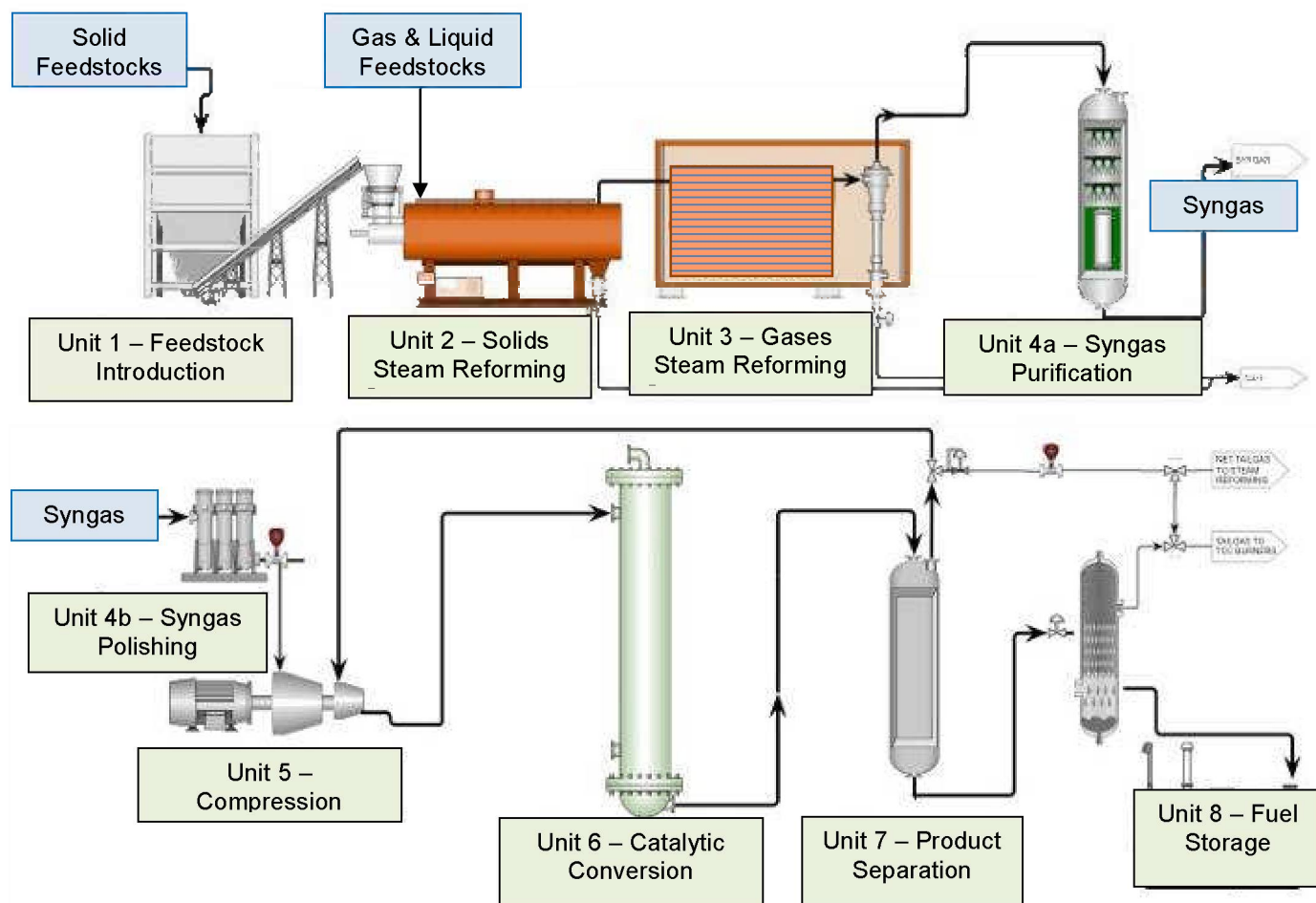
Figure IA.1: Primary Unit Operations and Process Flow Diagram for the IBR Plant

Figure IA.2: Completed Integrated Biorefinery (IBR) Plant

Figure IA.3: Thermochemical Conversion (TCC) System

Figure IA.4: Syngas Purification System
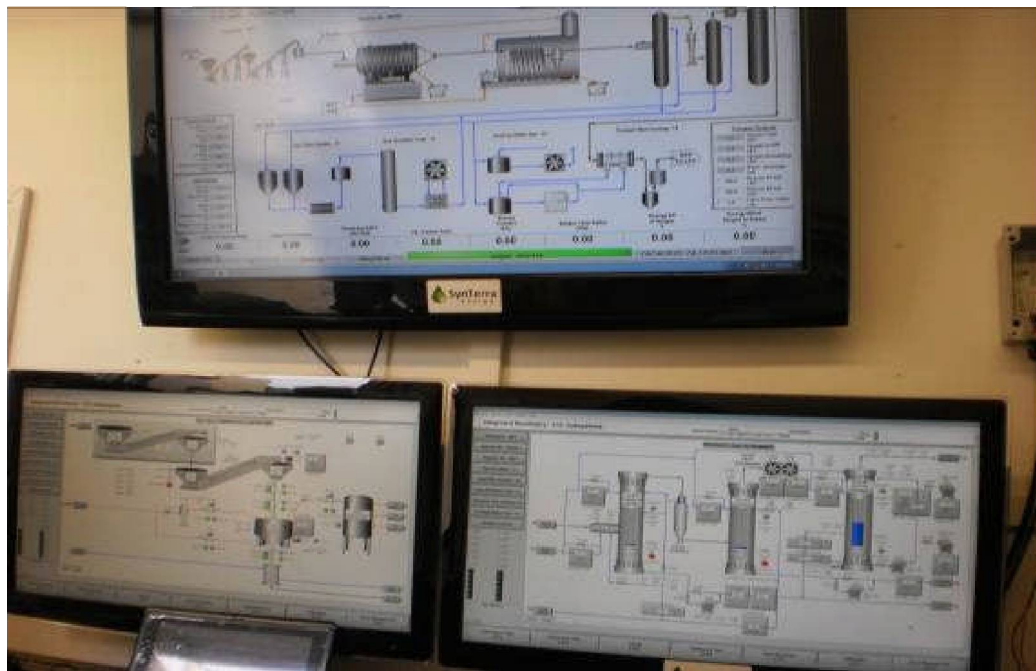
Figure IA.5: IBR Plant Central Control System

Figure IA.6: Liquid Fuel Production System (LFP) with the
Dual Catalytic Reactors and Diesel Fuel Storage Tanks (front view)

Figure IA.7: Liquid Fuel Production System (LFP) (back view)

Figure IA.8: Diesel Fuel Separation Process

Figure IA.9: Liquid Fuel Production System (LFP) Process Control

B. Project Objectives

The objective of this project was to design, build, test, optimize, and validate a 25 ton per day pilot integrated biorefinery (IBR) plant for efficiently converting biomass to synthetic diesel fuel. The major project objectives were as follows:

- Design, construct and validate the 25 ton per day pilot integrated biorefinery (IBR) plant for the direct, efficient conversion of biomass to "drop-in" fuels
- Operate the IBR plant:
  - Under a variety of conditions to determine the optimum parameters required for efficient fuel production
  - For sufficient time to collect operational data to validate these operating conditions
  - As required to collect technical and economic data for commercial deployment
- Demonstrate that the diesel fuel product is a high quality, "drop-in" fuel that can be used for in-use, current and future model vehicles
- Ensure that environmental and safety requirements are fully incorporated and properly implemented into the project's design and construction
- Present project results in the DOE comprehensive project reviews, public forums, and in technical journals
- Complete the proposed project in accordance with the allotted schedule and budget

1. Technical Targets (Predicted Performance Values)

The technical targets established initially for the IBR plant in December, 2009 are summarized in Table IB.1.

Table IB.1: Predicted Plant Performance
Specifications for the Conversion of Wood Feedstock to Fuel

Process Description	Average Plant Inputs and Outputs	Predicted Performance Values
Feedstock Properties	Feedstock size range (as delivered) (inches)	0.05-1.5
	Moisture content (wt. %)	10-35
	Carbon content (dry) (wt. %)	50.0
	Ash content (dry) (wt. %)	0.80
Feedstock Processing	Grinding energy use (kWh/daft)	None
TCC Conversion (pyrolysis/ steam reforming)	Slow pyrolysis (Unit Operation #2) Temp. ($^{\circ}$F)	1,450
	Gases steam reforming (Unit Operation #3) temperature ($^{\circ}$F) (reformer surface Temp.)	1,800
	Operating pressure (psia)	45
	Air & O_2 usage (lbs./daft)	0
	Steam usage (lbs. steam/lbs. feedstock) (with wood at 20 wt. % moisture)	2.0/1.0
	Syngas production (scf/daft)	45,000
	CO production (scf/daft)	9,450

Table IB.1 (continued): Predicted Plant Performance
Specifications for the Conversion of Wood Feedstock to Fuel

Process Description	Plant Inputs and Outputs	Predicted Performance Values*
Syngas Composition (exiting from TCC system)	H_2 / CO (volume and molar ratio)	2.0
	H_2 (volume %) (dry)	45
	CO (volume %) (dry)	22
	CO_2 (volume %) (dry)	20
	CH_4 (volume %) (dry)	12
	$C_2 - C_6$ (volume %) (dry)	1.0
	O_2 (ppm) (dry)	< 500
Syngas Contaminants (exiting from TCC system) before purification	Tars (ppm)	np
	Benzene (ppm) (dry)	np
	H_2S (ppb) (dry)	2,000
	NH_3 (ppb) (dry)	np
System Exit Gas Yield	Feedstock carbon conversion efficiency (to syngas carbon) (%)	85
	Thermochemical system energy efficiency (%)	70
Syngas Purification and final polishing)	Enviroscrub™ (gal/daft)	np
	Enviroscrub™ ($/gallon)	np
	Sulfur and NH_3 adsorbent replacement rate(s) (lbs./daft)	0.09
	Sulfur & NH_3 adsorbent cost ($/lb.)	13.60
	Tar conversion to syngas (wt. %)	Not Required

np: values not predicted

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Table IB.1 (continued): Predicted Plant Performance
Specifications for the Conversion of Wood Feedstock to Fuel

Process Description	Plant Inputs and Outputs	Predicted Performance Values
Syngas Composition (after syngas purification)	H_2 / CO (volume and molar ratio)	2.0
	H_2 (volume %) (dry)	45
	CO (volume %) (dry)	22
	CO_2 (volume %) (dry)	20
	CH_4 (volume %) (dry)	12
	$C_2 - C_6$ (volume %) (dry)	1.0
	O_2 (ppm) (dry)	< 500
Syngas Contaminants (after syngas purification)	Particulates ($\mu g/m^3$)	< 500
	Benzene (ppm)	np
	H_2S (ppb) (dry)	< 20
	NH_3 (ppb) (dry)	< 50
Conversion of Syngas to Fuel	Catalyst usage (based on 3.0 yr. life) (lbs. / daft) for IBR program	0.032
	Catalyst cost ($/lbs.) for IBR program	31.00
	H_2 usage in hydro-cracking (kg/kg biomass feed)	None required
	Syngas conversion to biofuel(s) (gal/10,000 scf CO at 90% CO conversion)	54
	Energy efficiency across biofuel(s) synthesis (%)	60

np: values not predicted

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Table IB.1 (continued): Predicted Plant Performance
Specifications for the Conversion of Wood Feedstock to Fuel

Process Description	Plant Inputs and Outputs	Predicted Performance Values
Overall Process Yield from Biomass	"Drop-in" fuel (gallon/daft) (with wax and tailgas recycle)	54
	"Drop-in" fuel (gallon/daft) (without wax and tailgas recycle)	44
	Export power (KWhr/daft)	None
	Commodity chemicals (benzene) (gallon/daft)	np
	Wax side-product (gallon/daft)	6.6
	Tailgas side-product (scf/daft) (used for plant gas burners)	12,000
	Commercial plant energy efficiency (%)	40
	Commercial plant carbon conversion efficiency (%)	40
Plant Effluents	Water discharge from TCC scrubbers (gallons/daft)	29
	Water discharge from Liquid Fuel Production	np
	Air Emissions (tons/day)	np

*np: values not predicted

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II. Project Management

A. Program Management

1. Organization

The Renewable Energy Institute International (REII) was the primary organization responsible for management of this project. The primary subcontractors to REII were Greyrock Energy (formerly Pacific Renewable Fuels) and Red Lion Bio-Energy (RLB). Leidos (formerly R.W. Beck) served as the Independent Engineer (IE). REII also managed the work of several secondary subcontractors as shown in Figure IIA.1.
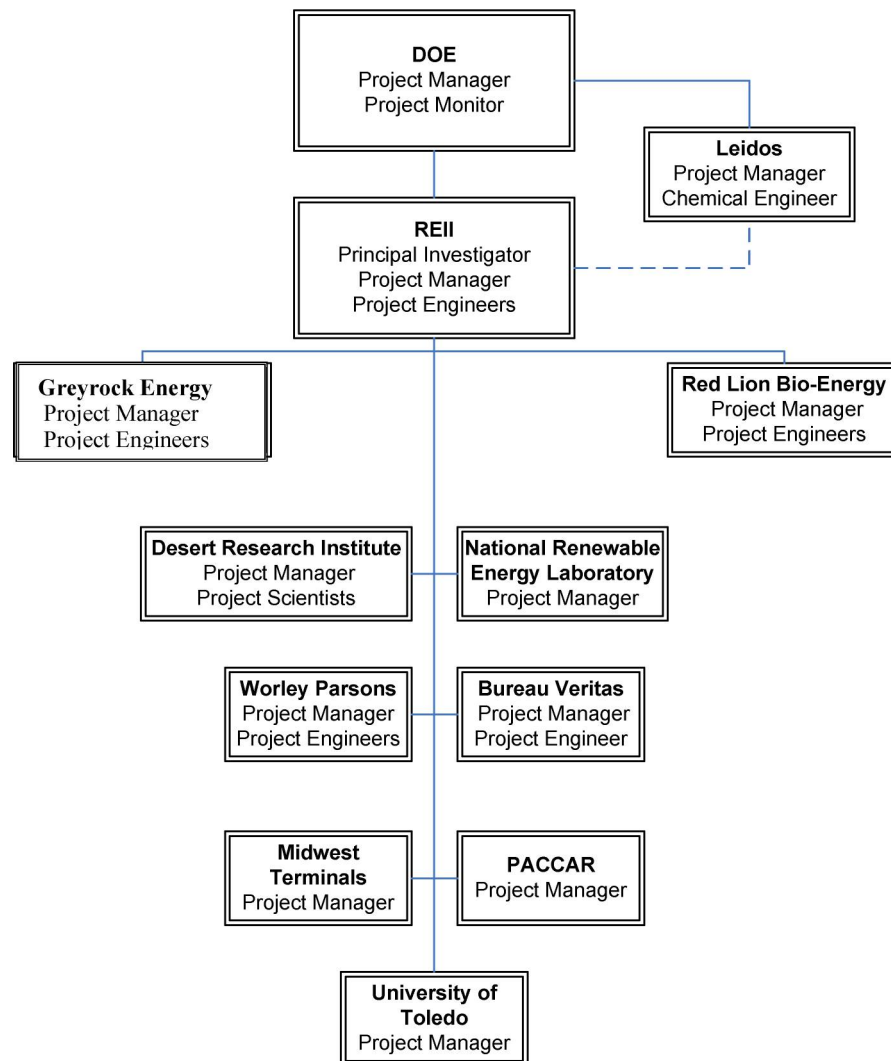
Figure IIA.1: IBR Project Organization

Project information was divided into technical, financial, and project management categories. Technical information was gathered by Project subcontractors and communicated to the Project Engineer, Project Manager, and Principal Investigator.

Financial information was gathered by the Project Manager from the subcontractors and by Project Accounting from Project staff. Project management information was gathered by the Project Manager from the subcontractors; financial information was a component of project management information and that was gathered from Project Accounting. Figure IIA.2 illustrates the flow of information between internal and external project entities.
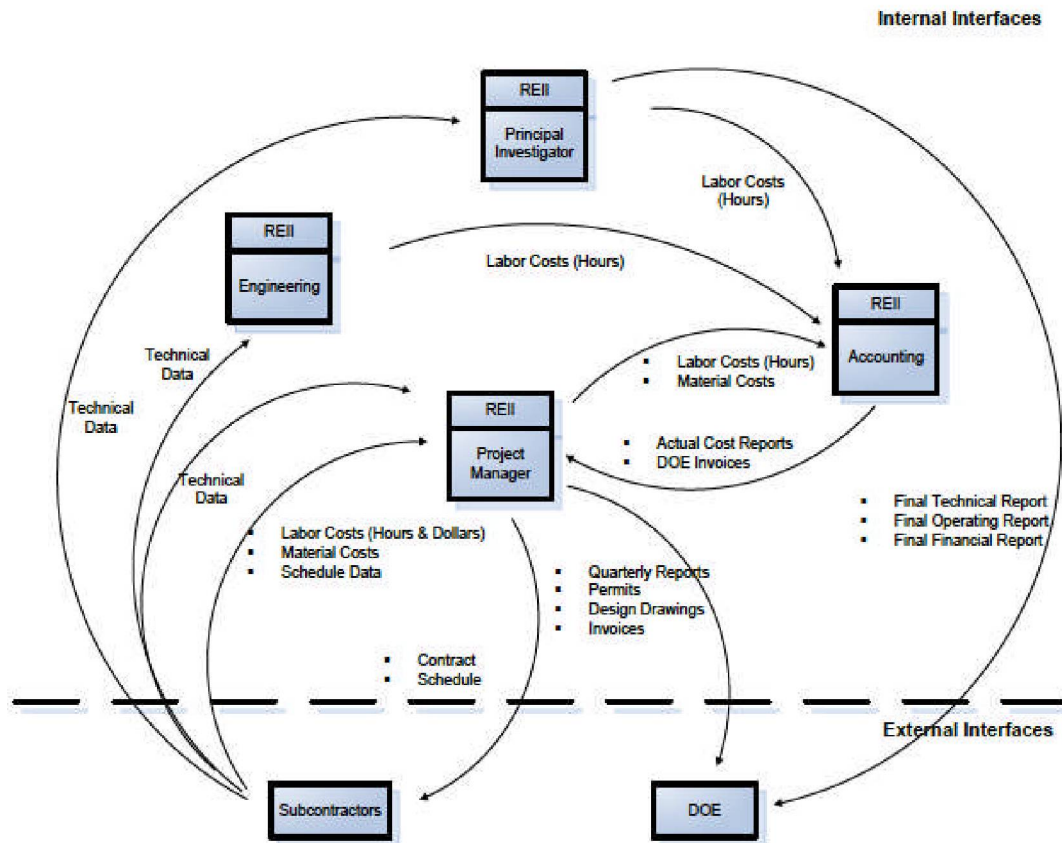
Figure IIA.2: Internal and External Data Flows for the IBR Project

2. Management Process

REII employed several key processes during the management of this project. These processes included:

- Management by Objectives
- Earned Value Management
- Project Milestone Reporting

3. Schedule and Milestones

The IBR project was divided into two budget periods.

Budget Period 1 (BP1) was comprised of design and permitting. This phase allowed the project team to complete preliminary engineering on the TCC and LFP systems as

well as integration engineering between these two technologies. BP1 also included selected laboratory tests to help determine the optimum operating conditions for the TCC system. The major milestones completed for BP1 included:

- Development of preliminary design documents for the TCC system, LFP system, and integrated biorefinery.
- Permits to operate the integrated biorefinery
- Completion of External Independent Review (EIR1)

Budget Period 2 (BP2) included final design, procurement, construction, operations, and project management. Major milestones for BP2 included:

- Issuance of final design documents including Process and Instrumentation Diagrams (P&IDs) and Process Flow Diagrams (PFD)
- Site Layout Drawings – 3D Drawings
- Issuance of purchase orders for long lead items
- Feedstock procurement contracts complete
- Mechanical completion of the integrated biorefinery
- Completion of biorefinery check-out
- Start of Operations of the integrated biorefinery
- Completion of the Independent Engineer's Performance Test

4. Project Financing

The funding for this project was provided by both public and private sources. The DOE provided $19,980,930 through the American Recovery and Reinvestment Act (ARRA). The project participants provided more than $7,028,395 of cost share through both cash and in-kind contributions. Figure IIA.3 provides a summary of the project cost performance versus the project baseline where AC and PV are the actual cost and present value, respectively.
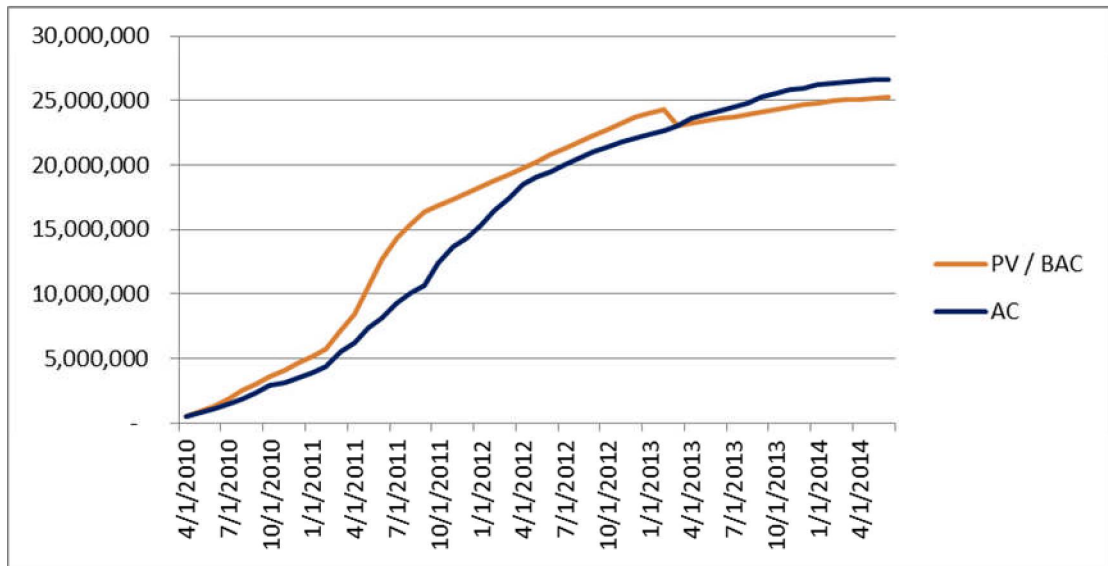
Figure IIA.3: Project Performance against Baseline Costs

B. Plant Site and Supporting Infrastructure

1. University of Toledo Energy Center

The project site is located in Toledo, Ohio at University of Toledo (Medical Center) Energy Center (UT Energy Center). The UT Energy Center consists of a natural gas steam plant, which provides steam to the nearby Medical Center. The UT Energy Center provided steam to the project as well as provided a location to connect to the electrical grid and provided an entry point for the disposal of process water from the operations of the integrated biorefinery.

2. Port of Toledo – Midwest Terminals

Midwest Terminals of Toledo International (MTTI) is the operator of the Port of Toledo. MTTI is a full service U.S. port at the mouth of the Maumee River at the west end of Lake Erie. MTTI provides logistics management services to domestic and international businesses operating in the Midwest. For the project, MTTI handled, stored, and transported biomass feedstocks used during the operations period of the project.

3. Environmental Permitting

The REII Project Team modified existing permits for the project site to allow for the expansion of the integrated biorefinery. Permits and plans developed for this project included:

- Air Pollution Permit-to-Install and Operate (PTIO) issued by the State of Ohio Environmental Protection Agency
- Building and occupancy permits
- Storm water discharge permit

- Storm Water Pollution Prevention Plan
- Spill Prevention Control and Countermeasures Plan

C. Technology Partners

This project brought together organizations from industry, academia, and the public sector in which 15 organizations were directly involved with this project. REII acted as the project lead for this effort and provided overall program management, engineering and scientific expertise, and third-party technical performance tests for the integrated system. REII's staff has extensive expertise in thermochemical processes, catalysis, material science, control systems, chemical engineering, fuel chemistry, manufacturing processes, environmental science and engineering, and analytical sciences. REII built an exceptional program management capability by implementing industry best practices in program management planning, systems, and processes, allowing the efficient execution of this project.

Two primary technology vendors provided the technical solutions for this project as subcontractors to REII:

1. Red Lion Bio-Energy (RLB)

RLB designed, constructed, and validated the Thermochemical Conversion (TCC) system that converts biomass to syngas. The RLB staff consists of an experienced team of engineers, scientists, and project developers with a proven track record of successfully designing, building, financing and operating complex systems similar to the integrated biorefinery built for this project and future commercial facilities.

2. Greyrock Energy

Greyrock designed, constructed, and validated the Liquid Fuel Production (LFP) system that converted the syngas to fuels. The Greyrock technology employed direct diesel fuel production catalysts, catalytic reactors, and adaptive control systems. The Greyrock staff consists of an experienced team of industry leading scientists and engineers engaged to develop novel technologies and processes capable of converting syngas into clean, renewable diesel fuel. The Greyrock team has experience with technology research, development and commercialization in the refinery, process, automotive, chemical, and alternative fuel industries having brought together experts from companies such as Air Products, Johnson Matthey, Chevron, Ford Motor Company, and other world-class organizations.

The solid experience of both partners has proven to be vital for the commercial success of the technologies demonstrated under this program.

D. Technical Support

In addition to the team members mentioned above, REII selected key organizations to assist in achieving the project objectives. These organizations included:

1. National Renewable Energy Laboratory (NREL)

NREL (Golden, CO) is the Department of Energy's principal laboratory for renewable energy research. NREL has R&D expertise in renewable fuels, renewable electricity, integrated system engineering and testing, and strategic energy analysis. NREL developed the Transportable Molecular Beam Mass Spectrometer (TMBMS) for the real-time characterization of syngas constituents. This instrument was used to monitor syngas contaminants in the hot syngas collected before syngas purification.

2. University of Toledo (UT)

The UT School of Engineering (Toledo, OH) provided technical and laboratory support to RLB during the project.

3. Desert Research Institute (DRI)

DRI (Reno, NV) is an internationally recognized environmental research center, which conducts applied research in air, land and water quality. DRI's Division of Atmospheric Sciences maintains an extensive organic and inorganic analytical laboratory with state-of-the art instrumentation. DRI developed and utilized advanced analytical methodologies for the characterization of over 200 organic and inorganic syngas contaminants from the TCC system and tail gas constituents from the LFP system.

4. Bureau Veritas (BV)

BV (Novi, MI) is an industry leader in measurement and analysis of chemical constituents in air, wastewater, and solid waste samples. BV helped develop protocols for the collection and analysis of syngas and tailgas from the catalytic reactors.

5. Grace Davison (GD)

GD (Columbia, MD) is an international chemical and catalyst company that was founded in 1832. Grace collaborated with Greyrock to develop and manufacture the catalyst support used for the direct fuel production catalyst.

6. pH Matter Laboratory (PHM)

PHM (Columbus, OH) designed and built a laboratory reactor that was designed to simulate the conditions of the IBR TCC (Figures IID.1 and IID.2). This laboratory reactor is capable of converting solid biomass, liquids, or gases to syngas. In addition, condensables and char were collected and characterized.
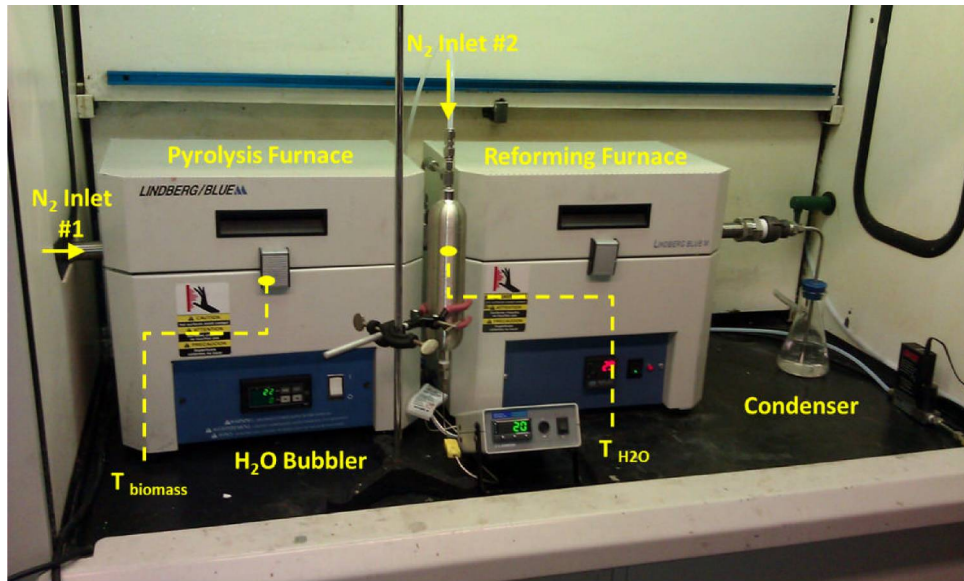
Figure IID.1: pH Matter Laboratory Simulator
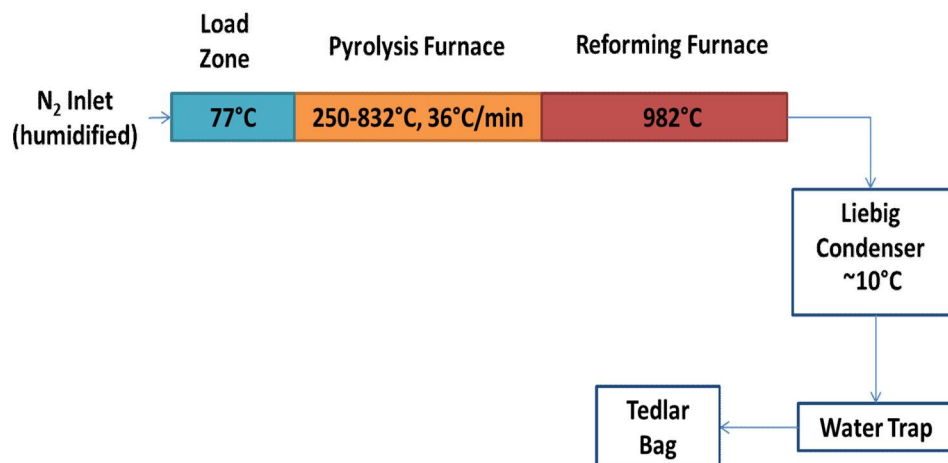
Figure IID.2: pH Matter Laboratory Simulator Schematic

7. SolarTurbines (ST)

ST (San Diego, CA), a subsidiary of Caterpillar Inc., is one of the world's leading manufacturers of industrial gas turbines, with more than 14,500 units and over 2 billion operating hours in 100 countries. Products from ST play an important role in the development of oil, natural gas, and power generation projects around the world. SolarTurbines' products include gas turbine engines (rated from 1,590 to 30,000 horsepower), gas compressors, and gas turbine-powered compressor sets, mechanical-drive packages and generator sets (ranging from 1.1 to 22 megawatts).

ST supported this project by assessing the compatibility of the IBR tailgas in current gas turbines for the generation of power for the commercial scale IBR plants. In the first budget period of this effort, the data developed by the project team was used prior to the completion of the operations period of the Integrated Biorefinery Project. The BP 2 effort utilized data developed during the operations period of the IBR test campaigns to update and finalize the report developed during BP 1.

8. WorleyParsons (WP)

WP is a leading provider of professional services to the resources & energy sectors and complex process industries. In delivering engineering, procurement, and construction management services, WorleyParsons possesses the versatility and flexibility to serve as the sole supplier, member of a joint venture, a subcontractor or contract services locally. In order to respond more effectively to customer needs, WorleyParsons also promotes and has formalized alliances, partnerships, and consortiums.

The objective of the WP support was to determine the compatibility of the fuel products produced by the integrated biorefinery with existing refinery and transportation infrastructure. The scope of work was completed in two budget periods. The first budget period utilized data developed by Greyrock prior to the completion of the operations period of the IBR project. The study deliverable for BP 1 was a draft report and BP 2 utilized data developed during the operations period of the IBR test campaigns to update and finalize the report developed during BP 1.

9. PACCAR

PACCAR is the 3rd largest global manufacturer of medium and heavy-duty trucks, marketed under the Peterbilt, Kenworth, and DAF brands. The IBR synthetic diesel fuel was tested on PACCAR's heavy-duty diesel engines at their technical center in Mount Vernon, WA (Figures IID.3 and IID.4).

Figure IID.3: PACCAR Technical Center in Mount Vernon, WA

Figure IID.4: PACCAR Heavy-Duty Engine Test Facility

10. Surface Combustion

Surface Combustion has designed and supplied thermal processing equipment to industry for nearly a hundred years. Surface combustion, in collaboration with RLB, designed the Solid Steam Reforming process (Figure IA.1 – Unit 2).

E. Feedstocks

This project utilized two feedstocks during the operations period; wood chips and rice hulls. These feedstocks were selected for two reasons: 1) The FOA required that applicants had previously tested and were able to provide data on feedstocks proposed for the project (these feedstocks had been tested under a separate program), and 2) the commercial plants planned for this technology will utilize these feedstocks. Data generated under this program will influence the design of future facilities.

The wood chips were sourced from a hardwood pellet mill operator in southwest Michigan. The wood chips were sized to 0.10-2.5 inches, partially dried using the pellet mill kiln, and then transported to the Port of Toledo for storage. During operations, the woodchips were transported to the project site as needed to operate the integrated biorefinery. Feedstock specifications were determined based on 1) previous testing done on the TCC system, 2) process models developed for the TCC systems that show how particle size impacts the conversion of biomass to synthesis gas, and 3) the desire to test a range of feedstock parameters based on the designs of future commercial plants.

Rice hulls were procured from Arkansas and Louisiana. No additional processing of the rice hulls was required prior to use as feedstock in the integrated biorefinery. The rice hulls were delivered by truck to the Port of Toledo for storage, and then transported to the project site during operations. Figure IIE.1 shows the rice hulls stored at the IBR plant site.

Figure IIE.1: Rice Hulls Stored at the IBR Plant Site

Table IIE.1 shows that the rice hulls obtained for the IBR test from Louisiana and Arkansas contained 1.3% less carbon and 2.0% more ash than rice hulls obtained from Northern California.

Table IIE.1: The Composition of Rice Hulls obtained from
Louisiana & Arkansas Compared to Rice Hulls from California

Property	Rice Hull Composition (Wt. %)	
	California Samples	Toledo IBR Samples (from Louisiana and Arkansas)
Carbon	37.8	36.5
Ash	19.9	21.9

Throughout the operations phase of the project there were several lessons learned that will be applied to future projects. Some of these lessons are listed below:

- The establishment of a system for removing fines and over-sized material will increase operational efficiency. Fines were not effectively removed from the feedstock after size reduction, which caused issues with gate valves in the feed

handling system during early tests. This was corrected in later runs and operations were more consistent with a tighter feedstock specification.

- The designation of a large area for biomass storage will reduce feedstock costs and improve feedstock quality. Larger volumes of feedstocks were stored at the Port of Toledo, then transported to the facility during operations as needed. The added handling and transport of the feedstock increased the cost to the project. In addition to increased cost, the storage of feedstock at an offsite location increased the possibility of feedstock contamination. During inspection of biomass feedstock on site, small rocks, asphalt, and dirt often had to be removed from feedstock piles prior to entering the feed handling system.

F. Risk Management / Mitigation Analysis

A Risk Mitigation Plan (RMP) was developed to identify, assess, report and effectively mitigate potential risks to the project. This RMP was administered by the REII Project Manager and was updated throughout the project. REII Project Management was responsible for leading the risk management process and maintaining the related documentation. Each subcontractor was responsible for carrying out mitigations for their respective areas of responsibility subject to the review of the REII Project Manager.

This Risk Mitigation Plan utilized methodologies described by several U.S. government organizations. This document also addressed recommendations on risk areas provided by the Independent Project Analysis (IPA) organization.

All risks identified were assessed to identify the range of possible project outcomes. It was then determined which risks were the top risks to address with a formal risk mitigation write up and which risks are considered minor, and could be easily mitigated.

The probability and impact of occurrence for each potential project risk was assessed by the REII Project Manager, with input from the project team and sub-contractors using a "Risk Probability" and "Potential Risk Impact" approach.

The "Risk Probability" was used to assess the probability that the risk will occur and the "Potential Risk Impact" was the potential impact that the risk could have if it did occur.

REII used the U.S. CDC, U.S. DOD and CA Risk Management templates as well as the IEC Risk Management Standards #62198 for the development of this Risk Mitigation Plan. A 3x3 Risk Graphic was chosen to represent the combination of the probability and impact of any given risk. This matrix was used for every risk outlined in this plan. An example of final output is shown in Figure IIF.1 in which the risk probability is low and the potential impact is medium.

Figure IIF.1: Risk Probability/Potential Risk Impact Graphic

A robust risk mitigation plan was developed for those elements that were labeled as red and a more modest mitigation plan was developed for those elements that were labeled as yellow. Risk mitigation plans were not required for those elements labeled green, however a discussion on how the risk is being addressed was included.

The application of the risk identification and impact assessment processes included risks associated with the following project elements:

- Project Scope
- Project Schedule
- Project Budget
- Human Resources/Subcontractors
- Technology (included Failure Modes Effects Analysis [FMEA])

A separate scoring technique was used for the FMEA and the outcome of this score was translated to an overall risk score and assigned a red, yellow or green Impact Rating for risks that came out of the Technology Risks Section.

G. Safety and Health

REII developed, in cooperation with RLB and Greyrock, a comprehensive Environmental, Health and Safety (EH&S) program for the project. This program was administered through the development of corporate policies; continuous staff education/training on topics related to environmental impacts, health and worker safety; and weekly project meetings.

As a result of this close attention to safety and health, no safety or health issues were encountered during the project period. In addition, the project team received recognition from the State of Ohio for its outstanding safety record.

III. Plant Engineering and Design

A. Engineering Management Processes Employed

The following engineering processes were employed for the design, manufacturing and construction of the IBR plant:

- Value Engineering
- Concurrent Engineering
- Piping and Instrument Design (P&ID)
- 3-D Drawings
- Materials Science and Engineering
- Design for Manufacturing
- Failure Mode and Effects Analysis (FMEA)

Details on these engineering processes are provided in the following sections.

1. Value Engineering

Value Engineering (VE) is a systematic method that was used to improve the "value" of the IBR process/system by using an examination of functions. Value, as defined, is the ratio of function to cost. Value can therefore be increased by either improving the function and/or reducing the cost. It is a primary tenet of value engineering that basic functions and safety characteristics be preserved and not be reduced as a consequence of pursuing value improvements. Many of the improvements made to date have been achieved by evaluating each unit operation and removing non-value added equipment and/or simplifying the process. An important part of VE is a process called "Design for Manufacturing".

This section summarizes how Value Engineering (VE) was used to reduce IBR system complexity, costs and risks. This VE methodology was also used for design and deployment of the commercial scale IBR technology (Section XII).

During the past several years, REII has developed and utilized "5E" VE Process models to evaluate candidate biomass to renewable fuel and energy conversion processes as follows:

(E1) - Evaluations that assess the scientific and engineering feasibility/practicality of each unit process in terms of chemistry, physics, material science, biology, chemical engineering, systems engineering and other technically relevant processes

(E2) - Energy and mass conversion balances and efficiencies

(E3) - Environmental impact assessments

(E4) - Economic analyses

(E5) - **E**ffectiveness of the proposed socio-political processes that will be used to obtain government and private stakeholder support for the deployment of commercial scale plants. Socio-political effectiveness evaluates factors such as government regulations, organizational objectives, societal benefits, environmental stewardship, and stakeholder needs and concerns.

As a result of this"5E" VE analysis, five complex and costly processes were completely eliminated (**orange font**), twelve processes were significantly improved (**blue font**), and three processes were found to perform well and therefore not modified for the IBR design (black font). The results of these analyses are summarized in Table IIIA.1.

In addition, the "5E" VE model was used in an iterative process to recalculate energy and mass balances, estimated capital and O&M costs, predict reliability, etc. for the 240 daft/day commercial scale plant design (see Section XII).

Table IIIA.1: Results of "5E" Value Engineering Process
Applied to the Final Design of the IBR Plant

Original Pilot Plant Processes	Results from "5E" Value Engineering	Resulting Improved Design For IBR Project
1). Biomass Processing	**Grinding biomass to < 3/16" adds significant cost**	**The need to grind biomass to small size was eliminated by modifying the biomass introduction process & improving the heat transfer efficiency for the pyrolysis/steam reforming processes**
2). Dryer	**Biomass drying reduces plant energy efficiency and increases costs**	**This step was not needed since water is necessary for the pyrolysis/steam reforming processes**
3). Biomass Introduction	**The screw and fluidized feed systems were not reliable and allowed air introduction**	**A simplified feeder design (the ram charge feeder) was developed**
4). Slow Pyrolysis	**Heat transfer to biomass was not acceptable**	**A new design was employed**
5). Steam Reforming	Steam reforming system performed as expected	The original design was incorporated
6). Ash Collection	**The ash collector release valve may overheat resulting in failure**	**The ash collector was redesigned to eliminate possible heat failure**
7). Steam Production	This is a well-known & defined process	No action/modification required
8). Natural Gas Heaters	This is a well-known & defined process	No action/modification required
9). Cyclones	**The cyclones need to be carefully designed to maximize particle collection efficiency**	**Cyclones re-designed to meet collection efficiency specifications**

Table IIIA.1 (continued): Results of "5E" Value Engineering Process
Applied to the Final Design of the IBR Plant

Original Pilot Plant Processes	Results from "5E" Value Engineering	Resulting Improved Design For IBR Project
10). HEPA Filter	This filter has a poor reliability and high maintenance resulting in a high down-time risk	The efficiency of cyclones and water scrubber were improved, thus eliminating the need for the HEPA filter
11). Water Scrubber	Water scrubber didn't have sufficient syngas purification efficiency	Incorporated a high efficiency scrubber at nominal incremental cost which effectively reduces contaminants
12). Syngas Oil Scrubber	This is an expensive process that produces a waste product	This process was eliminated as a possible plant improvement since it is not necessary and does not add value.
13). PSA System	This system adds unnecessary capital and O&M costs	This system is not needed since syngas is produced with the proper H_2 / CO ratio for fuel production.
14). Guard Beds	Is was determined that 3 guard beds were not necessary	Incorporate efficient, low-cost guard beds for H_2S and NH_3
15). Compressor	The cost and energy requirements for ~1,000 psi compressors are prohibitive	Incorporate an improved, economical catalyst that meets direct fuel production specifications below 400 psi.
16). Catalyst	Currently available catalysts produce a wide variety of products, which need to be further refined using expensive and complicated refinery type processes	Incorporate improved, economical catalysts that directly produces diesel fuel while minimizing undesirable side-products, which would require further refinery-type processing steps
17). Condensers	At least two product condensers were required, which were difficult to maintain	The number of condensers was reduced to one by designing a new, high efficiency system
18). Refinery Processing	These are expensive processes that will be difficult to operate and maintain at the site of a commercial, distributed scale plant	Refinery processing of the IBR plant products is not needed since "drop-in" fuels are produced directly.
20). Storage	The need for separate storage tanks for fuel, water and wax will add cost	The IBR plant will only require fuel tanks. Disposal of the wastewater in the Toledo sanitary sewer is acceptable. Storage of fuel and water at commercial scale facilities will be evaluated on a case-by-case basis.

2. Concurrent Engineering

Concurrent engineering was used for the IBR plant design, which was more time efficient than the more traditional sequential design engineering. Traditional sequential design engineering typically moves in a linear fashion by starting with user requirements and moving forward step by step until the final plant design is completed. The difference between these two design processes can be visualized by Figure IIIA.1
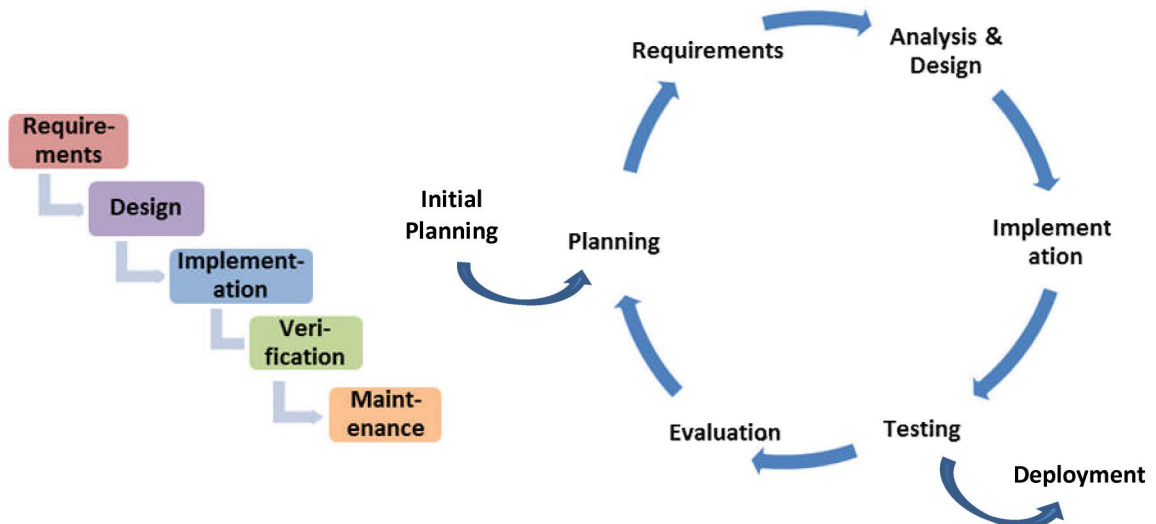
Figure IIIA.1: Sequential compared to the IBR Project Concurrent Engineering Approach

This concurrent engineering approach integrated the functions of design engineering, manufacturing engineering and other functions to reduce the elapsed time required to complete the final design. All elements of the plants' life-cycle, from functionality, producibility, assembly, testability, maintenance issues, environmental impact, and finally disposal and recycling were taken into careful consideration in the early design phases.

3. Piping and Instrument Design (P&ID)

The P&IDs were used to demonstrate the physical sequence of equipment and systems and how these systems inter-connect. During the design stage, the P&ID diagrams provided the basis for the development of system control schemes, allowing for further safety and operational investigations such as the Hazard Analysis and Operability Study (HAZOP). The P&IDs for the IBR plant included:

- Instrumentation and designations
- Mechanical equipment with names and numbers
- All valves and their identifications
- Process piping, sizes and identification
- Miscellaneous - vents, drains, special fittings, sampling lines, reducers, increasers and swaggers

- Permanent start-up and flush lines
- Flow directions
- Interconnections references
- Control inputs and outputs, interlocks
- Interfaces for class changes
- Computer control system input
- Identification of components and subsystems delivered by others

The P&IDs also included basic start up and operational information and control and shutdown schemes.

4. 3-D Drawings

3-D Drawings were used to lay out equipment, design piping runs and improve visualization of the processes. 3-D Drawings improved the efficiency of the project by reducing dimensional errors and limiting the amount of re-work required during construction.

5. Materials Science and Engineering

Since several materials used in components that make up the various unit operations are exposed to abrasive materials (e.g. rice hulls and rice hull ash) and hot syngas, it is important that the proper materials are selected to insure component robustness. Two materials experts were engaged as consultants to help choose the proper materials.

6. Design for Manufacturing

A 'design for manufacturing' approach was employed to reduce the cost and improve the reliability of plant components. This methodology was used to design and construct individual unit operations as modular units, such as the pyrolysis chamber, the steam reforming reactor and the catalytic reactors. In this manner, specific modular units, such as the fixed bed reactors were assembled at a specified manufacturing location and shipped to the Toledo IBR site for integration with the other unit operations (Figure IIIA.2). This approach assured the quality and integrity of each modular unit. Furthermore, the time and cost was significantly reduced for integration of modular units at the plant site.

Figure IIIA.2: Installation of the Modular Fixed Bed Reactors

7. Failure Mode and Effects Analysis (FMEA)

FMEA was used as a design tool to systematically analyze postulated component failures and identify the resultant effects on system operations. FMEA's were carried out and completed concurrently with the design described in Section IIIA.1. They were used to identify all potential part failure modes so they can be eliminated or minimized through design modification at an early point in the IBR plant development effort. Some possible component failures and fixes/upgrades that were identified as a result of the FMEA analyses were implemented in the final IBR system design.

B. Description of Unit Operations

Figure IIIB.1 illustrates a process flow diagram (PFD) for the IBR plant. Unit Operations #1-#4 are referred to as the Thermochemical Conversion (TCC) process and Unit Operations #4b-#8 are referred to as the Liquid Fuel Production (LFP) process.

The TCC process is comprised of #1 - Feedstock Introduction, #2 - Solids Steam Reforming, #3 - Gases Steam Reforming and #4a – Syngas Purification
Unit Operation #2 utilizes high-temperature steam to convert the solid-phase carbon to gas-phase carbon species in the absence of oxygen ($O_2 < 500$ ppm). This process can be compared in concept to the steam reforming of methane, except that this is the first

efficient steam reforming process that has been successfully developed and validated (at the pilot scale) for the conversion of solid-phase carbon containing compounds in various feedstocks to gas-phase carbon containing products. Unit Operation #2 is a specifically designed retort chamber that operates in the 1,400 to 1,550 °F range. The steam-to-feedstock carbon ratio is controlled to maximize the conversion of solid-phase carbonaceous compounds into gas-phase carbonaceous products.

Unit Operation #3 was designed to steam reform the gas-phase products from Unit Operation #2 into syngas. This conversion occurs at 1,790-1,815°F with gas residence times of 4-8 seconds.

Unit Operation #4a utilizes several process to purify the syngas including:

- ✓ A cyclone to remove particles greater than about 3 microns in size.
- ✓ A high-efficiency venturi water scrubber which cools the syngas and then removes tars and other fine particulates.
- ✓ A packed bed scrubber tower and chemical scavengers to remove sulfur compounds (e.g., H_2S, ammonia, and oxygenated hydrocarbons).

The Liquid Fuel Production (LFP) process is comprised of: #4b – Syngas Polishing, #5 - Compression, #6 - Fuel Synthesis, #7 - Product Separation, and #8 - Fuel Storage. The catalytic conversion process employed a novel catalyst that converts syngas directly to reformulated gasoline blendstock and synthetic diesel fuel.
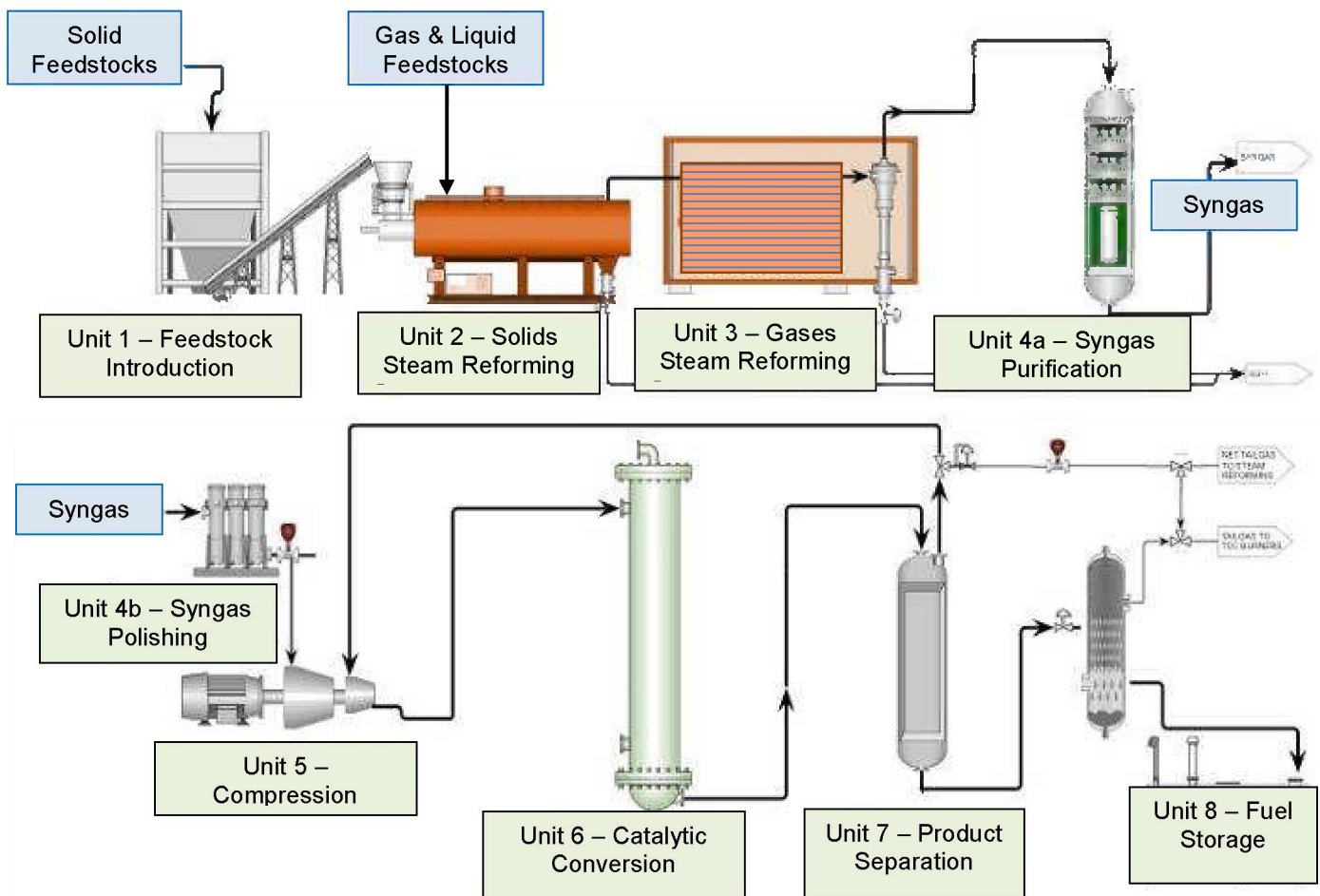
Figure IIIB.1: Primary Unit Operations and Process Flow Diagram for the IBR Plant

1. Feedstock Introduction

For ease of operation and capital cost considerations, no biomass sizing hardware, such as chippers and grinders were included in IBR facility. Instead, the feedstock was bought and delivered pre-sized, and rice hulls were delivered as-is. Commercial systems will require on-site sizing equipment for woody biomass.

Drying of the biomass was not required. Unlike traditional gasification or pyrolysis, which requires dry, finely sized feedstock, this conversion system operates in a steam reforming mode which can accept moisture laden feedstock.

The IBR project utilized an existing conveyor and transfer hopper while the feed hopper and air lock systems were upgraded (Figure IIIB.2). New slide gate valves with hardened surfaces, designed for handling and metering solid material flows, were installed on the air lock. These valves were designed for high temperature, high abrasion use.
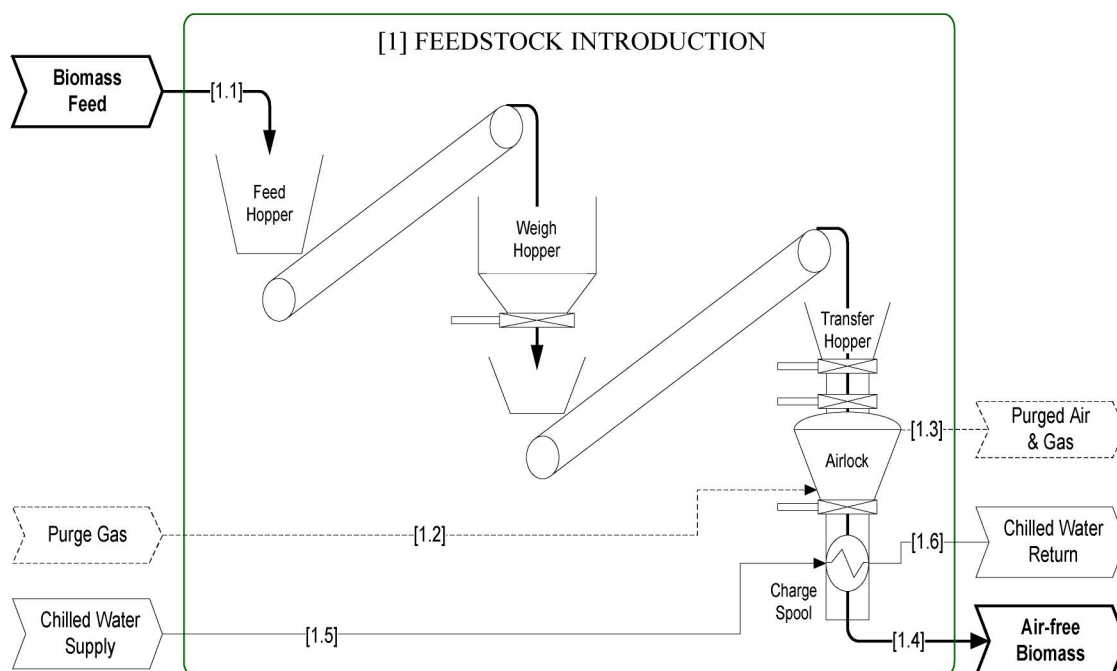
Figure IIIB.2: Feedstock Introduction

The feed hopper, conveyor, and storage hopper work together in a continuous process. The feed hopper stores approximately 12.5 dry tons of biomass and loads the conveyor, which in turn loads the storage hopper. The air lock moves feedstock into the process at a set rate in a batch/continuous mode. The batch process was set up on 1 minute intervals and the size of each batch was determined by conveyor speed which was established by the desired feed rate.

2. Solids Steam Reforming

Unit Operation # 2 is the first conversion stage of the thermochemical process in which solids are steam reformed in a unique "retort style" rotating heated vessel (Figure IIIB.3). The system is designed to operate under reducing conditions, in the absence of oxygen, and at a pressure of up to 36 psig. The gaseous products exit the system at a temperature of 1,480-1,530 °F. Unconverted carbon and ash particles exit the solid steam reforming system via an auger system.

[2] SOLIDS STEAM REFORMING

Burner Fuel [12.3] — [2.8] — Single-End Radiant Burner Tubes — [2.10] — Burner Exhaust

Combustion Air — [2.9]

Air-free Biomass — [2.1] — [2.6] — Gaseous Products

RAM — EM

[11.13] Product Water Recycle (option) — [2.2]

[12.2] Tailgas Recycle (option) — [2.3]

[11.3] Liq. Wax Recycle (option) — [2.4]

M

Steam Input (option) — [2.5]

[2.12] — Cooling Water Return (CWR)

Cooling Water Supply (CWS) — [2.11]

Ash Bin — [2.7] Ash
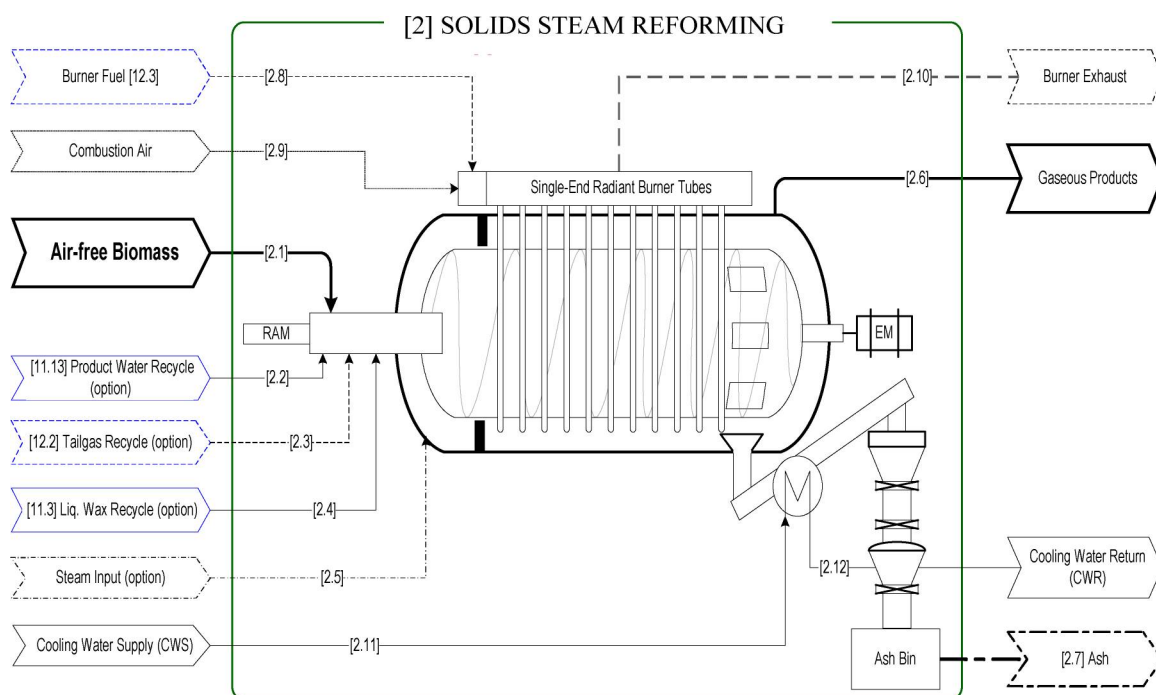
Figure IIIB.3: Unit Operation #2 - Solids Steam Reforming

Retort Assembly: The retort is a long cylinder with a series of internal spiral flights. The retort rotates around its longitudinal axis such that the spiral flights convey the feedstock from end to end in a defined period of time. Various devices (e.g., bars and rakes) are used between the flights to cause the feed stock to tumble and improve the rate of heat transfer.

Heating System: The heating system consists of thirty six (36) Single-Ended Radiant (SER) tubes and burners arranged along the sides the retort. Each radiant tube assembly consists of the components listed in Table IIIB.1.

Table IIIB.1: Unit Operation #2 - Radiant Tube Assembly Components

Hot Air Burner	Alloy Outer Tube
Exhaust/Air Recuperator	Air and Gas Flow Control Valves
Silicon Carbide Inner Tube	Electronic Flow Controller

Natural gas is used to fire the SER burners during startup operations, but once steady state conditions have been achieved, then tailgas (a methane enriched syngas) from the Liquid Fuels Production process may be substituted.

Slagging of silica in the feedstock was limited by keeping the temperature below 1,600°F in Unit Operation #2. Silica's normal melting point is above 3,092°F; however the presence of small amounts of potassium (2-3%) will reduce the silica melting point

to about 1,800°F (Thy et. al, 2006). Since rice hulls can contain up to 1.6 wt. % K_2O, slagging was not a problem below 1,600°F.

Ash is removed at the end of the retort with an integrated water-cooled auger system. The ash is depressurized to ambient conditions through a valve-lock/hopper system. The solid particles are composed primarily of unconverted carbon, silica, metal oxides, and trace minerals. The ash has commercial applications including as a soil enhancer and in ceramics manufacturing.

Controls: The heating system is divided into three equal and independent zones of temperature control. Control of all the zones is implemented in the process control programmable logic controller (PLC). An infrared temperature sensor is provided in each zone to monitor and record the retort temperature profile.

A pressure transmitter is provided to monitor and record the pressure inside the solid steam reforming chamber. Control of this pressure is affected by downstream equipment. For example, the chamber pressure will rise if the discharge flow is reduced. Likewise, the pressure will decline if the discharge flow is drawn away faster than the feedstock is supplied. A pressure relief device is provided in the event of a high-pressure control malfunction in downstream equipment.

The retort of the solids steam reforming system was manufactured from a wrought alloy, RA-330, that is suitable for the temperature range (i.e., 1700°F maximum) and the pyrolysis compounds. RA-330 was selected for its high temperature strength and corrosion resistance. The outer casing was designed to withstand 50 psig internal pressure. The vessel and dished ends were constructed of mild steel plates per American Society of Mechanical Engineers (ASME) boiler pressure vessel codes. Ceramic fiber modules, 10" thick, 10 pounds per cubic foot density, were provided and stud welded to the furnace sidewalls, roof, and discharge end wall.

3. Gases Steam Reforming

Figure IIIB.4 illustrates the unit operation used for steam reforming of the gases generated in Unit Operation #2. This unit operation operates at a tube temperature of 1,790-1,815°F and a pressure of up to 50 psig. The gas-phase products from the solids steam reforming process and superheated steam are injected into this unit operation for conversion into syngas. The resulting syngas is composed primarily of hydrogen (H_2), CO, along with some methane (CH_4), and CO_2.
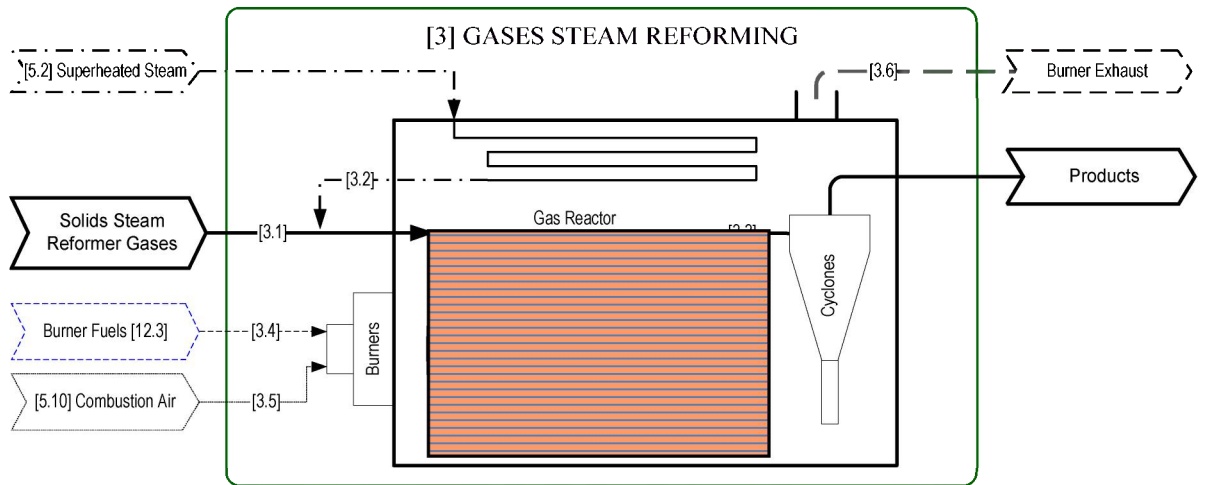
Figure IIIB.4: Gases Steam Reforming

The hardware for Unit Operation #3 was constructed from an Iron/Nickel/Chromium-based alloy. This material was selected for its high temperature tensile strength and abrasion resistance.

4. Syngas Purification

Figure IIIB.5 shows Unit Operation #4a-1 which is used to separate the ash from the syngas from Unit Operation #3.
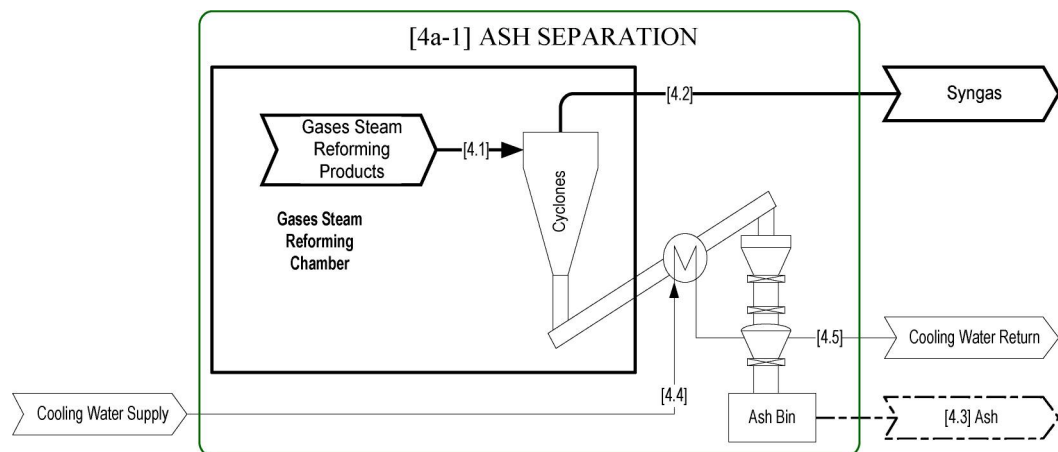
Figure IIIB.5: Cyclone Ash Removal

At the end of the gases steam reforming system the hot syngas is sent through cyclones to remove any entrained particles before they reach the syngas purification process. The cyclones are installed inside the reforming chamber and operate at the elevated temperature of the chamber. This location limits the potential for condensation of unconverted higher molecular weight gaseous components inside the cyclones which would cause fouling and plugging problems and also preserves the thermal energy in

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the syngas for heat recovery opportunities. Ash is collected from the cyclones and cooled via a water jacketed auger and valve lock system.

Figure IIIB.6 illustrates Unit Operation #4a-2 which is used to superheat the steam for injection into Unit Operation #2.
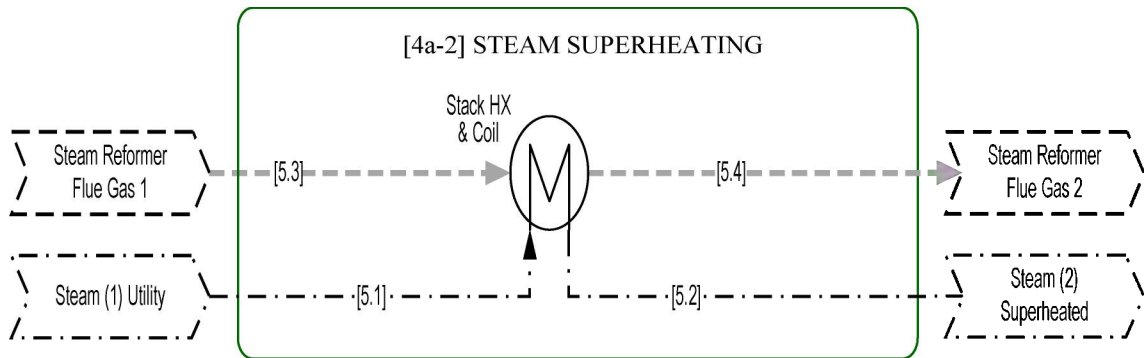
Figure IIIB.6: Steam Superheating Heat Recovery

Steam for injecting into the Unit Operation #3 is superheated with the exhaust from the steam reforming chamber burners. Plant steam is supplied at 350°F (177°C). The heat exchanger / recuperator is constructed from an iron/nickel/chromium-based alloy selected for its high temperature tensile strength, longevity, and low maintenance.

Following the cyclones, the hot syngas is routed through a quench venturi scrubber system as illustrated in Figure IIIB.7 (Unit Operation #4a-3) to cool and scrub any remaining particulates, condensable tars, gases, and contaminants.

First, hot syngas from the cyclones is passed through a series of water-spray quench vessels, which cool the syngas and coagulate and remove the bulk of micro-particles and contaminants. The cooled syngas then passes through a venturi scrubber to remove particles down to 0.5-1 microns in size. The syngas is next routed through an optional air cooler and then into a vertical packed-bed tower scrubber system.

The first quench spool is constructed of Hastelloy™ to handle the high temperature incoming syngas. All following vessels, lines, the venturi, and packed bed are constructed of 316 stainless steel.

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[4a-3] GAS CLEANING

Scrubbed Syngas

Emergency Fresh Water Supply

[42] Syngas from Cyclones [6.1]

Quench Spool

Quench Vessel

Venturi

[6.3]

Separation Vessel

KO

Packed Bed Scrubber

Settling Tanks

[6.11]

[78] Syngas Condensate

Filter Press

[6.12]

Filter Press Solids

[6.14]

[6.13]

[6.17]

Overflow

Storage Tanks

[6.15]

[910] Stm Cond

[6.16]

[6.19]

Tower water loss

Scrubbing Cool Twr

[6.5]

[6.6]

[6.8]

[6.9]

[6.10]

[6.7]

[6.2]

Triazine

[6.4]

[6.2]

Makeup Water

[6.18]

Figure IIIB.7: Syngas Cleaning

The vertical packed tower is used to scrub the syngas of sulfur species (such as SO_2, H_2S, and a sulfinoxyl precipitate) using scavenger chemicals. During the first few tests, sodium hydroxide and hydrogen peroxide were the chosen chemicals to scrub H_2S and other contaminants from the syngas stream. For these chemicals to be effective it was determined that the scrubber water pH needed to be maintained at about 10. However, it was difficult to maintain the proper levels of NaOH and H_2O_2 during these tests and therefore a change was made to using Enviro-Scrub®, a triazine derivative sulfur scavenging chemical. This reagent was supplied by Quaker Chemical.

Scrubbing water was recycled after passing through a press filter and chiller. The discharge of scrubber water was established as 2.5 gallons/minute at the maximum biomass input of 25 dtpd and the Enviro-Scrub™ input was 1.0 gallon/hr for this water discharge rate. However, after a quantitative analysis of the contaminants in this discharged water, it was determined that this water discharge rate was about eight times higher than necessary. Further details on this analysis are provided in Section VIIIA.5.

After run #9 during December 10-14, 2012 (see Table VI.1), the scrubber components were disassembled and examined. A minor buildup of tar was observed on one of the connectors in the gas cleanup system, but all other components were relatively clean.

Figure IIIB.8 illustrates Unit Operation #4a-4 which is used to cool and dry the syngas.

Figure IIIB.8: Cooling & Drying

Following the Packed Tower, the scrubbed, saturated syngas is further cooled through a chilled water heat exchanger. The chilled water is supplied at 55°F (13°C) to cool the syngas to 77°F (25°C). Condensate is removed with a knock out vessel and a coalescing filter and sent to the Settling Tanks of Unit Operation 4.

Also shown in this unit operation is the cooling loop for the two ash auger systems. The return water is collected and cooled with a fin-tube air cooler.

Figure IIIB.9 illustrates Unit Operation #4b which is the first of the LFP unit operations. As the final cleanup step before the LFP catalyst beds, the feed syngas was passed through packed beds of polishing catalysts/absorbents to remove trace gaseous contaminant species down to ppb levels. These are followed by a high efficiency particle filter as a final safeguard before the compressor inlet.

Table IIIB.2 lists the contaminant species of concern and their maximum recommended levels in order to assure that the LFP catalyst will have a lifetime of 3+ years.
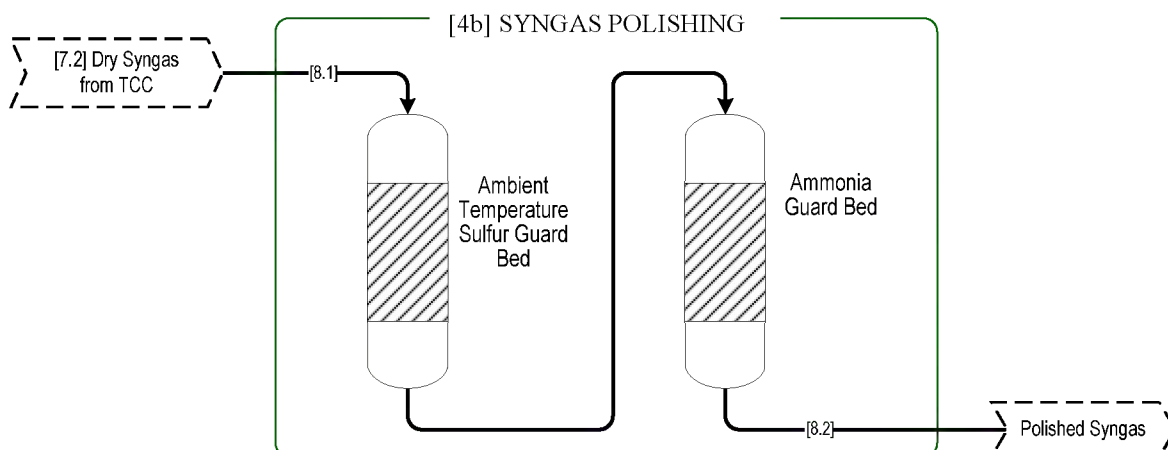
Figure IIIB.9: Syngas Polishing

Table IIIB.2: Maximum Recommended Contaminant Levels for
Efficient Diesel Fuel Production using the LFP Catalysts

Catalyst Contaminants	Maximum Specified Contaminant Levels	Average Contaminant Concentrations Measured
Sulfur Species		
Hydrogen Sulfide (H_2S)	< 20 ppb	< 3 ppb
Sulfur Dioxide (SO_2)	< 200 ppb	< 100 ppb
Nitrogen Species		
Ammonia (NH_3)	< 5 ppm	50 ppb
Hydrogen Cyanide (HCN)	< 20 ppb	Not determined
Nitrogen Oxides (NO_x)	< 200 ppb	< 100 ppb
Other Species		
Hydrogen Chloride (HCl)	< 50 $\mu g/m^3$ (34 ppb)	< 0.5 $\mu g/m^3$
Oxygen (O_2)	< 500 ppm	225 ppm
Total Particulate Matter ($PM_{2.5}$)	< 500 $\mu g/m^3$	425 $\mu g/m^3$

A variety of sulfur removal catalysts are commercially available. Unicat's TSR-122 copper carbonate catalyst/adsorbent was selected for this project due to its ability to operate in an environment containing high percentages of H_2, CO, CO_2 and moisture. Other advantages include the ability to operate at ambient temperature conditions (simplifying system design) and to remove many organic sulfur species including H_2S, carbonyl sulfide (COS), and mercaptans.

5. Syngas Compression

Figure IIIB.10 illustrates Unit Operation #5 which is used to compress the syngas. The polished feed syngas needs to be compressed before introduction to the LFP reactors. The compressor was a 4 cylinder reciprocating unit, electrically driven, with 3 cylinders/stages for feed compression and 1 cylinder/stage for recycle. Flow control and turndown were provided by internal spillback.

The unit compresses the feed syngas from 15 to 410 psig in 3 stages, with intercooling after stages 1 and 2. The 4th stage on the compressor boosts recycled syngas from approximately 310 to 410 psig. The compressed recycle stream is then heated with utility steam and then combined with the feed syngas and sent to the reactors.
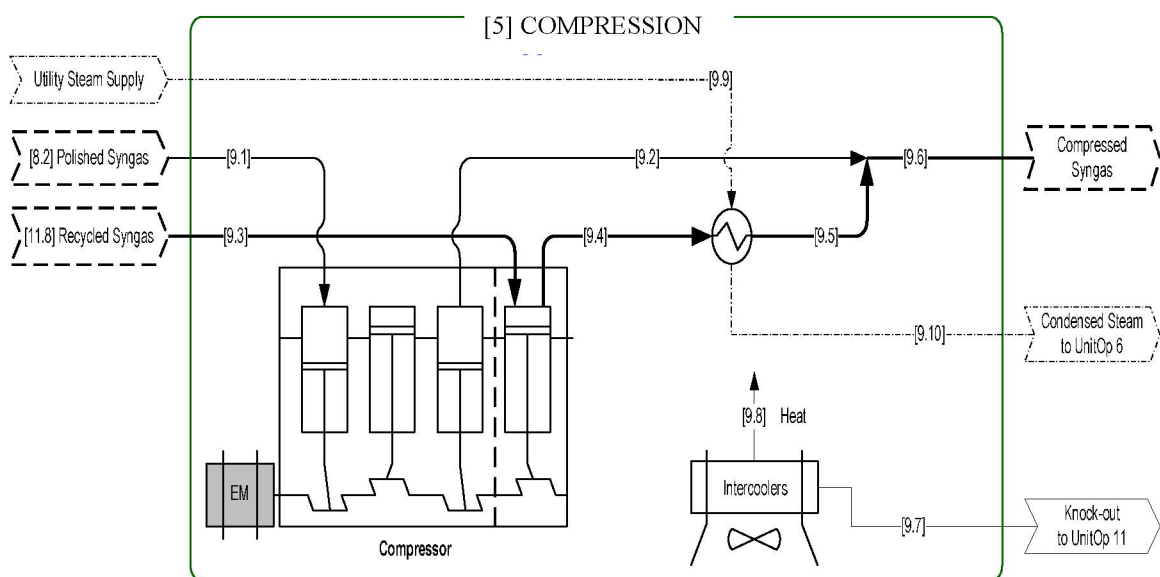
Figure IIIB.10: Syngas Compression

6. Fuel Synthesis

Figure IIIB.11 illustrates Unit Operation #6 which is used to convert the syngas directly into drop-in fuels. In the fuel synthesis unit operation (#6), the compressed syngas is converted into fuel using the proprietary, designer catalyst in a multi-tubular, fixed-bed, steam-raising reactor. Following the catalytic reaction, the product gas is cooled to condense the fuels from the unconverted syngas.
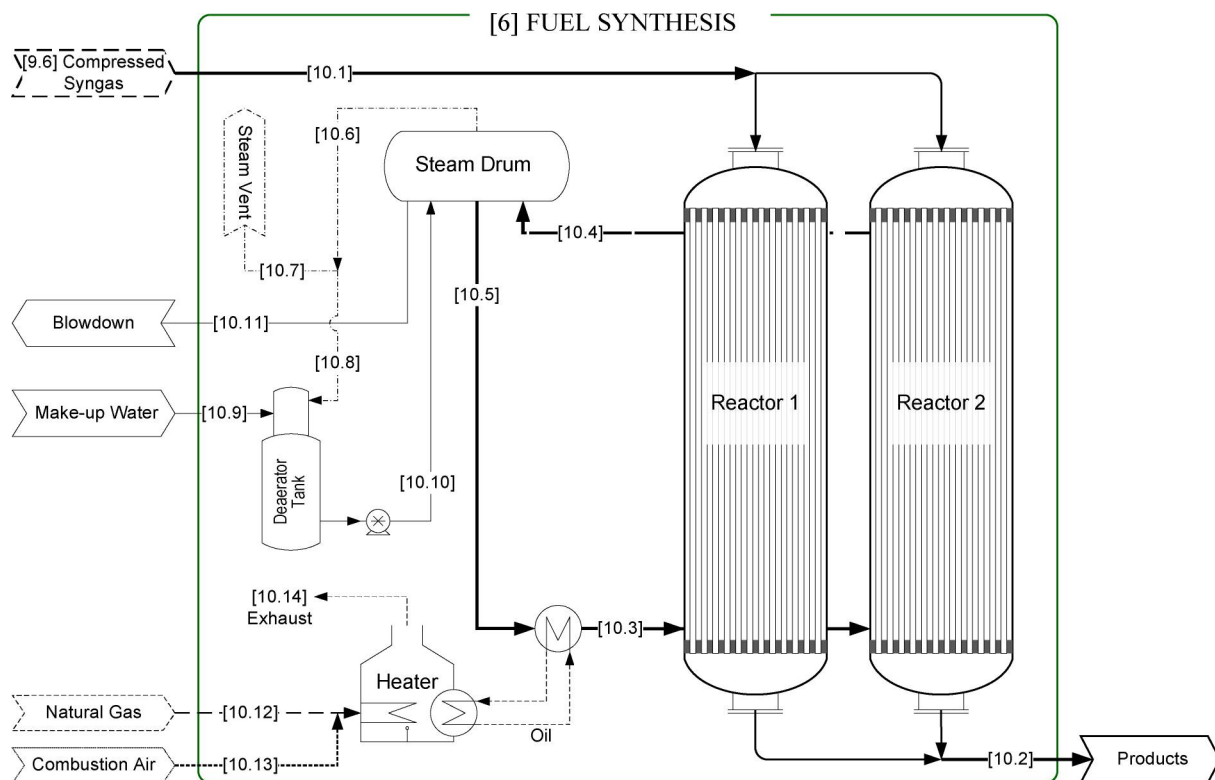
Figure IIIB.11: Direct Fuel Synthesis

Catalyst –Greyrock began development of their designer catalyst in 2006 and successfully completed development, large-scale catalyst manufacturing and pilot demonstration during the 4th quarter of 2009. Greyrock is the only organization that has been able to successfully develop, manufacture and validate a distributed commercial scale, catalytic process that can directly convert syngas into premium, "drop-in" fuels.

During the past eight years, Greyrock has carried out thousands of hours of catalyst testing and fundamental research studies to understand the chemical processes that make it possible for the Greyrock catalyst to produce minimal or no wax (C_{25}-C_{40} hydrocarbons) while producing primarily diesel fuel range hydrocarbons with high productivity.

The Greyrock "designer" catalyst was formulated:

- To utilize economical and readily available transition metals
- To achieve maximum activity and production efficiency in the desired HC selectivity range with minimal or no wax formation (C_{25}-C_{40})
- So that it can be activated *in situ* at moderate temperatures and pressures

The catalyst manufacturing process was developed to economically produce multi-ton quantities of high-quality catalysts using:

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- Standardized manufacturing processes that are reproducible at large, multi-ton scales.
- Highly dispersed (high surface area), catalytically active materials with optimum metal oxide crystallite dimensions
- Catalytically active materials that are strongly bonded to the substrate

Greyrock scientists have delineated the primary free-radical reactions that result in the product distribution produced at the commercial demonstration scale. It was found that the catalyst's formulation takes advantage of particular thermodynamic properties of the hydrocarbon product to kinetically enhance chain termination relative to chain growth that typically produces heavier intermediates.

The catalyst substrate was developed to optimize its pore structure, surface acidity, and surface area. As a result, this substrate exhibits:
- Superior hardness
- High surface area
- A unique shape that has good void space at substrate dimensions to minimize catalyst bed pressure drop at high gas linear velocities
- Low surface acidity
- Other optimized properties to achieve the desired results

The Greyrock catalyst coating was formulated:
- To utilize economical and readily available transition metals
- To achieve maximum activity and production efficiency in the desired HC selectivity range with minimal or no wax formation (C_{25}–C_{40} hydrocarbons)
- So that it can be activated *in situ* at moderate temperatures and pressures

The Greyrock manufacturing process was developed to economically produce multi-ton quantities of high-quality catalysts using:
- A catalyst production method as an easy to scale, reproducible catalyst manufacturing process
- Highly dispersed (high surface area), catalytically active materials with optimum metal oxide crystallite dimensions
- Catalytically active materials that are strongly bonded to the substrate

It has been demonstrated that the Greyrock catalyst does not produce hydrocarbons through free radical propagation and termination reactions that are typical for the Fischer-Tropsch (F-T) catalysis of syngas. As a result, the Greyrock catalyst does not follow the typical F-T Anderson-Schulz-Flory product distribution.

Catalytic Reactor – Greyrock worked for several years on a variety of reactor designs that enable ease of operation and reasonable construction costs. The catalytic reactor chosen was based upon an improved tube and shell design. The reactor consists of

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stainless steel tubes filled with catalyst. The tubes are arranged in an offset pattern with a center-to-center pitch that allows for efficient heat extraction. The exothermic heat of reaction is removed via boiling of pressurized water in the shell. The shell-side pressure is controlled so that the water bubble point temperature and heat removal rate create the desired catalyst temperature. Shell-side tube support sheets double as baffles to create efficient water flow. Multipoint thermocouples inside several tubes provide temperature information and control points.

7. Product Separation

The gaseous products that exit the reactor are cooled, condensed, and separated into diesel, water, and gas fractions. Before cooling, however, the flow is first sent through a "wax" knock-out separator to capture any longer-chain liquid hydrocarbons. The gaseous products that exit the wax separator are cooled using a fin-fan followed by a chilled water exchanger. The fin tube air cooled exchanger lowered the temperature from approximately 410 to 110°F (210 to 43°C). Fan speed was modulated as needed to correct for environmental variation or process needs. The second heat exchanger used 55°F (13°C) chilled water to cool and fully condense the liquids products.

Figure IIIB.12: Product Separation

The condenser output flows into a high pressure, three phase separator vessel that separates the liquid hydrocarbons and product water from the unconverted syngas. The gases are recycled to the compressor and then reactor, with the balance purged, while the two liquid fractions are depressurized into separate low pressure knock out vessels. Pressure reduction releases absorbed gases from the liquids which are collected and combined with the purged syngas to become Tailgas.

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The hydrocarbon fraction is the directly usable diesel fuel and the primary biofuel produced using this process. This synthetic diesel fuel can be used as a blend with petroleum derived diesel or used neat.

8. Fuel Storage

The final fuel product was stored in two 3,850 gallon storage tanks. The vertically oriented tanks were constructed of carbon steel with a flat bottom and a conical roof. Each tank has one 24" diameter manhole, assorted threaded NPT openings for filling, discharge, venting, gauge spare, etc. The tanks were complete with two ASME-designed support saddle assemblies providing 12" of clearance under tanks, exterior primer painted, and lifting lugs. The tanks were outfitted with both normal and emergency vent assemblies, per the appropriate code requirements.

Figure IIIB.13: Fuel Storage Tanks

9. Fuel Distillation

Intertek (Pittsburgh, PA) was contracted to carry out batch atmospheric distillations of fuel produced from the IBR plant. Results of this distillation for which the gasoline (IBP to 250 °F) and diesel fractions (260 to 690 °F) comprised an average of 29.4 wt. % and 70.6 wt. %, respectively.

IV. Control and Data Acquisition Systems

The IBR plant was divided into two data acquisition and control systems. The thermochemical process control system controlled Unit Operations #1-4a and the Liquid Fuel Production system controlled Unit Operations #4b-#8. Field data was fed into the control room.

A. Central Control System

The plant central control system (Figure IVA.1) was developed to run in an automatic mode with operator interaction as necessary.

Figure IVA.1: Plant Central Control Center Building

All of the data generated from the various unit operations were transferred to a control room in which the distributed control systems (DCS) are located. Figure IVA.2 shows the TCC control system screens and Figure IVA.3 shows the LFP control system screens.

- The control platform allowed for automatic settings to be changed during operations such as setting alarm conditions. As the plant was operated, experience dictated the alarm conditions that needed to be changed. The Proportional-Integral-Derivative (PID) parameters were initially set based upon engineering expectations and tuned during operation as expected. The color of the screen icons were designed to indicate various states of operation. Equipment that was out of service or disabled was shown in darker grey.
- Equipment that was operating without issue was shown as white or a lighter grey.

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- Abnormal operating situations displayed red for alarms requiring action and orange was used for alerting the operators.

Figure IVA.2: Thermochemical Conversion (TCC) Control System Screens

The number of alarms displayed was limited and the highest priority alarms were shown first. The operator was able to "silence" an alarm to allow better troubleshooting during abnormal situations. Additionally, the operator could select to see the "first" received alarm to allow better troubleshooting during abnormal situations.

The screens were mounted above eye level to allow easy visual observation by everyone in the control area. These screens provided a steady "dashboard" of the most critical unit operations, measurements, statuses, and trends in the plant. The items were not moveable or alterable by the operator. The philosophy was to not burden the operator with excessive indications but to make sure that all information was at the same place in the screen at all times to allow rapid location and evaluation of conditions (e.g. the temperature profile in the reactor is always in the same location).

Figure IVA.3: Liquid Fuel Production (LFP) Control System Screens

The primary functions of the system dashboard are:

- *Alarm Status Box* – high priority alarms are displayed here. The priority of alarms was based on approaching design limits, operational or safety hazards that could cause a plant shut down. The overall P&ID display includes:

  - Compressor status
  - Recycle flow through compressor
  - Feed flow through compressor
  - Reactor status
  - Reactor pressure
  - Reactor temperature at highest point and status (and possibly the reactor temperature profile)
  - Reactor CO per pass conversion
  - Separator system status
    - Temperature of cooling exit flow
    - Pressure at exit of separator system
    - Diesel fuel flow rate
    - Aqueous (water / F-T water) flow rate
    - Overall flow of tailgas
    - Flow to TCC Pyrolysis system
    - Flow to TCC Pyrolysis burner system
    - Inputs from TCC system
  - Calculations
    - Overall CO conversion

- Fuel Production - the composition and flow of syngas into the LFP was compared against the composition and flow of the fuel, tailgas and water produced by the LFP system.
- Last diesel yield per dry ash free ton (daft)
- Trends displayed:
  - Total flow from compressors
  - Reactor temperature
  - Reactor per pass CO conversion
  - Reactor pressure
  - Syngas flow from TCC system

V. Plant Construction

Upon completion of final design of the IBR plant, the Project Team started procuring long lead items during March of 2011. Procurement was completed prior to plant checkout. Construction activities commenced in April 2011 and were completed in March 2012. Checkout of the integrated facility was started in December 2011 and was completed in April 2012. All activities were completed on time and within the allotted budget. The following section further describes each project element and the methodologies employed during the period of performance.

A. Procurement

The REII Project Team's standard resource acquisition process can be summarized as follows:

- Plan
- Prepare requisition
- Issue requests for quote
- Evaluate supplier responses
- Issue contract/purchase order
- Receive supplies/services
- Review supplies/services for completeness
- Pay supplier
- Track inventory if applicable

Competitive bids were solicited from qualified suppliers when practical. For unique skills or services, justification for sole source procurement was required. In all cases, cost/price analysis was made and documented in the procurement file. During the course of initial investigations and subsequent development of the proposed technologies, the REII Project Team identified specific technology vendors who have the ability to provide the unique resources required to take the biorefinery to the next level of scale-up. Those vendors committed to being members of the project team, and provided essential information for estimating both project cost and schedule.

Although it was recognized that competitive bids are desirable, the competitive bid process is sometimes constrained by the unique nature of the resources required; where there were no known alternative suppliers who can meet project requirements, including the need to protect proprietary data, sole source justifications were required. Payment schedules were defined in the awarded contracts.

REII categorized purchases within the federal definitions, where small purchases were defined as being $25,000 or less, and micro purchases are defined as $5,000 or less. Provisions were applied at the appropriate levels, as described in Federal Acquisition Regulation (FAR) 600.148 and included:

- A clear and accurate description of the material, products, or services to be procured as well as a detailed budget and timeline.
- Provisions that allow for administrative, contractual, or legal remedies in instances where subcontractors violate or breach contract terms, and provide for such sanctions and penalties as may be appropriate.
- Provisions for termination, including termination procedures and the basis for settlement.
- Additional requirements specified in the appropriate OMB Circulars and/or federal regulations.

All subcontracts also incorporated language conforming to FAR provisions including:
- Standard of Performance
- Nondiscrimination Requirements
- Indemnification
- Rights of Parties Regarding Intellectual Property
- Intellectual Property Items Developed Prior to this Agreement
- Travel and Per Diem
- Equipment
- Disputes
- Confidentiality
- Recordkeeping, Cost Accounting, and Auditing
- Access to Sites and Records
- Legal Notice
- Recordkeeping, Cost Accounting and Auditing
- Audit
- Equipment
- Rights of Parties Regarding Intellectual Property
- Access to Sites and Records
- Davis Bacon Act Compliance

During the Procurement period of the project, RLB and Greyrock confirmed progress made by key vendors for major equipment and long lead items. This was done through scheduled conference calls, emails, and site visits. Figure VA.1 shows the TCC pressure vessel casing during an RLB vendor site visit.

Figure VA.1: TCC Pressure Vessel Casing

Figure VA.2 shows a picture of the LFP compressor prior to completion during a Greyrock vendor site visit.

Figure VA.2: LFP Compressor Prior to Completion

Figure VA.3 shows the LFP compressor at completion being loaded onto a truck for transport to the project site during a Greyrock vendor site visit.

Figure VA.3: LFP Compressor Complete at the Greyrock Vendor Site

After final checkout at the vendor's fabrication facility, large equipment was delivered to the project site. Figure VA.4 shows the delivery of the TCC pyrolysis unit. Final assembly was completed at the project site.

Figure VA.4: TCC Pyrolysis Reactor Delivery to Project Site

B. Site Preparation

The integrated biorefinery project was located at the existing RLB TCC facility at the University of Toledo (UT) Energy Center. The upgrade of the facility included site work to allow for expansion and modification of TCC system and the addition of the Greyrock LFP system. Site preparation activities included:

- Tracing all existing utility lines in the project area,
- Inspection of existing RLB TCC conduit,
- Installing a water discharge line to the sanitary sewer,
- Installing a security fence, and
- Pouring a concrete pad to allow for the expanded facility footprint.

C. Utilities

Utilities required for the project included power, natural gas, water, and steam. The existing facility had a pre-existing connection from the UT Energy Center to power the RLB TCC facility. A new power line was installed to meet the power needs of the Greyrock LFP system from the UT Energy Center.

A pre-existing natural gas line was connected to the project site from the UT Energy Center. No modification of this line was required for the project.

In order to insure that the water quantity and quality specifications of the integrated biorefinery could be met, a new water line was installed to connect the integrated biorefinery to the City of Toledo municipal water supply.

A pre-existing steam line was connected to the project site from the UT Energy Center. No additional modifications of the steam line were required for the project.

D. Assembly

The assembly of the IBR plant was completed as major equipment and supporting material were delivered, inspected, and accepted at the project site. Major equipment, including the solids steam reforming system, compressor, catalytic reactors, and the product separation skid were primarily fabricated off-site with final assembly occurring at the IBR project site. The following provides additional detail on the assembly of selected plant components.

Solids Steam Reformer – The Solids Steam Reformer was partially assembled off-site at the manufacturer's facility. Ready to ship inspections were done at the manufacturers facility and final acceptance of the equipment was done at the IBR site after the system was assembled and operated for a period of time acceptable to the Project Team. Site assembly included installation of insulation, burners, internal chamber, and mechanical and electrical systems. The manufacturer (Surface Combustion) was present for the start-up of the Solids Steam Reformer (Unit Operation #2).

Compressor – The LFP Compressor was wholly assembled at the manufacturer's facility. A factory acceptance test was completed at the manufacturer's site prior to shipment to the IBR project site. Once the compressor was received at the project site final piping and electrical connections were made. The manufacturer oversaw the installation and start-up of the compressor.

Catalytic Reactors – The Catalytic Reactors were fully assembled at the manufacturer's sites. Once received on-site, the reactors were set in place with a crane, attached to the reactor super-structure, and piping connections were completed.

Separation Skid – The Separation Skid was fully assembled by the manufacturer at their site. A factory acceptance test was completed at the manufacturer's site prior to shipment to the IBR project site. The Separation Skid was set in its final position by a crane (Figure VA.5). Final piping and electrical connections were completed after the skid was set.

Figure VA.5: Installation of the Separation Skid

Thermal Fluid Heater – The Thermal Fluid Heater was fully assembled by the manufacturer at their site. The Thermal Fluid Heater was set in its final position by a crane. Final piping and electrical connections were completed after the skid was set in place. The manufacturer administered final installation and start-up of the Thermal Fluid Heater prior to the start of operations.

Piping – Piping of the TCC and LFP systems was completed as equipment was set in its final position. Pressure and leak testing was done to insure that all connections were properly sealed. The TCC system had fewer piping connections and therefore sourced pipe and made final sizing determinations on site. Because the LFP system had many more piping connections, the pipe spools were fabricated off-site and installed as equipment was

set in place. This allowed for the Project Team to expedite the installation of the LFP system.

Instrumentation & Controls – Instrumentation and controls were installed as piping was installed throughout the IBR plant.

E. Equipment and Systems Check-Out

The IBR checkout and commissioning was performed in a manner that safely insured that all construction had been performed in adherence to the P&ID in a quality manner and that the systems functioned together as designed. Checkout and commissioning of the IBR plant insured that all components were installed correctly and were able to operate per the manufacturers design specifications. The checkout and commissioning of the IBR plant included the following:

- *Equipment Validation* – This task included the receipt and acceptance of equipment to the IBR Project Site. Equipment was initially checked to make sure no damage had been incurred during transport. After the initial damage inspection, equipment was inspected for accuracy against equipment specification sheets. Any discrepancies identified during the inspection were resolved prior to acceptance of equipment.
- *Piping Inspection* – All piping inspections were conducted by either a representative of Red Lion Bio-Energy for TCC piping or Greyrock for LFP piping as the piping contractors completed work.
- *Component Checkout and Commissioning* – Component checkout and commissioning was conducted to insure proper installation of all piping, equipment, and devices. The process for components checkout and commissioning is further described below.
- *Subsystem Commissioning* – Subsystem commissioning included the verification of proper controls communication, temperature and liquid level sensor verification, and plant simulated testing without biomass.

The following describes the process by which checkout and commissioning of the IBR facility was conducted and documented:
- *Individual Components*
  o All components on the P&ID were checked for proper installation
  o Instruments were checked for proper function and communication with control room
  o Electric motors were tested for proper function
  o Check list for components were completed
- *Piping Checks*
  o All installed pipes were checked for proper size and routing
  o Piping was inspected for adherence to the piping classification document
- *Pressure Test*
  o Entire Plant was pressure tested

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- o Soap bubble checks were completed throughout the facility. In addition to the soap bubble checks, the facility was tested to insure that it could maintain plant pressure for period of time.
- *Water Flow Test*
  - o Water systems were filled and operated
  - o Flow meters and other relevant instruments were checked
- *Feed Entry*
  - o Weigh bins were tested and calibrated
  - o Conveyors were tested and calibrated
  - o Gate valves were actuated and calibrated with the controls system
  - o Ram charge feeder was tested without biomass and calibrated
- *Pyrolysis Chamber*
  - o Rotation of retort was tested
  - o Burners were tested
  - o Compressor was run on N_2 and tested
  - o LFP Thermal Fluid Heater was tested
  - o LFP Reactors were tested for proper flow
- *Analytical Instrumentation*
  - o Analytical instrumentation was calibrated with bottled gas and known liquids
- *Safety Systems*
  - o Start up and shut down procedures were reviewed
  - o Gas monitoring devices were tested
  - o Over temperature and pressure conditions were tested
- *Utilities*
  - o Natural gas supply line and meters pressure tested
  - o Electrical supply and meters tested
  - o Water supply and meters tested
  - o Steam supply and meters tested

A spreadsheet was developed to document inspection, commissioning and any fixes that were required. To assist in this process, wireless tablets were used to operate devices in the field. This enabled a more effective and efficient checkout process.

Upon completion of checkout and commissioning of the IBR facility, start-up and shutdown procedures were performed to insure that the proper sequence of events was followed and subsystems responded correctly.

The final step in the system checkout was to bring the TCC system up to full operational mode and operate the plant on steam only, no feedstock. The LFP performed runs on Nitrogen to test compression and system flows.

F. Training

Prior to start-up of the IBR plant, a comprehensive training program was developed for the plant operators. Operator training included:

- ***Review of Roles and Responsibilities*** – The roles and responsibilities for each Team were discussed which included:
  - o Safety Team – responsible for all aspects of operator and site safety.
  - o Management Team – responsible for the overall management of each test campaign and interfacing between the TCC and LFP Teams.
  - o TCC Team – responsible for the operations of the TCC system.
  - o LFP Team – responsible for the operations of the LFP system.
  - o Analytical Team – responsible for maintenance of analytical equipment, sampling, and data logging.

- ***Safety Training*** – The standard safety requirements for operators was reviewed which included the following topics:
  - o Personal Protective Equipment (PPE) – including hard hats, safety glasses, shoes, hearing protection, fire resistant jumpsuits, and gas monitoring devices
  - o Evacuation procedures
  - o Hazard Communication – including a review of materials on site and Material Safety Data Sheets (MSDS)
  - o Gas cylinder storage and handling
  - o Basic site safety rules – including compliance with applicable rules and regulations, injury reporting, OSHA safety standards, tool maintenance, site speed limit, unsafe conditions reporting, warning signs, barricades and tags, and general housekeeping
  - o Review of emergency shut-down procedures

- ***Site Access and Authorizations*** – The following topics were discussed prior to each test campaign:
  - o Operating Conditions – A review of standard operating conditions of the TCC and LFP Teams were reviewed.
  - o Control Parameters – Control parameters that required monitoring and maintenance were reviewed with the operators.
  - o Site Walk – A site walk was done with all operators to view and discuss the operations of each unit operation.
  - o Controls Training - Hands-on control room training was carried out with all operators to train on the operations of controls screens, alarms, administrative functions, and charts and trends.
  - o Analytical - Sample gathering and data logging training for operators and the analytical team was completed, including: sampling locations, methods, and frequency.

An on-going operator training program was established during the operations period to address operational changes from plant improvements and for any new operators that may not have been trained in previous training sessions.

VI. Plant Tests

Seventeen test campaigns were carried out during which the IBR plant was operated as an integrated system for a total of 992 hours (Table VI.1) from May 9, 2012 to September 20, 2013. The plant start-up and shut down periods of 48-60 hours for each run are not included in the total run times summarized in Table VI.1. The TCC system was run alone for 186 hours and the standard reference materials, which included CH_4/CO_2, methanol/CO_2 and glycerol/CO_2 mixtures, were run in an integrated mode for 220 hours. Wastewater bio-solids were run for a period of 4 hours during run #12 (not included in the 38 hr. total for that run).

The comprehensive data generated from these performance and validation studies was used to establish the optimum operating conditions for the plant and a summary of the results and conclusions are provided in Section IX.

Table VI.1: Plant Integrated Operation Periods for the Wood, Rice Hull and Other Feedstocks during the Seventeen IBR Plant Test Campaigns

Run #	Dates	Plant Operation Period (hrs.)				TCC Only	Average and (Maximum) Feed Rate (tons/day)
		Total Integrated Operation					
		Wood	Rice Hulls	Standard Reference Materials	Total	Total	
2012							
1	5/9 - 5/11	16	-	-	16	16	2.5 (4.0)
2	5/21 - 5/27	96	-	-	96	32	6.0 (8.5)
3	6/26 - 6/27	18	-	-	18	0	11.0 (11.0)
4	7/9 - 7/13	68	-	-	68	12	14.0 (15.5)
5	7/28 - 8/06	121	-	55	176	24	10.5 (11.7)
6	8/20 - 8/25	-	75	-	75	5	10.0 (12.3)
7	9/5 - 9/8	52	-	-	52	4	7.5 (9.4)
8	11/7 - 11/16	126	-	-	126	24	11.8 (12.5)
9	12/10 - 12/14	68	-	-	68	0	13.1 (18.0)
Sub-Total Hrs. (2012)		565	75	55	695	117	-

Table VI.1 (continued): Plant Integrated Operation Periods for the Wood, Rice Hull and Other Feedstocks during the Seventeen IBR Plant Test Campaigns

Run #	Dates	Plant Operation Period (hrs.)					Average and (Maximum) Feed Rate (tons/day)
		Total Integrated Operation				TCC Only	
		Wood	Rice Hulls	Standard Reference Materials	Total	Total	
2013							
10	2/15 - 2/18	22	-	26	48	8	15.5 (15.5)
11	3/2 – 3/4		28	-	28	0	13.4 (15.2)
12	3/4 - 3/7	32		6	38	0	20.2 (24.0)
13	3/21 - 3/25	-	34	-	34	22	12.5 (13.6)
14	6/10 - 6/15	-	26	-	26	30	14.0 (14.8)
15	7/14 - 7/18	42	-	36	78	0	16.2 (18.0)
16	8/11 - 8/18	70	-	73	143	9	11.5 (12.8)
17a	9/8 - 9/21	30	-	24	54	0	8.9 (11.6)
17b	9/8 – 9/21		68	-	68	0	5.4 (5.4)
Sub-Total Hrs. (2013)		196	156	165	517	69	-
Total Hrs.		761	231	220	1,212	186	-

A. Startup and Commissioning

The startup and commissioning processes employed included:

- *Management Processes* – Commissioning Manager, Dedicated Staff and Maintenance Support Identified; Operations & Safety Training; Checkout and Startup Procedures; Progress Monitoring Procedures
- *Engineering Processes* – Pipe and Vessel Cleanliness; Temperature and Pressure Acceptance Tests; Instrument and Sensor Calibration; Data Acquisition; Advanced Data Analysis; Performance Optimization; Syngas Composition and Purity Tests; Synthetic Diesel Fuel Quality and Quantity Tests

B. Test Campaigns

Each test campaign had its own set of specific objectives and built upon the results from the previous campaign. The final assessment was the Independent Engineer (IE) test (test #17), which was carried out during September 8-21, 2013.

A brief description of each campaign is described in the following sections.

1. Test Campaign #1

Test campaign #1 focused on the initial operation of the newly commissioned IBR plant. The unit was run at half capacity only using wood feedstock, as the main purpose was to characterize and optimize the IBR plant operation. This campaign was used to establish the base line operating performance of a single catalyst reactor tube for diesel fuel production. The objectives that were successfully completed are summarized as follows:

- The TCC system was operated from 2.5-24 tons per day input capacity under varied conditions to establish baseline operational data.

- The TCC system was effectively integrated with the LFP system to test and optimize the direct production of synthetic diesel fuel.

2. Test Campaign #2

The objectives of this campaign were to operate the fully integrated TCC and LFP systems up to half capacity, using wood and rice hulls to establish IBR plant operating performance within the range of operating conditions listed in Tables VIB.1 and VIB.2.

Table VIB.1: Plant Operating Ranges for the Thermochemical Conversion System

Thermochemical Conversion System		
Process Variable		**Operating Conditions**
F	Feedstock type	Wood (0.15"-2.00") Rice hulls (ground or whole)
F_M	Feedstock moisture content (as received)	10-35 weight %
$F1_R$	Feedstock input rate	2.5-25 tons/day
$R2_S$	Rotation speed of Unit Operation #2	0.5-2.0 revolutions/min
$R2_L$	Length of Unit Operation #2 reactor	23 feet
$R2_T$	Temperature of Unit Operation #2 reactor	1,350-1,550°F
$R2_{H2O/C}$	Mass of H_2O to feedstock C in #3 reactor	0.2-0.5 to 1.0
$R2_P$	Pressure of Unit Operation #2 reactor	15-20 psi
$R2_t$	Feedstock residence time	12-46 minutes
$R3_T$	Temperature of Unit Operation #3 reactor	1,650-1,815°F
$R3_t$	Gas residence time	4-8 seconds
$R3_{H2O/C}$	Mass of H_2O to feedstock C in #3 reactor	1.0-1.5 to 1.0

Table VIB.2: Plant Operating Ranges for the Liquid Fuel Production System

Liquid Fuel Production System	
Process Variable	**Operating Conditions**
FP_P Pressure of unit operation #6 reactors	Up to 400 psig
FP_T Temperature of unit operation #6 reactors	Approximately 400 °F

3. Test Campaign #3

The objectives of this test campaign were to:

- Validate carbon conversion efficiencies for wood and rice hulls at the optimum integrated, plant operating conditions determined from test campaign #2.

- Determine catalyst efficiency and diesel fuel production (gallons per dry [ash free] ton of feedstock)

- Assess the quantity and composition of the following plant by-products:
    1. Ash
    2. Tars
    3. Water effluents
    4. Air emissions
    5. Wax

- Determine the chemical and physical properties of the "drop-in", synthetic diesel fuel.

- Determine the air emissions from the gas burners in Unit Operations #2 and #3.

- Carry out third party analytical measurements (DRI and BV).

- Modify the commercial plant design using data and improvements developed as a result of testing campaigns #1-#3.

4. Independent Engineer Test

DOE selected Leidos as the Independent Engineer (IE) for the final performance test. This IE Test was carried out during September of 2013. The primary purpose of the IE plant performance testing was to establish a technical performance baseline in support of the financial objectives for commercialization of this technology. The collection of data was intended to be sufficient for establishing a heat and material balance and to allow the evaluation of emissions and key process parameters such as energy use and chemicals consumed. *The purpose of the IE Test was not to verify guarantees that the facility has established or may require from an EPC contractor, nor was the test designed to be pass/fail.*

a) Plant Testing Plan

The IE Testing Plan included the 1) IE Pre-Performance Test Conditions; 2) Plant operating conditions for IE Test; 3) Plant check-out and approval; 4) Plant warm-up period; 5) Plant stabilization period; 6) IE Test period; 7) Plant shut-down; 8) Data analysis; and 9) IE performance test report.

The objective of the IE Test was to establish a performance baseline for operation of the integrated biorefinery. During the IE Test, the REII Team gathered data in support of the operations and provide the performance data to the Leidos Independent Engineer and DOE Project Manager for review. The data gathered during the IE Test was compared against the technical targets established at the beginning of the project.

It was decided that if a minor plant problem (e.g. disruption in feedstock flow, non-operating pump, etc.) occurred, the test would continue while the item was being repaired or replaced. If the problem was more serious such as a clogged ash removal auger, that unit operation will be shut down and repaired, during which time the other unit operations will remain under operating conditions. The plant would then commence operation once the repair had been completed and that unit operation was again operating at specified conditions. A risk management plan for potential plant upsets is provided in Table VIB.3.

Prior to the IE Test, it was determined by the project team (REII, RLB, and Greyrock) that there was sufficient biomass, gases, power, natural gas and other materials needed to run the plant during the IE Test performance period. In addition, all devices for measuring biomass input, system pressures, temperatures and gas flows as well as the use of chemical standards for calibration of analytical instruments were calibrated and standardized. The IE Test was carried out as follows:

Day 1 – This first day was used to set up and calibrate instrumentation, check-out control systems software and bring the plant up to operating conditions (e.g., temperatures, pressures, etc.). The details of the plant operation for the IE Test were reviewed and improved including:

- Plant operating conditions for the IE Test

- Locations and procedures for the measurement of solid and gas mass flows, temperatures and pressures

- Locations and procedures for the monitoring, collection and characterization of gas, liquid and solid phase samples

- The analytical instrumentation and procedures to be used for quantifying gas, liquid and solid phase samples

- The central computer systems used for monitoring and controlling plant operation

- The collection of operating data and how that data will be evaluated in real-time

All unit operations were brought up to the desired temperatures, pressures, and gas flows; which took about 16 hours.

Table VIB.3: Risk Management Plan for Potential Plant Upsets during the IE Test

Potential Effect of Upset on IE Test	Potential Plant Upset	Solution
Low	Feedstock not flowing from feedstock hopper to ram charge feeder	Manually break up obstruction while keeping all other processes under operating conditions
Medium	Minor problem with ram charge feeder	Repair while keeping all other processes under operating conditions
Medium	Major failure of ram charge feeder	Cool down Unit Operation #2 and repair while keeping all other processes under operating conditions
Low	Burners in Unit Operation #2 not controlling T within specifications	Repair while keeping all other processes under operating conditions
Medium	Ash auger clogged	Repair while keeping all other processes under operating conditions
Very Low	Major failure of Unit Operation #3 (e.g. leak)	Cool down Unit Operation #3 and repair while keeping all other processes under operating conditions
Low	Minor problem with syngas purification system	Repair while keeping all other processes under operating conditions
Low	Minor problem with compressor	Repair while keeping all other processes under operating conditions
Very Low	Major problem with compressor	Keep Unit Operations #1-4a operating and flare syngas until problem is fixed
Low	Minor problem with Unit Operation #10	Keep Unit Operations #1-4a operating and flare syngas until problem is fixed
Very Low	Major problem with Unit Operation #10	Keep Unit Operations #1-4a operating and flare syngas until problem is fixed
Very Low	Minor problem with Unit Operations #11 and #12	Keep Unit Operations #1-4a operating and flare syngas until problem is fixed

Day 2 – Pure syngas was generated in the TCC system by introducing reference materials with the proper ratio to produce H_2/CO with a ratio of ~2.2/1.0 for standardization and calibration of the plant to:

- Confirm that Unit Operations #2 and #3 were operating under optimum conditions

- Determine the accuracy of the syngas mass flow meters and argon flow tracer technique

- Assess that the syngas purification system (Unit Operations #4a) was operating properly

- Check the stability and accuracy of the analytical instrumentation for quantitative determination of syngas composition and syngas contaminants

- Gauge that the syngas polishing (Unit Operation #4b) and compressor (Unit Operation #5) were operating properly.

- Test the operation of the recycle loops

- Measure the performance of the catalytic conversion system (Unit Operation #6) for the production of diesel fuel

- Evaluate the efficiency of the product separation system (Unit Operation #7)

During the baseline test, the operation of each unit operation was modified as necessary to optimize their performance.

Days 3-4 – The plant was run in a hybrid mode using mixtures of reference materials with increasing inputs of rice hulls.

Day 5 – The plant was run on rice hulls at 5-6 tpd input.

Day 6-7 – The plant was run on wood at 6-12 tpd input.

Day 8 – This final day of the IE Test was used to determine if there were significant changes in operation of the plants unit operations. The plant was run using methanol with the proper ratio of CO_2 to produce H_2/CO with a ratio of ~2.3/1.0 for comparison of the results generated from Day 1 to confirm:

- That Unit Operations #2 and #3 were still operating under optimum conditions

- That the calibration of the syngas flow meters have not changed

- To assess that the syngas purification system (Unit Ops #4a-#4b) has been operating properly

- To confirm the accuracy of the analytical instrumentation for quantitative determination of syngas composition and syngas contaminants

- To gauge that the syngas polishing (Unit Operation #4b) and Compressor (Unit Operation #5) have been operating properly.

- To check the performance of the catalytic conversion system (Unit Operation #6) for the production of diesel fuel

- To evaluate the efficiency of the product separation system (Unit Operation #7)

Day 9 – The plant was brought back to non-operating conditions and data files were compiled for analysis and modeling.

b) IE Test Operating Conditions

Tables VIB.4 and VIB.5 summarize the plant operating conditions chosen for the IE Test. Wood chips (~0.15" to ~2.0" diameter) and rice hulls (~1/2" diameter) were used as the feedstocks.

Table VIB.4: Optimum Thermochemical Conversion System Operating Specifications Chosen for the IE Test

Thermochemical Conversion System	
Process Variable	**Operating Conditions**
F Feedstock type	Wood: 0.15"-2.00" Rice hulls (whole)
F_M Feedstock moisture content (as received)	Wood: 14.5-16.1 weight % Rice hulls: 9.7-11.5 weight %
$F1_R$ Feedstock input rate	2.5-25 tons/day
$R2_S$ Rotation speed of Unit Operation #2	1.0 revolutions/min
$R2_L$ Length of Unit Operation #2 reactor	23 feet
$R2_T$ Temperature of Unit Operation #2 reactor	1,450-1,550°F
$R2_{H2O/C}$ Mass of H_2O to feedstock C in #3 reactor	0.4-0.6 to 1.0
$R2_P$ Pressure of Unit Operation #2 reactor	15-20 psi
$R2_t$ Feedstock residence time	23 minutes
$R3_T$ Temperature of Unit Operation #3 reactor	1,750-1815°F
$R3_t$ Gas residence time	4-8 seconds
$R3_{H2O/C}$ Mass of H_2O to feedstock C in #3 reactor	1.2-1.4 to 1.0

Table VIB.5: Optimum Liquid Fuel Production System
Operating Specifications Chosen for the IE Test

Liquid Fuel Production System	
Process Variable	**Operating Conditions**
FP_P Pressure of Unit Operation #6 reactor	Up to 400 psi
FP_T Temperature of Unit Operation #6 reactor	Approximately 400°F

C. Physical Measurements

Figure VIC.1 illustrates a process flow diagram (PFD) for the 25 ton per day IBR plant and the locations at which solids and gas mass flows, temperatures and pressures which were monitored and Table VIC.1 describes the parameters measured at these locations.

Table VIC.1: Locations for the Measurement of Solids and Gas
Mass Flows, Temperatures and Pressures for the IBR Plant

Location	Parameters Measured
1	Feedstock input rate (tons/hr.)
2	CO_2 purge volume and time
3	Average temperature (°F) for Unit Operation #2
4	Ash mass flow rate (tons/hr.)
5	Steam injection mass flow rate (lbs./hr.) for Unit Operation #3
6	Average temperature (°F) for Unit Operation #3
7	Mass flow rates for reference gases (*for parametric studies and system calibration*)
8	Syngas mass flow rate (scfm)
9	Scrubber water temperature (°F)
10	Syngas pressure (psi) and temperature (°F)
11	Syngas mass flow rate (scfm)
12	Average catalytic reactor temperature (°F)
13	Tail gas recycle mass flow rate (scfm)
14	Diesel fuel production rate (gallons/hr. & lbs./hr.)
15	Wax production rate (lbs./hr.)
16	Water production rate (gallons/hr. and lbs./hr.)

Figure VIC.1: Locations for the Measurement of Solids and Gas Mass Flows, Temperatures and Pressures for the IBR Plant

1. Feedstock Input Rate

A batch weigh hopper on the conveyor system (Unit Operation #1) was used to weigh the feedstock (Figure VIC.1- location #1). The weigh hopper stands on four 50 lb. load cells. The hopper was calibrated using a 200 lbs. weight during plant commissioning. This weight data was sent directly to the control system, where it is used directly and averaged over time to obtain feedstock mass introduction rates.

2. CO₂ Purge Volume and Time

After the feedstock filled the feedstock introduction system, the gate valve was closed and the feedstock flushed with CO_2 for 10-15 seconds to remove entrained air (Figure VIC.1 – location #2). The CO_2 enters through eight ports in the bottom of the purge vessel. Roughly two vessel volumes (24 cubic feet) of CO_2 are sent through the feedstock introduction system during each cycle.

3. Plant Standardization and Calibration

Several gas-phase mixtures were tested as potentially viable materials for IBR plant standardization, calibration and validation. The mixtures tested included:

- Methanol / CO_2 blends
- Glycerol / Methanol blends
- Natural Gas / CO_2 blends

The objective was to utilize these mixtures to standardize, calibrate and validate:

- Syngas mass flow meters
- Analytical instruments
- Transfer efficiency of syngas from the thermochemical conversion system (TCC) to the liquid fuel production system (LFP)
- Adjustment of syngas residence time (space velocity) and catalyst operating temperature
- Quantification of catalyst productivity
- Optimization of TCC System (for example, validation of burner/heat control in the TCC system before biomass enters the system)

These gas-phase mixtures were injected at location #3 (Figure VIC.1)

4. Comparison of Laboratory and IBR Plant Tests

A laboratory simulator (see Figure IID.1) was employed to help determine the optimum operating conditions for the IBR TCC system and to help choose which of the three mixtures (methanol/CO_2, glycerol/methanol, and natural gas/CO_2) would be the best choice for calibration and validation of the plant.

The total carbon conversion (feedstock carbon to syngas carbon) for methanol/CO_2, glycerol/methanol, and natural gas/CO_2 mixtures averaged 80%, 80%, and 35%, respectively. In comparison, the carbon conversion for wood and rice hulls averaged 85%.

The methanol/CO_2 mixture was feed into the IBR plant at the same ratio as the laboratory simulator and under similar conditions of temperature and pressure. As shown in Table VIC.2, the laboratory reactor and IBR plant produced syngas with similar composition. It was also found that:

- The introduction of these mixtures into the IBR plant was straightforward.
- A constant flow of syngas could be generated over extended periods of time.
- The ratio of H_2 / CO averaged 2.2 ± 0.2.
- The production of CO was efficient and stable ($14,080 \pm 800$ scf/1,000 lbs. of carbon input).

- The production of fuel was efficient and stable

As a result, the methanol/CO_2 mixtures were chosen as the best gas-phase mixtures for plant standardization and calibration

Table VIC.2: A Comparison of the Composition of Syngas from the Laboratory Simulator (see Figure IID.1) and IBR plant for the Thermochemical Conversion of Methanol and CO_2

Syngas Constituents	Concentration (Volume %)	
	Laboratory Reactor	IBR Plant
H_2	55	56
CO	28	25
CO_2	17	18
CH_4	0.0	0.6

5. Unit Operation #2 Temperature

Unit Operation #2 temperatures were determined as an average of the thermocouples in zones 434, 435, 436, 437, 438, 439, 440, 441, 442, 443 and 444. The thermocouples are located along the outside wall and protrude six inches from the surface. This average temperature was transmitted to the DCS every second.

6. Ash Mass Flow Rate

The ash produced in Unit Operation #2 was removed through the ash interlock system (see Figure VIC.1 – Location #4). The ash was collected in a bin, and when the bin was filled, it was taken to an electric scale on palettes. It was then weighed and tarred with respect to the weight of the bin. The weight of the ash was manually recorded.

7. Steam Injection Mass Flow Rate for Unit Operation #3

It was not necessary to inject much steam into Unit Operation #2 since the pyrolysis of wood produces steam as described in Section VIII.B. Although some of the water, evaporated from the wood and produced during the pyrolysis process, reacts with the wood or pyrolysis products in Unit Operation #2, most of the water will react with the gas-phase pyrolysis products in downstream Unit Operation #3. Steam injection is controlled by manually adjusting a feed valve (FE-752), which sends saturated steam through a super heater coil located in the convection section of Unit Operation #3 (Location #5). This heats the steam to roughly 1,400°F before merging with the process gas entering Unit Operation #3. The amount of steam is monitored by a flow element. The recommended steam injection into Unit Operation #3 is provided in Table VIC.3 as a function of wood feedstock input.

Table VIC.3: Steam Injection into R2 (Unit Operation #3) as a
Function of Feedstock Input

Wood Feedstock Input			Steam Injection into Unit Operation R2
As Received (ton/day)	As Received (lb./hr.)	As Carbon (lb./hr.)[1]	(lb./hr.)[2]
2.5	208	93	112
5.0	416	186	223
7.5	624	279	335
10.0	832	370	444
12.5	1040	465	558
15.0	1248	558	670
17.5	1456	651	781
20.0	1664	744	893
22.5	1872	837	1004
25.0	2080	930	1116

[1] *lb./hr. (as Carbon) = lb./hr. (as received) x (0.445)*
[2] *Steam Injection (lb./hr.) = Carbon (lb./hr.) x 1.2*

8. Unit Operation #3 Temperature

The Unit Operation #3 temperatures are collected by 5 thermocouples placed in thermo-wells along the length of the coil to get a temperature profile of the process gas temperature. There are also a dozen thermocouples distributed at various locations that measure the external skin temperature of the coil for the purpose of making sure not to exceed mechanical stability of the unit. These temperatures were sent to the DCS every second.

9. Syngas Mass Flow Rates

A rotometer, a thermal mass online flow element, and a vortex shedding volumetric flow element (see Figure VIC.1 – Location 6) were used to monitor the syngas flow in the TCC system. The thermal mass flow meter was unreliable due to condensation and coating of the thermal element, preventing accurate measures. The vortex shedding volumetric flow meter performed reliably, but the noise was high due to pulsation from the reciprocating compressor downstream. The volumetric flow had to be converted to mass flow via pressure and temperature corrections internal to flow meter as well as composition received from the online mass spectrometer. Similar corrections were made for the rotometer, which was calibrated using air at standard temperature and pressure. Another vortex shedding volumetric flow meter (Figure VIC.1 – Location #10) was used to measure the flow of pure, dry syngas after compression before it mixes with the recycle gas and enters the catalytic reactor.

As described earlier, methanol/CO_2 mixtures were injected into Unit Operation #2 to generate specific syngas flows and syngas compositions for plant standardization and calibration.

The most accurate method for determining the mass flow in scfm of the syngas was by injecting argon into the syngas stream before Unit Operation #4a (injection port #7) at a fixed flow rate using a Sierra Instruments mass flow controller. The online mass spectrometer #2 was used to quantify the volume of argon (Ar) in the syngas sampled from port #10. The flow rate of the syngas stream was determined by the following equation.

Syngas Flow Rate (scfm) = (100% / Vol. % Ar (port #10)) * Argon Mass Flow (scfm)

Figure VIC.2 illustrates the correlation between Ar mass flow measurement and the LFP mass flow meter for 135 measurements made during run #17. It is seen that the correlation is good between 100 and 350 scfm but there is increasing discrepancy below 100 scfm and above 350 scfm. It appears that the upper limit of the LFP flow meter was 350 scfm. Therefore, the Ar mass flow measurement was used as the most accurate syngas mass flow measurement method below 100 scfm and above 350 scfm.

10. Scrubber Water Temperature
The scrubber water temperature was measured (see Figure VIC.1 – Location #9) to determine if there was proper water flow to adequately cool and scrub the raw syngas. In addition, if the scrubber water temperature was too high, the purified syngas was found to contain excess water, which condenses downstream in the compressor and analytical sampling lines.

11. Syngas Pressure and Temperature
The syngas pressure and temperature of the syngas exiting Unit Operation 8 (syngas polishing unit) (see Figure VIC.1 – Location #10) was monitored and the data recorded by the DCS.

12. Syngas Mass Flow Rates
A second volumetric flow meter (see Figure VIC.1 – Location #10) was used to measure the flow of pure, dry syngas before it mixed with the recycled syngas and entered the catalytic reactor. Argon injection was also used to check the calibration of this mass flow device. Another volumetric flow meter of the same style measured the recycled syngas before it merged with the fresh syngas stream and entered the catalytic reactor (see Figure VIC.1 – Location #11).
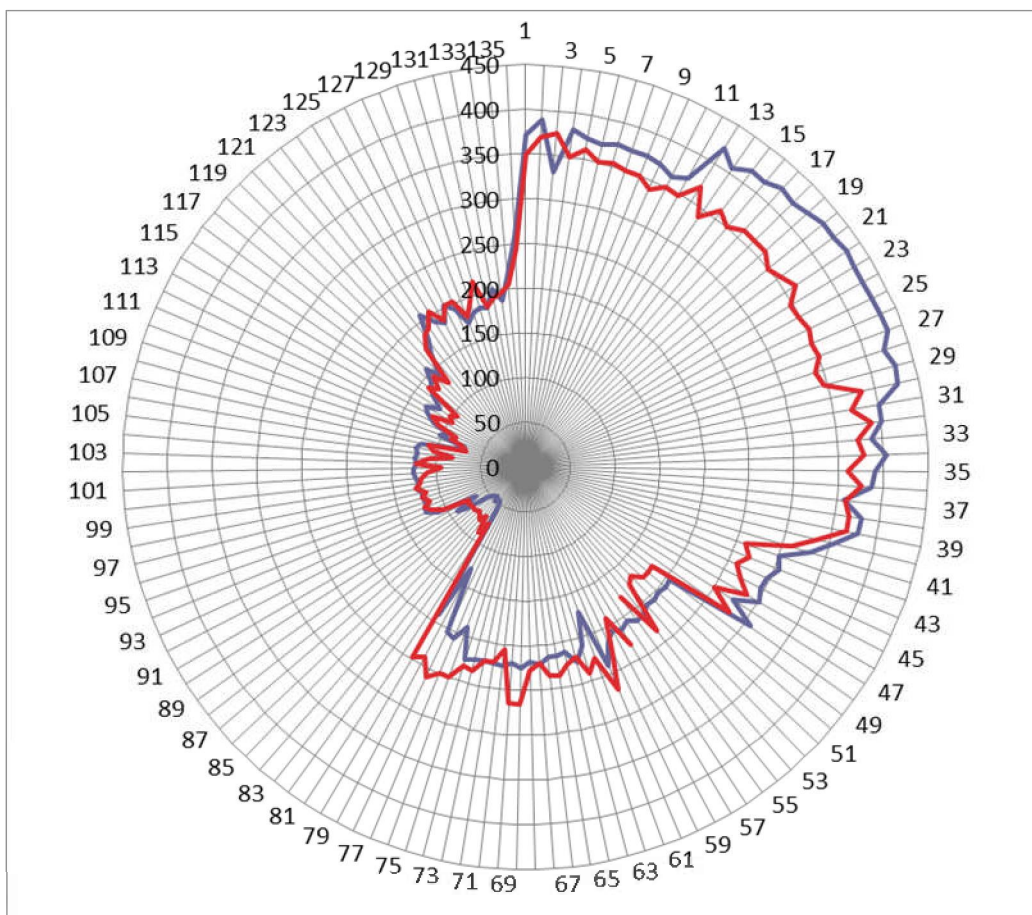
Figure VIC.2: Correlation between the Syngas Mass Flows using the
Ar Tracer Technique (blue) with the LFP Mass Flow
Meter in scfm (red) at Location #11 (Figure VIC.1)

13. Catalytic Reactor Temperatures and Space Velocities

The temperature of each catalytic reactor was monitored using five sets of
thermocouples, consisting of 12 thermocouples per set (see Figure VIC.1 – Location
12). Each thermocouple set is located in the middle of a catalyst filled tube with the 12
thermocouples distributed across the length to get a temperature profile. One set of
thermocouples in each reactor is placed in a catalyst tube that does not receive flow.
This allows for the comparison of a reacting tube to a non-reacting tube. These
temperatures were continuously monitored on the Central Control System screen and
recorded by the DCS. The space velocity was calculated in real time by summing the
volumetric flow rates of the fresh and recycled syngas and then dividing by the volume
of catalyst.

14. Tailgas Recycle Mass Flow Rates

The catalyst tailgas was recycled back through the catalytic reactor an average of about
three times (see Figure VIC.1– Location 13). The recycle volumetric flow rate was
continuously monitored and recorded by the DCS. The mass flow rate was calculated

using the volumetric flow rate and a density calculation based on the temperature, pressure and composition of the stream. The gas composition was monitored in real time using the online mass spectrometer #2.

15. Tailgas Outlet Flow Rates

The flow rate of tailgas from the LFP was monitored using a volumetric flow meter. The mass flow rate was calculated using the volumetric flow rate and a density calculation based on the temperature, pressure and composition of the stream. The composition was monitored in real time using the on-line mass spectrometer. The tailgas has some additional compositional complexity due to the presence of higher molecular weight compounds from separation off-gas streams that the on-line mass spectrometer was not able to be calibrated for. The mass flow rate accuracy was improved by using on-line GC measurements of the composition when required.

16. Fuel Production Rates

Two methods were used to quantify fuel production rates:

- A measurement of the height of the fuel in the fuel tank used for the storage of the synthetic fuel
- A real-time, automatic fuel counter

a) Fuel Storage Tanks

The IBR plant has two 3,850 gallon capacity storage tanks, one of which is used for the storage of the bulk fuel product as illustrated in Figure VIC.3

Figure VIC.3: 3,850 Gallon tanks used for the
Storage of the Synthetic Fuel and Water

Figure VIC.4 provides the dimensions for each tank. Each tank is full when the fuel reaches 123" from the bottom of the tank. Approximately 24" is left at the top of

the tanks for headspace. The volume of fuel as a function of height in the tank was determined from the following calculation (3,850 gallons/123 inches = 31.3 gallons/1.00 inch at 75°F).
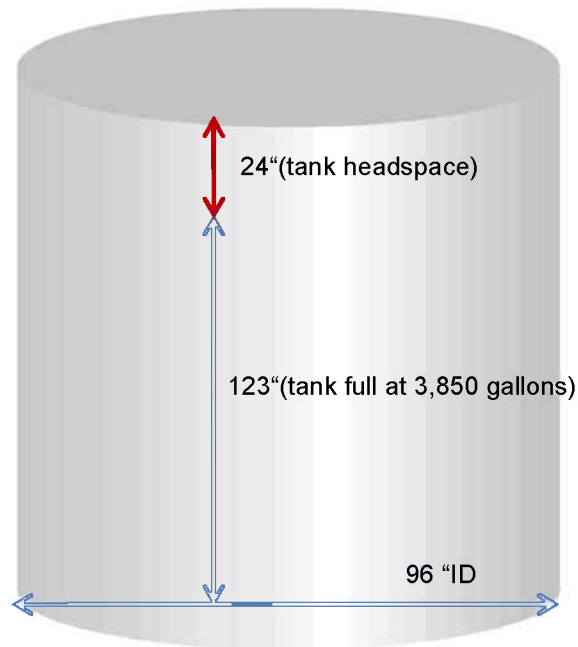
Figure VIC.4: Dimensions of the 3,850 gallon synthetic diesel fuel tank

b) Automatic Fuel Counter

An automatic fuel counter was developed to measure fuel production in real-time. The automatic fuel counter and water counter are not actual flow meters, but a calculated value based on valve positions and differential pressures across the respective valves. These values are then integrated over time. Values were calculated every second and recorded in the log file every 30 seconds. The valves used for these counters are the valves immediately exiting the 3-phase separator and are normally PID controlled via liquid level or interface level. For the water counter, there is only one valve that is used to totalize the amount of water produced, level control valve (LCV) LCV-1940, which drains water from the bottom of the 3-phase separator and is controlled via the interface level of the fuel and water. It is important to maintain a low interface level, because if it's high enough, water can spill over the weir that receives the bulk fuel product and exit with said bulk fuel through LCV-1941. LCV-1941's valve position is the primary source of the automatic fuel counter's value, and is controlled by the level of the fuel in the weir, which has spilled over. There are two more valves that can collect fuel product and tally it via the automatic fuel counter: LCV-1941 and LCV-1942, which collect fuel from the cyclones and the mesh pad respectively inside of the 3-phase separator.

Because the fuel counter depends on all of these instruments working properly, it has led to some errors and variations, but on average, the fuel counter worked well.

But there can be errors, nonetheless. One such error is that it requires accurate control via the level using PID and will not work if left in manual where the level is allowed to go to 0%. It requires that the valve be correctly calibrated so that 0% open is actually closed and anything higher than 0% results in an equal-percentage Cv consistent with Kimray's (valve manufacturer's) Cv curve. The valve was calibrated before the IE Test, but there were occasions where waxy material may have clogged the orifice and resulted in less material passing through than would have been reported by the automatic fuel counter. Suspicions of this happening resulted in a couple of cases when switching over the level control valve (LCV) to manual and cycling it between 0 and 100% to break up any clog.

Another instance of possible error may be in the interface level. On occasion, the interface seemed to be inaccurate and water would spill over the weir. This would increase the amount of fuel recorded because the level in the weir would have been raised to include the volume of water spilling over as well as the fuel. This effect was found to small however. At the end of the run, the bottom of the bulk fuel tank was drained and only 2-3 gallons of water were recovered. When water passing over was discovered, it was remedied by lowering the water-fuel interface. Because of the decrease in water volume from lowering the interface, the fuel height also decreased resulting in a period of time where no fuel left the separator, even though fuel was being produced. The water and fuel produced during that period went to re-establishing enough fuel to send it over the weir again. During a flush out period for when feedstocks were changed, the water-fuel interface level was pushed up, to push as much fuel over the weir as possible before receiving new fuel from the new feedstock. The fuel-water interface would have then been lowered to prevent spillover, and thus would have had the lag time of zero production as well.

Those were the primary challenges and sources for error in the automatic fuel counter. They compared favorably with the actual tank volume measurements that were physically measured. The tank fuel volume measurements were achieved by connecting a transparent tube to the bottom of the bulk tank and then running the tube up along the exterior of the tank and visually inspecting the resulting fuel height.

c) **Comparison of Fuel Tank and Automatic Fuel Counter Measurements**

Table VIC.4 compares incremental fuel production using the fuel tank and automatic fuel counter measurements taken during the IE Test (run #17) during September 2013. Overall, the tank and fuel counter measurements agreed to within 6 % for the IE Test runs.

Table VIC.4: A Comparison of Incremental Fuel Production using
Fuel Tank and Automatic Fuel Counter Measurements

Incremental Fuel Production		
Fuel Tank (Actual Physical Measurements) (gallons)	Automatic Fuel Counter (gallons)	Actual/Counter
272	263	1.03
200	217	0.92
301	252	1.19
222	238	0.93
204	171	1.19
287	275	1.04
1486	1416	1.05 (average)
15*	-	-
1501 (total)	1416	1.06 (average)

** About 15 gallons of additional fuel was collected throughout the IE Test
for subsequent testing and analysis.*

17. Wax Production Rates

The wax produced from the catalytic reactor was collected in a condenser held at approximately 380°F and transferred in a batch mode to the wax tank. The wax production rate was determined accurately by collecting wax in the wax condenser for 24 hours (see Figure IIC.1 – Location 14) and emptying the hot wax into a 42 gallon drum. The drum was weighed to determine the quantity of wax produced.

It was found that the wax production rate was typically less than 0.5% of the fuel produced. It was determined that this is too small of a wax production rate to warrant the cost of recycling wax into the TCC system to produce additional syngas. The amount of diesel fuel trapped in the wax was determined by gas chromatography. This analysis showed that the wax contained 50-65 wt. % of diesel fuel.

18. Water Production Rates

The water separated from the fuel was transferred to a separate tank where it is stored until used as a recycle stream into the TCC system. Water production rates were measured in the same manner as the automatic fuel counter.

D. Chemical Measurements

Figure VID.1 illustrates a process flow diagram (PFD) for the IBR plant and the locations for the collection of samples. Table VID.1 summarizes the type of samples that were

collected at each sampling location, and Table VID.2 summarizes the chemical species that were measured.
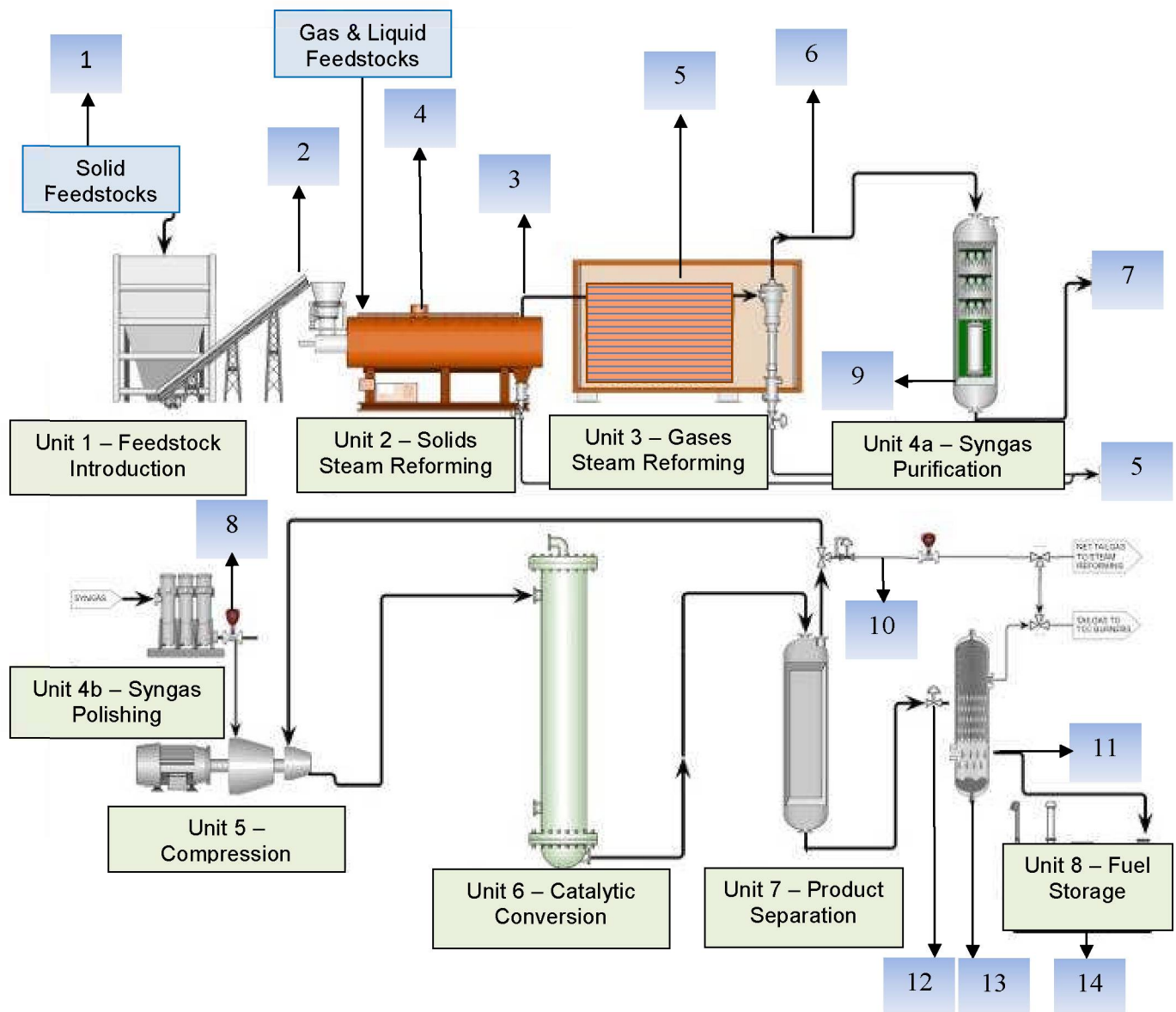
Figure VID.1: Locations for the Monitoring and Collection of Samples for the IBR Plant

Table VID.1: Description of the Sampling Locations, Sampling Procedures, Sample Sizes and Sampling Intervals

Location	Sample Locations	Sampling Procedures	Sample Sizes	Sampling and Analysis Procedures
1 & 2	Feedstock storage and introduction	Grab	2 x 100 g	24 hr. samples combined for analysis (Section C1a, C1b)
3	Gases from solids steam reforming	Integrated SS cylinder	2 x 1.0 liter	No testing planned
4	Stack emissions from gas heaters	EPA stack methods	EPA protocol	3rd Party test objective (1-2 months before IE Test)
5	Ash augers	Grab	2 x 100 g	Composite 24 hr. samples for analysis (Section C3a)
6	Hot syngas (after cyclones)	NREL on-line TMBMS	Continuous sampling	3rd Part test objective
7	Syngas before polishers	Dräger tubes and on-line MS	Various	See Sections C3a-C3e
8	Syngas after polishers	On-line Jerome™ instrument	Various	See Sections C4a-C4d
9	Water scrubber tank	Grab	2 x 1.0 liter	See Sections C5a-C5b
10	Syngas recycle stream	On-line GC	GC sample loop	See Sections C6a-C6b
11	Fuel from fuel fraction collector	Grab	2 x 100 mL	See Sections C7a-C7b
12	Wax from wax fraction collector	Grab	2 x 25 g	See Section C8a
13	Water from aqueous collector	Grab	2 x 100 mL	See Section C8b
14	Fuel from 3,850 gallon tank	Grab	2 x 100 mL	The fuel is transferred to Port of Toledo tank storage as required per site permits

Table VID.2: Description of the Sampling Locations, the
Chemical Species to be measured and the Analytical Procedures Employed

Location	Sampling Location Identification	Species to be Quantified
1&2	Feedstock Introduction	H_2O content; proximate and ultimate analysis
3	Gases from solids steam reforming (before polisher)	H_2; CO; CH_4; CO_2; total C_4-C_8 HC's; benzene and toluene
4	Gases from solids steam reforming (after polisher)	H_2; CO; CH_4; CO_2; total C_4-C_8 HCs; benzene and toluene
5	Ash from SSR and cyclones	Elemental carbon; volatile carbon;
7	Syngas before sulfur and ammonia polishers	H_2; CO; CH_4; CO_2; total $C_4 - C_8$ HCs); benzene and toluene; total particulates; H_2S; NH_3
8	Syngas after sulfur and ammonia polishers	H_2; CO; CH_4; CO_2; $C_4 - C_8$ HCs; benzene and toluene; total particulates; H_2S; NH_3
9	Water scrubber tank	TOC; solids; several anions and cations
10	Syngas recycle stream	H_2; CO; CH_4; CO_2; $C_4 - C_8$ HCs; benzene and toluene
11	Diesel fuel from fuel fraction collector	$C_6 - C_{24}$ HCs
12	Wax from wax fraction collector	C_{10}-C_{40} HCs
13	Water from aqueous fraction collector	C_1-C_5 alcohols; total organic carbon (TOC); pH
14	Fuel from 3,850 gallon tank	$C_6 - C_{24}$ HCs

1. Characterization of Feedstocks

Approximately 2 liters of feedstock were collected every 4 hours during plant operation. These samples were typically consolidated into a 24 hour composite sample, which was used for moisture, proximate and ultimate analysis.

Figures VID.2 and VID.3 illustrate the typical size distribution of the wood chips and rice hulls, respectively. The wood chips ranged from 0.15" to 2.5" in size. Wood chips less than 0.15" were removed by screen segregation. The rice hulls averaged about 0.50" in length.

Figure VID.2: Size Distribution of the Wood Chips

Figure VID.3: Size Distribution of the Rice Hulls

a) Moisture Analysis

The moisture content of the feedstocks was used to determine how much steam should be fed into the TCC system as well as for determining the feedstock carbon conversion efficiency to fuel. Feedstock moisture analysis was carried out using a drying oven following ASTM method #D442 and an AGS 100 Moisture Analyzer purchased from Torbal Scales.

ASTM method #D442 was found to be the more accurate method for determining moisture content. Approximately 10 g samples of the wood chips were added to a beaker and weighed. The sample was placed in an oven heated to 210-220 °F and kept there until no appreciable weight change occurred. The moisture content was determined using the following formula:

Moisture (%) = ((Wood Chip Wt. - Oven Dry Wt.)/Oven Dry Wt.)) (100)

The AGS 100 Moisture Analyzer utilizes a drying oven that uses two halogen heating elements to provide high speed infrared heating. Each element is operated at half of its rated voltage, thereby providing for reliable operation and greatly extended life. Temperature is sensed in good proximity to the samples for better control. This instrument is set-up in a laboratory which is about 500 feet from the IBR plant. Although this analyzer produces quick results, we believe that does not provide results that are as accurate as the ASTM method.

Table VID.3 summarizes the moisture content of wood and rice hull feedstocks collected during various IBR plant tests using ASTM method #D442.

Table VID.3: The Moisture Content of Wood and Rice Hull Feedstocks Collected During Various IBR Plant Tests

Sample ID	Feedstock Sample	H_2O (%)
Run #17 - 9/15/2013 (11:00 am) to 9/17/2013 (11:00 am)	Rice Hulls	9.7
Run #17 - 9/17/2013 (11:00 am) to 9/18/2013 (7:00 am)	Rice Hulls	11.5
Run #17 - 9/18/2013 (7:00 am) to 9/19/2013 (7:00 am)	Wood Chips	14.5
Run #17 -9/19/2013 (7:00 am) to 9/19/2013 (3:00 pm)	Wood Chips	16.1

b) Proximate and Ultimate Analysis

Proximate and ultimate analysis of the wood feedstock was carried out by SGS Labs (South Holland, Illinois) and Hazen Labs (Denver, CO).

Table VID.4 summarizes the composition of the wood and rice hull feedstocks collected during run #17 using ASTM method #D442. The ash content of the wood and rice hulls averaged 0.75 and 21.8 wt. %, respectively. The high ash level of the rice hulls are primarily due to the high levels of silica. The carbon content of the wood and rice hulls averaged 49.6 and 37.0 wt. %. The total hydrogen, oxygen and nitrogen averaged 41.4 wt. % for the rice hulls and 47.1 wt. % for the wood.

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Table VID.4: Summary of Typical Feedstock and
Biochar Composition Results

Sample #	Sample Type	Weight %					
		C	**Ash**	**O, H**	**N**	**S**	**Total (%)**
Run #5	Wood Chips	49.3	0.71	49.9	0.06	0.013	100.0
Run #17		50.0	0.80	49.1	0.06	0.015	100.0
Run #5	Wood Chip Biochar	80.9	10.3	8.4	0.39	0.048	100.0
Run #17		7	11.8	8.3	0.43	0.037	100.0
Run #13	Rice Hulls	37.5	22.5	39.3	0.52	0.130	100.0
Run #17		35.5	21.2	42.7	0.48	0.110	100.0
Run #13	Rice Hull Biochar	35.2	59.8	4.3	0.69	0.030	100.0
Run #17		41.7	53.3	4.3	0.65	0.022	100.0

Table VID.5 summarizes the average volatile organic carbon and fixed (elemental) carbon constituents in the total feedstock carbon content. For example, 86.2 and 13.8 weight % of the 49.6 weight % of carbon in the wood feedstock is volatile organic carbon and fixed (elemental carbon), respectively.

Table VID.5: Average Volatile Organic Carbon and
Fixed (Elemental) Carbon Constituents in Total Feedstock
Carbon Content (Composite Sample from Run #17)

Property	Wood (Wt. %)	Rice Hulls (Wt. %)
Volatile Organic Carbon	86.2	79.7
Fixed (Elemental) Carbon	13.8	20.3

2. Characterization of Ash and Tars

a) Ash from Solids Steam Reformer and Cyclones

Samples were collected from the Unit Operation #2 ash bin and cyclone ash augers every 1-2 hours. After the ash was cooled, the samples were weighed, sealed in glass containers, and labeled.

Table VID.6 summarizes the average moisture content of the wood and rice hull biochar for a composite sample from run #17. The higher concentration of water in the rice hull ash may be due to the hydroscopic nature of the ash, which is primarily silica.

Table VID.6: Average Moisture Content of Wood and Rice Hull
Biochar (Composite Sample from Run #17)

Property	Wood (Wt. %)	Rice Hulls (Wt. %)
% Moisture Content	20.5 ± 1.0%	17.5 ± 1.5%

Table VID.7 summarizes the average elemental composition of wood and rice hull biochar for a composite sample from run #17.

Table VID.7: Elemental Composition of Wood and
Rice Hull Biochar (Composite Sample from Run #17)

Property	Wood (Wt. %)	Rice Hulls (Wt. %)
Carbon	71.5 ± 2.5%	38.5 ± 3.5%
Ash (All Other Elemental Constituents)	29.5 ± 2.5%	61.5 ± 3.5%

Table VID.8 provides the average proportion of volatile organic carbon and fixed (elemental) carbon in the total biochar carbon content for the wood feedstock.

Table VID.8: Characterization of Ash from the
Conversion of Wood to Syngas

Property	Wt. %
Fixed (Elemental) Carbon	90.8
Volatile Organic Carbon	5.3
Inorganic Components (ash)	3.9

b) Tars from the Tar Collector

Figure VID.4 illustrates the sub-processes in Unit Operations #4a-1, 4a-2, 4a-3 and 4a-4 that are employed to purify the syngas generated from Unit Operation #3. The tars generated from the IBR plant are classified into two types:

- *Type A Tars* - Aromatic compounds with 2-3 rings (volatile and semi-volatile tars) such as Naphthalene and Anthracene.

- *Type B Tars* - Aromatic compounds with 4 or more rings (non-volatile tars) such as Pyrene and Benzo (a) pyrene

Volatile hydrocarbons, such as guaiacol, benzene, toluene, and phenol, will pass through the catalyst bed unreacted and become included with the diesel fuel fraction. Therefore, these volatile HCs are not classified as tars.

#4a-1   #4a-2   #4a-3   #4a-4

```
┌──────────┐   ┌─────────┐   ┌─────────┐   ┌──────────┐   ┌──────────┐
│   Unit   │──▶│ Cyclone │──▶│  Quench │──▶│  Water   │──▶│  Water   │
│Process #3│   │         │   │  Column │   │ Scrubber │   │ Scrubber │
└──────────┘   └─────────┘   └─────────┘   │   #1     │   │   #2     │
                                  │        └──────────┘   └──────────┘
                                  ▼             ▼              ▼
                             ┌─────────┐   ┌─────────┐   ┌──────────┐
                             │   Tar   │   │  Waste  │   │  Syngas  │
                             │Collector│   │  Water  │   │   Flow   │
                             └─────────┘   │  Sludge │   │  Meters  │
                                           └─────────┘   └──────────┘
```
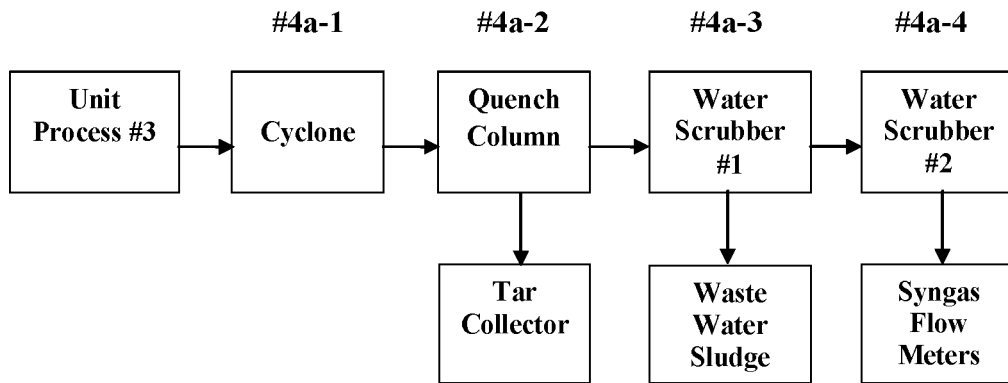
Figure VID.4: Syngas Purification #4a-1 to #4a-4 Unit Operations

Since it was found that some tars were being collected in the transfer pipe between 1) the cyclone and quench column and 2) the quench column and water scrubber, tar collectors were designed and installed to trap and collect tars.

About 900 grams of tar was collected in the tar collector in run #9 during which 585,400 ft^3 (15,570 m^3) of syngas was generated from approximately 20,000 lbs. of wood input at an average feedstock rate of 10.7 dry (ash free) tons/day.

From this data, it is estimated that the concentrations of Type A and Type B tars collected in the tar collector were about 9.1 ppm or 56 mg/m^3. From the data in VID.10 another 1.13 ppm of tar was collected in the transfer pipe between the quench column and water scrubber, the transfer pipe between water scrubber #1 and water scrubber #2 and the syngas flow meters.

Much smaller quantities of tar were found after the water scrubber, the sulfur scrubber and the syngas flow meters. The concentrations of Type A and Type B tars were determined and the ratios of Type A tars and Type B tars are summarized in Table VID.9.

The composition of the Type A and Type B tars in Tar Collector #1 and deposited on the syngas flow meters are summarized in Section XIIIC. The concentration of benzene measured during this run using the mass spectrometer averaged about 3,800 ppm for the wood feedstock. Therefore, the ratio of benzene to tars was 704/1.0.

Table VID.9: Ratios of Naphthalene to Benzo (a) pyrene (BaP) for
Samples Collected at Various Points in Unit Operations #4a-1 to #4a-4

Sample Location (See Figure VID.4)	Total Material Collected (ppm)	Type A PAHs (ppm)	Type B PAHs (ppm)	Ratio Type A/B PAH's
Tar Collector #4a-2	5.4	4.6	0.81	0.57
Transfer Pipe between Quench Column and Water Scrubber	0.34	0.33	0.011	29.5
Transfer Pipe between Water Scrubber #1 and Water Scrubber #2	0.23	0.23	0.0035	65.7
Syngas Flow Meters	0.17	0.17	< 0.002	> 87
Total	6.14	5.33	0.82	-

Since the ratio of Type A tars to type B tars increased as the syngas flowed through the different syngas purification processes (0.57/1 to > 87/1), it was concluded that the nearly all of the Type B tars were removed by the time the syngas reached the syngas flow meter. This conclusion was confirmed by opening up the flow meter and piping. After several hours of exposure to the atmosphere, all of the Type A tars evaporated. These vapors from this exposure had the characteristic naphthalene odor. After the Type A tars had evaporated, Type B tars were not observed on the surfaces. Table VID.10 summarizes the concentrations of Type A and Type B tars collected in the tar collector compared to the concentrations of benzene and toluene measured using the on-line mass spectrometer.

Table VID.10: A Comparison of Tars, Benzene and Toluene
Generated from Unit Operation #3 before Syngas Purification

Syngas Contaminant	Concentration (ppm)
Benzene	3,800
Toluene	29
Type A Tars	4.6
Type B Tars	0.81

The real-time particulate analyzer measured an average of 25 micrograms/m^3 in the purified sygnas over several runs. Therefore, the efficiency of Unit Operations #6-7 for removal of Type B tars was better than 99.85% (1.3/<0.002 from Table VID.9). Although some naphthalene remained in the syngas (0.174 ppm) before the compression step, no naphthalene has been detected in the fuel to date.

Figure VID.5 illustrates the relationship between the concentrations of benzene in ppm as a function of rice hull input in tons per day. The background concentration of benzene in the IBR plant was about 150 ppm when no rice hulls were being introduced into the plant. It is seen that the concentration of benzene was not dependent upon the quantity of rice hulls being converted to syngas.
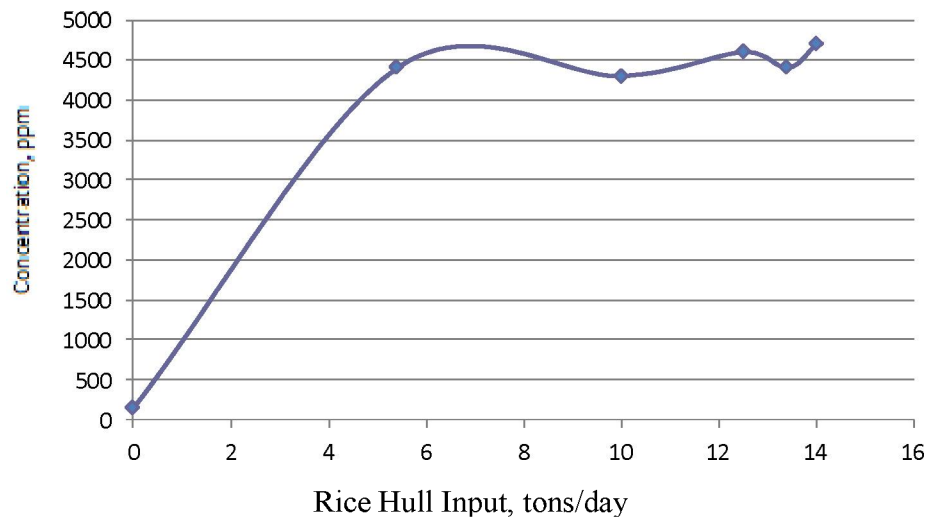
Figure VID.5: The Concentration (ppm) of Benzene in the Syngas as a Function of Rice Hulls Input (Tons/Day)

3. Characterization of Syngas and Syngas Contaminants

The National Renewable Energy Laboratory (NREL) shipped and installed their Transportable Molecular Beam Mass Spectrometer (TMBMS) (Figure VID.6) at the Toledo IBR plant site during September 2013.

This instrument was used to characterize hot syngas (at approximately 650 °C) generated after Unit Operations #3-4 (after the cyclones and before the scrubbers) and purified, syngas after Unit Operation #8 in real-time during the Independent Engineer (IE) test carried out during September 8-20. This instrument was able to monitor higher molecular weight compounds than could be measured using the Ametek mass spectrometers which had a mass limit of 100 AMU (Section VID.3).

A comparison of syngas contaminants measurements in the hot syngas and the purified syngas provided valuable data on the efficiency of the syngas purification systems for the removal of syngas contaminants.

Figure VID.6: NREL TMBMS Instrument Collecting Syngas
Data at the Toledo IBR Plant Site

Figure VID.7 shows a typical mass spectrum generated from the analysis of hot syngas (at 650 °C) generated from the conversion of rice hulls using the NREL TMBMS instrument. The tar species observed in the raw syngas were typical of those generated during biomass gasification, and were dominated by benzene, small amounts of polycyclic aromatic hydrocarbons (naphthalene, phenanthrene, pyrene), and trace amounts of fused-ring and alkyl derivatives (toluene, indene, acenaphthene).

The inset shows the portion of the spectrum from m/z 100-300, zoomed in to 5% of the base peak (methane). Omitted from the scan were m/z 18, 28, and 44 (H_2O, $CO/N_2/C_2H_4$, and CO_2, respectively) due to concerns over saturating the detector. The grouping of peaks seen between methane and benzene are primarily attributable to fragment ions and isotopes of high-concentration products, e.g. m/z 29 and 45 from ^{13}CO and $^{13}CO_2$.
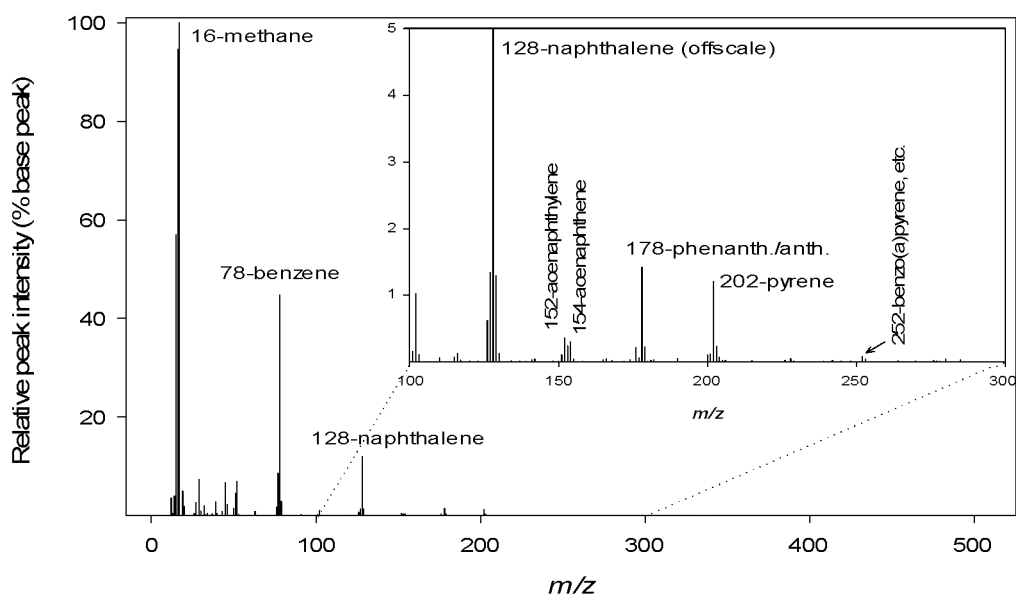
Figure VID.7: Averaged Mass Spectrum Showing Hot Syngas Products
Observed during 5.0 tpd Rice Hull Gasification (Run #17)

Benzene and naphthalene were the predominant aromatic compounds in the syngas
samples from the thermochemical conversion of wood and rice hulls (Table VID.11).
The background levels for the benzene and naphthalene were 19 and 2 ppmv,
respectively.

The benzene in the partially purified syngas averaged 6,080 ppm for the rice hulls and
4,470 ppm for the wood. The concentration of benzene was not affected by the amount
of biomass being reformed and it was not removed by the syngas purification system.
In contrast, greater than 95% of the naphthalene was removed and all other PAH
compounds were removed with an efficiency of greater than 99.9%.

Table VID.11: Concentrations of Benzene, Toluene,
Type A Tars and Type B Tars in the Hot (Unpurified Syngas) and the
Partially Purified Syngas (after Unit Operation #6) from the
Thermochemical Conversion of 5.4 tons/day of Rice Hulls

Component	6.3 Tons/Day (ppm) (bd: below detection)			11.6 Tons/Day (ppm) (bd: below detection)		
	Hot Syngas	Partially Purified Syngas	Hot Syngas	Partially Purified Syngas	Hot Syngas
Benzene	1712	4682	1606	4252	2123
Toluene	20	90	19	63	33
Type A Tars					
Phenol	bd	15	bd	bd	bd
Naphthalene	231	25	236	15	348
Phenanthrene	27	2	33	bd	64
Type B Tars					
Pyrene	29	3	36	bd	bd
Tars Heavier than Pyrene	bd	bd	bd	bd	bd
Total Tars					
Total Tars (excluding benzene and toluene)	287	45	305	15	529
Estimated H$_2$O Content (%)	67%	23%	68%	25%	71%

a) Characterization of Syngas After Purification

Several on-line and batch analytical techniques were employed for the characterization of the syngas after purification. These analytical techniques are described in this section.

One quick method to determine the purity of the syngas at this stage was to exhaust some of the purified syngas through the syngas flare. As noted in Figure VID.8 this flare was not visible when the syngas is free of impurities, whereas the raw, unpurified syngas produced a visible flame.

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Figure VID.8: Flaring of the Raw, Unpurified
Syngas (left photo) and Purified Syngas (right photo)

b) Real Time Syngas Analysis

Teflon sampling lines were used to transfer the purified syngas from the line after the polishers to the real-time instruments and the integrated sampling systems in Analytical Trailer #1.

During the initial tests in May of 2012, condensed water collected in the sampling lines to the analytical trailer, which adversely effected the measurements. Therefore, the sampling lines were modified to reduce this problem. The sampling lines to the second MS in Analytical Trailer #2 did not have a water condensation problem and therefore the sampling system was not modified.

Two Dycor Proline™ Process Mass Spectrometers from Ametek™ Process Instruments was used to measure major components of syngas (greater than 1.0 volume %) on a real-time basis. The specifications for this instrument are included in Table VID.12. These mass spectrometers served as the primary instrument for syngas analysis. Its sampling speed is 6 samples per minute, which provides high speed analysis for true process control. It also performs simultaneous specific gravity and syngas BTU calculations.

Table VID.12: Specifications for the Dycor Proline Mass Spectrometer

Measurement Specifications	Values
Mass Range	0-100 AMU (mass units)
Detection Range	100 ppm to 100%
Accuracy	> 0.5% for argon in air
Outputs	RS-485, RS-232, 4-20mA
Response time	Less than a minute

The calibration gas standards contained 1% butane in addition to the regular syngas constituents.

Some of the chemical species that have the potential of being detected at various masses (AMU) are summarized in Table VID.13. The syngas components that were measured are highlighted in **bold font**. The concentrations of benzene and toluene were monitored as chemical markers for the possible formation of tars.

It is well known that benzene and toluene are typically formed at ratios of 2/1 to 5/1 from the combustion of fuels and the thermal steam reforming of carbonaceous feedstocks (Schuetzle, 1983). This is most likely the case for the steam reforming of wood and rice hull feedstocks in Unit Operation #2. However, the high temperature steam reforming of the gases formed in Unit Operation #2, reduces the concentration of the more reactive toluene compared to the chemically stable benzene, resulting in a 95/1 benzene to toluene ratio. Since the Type A and Type B tars, are also relatively easy to steam reform at 1,750-1,800 °F, the monitoring of toluene serves as a good surrogate for the presence of PAHs in the syngas.

Table VID.13: Potential Chemical Species in Syngas (N_2 free) that can be Selectively Detected in the 1-100 AMU Range

Chemical Species	Mass (AMU)
Hydrogen	**2**
Methane	**16**
Ammonia	17
Carbon Monoxide	**28**
Nitrogen	28
Ethane	30
Ethanol	31
Oxygen	32
Hydrogen Sulfide	34
Argon	**40**
Total Hydrocarbons (as butane)	**43**
CO_2	**44**
Ethanol	46
Carbonyl Sulfide; Acetic Acid	60
Sulfur Dioxide	64
Benzene	**78**
Toluene	**92**
Phenol	**94**
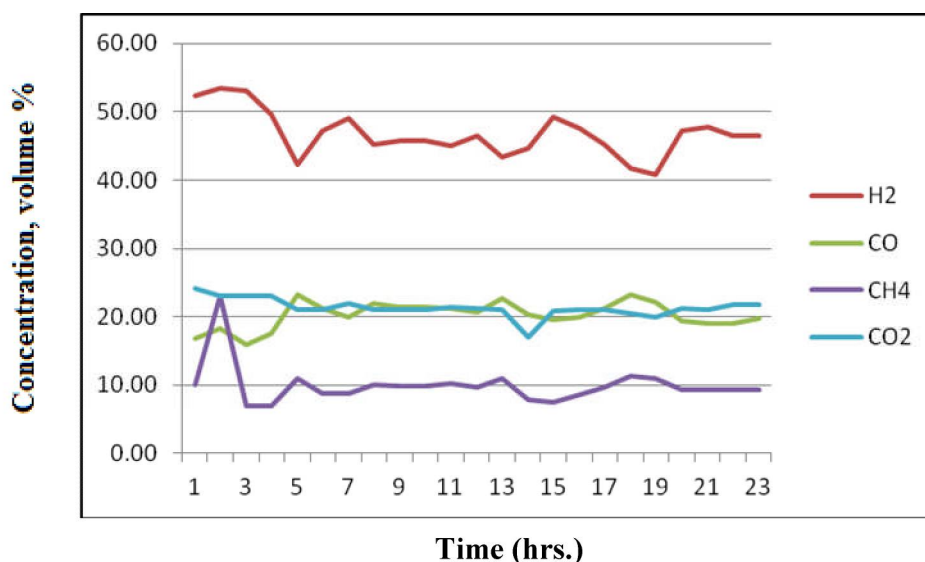
Time (hrs.)

Figure VID.9: Monitoring of Syngas Produced from the Thermochemical Conversion of Rice Hulls [volume % vs time (hrs.)]

c) Real-Time Particulate Analysis

The particulate levels in the syngas were measured in real-time using a Dustrak DRX Aerosol monitor, which simultaneously measures both particulate mass and size fraction. This monitor is a battery-operated, data logging, light scattering laser photometer that gives real-time aerosol mass readings corresponding to PM1, PM2.5, PM10, and Total PM. It has 5 MB of on-board data memory (which is greater than 60,000 data points). The specifications for this unit are listed in Table VID.14.

Table VID.14: Specifications for the TSI 8533
Dustrak DRX PM Analyzer

Measurement Specifications	Values
Detection Range	$1 \ \mu g/m^3$-$150 \ mg/m^3$
Resolution	$\pm 0.1\%$
Response Time	1 to 60 sec, user adjustable
Sample flow	3.0 L/min

d) Integrated H₂S, SO₂ and NH₃ Analysis

Dräger tubes were used to monitor the concentration of the syngas contaminants, H_2S, SO_2 and NH_3. Dräger tubes are glass tubes (Figure VID.10) packed with specific chemical reagents that react with selected chemical compounds that produce a colored product. When a specific gas, such as hydrogen sulfide (H_2S), is passed through a Dräger Tube it reacts with the specific chemical reagent to produce a colored reaction product. When a gas sample containing a specific substance is passed through the tube at a specific sampling rate, the length of discoloration in the tube is directly proportional to the concentration of that specific substance.

A scale is printed on each tube to allow a direct reading of the concentration of the desired substance (Figure VID.10). Thus, calibration by the user is not necessary. The length of the discoloration on the printed scale allows a direct reading of the concentration. The calibration scale is typically provided in ppb, ppm or volume % units.

The Dräger Tubes are used for the integrated analysis of H_2S, SO_2, NH_3 and toluene in the syngas samples. The sampling times required for various concentration ranges are summarized in Table VID.15.

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Table VID.15: Sampling Times and Concentration Ranges for
Syngas Contaminants using Dräger Tubes

Chemical Species	Gas Sample Required	Tube Calibration Range	Notes
H_2S	1,000 mL	0.10-5.0 ppm	Use tube scale
NH_3	1,000 mL	0.15-3.0 ppm	Use tube scale

Figure VID.10: Example of a H_2S Dräger Tube before (left) and
After Elution with 2.0 ppm of H_2S in Air (right)

e) Real-Time Analysis H_2S Analysis

A Jerome J605 H_2S analyzer was used for the real-time analysis of H_2S after the polishers. The specifications for this analyzer are provided in Table VID.16.

Table VID.16: Specifications for the Jerome J605 H_2S Analyzer

Measurement Specifications	Values
Detection Range	3 ppb - 10 ppm
Resolution	20 ppt (0.02 ppb)
Response Time	12-52 seconds

This instrument does not require PC software since it incorporates an on-board data logger that stores the date, time and H_2S concentration. The data logger has a storage capacity of 20,000 data points and a USB interface for data transfer. It also has SCADA interface capabilities with 4-20 ma output.

f) Integrated NH_3 Analysis

Ammonia Dräger tubes were used to measure the concentration of ammonia in the syngas after the polishers.

4. Characterization of Water Scrubber Constituents

The testing for scrubber water and wastewater quality was carried out by Jones and Henry Labs (Northwood, Ohio).

a) Scrubber Water

Table VID.17 provides a typical analysis of scrubber water from the characterization of the scrubber water from IBR plant test #9. The pyrolysis of wood forms phenolic and organic acids, most of which will be reformed in Unit Operation #3. If some of these compounds are not reformed, then they will be removed in the water scrubber since phenolics are partly soluble in water. The concentration of total organic carbon in the water sample was very low (38 Mg/L) which confirms that the steam reforming process was very efficient.

It was expected that sulfide wouldn't be found in this water sample, since hydrogen sulfide would not be removed from the gas stream at the nearly neutral pH conditions. However, sulfates (161 Mg/L) will be removed from the gas stream since they are very soluble in water.

Table VID.17: Results from the Characterization of Scrubber
Water from IBR Plant Test #9

Test Parameter	Results	Units
pH at 25°C	7.13	Std.
Conductivity at 25°C	1860	μmhos/cm
Turbidity	14.1	NTU
Alkalinity as CaCO$_3$	744	Mg/L
Cyanide, Total	58.1	Mg/L
Chloride	112	Mg/L
Chemical Oxygen Demand	516	Mg/L
Oil & Grease	Not detected	Mg/L
Total Organic Carbon	**38**	**Mg/L**
Total Solids, 104°C	962	Mg/L
Suspended Solids, 104°C	192	Mg/L
Volatile Suspended Solids, 550°C	164	Mg/L
Dissolved Solids, 180°C	730	Mg/L
Silica, molybdate reactive	45.2	Mg SiO$_2$/L
Sulfate	**161**	**Mg/L**
Sulfide	Not detected	**Mg/L**
Nitrogen, nitrate + nitrite	0.45	Mg/L
Phosphorous	4.77	Mg/L
Calcium, total	64.3	Mg/L
Magnesium, total	29.9	Mg/L
Potassium, total	87	Mg/L
Sodium, total	48.5	Mg/L
Aluminum, total	62	μg/L
Arsenic, total	8	μg/L
Barium, total	104	μg/L
Boron, total	630	μg/L
Cadmium, total	Not detected	μg/L
Chromium, total	Not detected	μg/L
Cobalt, total	6	μg/L
Iron, total	277	μg/L
Lead, total	Not detected	μg/L
Manganese, total	1500	μg/L
Mercury, total	Not detected	μg/L
Nickel, total	408	μg/L

GC and GC/MS was used to identify and quantify the organic constituents in the
scrubber water. C_2-C_6 hydroxy-alkanes were the predominant organic species
identified in the water (Figure VID.11). The concentration of the hydroxy-alkanes
in this sample totaled 1.02%. A small quantity (0.05%) of benzene was also found
in this water sample. Although low concentrations of benzene were found in most
of the water scrubber samples from the thermal reforming of rice hulls and wood,

no benzene was detected in the water samples generated from the methanol/CO_2 mixtures.
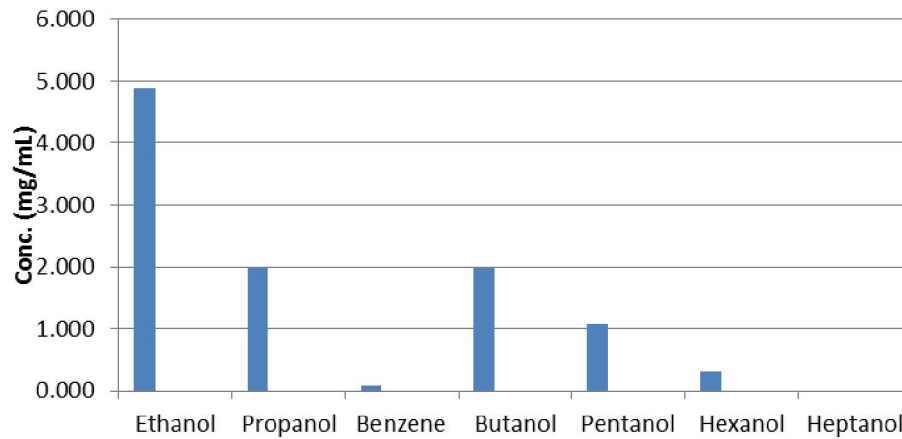
Figure VID.11: The Identification of Organic Constituents in the Scrubber Water Generated from the Thermal Reforming of Wood

b) Scrubber Water Solids

The scrubber water from the TCC process was sent to the filter press to filter any suspended solids. This solid filtered material is called the filter press cake. Although the amount of filter press cake was expected to be minimal, the chemical composition of this cake was used for the mass balance calculations. Sampling of the filter press cakes were carried out at the end of each test. A typical analysis is presented in Table VID.18.

A total of 20 lbs. of scrubber water solids were collected during this plant test #9 over a period of 20 hrs. The average dry (ash free) wood input rate over this time period was 10.7 tons/day or a total of 20,000 pounds. It can be concluded that the cyclones are very efficient in collecting particulates since very little particulate matter is collected in the scrubber water. The organic carbon fraction probably consists of unconverted light, Type A tars.

Table VID.18: Results from the Characterization of Scrubber Water Solids from IBR Plant Test #9

Component	Method	Composition (dry) (Wt. %)
Ash	ASTM D3174/D7582	4.0
Fixed Carbon	ASTM D3172	67.1
Organic Carbon	ASTM D5373	25.0
Carbonates	ASTM D1756	1.1

5. Characterization of Recycle and Tail Gases from the Fuel Production System

A second Ametek mass spectrometer was used to continuously characterize syngas recycle gas from the Fuel Production System (Figure VID.1 - sampling location #10). In addition to monitoring H_2, CO, CO_2 and CH_4, this instrument was capable of monitoring total C_2-C_8 HCs and benzene. Argon was injected into the TCC system and used as an internal standard. In addition, DRI utilized their real-time instruments and integrated sampling systems to collect and quantify the chemical components in the tail gas (see Section XIIIB.2).

a) Catalyst Recycle Gas

The catalyst recycle syngas was monitored using the second quadrupole mass spectrometer. These measurements were used to help adjust the recycle to tailgas exhaust ratios so that the catalyst could be operated to achieve > 90% conversion for CO.

b) Tail Gas (After Fuel Collection)

Diluted tailgas samples collected downstream of the liquid fuel production (LFP) unit were characterized by GC/MS. Total VOC concentrations (in undiluted tailgas) were approximately 1-3 vol. %. These VOCs consisted primarily of C_2-C_6 alkanes and alkenes. SVOCs were present in lower concentrations (< 2 %), and consisted primarily of C_8-C_9 alkanes and alkenes. The overall low concentrations of VOCs and SVOCs in tailgas confirmed that both the catalytic LFP unit and the diesel fuel collection system within the IBR were functioning properly (see Section XIIIB.2 for additional details).

6. Characterization of Fuel Products

Duplicate 3.0 mL fuel samples were collected in 4.0 mL glass vials with Teflon lined polypropylene caps directly from the plant fuel production process every 8 hours.

a) Speciation and Quantification of Fuel Constituents

One of the 3.0 mL samples was archived and the other 3.0 mL sample was used for the characterization of C_4-C_{24} alkanes, alkenes, aromatics, and hydroxy-alkanes using an HP 5890 capillary column GC.

b) ASTM Tests

The fuel samples were characterized using ASTM test procedures. Table VID.19 summarizes the average results from those tests compared to EPA and CA #1 and #2 diesel fuels.

Table VID.19: The Average Properties of the Synthetic Diesel Fuel
Produced from the 2012-13 IBR Plant Runs Compared to
ASTM Diesel #1 and #2 Specifications (nd: not determined)

Fuel Specifications (ASTM Test #)	Synthetic Diesel	ASTM Diesel #1 - #2 Specs. (U.S.)*	ASTM Diesel #1 - #2 Specs. (CA)*
Cetane Index (D 976)	70	> 42-45	> 53
Fuel Energy Content (BTU/gallon)	123,500	No Specs.	**122,500-128,700**
Flash Point (°F) (D 93)	105	100-125	100-130
Cloud Point (°F) (D 2500)	7	10	10
Pour Point (°F) (D 97)	-0.4	-5.8	-5.8
Density (g/mL) (68°F)	0.76	No Specs.	**0.81-0.84**
Lubricity (HFRR) (max.) (D 6079)	371	520	520
Viscosity (mm^2/s) (104°F) (D 445)	2.0	1.3 - 4.1	1.8 - 4.1
Copper Corrosion (122°F) (D 130)	Class 1a	Class 3	Class 3
Oxidative Stability (D 2274) (mg/0.1 L)	0.1	1.5	1.5
API Gravity (104°F)	54.7	No Specs.	> 37
High Temperature Stability (D 6468)	99	**99**	**99**
Sulfur (ppm) (max.) (D5453)	< 0.1	15	15
Aromatics (%) (max.) (D1319)	< 0.3	35	< 21
PAHs (%) (max.) (D5186)	< 0.1	3.5	3.5
Benzene (%)	< 0.1	No Specs.	No Specs.
Olefins (%)	1.5	No Specs.	No Specs.
Oxygen Content (%)	0.21	No Specs.	No Specs.
5% Point (max.) (D86)	342	363	No Specs.
50% Point (max.) (D86)	478	504	560
90% Point (max.) (D86)	636	640	610
Final Boiling Point (max.) (D86)	696	689	660

*Values in **blue font** are typical values for California diesel fuels in cases where there are no established fuel specifications.

c) Distillation

Intertek Corporation (Pittsburgh, PA) was contracted to distill the fuel produced from the IBR plant. The objective of this distillation was to fractionate about 20 gallons of fuel as follows:

- Batch fractionate the fuel to generate an IBP to 225°F fraction;
- Collect subsequent fractions in 25°F increments until the maximum possible cut point is reached;
- Characterize each fraction including the bottoms fraction.
- Combine fractions to generate a syndiesel targeting a flash point specification meeting diesel fuel specifications and with a 90% distillation point at 640°F.

7. Characterization of Side-Products

a) Wax

Wax samples were collected from the Product Separation System (Unit Operation #7) every 8 hrs. Much less wax was produced from the IBR plant than projected from the laboratory and process development unit (PDU) tests. This reduction in wax production resulted in additional diesel fuel production. It was found that the wax typically contained about 50% fuel. Although the Toledo IBR plant doesn't have a distillation column to remove this fuel fraction from the wax fraction, the first commercial plant has been designed to include distillation (see Section XII.E).

b) Water

Table VID.20 lists the organic constituents identified in the water generated from the catalytic conversion of the syngas.

Table VID.20: The Identification of Organic Constituents in the Water generated from the Catalytic Conversion of Syngas (Run #16)

Compound	Wt. %
Methanol	0.469%
Ethanol	0.542%
1-Propanol	0.224%
1-Butanol	0.141%
Pentanol	0.097%
1-Hexanol	0.033%
1-Heptanol	0.005%
1-Octanol	0.001%
1-Nonanol	0.000%
1-Decanol	0.000%
Total	**1.51%**

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8. Air Emissions from Gas Burners

Since the gas burners are well-defined components, it was decided that testing of the emissions generated from these burners was not necessary. Table VID.21 summarizes the emissions factors for the gas burners used in the IBR plant.

Table VID.21: Emission Factors for the Gas
Burners used in the IBR Plant

Emission Constituent	Emission Factors (lbs./10^6 scf)	Emission Factors (lbs./10^6 scf) with SCR NOx Control
Hydrocarbons	11.0	11.0
Methane	2.3	2.3
Carbon Monoxide	84.0	84.0
Nitrogen Oxides	50.0	5.0
Nitrous Oxide	0.64	0.06
Sulfur Dioxide	0.60	0.60
Particulates (Total)	7.6	7.6
Particulates (Condensable)	5.7	5.7
Particulates (Filterable)	1.9	1.9
CO_2	1.17×10^5	1.17×10^5

VII. Data Analysis

A. Feedstock Carbon Conversion Efficiency

The carbon conversion efficiency was determined by utilizing a couple of approaches as follows:

1. Approach #1

This approach compares the mass input of carbon in the feedstock (FS_c) to the mass output of carbon in the ash (Ash_c) for determining the carbon conversion efficiency as follows:

$$\% \text{ Carbon Conversion Efficiency} = (FS_c - Ash_c)/FS_c \times 100$$

2. Approach #2

This approach compares the mass of carbon introduced into the thermochemical conversion system with the mass of carbon containing compounds (CO, CO_2, and C_2-C_8 HCs) produced. An example of that calculation is shown in Table VIIA.1 for wood. In this example, the carbon conversion efficiency was found to be 86.1%.

Table VIIA.1: Carbon Mass Balance for Wood Conversion to Syngas (Run #9)

Syngas Component	Mole% in Syngas	Total Syngas Moles	Total Syngas Mass (lb.)	Total Carbon Mass (lb.) in Syngas	% Carbon Mass (lb.) in Syngas
Hydrogen	45	1,946,244	0.0	0	0
Carbon monoxide	24	1,037,997	640.7	274.6	43.3%
Methane	12	518,999	183.1	137.3	21.7%
CO_2	19	821,748	797.1	217.4	34.3%
Total HCs	0.1	4,325	5.5	4.6	0.7%
Total	100.1	4,329,312	1,626.4	633.9	100.0%

Syngas produced	34,440	Cubic ft.	968,797	Liters
	574	Cubic ft./min		

Calculation of Carbon Conversion (%)

Carbon in syngas	633.9	lbs.
Carbon in feed	736.0	lbs.
% Conversion	86.1	%

Table VIIA.2 summarizes the results from the laboratory steam reforming of wood. The mass conversion for the wood to biochar was 17.2%, which was similar to the average determined from the IBR plant of 16.3% (see Figure VIIIA.8).

Table VIIA.2: Laboratory Steam Reforming of Wood

Component	Weight (g)	% of Input
Inputs		
Wood (dry)	2.50	-
H_2O	5.44	-
Products		
Gases	1.89	75.6 %
Biochar	0.43	17.2 %
Condensate		
H_2O	5.53	+1.7 %

B. Diesel Fuel Production Yield

The following products are formed from the catalytic reaction of hydrogen and carbon monoxide:

- Non-condensable hydrocarbon gases (C_1-C_4)
- Condensable hydrocarbon gases (fuels)
- Reformulated gasoline blendstock (C_5-C_8)
- Diesel (C_8-C_{24} hydrocarbons)
- Wax (C_{25}-C_{40} hydrocarbons)

The calculation of diesel fuel production yields is determined by measuring the number of gallons of fuel produced every 24 hours divided by the tons of dry biomass (wood) introduced into the plant. There are three sources of fuel from this process:

- The amount of reformulated gasoline blendstock and diesel fuel collected by the liquid fuel condenser. This is a direct measurement of the gallons of fuel produced per unit time
- The amount of diesel fuel collected in the wax condenser (entrained in the wax). The amount of diesel fuel in the wax is determined by GC analysis as described in Section IIID.7a.
- The amount of diesel fuel not collected by the liquid fuel condenser or entrained in the wax is determined by GC analysis of the catalyst tail gas.

Therefore, the fuel yield per dry ash free ton (daft) is calculated as follows:

Fuel yield (gallons/daft) = Sum of fuel collected from sources #1-#3/daft

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C. Wax Production Yield

The wax fraction is defined as C_{25}–C_{40} hydrocarbons. The hot, liquid wax was collected in a 5 gallon bucket every few hours.

D. Production of Side Products

Water is a major side product from the catalytic reaction. Assuming that the average composition of the fuel product is $C_{12}H_{26}$, then the stoichiometry of this reaction for 100% conversion efficiency is:

$$36\ H_2 + 16\ CO \rightarrow C_{12}H_{26} + 15\ H_2O + 4\ CH_4 \text{ (Reaction 1a)}$$
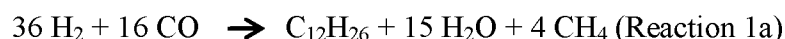
Reaction 1a assumes CH_4 is the only non-condensable product) (15% conversion efficiency from CO). Assuming that 4% of the H_2 will react with the catalyst as follows:

$$1\ H_2 + \text{Catalyst-O} \rightarrow H_2O \text{ (Reaction 1b)}$$
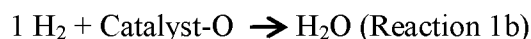
Adding Reactions 1a and 1b, the total stoichiometry for 100% CO conversion is:

$$37\ H_2 + 16\ CO \rightarrow C_{12}H_{26} + 16\ H_2O + 4\ CH_4$$
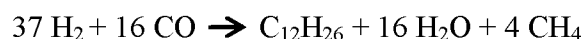
The % molar concentrations for the reactants are:

$$H_2 = 69.8\%$$
$$CO = 30.2\%$$

Therefore, the ideal molar ratio of H_2/CO is:

$$H_2/CO = 37/16 = 2.31$$

And the molar ratio of water to fuel is:

$$H_2O/C_{12}H_{26} = 16.0$$

Therefore, the volume ratio of water to the diesel fuel product is:

$$H_2O/C_{12}H_{26} = 1.69$$

In conclusion, a measure of the water to diesel fuel ratio was used to help determine if the fuel production yields were reasonable.

VIII. Assessment and Optimization of Plant Operating Conditions

During May 9, 2012 to April 1, 2013, twelve test campaigns were carried out to generate operational data to determine under which conditions the IBR plant should be operated to maximize fuel production.

A. Determination of Optimum TCC and LFP Operating Conditions

As described earlier, the thermochemical process for the efficient conversion of biomass to syngas was carried out in Unit Operations #1 - #4a. The following sections summarize the comprehensive data generated from these IBR tests and how this data was used to determine the optimum TCC operating conditions for the production of purified syngas with a composition suitable for the production of diesel fuel from Unit Operations #4b - #8.

1. Unit Operation #1 (Feedstock Introduction)

The preponderance of the durability problems encountered during the IBR tests occurred during the introduction of wood feedstock into Unit Operation #2. These problems were as follows:

- The degradation of the gate valve seal from exposure to the heat and steam from Unit Operation #2. These seals were replaced with seals that had higher temperature specifications.

- The introduction of very fine biomass particles (< 1/8") into Unit Operation #1 caused the build-up of particle fines on the seals between Unit Operation #1 (biomass introduction system) and #2 (solids steam reforming) and some of these fine particles were entrained into unit operation #3 (gases steam reforming) causing excessive tar formation and unconverted biomass fines. These particles and tars resulted in plugging of selected components in the syngas purification system (Unit Operation #4). In order to lessen this potential problem, it is specified that biomass be screened to reduce fines less than about 1/8".

After run #8a and #8b (Table VI.1), the biomass ram charge feeder was disassembled and examined with the following results:

- No buildup of wood fines on the seals and surfaces were observed
- All of the seals looked good (free of cracks and intact)

2. Unit Operation #2 (Solids Steam Reforming)

Unit Operation #2 is a slow pyrolysis process, which produces different products than those generated from the more widely employed fast pyrolysis process. Table VIIIA.1 provides typical data on the average distribution of ash, ash, condensable gases (pyrolysis oil), and non-condensable gas (primarily syngas) formed from the slow pyrolysis of wood.

Table VIIIA.1: The Average Composition of
Products formed from Wood in Unit Operation #2 at 1,450°F

Product	Product Distribution (Wt. %)
Ash (Elemental and Organic Carbon Species)	11%
Non-Condensable Gases (Syngas)	20% [1]
Condensable Gases at 40°F (Pyrolysis Oil)	69% [2]
Total	100%

[1] *Excludes water fraction*
[2] *See Table VIII.A.2 for non-condensable gas composition*
[3] *See Table VIII.A.3 for condensable gases (pyrolysis oil) composition*

Table VIIIA.2 summarizes the composition of the non-condensable gases (mole %) shown in Table VII.A.1. It is seen that H_2 and CO are the primary constituents of this fraction.

Table VIIIA.2: The Composition of Non-Condensable
Gases (mole %) Generated from Unit Operation #2

Non-Condensable Gas	Mole %
Hydrogen	48
Carbon Monoxide	27
CO_2	12
Methane	12
C_2+ Hydrocarbons	<1
Total	100%

Table VIIIA.3 summarizes the properties of the condensable gases (pyrolysis oil) generated from Unit Operation #2 at 1,450°F.

Table VIIIA.3: Chemical and Physical Properties of Condensable Gases (Pyrolysis Oil) Generated from Unit Operation #2

Value	Chemical and Physical Properties
Elemental Composition (wt. %)	
Carbon	70
Hydrogen	8.0
Oxygen	20
Nitrogen	1.5
Other Properties	
Insoluble Constituents (wt. %)	< 0.05
pH	3.5
H_2O Content (wt. %)	20
Viscosity [Centipoise (CPS)] (1 hr. after collection at 30°C)	14
Heat Value (BTU/lb.)	11,400
Density (g/cc) at 25°C	1.10 (9.1 lbs./gallon)
TAN number	40
Color	Light Tan
Odor	Mild Smokey

Table VIIIA.4 compares the results from the chemical analysis of wood and that of the average molecular composition. It is observed that there is good agreement between these two sets of data.

Table VIIIA.4: A Comparison of the Elemental Composition of Wood with the Average Molecular Composition ($C_8H_{14}O_5$)

Elemental Composition	Wood Elemental Analysis (Weight %)	Wood Average Molecular Composition ($C_8H_{14}O_5$) (Weight %)
Carbon	49.8	50.5
Oxygen	43.3	42.1
Hydrogen	6.9	7.4

As based upon the data presented above, the general chemical process in Unit Operation #2 can be expressed by Equation 1 where $C_8H_{14}O_5$ is the average elemental composition of wood and $C_7H_8O_2$ is the average elemental composition of the pyrolysis oil.

$$C_8H_{14}O_5 \rightarrow C_7H_8O_2 + H_2 + CO + 2\ H_2O \quad \text{(Eq. 1)}$$
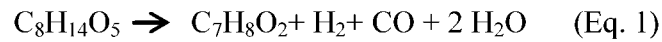
$C_7H_8O_2$ most closely matches the molecular composition of Guaiacol, a major constituent identified in pyrolysis oil.

Figure VIIIA.1 illustrates the relationship between the final syngas flow rate (scfm) and Unit Operation #2 Temperature. This data is normalized to a wood feedstock input of 11.0 tpd and a Unit #3 Process Temperature of 1,725 °F. It is seen that once Unit Operation #2 reaches 1480 °F, there is no change in the syngas production up to 1,550 °F.
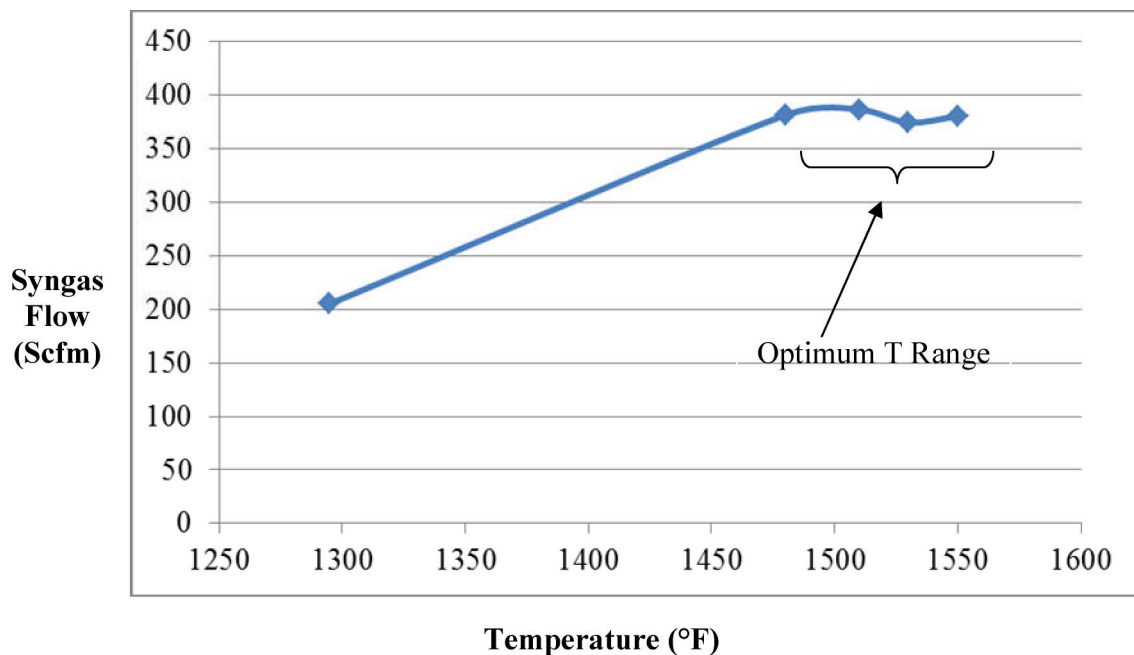
Figure VIIIA.1: The Effect of Unit Operation #2 Temperature on Syngas Flow (Scfm) (with Unit Operation #3 @ 1800 °F)

3. Unit Operation #3 (Gases Steam Reforming)

Unit Operation #3 is a steam reforming process, carried out at about 1,800 °F with a 3-10 sec residence time, to reform the condensable organics formed in Unit operation #2. As based upon the IBR plant data generated during 2012, it is proposed that the

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chemical reactions that take place in this process can be illustrated by Equations #2 and #3.

$$C_7H_8O_2 + 5\ H_2O \rightarrow 5\ H_2 + 3\ CO + 2\ CO_2 + 2\ CH_4 \text{ (Eq. 2)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \text{ (Eq. 3)}$$
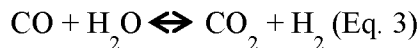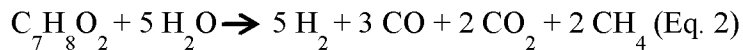
The resulting reaction stoichiometry and syngas composition from the TCC system can be determined by combining Equations #1-3 as illustrated by Equation #4.

$$C_8H_{14}O_5 + 4\ H_2O \rightarrow 7\ H_2 + 3\ CO + 3\ CO_2 + 2\ CH_4 \text{ (Eq. 4)}$$
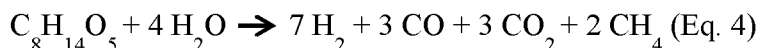
$$H_2O/C \text{ mass ratio} = 0.75/1.0$$
$$H_2O/C \text{ mole ratio} = 4.0/1.0$$

The overall process reaction stoichiometry (equation 4) demonstrates that at least a mass ratio of H_2O/C of $0.75/1.0$ is required in Unit Operation #3 for the reforming of the organic pyrolysis products produced from Unit Operation #2. Furthermore, additional steam is needed to prevent the formation of elemental carbon in Unit Operation #3. As elemental carbon is formed, it is converted into syngas by steam (Equation 5). The excess steam also helps to reform methane into syngas (see Equation 6).

$$C + H_2O \rightarrow CO + 3\ H_2 \text{ (Eq. 5)}$$

$$CH_4 + H_2O \rightarrow CO + 3\ H_2 \text{ (Eq. 6)}$$

Figure VIIIA.2 shows the relationship between steam injections into Unit Operation #3 and the production of syngas. It is observed that the maximum production of syngas occurs at a H_2O/Feedstock C mass ratio of about 1.2. There is a slight decrease in syngas production at higher H_2O/Feedstock C mass ratios, which may be due to the following reasons:

- The addition of extra 1,400 °F steam decreases the optimum reforming temperature of 1,800-1815 °F thus reducing the gas reforming efficiency.
- The addition of extra steam increases the gas flow rate, which decreases the residence time for the steam reforming reactions to occur.

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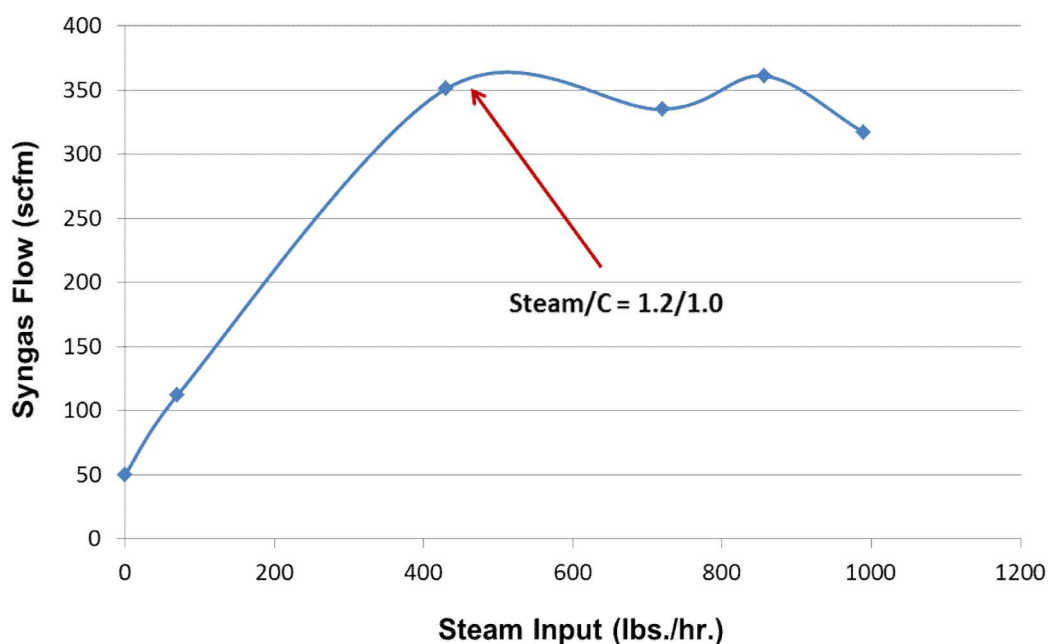
Figure VIIIA.2: The Effect of Steam/Feedstock
Carbon on Syngas Flow

As based upon the above results and conclusions, the recommended steam injection into Unit Operation #3 as a function of feedstock input is provided in Table VIIIA.5.

Table VIIIA.5: Steam Injection into Unit Operation #3 as a
Function of Feedstock Input

Wood Feedstock Input			Steam Injection into Unit Operation #3
Ton/Day (as received)	As Received Lbs./Hour	As Carbon Lbs./Hour[1]	Lbs./Hour[2]
2.5	208	93	112
5.0	416	186	223
7.5	624	279	335
10.0	832	370	444
12.5	1040	465	558
15.0	1248	558	670
17.5	1456	651	781
20.0	1664	744	893
22.5	1872	837	1004
25.0	2080	930	1116

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Figure VIIIA.3 illustrates the effect of the reformer tube wall temperature in Unit Operation #3 on the production of syngas. It is seen that the temperature of Unit Operation #3 has a significant effect on the production of syngas.
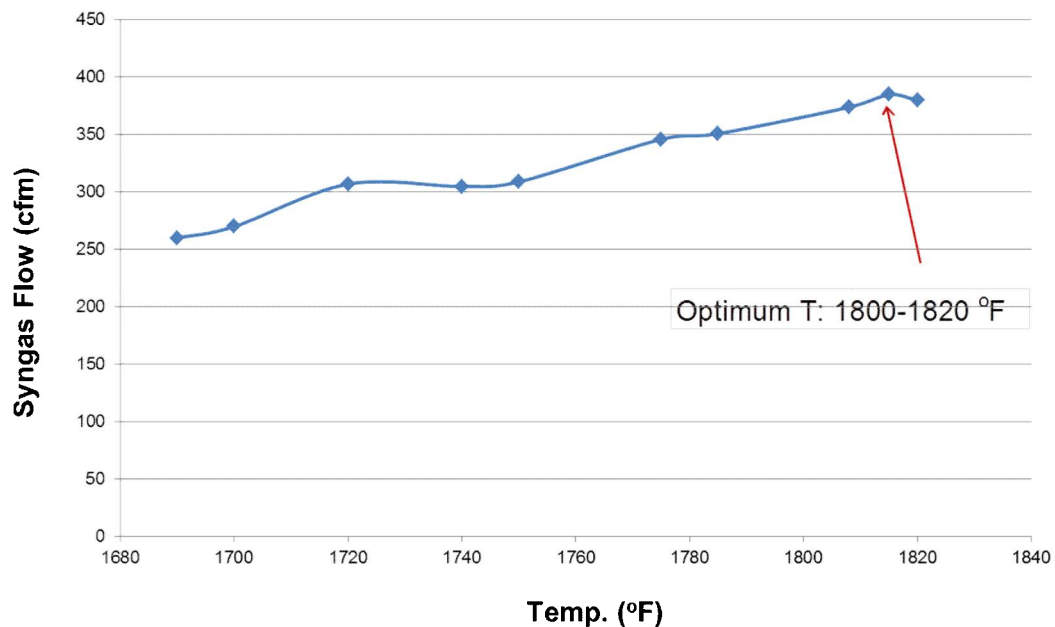
Figure VIIIA.3: The Effect of Unit Operation #3 Temperature on the Production of Syngas (with Unit Operation #2 at 1520°F)

Figure VIIIA.4 illustrates the effect of the reformer tube temperature in Unit Operation #3 on the concentration of CO_2 in syngas. It is observed that higher temperatures reduce the concentration of CO_2. However, there is no change in the CO_2 above about 1,790°F.

The proposed reaction for this observation is given by Equation 7 in which the formation of CO and H_2 from CO_2 and H_2O is favored at higher temperatures.

$$CO_2 + H_2O \longleftrightarrow CO + H_2 \text{ (Eq. 7)}$$
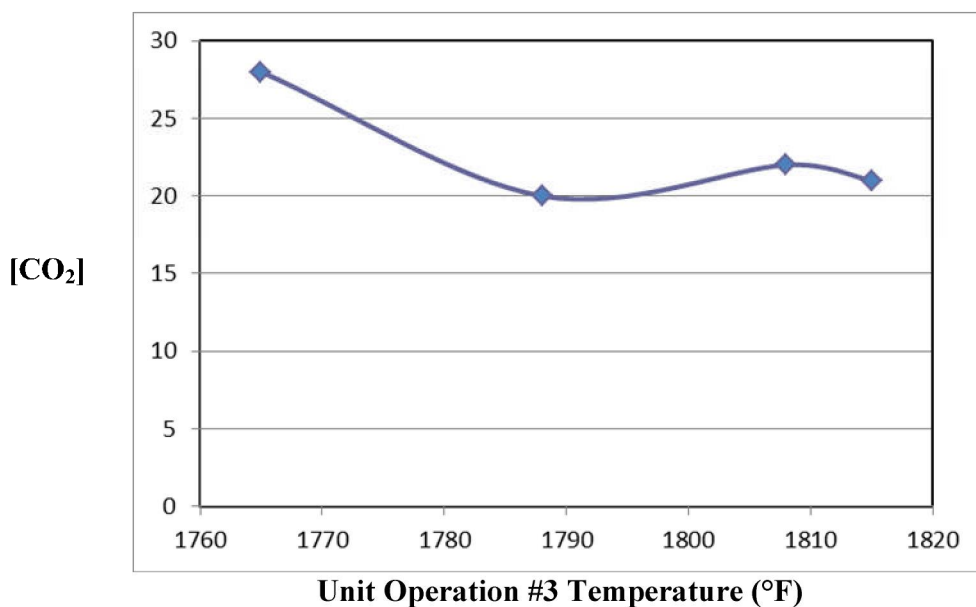
Figure VIIIA.4: The Effect of Unit Operation #3 Reformer
Tube Surface Temperature on the Concentration of CO_2 in Syngas

Figure VIIIA.5 illustrates the effect of reformer tube wall temperature in Unit
Operation #3 on the concentration of CH_4 in the syngas. It is observed that higher
temperatures reduce the concentration of CH_4. However, there is no change in $[CH_4]$
above 1,790°F. This data is consistent with Equation 6.
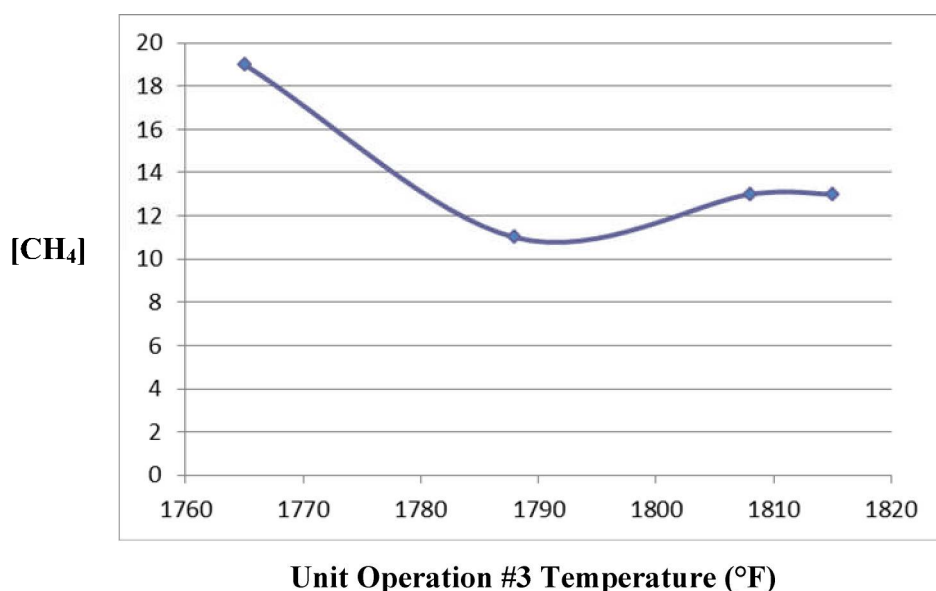
Figure VIIIA.5: The Effect of Unit Operation #3
Temperature on the Concentration of CH_4 in Syngas

Figure VIIIA.6 illustrates the effect of the reformer tube wall temperature in Unit
Operation #3 on the concentration of CO in the syngas. It was found that higher

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temperatures increase the concentration of CO which is consistent with the reactions summarized by Equations 5, 6, and 7.
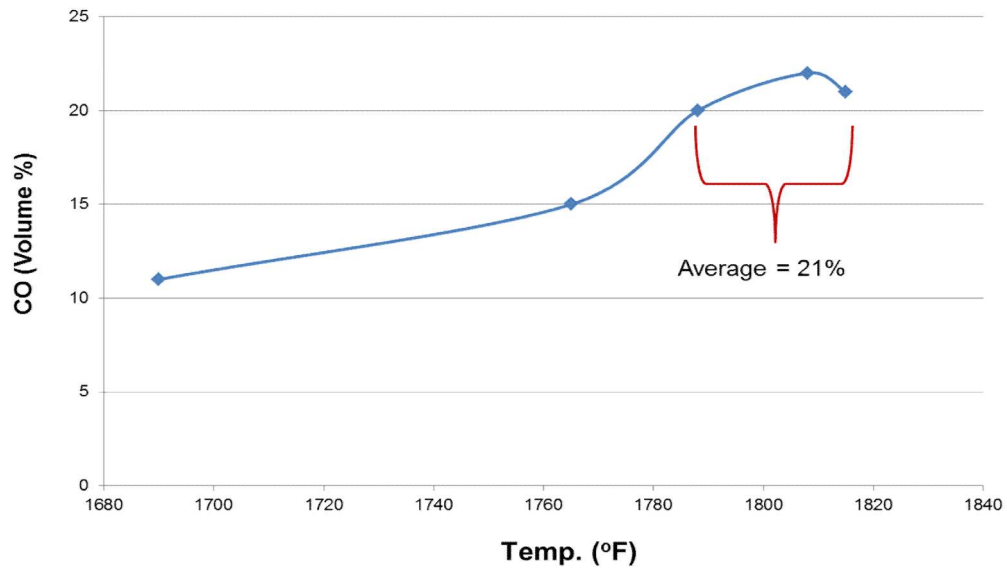
Figure VIIIA.6: The Effect of Unit Operation #3 Temperature on the Concentration of CO in Syngas

Figure VIIIA.7 shows the effect of temperature on the concentration of H_2 in the syngas. It is observed that higher temperatures increase the concentration of H_2, which is consistent with the reactions summarized by Equations 5, 6 and 7.
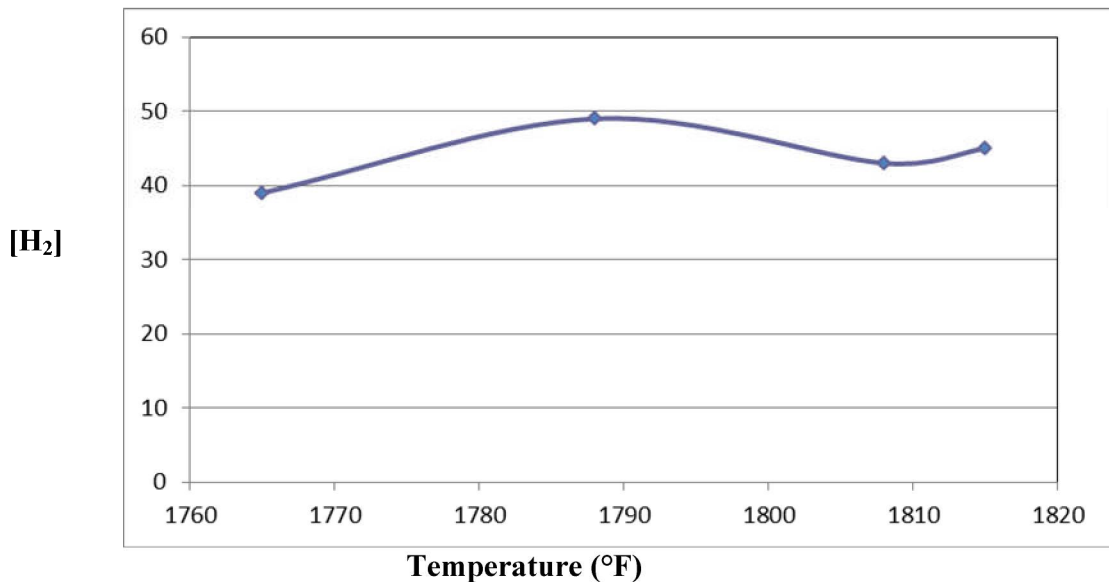
Figure VIIIA.7: The Effect of Unit Operation #3 Temperature on the Concentration of H_2 in Syngas

4. Unit Operations #2 and #3 Combined

This section uses the data generated from the first 13 test campaigns to determine the combined effects of Unit Operation #2 operating conditions on the final syngas production rate (after Unit Operation #3).

Experiments were carried out in which 300°F steam was injected into Unit Operation #2 in addition to the 1,400°F steam injected into Unit Operation #3. Table VIIIA.6 summarizes the effect of syngas flow on the injection of steam into Unit Operation #2 (this data is normalized to 11.0 tpd of wood input, a Unit Operation #2 temperature of 1,490°F and a Unit Operation #3 reformer surface temperature of 1,750°F).

Table VIIIA.6: The effect of Steam Injection into
Unit Operation #2 on the Syngas Flow from Unit Operation #3

Steam Input (Steam/Biomass C Input)		Syngas Flow (Scfm)
Unit Operation #2	Unit Operation #3	
0.00	1.80	335
0.29	1.31	340
0.30	1.15	328

This data demonstrates that the addition of steam into Unit Operation #2 does not increase the syngas flow from Unit Operation #3.

It was shown previously that the pyrolysis of wood produces water according to Equation 1. In addition, the wood used in these tests had an average water content of 15 weight %.

$$C_8H_{14}O_5 \rightarrow C_7H_8O_2 + H_2 + CO + 2 H_2O \quad \text{(Eq. 1)}$$
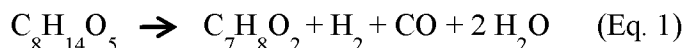
It is concluded from these results, that it is not necessary to inject much steam into Unit Operation #2. It is predicted that very little of the water produced during the pyrolysis process reacts with wood or pyrolysis products in Unit Operation #2 and therefore most of the water produced will be utilized in Unit Operation #3 for the steam reforming of the gas-phase pyrolysis products as shown by Equation 2.

$$C_7H_8O_2 + 5 H_2O \rightarrow 5 H_2 + 3 CO + 2 CO_2 + 2 CH_4 \quad \text{(Eq. 2)}$$
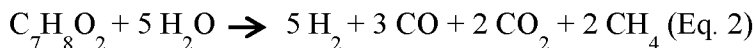
It was demonstrated in Section III.B.2.a that the overall reaction stoichiometry can be expressed by Equation #3.

$$C_8H_{14}O_5 + 4 H_2O \rightarrow 7 H_2 + 3 CO + 3 CO_2 + 2 CH_4 \quad \text{(Eq. 3)}$$
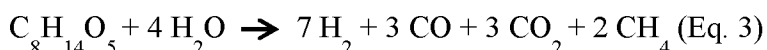
a) Syngas Production and Composition

Table VIIIA.7 provides a comparison of the overall reaction stoichiometry from Equation 3 with the syngas composition from the IBR plant when operated under ideal conditions.

Table VIIIA.7: Comparison of the Overall Reaction Stoichiometry with the Syngas Composition from the IBR Plant when operated under Ideal Conditions

Results	Syngas Composition (Volume %)			
	H_2	CO	CH_4	CO_2
Reaction Stoichiometry (from Eq. 3)	47	20	13	20
IBR Plant Tests	46	23	12	19

This close correspondence between the reaction stoichiometry derived from Equation 3 and the performance tests indicate that the plant is operating at or near the optimum conditions.

b) Carbon Conversion Efficiency

The biomass carbon conversion efficiency for Unit Operations #2 and #3 was determined by utilizing a couple of approaches.

Approach #1 - This approach compares the mass input of carbon in the feedstock (FS_c) to the mass output of carbon in the ash (Ash_c) for determining the carbon conversion efficiency as follows:

$$\% \text{ Carbon Conversion Efficiency} = (FS_c - Ash_c)/FS_c \times 100$$

Approach #2 - This approach compares the mass of carbon introduced into the thermochemical conversion system with the mass of carbon containing compounds (CO, CO_2 and C_2-C_8 HCs) produced.

Figure VIIIA.8 shows the carbon mass conversion efficiency for nine of the test campaigns carried out during 2012-13. As observed, the carbon conversion calculated using Approach #2 gave a bit higher conversions (average of 90%) than Approach #1 (average of 84%).
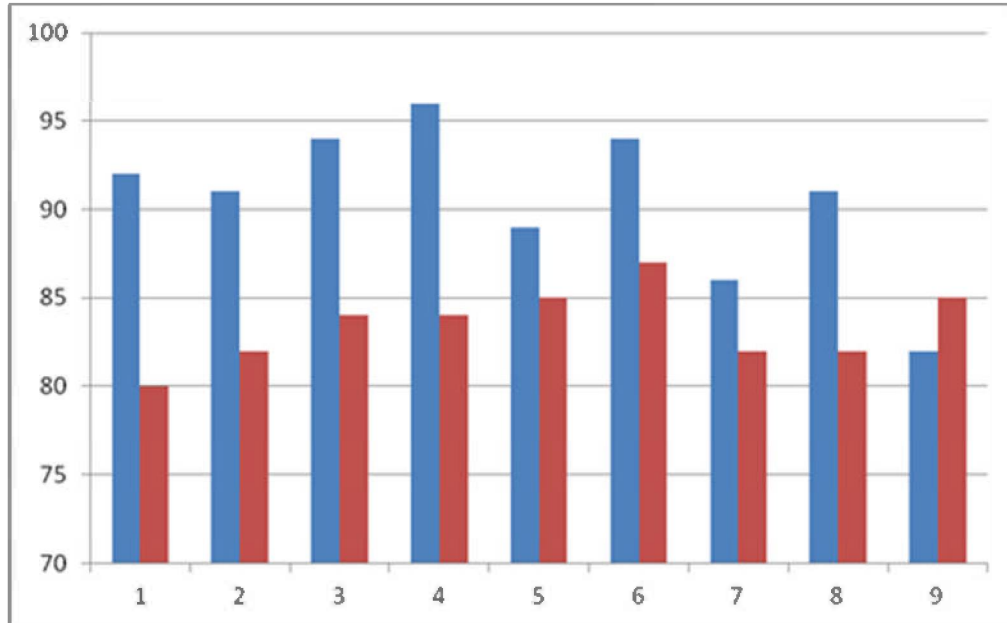
Figure VIIIA.8: % Carbon Conversion Efficiency of the TCC System for Wood
C in Biochar / C in Feedstock x 100 ■
C in Syngas / C in Feedstock x 100 ■

5. Unit Operations #4a-1 to #4a-4 (Syngas Purification)

Figure VIIIA.9 illustrates the main components used for purification of the syngas as follows:

- A heat exchanger produces ~1,400 °F steam which is injected into Unit Operation #3 to increase the H_2O/C ratio as necessary for efficient steam reforming.

- Particles greater than about 3 microns in diameter are removed from the syngas from Unit Operation #3 using high efficiency cyclones.

- Type B tars are removed using a condenser held at about 250 °F.

- Two scrubbers are used to remove particles less than about 3 microns in diameter and to scrub inorganic gases (e.g. H_2S) and soluble organic gases (e.g. phenols) from the syngas.

- The volume of syngas is measured using two different types of mass flow meters.

#4a-1	#4a-2	#4a-3	#4a-4

Unit Process #3 → Cyclone → Quench Column → Water Scrubber #1 → Water Scrubber #2

Quench Column → Tar Collector

Water Scrubber #1 → Waste Water Sludge

Water Scrubber #2 → Syngas Flow Meters
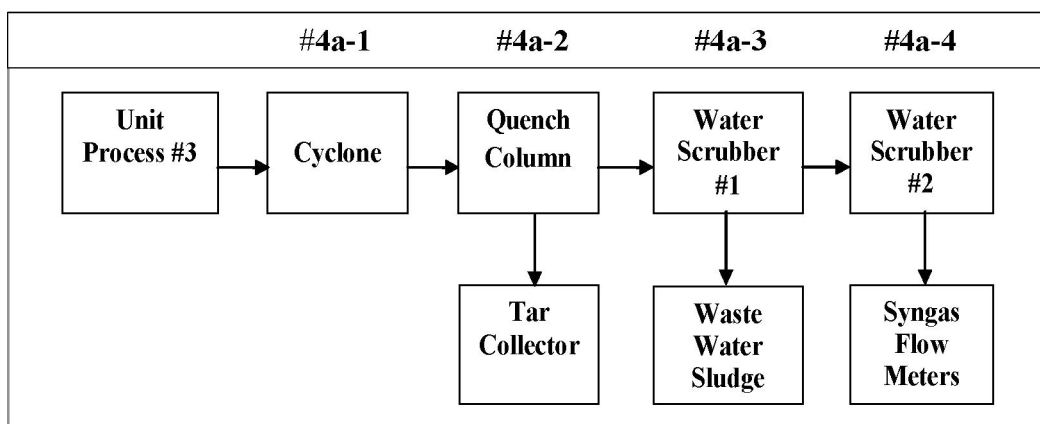
Figure VIIIA.9: Unit Operations #4a-1 to #4a-4 (Syngas Purification)

Sodium hydroxide/hydrogen peroxide ($NaOH/H_2O_2$) mixtures were used in the water scrubbers in the first few tests to remove H_2S and other inorganic gases. However, it was found that the hydrogen peroxide reacted rapidly with particles, dissolved organics and other constituents, the reactions of which heated the scrubber water and reduced scrubbing efficiency. Furthermore, it was necessary to continuously replenish the H_2O_2, which was costly.

Therefore, only NaOH was used in the scrubber and the pH was maintained at 9.0-9.5. However, it was found that the H_2S scrubbing efficiency decreased for extended runs (e.g. Test Run #8). Therefore, a new scavenging additive, Enviro-Scrub™, was tested in Test Run #9.

Enviro-Scrub™ is a liquid triazine solution which is added to scrubber water to remove H_2S and mercaptans from gas streams. Figure VIIIA.10 shows the reaction of the triazine with H_2S. The product, dithazine, is a non-hazardous, stable compound. The reacted solution is water soluble, forms no solids, and is readily biodegradable.

The Enviro-Scrub™ solution consists of a 10% solution of triazine maintained at a pH of 10.0-11.5. The Enviro-Scrub™ was maintained at a concentration of 0.07% in the scrubber water. As based upon the concentration of contaminants in the scrubber water (see section VID.4), it was determine that the discharge of scrubber water was about eight times higher than necessary. This determination was based upon the typical TOC and BOD limits of 300-500 mg/liter for discharge of wastewater to a sanitary sewer.
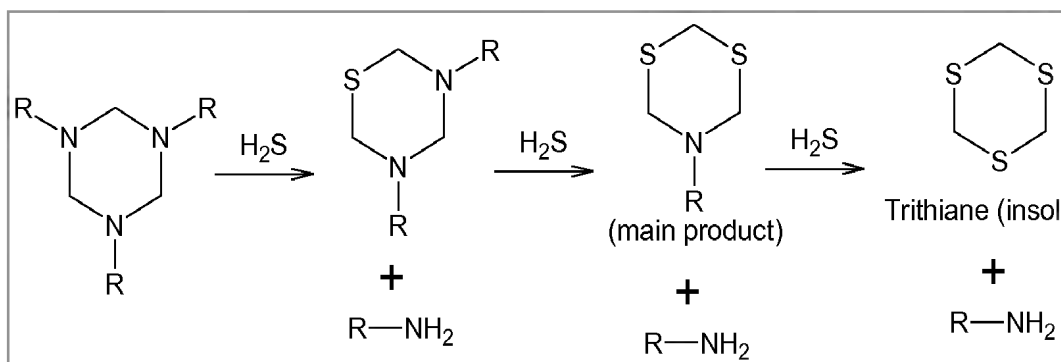
Figure VIIIA.10: The Reaction of Triazine with
Hydrogen Sulfide in Aqueous Solution

In conclusion, the optimum scrubber water discharge rate was 0.31 gpm or 18.8
gallons/hr and the optimum triazine input rate 0.016 gallon/hr at the maximum biomass
input rate of 1.04 daft/hr. Since the cost of the triazine (delivered to the site) was
$9.67/gallon, the cost of this triazine additive per daft of biomass input was $0.15/daft.

The Enviro-Scrub™ was tested over a period of about nine months and 500 hours of
TCC run time. It was found to be much more efficient than NaOH in reducing
hydrogen sulfide in the syngas – this additive reduced H_2S to very low levels (<5 ppb).

6. Unit Operation #8 (Syngas Polishing)

Table VIIIA.8 reviews the maximum recommended contaminant levels for efficient
diesel fuel production using the LFP catalysts and when the hydrogen sulfide and
ammonia syngas polishing guard beds were used. Turk et al (2013), recommends that
HCN be kept below 10 ppb, NH_3 below 10 ppm, NOx below 0.2 ppm and sulfur below
60 ppb.

Table VIIIA.8 summarizes the average concentrations of contaminants measured in the
purified syngas. As shown in this table, the average contaminant concentrations in the
syngas were within the maximum recommended contaminant levels.

Table VIIIA.8: Maximum Recommended Contaminant Levels for
Efficient Diesel Fuel Production using the LFP Catalysts

Catalyst Contaminants	Maximum Recommended Contaminant Levels	Average Contaminant Concentrations Measured in the Purified Syngas
Sulfur Species		
Hydrogen Sulfide (H_2S)	< 20 ppb	0.1 ppb
Sulfur Dioxide (SO_2)	< 200 ppb	0.7 ppb
Nitrogen Species		
Ammonia (NH_3)	< 5 ppm	53 ppb
Hydrogen Cyanide (HCN)	< 20 ppb	Not determined
Nitrogen Oxides (NOx)	< 200 ppb	See DRI data
Halogen Species		
Hydrogen Chloride (HCl)	< 50 $\mu g/m^3$ (34 ppb)	< 0.5 $\mu g/m^3$
Other Species		
Oxygen (O_2)	< 500 ppm	225 ppm
Total Particulate Matter ($PM_{2.5}$)	< 500 $\mu g/m^3$	460 $\mu g/m^3$

7. Unit Operation #9 (Syngas Compression)

After syngas polishing, the syngas was compressed to between 250 and 400 psi.
Additional water in the syngas was removed during this compression step as well as
some particulate and gas-phase contaminants.

8. Unit Operation #10 (Catalytic Conversion)

The accurate determination of catalyst productivity for fuel production requires the
accurate measurements of 1) syngas composition, before and after the catalyst, and 2)
the relative distribution of diesel fuel, reformulated gasoline blendstock, wax and
tailgas.

As described earlier, since varying mixtures of methanol and CO_2 are easily reformed
in the TCC system to produce high purity syngas at various flow rates and with
different H_2/CO ratios, this standardization process was used successfully to develop
parametric data for the LFP by varying the following catalyst operating conditions over
a 50 hour test period:

- Syngas H_2/CO: 1.47-3.59
- Catalyst Temperature: 390-428°F

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- CO Conversion (single pass): 13-81%
- CO Conversion (two recycles): 42-95%

These optimum operating conditions validate the parametric model developed from our previous laboratory and pilot results for this catalyst. The above results are also similar to the LFP operating conditions we have been using in our commercial model.

9. Unit Operation #11 (Product Separation)

The on-line mass spectrometer was used to assess the quantity of diesel fuel that wasn't efficiently collected in the fuel condenser. This was determined by monitoring the mass 43 peak which is the major fragment peak in the mass spectra for pentane (C_5) to nonane (C_9). It was found that the total concentration of C_4-C_8 HCs in the tailgas at the optimum operating conditions presented above was 5.4 ± 1.5 volume %. Since this value is at the low concentration end of what is expected in the tailgas from the catalytic reaction (5-10 volume % as shown in Table 30 below), it is concluded that the fuel condenser was very efficient in collecting the hydrocarbons.

Very little wax was produced during test runs. It is estimated that the wax fraction represented less than 0.5 volume % of the total catalyst products.

The tail gases after the diesel fuel collection system were characterized and it was determined that when the syngas flow is within typical operating conditions, then the fuel collection efficiency is acceptable (> 98% efficiency).

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IX. Results and Conclusions from Plant Tests

The key results and conclusions for the sixteen months of integrated IBR plant testing are summarized in this section.

A. Thermochemical Conversion (TCC) System

1. The fully integrated system was operated at 10-96% input capacity (2.5-24.0 tons/day) for the wood and at 22-56% capacity (5.4-14.0 tons/day) for rice hulls under various operating conditions to establish baseline operational data.
2. Feedstock carbon was efficiently converted to syngas with the proper stoichiometric H_2/CO ratio of 2.0 ± 0.2 for the efficient conversion to fuel. In comparison, the syngas generated from most other thermochemical conversion systems produces H_2/CO ratios that are far from ideal as summarized in Table IXA.1.
3. It has been demonstrated that this integrated technology is able to efficiently convert nearly any type of biomass into "drop-in" liquid fuels. A distinctive advantage is that this process can accept biomass from 0.15" to 2.50" in size and water content from 0 to 35 weight%.
4. The introduction of very fine biomass particles (< 0.15") into the TCC system caused the build-up of particle fines on the seals between Unit Operation #1 (biomass introduction system) and #2 (solids steam reforming) and some of these fine particles were entrained into Unit Operation #3 (gases steam reforming) causing excessive tar formation and unconverted rice hull fines. These particles and tars resulted in plugging of selected components in the syngas purification system (Unit Operation #4a). Therefore, biomass that is less than about 0.15" in size is not suitable.
5. The ideal operating temperatures for the slow pyrolysis system (Unit Operation #2) was found to be in the 1,480-1,530 °F range and 1,790-1,815 °F (reformer tube temperature) for the gases steam reforming system (Unit Operation #3). These operating temperatures minimized the formation of tars and CO_2.
6. The ideal steam injection rate for the process was 1.2 lb. of steam per lb. of feedstock carbon when the feedstock was input at 20 wt. % moisture. The addition of additional steam did not increase the production efficiency of syngas or carbon monoxide. In fact, the introduction of additional steam reduced slightly the efficiency for steam reforming of the gas-phase hydrocarbons. This reduction in reforming efficiency was probably due to a reduction in the gas residence time for reforming. The addition of too much steam into Unit Operation #2 adversely affected the flow of biomass due to the formation of "wet particle lumps" which formed in the ash removal system, making the removal of ash more difficult.
7. When Unit Operations #1-#4a were operated under the optimum conditions recommended above, the conversion efficiency of wood carbon to syngas carbon averaged 85% over a wood feedstock input range of 2.5-24.0 tons/day. There was good agreement between carbon conversion as determined by comparing C in wood input to C in biochar output with C in wood input to C in syngas output.

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8. The scrubber water additive (Enviroscrub™, a triazine additive) was much more efficient than mixtures of NaOH and H_2O_2 in reducing hydrogen sulfide in the syngas – this additive efficiently reduced H_2S to very low levels (< 5 ppb).

9. The on-line instruments for real-time measurements of syngas composition (mass spectrometer), particulates and hydrogen sulfide worked well. The monitoring of benzene by MS was found to be a good surrogate compound for the potential formation of tars. However, the inefficient removal of water from the syngas caused condensation in the syngas sampling lines, which adversely affected the analytical instruments.

Table IXA.1: The Composition of Syngas Generated from the IBR Plant Compared to the Syngas Generated from Other Thermochemical Conversion Systems

TCC Technology	H_2	CO	H_2/CO	CH_4	CO_2	N_2/Ar
DOE IBR Toledo Plant (1,500°F/1,800°F)	46	22	2.0 ± 0.15	12	20	<1
Circulating Fluidized Bed Air Blown System (1,650°F)	6	13	0.46	6	13	62
Downdraft Air Blown System (1,560°F)	22	19	0.86	ND	9	50
Fluidized Bed Air Blown System (1,560°F)	21	23	0.91	<1	10	42
Downdraft Air Blown System (930°F)	2	18	0.11	<1	25	55
Circulating Fluidized Bed Oxygen Blown System (1,650°F)	15	47	0.32	18	15	<1
Plasma Arc Air Blown System (>3,000°F)	8	22	0.36	<1	20	50

10. The overall tar concentrations, excluding benzene and toluene, in the raw syngas ranged from 210-530 ppmv. The syngas purification system effectively removed these tars from the syngas (>98% for naphthalene and ~100% for heavier tars).

B. Liquid Fuel Production (LFP) System

1. The quality and composition of the syngas monitored after the syngas polisher (Unit Operation #8) exceeded operating specifications (< 3 ppb H_2S and 25 $\mu g/m^3$ particulates).
2. The diesel fuel production catalyst was efficiently reduced in-situ under the operating specifications developed from previous laboratory and pilot studies.
3. The on-line mass spectrometer was effective for the real-time monitoring of the syngas, before and after catalytic conversion.
4. The results for the optimized LFP system are summarized in Table IXB.1

Table IXB.1: Syngas Conversion Efficiencies and
Fuel and Side Product Distribution

Average Fuel and Side Product Distribution	
Wax Production (C_{25}-C_{40})	0.5%
Diesel Fuel (C_8-C_{24})	71.5%
Reformulated Gasoline Blendstock (C_5-C_8)	28.0%

5. Table IXB.2 summarizes the fuel production results from Run #17. It was determined that the % carbon conversion (feedstock carbon compared to syngas carbon) for the rice hull and wood feedstocks averaged 85 +/- 3%. The fuel production averaged 57 +/- 4% gallons/1,000 lbs. of carbon input for the rice hulls and 56 +/- 3% gallons/1,000 lbs. of carbon input for the wood feedstocks when the plant was operated under the proper number of recycle loops to convert 90% of the CO to fuel. As expected, the fuel productivity in terms of gallons/daft and gallons/1,000 lbs. of carbon input were similar. These fuel production rates were achieved without recycling of the minor side products (e.g. catalyst tailgas and wax).

The % carbon conversion (feedstock carbon compared to syngas carbon) for the methanol/CO_2 standard mixtures average 80% +/- 3% which was similar to that of the carbon conversion for the wood and rice hulls. The fuel production from this standard mixture averaged 53 +/- 2% gallons 1,000 lbs. of C input.

Run #8b was carried out during November 9-13, 2012 and runs #17e and #17f were carried out during September 8-20, 2013 (see Table VI.1). As shown in Table IXB.2, the fuel productivity increased slightly over this 10-month period (56 gallons/1,000 lbs. of C vs. 53 gallons/1,000 lbs. of C). These differences are probably the result of the plant running under more optimum conditions during run #17 compared to run #8. In any case, this data demonstrates that the catalyst productivity remained relatively constant over this time period.

Table IXB.2: Feedstock Carbon Conversion and
Fuel Production from Various Feedstocks

Run #	Feedstocks				% C Conversion	Fuel Production	
	MeOH Carbon (lb. /hr.)	CO₂ Carbon (lb. /hr.)	Rice Hulls Carbon (lb. /hr.)	Wood Carbon (lb. /hr.)	C input Compared to syngas C out	Gal per 1,000 lb. of C input	Gal per daft of biomass input
8b	0.0	0.0	0.0	833	86%	53	53
16a	232	110	0.0	0.0	83%	54	-
17a	222	143	0.0	0.0	81%	51	-
17b	216	0.0	87	0.0	94%	53	-
17c	91	0.0	110	0.0	85%	53	-
17d	0.0	0.0	142	0.0	86%	61	61
17e	0.0	0.0	0.0	220	84%	54	54
17f	0.0	0.0	0.0	524	85%	58	58
17g	149	95	0.0	0.0	83%	52	-

[1] *Normalized to 90% CO conversion from the actual % CO conversion measured during the runs.*

C. Fuel Composition and Properties

GC and GC/MS was used to determine the quantity of reformulated gasoline blendstock (C_5-C_8 constituents), premium diesel (C_8-C_{24} constituents) and wax (C_{25}–C_{40} constituents) produced during the seventeen IBR tests. Table IXC.1 summarizes the concentration of fuel hydrocarbon constituents produced from the feedstocks tested in run #17 (IE Test). The reformulated gasoline blendstock varied from 23.0-29.3 volume % and the premium diesel varied from 69.3-76.8 volume % of the total fuel produced from this run.

Table IXC.1: Distribution of Reformulated Gasoline Blendstock, Synthetic Diesel Fuel and Wax Side Product Produced from Various Feedstocks (Run #17)

Feedstock Types	MeOH & CO_2	MeOH & CO_2 & Rice Hulls	MeOH & CO_2 & Rice Hulls	Rice Hulls	Wood	MeOH & CO_2
"Drop-in" Fuel Products	Concentration (Volume %)					
Reformulated Gasoline Blendstock (C_5-C_7)	29.3	23.3	29.3	28.4	28.6	23.0
Premium Diesel (C_8-C_{24})	70.5	75.6	69.3	69.5	68.5	76.8
Wax (C_{25}-C_{40})	0.2	1.1	1.4	2.1	2.9	0.2
Total	100.0	100.0	100.0	100.0	100.0	100.0

1. Premium Synthetic Diesel Fuel

Table IXC.2 summarizes the average properties of the synthetic diesel fuel generated from the IBR plant during the 2012-13 IBR plant runs. This premium diesel fuel will be marketed as "Greyrock Premium Diesel." The Greyrock fuel is a synthetic fuel product that exceeds or meets all ASTM fuel specifications that have been established for #1 and #2 diesel fuels. Table IXC.2 compares the ASTM test results for the Greyrock diesel (GD); petroleum #1 diesel (#1D); petroleum #2 diesel (#2D); a 20 volume % blend of the GD with #2D; a synthetic diesel fuel produced by Sasol and Shell (SD); and a bio-diesel produced from rapeseed oil (BD). The results in **green** denote ASTM specifications for fuels that exceed those established for #1 and #2 diesel fuels and the results in **red** denote those results that just meet or don't meet ASTM specifications.

Table IXC.2 demonstrates that the Greyrock synthetic diesel is very similar in chemical and physical properties to the synthetic fuels currently being produced by Sasol, Shell, Exxon-Mobil, and others in large multi-billion dollar refineries, with the exception of fuel lubricity (note that the lower the HFRR number the better the fuel lubricity). The major advantage of the Greyrock synthetic diesel compared to the Sasol, Shell, and Exxon-Mobil synthetic diesels is the excellent lubricity of the Greyrock fuel (**371**) vs **520**. As a result, Sasol, Shell, Exxon-Mobil, and others need to add lubricity enhancers to their fuel to improve fuel lubricity to 520 or better (Schaberg, 2005). Shell sells their reformulated synthetic diesel under the V-Power diesel brand in Europe (Shell, 2010).

Table IXC.2: The Average Properties of the Greyrock Diesel Fuel compared to EPA #1, EPA #2 and Sasol/Shell Synthetic Diesel Fuels (nd: not determined)

Fuel Specifications (ASTM Test #)	Greyrock Synthetic Diesel (GD)	EPA #1 Diesel (#1D)	EPA #2 Diesel (#2D)	20% GD/ 80% #2D Blend	Sasol/Shell Synthetic Diesel (SD)	Bio-Diesel (BD)
Cetane Index (D 976)	70	40	40	53	70	50
Fuel Energy Content (BTU / gallon)	123,500	122,300	128,700	127,600	123,400	118,170
Fuel Energy Content (MJ / kg)	45.3	43.2	43.1	43.6	45.4	37.2
Flash Point (°F) (D 93)	105-125	100	125	121	125	220
Cloud Point (°F) (D 2500)	7	-54	7	7	10	36
Pour Point (°F) (D 97)	-0.4	-71	-10	-4	2	33
Density (g/mL)(68°F)	0.76	0.81	0.84	0.82	0.76	0.88
Lubricity (HFRR)(D 6079)	371	520	520	404	520	350
Viscosity (mm^2/s) (cSt)(D 445)	2.0	1.9	2.6	2.4	2.0	4.5
Copper Corrosion (D 130)	Class 1a	Class 1a	Class 1a	Class 1a	Class 1a	Class 1b
Oxidative Stability (D 2274)	0.1	1.5	1.5	1.2	0.4	3.8
High Temp. Stability (D 6468)	99	99	99	99	99	nd
Sulfur (ppm)	< 0.1	15	15	12	< 5	8
Aromatics (%)	< 0.3	21	20	16	< 1.0	< 0.02
Benzene (%)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.3	nd
Olefins (%)	6	2	13	12	2	nd
Oxygen Content (%)	0.21	ND	ND	ND	< 0.01	10
Methanol / Ethanol Content (%)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.45
Initial Boiling Point (IBP)(D86)	266	275	360	318	309	572
5 % Point (D86)	342	336	363	358	345	nd
50 % Point (D86)	478	412	504	498	471	nd
90 % Point (D86)	636	482	640	634	667	nd
Final Boiling Point (FBP)(D86)	696	523	689	694	690	648
Recovery (%)	98.5	98.2	98.0	98.0	98.5	nd
Residue (%)	0.50	1.00	1.00	1.00	0.50	nd
Loss (%)	1.00	1.00	1.00	1.00	1.00	nd

Even conventional U.S. diesel fuels typically have poor lubricity (**520** and higher) due to the refining processes that removes fuel sulfur. The Greyrock fuel, even when blended with #2 diesel fuel at 20 volume %, demonstrates significantly improved #2 diesel fuel lubricity (**404**) which results in much less engine wear, longer diesel engine life and improved fuel economy over long term operation.

The Greyrock and Sasol/Shell synthetic diesels are high Cetane (ASTM, 1980), premium fuel products that contain no sulfur and have very low concentrations of aromatics. Numerous published studies over the past 25 years have demonstrated that these synthetic fuels reduce emissions, improve engine performance and fuel economy compared to petroleum diesel, depending upon the engine model, age, calibration, emission control strategies and driving cycle (Zannis et al, 2008).

During the past three decades, these studies have determined the benefits of synthetic fuels in many categories of diesel engines. Examples of such engines include light-duty and heavy-duty diesel engines used for on-road vehicles, off-road vehicles, aircraft, military and marine vehicles. Since the Greyrock and Sasol/Shell synthetic fuels are similar in chemical and physical properties, except for lubricity, the results from many of these studies are directly relevant to the Greyrock fuel. In addition, the Greyrock fuel has been tested as a 20 volume % blend by PACCAR during 2013 in their most advanced heavy-duty diesel engine and the findings from the PACCAR tests are compared with these published studies in the Appendices.

Sasol and Shell market their synthetic diesel in Europe as premium products. The Shell synthetic diesel product is called V-Power diesel. This product has been reported to improve average fuel economy by 2-3% when vehicles are driven under typical freeway conditions. Shell (Shell, 2010) and Sasol charge an additional 3-5 cents/gallon for their premium diesel fuels. These synthetic diesel fuels have not yet been marketed in North America because of the high demand for diesel fuel in Europe. Some additional advantages of the Greyrock synthetic fuel are that it:

- Is a relatively simple blend of C_8-C_{24} normal paraffins with a high Cetane index of 70 which delivers enhanced engine auto-ignition qualities and improved combustion (California petroleum derived diesel #2 has an average Cetane index of 45 (and is often lower).

- The Cetane index of diesel fuel is an indicator of how readily and completely the fuel burns in the engine combustion chamber. The higher the Cetane index, the faster the fuel ignites and the more completely it combusts with a resulting improvement in fuel economy. These attributes are important because as the fuel burns faster and more completely, the engine also experiences better performance and produces fewer emissions.

- U.S. Diesel fuel has a typical Cetane index of 40-45, which is lower than that for diesel fuels from many other regions of the world. Since many current engines equipped with electronically controlled high-pressure fuel injection require fuels

with higher Cetane, Europe recommends a Cetane level of 50-51. Because of the current low Cetane of U.S. diesel fuels and the potential resulting negative impact on performance and engine lifetime, many diesel vehicle operators have found it necessary to raise the Cetane number by adding a Cetane improver, such as 2-ethyl hexyl nitrate. These Cetane improvers are marketed under several brand names.

- Several studies have demonstrated that once a diesel fuel reaches a Cetane index of 50-51, a further increase in Cetane does not provide the additional benefits listed above. As presented in Table 1, a 20 volume % blend of the Greyrock fuel produces a 53 Cetane fuel. Therefore, this is the recommended blend level of the Greyrock synthetic fuel with petroleum #2 or #1 diesel.

- Has excellent lubricity. As described earlier, Greyrock fuel, when blended with #2 diesel fuel at 20 volume %, demonstrates significantly improved #2 diesel fuel lubricity (404) compared to a lubricity value of 371 for the neat Greyrock fuel. Since blend levels above 20 volume % provide little additional engine lubrication, the recommended blend level of 20 volume % is optimal.

- Has higher energy content per unit mass than that of #2 diesel fuel (45.2 MJ/kg vs 43.1 MJ/kg) and #1 diesel fuel (45.2 MJ/kg vs. 43.2 MJ/kg). Since the Greyrock fuel density is less than that of #2 diesel (0.76 vs. 0.83), the energy content per volume is less (123,500 BTU/gallon vs. 128,700 BTU/gallon) but greater than that of #1 diesel (123,500 BTU/gallon vs. 122,300 BTU/gallon). Therefore, under a wide range of engine operating conditions, the Greyrock fuel may yield 0.8% lower fuel economy than #2 diesel as a 20 volume % blend and 0.2% better fuel economy than #1 diesel.

- Sasol, in collaboration with Chevron, has found that for most engines in current operation, fuel consumption for synthetic fuels are comparable to conventional #2 diesel fuel (Sasol-Chevron, 2013). They conclude that these results are probably due to the following factors: 1). Most diesel engines are typically operated under a fairly narrow range of speed and load conditions; 2). It is possible to operate the engine under a more efficient control strategy because of the lower emission benefits associated with the combustion of the synthetic diesel fuel and 3). Engines specifically designed to exploit the benefits of a higher Cetane number and other characteristics of synthetic fuels are expected to achieve a performance advantage over conventional diesel fuel. Sasol-Chevron is continuing to investigate these advantages in a number of development programs.

- Does not contain methanol and ethanol. Such alcohols are often harmful to fuel storage tanks, fuel lines and components typically used in small engines and other engines not specifically designed for alcohol/fuel blends.

- Has no sulfur (< 0.1 ppm) compared to about 15 ppm for #1 and #2 diesel fuels. This sulfur oxidizes in the engine to form sulfates and these sulfates deposit/collect on the catalyst and particulate trap surfaces.

- The Greyrock diesel also contains less than 0.3% of aromatics compared to EPA#2 diesel fuel which contains about 20 % aromatics. Aromatics increase the formation of particulates during combustion which accumulate in the diesel particulate trap, requiring that the diesel particulate trap be re-generated more often.

- Has lower density (0.76 g/mL compared to 0.84 g/mL for petroleum diesel) and viscosity than current fuels resulting in improved high-pressure fuel injector fuel spray formation, enhanced combustion efficiency and improved engine performance. Other potential benefits include improved cold starts and fuel economy, reduced warm-up time, fewer misfires and lower exhaust emissions of nitrogen oxides, hydrocarbons, carbon monoxide and particulate matter.

- It doesn't contain interior olefins (2, 3 and 3, 4 olefins) and other fuel constituents that can easily oxidize during storage in fuel tanks and fuel lines. As a result, the Greyrock diesel fuel has a very long storage lifetime, unlike traditional gasoline, diesel or biodiesel. For example, Greyrock has established that no chemical or physical changes occur even when the fuel is stored at room temperature for more than five years in ambient, office light.

A recent publication (HEI, 2011) further describes the benefits of synthetic diesel fuels such as this synthetic diesel fuel and describes some of the problems associated with the blending of food stock derived biodiesel and bio-alcohol fuels with petroleum derived diesel fuels.

2. Reformulated Gasoline Blendstock

The reformulated gasoline blendstock (RGB) comprises and average of about 28% of the fuel product produced from the wood, rice hull and natural gas/CO_2 feedstocks, whereas the diesel fraction comprises an average of about 72% of the fuel product.

Figure IXC.1 illustrates a typical gas chromatogram for the RGB fuel. The main HC constituents in the RGB consist of pentane, hexane, benzene, heptane, and octane. Since hexane, benzene, and heptane have quite different boiling points (154, 176, and 209°F); the benzene is easy to remove from these hydrocarbons in the final distillation process. It was found that the benzene comprised about 1/3 of the volume of the RGB fuel produced from wood and rice hulls, whereas no benzene was found in the fuel produced from the NG/CO_2 feedstock. Therefore, the distribution of products from the wood and rice hull feedstocks averaged 19 volume % RGB, 72 volume % diesel and 9% benzene.

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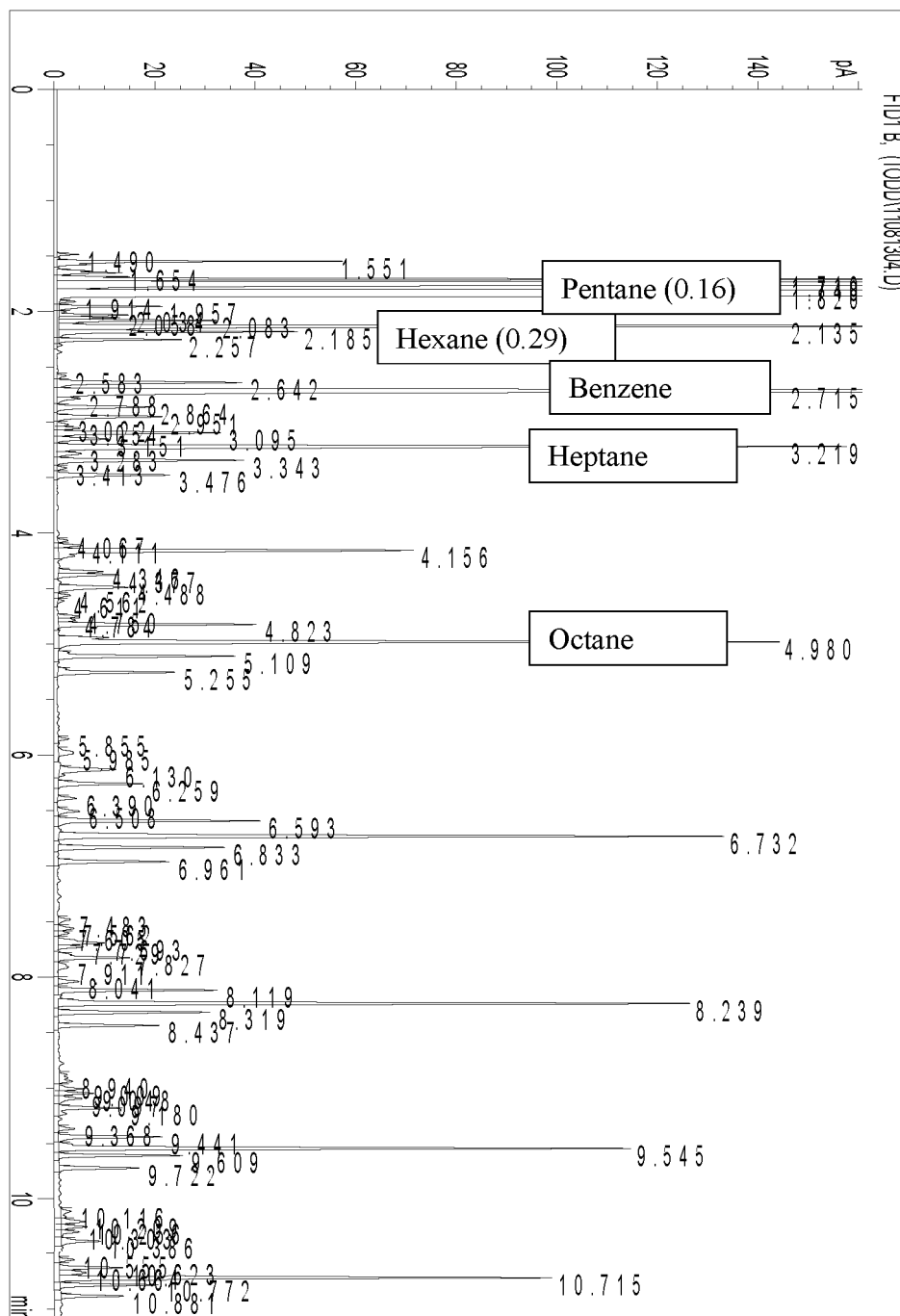
Figure IXC.1: Chromatogram of the RFG Fuel Produced from Wood

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Table IXC.3: Composition of the Reformulated Gasoline Blendstock
Produced from Rice Hull, Wood and NG/CO$_2$ Feedstocks

Reformulated Gasoline Blendstock Composition	Rice Hull Feedstock	Wood Feedstock	Natural Gas/CO$_2$ Feedstock
	Volume %		
N-Alkanes (C$_5$-C$_7$)	40.5	35.2	81.1
Normal 1-Alkenes (alpha-olefins) (C$_5$-C$_7$)	5.3	8.9	3.9
Normal 1-Hydroxy-Alkanes (C$_5$-C$_7$)	7.4	7.5	3.3
Iso-Alkanes (C$_5$-C$_7$)	11.3	11.9	11.4
Benzene	34.9	35.8	0.0
Toluene	0.85	0.82	0.0
Total	100.1	100.1	99.8

Since benzene is a valuable commodity chemical used as an intermediate for the production of other chemicals, our major oil/gas company partners recommend that we separate the benzene from the RGB and market it as a commodity chemical since benzene is currently selling at a much higher price that gasoline or diesel fuel. The current wholesale price for benzene is $5.00 / gallon in 2014. Therefore the benzene is easily removed from the RGB fraction using distillation. Table IXC.4 provides the composition of the RGB after the benzene has been removed.

Table IXC.4: Composition of the Reformulated Gasoline Blendstock Produced from Rice Hull, Wood and NG/CO$_2$ Feedstocks with Benzene Removed

Reformulated Gasoline Blendstock Composition	Rice Hull Feedstock	Wood Feedstock	Natural Gas/CO$_2$ Feedstock
	Volume %		
N-Alkanes (C$_5$-C$_7$)	62.0	54.7	81.1
Normal 1-Alkenes (alpha-olefins) (C$_5$-C$_7$)	8.1	13.8	3.9
Normal 1-Hydroxy-Alkanes (C$_5$-C$_7$)	11.3	11.7	3.3
Iso-Alkanes (C$_5$-C$_7$)	17.3	18.5	11.4
Benzene	0.0	0.0	0.0
Toluene	1.3	1.3	0.0
Total	100.0	100.0	99.8

Table IXC.5 summarizes the average properties of the reformulated gasoline blendstock produced from the 2012-13 IBR plant runs compared to EPA gasoline fuel. The octane rating (RON+MON)/2 for this blendstock varied from 60-65 compared to an octane rating of 87-89 for EPA summer gasoline. However, when the RGB is blended with EPA summer gasoline at 10 volume %, the octane rating for the blend should not be affected due to the presence of the 1-alkenes and 1-hydroxy alkanes.

The energy content of the RGB averages 116,500 BTU/gallon which is about 2% higher than that for EPA summer gasoline (114,000 BTU/gallon). As a result, the RGB, when blended with EPA summer gasoline at 10 volume %, should improve fuel economy by about 0.4%.

The RGB has a low flash point that is similar to that of gasoline and therefore it can be stored and distributed using the same infrastructure as that for gasoline. The distillation points (5%, 50%, and 90%) for the RGB and EPA summer gasoline are similar.

The RGB has very low benzene content (< 0.1%) compared to 1.8% for EPA summer gasoline. The alkene content varies from 3.9 to 8.9%, compared to gasoline, which can have an olefin content as high as 30%. The sulfur content of the RGB is less than 1 ppm.

Table IXC.5: The Average Properties of the Reformulated Gasoline Blendstock Produced from the 2012-13 IBR Plant Runs Compared to EPA Gasoline Fuel

Fuel Specifications (ASTM Test #)	RGB	EPA Gasoline (Summer)
Octane (RON+MON)/2	60-65	87-89
Fuel Energy Content (BTU/gallon)	116,500	114,000
Flash Point (°F) (D 93)	- 9°C	- 43°°C
Reid Vapor Pressure (psi)	9.0	9.0
Density (g/mL) (68°F)	0.680	0.745
Viscosity (mm^2/s) (104°F) (D 445)	1.85	1.17
Sulfur (ppm)	0	10
Aromatics (%)	< 0.1	32
Benzene (%)	< 0.1	1.8
Olefins (%)	11	18
Oxygen Content (%)	4.5	3.0
Initial Boiling Point (IBP)	84	81
5% Point	93	90
50% Point	116	118
90% Point	304	315
Final Boiling Point (FBP)	382	394
Recovery (%)	99	98
Residue (%)	0.5	1.0
Loss (%)	0.5	1.0

D. Wax Composition and Properties

The small amount of wax produced from this process is classified as a soft wax with a hydrocarbon distribution primarily in the $C_{25} - C_{40}$ range.

Table IXD.1: The Average Properties of the Wax Fraction Produced from the 2012-13 IBR Plant Runs Compared to Petroleum Paraffin Wax

Properties	IBR Wax	Petroleum Paraffin Wax
Composition	$C_{15} - C_{40}$ Normal Hydrocarbons	$C_{15} - C_{40}$ Branched Hydrocarbons
Density (g/cc) at 68 °F	0.90	0.90
Physical Properties	Macro-Crystalline (large crystals)	Micro-Crystalline (small crystals)
Melting Temperature °F	115-150	120-150
Aromatics	< 1 ppm	Not determined
Sulfur	< 1 ppm	Not determined

E. Engine and Vehicle Studies

A 2013 PACCAR MX-13 12.9 liter on-highway diesel engine was operated on an engine dynamometer to compare emissions and performance data from a Greyrock 20% synthetic diesel fuel blend with ultra-low sulfur diesel certification fuel to a neat (100%) certification fuel. These tests were carried out over a period of two days in April 2013 at the PACCAR Technical Center in Mount Vernon, WA.

Testing consisted of a 300-second torque map, pre-conditioning, one cold- and three hot-start heavy-duty transient cycles, and one ramped modal cycle supplemental emissions test (RMC SET) for each fuel. Two baseline tests with neat PACCAR certification diesel fuel bracketed one fuel blend with 20% Greyrock / 80% certification diesel fuel.

In general, performance and emissions were similar with 20% synthetic diesel blend and neat PACCAR fuel. Table 1 shows engine-out, brake-specific emissions differences between test fuels (negative values indicate a reduction in emissions with 20% synthetic fuel). The key findings from these performance and emissions tests are as follows:

1. There was a reduction in THC, NMHC, CO and opacity with the 20% synthetic blend. These reductions were likely due to the higher cetane number and lower concentration of aromatics for the 20% synthetic blend.
2. Due to the slightly lower energy density of the 20% synthetic blend, power was

approximately 1% lower across the operating range of the engine.
3. CO_2 emissions were reduced by 1.0% with the 20% blend.
4. There was no change in NOx emissions. It is likely that the engine out NOx control technology may have compensated for any potential NOx emission changes.
5. Mass-based brake-specific fuel consumption showed a slight reduction (improved efficiency) with 20% synthetic fuel based on triplicate hot-start HDT cycles. However, due to lower density of synthetic fuel, volume-based brake-specific fuel consumption increased over the wide range of test conditions.

Table IXE.1: Engine-out Emissions over Cold/Hot Composite, Hot-Start Average and RMC SET: Emission Test Results between 20% Synthetic Fuel and Neat Certification Diesel Fuel

Test Description	Engine-Out Brake-Specific Emissions (% Difference)							BSFC[2] (% Difference)	
	THC	CH$_4$	NMHC	NOx	CO	CO$_2$	PM_k[1]	g/(kW·hr)	L/(kW·hr)
Cold/Hot Comp	-8.0	N/A[3]	-8.0	N/A[3]	-8.6	0.1	-17.8	-0.2	1.9
Hot Start Ave	-9.5	N/A[3]	-9.5	N/A[3]	-11.3	-0.8	-21.1	-0.6	1.5
RMC	-9.7	N/A[3]	-9.7	N/A[3]	-9.5	-1.0	N/A[3]	-0.7	1.4

[1] PM calculated from opacity measurements
[2] Brake-Specific Fuel Consumption on a mass basis (g/kW-hr) and a volume basis (L / (kW-hr))
[3] Not Applicable – no measurable changes in emissions

The Cetane value of diesel fuel is an indicator of how readily and completely the fuel burns in the engine combustion chamber. The higher the Cetane number, the faster the fuel ignites and the more completely it combusts with a resulting improvement in fuel economy (Cataluña et al, 2012). These attributes are important because as the fuel burns faster and more completely, the engine also experiences better performance and produces fewer emissions. In addition, the lower density of the syndiesel (compared to petroleum diesel) results in more efficient fuel atomization, producing more power, lower emissions and improved fuel economy. In summary, the use of the IBR syndiesel fuel results in:

• More complete combustion
• Improved cold starts
• Improved fuel economy
• Less engine noise and knocking
• Reduced smoke and warm-up time
• Fewer misfires

- Lower exhaust emissions: nitrogen oxide, hydrocarbons, carbon monoxide and particulate matter.

Figure IXE.2 summarizes the reduction in emissions from neat synthetic diesel fuels (produced by Sasol and Shell) relative to petroleum derived diesel fuel from 2008-2012 diesel vehicles.
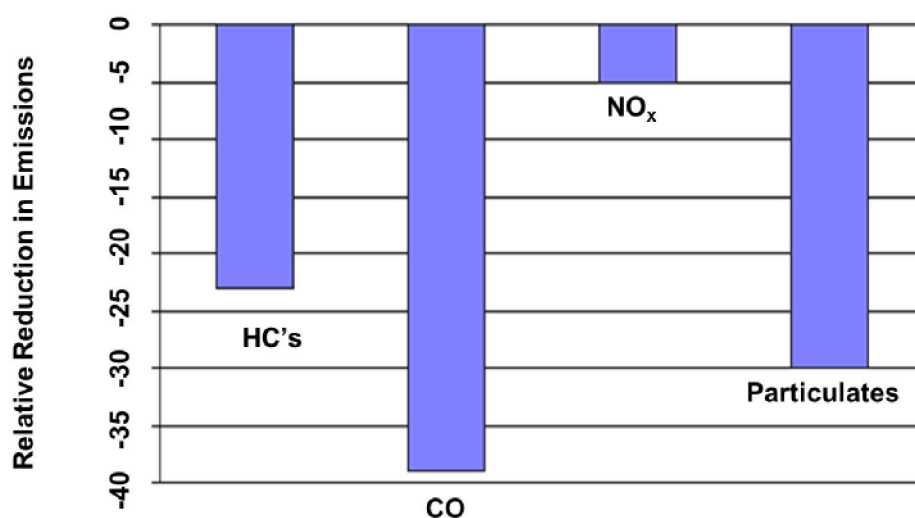
Figure IXE.1: **Figure 1:** The Reduction in Emissions using Synthetic Diesel Compared to Petroleum Derived Diesel Fuel for In-Use (2008-2012) Passenger Vehicles

Several published studies have demonstrated that fuel economy can be improved by 3-4% when using neat, synthetic fuels compared to petroleum derived fuels (U.S. Department of Transportation, 2010; Uchida, 2012; Shell, 2010).

F. Plant Performance Specifications

This section summarizes the optimum plant performance specifications as determined from the sixteen months of IBR plant testing encompassing over 992 hours of integrated operation. These validated performance specifications are compared to the technical targets that were forecast when the project was initiated in early 2010. These validated performance specifications were used in REII's techno-economic analysis (TEA) model to determine the production volumes of premium diesel fuel, reformulated gasoline blendstock and biochar. This TEA model was also used to determine the plant energy efficiency, the efficiency of feedstock carbon to product carbon, water effluents and air emissions.

1. Carbon Mass Balance Analysis

Table IXF.1 summarizes the distribution of plant carbon inputs and outputs generated from the conversion of 1,000 lbs. of biomass carbon to products and the carbon mass balances for the TCC and LFP systems as well as the total integrated plant. The energy conversion efficiencies for the conversion of biomass to syngas and biochar, syngas to fuel production, and the total integrated plant are included in this table.

a) Column A – Lbs. of C in Products from the TCC

The primary products from the TCC conversion of wood include syngas, biochar, tars and organic contaminants removed from the syngas by the water scrubber. The total carbon quantified in these products represented 97.9% of the carbon input into the TCC.

b) Column B – Total Lbs. of C for the Integrated Plant

The total amount of carbon in all of the plant products is shown in column B.

The tailgas consists of remaining H_2 and CO from the catalytic reaction; CH_4; CO_2 and C_2-C_7 HCs. This tailgas mixture can be used as fuel for the plant gas burners or recycled to produce additional diesel fuel. This tailgas has an energy value of about 650 BTU/scf.

The total % carbon conversion efficiency of biomass to CO was 42% and CO to fuels was 91%. The % carbon conversion efficiency of biomass carbon to fuel carbon was 40% and biomass carbon to fuel & biochar carbon was 53%.

The total % energy efficiency for the conversion of 1000 lbs. of feedstock carbon to syngas, biochar, tars and organic carbon in the scrubber water was 72%.

Table IXF.1: Distribution of Plant Carbon Inputs and Outputs
Generated from the Conversion of 1,000 lbs. of Biomass
Carbon to Products and Carbon Conversion Efficiencies

Components	A - Lbs. of C in TCC Products	B - Lbs. of C Output from the Plant
H_2	0.0	0.0
CO	417.0	38.4
CH_4	285.0	345.5
CO_2	122.6	97.4
C_2-C_5 HCs	4.2	42.5
Fuels (C_5-C_{24} HC's)	0.0	396.6
C_1-C_4 Alcohols in LFP Water	0.0	8.8
Wax	0.0	4.0
Biochar	135.5	135.5
Tars	1.6	1.6
C in Scrubber Water	13.0	13.0
Total Lbs. Carbon	979	1079
% C Conversion Efficiency	Biomass to CO & Biochar (56%)	Biomass to Fuels & Biochar (53%)

2. Comparison of Predicted and Validated Plant Performance Specifications

Table IXF.2 compares the validated plant performance specifications with the predicted values for the conversion of wood and rice hull feedstocks to "drop-in" fuels. All of the predicted performance values were either met or exceeded. The validated performance values in **green font** are specifications that have been surpassed or not originally specified. The reasons that some specifications were surpassed are described in this section.

a) Feedstock Size Range (as delivered)

The predicted optimum feedstock size range was 0.05"-1.5". However, it was found that feedstocks that were very small (less than about 0.10") can be entrained into the syngas stream flowing into Unit Operation #3. Since the syngas purification system was not designed to remove large quantities of biochar, this system became clogged with particulates after about 12 hrs. Therefore, the

feedstock size specification was increased from 0.05" to 0.15" and the wood feedstocks were screened to remove the fines less than 0.15".

The wood chips used in the plant tests were as large as 2.5". After the slow pyrolysis process, the wood biochar carbon was composed of elemental carbon (~95 %) and organic carbon (~5%). Since the wood biochar retained the same shape as the original wood chips, the wood biochar was easily segregated into 0.15"-1.25" and 1.25"-2.50" size ranges. It was found that the ratio of elemental to organic carbon in these two assemblages of samples were nearly the same, which demonstrated that the slow pyrolysis process can accommodate biomass materials up to 2.5".

b) Feedstock Moisture Content

The original specification for feedstock moisture content was 10-35 wt. %. Since the moisture content of the wood and rice hull feedstocks varied from 15-20 wt. % and 5-15 wt. %, respectively, enough steam was added to reach the optimum 1.4 lbs. of steam to 1.0 lbs. of feedstock carbon level. As based upon this optimum steam to carbon level, feedstocks with moisture content from 0-35 wt. % are acceptable.

c) Feedstock Carbon Content

The wood and rice hull feedstocks are comprised of 0.75 wt. % and 22 wt. % of ash, respectively. As a result, the carbon content of these feedstocks are 49.6 wt. % for wood and 36.5 wt. %, respectively.

d) Slow Pyrolysis Temperature (°F)

When the IBR project was initiated, it was predicted that the optimum temperature for the slow pyrolysis process (Unit Operation #2) would be 1,450 °F. However, it was demonstrated in Section VIIIA.1 (Figure VIIIA.1) that the pyrolysis process was not efficient at the original specified temperature of 1,450 °F and that the optimum temperature needs to be higher and in the 1,480-1,530 °F range.

e) Gases Steam Reforming Temperature (°F)

The predicted optimal performance temperature for this Unit Operation #3 was 1,800°F (surface temperature of the reforming coils) and it was found that the optimum temperature range for this process was 1,790-1,815 °F. Since the upper operating temperature limit of the Incoloy 800 HT coils was 1,825-1,850 °F, optimization studies were not carried out above 1,815 °F.

f) Operating Pressure (psia)

It was determined that a TCC operating pressure of 30 psia was sufficient for efficient plant operation since the system back pressure was typically in the 6-9 psi range (difference between the pressure in Unit Operations #6 and #2).

g) Air & O_2 Usage (lb./daft)

Since it has been demonstrated that oxygen levels greater than 500 ppm result in additional tar formation, the biomass was flushed with CO_2 to eliminate the introduction of O_2. In addition, any O_2 left in the syngas entering the LFP system can re-oxidize and de-activate the catalyst.

h) Steam Usage (lb. steam/lb. feedstock)

The original specifications for the optimum steam/lb. feedstock ratio for wood were 2.0/1.0. It was demonstrated in Sections VIIIA.2 and VIIIA.3 that a steam ratio of 1.4/1.0 would be efficient in steam reforming the feedstock and the gases generated from pyrolysis of the feedstock. It was found that any additional steam reduces the plant energy efficiency.

i) Syngas Production (scf/daft)

The production volume of syngas averaged 44,600 for the wood and 43,800 for the rice hulls (dry ash free ton basis). These similar results are not surprising since the ash free compositions of these feedstocks are similar.

j) CO Production (scf/daft)

Since the wood and rice hulls produce the same volume % of CO then the CO production in terms of scf/daft were similar.

k) Syngas Composition (exiting from TCC system)

The composition of the primary syngas constituents from the wood and rice hulls were similar as expected.

l) $C_2 - C_6$ Hydrocarbons

The quantity of $C_2 - C_6$ hydrocarbons in the syngas is an indicator of the efficiency of the slow pyrolysis and gases steam reforming processes. As these processes become more efficient, the concentration of these hydrocarbons will decrease. It was originally predicted that the concentration of $C_2 - C_6$ HCs would be about 1.0 volume %. It was found that the concentration of these HCs averaged 0.15%, which demonstrates further that the IBR plant was operating at its optimum operating conditions.

m) Tars (before and after purification)

The tars (in ppm) exiting from the TCC system averaged 260 ppm for wood and 296 ppm for the rice hulls as based upon NREL's measurements. When the plant is operating at 12.5 daft/day with biomass feedstock, this feedstock is converted to 10,625 lbs. of carbon containing products. Therefore as based upon these measurements, 2.8 – 3.1 pounds of tar would be produced per day.

As previously described, about 1020 grams (2.3 pounds) of tar was collected during run #9 during the time in which 585,400 ft^3 (15,570 m^3) of syngas was generated from approximately 10,000 lbs. of wood carbon input at an average feedstock rate

of 10.7 dry (ash free) tons/day. Therefore, the quantity of tar collected and the NREL tar measurements are in good agreement.

n) Benzene (before and after purification)

When this project was initiated, predicted concentrations of benzene in the syngas were not specified. It was determined that benzene was present at 4,900 ± 800 ppm in the syngas exiting from the TCC system (before purification) and 4,600 ± 850 ppm in the purified syngas for the wood feedstock. These values are similar to that for the rice hulls, which produced 4,600 ± 800 ppm in the syngas exiting from the TCC system (before purification) and 4,500 ± 800 ppm (after syngas purification. These data demonstrate that the TCC purification system didn't remove benzene from the syngas stream. Since benzene was not modified in the LFP catalytic system, all of this benzene is found in the fuel.

o) Sulfur and NH_3 Adsorbent

The required amount of these adsorbents was much less than originally specified (0.0044 vs. 0.09 lb. / daft feedstock) since the water scrubber was much more efficient in removing these contaminants than originally expected.

p) Conversion Efficiency (%) for Feedstock C to Syngas C

The validated % conversion of feedstock C to Syngas C matched that which was predicted (85%).

q) Thermochemical System Energy Efficiency (%)

The thermochemical system energy efficiency was slightly better (73%) than originally predicted (70%). This energy efficiency is based upon the commercial plant energy models, which utilize readily available heat recovery and use technologies.

r) Syngas Purification and Final Polishing

The use of Enviroscrub™ for the efficient removal of H_2S in the syngas stream was an innovation that was developed during the IBR tests. The amount of Enviroscrub™ required for efficient H_2S removal was 0.0132 gallons/daft of feedstock. The quantity of sulfur and ammonia adsorbent used in the guard beds was 0.0044 lbs. per daft.

s) Syngas Composition (after syngas purification)

The syngas composition data summarized in Table IXF.1 demonstrates that the concentrations of H_2, CO, CO_2, and CH_4 were not modified by the syngas purification system.

t) H_2S in Syngas (before and after purification)

The hydrogen sulfide in the syngas before purification averaged 2,300 ppm and 3,400 for the wood and rice hulls, respectively. The syngas purification system effectively reduced the H_2S to less than 3 ppb.

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u) NH₃ in Syngas

The ammonia in the syngas before purification averaged 4,100 and 5,500 ppm for the wood and rice hulls, respectively. The syngas purification system effectively reduced the NH_3 levels to $\leq$ 50 ppm.

v) Catalyst Usage

The fuel productivity of the catalyst increased slightly over the period of the IBR validation tests. This finding demonstrates that the catalyst was more robust than expected and that it is likely that the catalyst lifetime will be greater than 3 years. However, the catalyst usage rate in Table IXF.1 of 0.014 lbs. per daft was based upon a 3.0 year lifetime.

w) Syngas Conversion to Biofuels

It was predicted that 54 gallons of fuel would be produced from 10,000 scf of CO (at 90% CO conversion). However, the productivity of the catalyst was better than expected, producing 55.1 ± 1.4 gallons of fuel per 10,000 scf of CO at 90% CO conversion.

x) "Drop-in" Fuel (with wax and tailgas recycle)

The predicted performance of the plant for fuel production with wax and tailgas recycle was 54 gallons/daft. However, 56.0 ± 2.0 gallons/daft of fuel were produced without wax and tailgas recycle.

y) Production of Commodity Chemicals

It was not expected that any commodity chemicals would be produced from this process. However, since benzene is formed in this process and since benzene is a valuable commodity chemical used as an intermediate for the production of other chemicals, the benzene from the RGB fuel can be marketed as a commodity chemical since benzene is currently selling at a much higher price that gasoline or diesel fuel. The average wholesale price for benzene was about $5.00/gallon during the last half of 2013, compared to $3.10/gallon for diesel fuel and $2.65/gallon for gasoline. It was determined that 5.3 ± 0.5 gallons/daft of benzene is produced from this process.

z) Wax Side-Product

It was originally predicted that about 6.6 gallons/daft of wax would be produced from this process. However, through optimization of the fuel production process, wax production was reduced to 0.5 ± 0.2 gallons/daft.

aa) Commercial Plant Energy Efficiency

The current techno-economic modeling for the 240 daft/day commercial plant shows that this plant will achieve an energy efficiency of 53.9% compared to the original predicted 40% energy efficiency. This energy conversion efficiency is

comparable to the $25 billion Shell Bintulu plant that has 40-45% energy conversion efficiency for NG to fuels.

bb) Plant Effluents (water discharge)

The predicted quantity of water discharged from the commercial plant was 29 gallons/daft. However, since this process requires water input and the water generated from the catalytic conversion of syngas is used to generated steam for Unit Operation #2, the only water discharged from the syngas water scrubbers was 5.5 gallons/daft.

When wood is used with the typical 20 wt. % water content, 52 gallons/daft of water is produced. Since this water, contains small quantities of easily biodegradable organics at below the 1 volume % level, this water should be suitable for agriculture use.

cc) Plant Effluents (air emissions)

When this project was initiated, predicted concentrations of from a proposed commercial plant were not specified. Table VID.22 summarizes the air emissions that would be expected from the 240 dtpd commercial plant.

Table IXF.2: Predicted and Validated Plant
Performance Specifications for the Conversion of Wood and
Rice Hull Feedstocks to Fuel (np: not predicted)

Process Description	Average Plant Inputs and Outputs	Predicted Performance Values	Validated Performance	
			Wood	**Rice Hulls**
Feedstock Properties	Feedstock size range (as delivered) (inches)	0.05-1.5	**0.15–2.5**	**As received**
	Moisture content (Wt. %)	10-35	15-20	5-15
	Carbon content (dry) (Wt. %)	50.0	49.6 ± 0.7	36.5 ± 0.8
	Ash content (dry) (Wt. %)	0.80	0.75 ± 0.2	22.0 ± 1.0
Feedstock Processing	Grinding energy use (kWh/daft)	None	None	
TCC Conversion (pyrolysis / steam reforming)	Slow pyrolysis (UP #2) temperature (°F)	1,450	**1,480-1,530**	
	Gas steam reforming (UP #3) surface T	1,800	1,790-1,815	
	Operating pressure (psia)	45	**30**	
	Air & O_2 usage (lb./daft)	0	0	
	Steam usage (lb. steam / lb. feedstock carbon)	2.0/1.0	**1.4/1.0**	
	Syngas production (scf/daft)	45,000	44,660 + 2,100	43,800 + 2,400
	CO production (scf/daft)	9,450	**10,260 + 440**	**10,075 + 460**

Table IXF.2 (continued): Predicted and Validated Plant Performance Specifications for the Conversion of Wood and Rice Hull Feedstocks to Fuel (np: not predicted)

Process Description	Plant Inputs and Outputs	Predicted Performance Values*	Validated Performance Values	
			Wood	Rice Hulls
Syngas Composition (exiting from TCC system)	H_2 / CO (molar ratio)	2.0	2.00 ± 0.15	
	H_2 (volume %) (dry)	45	46 ± 2.0	
	CO (volume %) (dry)	22	23 ± 1.3	
	CO_2 (volume %) (dry)	20	18 ± 1.2	
	CH_4 (volume %) (dry)	12	12 ± 0.8	
	$C_2 - C_6$ (volume %) (dry)	1.0	**0.15 ± 0.10**	
	O_2 (ppm) (dry)	< 500	< 500	
Syngas Contaminants (exiting from TCC system) before purification	Tars (ppm)	np	260 ± 39	296 ± 44
	Benzene (ppm) (dry)	np	**$4,900 \pm 800$**	**$4,600 \pm 800$**
	H_2S (ppb) (dry)	2,000	$2,300 \pm 1,000$	**$3,400 \pm 1,200$**
	NH_3 (ppb) (dry)	np	**$4,100 \pm 500$**	**$4,500 \pm 650$**
System Exit Gas Yield	Conversion efficiency (%) for feedstock C to syngas C	85	85 ± 3	
	Thermochemical system energy efficiency (%)	70	73 ± 2.5	
Syngas Purification and Final Polishing	Enviroscrub™ (gallon/daft)	np	**0.015**	
	Enviroscrub™ ($/gallon)	np	**$9.67**	
	Sulfur and NH_3 adsorbent (lb./daft)	0.09	**0.0044**	
	Sulfur & NH_3 adsorbent cost ($/lb.)	13.60	14.40	
	Tar conversion to syngas (Wt. %)	np	Not Required	

*ND: Not Determined

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Table IXF.2 (continued): Predicted and Validated Plant Performance Specifications for the Conversion of Wood and Rice Hull Feedstocks to Fuel (np: not predicted)

Process Description	Plant Inputs and Outputs	Predicted Performance Values	Validated Performance Values	
			Wood	**Rice Hulls**
Syngas Composition (after syngas purification)	H_2 / CO (molar ratio)	2.0	2.00 ± 0.15	
	H_2 (volume %) (dry)	45	46 ± 2.0	
	CO (volume %) (dry)	22	23 ± 1.3	
	CO_2 (volume %) (dry)	20	18.5 ± 1.2	
	CH_4 (volume %) (dry)	12	12 ± 0.8	
	$C_2 - C_6$ (volume %) (dry)	1.0	**0.15 ± 0.10**	
	O_2 (ppm) (dry)	< 500	< 500	
Syngas Contaminants (after syngas purification)	Particulates ($\mu g/m^3$)	< 500	700 ± 105	180 ± 27
	Benzene (ppm)	np	**$4,600 \pm 850$**	**$4,500 \pm 800$**
	H_2S (ppb) (dry)	< 20	< 3	
	NH_3 (ppb) (dry)	< 50	< 50	
Conversion of Syngas to Fuel	Catalyst usage (based on 3 yr. life) (lb./daft) for IBR plant	0.032	**0.014**	
	Catalyst cost ($/lb.) for IBR plant	31.00	33.20	
	Catalyst cost ($/daft) for IBR plant	$0.98	$1.12	
	H_2 usage in hydro-cracking (kg/kg biomass)	Not required	Not required	
	Syngas conversion to biofuel(s) gal/10,000 scf CO at 90% CO conversion)	54 (*with wax and tailgas recycle)*	**55.1 $\pm$ 1.4 (*without wax and tailgas recycle)***	
	Energy efficiency across biofuel(s) synthesis (%)	60	61	

Table IXF.2 (continued): Predicted and Validated Plant
Performance Specifications for the Conversion of Wood and
Rice Hull Feedstocks to Fuel (np: not predicted)

Process Description	Plant Inputs and Outputs	Predicted Performance Values	Validated Performance Values	
			Wood	**Rice Hulls**
Overall Process Yield from Biomass	"Drop-in" fuel (gal/daft) (with wax and tailgas recycle)	54	**There is too little wax to recycle and tailgas will be used for heat/power for the plant**	
	"Drop-in" fuel (gal/daft) (without wax and tailgas recycle and excluding benzene)	44	**51.3 ± 3 (79.5% diesel & 20.5% gasoline)**	
	Export power (kW-hr/daft)	None	None	
	Commodity chemicals (benzene) (gal/daft)	np	**5.3 ± 0.5**	
	Wax side-product (gal/daft)	6.6	**0.25 ± 0.2**	
	Biochar (lbs./daft)	np	**297**	
	Tailgas side-product (scf/daft) (used for plant gas burners)	12,000	12,200 ± 1,300	
	Commercial plant energy efficiency (%)	40	**53.9 ± 1.5**	
	Commercial plant carbon conversion efficiency (%)	40	**43.8 ± 1.2**	
Plant Effluents	Water discharge (gal/daft)	np (from LFP)	**52 (recycled back to TCC)**	
		29 (from scrubbers)	**19 (for treatment)**	
	Air Emissions (tons/daft)	np	**CO (2.21 x 10^{-4})**	
			PM (3.75 x 10^{-5})	
			NOx (3.83 x 10^{-5})	
			CO$_2$ (0.801)	

X. Results and Conclusions from Project Management

The following section summarizes the project management activities performed for this project.

A. Coordination of Project Partners

The overall project management of this project was carried out by REII. REII managed the project partners and their workflow to insure timely completion of deliverables. The Project Team consisted of:

- Red Lion Bio-Energy (Key Partner)
- Greyrock Energy (Key Partner)
- National Renewable Energy Laboratory
- Desert Research Institute
- PACCAR
- Bureau Veritas
- Grace Davison
- pH Matter
- University of Toledo
- Midwest Terminals
- WorleyParsons
- Solar Turbines

Weekly teleconferences were conducted with REII and the Key Partners to manage project costs, scope, schedule, and deliverables. Meetings with other members of the Project Team were conducted as needed to allow for the appropriate flow of information.

B. Design for Manufacturing (Modular Design)

The design of the IBR facility was based on the need to demonstrate a modular design, which could be supported during future scale-ups of the technology. More specifically, a design for manufacturing approach was taken, which allowed the Project Team to control costs and schedule during the Procurement and Construction phases of the project. The modular design of components also allowed Red Lion Bio-Energy and Greyrock to ship equipment using conventional trucks, removing the need for oversized loads that could have resulted in delays or additional project costs.

Based on the successful use of the design for manufacturing concept on this project, future facilities will be deployed using a similar methodology.

C. Procurement and Delivery of Major Components

Overall, the procurement and delivery of major equipment components was completed on schedule and within budget. Any delays in procurement were identified early and remedied to insure the project could maintain its schedule and budget allocated to the task. Lessons learned during procurement and delivery included:

- Early in the procurement phase it was important to insure that all team members and contractors/vendors understand specifications, payment terms, schedule, and roles and responsibilities. This was accomplished by 1) establishing a data room for consolidating all of the documents related to procurement and delivery, 2) standardizing contracts and payment terms (where possible) and storing contracts in the data room, and 3) establishing weekly calls with contractors and vendors to maintain open lines of communication.
- Establishing a single point of contact for key equipment and key contactors/vendors improved communication efficacy and efficiency.
- Establishing a system for tracking, reporting, and mitigating any scope, cost, or schedule changes that could affect the project.

D. Plant Component and Process Reliability

During the operations phase of the project, component and plant durability were monitored throughout the 17 test campaigns. However, there were a number of components that needed to be redesigned. The following provides a summary of plant durability issues and the solutions developed during the execution of the project.

- Feed handling system gate valves – During the operation of the IBR plant, the gate valves failed due to inadequate materials of construction. The solution employed by the Project Team involved exchanging the Teflon slides with a more robust material (brass), which eliminated the failures.
- Feed handling system seals – Due to several seals deteriorating under normal plant operating conditions, more robust seals were installed. The Project Team also tightened feedstock specifications, which helped to keep the integrity of the upgraded seals.
- Ram Charge Feeder plugging – At higher feed rates the Ram Charge Feeder experienced plugging, which required either the removal of the impacted material or the stopping of an operational campaign. The Project Team addressed the issue by 1) tightening the feedstock specification, 2) more slowly increasing feed rate input the during ramp-up of the system, and 3) closely monitoring the performance of the Ram Charge Feeder during operations to identify any early signs that the system was not operating under optimal conditions. An improved design of the Ram Charge Feeder is in development for future commercial facilities.
- Solids Steam Reforming seals – Seals on the Solids Steam Reforming system that had been designed to withstand a high temperature syngas environments failed early in the testing program. The Project Team replaced the seals and installed a water cooling system around the seals to prevent the seals from overheating.
- Solids Steam Reforming mechanical drive – Later in the operations period of the project a weld broke on the mechanical drive end of the Solids Steam Reforming system. The weld was re-welded and reinforced with bolts, which solved the problem.
- Ash Auger plugging – At higher biomass feed rates to the Solids Steam Reformer, the Ash Auger was unable to remove ash from the system fast enough, which resulted in plugging and continued maintenance. The Project Team closely monitored the performance of the Ash Auger during operation of the IBR and frequently had to

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unclog the system at higher feed rates. Future commercial plants will take a larger ash auger into consideration.

- Syngas cooling and water removal – At times during the operation of the IBR the ability of the system to adequately remove water from the syngas after the Gases Steam Reforming system was inadequate. This led to the disruption of flow meter readings and migration of water to downstream processes. The Project Team was able to reduce the water content of the syngas through heat exchangers, but was not able to fully remove all of the water in the syngas.

XI. Future Efforts

A. Modification of Unit Operations to Improve Commercial Plant Performance, Reliability and Economics

1. Unit Operation #1 (Feedstock Introduction)

The weigh bins and conveyors utilized in Unit Operation #1 worked well during the test campaigns. Future upgrades to this system will include automated, real-time feedstock input calculations to better monitor and manage the feed rate of biomass to the Solids Steam Reforming system. The valves used in the feed introduction system have been modified from the manufacturer's design to better accommodate biomass feedstocks and the operating conditions of the IBR (Figure X1A.1). This section describes modifications to the Feedstock Introduction system that our technical consultants recommend to ensure trouble free operation for the 240 daft/day commercial plants.

As described previously, the 25 tpd biomass feeding system has a *lock hopper* and a *piston injection system*. The main functions of this system are to pressurize the biomass and provide reliable sealing to prevent the backflow of gasses from the pyrolysis reactor. The lock hopper system receives biomass at atmospheric pressure and after pressurization with carrier gas; the biomass is discharged via gravity into the injection line where the piston pushes it into the reactor. Although the system was designed to operate at 50 psig, all the tests conducted so far have been done at 15 – 20 psig.
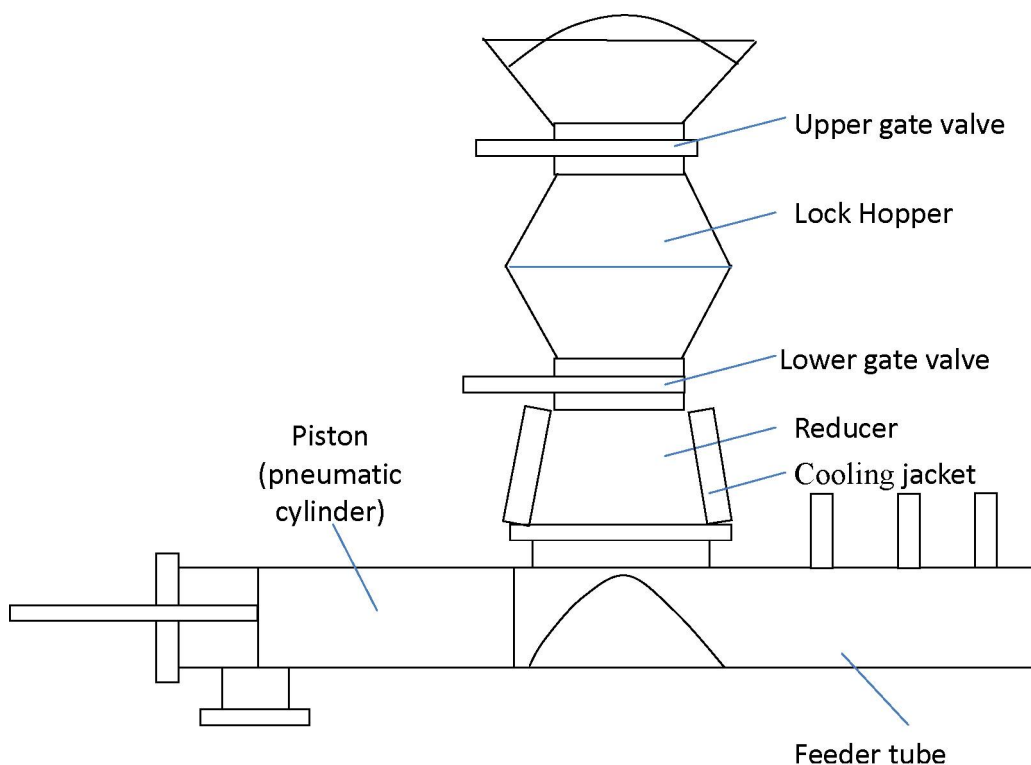
Figure XIA.l: Feedstock Introduction System

Piston feeders are sometimes more complicated to design and operate than other feeding systems. Typical problems encountered with the operation of these systems are mechanical wear, gas leakage, and feeding fluctuations.

The Toledo IBR plant encountered intermittent problems with the feedstock introduction (mainly clogging and compaction). When the Ram Charge Feeder (RCF) was operated with ground rice hulls, it compacted near the top of the piston at full extension. The compaction was also significant with wood chips that were less than 0.15". After 18 hours of operation, the piston started to stick at the ends when small particles slipped and became trapped in the cylinder area.

Extensions/stages were added to the end of the piston to help break up the compacted biomass. Then, the piston was sent to a machine shop to expand the ends to be flush with the entire piston. These modifications improved the operation of the biomass feeder.

No feeding system is ideal. In fact, according to industrial data, approximately 80% of biomass feeders encounter significant problems. Figure XIA.2 shows a "Cause and Effect Evaluation Diagram" that illustrates and categorizes the potential causes of the problems in the operation of the biomass feeder. This diagram was built based on the information developed during the 16 months of IBR plant testing, information reported in the literature and the experience of technical consultants.

The main variables affecting the operation of biomass feeding systems are: *biomass physico-chemical properties* (type of biomass processed, particle shape, size distribution, moisture content, bulk density, contaminants, compressibility), *operational variables* (feeding rate, temperature in the feeding tube, pressure, pressure drop in the feeding system, piston frequency, feeding rate, flow, pressure and temperature of carrier gas used, shoot-down and start-up conditions), *design variables* (type of feeder, shape of the piston, piston size, hopper and feeding line, dimension of hopper and feeding tube, maximum design torque, instrumentation and control system, cooling system used, distance between the piston and the cylinder and lubrication method). Each of the possible causes of the reported problems is discussed in the following sections.

a) Biomass Physico-Chemical Properties

This category groups all the variables related to physico-chemical properties of the biomass that are relevant to its behavior in the feeding system.

Type of biomass: Biomass particles, whether derived from wood or agricultural feedstocks vary greatly in size, shape, density, moisture content and compressibility. Some of these properties can affect bridging and blockage during feeding. Some of these physical variables together with the actual chemical composition of the biomass have an impact on the cohesive/adhesive characteristics of these materials.

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Size distribution: The performance of feeding systems is affected by biomass particle size distribution. Uniformly sized feedstocks (e.g. pellets) are easier to feed. Oversized particles (> 2.0") with extreme shapes, high density, and stiffness are often responsible for the blockage of feeding systems and should be removed. The cohesion and adhesion of fine particles (< 0.10") can cause bridging and blockage. The introduction of biomass particles finer than about 0.10" should be limited to 10 % to maintain reliable operation.

Particle shape: The particle shape can induce friction and mechanical interactions between particles, impacting biomass flow properties and creating bridges across openings. Hook-shaped or long, thin particles have higher tendency to bridge.

Moisture content: The cohesive strength of the biomass increases with the moisture content. Thus, long thin particles with high moisture content have higher tendency to bridge and block biomass feeding systems.

Bulk density: Bulk density directly affects biomass flow properties and feeding capacity. A bulk density between 1,000 and 1,700 kg/m^3 is needed to create a mechanically stable plug (compact biomass) of low gas permeability.

Compressibility: While hard particles with large strength tend to be incompressible and flow readily, compressible solids resist motion. Hard particles, on the other hand, can cause blockages if the outlet dimensions are too small.

Contaminants: Serious wear and stoppage in the feeding system can happen if stones, dirt, and metals are not removed.

b) Operational Variables

This category groups all the variables that can be controlled by the operator. To ensure smooth operation the feeding line temperature and pressure, feed hopper level, piston frequency, power consumed by the piston, should be monitored continuously

Temperature: When the feeding line reaches torrefaction and pyrolysis temperatures, severe tar accumulation occurs. This tar can act as glue and can block the feeding system.

Biomass feeding rate: Measuring and controlling the biomass feeding rate on real-time is critical to ensure a smooth operation of the system and to evaluate the performance of the system.

Piston frequency: Piston feeders are positive displacement devices with feed rate proportional to the piston frequency if the cylinder is always filled to the same level.

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Carrier gas used: For some systems, pressurizing the feed line with air or inert gas (usually nitrogen or CO_2) is required to prevent backflow and avoid dust explosions.

Start-up conditions: The motor should be big enough to start the operation of the piston and to overcome blockage problems. The design of the piston should account for the high initial shear stress during start up caused by confined solids as well as the extra torque needed to overcome a blockage. Before starting up the operator should make sure that the feeding system is empty to avoid excessive thermal degradation of the biomass.

Shut-down conditions: The feeding system should be emptied before stopping the reactor otherwise the biomass could stay in the feeding system for too long and pyrolysis could occur.

Pressure: To avoid backflow the pressure in the feeder should be higher than the pressure in the reactor. Avoiding backflow is critical because the vapors in the pyrolysis chamber contain high content of tars that could condense on the cold surfaces.
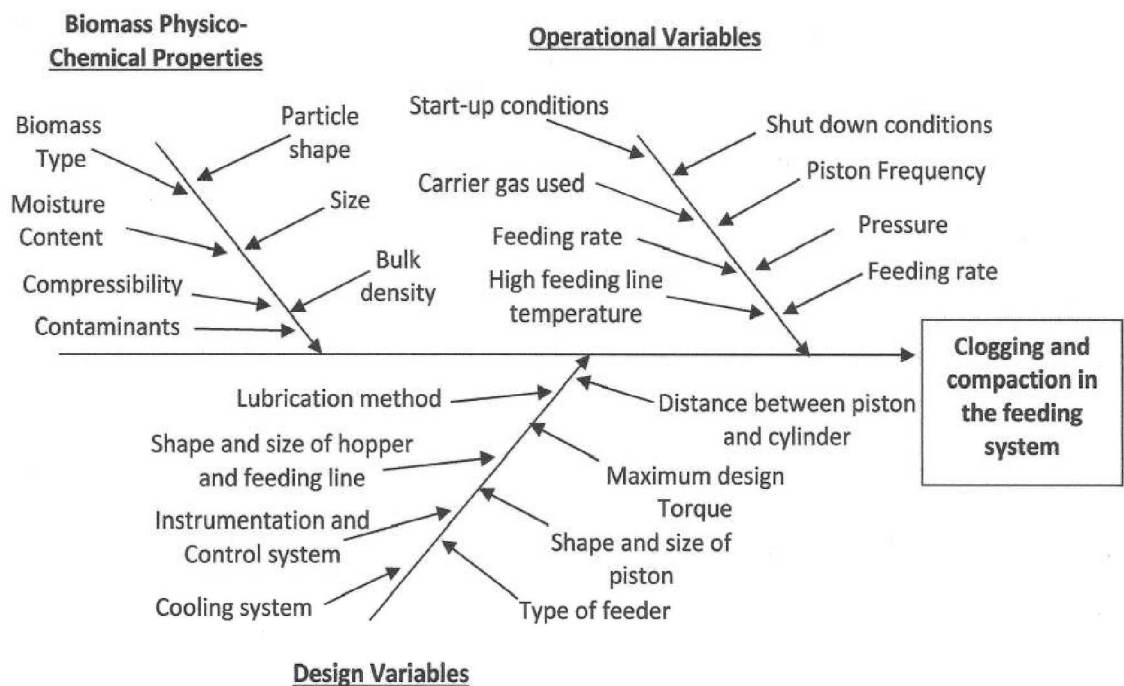
Figure XIA.2: Cause and Effect Evaluation Diagram Developed for Upgrading of the IBR Feedstock Introduction System

c) Design Variables

The following items summarize the modifications to be considered during the re-design of the system.

Type of feeder: The most common feeders used in biomass thermochemical conversion systems are: hopper and lock hopper systems, screw feeders (including single and twin-screw feeders), rotary valve feeders, piston feeders, belt feeders, vibratory feeders, reciprocating pan feeders and rotary table feeders. The choice of the system will depend on the kind of material processed. Most feeders work well for specific feedstocks and feeding conditions.

Cooling system: The addition of a cooling jacket to the feeding line is one of the most common methods emplyed to maintain the temperature in the feeding line below pyrolysis conditions.

Hopper: Conical or wedge shaped hoppers and lock feeders are the most common devices used in biomass feeding systems. These systems typically include a converging sloped wall section at the bottom. The lock hopper is typically used as an air lock to receive the biomass at atmospheric pressure and after pressurization discharge the biomass by gravity. The main factors that have to be taking during hopper design are: hopper type, configuration, and dimensions as well as pressure, filling level, and refilling procedures.

Feeding Line: The feeding line is the tube connecting the feeder and the reactor. This line is exposed to high heat flow from the reactor and if not properly designed, blockage and compaction occur.

Piston: The dimensions of the piston, its displacement and frequency determine the capacity of the piston feeder. The design of the piston also impacts power consumption.

Piston-Cylinder Distance: The piston ring and cylinder are two very important components of the feeder since they slide against each other leading to severe wear. Leaving too much space between the cylinder and the piston could lead to the accumulation and compaction of fines.

Instrumentation and Control: Reliable instruments (pressure, temperature, torque) and a robust control system are very important to detect blockages and compaction and restore feeding. Torque meters, and revolution counters, are among the simplest instruments to monitor and adjust the feeding systems. Some of the actions that could be implemented in the event of feeding blockage can be: start up mechanical or pneumatic aids and injecting pressurized gas.

Maximum Torque: The motor and the transmission mechanisms should be designed to overcome starting torque and the torque needed to break compacted biomass responsible for the blockage of the feeder. The torque needed under these

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conditions is much higher (often 1.5 – 3 times) the torque needed for continuous operation.

Lubrication Method: Graphite is often employed as a self-lubricating material due to its heat resistance, thermal expansion, mechanical properties and cost. The wear between the piston ring and the cylinder is commonly reduced by the use of lubricating oil.

d) Identification of Problems and Recommended Modifications

The following four causes of feedstock introduction problems were identified as follows:

- The overfilling of the feeding tube and compaction of the biomass when the piston pushes the biomass towards the discharge elbow of the reducer

- High temperature in the feeding line due to an inefficient cooling system

- Lack of instrumentation to follow variables associated with clogging and compaction (temperature, pressure, torque) in the feeding system

- Lack of operational strategies to handle the feeding system in conditions of incipient clogging and compaction.

It was determined that major design modifications to the existing feeder were not required. The alternatives proposed to mitigate the effect of the main causes identified in the previous section were:

- The overfilling of the feeding tube can be avoided by limiting the mass of biomass fed into the lock hopper to the volume of the feeding tube underneath. The main drawback of this alternative is that it could limit the capacity of the feeder. The capacity could be improved by increasing the feeding frequency but this could increase the wear of the valves. The operation of the feeder and the piston should be synchronized.

- The high temperature in the feeding line can be mitigated if a high volume of an ambient temperature pressured carrier gas is used. The use of tail gas as carrier gas is recommended.

- The feeding system should be monitored so that the clogging and the compaction of biomass can be detected on real time and appropriate operative actions can be implemented. It is recommended that a thermocouple be added to the feeding tube, a pressure sensor, to measure the pressure drop on the feeding tube and to measure the power consumed by the piston. When the operator identifies abnormal conditions in the feeder he/she should take corrective actions. Some of the corrective actions recommended when clogging formation is detected are: (a) reduce biomass feeding rate, (b) increase the flow of carrier gas, and/or (c) reduce the frequency and the displacement of the piston. Normal feeding conditions can be resumed after removing the compacted biomass.

- Special care should be taking during shut-down and start-up to avoid biomass in the feeding system exposed to high temperature for prolonged periods of time.

It is recommended that a lock hopper system be used that is similar to the one used in the IBR unit to pressurize the biomass plus an auxiliary feeder. In order to effectively scale up the current Ram Charge Feeder, it is recommended that the solutions listed in the previous section be implemented in addition to the following:

- To prevent pyrolysis reaction in feeding line, we recommend installing a cooling jacket (see Figure XIA.3) to prevent biomass from heating.

- The aim of most of the piston feeders is to create a plug that seal the feeding system and avoid backflow. To create this plug, most of the feeding lines use reducers before entering the reactor. Because the seal is provided by the lock hopper, we propose to expand the diameter of the feeding line and in this way reduce the shear stress and the compaction of the biomass in the feeder.

These modifications to the ram charge feeder will be made and tested over long periods of time to insure the robustness of the upgrades. These upgrades will be incorporated into future commercial facilities to improve reliability.
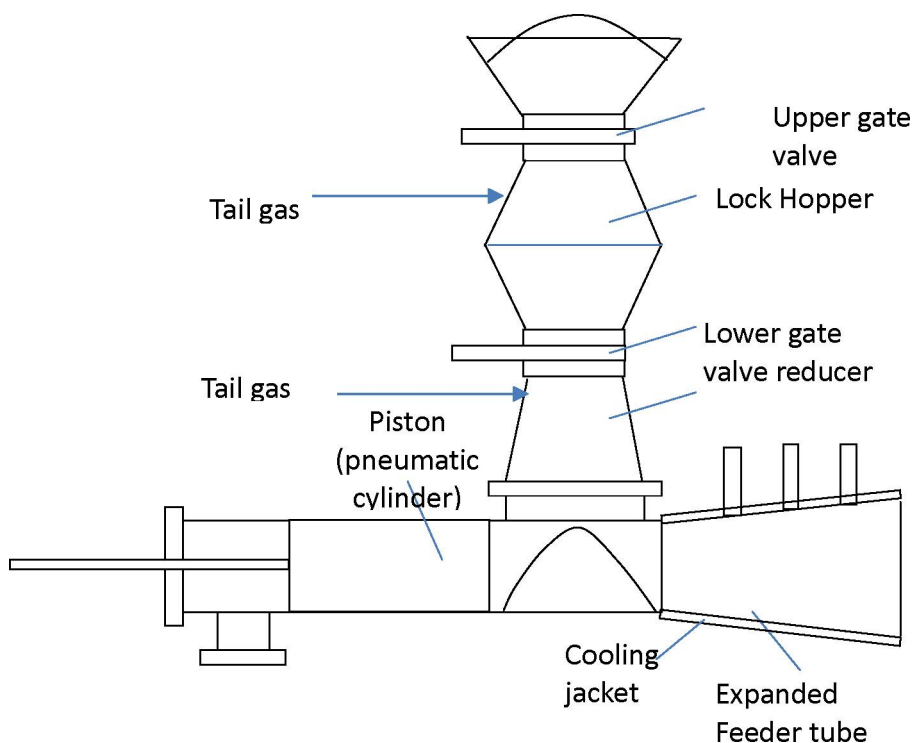
Figure XIA.3: Recommended Modifications to the Feedstock Introduction System

2. Unit Operation #3 (Gases Steam Reforming)

The gases steam reforming process performed well. However, a more energy efficient and economical design has been developed which will be validated at the Toledo IBR plant for use in future commercial facilities.

3. Unit Operations #4a & #4b (Syngas Purification)

The Syngas Purification system worked well during the operation of the IBR. Additional work will be carried out to assess whether or not Type A Tars, primarily naphthalene, can be further reduced through system upgrades. Although the management of these tars is not a primary concern for the deployment of commercial facilities, their reduction will reduce O&M costs.

4. Unit Operation #5 (Syngas Compression)

The syngas compressor worked as expected during the operation of the IBR plant. Therefore, no further work will be required on this unit operation.

5. Unit Operation #6 (Catalytic Conversion)

The Catalytic Conversion unit operation exceeded expectations during the operation of the IBR. No further work will be required on this unit operation.

6. Unit Operation #7 (Product Collection)

This product collection Unit Operation met expectations. Therefore, no further work on this Unit Operation will be required.

7. Unit Operation #8 (Fuel Storage)

The fuel tanks used for storage of the fuel met expectations.

8. Unit Operation #9 (Distillation)

Additional validation work will be carried out on the proposed distillation Unit Operation prior to the deployment of the first commercial plant.

B. REII "5E" Assessments for Commercial Plant Deployment

During the past decade, REII developed and utilized a rigorous assessment methodology for current and emerging production technologies for renewable fuels, renewable energy and renewable chemical products. The components of this 5E assessment methodology are: (E1) technology evaluations at the research, development, demonstration and deployment stages (R3D); (E2) determination of energy and mass conversion efficiencies for each Unit Operations and the entire biorefinery; (E3) environmental impact assessments; (E4) economic analyses and; (E5) appraisals of socio-political effectiveness. Socio-political effectiveness evaluates factors such as government regulations, organizational objectives, societal benefits, environmental stewardship, and stakeholder needs and concerns. This "5E Assessment" has been utilized by REII for several years to:

- Determine the viability of promising technologies for the conversion of various feedstocks to renewable energy, renewable fuels and renewable chemical products.

- Compare the development of alternative fueling infrastructures (e.g. renewable diesel and ethanol fuels) from various waste biomass feedstocks.
- Assess the likelihood that the automotive/vehicle industry will be able to produce these alternative fueled and next-generation vehicles which are acceptable to the public in the foreseeable future.
- Verify that future engines will be able to effectively utilize these alternative fuels.

REII will continue to utilize this "5E Assessment" methodology to advance the development of the technologies utilized in the IBR to inform commercial plant performance, plant economics and reduce the environmental impact of future IBR facilities.

C. Future Uses of IBR Plant

The IBR facility will continue be used as a testing and training facility for the TCC and LFP technology platforms. As outlined above, there are several Unit Operations that will continue to be tested prior to the deployment of a commercial scale IBR. It will also be used to provide future operators on-the-job training to address actual operational challenges, work-a-rounds, and provide a better base of knowledge from which the operators can operate commercial facilities.

XII. Commercialization of IBR Technology

SynTerra Energy was established as a 50/50 joint venture between Greyrock and Red Lion Bio-Energy (RLB) in 2012 to commercialize this IBR technology for the conversion of biomass residues to synthetic diesel fuel and reformulated gasoline blendstocks. Since that time, SynTerra Energy business and technical leaders have met with numerous equity investors, energy companies, private investors and oil and gas companies to obtain funding for the first commercial scale plant designed to convert 240 dry ash free tons of biomass to 4.40 million gallons of fuel. Although many of these investors agreed that SynTerra has established leadership in this application, and that techno-economic assessments of this this technology estimate that the potential return on investment is about 11% (without fuel incentives) and 21% (with fuel incentives) (based upon 2014 economics and $90/barrel oil), the recent failure of some competing technologies have made these investors wary of additional funding support for such projects.

A. Plant Site

Figure XIIA.1 shows the proposed area for siting of the proposed commercial scale biomass to liquid fuel (BTL) plants in the Sacramento Basin Province. The agriculture towns within this area are representative of hundreds of such towns in the U.S. The primary agriculture products within the 960 square mile (520,000 acre) encircled area includes rice, nuts, alfalfa, olives and a wide variety of fruits and vegetables. These agriculture products produce large quantities of biomass residues (see Section XIIB).
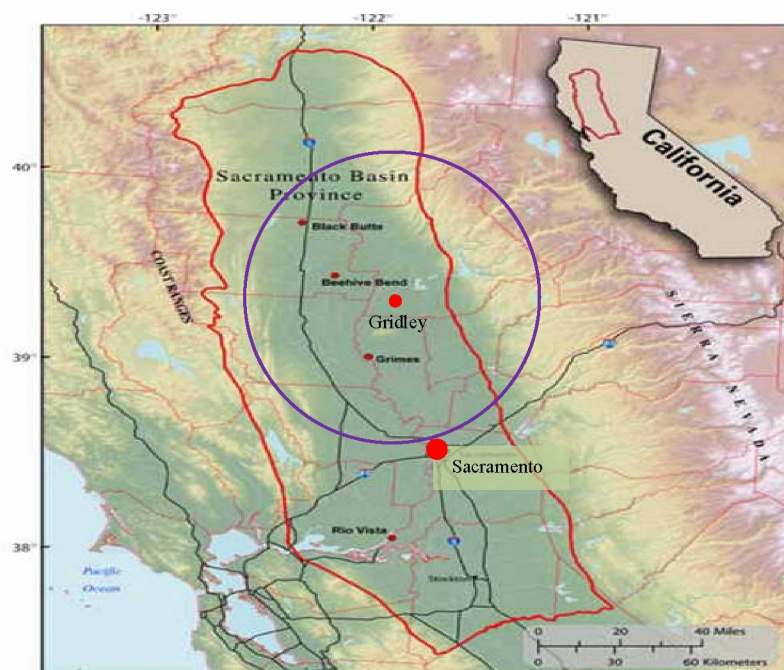
Figure XIIA.1: Proposed Area for the Commercial Scale BTL Plants in the Sacramento Basin Province

The Sacramento Basin oil and gas province (Figure XIIA.1 – heavy red line) covers an area of nearly 12,000 square miles and forms the northern part of California's Central Valley. The province is bordered on the west by the Coast Ranges, on the north by the Klamath Mountains, on the east by the Sierra Nevada, and on the south by the Stanislaus-San Joaquin County line (the thin red lines show county boundaries).

The U.S. Geological Survey (USGS) recently completed an assessment of undiscovered natural gas resources of the Sacramento Basin Province of California. Using a geology-based assessment methodology, the USGS mean estimates of undiscovered, technically recoverable resources are 534 billion cubic feet of natural gas and 323 thousand barrels of natural gas liquids in the Sacramento Basin Province. Currently there are several natural gas power plants and stranded gas wells (Figure XIIB.2) in this area.

B. Biomass Residues

Table XIIB.1 summarizes the biomass residues available within this 962 square mile (5,193,000 acre) area. The average quantity and estimated cost ($/dry ton delivered to the plant site) for each feedstock produced during the 2013 harvest are provided in this table.

Table XIIB.1: Biomass Residues Available within the 962 Square Mile Area Shown in Figure XIIA.1

Biomass Residues	Average Quantity Available (kiloton/year)	Estimated Cost ($/dry ton)
Rice hulls	332	20
Rice straw	910	35
Orchard and Domestic Wood Residues	170	30
Nut shells	460	40
Wild-Land Remediation Wood Residues	120	55
Fruit Processing Residues	80	15

1. Rice Hulls

California is the second largest producer of rice in the United States and about 65% of this rice is grown within a 35 mile radius of the proposed plant site. During the 2013 season, 561,000 acres of rice were harvested in California with 365,000 acres harvested within the 35 mile radius. The yield of un-processed rice (rice kernel and hull) was about 4.1 tons/acre (The Crop Site, 2014).

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All of the rice is processed locally. Rice milling generates a byproduct known as rice husks. During milling, rice & bran represents 78 weight % and the rice husks represent 22 weight % (Figure XIIB.1 shows a typical rice mill). Therefore, about 512,000 tons of rice husks by-products were produced during 2013 with 332,000 tons produced within the 35 mile radius (Table XIIB.1). Since there wasn't much demand for rice hulls, the price was about $20/ton delivered in 2013.

2. Rice Straw

As shown in Table IIB.1, rice straw is the most abundant biomass resource available within the 35 mile radius with 910,000 tons produced during 2013.

The farmers within the zone of biomass collection, have sufficient equipment to effectively collect the rice straw. This equipment includes swathers, balers, stack-wagons and loaders.

Figure XIIB.2 shows a self-propelled rotary swather with cutter, stripper and header accessories in the process of harvesting rice straw in the Sacramento Basin Province. After rice harvest, the swather can also cut the remaining stubble by a conventional header harvester to maximize the volume of straw per acre collected. Swathing rice straw is expensive at approximately $12 per acre.

Figure XIIB.1: Bunge Rice Processing Mill in Woodland, CA

Figure XIIB.2: Rotary Swather Harvesting Rice Straw

Figure XIIB.2 illustrates a Hesston large-bale baler producing 36"x48"x96" bales that weigh between 975 to 1025 pounds with a moisture content of 11%–15%.

Figure XIIB.3: A Large Baler for Baling Rice Straw

Road-siding consists of moving bales from the interior of a rice field to the edge of the field where the bales are accessible for loading onto trucks. The road-siding operation may include transport of up to a mile or more to a local storage area, with no additional interim stacking and loading operations. Typically, road-siding operations involve either stacking bales at the edge of the field for later retrieval and loading on trucks, or directly loading bales on trucks during the road siding operation. Figure XIIB.3 illustrates one method of retrieving large bales from the field. This machine's capability is 8 bales per load.

Figure XIIB.4: A Freeman Stack Wagon Retrieving Bales from the Field

Rice straw is being stored at convenient locations throughout the rice growing area. Figure XIIB.4 illustrates the stacking of the large rice straw bales. These stacks are 32 feet wide and 30 feet high at the peak. Each stack contains approximately 1,000 dry tons of rice straw.

Figure XIIB.5: Storage of Large Rice Straw Bales

It is necessary to grind the rice straw to a suitable size for introduction into the IBR plant. Experiments on the introduction of rice straw have demonstrated that the straw will need to be ground to less than ½" long pieces. Straw much larger than ½" tends to bind together, like Velcro, thus making its introduction somewhat difficult.

3. Orchard Wood Residues

About 170 thousand dry tons of orchard and domestic wood waste is available in this area each year. This wood is primarily produced from pruning of fruit and nut trees. In addition, after many years these trees decline in production and therefore they are removed and replaced with new trees.

4. Nut Shells

During the 2013 season, 2.7 million tons of nuts were produced in California. The primary nut varieties include almonds, English and black walnuts, pecans and pistachios. On the average, the nut kernel represents about 60 weight % of the nut; therefore the shells represented about 1.08 million tons. 40% of these nuts were produced within a 35 mile radius of the proposed plant site resulting in about 460 tons of nut shells.

5. Fruit Processing Residues

About 80 thousand dry tons of fruit processing waste is available each year in this area. The primary fruit varieties include apples, apricots, kiwifruits, olives, peaches, pears, plums, prunes, wine and table grapes, oranges and lemons.

C. Commercial Plants

This section describes the design of a commercial-scale biomass to liquid fuels (BTL) plant for the Northern Sacramento Basin and the results from the techno-economic analysis (TEA) for this commercial plant. In addition, a biomass and natural gas to liquid fuels (BGTL) plant was designed for possible commercial deployment in this area and the results from the TEA for this plant are summarized.

1. BTL Plant

Figure XIIC.1 provides the inputs and outputs for the commercial scale BTL plant. This plant will produce about 4.4 million gallons/year of "drop-in" fuels from 240 dry ash free tons (daft)/day of biomass feedstock. These "drop-in" fuels consist of reformulated gasoline blendstock (29 %) and premium diesel fuel (71%). The energy efficiency of this BTL plant is 53.9% (HHV), the carbon conversion efficiency for biomass to fuel is 39.7% and 53.2% for biomass to fuel and biochar.

About 36 tons/day of biochar is produced from this plant. Since this biochar has been demonstrated to be a soil enrichment additive, it has a commercial value and a conservative value of $100/dry ton was used in the TEA model.

About 3.5 gallons of fresh water are produced for each gallon of fuel produced. 0.92 gallons of wastewater is produced for each gallon of fuel produced. However, this discharged water is expected to be suitable for agriculture use in many cases.
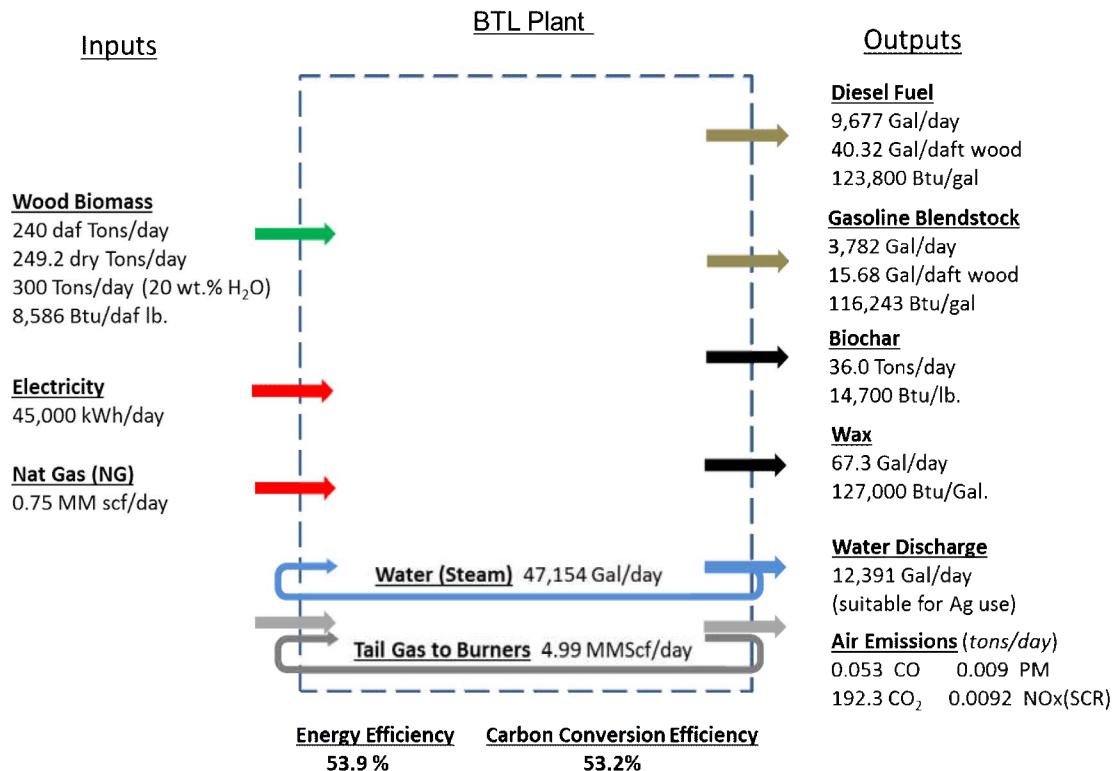
Figure XIIC.1: Inputs and Outputs for the 240
Dry Ash Free Ton (daft)/day Commercial BTL Plant

These inputs and outputs are used as inputs to the techno-economic analysis (TEA) for this BTL plant as based upon 2014 economics. The data inputs and results for this analysis are provided in Table XIIC.1. The total capital cost of the plant is $40.4 million which results in a Capex of $9.18/gallon for the first full year of operation. The Operating and Maintenance costs are $4.21 million/year excluding feedstock costs. The estimated feedstock cost is $35 / daft as based upon using 50% rice hulls and 50% wood residues (see Table XIIB.1).

Table XII.C.2 summarizes the input variables and the corresponding low, base, and high inputs to the TEA. The base IRR is 10.6%. If a fuel production incentive of $1.00 is available then the IRR increases to 21.0%. As based upon this IBR project, it was found that the average yield of fuel from 1.00 daft ton of wood and rice hulls was 56 gallons. If the fuel yield is lower (52 gallons/daft) then the IRR drops to 7.4% and at a higher yield of 60 gallons/daft, the IRR increases to 13.5%.

Table XIIC.1: Techno-Economic Analysis for the Sacramento Basin BTL Plant

Metric	Values
Biomass Input (dry ash free tons/day)	240
Natural Gas Input (million scf/day)	na
"Drop-in" Fuel Production (millions gallons)	4.40
Process Capital Cost ($ millions)	31.3
Site Development Cost ($ millions)	4.6
Assembly & Validation Cost ($ millions)	4.5
Total Capital Cost ($ millions)	40.4
Capex ($/gallon) for first full year of operation	9.18
Plant Opex (O&M) Costs (excludes feedstock) ($ millions/year)	4.21
Feedstock Cost (50% rice hulls & 50% wood residues) ($/daft)	35.00
Personnel (FTEs)	13
Financing Assumptions	100% equity
Internal Rate of Return (IRR)	10.6%

The current estimated capital cost of the plant is $40.4 million. If the capital cost drops to $35.0 million, the IRR increases to 12.8%, but drops to 8.7% if the capital cost is higher ($45.0 million). The IRR varies from 7.3% to 13.7% with high and low inputs of $3.21 million and $5.21 million for the plant Opex, respectively.

A variation in biomass cost from $25.00/daft to $45.00/daft results in an IRR variation of 8.0% to 13.0%, respectively, and a range in value for the biochar of $50/dry ton to $150/dry ton changes the IRR from 8.9% to 12.2%, respectively. In this analysis, it was anticipated that the plant would have a 93.5% uptime. A variation in uptime from 85% to 97% changes the IRR from 7.4% to 11.7%, respectively.

Table XII.C.2: Low, Base and High Data Inputs for the BTL-TEA Analysis

Variable	%IRR			Parameter Value			Units
	Low	Base	High	Low	Base	High	
Product Price	10.6	10.6	21.0	0.00	0.00	1.00	$/gal
Fuel Yield	7.4	10.6	13.5	52	56	60	gal/ton
Plant Capex	8.7	10.6	12.8	35.0	40.4	45.0	$MM
Plant Opex	7.3	10.6	13.7	3.21	4.21	5.21	$MM/yr.
Biomass Price	8.0	10.6	13.0	25.00	35.00	45.00	$/daft
Ops. Reliability	7.4	10.6	11.7	85	93.5	97	%
Biochar	8.9	10.6	12.2	50	100	150	$/ton

Figure XIIC.1 illustrates the variability in the IRR for the BTL plant using the range of inputs summarized in Table XII.C.2.
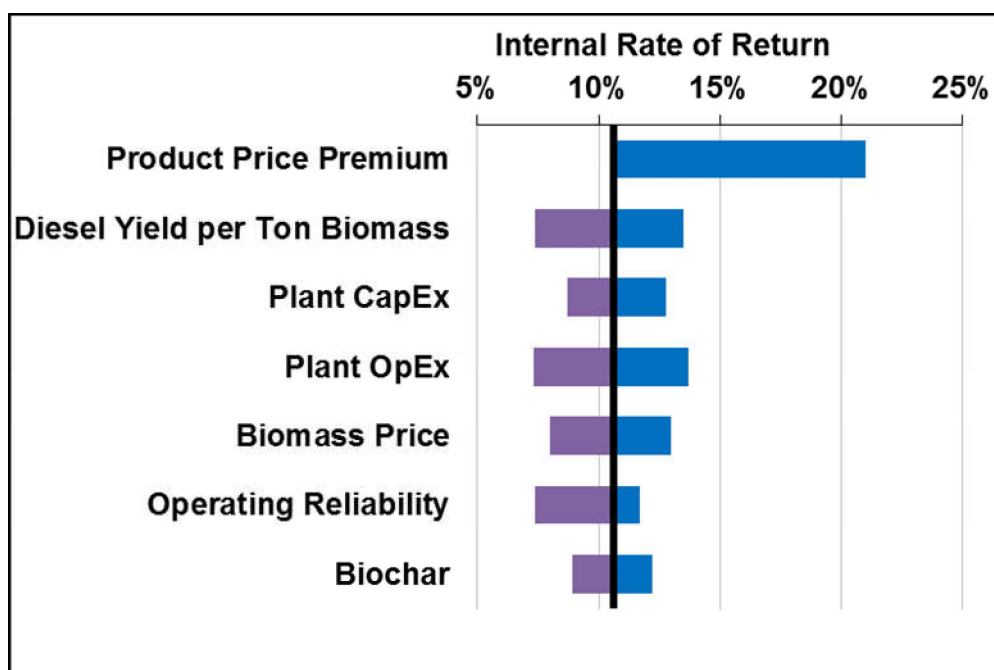
Figure XIIC.1: IRR Economic Variance Analysis (2014 Economics) for the Sacramento Basin BTL Plant

2. BGTL Plant

As described previously, Greyrock's one-step liquid fuel production (LFP) process performed very well during the 16 months of validation tests. As a result, the potential of this technology in the marketplace has become recognized as "next-generation" technology and several major investors and corporations believe that this LFP process has the potential of economically producing liquid fuels from natural gas. Since NG is widely available at low cost and since NG can be effectively converted to syngas using established technologies, it was recommended that Greyrock actively pursue the design of plants that utilize natural gas as a feedstock for the production of the synthetic diesel fuel and reformulated gasoline feedstocks.

As a result, Greyrock Energy designs and builds distributed gas-to-liquids (GTL) plants in addition to the biomass to liquid (BTL) plants with Red Lion Bio-Energy. It was determined that a hybrid of the GTL and BTL technologies for the production of "drop-in" fuel could provide the following advantages:

- Reduce plant capital and O&M costs resulting in improved return on investment
- Increase plant energy and carbon conversion efficiencies
- Lower greenhouse gas emissions

This approach supports a recent, cooperative DOE effort between the Office of Energy Efficiency and Renewable Energy (Bioenergy Technologies Office (BETO)) and Office of Fossil Energy (National Energy Technology Laboratory (NETL)) to examine the potential of combining GTL and BTL technologies for the reasons summarized above. The combination of these technologies will be referred to as BGTL in this report.

Figures XIIC.2 and XIIC.3 show generic layouts for the BGTL plant designed for commercial deployment by Greyrock and SynTerra in Northern California. The BGTL plant will have the capability of converting 240 daft/day and 4.0 million standard cubic foot of natural gas to 8.70 million gallons/year of premium diesel fuel and reformulated gasoline blendstock when the plant is operated for 329 days/year.

Figure XIIC.4 summarizes the inputs and outputs for the BGTL plant. The co-products include biochar at 36.0 tons/day production, benzene at 1,159 gallons/day and wax at 67.3 gallons/day production. The plant has a carbon conversion efficiency of 53.1% and an energy efficiency of 42.5%. The plant tail gas is used as fuel for burners and for the generation of about half of the plant's power requirements.
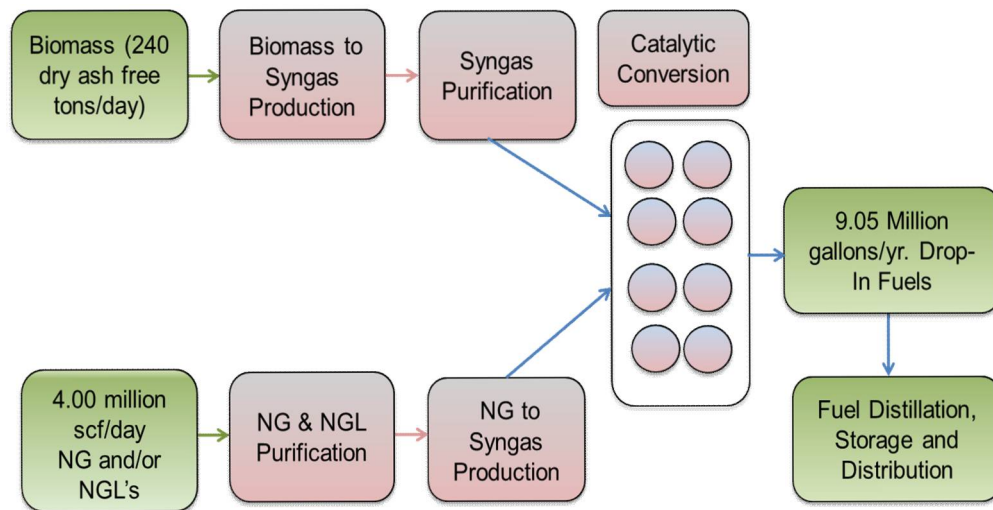
Figure XIIC.2: Sacramento Basin BGTL Production Plant
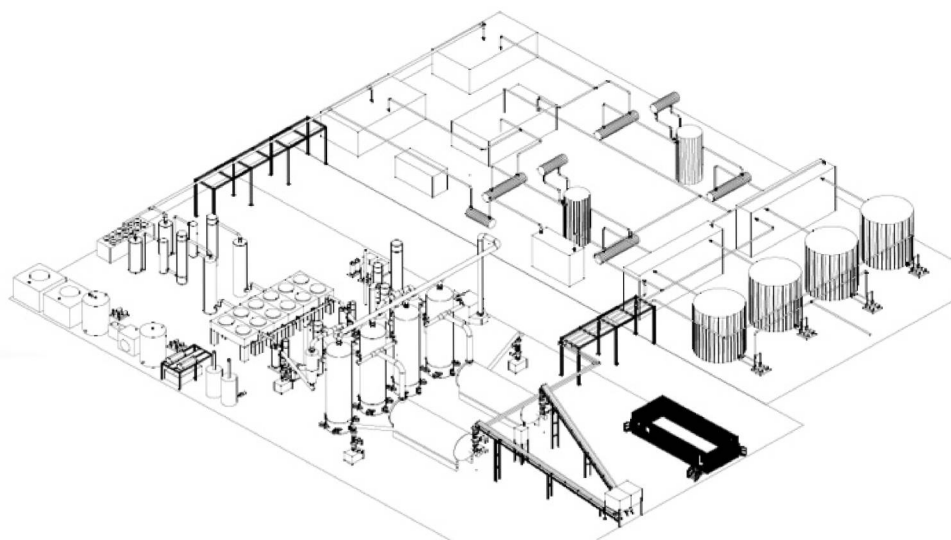
Figure XIIC.3: Footprint for the BGTL Commercial Plant (375' x 375')

Inputs

Biomass
240 daft/day
8,586 Btu/daf lb.

Nat Gas (NG)
4.75 MM scf/day

Fresh Water
17,906 Gal/day

Electricity (E)
45,000 kWh/day

BGTL Plant

Water (Steam) (47,154 Gal/day)

Electricity (Generated from plant process tailgas @ 30,000 kWh/day)

Tail Gas to Burners (4.99 MM Scf/day)

Energy Efficiency **Carbon Conversion Efficiency**
47.9%   53.1%

Outputs

Diesel Fuel
19,152 Gal/day
40.32 Gal/daft wood
23.7 Gal/10,000 scf NG
123,800 Btu/gal

Gasoline Blendstock
7,566 Gal/day
15.68 Gal/daft biomass
9.46 Gal/10,000 scf NG
116,243 Btu/gal

Biochar
36.0 Tons/day
14,700 Btu/lb.

Water Discharge
13,571 Gal/day
(suitable for Ag use)

Wax
67.3 Gal/day
127,000 Btu/Gal

Air Emissions (*tons/day*)
0.101 CO   0.017 PM
305.0 CO_2 0.023 NOx

Figure XIIC.4: Inputs and Outputs for the Sacramento Basin BGTL Plant

These inputs and outputs are used as inputs to the techno-economic analysis (TEA) for this BGTL plant. The financing assumptions are that the plant will be funded with 100% equity. The data inputs and results for this analysis are provided in Table XIIC.3. The total capital cost of the plant $56.2 million which results in a Capex of $6.45/gallon for the first full year of operation. The Operating and Maintenance (O&M) costs are $5.42 million/year, excluding feedstock costs. The estimated feedstock cost is $35 / daft as based upon using 50% rice hulls and 50% wood residues.

Table XIIC.3: Techno-Economic Analysis for the
BGTL Plant (2014 Economics)

Metric	Values
Biomass Input (dry ash free tons/day)	240
Natural Gas Input (million scf/day)	4.00
"Drop-in" Fuel Production (millions gallons/year) (based upon 329 days/year of operating time)	8.70
Process Capital Cost ($ millions)	45.4
Site Development Cost ($ millions)	5.1
Assembly & Validation Cost ($ millions)	5.0
Total Capital Cost ($ millions)	56.2
Capex ($/gallon) for first full year of operation	6.45
Plant O&M Costs (excludes feedstock) ($ millions/year)	5.42
Feedstock Cost (50% wood and 50% rice hulls) ($/daft)	$35.00
Personnel (FTEs)	14
Financing Assumptions	100% equity
Internal Rate of Return (IRR)	21.8%

Table XII.C.4 summarizes the input variables and the corresponding low, base, and high inputs to the TEA. The base IRR is 21.8%. If a fuel production incentive of $1.00 is available then the IRR increases to 28.4%. As based upon this IBR project, it was found that the average yield of fuel from 1,000 lbs. of carbon input (from biomass and natural gas together) was 70.1 gallons. If the fuel yield is lower (66.6 gallons/daft) then the IRR drops to 19.8% and at a higher yield of 73.6 gallons/daft, the IRR increases to 23.2%.

The current estimated capital cost of the plant is $56.2 million. If the plant capital cost drops to $51.2 million, the IRR increases to 24.0%, but drops to 20.0% if the capital cost is higher ($61.2 million). The IRR varies from 19.9% to 23.7% with high and low inputs of $4.42 million and $6.42 million for the plant Opex, respectively.

A variation in biomass cost from $25.00/daft to $45.00/daft results in an IRR variation of 21.1% to 23.3%, respectively, and a range in value for the biochar of $50/dry ton to $150/dry ton changes the IRR from 20.8% to 22.8%, respectively. In this analysis, it

was anticipated that the plant would have a 93.5% uptime. A variation in uptime from 85% to 97% changes the IRR from 20.6% to 23.0%, respectively. This data is shown graphically by Figure XIIC.5.

Table XIIC.4: Low, Base and High Data Inputs for the BGTL-TEA Analysis

Variable	%IRR			Parameter Value			Units
	Low	Base	High	Low	Base	High	
Product Price	21.8	21.8	28.4	0.00	0.00	1.00	$/gal
Diesel Yield	19.4	21.8	23.2	66.6	70.1	73.6	gal/ton
Plant Capex	20.0	21.8	24.0	51.2	56.2	61.2	$MM
Plant Opex	19.9	21.8	23.7	4.42	5.42	6.42	$MM/yr.
Biomass Price	21.1	21.8	23.3	25.00	35.00	45.00	$/daft
NG Price	19.3	21.8	23.1	3.50	4.00	4.50	$/mcf
Ops. Reliability	20.6	21.8	23.0	85	93.5	97	%
Biochar	20.8	21.8	22.8	50	100	150	$/ton
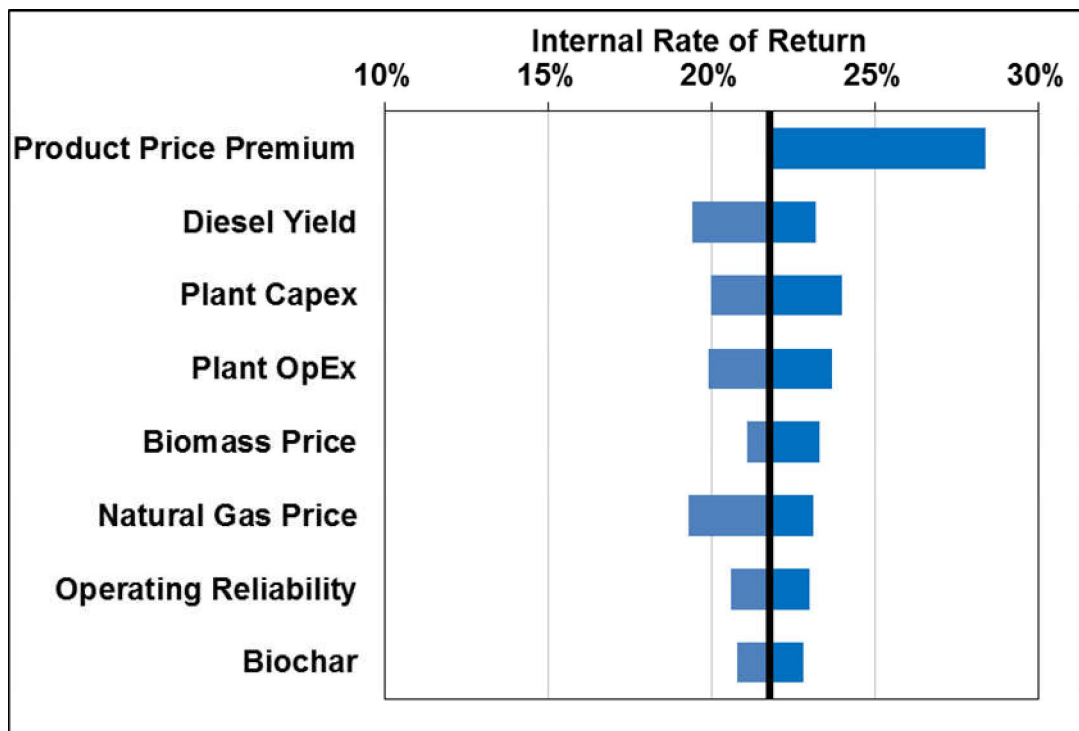
Figure XIIC.5: IRR Economic Variance Analysis for the GBTL Plant (2014 Economics)

Figure XIIC.6 below shows other potential U.S. locations for the BTL and GBTL plants. This figure demonstrates that the potential for commercialization of this technology is excellent.
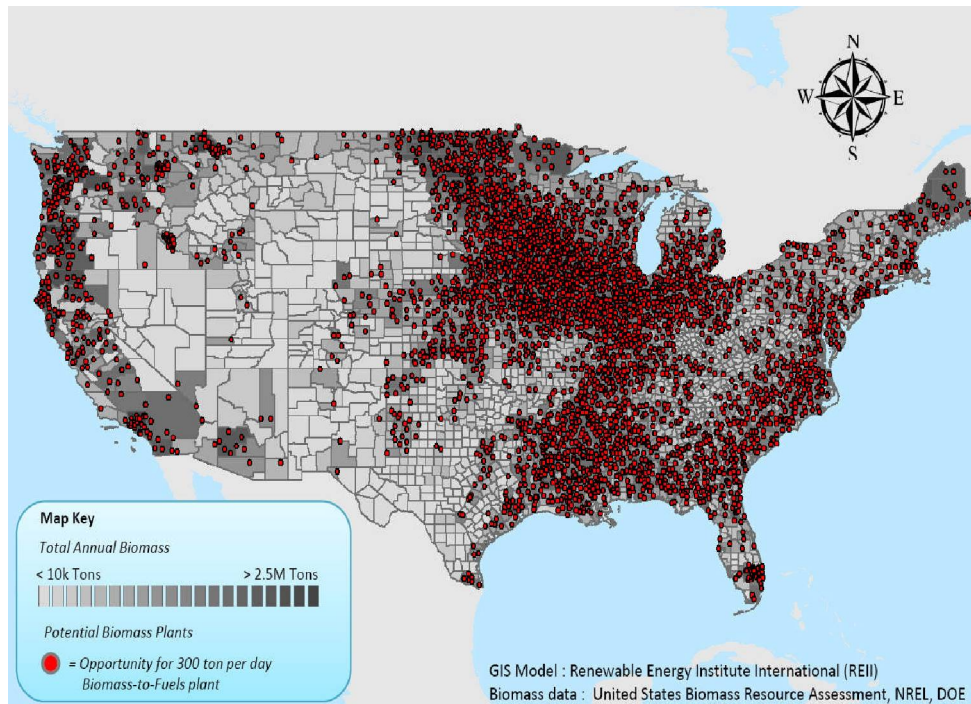
Figure XIIC.6: Other Potential U.S. Locations for the BTL and BGTL Plants

D. Fuel Products, Off-take and Blending

The compatibility of the premium, synthetic diesel fuel (syndiesel) and reformulated gasoline blendstock (RFG) for blending with existing petroleum fuels and infrastructure was evaluated using the following parameters:

- Storage issues including contamination and degradation
- Transportation cost
- Transportation issues, cold-weather freezing, etc. including types of packaging and projected transport requirements
- High-level approximation of fuels blending opportunities, applications and challenges
- Potential product compatibility issues

Each of the products and product parameters were evaluated for ambient cases of summer and northern extreme locations in the Midwest of the United States during winter and summer fuel seasons and located either far from or near to a location where the fuel product is blended with conventional fuels. These possible locations include refineries, fuel terminals and pipelines. Table XIID.1 summarizes the cases considered.

Table XIID.1: Cases Considered for the Synthetic Diesel Fuel
Production, Fuel Off-take and Fuel Blending

Study Cases	Case ID
Summer Northern Midwest / Far from fuel blending	A
Summer Northern Midwest / Close to fuel blending	B
Winter Northern Midwest / Far from fuel blending	C
Winter Northern Midwest / Close to fuel blending	D
Summer Southern Midwest / Far from fuel blending	E
Summer Southern Midwest / Close to fuel blending	F
Winter Southern Midwest / Far from fuel blending	G
Winter Southern Midwest / Close to fuel blending	H

Minnesota was chosen as Northern Midwest location and Louisiana was chosen as the
Southern Midwest location for this study. Considering the number of products, parameters
to consider and the ambient cases, one can arrive at the parameter evaluation matrix
provided by Table XIID.2.

Table XIID.2: Parameter Evaluation Scenarios Matrix

Case ID	Parameters				
	Storage	Transport Cost	Transport Issues	Blending	Compatibility
Greyrock Premium Synthetic Diesel (syndiesel)					
A	M1A	M2A	M3A	M4A	M5A
B	M1B	M2B	M3B	M4B	M5B
C	M1C	M2C	M3C	M4C	M5C
D	M1D	M2D	M3D	M4D	M5D
E	M1E	M2E	M3E	M4E	M5E
F	M1F	M2F	M3F	M4F	M5F
G	M1G	M2G	M3G	M4G	M5G
H	M1H	M2H	M3H	M4H	M5H
Greyrock Reformulated Gasoline Blendstock (RGB)					
A	N1A	N2A	N3A	N4A	N5A
B	N1B	N2B	N3B	N4B	N5B
C	N1C	N2C	N3C	N4C	N5C
D	N1D	N2D	N3D	N4D	N5D
E	N1E	N2E	N3E	N4E	N5E
F	N1F	N2F	N3F	N4F	N5F
G	N1G	N2G	N3G	N4G	N5G
H	N1H	N2H	N3H	N4H	N5H
Light Wax					
A	W1A	W2A	W3A	W4A	W5A
B	W1B	W2B	W3B	W4B	W5B
C	W1C	W2C	W3C	W4C	W5C
D	W1D	W2D	W3D	W4D	W5D
E	W1E	W2E	W3E	W4E	W5E
F	W1F	W2F	W3F	W4F	W5F
G	W1G	W2G	W3G	W4G	W5G
H	W1H	W2H	W3H	W4H	W5H

The syndiesel and RGB fuels were evaluated by reviewing a number of potential bio-refinery locations, product separation and fuel handling options.

1. Premium Synthetic Diesel Fuel

The chemical and physical properties of the syndiesel were described in Section IXC and summarized in Table IXC.4. It was found that the syndiesel has properties that are between that of CA #1 and CA #2 diesel fuels. Therefore, storage of the syndiesel during summer seasons in either location (scenarios D1A, B and D1E, F in Table

XIID.2) can be accomplished in storage tanks and fuel distribution systems that are normally used for petroleum based #1 and #2 diesel.

The syndiesel has a high stability to oxidation since the alkanes are predominately normal alkanes and the olefins are terminal olefins (alpha-olefins). The C_3-C_{14} hydroxy-N-alkanes (aliphatic alcohols) in the syndiesel serve to help reduce metal corrosion and fuel oxidation. In addition, these hydroxy-N-alkanes contribute to the excellent lubricity of the fuel. Samples stored at room temperature and in the light for more than five years have not undergone any observable chemical or physical changes. In comparison, petroleum derived diesel fuel has a relatively poor oxidation stability since this fuel contains primarily iso-alkanes and interior olefins which are subject to oxidation during storage. In conclusion, the syndiesel can utilize the same storage and distribution system as that already available for the petroleum derived diesel fuels.

Since it is recommended that the syndiesel be blended at about 20% with #1 or #2 petroleum diesels, the precautions typically employed storing these petroleum diesel feedstocks need to be employed. These precautions include keeping fixed roof tanks full, avoiding the use of copper and copper containing alloys since they promote fuel degradation. Zinc coatings should also be avoided since they can react with water or organic acids in the fuel to form gels that can plug fuel filters.

Typically, sediment may build-up in diesel fuel systems. Therefore, it is recommended that storage tanks have a dispenser filter installed to keep any contamination from being passed along to vehicles.

Table XIID.3 summarizes the tenth percentile minimum ambient air temperatures for Minnesota and Louisiana. This data was used to determine the maximum blending volume for the syndiesel with the #2 diesel during the coldest periods at these two locations.

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Table XIID.3: Tenth Percentile Minimum Ambient Air
Temperatures for Minnesota and Louisiana

Month	Minnesota	Louisiana
January	-34	-4
February	-31	-2
March	-24	1
April	-9	6
May	-2	13
June	4	19
July	8	21
August	7	20
September	-1	14
October	-4	5
November	-18	-1
December	-30	-3

Trucks, rail and barges are currently used to transport biodiesel (methyl ester or hydro-cracked triglycerides) are mainly trucks, rails and barges. The selection of the best mode of fuel transport is determined by considering the:

- Volume and distance of the shipment
- Whether both shipping and receiving ends have proper infrastructure e.g. trucks offloading capacity, railroads or river/water access for barges.
- Cost and timing considerations

Table XIID.4 summarizes the typical transportation costs, on a per-barrel per-mile basis, for each of the fuel transport choices listed above.

Table XIID.4: Typical Liquid Fuel Transportation Costs

Transportation costs			
Transportation Mode	**Requirements**	**Capacity (Gallons)**	**Typical Cost ($ per barrel per mile)**
Trucks	~300 Miles; Loading & Unloading Infrastructure	6,600-7,200	0.53
Rail car	~300 Miles; Rail Access	23,000-30,000	0.265
Barges	River Access	400,000	0.05 – 0.25
Pipelines	Pipeline Infrastructure	-	0.08

The volume of fuel production will influence the choice of transportation. A nominal 300 bpd plant will produce approximately 220 bpd (9,240 gallons/day) of premium syndiesel, which is the largest product produced by the refinery. Since most rail tank cars have a 20,000 to 34,500 gallons capacity, it would take 2-4 days to fill one tank car. This would only make economic sense if a spur rail line was already located next to the plant, which is not very probable. Therefore, tanker trucks will be the most flexible and economical method of transporting the fuel to fuel blenders.

Therefore, it would be most flexible and economical to transport the fuel by tanker truck to an existing refinery or a fuel blending terminal located within 300 miles of the production facility. As discussed above, trucks are the sole reasonable transportation choice if the distance is about 300 miles or less. Some of the largest methyl ester biodiesel production facilities are approximately 100 MM gal/year, a volume which typically justifies rail infrastructure, but typically not a pipeline.

The syndiesel can be blended with the EPA #1 or EPA #2 fuel using in-line blending or splash blending. In-line blending is done directly at the refineries and pipeline terminals. The syndiesel stream is added to a stream of diesel fuel as it travels through a pipe in such a way that the synthetic diesel and diesel fuel becomes thoroughly mixed by the turbulent movement. It is the preferred method as it ensures complete blending.

Splash blending is used where in-line blending is not available. Splash blending is carried out in the tank car or tank truck. For top loading trucks in warm weather, it is recommended to load both products at the same time through separate lines at high enough fill rates to sufficiently mix the products in the tank

Minnesota was arbitrarily selected as a representative North Midwestern location while Louisiana was selected as a representative South Midwest location. The ambient data for these locations were summarized in Table XIID.3.

As shown in Table XIID.5, the syndiesel may be blended with EPA #2 diesel fuel at levels up to 100% during April to October in the Northern Midwest. However, during the coldest months the syndiesel needs to be blended with EPA #1 fuel. The maximum blending volume is 38% during January and 90% during November. In contrast, the syndiesel may be blended with EPA #2 diesel fuel at any time of the year in the Southern Midwest.

The heavier HC ends of the diesel fuel (C_{21}, C_{22}, C_{23}, etc.) may be removed during the distillation step to further improve the cold weather tolerance of the syndiesel. Another option widely used for petroleum diesel is to add cloud and pour point improvers.

Table XIID.5: Estimated Maximum Blending Volumes for the North Midwest

Month	10th Percentile Minimum Temperatures (°F)	Cloud Point of the Blend (°F)	Estimated Maximum Blend Amounts (%) with EPA Diesel #2
April	16	16	100
May	28	7	100
June	39	7	100
July	46	7	100
August	45	7	100
September	30	7	100
October	25	7	100
Month	10th Percentile Minimum Temperatures (°F)	Cloud Point of the Blend (°F)	Estimated Maximum Blend Amounts (%) with EPA Diesel #1
November	-0.4	-0.4	90
December	-22	-22	50
January	-29	-29	38
February	-24	-24	46
March	-11	-11	68

Table XIID.6: Estimated Maximum Blending Volumes for the South Midwest

Month	10th percentile minimum temperatures (°F)	Cloud Point of the Blend (°F)	Estimated Maximum Blend Amounts (%) with EPA Diesel #2
April	43	7	100
May	55	7	100
June	66	7	100
July	70	7	100
August	68	7	100
September	57	7	100
October	41	7	100
November	30	7	100
December	27	7	100
January	25	7	100
February	28	7	100
March	34	7	100

2. Reformulated Gasoline Blendstock (RGB)

The composition of the RGB was summarized in Tables IXC.5 and IXC.6. This blendstock has a much higher octane (60-65) than that of typical refinery naphtha cuts (20-30).

Due to it purity and low aromatic content, the RGB is ideal for use as a gasoline blendstock at low addition rates. Our blending data demonstrates that it can be effectively blended up to 10 volume % in gasoline. It is expected that it will command a wholesale value in the range of 70-80% of wholesale gasoline prices, depending upon the specific blending opportunity.

3. Renewable Fuel Standard (RFS2)

The Renewable Fuel Standard (RFS) as developed and implemented by the US EPA ensures that a minimum volume of renewable fuel is sold in the United States. Since its creation in 2005 the RFS program (RFS1) has since been further expanded in several areas, some of which clarify the inclusion of fuel produced by the technologies demonstrated under this project. More specifically, the non-ester diesel fuel and gasoline blendstock produced by the technologies described in this report meet the minimum requirements to apply for the development of Renewable Identification Numbers (RINs).

E. Other Potential Commercial Products

1. Biochar

As described earlier, this IBR process produces approximately 300 pounds of biochar from every 2,000 lbs. of dry wood. This biochar has economic value since it has been found for over 2,000 years that this material improves soil fertility and decreases water pollution. However, the commercialization of this material has been slow primarily because of limited supplies and the absence of an established agriculture market. The International Biochar Initiative (IBI) was established to help set composition standards for biochar and to support its commercialization. IBI has established that biochar has a current market value of $100-$200/dry ton. Therefore, a conservative market value of $100/dry ton has been included in our economic models.

2. Water

The water discharge from the 240 daft/day plant is 52 gal/daft from the LFP. This water only contains 1.0-1.5 volume % of $C_1 - C_5$ alcohols and no inorganic materials.

One gram of these alcohols has a theoretical oxygen demand of about 1.05 grams/gram. The normal bacteria in soil will destroy 50% of these alcohols in 1-2 days and they will be virtually all metabolized in 1-2 weeks. Therefore, this water can be classified as "gray water" which will be suitable for agriculture use.

This water is also ideal for the steam reforming process in the thermochemical conversion process since the alcohols are easily reformed to syngas.

3. Wax

For the nominal 300 bpd plant, the soft wax production should be approximately 1.5 bpd. Since the wax will be collected in barrels, this will be the easiest method of transport to the various intended markets.

The soft wax generated from the IBR plant consists of normal hydrocarbons in the C_{25}-C_{40} range. Since this soft wax doesn't contain any olefins, it is very stable and does not degrade in UV light and heat. As a result, soft wax of this composition has a number of high value commercial uses. It is an ideal material:

- For waxing skis and snow-boards
- For protecting and giving a beautiful matte finish on painted furniture, cabinets and walls
- As a release agent for metal castings
- As a rubber additive to prevent cracking
- To prevent oxidation on steel and iron surfaces
- For waterproofing leather

4. Benzene

Benzene is a widely used industrial chemical which is used to make plastics, resins, synthetic fibers, rubber lubricants, dyes, detergents, drugs and pesticides.

Ethylbenzene → Styrene → Polystyrenes

Cumene → Acetone

Cumene → Phenol

Phenol → Bisphenol A

Bisphenol A → Polycarbonates

Bisphenol A → Epoxy resins

Phenol → Phenolic resins

Benzene → Ethylbenzene

Benzene → Cumene

Benzene → Cyclohexane

Benzene → Aniline

Benzene → Chlorobenzenes

Cyclohexane → Adipic acid → Nylon 6-6

Cyclohexane → Caprolactam → Nylon 6
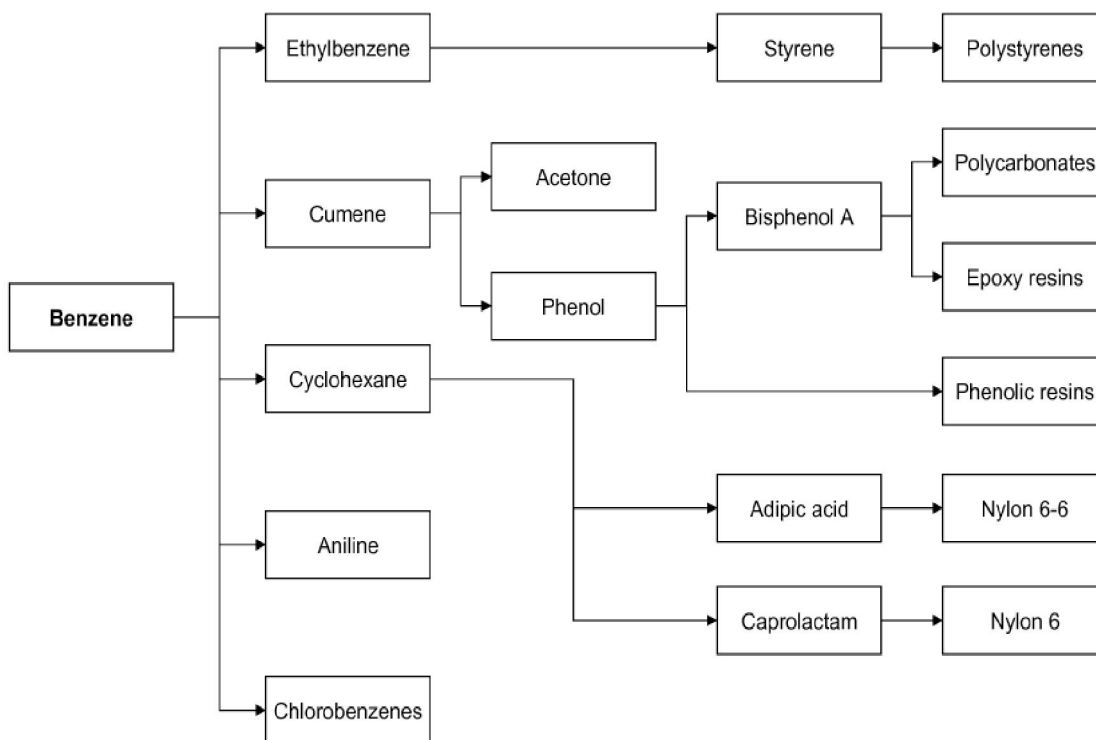
Figure XIIE.1: The Uses of Benzene as a High
Value Commodity Chemical

The 2014 market value of benzene averaged $5.00/gallon.

F. Environmental Evaluation

1. Water Effluents

The two sources of water effluents from the plant include the scrubber water from the TCC system and the water produced as a co-product from the LFP system.

a) TCC Scrubber Water

As described in previous sections, the wastewater from the TCC srubber system will need to be treated prior to discharge to a wastewater treatment plant. For future commercial facilities, water treatment options will be developed in accordance with the applicable Federal, State, and Local regulations.

b) LFP Water Co-Product

The water co-produced with the generation of fuels contains small quantities of alcohols. After analyzing the composition of this water, it has been determined that this water is ideal for steam reforming under the BTL and GTL scenarios. Therefore, no wastewater treatment will be required for this water stream.

c) Air Effluents

The primary source of air effluents from the plant are generated by the burners on the TCC system. The primary pollutants of concern are nitrogen oxides (NOx). These burners are utilized to heat up the TCC system and provide a constant temperature environment during operations. The burners utilize low NOx burner technology to reduce emissions. Future commercial facilities will continue to utilize low NOx burner technology and where necessary Selective Catalytic Reduction (SCR) will be used to further reduce NOx emissions to meet more stringent local regulations.

d) Greenhouse Gas Reduction Analysis

The Greet LCA model was used to estimate the expected greenhouse gas reductions from the BTL and GBTL plants. Details for these LCAs are provided in Section XIII.G.

XIII. Detailed Supporting Information

This section provides additional data, technical details and other information used to support the information provided in Sections I to XII of this report.

A. Biochar Composition

Biochar is the solid product collected in the ash removal system from Unit Operation #2. Biochar has many commercial uses. It can be used to produce activated carbon and different carbonaceous materials. Biochar samples generated from the plant runs were sent to Hazen Labs for ultimate and proximate analysis.

The elemental or ultimate analysis comprises the quantitative determination of carbon, hydrogen, nitrogen, sulfur and oxygen. Elemental analysis of the biochar was performed according to ASTM D 5373 and ASTM D 5291 standard test methods. The composition was determined according to ASTM D 3176. The empirical formulas, H/C, and O/C molar ratios were calculated from the elemental composition. The oxygen content of fuel was calculated as shown by Equation 1 instead of by direct analysis.

$$O\ (\%) = 100 - [Ash\% + Moisture\% + C\% + H\% + N\% + S\%] \quad Equation\ 1$$

The total sulfur was determined according to ASTM D 3177 and ASTM D 4294, respectively.

Table XIIIA.1 summarizes the ultimate analysis for the wood biochar for two runs. As shown in this table the composition of the biochar was similar for these runs as expected.

Table XIIIA.1: Elemental or Ultimate Analysis of the Wood Biochar

Measurement	Run #1	Run #13
Ash (%)	4.65	4.98
Volatile Carbon (%)	5.22	2.85
Fixed Carbon (by difference) (%)	90.1	87.3
Sulfur (%)	0.03	0.03
Caloric Value (BTU/lb.)	14,069	14,179
Hydrogen (%)	1.27	1.43
Nitrogen (%)	0.43	0.41
Oxygen (by difference) (%)	5.45	5.25

The parameters of proximate analysis are moisture, volatile matter, ash, and fixed carbon. The proximate analysis of different materials was carried out according to a group of test methods ASTM D 5142 and ASTM D 3172, or ASTM D 3173 and ASTM D

4442 for measuring moisture content, ASTM D 3174 and ASTM E 1755 for measuring ash content, ASTM D 872 and ASTM D 3175 for measuring volatile matter, respectively.

B. Syngas and Tailgas Composition

The National Renewable Energy Laboratory (NREL), Desert Research Institute (DRI), and Bureau Veritas (BV) were contracted to characterize major and trace syngas constituents during the test campaigns.

1. NREL

NREL's transportable molecular beam mass spectrometer (TMBMS) was employed to provide continuous, on-line chemical analysis of syngas produced by the Red Lion Bio-Energy TCC system. A summary of results from this analysis were provided in Section VID.3. Additional details and data are provided in this section.

Product gases/vapors arrive at the instrument sampling orifice by means of a heated sample transfer and conditioning system (described below). Here, the gases are extracted through a 300 µm diameter orifice into a three-stage, differentially pumped vacuum system, (Figure XIIIB.1). Sampled gases undergo a near-adiabatic, free-jet expansion, resulting in a rapid transition to molecular flow that prevents reactions and condensation. The central core of this expansion enters a 1 mm conical skimmer to form a molecular beam that enters into the ionization region of the mass spectrometer. Molecular components in the beam are ionized by 22.5 eV electrons and the resulting ions are analyzed by a commercial quadrupole mass spectrometer using an off-axis electron multiplier for detection.
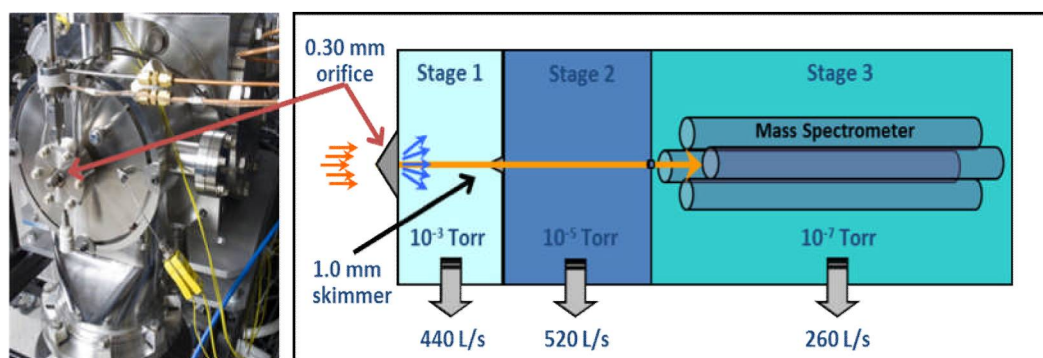
Figure XIIIB.1: Schematic of the 3-stage Molecular-Beam Vacuum System

The instrument is equipped with several integrated system controls that allow it to interface with and monitor a variety of chemical process streams. There are eight temperature control zones used to maintain gas/vapor temperature up to and through the sampling orifice. Two mass flow controllers introduce gases for sample dilution and internal standards. Additional mass flow meters measure the flow of a nitrogen purge used to prevent line plugging and buildup of hazardous process gases. Pressure transducers are used to monitor the differential pressure across a heated orifice flow meter, as well as the absolute pressure at the sampling orifice, to provide feedback for

flow control and pressure control valves. Information from each of these auxiliary channels is recorded once per minute, along with the mass spectral data, for use in quantitative analysis.

In order to achieve representative sampling, it is critical to maintain the compositional integrity of the hot product gas on route to the TMBMS. This can be difficult to accomplish due to the condensable and reactive nature of tar species present in the product gas. Maintaining a gas sample temperature comparable to that of reactor (~927°C or 1700°F in this case) prevents condensation, but would result in further thermal decomposition of the analytes. Moreover, the components used in the sampling system – heat tracing, valves, etc. – are not suitable for this temperature. Experience in the field has shown that sample transfer lines, kept as short as possible and maintained at 350°-400°C (660°-750°F), will minimize losses from condensation or thermal decomposition.


Figure XIIIB.2: TMBMS Instrument Installed at the
IBR Plant Site Showing the Heat Traced Sample Line (top right)

The sampling system consisted of a hot port (installed by REII staff), isolated in a block-and-bleed configuration with high temperature ball valves, and dual 3/8" o.d. stainless steel lines routed to the TMBMS sample conditioning oven in the trailer. The sample line was approximately 40' in length, resulting in a vapor residence time (at operating temperature) of roughly 15 s. The tubing and shut-off valves were heat traced using an 1800 W MI cable heater that was doubled back to provide roughly 44 W/linear ft. of heating. The entire assembly was wrapped with 2" of high temperature mineral wool insulation to maintain a nominally uniform temperature of 400°C (750°F).
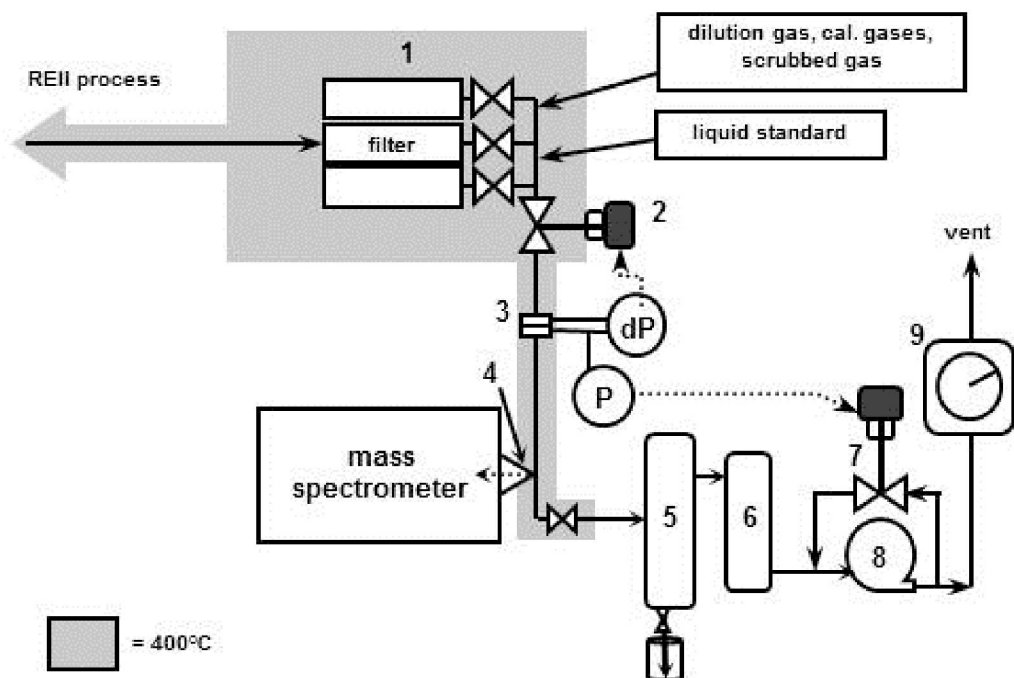
Figure XIIIB.3 shows a schematic of the IBR process, including the locations of the TMBMS sampling points (upper right), after the gases steam reforming process (Unit Operation #3) and the water scrubber (Unit Operation #4a). The samples after Unit Operation #3 are hot, un-purified syngas and the samples after Unit Operation #4a are the partially purified syngas. The final syngas purification process occurs in Unit Operation #4b.
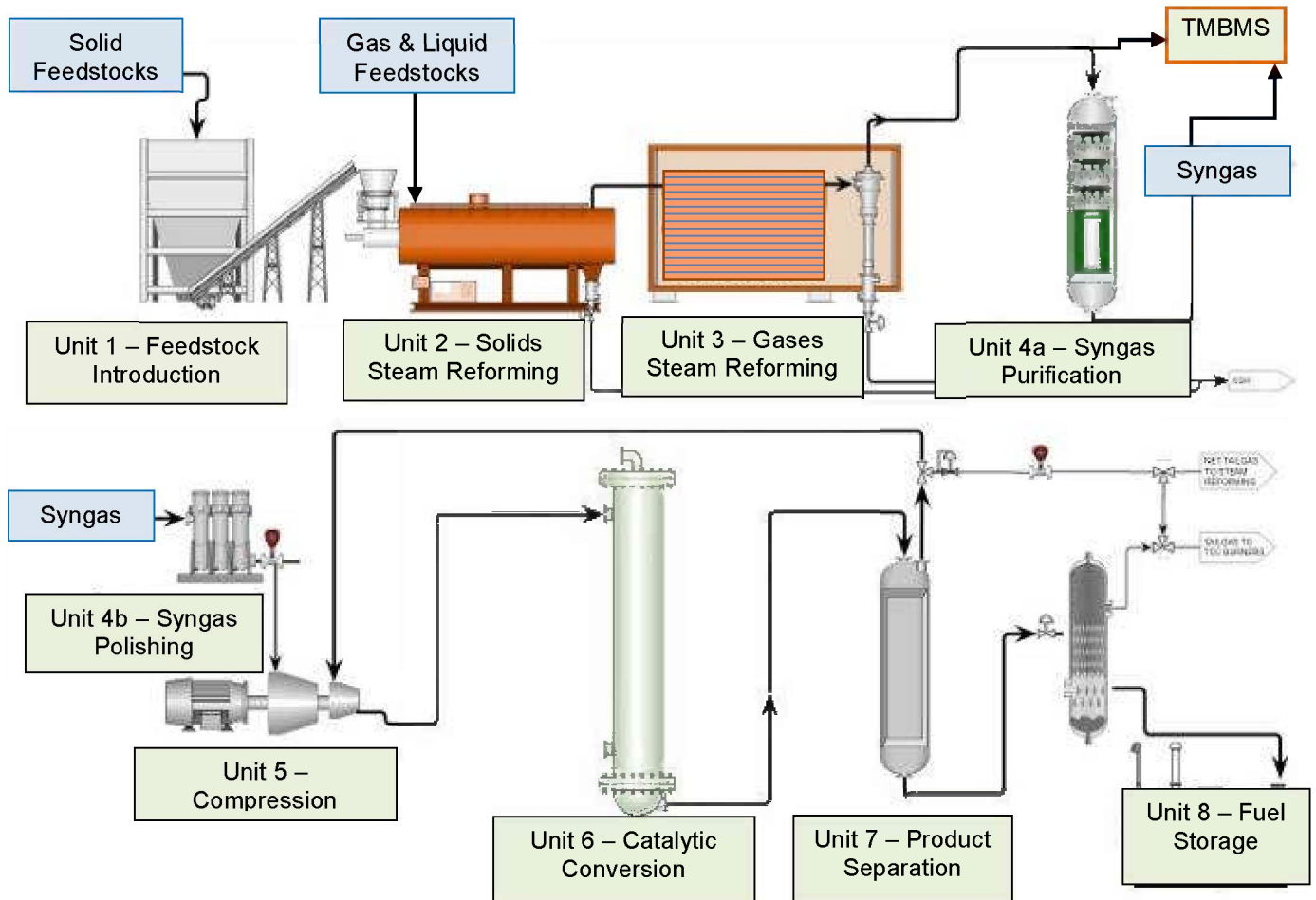
Figure XIIIB.3: Schematic of the IBR plant including the
Locations of the TMBMS Sampling Points

The sample oven, designed and built at NREL, was modified for this project and used to filter and control the flow of hot gas samples. Figure XIIIB.4 shows a schematic of the sampling system which includes the (1) sample conditioning oven; (2) flow control valve; (3) orifice-plate flow meter; (4) sampling orifice; (5) condenser; (6) coalescing filter; (7) back-pressure control valve; (8) sample pump; and (9) dry test meter.

Samples enter the oven, from the left in the schematic, and pass through a 10 μm stainless steel filter remove particulate material (char/ash) entrained from the process. The system was operated in "flow-by" mode, flowing roughly 2.5 standard liters per minutes (slm) of gas from the process past the orifice. This flow was controlled using a heated control valve and feedback from the pressure drop measured across the orifice flow meter. The sampling orifice extracted approximately 0.25 slm of the syngas for analysis, while the remainder continued on to a chilled water condenser to remove steam/tar, a coalescing filter to remove aerosols, sample pump and dry test meter (DTM) to measure dry gas flow. Another automated valve, located on the sample pump bypass loop, acted to control the upstream pressure using feedback from the pressure transducer on the downstream leg of the pressure drop measurement (equivalent to pressure at the sampling orifice).

Figure XIIIB.4: Schematic of the IBR plant including the Locations of the TMBMS Sampling Points

Figure XIIIB. 5 shows several critical sampling parameters that are tracked and/or controlled, typifying trends observed during an experiment. As seen in the Figure, the sample control pressure (green trace) and orifice nozzle temperature (blue trace) remain very constant throughout the day. The sample flow cycles with sample location (hot vs. cold). This is due to the removal of steam from the cold sample by the scrubbing system, resulting in a lower mass flow across the orifice for a constant control valve setting. The sample line temperature (red trace) was observed to increase by roughly 25°C during sampling from the hot port, likely due to heat transfer from the process,

which was much hotter than the sample line set point, being carried through the first several feet of sample line.
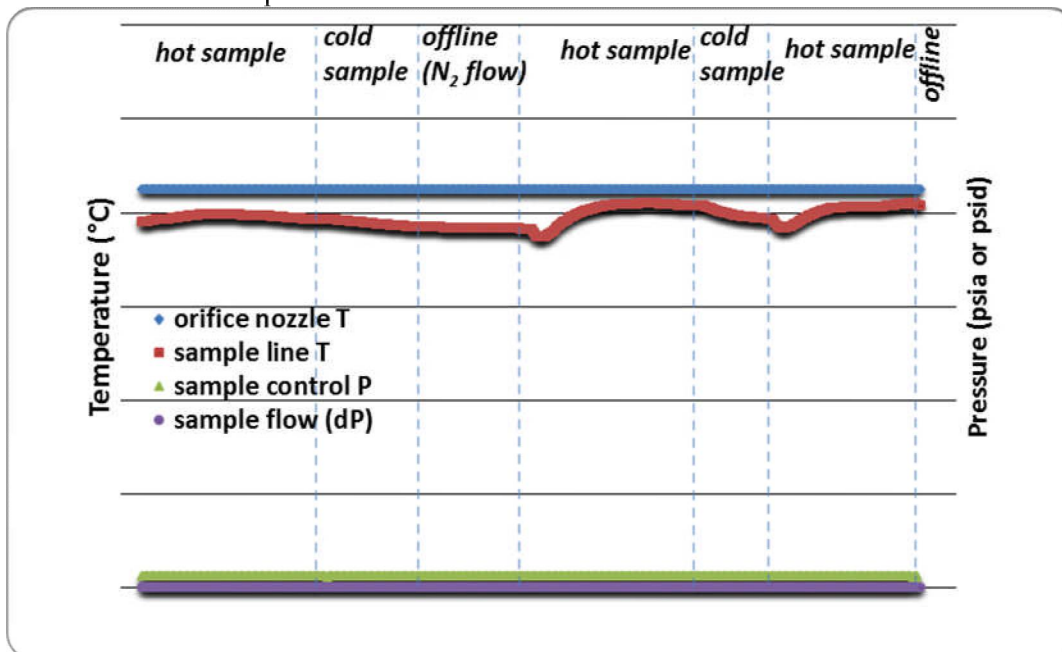
Figure XIIIB.5: Typical Trends for Critical Sampling Parameters during TMBMS Monitoring of Hot Syngas from the IBR Plant

Data collection and control of the mass spectrometer were automated using an acquisition and control system manufactured by Extrel™ CMS [3]. Mass spectra were recorded for m/z (10-500) along with auxiliary pressure data at a rate of 1 scan-sec^{-1}, with 30 s averages stored. Sample temperature, pressure, and flow were actively controlled and the data recorded using an OPTO 22 Ethernet-based I/O control system.

Absolute concentration data for selected tar compounds was achieved by carefully controlled injections of a liquid calibration standard into a heated capillary port upstream of the flow control valve (see Figure XIIIB.4). The mixed standard contained benzene, toluene, phenol, cresol, naphthalene, phenanthrene, and pyrene dissolved in methanol to represent predominant tar species typically observed in biomass-derived syngas. Table XIIIB.1 summarizes the composition of the liquid standard.

Table XIIIB.1: Composition of the Liquid Calibration Standard

Species	Molecular Weight	Liquid Concentration (wt. %)
Methanol	32	62.72
Benzene	78	11.18
Toluene	92	11.18
Phenol	94	5.97
Cresol	108	2.23
Naphthalene	128	4.47
Phenanthrene	178	1.11
Pyrene	202	1.09

To help negate potential matrix effects (i.e. changes to TMBMS response factors) caused by differences on bulk gas composition, tar standards were injected directly into the sampled process gas using two HPLC pumps – one feeding the standard, and the other feeding make-up methanol as needed to maintain a constant liquid flow. The standard additions were performed at two levels to generate response factors for each compound of interest, as shown for benzene in Figure XIIIB.6. The TMBMS response at zero added standards was proportional to the analyte concentration in the process gas stream at the time of the calibration. The uncertainties, reported as +/- 2 seconds, are typical of the scatter in the raw TMBMS data during sampling.

Lumped estimates for Type A and Type B tar were calculated by summing the uncalibrated peaks in the spectrum (i.e. compounds not included in the standard) and applying the response factors for naphthalene and pyrene, respectively. Here, the peaks used for the estimates were m/z 80-178 for Type A tar and m/z 179-500 for "heavy tar", but the designation is somewhat arbitrary. This method carries with it an increased potential for error since a single response factor is assumed for several species. Previous comparisons with impinger measurements have shown this error to be on the order of 20% (absolute basis). A method detection limit (MDL), equal to 3 times the standard deviation of the background signal, was estimated for each compound in the calibration mix.

Process sampling with the TMBMS began on Sept 17, 2013 at approximately 09:15. At this time the feed into the plant was being transitioned from standard mixture of methanol and CO_2 to rice hulls. By 11:00 the feed of the standard mixture had stopped and rice hulls were fed at a rate of 5.4 tons/day, with a steam feed rate of roughly 25 scfm, both of which were held constant throughout the day.
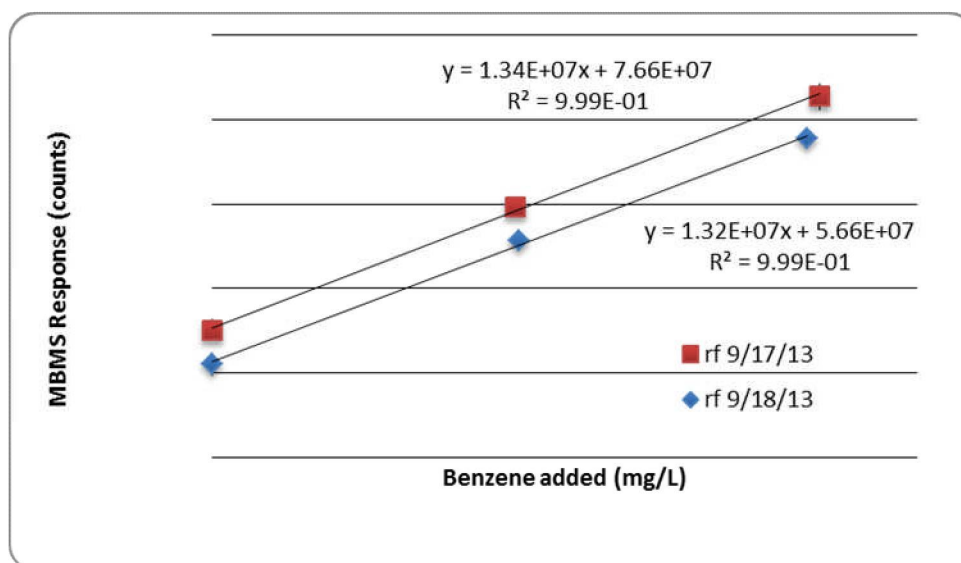
Figure XIIIB.6: An Example of the TMBMS Response Curves for Benzene

Using the response factors generated during the standard additions (Figure XIIIB.6), concentration vs. time plots were generated for individual tar species. The results are shown in XIIIB.7, where trends in syngas composition during the course of the day can be observed. After the initial transition to rice hulls, several hours of stable operation were achieved, where abrupt changes in signal intensity (labeled in graph) were caused by alternating between hot and cold gas sample ports, as well as tar standard additions. There was some periodicity observed in the mass spectral signal intensity, especially during the feed rate increase (09:15-10:00), which could have been due to the semi-batch nature of the retort feeding system. Figure XIIIB.8 show the same type of plot for the following day, where the feedstock was transitioned from rice hulls to 6.3 tons/day of wood chips.

The large decrease in TMBMS signals observed at approximately 8:15 (Figure XIIIB.8) was due to this change in feed material as wood was introduced to the system after the rice hulls had been consumed. The large signal deviations seen at 10:40-10:50 were due to an attempted standard addition that had to be aborted because of a malfunctioning TMBMS vacuum pump. The standard addition used for calibration can be seen roughly 30 minutes later after the problem was fixed. Overall, a small decrease (~10%) was observed in the raw concentration of tar species on a wet basis. This is consistent with the decrease in benzene concentration of roughly 20% (dry basis) that was measured by REII's online mass spectrometer.
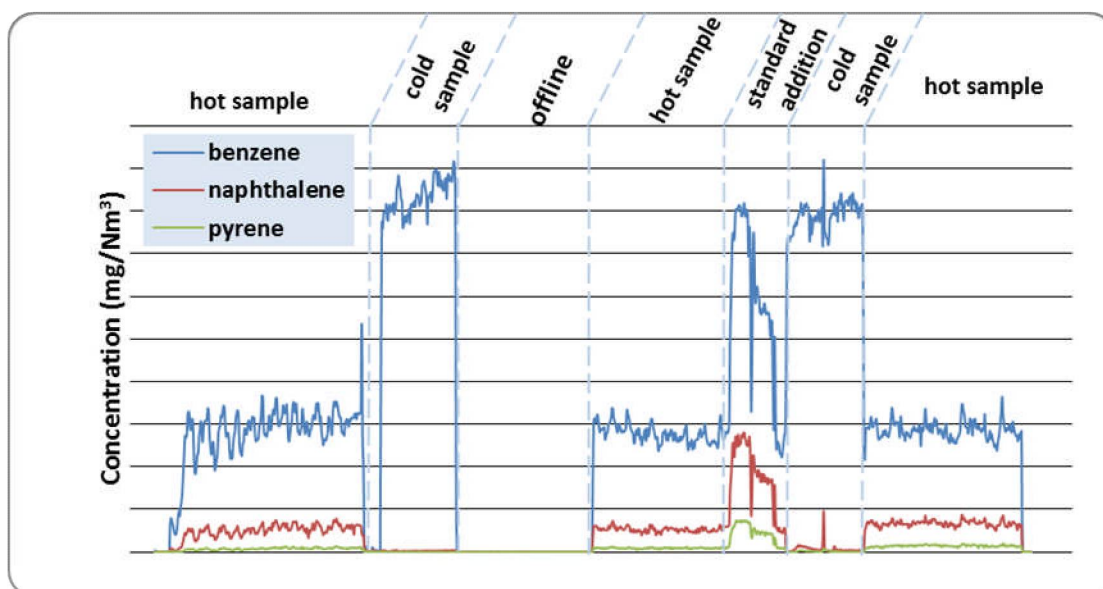
Figure XIIIB.7: Concentration vs. Time Plots for Benzene, Naphthalene and
Pyrene during the Conversion of 5.4 tons/day of
Rice Hulls in the Hot, Untreated Syngas
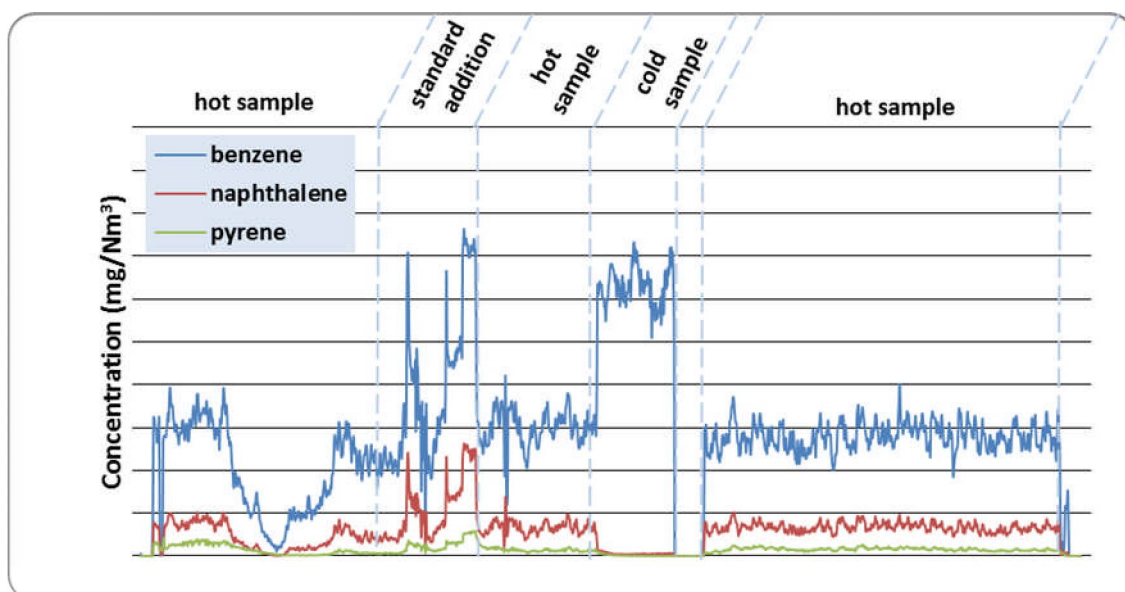
Figure XIIIB.8: Concentration vs. Time Plots for Benzene, Naphthalene and
Pyrene during the Thermochemical Conversion of 6.3 tons/day of
Wood in the Hot, Untreated Syngas

Figure XIIIB.9 shows the concentration vs. time trends when the wood feed rate was
increased to 11.6 tpd. At the higher feed rate, the process oscillations (roughly **8 min.**
cycles) became more apparent, and the tar concentration increased somewhat. The
TMBMS was taken offline just after noon to perform routine maintenance items.
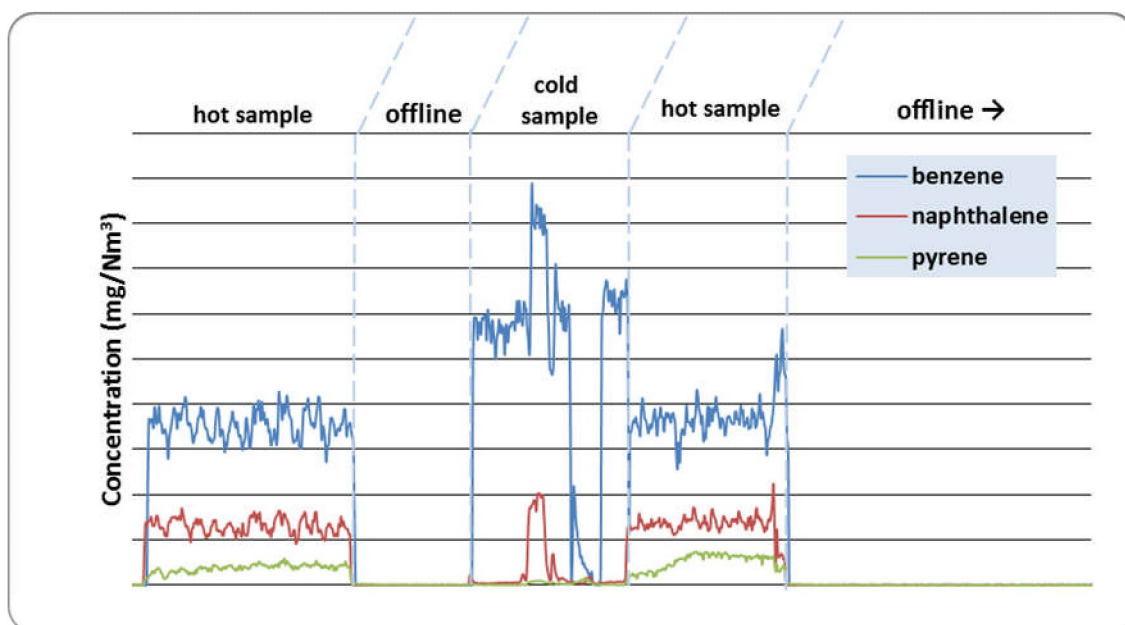
Figure XIIIB.9: Concentration vs. Time Plots for Benzene,
Naphthalene and Pyrene during the Thermochemical Conversion of
11.6 tons/day of Wood in the Hot, Untreated Syngas

2. Desert Research Institute

DRI employed an updated sampling and analysis system that was previously developed for REII in 2009 (Hoekman, 2013; Wang, 2011). A portable dilution sampling system previously developed for measuring multiple pollutant emissions from stationary and mobile sources was adapted for use in this project. A schematic of this system as deployed in previous field sampling experiments at the IBR plant is shown in Figure XIIIB.9. More detailed descriptions of this dilution sampling system's design, operation, and validation are provided elsewhere.

In the present IBR testing period, several modifications were made to the sampling system configuration shown in Figure XIIIB.10. First, because sampling of syngas (and tailgas) was done directly from ¼ in. analytical lines that were part of the plant's monitoring and control system, it was not possible to use a sample probe to introduce a fraction of the syngas into a larger pressure reducing chamber, as had been done before. Instead, a small fraction of the syngas was withdrawn from the sample line and introduced directly into the dilution sampling system through a needle valve.
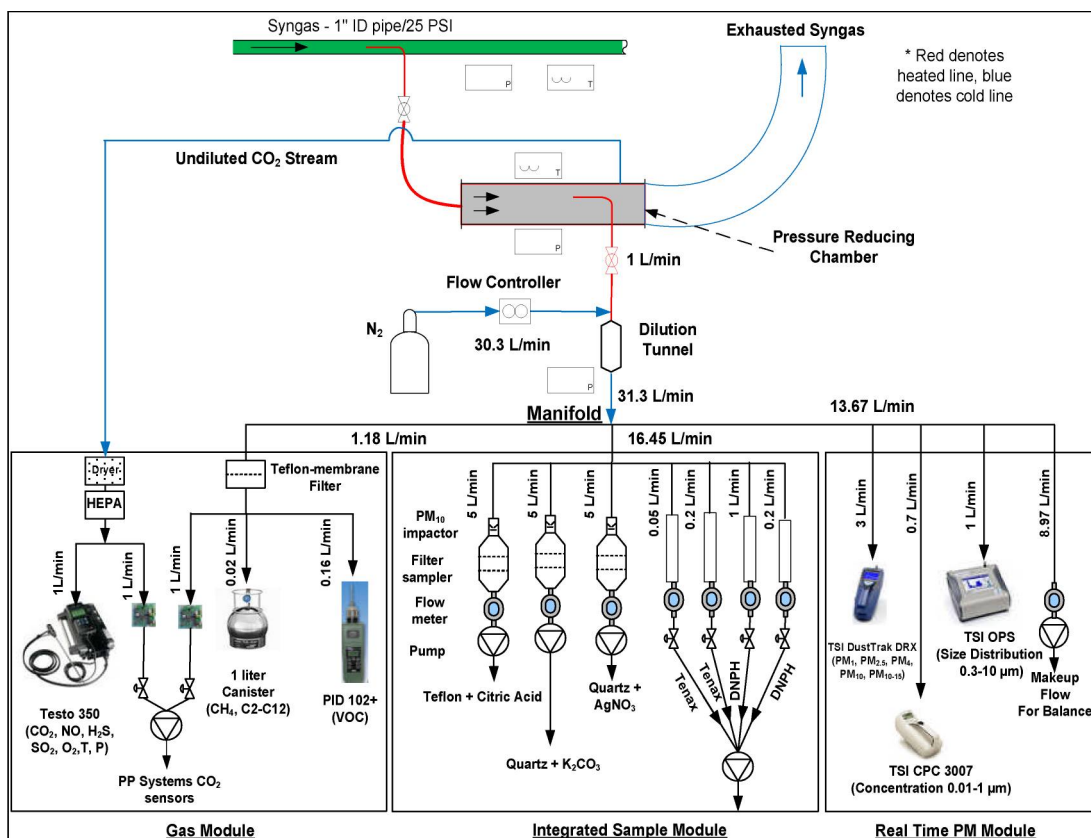
Figure XIIIB.10: Configuration of DRI's 1st Dilution Sampling System Developed for the Toledo IBR Plant

For the 2013 IBR plant test campaigns, some changes were also made to the Gas Module of the dilution sampling system. In the present testing effort, the Testo 350 real-time gas analyzer was not used. Although this instrument was originally quite attractive, as it has electrochemical sensors for many different gas species of interest (and it has proven useful in measurement of diluted engine exhaust), it is problematic when used to sample process gases. During previous sampling at the IBR plant, it was determined that some of the instrument's sensors are unreliable due to the high concentrations of CO and CO_2 in syngas, while other sensors (H_2S, SO_2, and O_2) are too insensitive to be of use in this application.

Another change within the Gas Module pertains to the HNU Systems Inc. photo-ionization detector (PID) instrument. The UV lamp for ionizing gaseous materials was changed from 10.2 eV to 9.5 eV. This reduction in ionization energy was used to improve the detector's sensitivity/selectivity for aromatics, olefins, and heterocyclic compounds, all of which are more easily ionized than the abundant aliphatic hydrocarbons. It was thought that this change would make the PID a more useful real-time indicator of the IBR plant's performance.

The Filter Module and the real-time PM Module of DRI's portable dilution sampling system were not changed from their previous configuration. The Filter Module (also

called the Integrated Sample Module) contained a variety of filter packs and adsorbent sampling media for collecting $PM_{2.5}$ (particles with aerodynamic diameter less than 2.5 µm), particle-phase ionic species, acid gases, ammonia, hydrogen sulfide (H_2S), higher MW organic compounds (C_8-C_{20}), and carbonyl species. The configuration of the filter packs used in the Integrated Sample Module and the species that are collected and analyzed are shown in Table XIIIB.2.

Table XIIIB.2: Configuration of Filter Packs used for Syngas Collection

| Filter Pack No. 1		Filter Pack No. 2		Filter Pack No. 3	
Filters	**Species Sampled**	**Filters**	**Species Sampled**	**Filters**	**Species Sampled**
Teflon Citric Acid	Total PM PM Elements NH_3	Quartz 1 K_2CO_3	OC/EC, Carbon Fractions HCl, HNO_3, H_2SO_4	Quartz 2 $AgNO_3$	NH_4^+, K^+, Na^+, Cl^-, NO_3^-, $SO_4^=$, H_2S

The Real-Time PM Module contained three continuous measurement instruments: (1) a DustTrak DRX aerosol monitor (Model 8534, TSI Inc., Shoreview, MN) for continuous measurement of PM mass in several size fractions (PM_1, $PM_{2.5}$, PM_4, PM_{10}, TPM), (2) a condensation particle counter (CPC; TSI Model 3007) for continuous measurement of particle number concentrations in the range of $\sim 0.01 - 1.0$ µm, and (3) an optical particle size classifier (OPS; TSI Model 3330) for continuous measurement of particle number concentration in the range of $0.3 - 10$ µm.

The configuration of the portable dilution sampling system as deployed at the IBR for syngas sampling in 2013 is illustrated in Figure XIIIB.11. As shown here, a slip stream of syngas was taken from the ¼-in tubing feeding the plant's analytical equipment, and was fed directly into the dilution tunnel of DRI's sampling system. Compressed nitrogen (N_2) gas was added to the dilution tunnel at a known flow rate. The dilution ratio (DR) could not be determined simply by flow rates because the syngas flow rate was not easily controllable (and was quite variable). Instead, DR was calculated based upon measurement of CO_2 in both the diluted and undiluted syngas stream
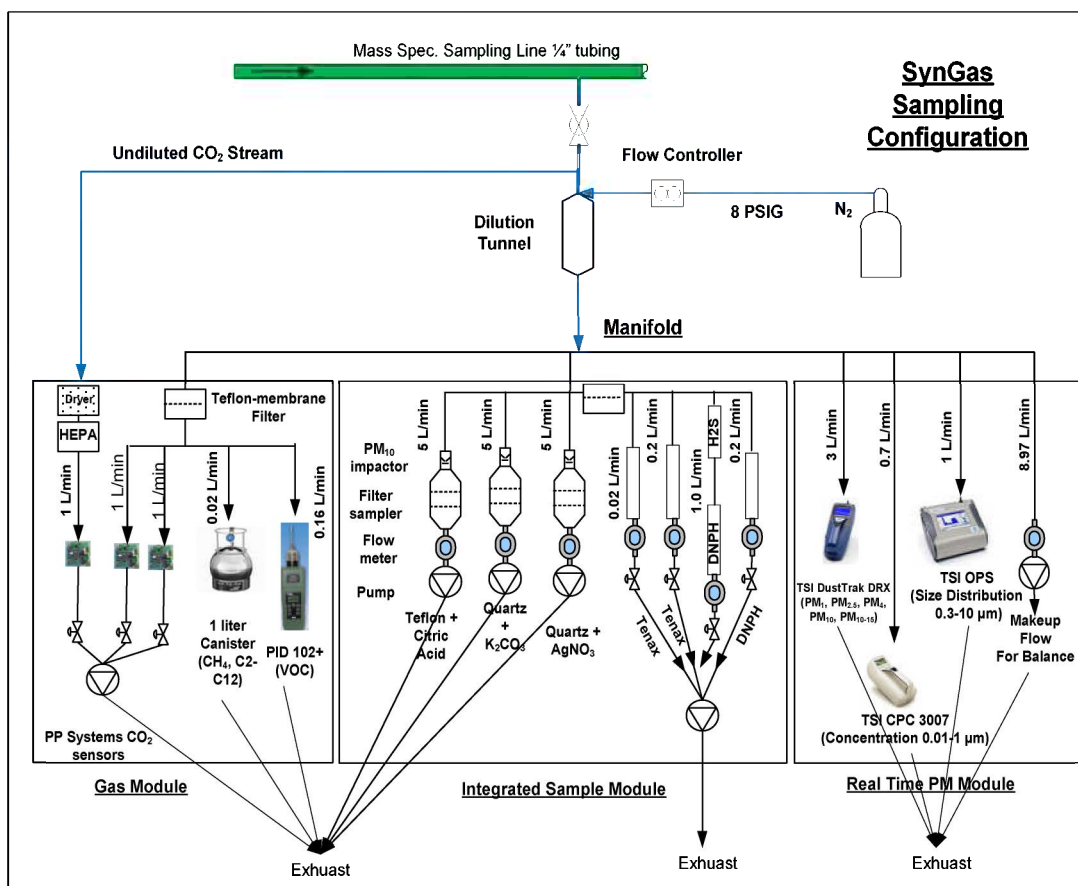
Figure XIIIB.11: Configuration of DRI's 2nd Generation Dilution Sampling System Developed for the 2013 Toledo IBR Plant Test Campaigns

For sampling tailgas, a simplified configuration of the dilution sampling system was used, as shown in Table XIIIB.12. The Gas Module and the Real-Time PM Module were used as before. However, no filter packs or DNPH cartridges were used; thus, the Integrated Sample Module contained only Tenax cartridges. As with syngas sampling, the dilution ratio for tailgas sampling was calculated by CO_2 measurements of the diluted and undiluted tailgas. However, this introduced complications, as it was discovered that tailgas samples contained very high levels of CO_2, which exceeded some of the instrument's range of operation. In addition, high concentrations of hydrocarbons in tailgas samples interfered with operation of the CO_2 instruments. As discussed later, corrective measures were taken to account for this, and provide improved estimates of the true dilution ratios when sampling tailgas.
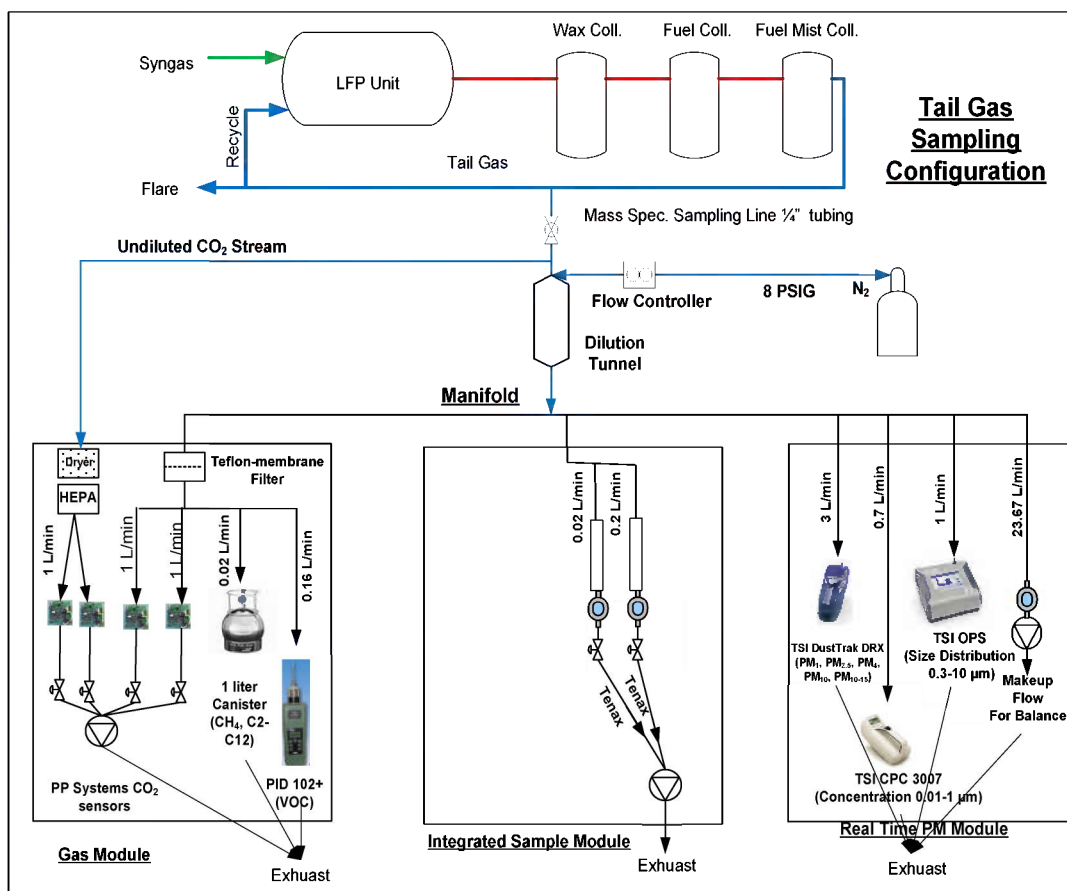
Figure XIIIB.12: Schematic of Tailgas sampling for the IBR Liquid Fuel Process (LFP)

Real-time measurements of CO_2, total VOC (by PID), and particulates (mass and number concentrations) from both syngas and tailgas were conducted on-site. Time-integrated samples (filters, cartridges, and canisters) were collected on-site, and shipped to DRI's analytical laboratories in Reno, Nevada, for off-line analysis. Details of these analytical methodologies have been reported previously but are also summarized briefly below. More detailed descriptions of these sampling and measurement protocols are provided in Appendix II. In addition, tabular summaries of sampling and analysis methods are provided in Table XIIIB.3 for syngas, and Table XIIIB.4 for tailgas.

a) Permanent Gases and light VOCs

Gaseous species were sampled using 1-L electro-polished canisters (Restek, Inc.) that had been cleaned and evacuated. After collecting a known volume of syngas, the canisters were returned to the lab for speciated analysis. CO, CO_2, and CH_4 were analyzed using GC (Shimadzu GC-17A) with flame ionization detection (GC-FID), following methanation of the column effluent. Other gas phase hydrocarbons (C_2-C_{11}) were analyzed from the canisters using an integrated GC/MS/FID method (Varian 3800 GC; modified US EPA TO-15 Method). Approximate method

detection limits (MDLs) are 0.1-0.2 ppbv for VOCs, 0.06 ppmv for CO, 0.2 ppmv for CH_4, and 3 ppmv for CO_2.

b) Higher MW VOCs

Higher MW VOCs [(C_8-C_{20}) also called semi-volatile organic compounds (SVOC)] in the gas phase were collected by drawing known amounts of syngas through cartridges containing Tenax-TA adsorbent material that was cleaned by solvent extraction (hexane/acetone) prior to use. After use, the Tenax cartridges were capped and returned to the laboratory for speciated analysis by GC/MS using a thermal desorption method. A Gerstel™ thermo-desorption System (TDS) was coupled to a Varian Saturn 2000 GC/MS system. MDLs for most identified species are in the range of 0.01-0.02 μg/cartridge.

c) Carbonyl Compounds

Carbonyl compounds (aldehydes and ketones) were collected by drawing known amounts of syngas through silica gel SepPak™ cartridges impregnated with acidified 2, 4-dinitrophenylhydrazine (DNPH). After use, the cartridges were capped and returned to the laboratory for analysis. The resulting hydrazone products were eluted from the cartridges with acetonitrile and analyzed by high performance liquid chromatography (HPLC) with a photodiode array detector.

d) Filter Samples

Three filter packs were used for sampling gaseous and particulate species in syngas, with each filter pack containing two 47-mm diameter filters in series. The identities and purposes of these filters are briefly described below.

Filter Pack No. 1: The front filter, a Teflon-membrane filter, was used to determine total $PM_{2.5}$ mass gravimetrically. This filter can also be used to measure individual elements by X-ray fluorescence (XRF) spectroscopy, although such analyses were not done in this study. The back filter, a citric acid impregnated filter, was used to collect ammonia (NH_3), which was measured as ammonium (NH_4^+) by the indol-phenol method, using an automated colorimetric analyzer.

Filter Pack No. 2: The front filter, Quartz-fiber Filter 1, was used for organic carbon/elemental carbon (OC/EC) analysis, determined by thermal optical analysis. The back filter, a K_2CO_3 impregnated cellulose filter, was used for acidic gases [HCl, HNO_3, H_2SO_4, and SO_2 (measured as $SO_4^=$)], determined by ion chromatography (IC), using a Dionex ICS-3000 IC instrument with a conductivity detector. Because SO_2 is converted to sulfate during the sample collection and work-up procedures, the IC measurement of $SO_4^=$ represents the sum of H_2SO_4 and SO_2 present in the original gas sample.

Filter Pack No. 3: The front filter, Quartz-fiber Filter 2, was used for particulate-phase, water-soluble ions. Anions (Cl^-, NO_3^-, $SO_4^=$) were determined by IC. Ammonium (NH_4^+) was determined by automated colorimetry. Other cations (K^+, and Na^+) were determined by atomic absorption (AA) spectrometry. The back

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filter, a silver nitrate-impregnated cellulose filter, was used for H_2S. During collection, H_2S present in the syngas is reacted to produce silver sulfide (Ag_2S), which is analyzed by XRF spectroscopy to determine the amount of sulfur on the filter. Another method for estimating H_2S concentrations involves the use of Dräger tubes. In this method, gas samples are passed through a glass cartridge containing mercuric chloride ($HgCl_2$), which reacts with H_2S to produce black-colored mercuric sulfide (HgS). The length of discoloration within the Dräger tube, combined with measurement of the sample flow rate, enables an estimation of the H_2S concentration in the syngas. Dräger tubes were inserted in the diluted syngas stream just prior to the high flow rate DNPH cartridges.

Table XIIIB.3: Summary of Syngas Sampling and
Analysis Methods for the Syngas (before Unit Operation #7)

Species of Interest	Sampling Method	Analysis Method
VOCs (C_2-C_{11}), COS	Canister	GC/MS/FID
CO, CO_2, CH_4	Canister	GC-FID (following methanation)
Higher MW VOCs (C_8-C_{20})	Tenax Cartridges	Thermal Desorption GC/MS
Carbonyls (C_1-C_7)	DNPH Cartridges	HPLC-UV/Visible diode array detector
HCl, HNO_3, H_2SO_4, and SO_2 (measured as $SO_4^=$)	K_2CO_3 impregnated cellulose filter (following Quartz 1 filter)	IC – conductivity detection
NH_3 (measured as NH_4^+)	Citric acid filter (following Teflon filter)	Automated colorimetry
H_2S	$AgNO_3$ impregnated filter (following Quartz 2 filter)	XRF
CO_2	Real-time monitoring (before and after dilution)	NDIR
Total VOC	Real-time monitoring	PID
Total $PM_{2.5}$ mass	Teflon Filter (preceding citric acid)	Gravimetry
OC/EC Total Carbon	Quartz Filter 1 (preceding K_2CO_3 filter)	Thermal Optical Analysis
Anions (Cl^-, NO_3^-, $SO_4^=$) Ammonium (NH_4^+) Other Cations (K^+, Na^+)	Quartz Filter 2 (preceding $AgNO_3$)	IC-conductivity detection Automated colorimetry Atomic Absorption
Elements *	Teflon Filter	XRF, ICP-MS
Particle number concentration	Real-time monitoring	Condensation Particle Counter (0.01-1.0 μm) Optical Particle Sizer (0.3-10 μm)
PM_1, $PM_{2.5}$, PM_4, PM_{10}, and TPM mass concentrations	Real-time monitoring	DustTrak DRX

* Not measured in this experimental program

Table XIIIB.4: Summary of Syngas Sampling and
Analysis Methods for the Tailgas (after Unit Operation #7)

Sample Type	Species of Interest	Sampling Method	Analysis Method
Tailgas: Gas Phase	VOCs (C_2-C_{11}), COS	Canister	GC/MS/FID
	CO, CO_2, CH_4	Canister	GC-FID (following methanation)
	Higher MW VOCs (C_8-C_{20})	Tenax Cartridges	Thermal Desorption GC/MS
	CO_2	Real-time monitoring (before and after dilution)	NDIR
	Total VOC	Real-time monitoring	PID
Tailgas: Particle Phase	Particle number concentration	Real-time monitoring	Condensation Particle Counter (0.01-1.0 µm) Optical Particle Sizer (0.3-10 µm)
	PM_1, $PM_{2.5}$, PM_4, PM_{10}, and TPM mass concentrations	Real-time monitoring	DustTrak DRX

The most comprehensive sampling and analysis campaign was carried out during
the IE test (Run #17). The complete list of 16 samples that were collected is
provided in XIIIB.5. Of these 16, 12 samples were syngas and 4 were tailgas.

Table XIIIB.5: Integrated Samples Collected from the IBR Plant (Run #17)

Sample No.	Date	Feedstock Type	Sample Type	Sample Time, min.	Calculated Dilution Ratio
1	9/9/13	MeOH/CO_2	Syngas	86	(1)
2	9/9/13	MeOH/CO_2	Syngas	45	143.1 ±326.5
3	9/9/13	MeOH/CO_2	Syngas	93	12.8 ±1.0
4	9/9/13	MeOH/CO_2	Tailgas	11	43.6 ± 34.9
5	9/10/13	Rice Hulls	Tailgas	10	43.0 ± 14.7
6	9/16/13	Rice Hulls	Syngas	90	13.2 ± 0.3
7	9/16/13	Rice Hulls	Syngas	90	15.0 ± 1.1
8	9/16/13	Rice Hulls	Syngas	91	17.8 ± 0.7
9	9/17/13	Rice Hulls	Syngas	96	27.1 ± 4.7
10	9/17/13	Rice Hulls	Syngas	90	27.2 ± 1.1
11	9/18/13	Rice Hulls	Syngas	31	(2)
12	9/18/13	Wood Chips	Syngas	90	23.5 ± 9.7
13	9/18/13	Wood Chips	Tailgas	10.5	93.9 ± 51.6
14	9/18/13	Wood Chips	Tailgas	11	77.0 ± 31.2
15	9/18/13	Wood Chips	Syngas	87	34.4 ± 15.3
16	9/18/13	Wood Chips	Syngas	60	28.6 ± 11.5

(1) Sample No. 1 occurred during initial setup – no reliable dilution ratios were obtained;

(2) Diluted CO₂ measurements are not available for Syngas Sample No. 11

Only a subset of these 16 samples was analyzed in DRI's laboratories. This subset was selected based upon (1) analysis of the real-time data for PM, CO_2, and VOC (by PID), (2) IBR plant feedstock used, and (3) knowledge of the IBR plant's operational performance. The subset of seven samples that were analyzed is highlighted in bold.

It was desirable to include samples of both syngas and tailgas from each of the three IBR feedstocks: (1) methanol/CO_2, (2) rice hulls, and (3) wood chips. To provide

useful information about repeatability, two syngas samples from wood chips were analyzed. The four syngas and three tailgas samples that underwent detailed analyses are shown below in Table XIIIB.6.

Table XIIIB.6: Integrated Samples Analyzed in DRI's Laboratories

Feedstock	Syngas		Tailgas	
	Sample #	Date	Sample #	Date
MeOH/CO$_2$	3	9/9/13	4	9/9/13
Rice Hulls	10	9/17/13	5	9/10/13
Wood Chips	15, 16	9/18/13	13	9/18/13

A list of real-time instruments that were used to sample the diluted and non-diluted gas streams (both syngas and tailgas) is shown below in Table XIIIB.7. Data plots from these instruments are included for each run in Appendix IV. These plots provide valuable insights into the plant operational conditions and sampling conditions that existed during each sampling period. Additional operational details for each of these instruments are provided in Appendix II.

Table XIIIB.7: Real Time Instruments Employed at the IBR Plant in 2013

Instrument	Parameter of Interest and Measurement Principles	Measurement Range	Time Resolution	Nominal Precision/ Accuracy
Condensation Particle Counter (CPC) Model 3007 (TSI Inc., Shoreview, MN, USA)	Particle number concentration by condensation growth and optical counting	Size: 10 nm–2.5 µm Number: 0–100,000 particles/cm^3	1 s	±20%
DustTrak DRX Model 8534 (TSI Inc., Shoreview, MN, USA)	PM mass concentration (PM$_1$, PM$_{2.5}$, PM$_4$, PM$_{10}$, and PM$_{15}$) by photometry and optical sizing	Size: ~ 0.1–15 µm Mass: 0.001–150 mg/m^3	1 s	±20% (for calibration aerosol)
Optical Particle Counter (OPS) Model 3330 (TSI Inc., Shoreview MN, USA)	Particle size distribution by light scattering	Size: 0.3–10 µm Number: 0.001–3,000 particle/cm^3 Mass: 0.001–275 mg/m^3	10 s	±5% at 0.5 µm per ISO 21501-1
PID analyzer Model 102+ (PID Analyzers, Pembroke, MA, USA)	Total VOC (as isobutylene equivalent) by photo-ionization detection	0.1–3000 ppm	1 s	± 1% of reading
CO$_2$ analyzers (100k) Model SBA–5 (PP Systems, Amesbury, MA, USA)	CO$_2$ (non-dispersive infrared) Diluted sample stream	0–100,000 ppm	~2 s	<1% of span conc.
CO$_2$ analyzers (30k) Model SBA–5 (PP Systems, Amesbury, MA, USA)	CO$_2$ (non-dispersive infrared) Diluted sample stream	0–30,000 ppm	~2 s	<1% of span conc.
CO$_2$ (65%) Model CM-0050 (CO$_2$meter.com, Ormond Beach, FL)	CO$_2$ (non-dispersive infrared) Un-diluted gas stream	0-650,000 ppm	2s	±5%
CO$_2$ (100%) Model CM-0006 (CO$_2$meter.com, Ormond Beach, FL)	CO$_2$ (non-dispersive infrared) Un-diluted gas stream	0-1,000,000 ppm	2s	±5%

Of the four different CO$_2$ analyzers used, two were used to sample the diluted gas stream (the 30k and 100k analyzers), and two were used to sample the un-diluted gas stream (the 65% and 100% analyzers). However, the 100k analyzer did not function properly throughout the sampling campaign, so provided no useable data. In addition to these continuous analyzers, a GC and a CAI-ZRE Gas Analyzer (that are components of the IBR plant's suite of analytical instruments) were used to

monitor gas concentrations from the undiluted gas stream by taking period snapshots.

The dilution sampling system is designed to draw from a sample gas stream, dilute it with air or nitrogen, and then measure the constituents. Since all samples were collected and analyzed from the diluted stream, determining the dilution ratio (DR) is important to properly calculate the concentrations of the original, non-diluted gas stream. The DR was calculated by measuring the CO_2 concentrations in the diluted gas stream, the undiluted gas stream, and the background air using multiple CO_2 analyzers as described in Table XIIIB.8. The dilution ratio can then be calculated by comparing the measurements of the non-diluted CO_2 concentrations to the diluted CO_2 concentrations as follows:

$$DR = \frac{CO_{2,Undil}}{CO_{2,Dil}}$$ (Equation 1)

Where:

$CO_{2,\,Undiluted}$ = undiluted CO_2 concentration (in ppm, corrected for background)
$CO_{2,\,Diluted}$ = diluted CO_2 concentration (in ppm, corrected for background)

Inconsistencies in the analyzers, however, required that different calculations be done for the syngas compared to the tailgas as follows. Average CO_2 concentrations in the undiluted sample gas streams as measured by the 65% and 100% real-time gas analyzers are shown in Table XIIIB.8, along with other snapshot measurements of CO_2 by GC and MS. These averages are over time periods that most closely correlate with the sampling time of each integrated sample. The 100% CO_2 analyzer did not work consistently, so the data from this analyzer could not be used. The 65% CO_2 analyzer worked well, and gave reasonable readings from the syngas stream, although these results did not agree closely with MS snapshot measurements taken during these runs. This may be due in part to interferences in the gas stream that affect the reading of the 65% sensor. For example, it is known that this sensor responds to high concentrations of hydrocarbons and CO, both of which may be present in undiluted syngas.

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Table XIIIB.8: CO_2 Concentration Readings from
Un-Diluted Gas Streams (Volume %)

Sample	Type	Feedstock	65% CO_2 (avg.)	100% CO_2 (avg.)	ZRE	GC	MS
3	Syngas	CO_2 / Methanol	48	-	-	-	-
10	Syngas	Rice Hulls	41	-	-	-	11.61
15	Syngas	Wood Chips	48	60	-	-	23.39
16	Syngas	Wood Chips	48	60	-	-	22.36
4	Tailgas	CO_2/ Methanol	max	-	41	49.16	-
5	Tailgas	Rice Hulls	max	-	36	70.0	-
13	Tailgas	Wood Chips	max	max	-	46.45	

To calculate the syngas dilution ratio, the continuous measurements from the 65% CO_2 analyzer (in the un-diluted stream), and the 30k analyzer (in the diluted stream) were compared. The raw data from the real-time, continuous dataset were first interpolated into 1-second time intervals, and then averaged into 20 second intervals. The 20-second average dilution ratio values were then calculated using Equation 1. It is these 20-second averaged DR values that are plotted in the real-time data displays shown in Appendix IV.). A single, overall average dilution ratio was then estimated for the entire run by integrating the instantaneous data. These overall average dilution ratios are shown in Table XIIIB.5.

As shown in Table XIIIB.9, the 65% CO_2 analyzer that was used to give the instantaneous readings for the undiluted syngas maxed out and did not provide reliable readings for tailgas. We believe this was caused by both higher actual CO_2 concentrations and by interferences from high concentrations of VOCs in the tailgas. Therefore, the only consistent CO_2 concentration measurement from the undiluted stream of tailgas was from the GC. In order to compute the dilution ratio, the single point GC reading was assumed as a constant undiluted concentration throughout the sampling period of the tailgas, and was compared to the 1-second averaged continuous data from the 30k analyzer using Equation 1. The average dilution ratio was then computed by integration, and is shown in Table XIIIB.5.

In the sections that follow, results from collecting and analyzing integrated samples of syngas and tailgas are presented. Where possible, the concentrations and compositions of syngas samples are compared with similar samples that were collected from the IBR plant in 2009 while operating on rice hulls and wood chips.

e) Total PM Mass in Syngas

The total PM mass in syngas was determined by weighing Teflon membrane filters before and after use. As expected, the syngas produced when using methanol/CO_2

as feedstock was very clean, having PM levels that were below detection limits. As shown in Figure XIIIB.9, significantly higher PM concentrations were measured in syngas produced from rice hulls (180 $\mu g/m^3$ or 34 ppb and wood chips (710 $\mu g/m^3$ or 135 ppb). These concentrations are within the desired purity specification of 1.0 mg/m^3.

The PM sample from Run 16 was also below the detection limits, partly due to the shorter collection time of that sample (60 minutes compared to 90 minutes in the other three runs shown). It should be noted that all filter mass measurements were close to detection limits. Even with the heaviest loaded filter (Sample No. 15), only a few micrograms was collected, which is difficult to determine on a filter that weighs approximately 160 mg.
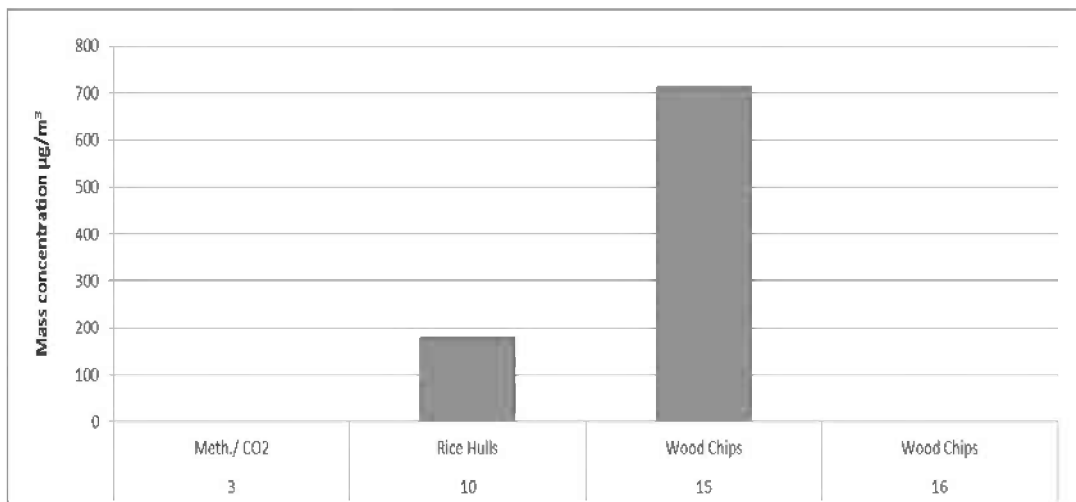
Figure XIIIB.13: The Concentration of Particulate
Matter in the Syngas (Run #17)

Table XIIIB.9: Summary of Syngas Contaminants in the Raw Syngas, after Purification Systems #4a and after Polishing System #4b

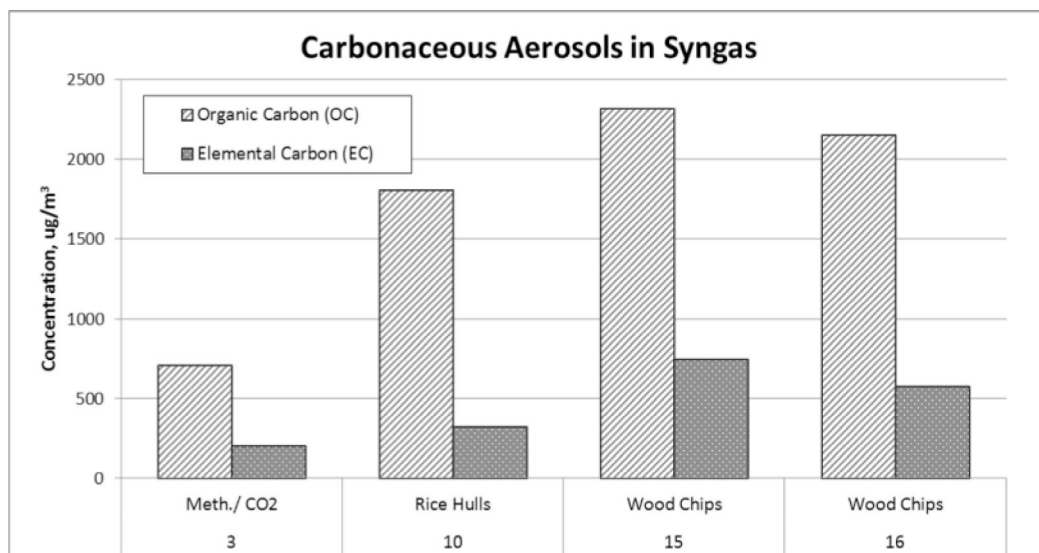|	Concentration (dry)		
	Raw Syngas	**After Purification System #4a**	**After Polishing System #4b**
Particulate Species			
Elemental Carbon	Not tested	Not tested	665 $\mu g/m^3$
Total Inorganics (anions and cations)	Not tested	Not tested	47 $\mu g/m^3$
Total Type A Tars	231 ppm	20 ppm	(< 70 $\mu g/m^3$)
Total Type B Tars	29 ppm	(< 70 $\mu g/m^3$)	(< 70 $\mu g/m^3$)
Gas Phase Species			
Benzene	5,303 ppm	5,508 ppm	5,340 ppm
Total Aliphatic HCs	Not tested	1,100 ppm	1,230 ppm
Toluene	76 ppm	Not tested	8.7 ppm

f) Carbonaceous Aerosol in Syngas

Classification of carbonaceous aerosol into organic carbon (OC) and elemental carbon (EC) was determined by thermal optical reflectance/thermal optical transmittance (TOR/TOT) analysis of material collected on quartz fiber filters. Results from the four syngas samples collected here are shown in Figure XIIIB.14. As was seen in 2009, considerably higher amounts of OC were seen compared to EC. This is attributed to positive sampling artifacts, whereby semi-volatile constituents in the syngas are adsorbed on the quartz filter during the long sampling period (60-90 min.), but are devolatilized and measured during conduct of the OC/EC instrumental analysis. The two wood chip samples (No. 15 and 16) show reasonably consistent OC/EC results. Consistent with the total PM mass results described above, the concentrations of OC/EC measured in the 2013 samples are about an order of magnitude higher than seen in 2009.

For Sample No. 15, the measured concentration of EC is in good agreement with the concentration of total PM mass. This further suggests that the total PM mass determined gravimetrically for Sample No. 16 was erroneously low, and that the actual PM mass concentration was close to a value of 500 $\mu g/m^3$, which was similar to that found in the EC measurement.

No significant levels of carbonaceous aerosols would be expected when operating the IBR plant with methanol/CO_2 as feedstock. Thus, the OC/EC concentrations seen for Sample No. 3 could be considered a functional system blank. The OC/EC

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seen in this sample could result from flushing the system of material that had formed from previous operation of the IBR plant.

Figure XIIIB.14: Carbonaceous Aerosol
Concentrations in the Syngas Samples (Run #17)

g) Hydrogen Sulfide (H_2S) in Syngas

H_2S concentrations were determined by XRF analysis of silver nitrate-impregnated cellulose filters. (H_2S reacts with $AgNO_3$ during sampling to produce Ag_2S; XRF is used to quantify S on the filter.) For all filters that were analyzed, the concentrations of S were below the detection limit. Considering the XRF analytical detection limit, and the relevant syngas dilution ratios, it is concluded that the concentrations of H_2S present in all undiluted syngas samples were less than 5 $\mu g/m^3$ (< 3 ppb).

During collection of each syngas sample, a Dräger tube was inserted in front of the high flow DNPH cartridge to provide an estimate of H_2S concentrations. During sampling, any H_2S present in the diluted syngas reacts with $HgCl_2$ on the Dräger tube to produce HgS, which is visible as a dark colored band that progresses throughout the calibrated tube. Of all 12 syngas samples collected, only Sample No. 6 showed a detectable visual band for H_2S. (This is the first sample collected following startup of the IBR plant on 9/16/13, after it had prematurely shut down a week earlier.) The H_2S concentration estimated from this tube was 3.5 ppm.

h) Particulate Ions in Syngas

Particulate matter in syngas samples was collected on quartz filters, which were subsequently extracted with water to obtain water-soluble anions and cations that were quantified by ion chromatography (anions) and atomic absorption (AA) spectrometry (cations). The ion results from the four syngas samples analyzed here

are shown in XIIIB.15. Ammonium and potassium are the main cations observed, while sulfate, nitrate, and chloride are the main anions observed.

As expected, higher total ion levels were measured in syngas from rice hulls and wood chips, as compared to syngas from methanol/CO_2. Again, the methanol/CO_2 sample could be considered a functional blank for the entire system. The replicate wood chip samples (#15 and 16) do not agree very closely, with Sample 16 having much higher levels of ammonium, potassium, and chloride compared to Sample 15. This suggests that formation and/or collection of these particulate ions is quite sensitive to slight changes in operation of the IBR plant.
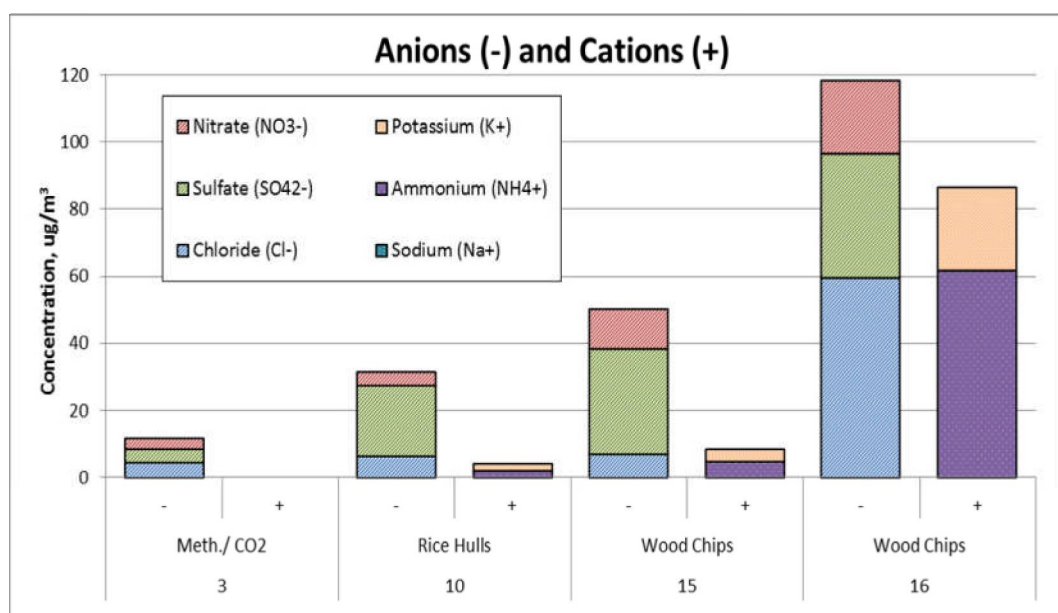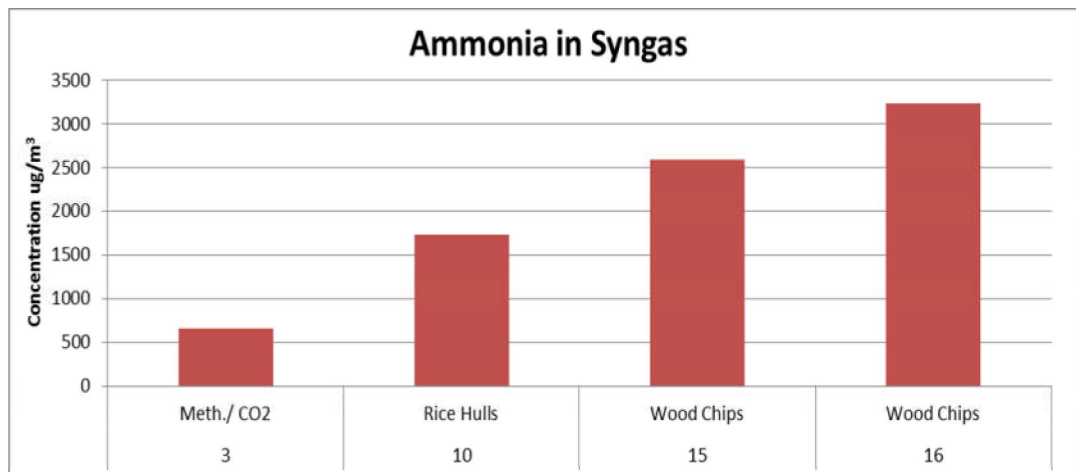

Figure XIIIB.15: The Concentration of Anions and Cations in the Particulates for Run #17

i) Ammonia in Syngas

Ammonia gas was collected by reaction with citric acid on a cellulose fiber filter to produce ammonium citrate. After water extraction, the ammonium ion was quantified using an indol-phenol colorimetric method. The results shown in Figure XIIIB.16 indicate higher amounts of ammonia than expected, although the concentrations are much higher in syngas from rice hulls and wood chips, compared to syngas from methanol/CO_2. The noticeable increase in ammonia from one sample to the next closely parallels what was seen with the ion concentrations discussed above. This suggests that the same sampling and plant operational factors affect both ions and free ammonia in a similar fashion. In general, the ammonia concentrations measured in 2013 are higher than those measured in 2009 by about an order of magnitude.

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It was subsequently learned that during this field sampling program, the ammonia scrubbing component within the syngas polisher (Unit Operation #8) was not being used (it was bypassed due to high backpressure). This may explain the elevated concentrations of ammonia (and possibly particulate ion species) that were measured in 2013 as compared to previous sampling.

Figure XIIIB.16: The Concentration of Ammonia in the Syngas Samples (Run #17) (500 $\mu g/m^3 NH_3$ = 720 ppb)

j) Acid Gases in Syngas

The acid gases present in syngas (HCl, HNO_3, and H_2SO_4) were collected by reaction with potassium carbonate on a cellulose fiber filter. The resulting potassium salts were extracted with water and analyzed by ion chromatography. As shown in Figure XIIIB.17, the four syngas samples that were analyzed all contained measureable amounts of HCl, HNO_3, and H_2SO_4. (It should be noted that gaseous SO_2 present in syngas will react on the potassium carbonate filter to produce potassium sulfate, and thus contribute to the measured H_2SO_4. The two replicate wood chip-derived samples do not agree very closely, with substantially higher concentrations of HNO_3 and H_2SO_4 seen in Sample No. 15, as compared to Sample No. 16. Reasons for these differences are not completely understood, but this suggests that the formation and/or collection of acid gases is quite sensitive to slight changes in operation of the IBR plant.
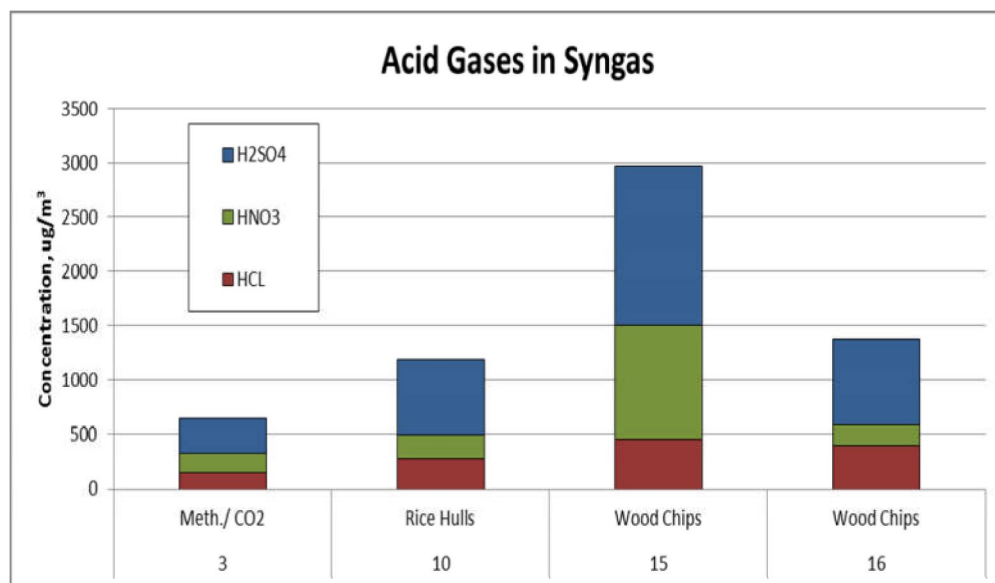
Figure XIIIB.17: The Concentration of Acid Gases in the Syngas Samples (Run #17) (1000 $\mu g/m^3$ H_2SO_4 = 125 ppb)

k) Carbonyls in Syngas

Carbonyl compounds were captured by reaction with 2,4-dinitrophenylhydrazine on silica gel cartridges. The resulting hydrazone products were eluted from the cartridges with acetonitrile, and were measured using HPLC with a photodiode array detector. The results are shown in Figure XIIIB.18. In all four samples, a large number of carbonyl compounds were measured – primarily in the range of C_1-C_6. The total carbonyl concentrations in syngas from wood chips are similar to those observed earlier, while the concentrations in rice hull-derived syngas are somewhat higher than observed previously.
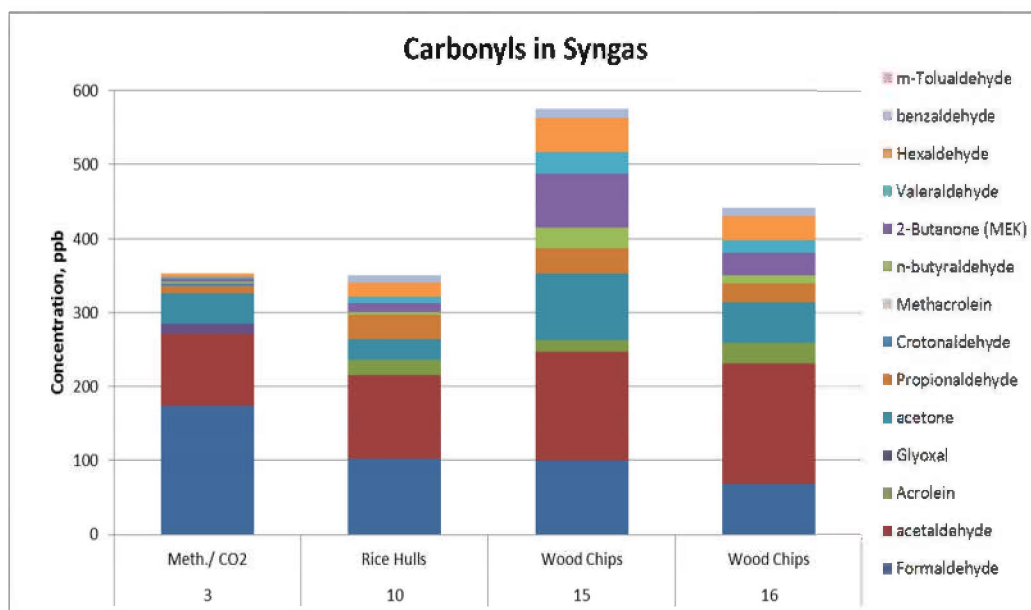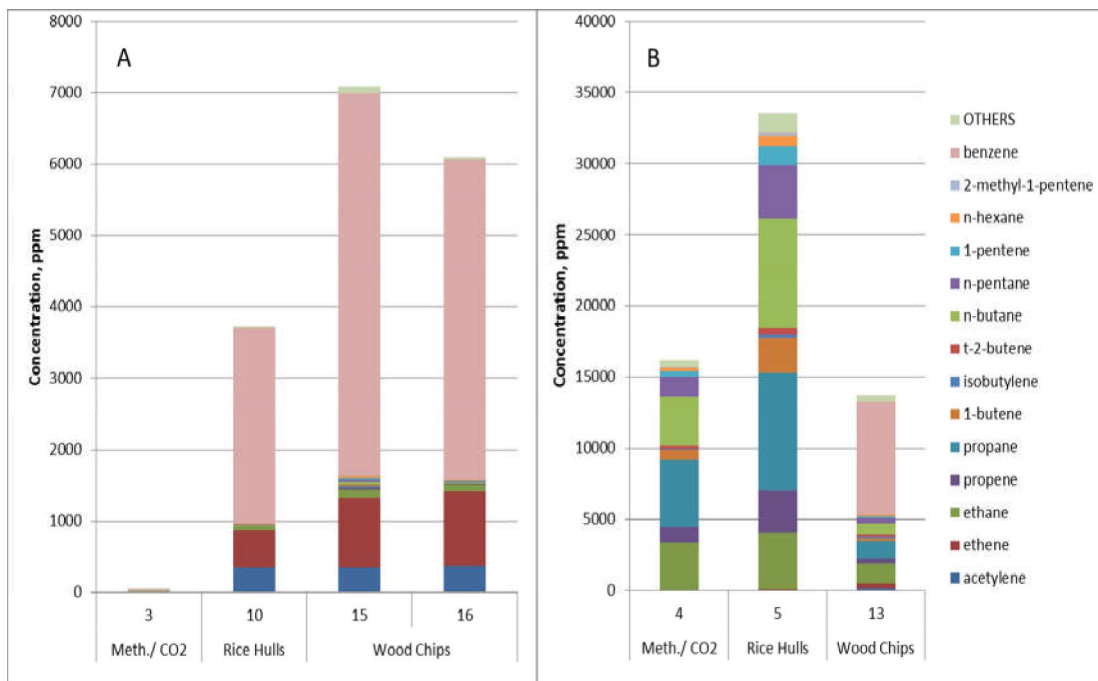
Figure XIIIB.18: The Concentration of
Carbonyls in the Syngas Samples (Run #17)

The higher concentration of formaldehyde when operating the IBR plant on
methanol/CO$_2$ is expected. In this case, Sample No. 3 cannot be considered a
functional system blank for formaldehyde (and possibly for acetaldehyde), but may
still serve as a blank for the higher molecular weight carbonyl species.

l) VOCs in Syngas and Tailgas

VOCs in both syngas and tailgas were collected in evacuated canisters and anlyzed
by an integrated GC-FID and GC-MS method. Light compounds (C$_2$-C$_4$) are
quantified by GC-FID; heavier compounds (C$_5$-C$_{11}$) are quantified by GC-MS.
VOC results for the syngas samples are shown in XIIIB.17. As expected, very little
VOC material was seen in syngas from methanol/CO$_2$. Syngas from rice hulls and
wood chips contained substantial levels of VOCs; the total concentrations are
similar to what was observed in 2009. However, the VOC composition is
somewhat different from previous samples. The compositions shown in XIIIB.19
are dominated by benzene, while acetylene and ethene were more dominant in the
2009 samples.

VOC composition of tailgas is much different, consisting primarily of a large
number of alkanes and alkenes in the range of C$_2$-C$_6$. No single species dominates
the overall tailgas composition, although benzene was the largest constituent in the
wood chip-derived tailgas (Sample No. 13). This high benzene concentration in
Sample No. 13 is unexplained. It perhaps results from sample contamination and/or
a temporary upset in the LFP unit. Some evidence of a slight LFP upset is
suggested by the fact that Sample No. 13 also had higher concentrations of
acetylene and ethene compared to Samples 4 and 5. However, the main reason for
the high benzene level in Sample No. 13 remains unknown.

Figure XIIIB.19: The Concentration of
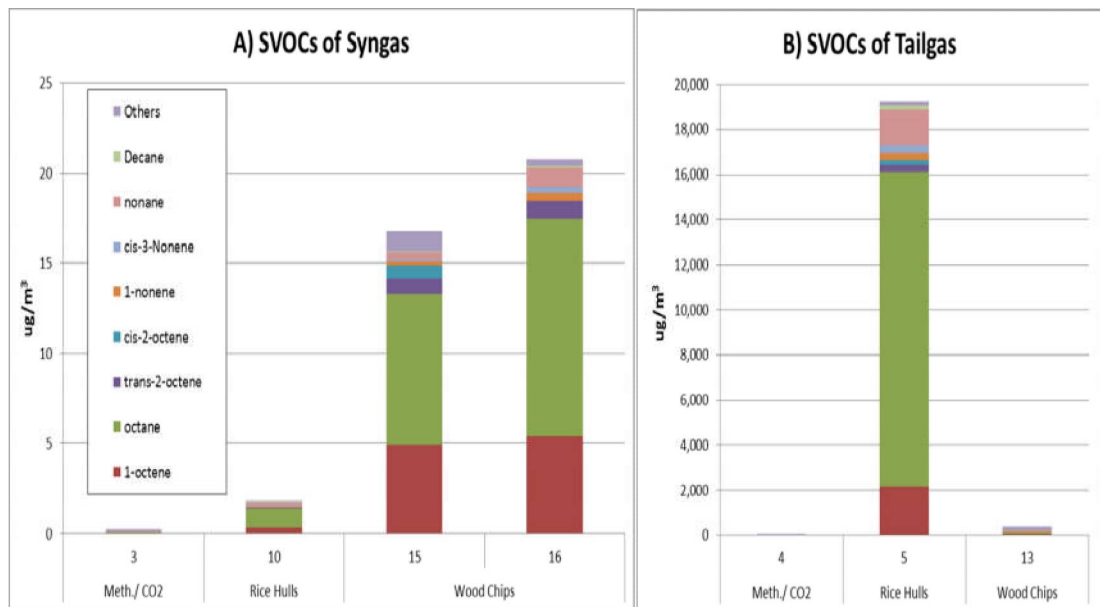VOC's in the Syngas (A) and Tailgas (B) Samples (Run #17)

This complex VOC composition of the tailgas samples is expected from the "designer catalyst" process used to produce liquid hydrocarbon fuels from syngas. The overall VOC concentrations in the three tailgas samples are quite low (approximately 1.5 – 3.5%), indicating that the fuel production and fuel collection units within the IBR plant were functioning well.

m) SVOCs in Syngas and Tailgas

Semi-volatile organic compounds (SVOCs) were captured by adsorption on Tenax cartridges. The cartridges were then thermally desorbed into a GC-MS instrument for speciation and quantification. In this report, we define SVOCs to be C_{8+} compounds. As shown in XIIIB.20, very low levels of SVOCs were present in all of the syngas samples, with the methanol/CO_2-derived syngas having nearly undetectable amounts. Total SVOC concentrations in syngas from rice hulls were very low at about 2 $\mu g/m^3$, while total concentrations from wood chip-derived samples were an order of magnitude higher. Reasonably good agreement (in both concentration and composition) was observed for the two replicate syngas samples, Nos. 15 and 16.

SVOC concentrations observed in the three tailgas samples were quite inconsistent, with relatively high levels in Sample No. 5 (rice hull feedstock), but nearly undetectable amounts in Sample No. 4 (methanol/CO_2) and Sample No. 13 (wood chips). The composition of the SVOCs is quite similar between syngas and tailgas samples, consisting primarily of C_8-C_9 hydrocarbons. The relatively high SVOC

concentration in Sample No. 5 suggests that the fuel condensation/collection system was not operating quite as efficiently during collection of this sample. Nevertheless, the overall low levels of SVOCs in all tailgas samples (< 2% even in Sample #5) confirm that the fuel collection/ condensation units within the IBR plant were functioning properly.

Figure XIIIB.20: The Concentration of
SVOC's in the Syngas (A) and Tailgas (B) Samples (Run #17)
(14,000 µg/m3 of octane = 3.5 ppm)

3. Bureau Veritas (BV)

BV collected and characterized integrated syngas samples from sampling location #8 (Figure VID.1) during the same period in which the mass spectrometer was generating quantitative data for H_2, CO, CO_2, CH_4, N_2, Ar and O_2.

C. Tar Composition

Tars were primarily collected in Tar Collector #1 as shown in Figure VID.4. The total material collected was 5.3 ppm in the raw syngas. In addition, a small amount of white material condensed on the syngas flow meters, the quantity for which was not determined. Analysis of the Type A PAHs and Type B PAHs was carried out by Bureau Veritas and that data is summarized in Table XIIC.2.

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Table XIIIC.1: The Concentration of Tars Collected at Various Locations in the Syngas Purification System

Sample Location (see Figure VID.4)	Total Material Collected (ppm)	Type A PAHs (ppm)	Type B PAHs (ppm)	Type A / Type B PAHs
Tar Collector #1	5.4	4.6	0.81	0.57
Transfer Pipe between Quench Column and Water Scrubber	Not determined	0.33	0.011	29.5
Transfer Pipe between Water Scrubber #1 and Water Scrubber #2	Not determined	0.23	0.0035	65.7
Syngas Flow Meters	Not determined	0.17	< 0.002	>87

Table XIIIC.2: The Composition of PAHs in the Material
Collected in the Tar Collector and Condensed on the Syngas Flow Meters

Compound	Tar Collector Sample	Syngas Flow Meter Sample
	Concentration in Samples (μg/g)	
Type A Tars		
Naphthalene	26,000	87,000
1-Methylnapthalene	<1,000	<1,000
2-Methylnapthalene	<1,000	<1,000
Dibenzofuran	1,000	<1,000
Phenanthrene	40,000	3,000
Anthracene	8,200	<1,000
Acenaphthene	8,000	3,000
1,1'-Biphenyl	1,800	<1,000
Fluorene	1,700	<1,000
Total	86,700	93,000
Type B Tars		
Pyrene	50,000	2,000
Fluoranthene	31,000	1,000
Benzo[a]pyrene	12,000	<1,000
Benzo[e]pyrene	9,400	<1,000
Chrysene	8,300	<1,000
Benzo[b]fluoranthene	8,300	<1,000
Benzo[g,h,i]perylene	8,000	<1,000
Indeno[1,2,3-cd]pyrene	5,500	<1,000
Benzo[a]anthracene	5,000	<1,000
2,3-Dihydrofluoranthene	5,000	<1,000
1,2-Benzoperylene	3,000	<1,000
4H-Cyclopenta[def]phenanthrene	2,900	<1,000
Benzo[k]fluoranthene	2,600	<1,000
2-Phenylnaphthalene	2,300	<1,000
Total	153,300	3,000

D. Fuel Composition

REII engaged EFT and California State University – Sacramento (CSU-S) Chemistry Dept. (Professor Roy Dixon) to characterize the synthetic diesel and reformulated gasoline blendstock samples from the IBR runs. Details on these analytical procedures are provided in this section.

1. Synthetic Diesel Fuel

The constituents were identified and quantified using GC and GC/MS. Standards consisting of mixtures of C_6 to C_{44} hydrocarbons were used to identify and quantify the alkanes. The alkenes and hydroxy-alkanes were quantified using standard mixtures of these components. Standards for benzene, toluene and naphthalene were also prepared. The standards were diluted in a mixture of CH_2Cl_2 and hexane with the addition of 1-cyclopentane (the internal standard).

All of the major peaks in the diesel samples were identified. The branched alkanes and branched alkenes, which eluted before the linear 1-alkene (alpha-alkenes) and linear alkane peaks, were relatively small. The mass spectra of the linear alkanes gave a major peak for the loss of an ethyl group. Some 2-alkene standards were used to help determine if there were any beta or gamma olefins present. It was found that very minor quantities of these olefins were present.

A number of samples were analyzed multiple times to determine the precision of the method.

Figure XIIID.1 illustrates the density of the fuel produced from the IBR plant. As described earlier, the reformulated gasoline blendstock and synthetic diesel fuel comprises this fuel mixture.
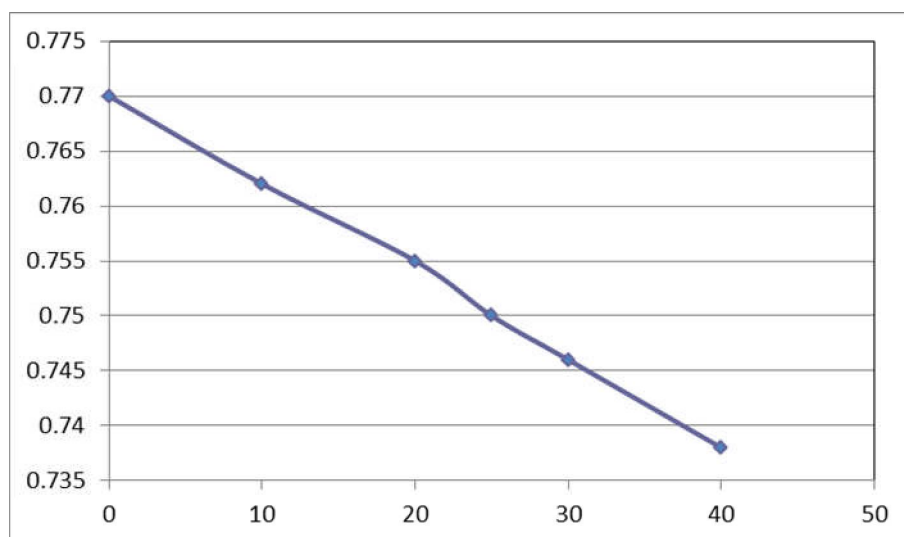
Figure XIIID.1: Fuel Density as a Function of Temp (°C)

E. Wax Composition

The wax samples were dissolved in decane, 1-dodecene was added as an internal standard and GC was used to characterize the samples. Figure XIIIE.1 shows the distribution of normal and branched (iso) alkanes in a typical wax sample collected from the IBR plant.
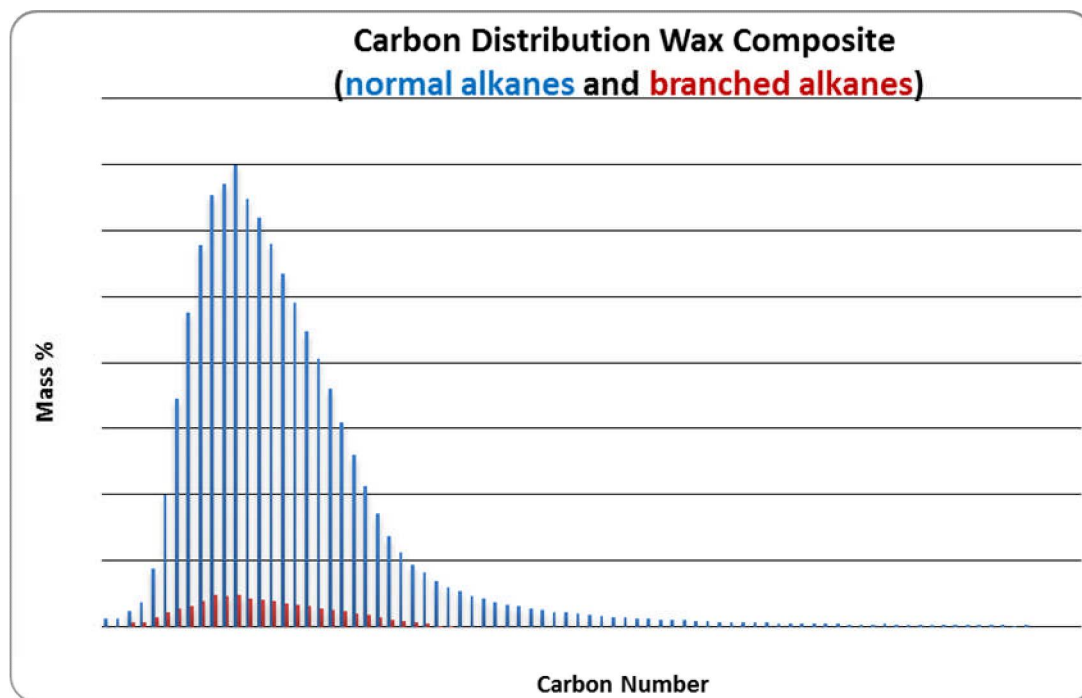
Figure XIIIE.1: Typcial Distribution of Hydrocarbons in the Wax from the IBR Plant

F. Composition of Plant Water Effluents

The two types of water effluents from the plant include the scrubber water and water produced from fuel production.

1. Scrubber Water

The wastewater and wastewater solids from the TCC scrubber system was characterized by the Jones and Henry laboratory utilizing standard ASTM procedures. An example of the results from Test Run #17 is provided in Table XIIIF.1

Table XIIIF.1: Characterization of the Scrubber
Water from Test Run #17

Measurement	Results
pH	6.24
Conductivity (micro-ohms/mL)	1130
Alkalinity as CaCO3	660 ppm
Total Organic Carbon	313 ppm
Nitrogen, Nitrate and Nitrite	Not detected
Nitrogen (ammonia)	73.2 ppm
Suspended Solids	540 ppm
Phenols	3.50 ppm
Sulfide	0.42 ppm
Sulfate	Not detected

2. Fuel Production Water

The organic constituents in the water produced from the catalytic reaction of the syngas was characterized by Roy Dixon, a Chemistry Professor at California State University – Sacramento, using two methods. An internal standard, 2-pentanone, was used for the quantitative analysis.

- Solid-phase micro-extraction (SPME) followed by GC analysis
- Methylene chloride extraction followed by GC analysis

Table XIIIF.2 summarizes the concentration of organic constituents in the fuel production water produced from the IBR plant using the MeOH/CO$_2$ feedstock (Test Run #16) and wood feedstock (Test Run #17).

Table XIIIF.2: The Concentration of Organic Constituents in the
Fuel Production Water for IBR Runs #16 and #17 (*1.0 mg/mL = 0.10%*)

Compound	Concentration (mg/mL)	
	MeOH/CO$_2$ Feedstock (Run #16)	Wood Feedstock (Run #17)
Ethanol	4.89	5.04
Propanol	1.97	1.93
Benzene	0.093	0.88
Butanol	1.98	2.53
Pentanol	1.08	1.38
Hexanol	0.31	0.29
Heptanol	0.11	0.06
Total	10.43	12.11

As expected, the concentrations of the $C_1 - C_7$ hydroxy-alkanes were similar (within experimental error) in the fuel production water generated from the MeOH/CO$_2$ and wood feedstocks. However, about 10 times more benzene was found in the wood feedstock sample than the MeOH/CO$_2$ sample since the wood feedstock produces benzene in the syngas, which is eluted unreacted through the catalytic reactors and condensed with the reformulated gasoline blendstock. Since the MeOH/CO$_2$ feedstock doesn't produce any benzene, the small quantity of benzene found in the Test Run #16 sample is considered a background concentration.

G. Life Cycle Assessments

1. Methodology

The Argonne GREET model (Version 2014) was used to conduct the Life Cycle Analysis (LCA) of the synthetic diesel fuel produced in the 2015-17 time frames for the commercial scale biomass to liquid fuels (BTL) and hybrid natural gas and biomass to liquid fuel (GBTL) plants. The material and energy inputs and outputs for the 4.4 million gallon/year BTL plant and 9.05 million gallon/year GBTL plant are provided in Figures XIIIG.1 and XIIIG.2, respectively.

This study was carried out in collaboration with the National Renewable Energy Lab (NREL) and Argonne National Lab (ANL) to predict the life cycle GHG emissions of diesel fuel and reformulated gasoline blendstock derived from biomass-to-liquids (BTL) conversion pathways and natural gas/biomass-to-liquids (GBTL) hybrid pathways. The modeling boundary for this study is Well-to-Wheels (WTW). The GREET model (Argonne National Lab, 2013) was modified and used to quantify and account for GHG emissions along the entire supply chain. The life cycle assessment (LCA) results of this analysis only consider greenhouse gas (GHG) emissions,

expressed as CO_2 equivalents (CO_{2e}) using the Intergovernmental Panel on Change (IPCC) 2007 100-yr global warming potentials (Fischer, 2007; Biorecro, 2010). The functional unit is g CO_{2e} per MJ of fuel. Note that BTL and GBTL plants produce both diesel fuel and reformulated gasoline blendstock, but they are combined and referred to as a single-"fuel" product for simplicity. Consequently, the current GHG emissions burdens are allocated among liquid output products (i.e., diesel and gasoline) according to their energy output shares of the plant. This is accomplished by applying the direct energy allocation method. Energy outputs are determined using the corresponding lower heating values (LHV).

2. BTL Plant

The commercial scale biomass to liquids (BTL) production plant has been designed to produce 4.49 million gallons/year of "drop-in" fuels from 240 daft/day of feedstock. Figure XIIIG.1 summarizes the life cycle inputs and outputs for this BTL plant. The energy efficiency of this BTL plant is 53.9% (HHV), the carbon conversion efficiency for biomass to fuel is 39.7% and 53.2% for biomass to fuel and biochar.
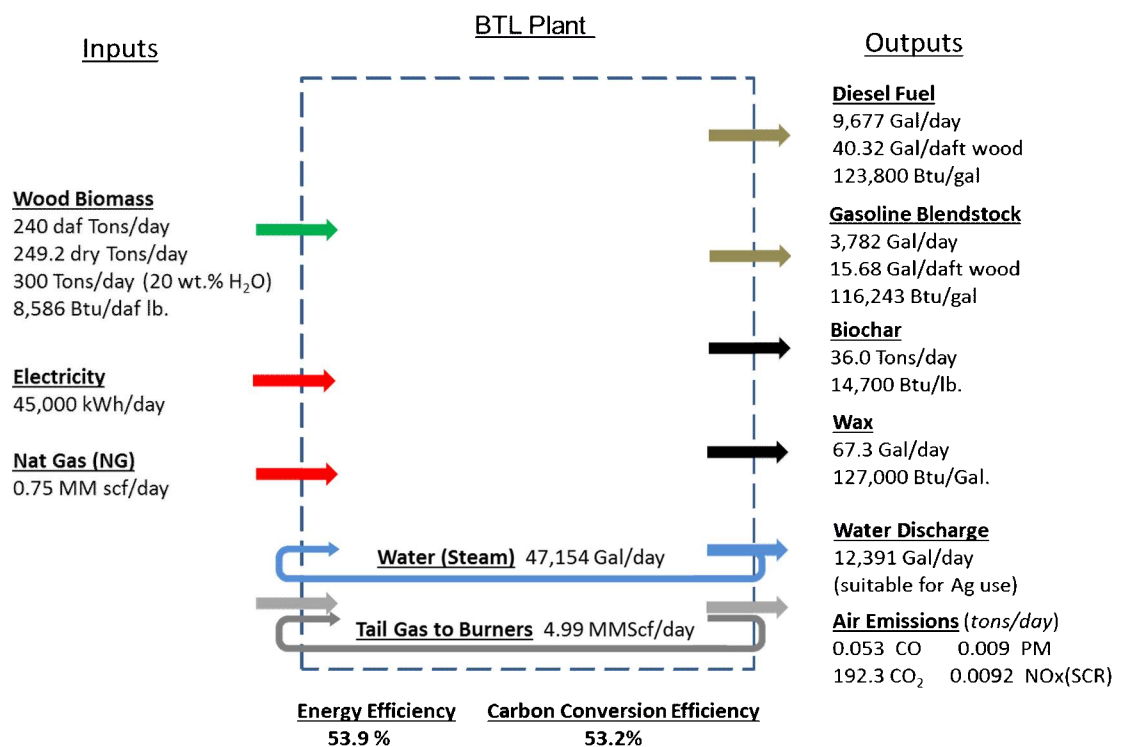
Figure XIIIG.1: LCA Inputs and Outputs for the 240 daft/day BTL Commercial Plant

Table XIIIG.1 summarizes the life cycle GHG emission results. The GHG LCA calculations show a 153-162% reduction in total greenhouse gas emissions (GHGs) for

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the conversion of wood to fuels and 152% for the conversion of rice hulls to fuels compared to the baseline petroleum diesel fuel case.

Table XIIIG.1: Life Cycle GHG Emission Results for Biomass to Liquid Fuel Production (g CO_2/MJ) for the 240 daft BTL Plant

Scenario	Life Cycle GHG Emissions (g CO_2/MJ)						% GHG Reduction (compared to Diesel)
	Biogenic CO_2 in Fuel	Biochar Use	Feedstock Production	Fuel Production	Fuel Transport & Use	Well to Wheels	
Oil to Gasoline	0.0	0.0	8.1	12.7	73.3	94.1	--
Oil to Diesel	0.0	0.0	8.1	12.5	75.0	95.6	0.0
Wood to Fuel (a)	-78.4	-46.7	25.3	-31.2	80.2	-50.8	-153
Wood to Fuel (b)	-78.4	-46.7	17.2	-31.2	79.8	-59.2	-162
Rice Hulls to Fuel	-79.1	-46.4	12.0	-17.3	80.9	-49.9	-152

Figure XIIIG.2 summarizes the life cycle inputs and outputs for this GBTL plant. The commercial scale natural gas and biomass to liquids (GBTL) production plant has been designed to produce 9.05 million gallons/year of "drop-in" fuels from 4.0 MM scf/day of natural gas and 240 daft/day of biomass. These GBTL plants will be located at sites where unprocessed or partially processed natural gas from relatively short pipelines from the well head will be utilized. In some cases, these plants may use natural gas that would otherwise be flared from a well head (DOE/NETL, 2013).

The "drop-in" fuel output from this plant includes 19,152 gallons/day of synthetic diesel fuel and 6,948 gallons/day of reformulated gasoline blendstock. The side products include biochar (36.0 tons/day) and benzene (1,159 gallons/day).
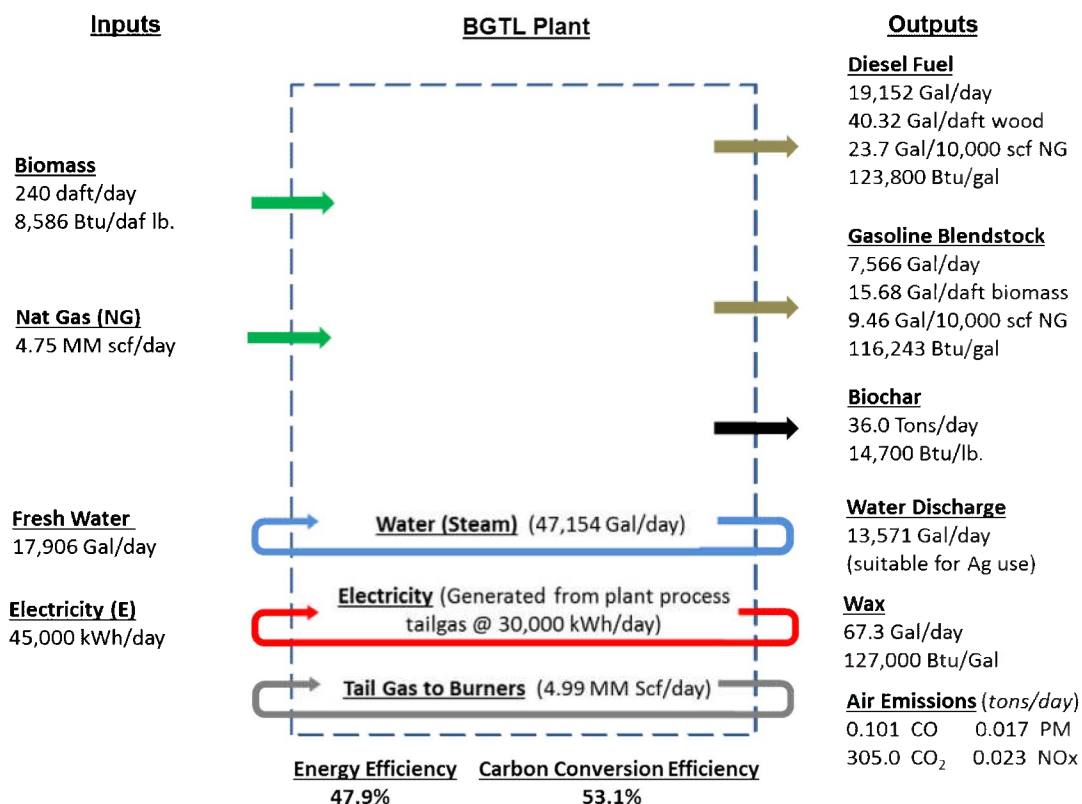
Figure XIIIG.2: LCA Inputs and Outputs for the GBTL Commercial Plant

Table XIIIG.2 summarizes the life cycle GHG emission and reduction results for the GBTL plant. The GHG LCA calculations show a 49% reduction in GHGs for the Well to Wheels co-conversion of natural gas and wood to fuels and a 45% reduction in GHGs for the Well to Wheels co-conversion of natural gas and rice hulls to fuels.

Table XIIIG.2: Life Cycle GHG Emission and Reduction Results for GBTL

	Life Cycle GHG Emissions (g CO_2/MJ)							% GHG Reduction (compared to Diesel)
	Biogenic CO_2 in Fuel	Biochar Use	Feedstock Produce	Fuel Produce	Fuel Transport & Use	Improved Fuel* Economy	Well to Wheels	
Oil to Gasoline	0.0	0.0	8.1	12.7	73.3	--	94.1	--
Oil to Diesel	0.0	0.0	8.1	12.5	75.0	--	95.6	0.0 (*baseline*)
GBTL – NG* & Wood to Fuel	-40.4	-23.6	19.6	16.4	78.2	-3.5	46.7	-48.9
GBTL – NG* & Rice Hulls to Fuel	-40.7	-23.4	16.1	23.2	78.8	-3.5	50.5	-45.1

*Since the synthetic diesel fuel has been demonstrated to improve fuel economy by 3.5% compared to petroleum derived fuel, the % GHG reduction was increased by 3.5%

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XV. Glossary of Terms and Acronyms

A. Definition of Terms

#1 Diesel Fuel (Ultra Low Sulfur) – A light distillate fuel oil that has distillation temperatures of 550 degrees Fahrenheit at the 90-percent point, meets the specifications defined in ASTM Specification D 975 and has a sulfur level no higher than 15 ppm. It is used in high-speed diesel engines generally operated under frequent speed and load changes, such as those in city buses and similar vehicles (EIA, 2014).

#2 Diesel Fuel (Ultra Low Sulfur) – A fuel that has distillation temperatures of 500 degrees Fahrenheit at the 10-percent recovery point and 640 degrees Fahrenheit at the 90-percent recovery point, meets the specifications defined in ASTM Specification D 975 and has a sulfur level no higher than 15 ppm. It is used in high-speed diesel engines that are generally operated under uniform speed and load conditions, such as those in railroad locomotives, trucks, and automobiles (EIA, 2014).

Cold Filter Plugging Point (CFPP) – This is the temperature under a standard set of conditions (ASTM D6371) at which the filter plugs. A sample is cooled and tested at intervals of 1°C until the wax crystals precipitate out of solution and are sufficient to slow or stop the flow of fuel through the filter (ASTM, 2014).

Cloud Point (CP) – Cloud Point defines the temperature at which a cloud or haze of wax crystals appears in the fuel under prescribed test conditions which generally relates to the temperature at which the wax crystals begin to precipitate from the fuel (ASTM, 2014; Wikipedia, 2014).

Heavy-Duty Diesel (HDD) Engine – A heavy-duty diesel engine is a diesel engine that is used in a vehicle, other than a diesel bus, that has a gross vehicle weight exceeding 8,500 pounds and is designated primarily for transporting persons or property (www.epagov) 2014.

HFRR Lubricity Test – The high-frequency reciprocating rig (HFRR) test was developed to determine the lubricity of diesel fuels and is a standard ASTM test (D6079). This test is important since diesel fuel injection equipment has some reliance on lubricating properties of the diesel fuel. A shortened life of engine components, such as diesel fuel injection pumps and injectors, has sometimes been ascribed to lack of lubricity in a diesel fuel. The trend of HFRR test results to diesel injection system pump component distress due to wear has been demonstrated in pump rig tests for some fuel/hardware combinations where boundary lubrication is believed to be a factor in the operation of the component.

The wear scar generated in the HFRR test is sensitive to contamination of the fluids and test materials, the temperature of the test fuel, and the ambient relative humidity. Lubricity evaluations are also sensitive to trace contaminants acquired during test fuel sampling and storage. Fuels with good lubricity have HFRR results below about 475 and fuels with

exceptional lubricity have HFRR results below about 400. Most diesel fuels purchased from fueling stations have HFRR's in the 475-550 range.

Pour Point (PP) – Pour Point is the lowest temperature at which a fuel is capable of flowing under very low forces. It is generally observed that the Cloud Point temperature of a fuel is higher than it Pour Point by several degrees (ASTM, 2014; Wikipedia, 2014).

Reformulated Gasoline Blendstock (RGB) – The term "Reformulated Gasoline Blendstock (RGB) includes fuels blended with gasoline to improve combustion and reduce emissions. These fuel blendstocks typically contain oxygenates. RGB excludes Reformulated Blendstock for Oxygenate Blending (RBOB).

Syngas – Syngas, or synthesis gas, is a fuel gas mixture consisting primarily of hydrogen and carbon monoxide, very often with some CO_2 and methane (Wikipedia, 2014).

B. Acronyms

AA	Atomic Absorption spectrometry
AMU	Atomic Mass Unit
Ag	Agriculture
Ar	Argon
ARRA	American Recovery and Reinvestment Act
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
BDT	Bone Dry Ton
BOD	Biochemical Oxygen Demand
BTL	Biomass to Liquids
BTU	British Thermal Units
BV	Bureau Veritas
°C	degrees Centigrade
CDD	U.S. Center for Disease Control
CFPP	Cold Filter Plug Point
CFR	Code of Federal Regulations
CH$_4$	Methane
CHP	Combined Heat and Power System
CO	Carbon Monoxide
CO$_2$	Carbon Dioxide
CP	Cloud Point
CPC	Condensation Particle Counter
DAF	Dry ash free
DCA	Distributed Control System
DDW	Deionized Distilled Water
DNPH	2, 4 - Dinitrophenylhydrazine
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DR	Dilution Ratio
DRI	Desert Research Institute
DTPD	Dry Tons per Day (biomass feed rate: dry, ash free basis)
EC/OC	Elemental Carbon/Organic Carbon
EH&S	Environmental Health & Safety
EIR	External Independent Review
EPA	Environmental Protection Agency
°F	degrees Fahrenheit
FAR	Federal Acquisition Regulation
FBP	Final Boiling Point
FID	Flame Ionization Detector
FMEA	Failure Modes Effects Analysis
F-T	Fischer-Tropsch
Cu.ft	Cubic Feet
FS$_C$	Carbon in Feedstock
GAL	Gallon

GBTL Natural Gas Biomass to Liquids
GC Gas Chromatography
GC-FID Gas Chromatography-Flame Ionization Detector
GC-MS Gas Chromatography-Mass Spectrometry
GD Grace Davison
GHG Greenhouse Gas
HAZOP Hazard and Operability Analysis
H₂ Hydrogen gas
H₂O₂ Hydrogen Peroxide
H₂S Hydrogen Sulfide
HC Hydrocarbon
HCN Hydrogen Cyanide
HHV Higher Heating Value (Btu/scf for syngas)
HFRR High-Frequency Reciprocating Rig
HPLC High Performance Liquid Chromatography
hr hour(s)
IBEP Integrated Biofuels and Energy Production System
IBP Initial Boiling Point
IBR Integrated Bio-Refinery
IC Ion Chromatography
ICP/MS Inductively coupled plasma mass spectrometry
IE Independent Engineer
IEC International Electro-technical Commission
IPA Independent Project Analysis
IPCC Intergovernmental Panel on Change
Kg kilograms
Lb pounds
LCA Life Cycle Assessment
LFP Liquid Fuel Production (process unit)
MB megabyte
μg/m³ Micrograms per cubic meter
Mj/kg mega joules per kilogram
m²/g square meters per gram
MDL Measurement Detection Limit
MeOH Methanol
MM Million
Ml milliliter
MSDS Material Safety Data Sheet
MTTI Midwest Terminals of Toledo International
MW Molecular Weight
N₂ Nitrogen gas
NaOH Sodium Hydroxide
NDIR Non-dispersive Infrared
NETL National Energy Technology Laboratory
NG Natural Gas
NH₃ Ammonia

NIST National Institute of Standards and Testing
NMOC Non-Methane Organic Compound
NO$_X$ Nitrogen Oxides
NREL National Renewable Energy Laboratory
O&M Operations and Maintenance
OC/EC Organic Carbon/Elemental Carbon
OH Ohio
OMB Office of Management and Budget
OPS Optical Particle Sizer
OSHA Occupational Safety and Health Administration
PDU Process Development Unit
PID Photo-Ionization Detector
PID Proportional-Integral-Derivative
P&ID Piping and Instrumentation Drawing
PFD Process Flow Diagram
PHM pH Matter
PLC Programmable Logic Controller
PM Particulate Matter
PM2.5 PM with aerodynamic diameter less than 2.5 μm
PP Pour Point
ppb parts per billion
PPE Personal Protective Equipment
ppm parts per million
ppbv parts per billion by volume
ppm parts per million
ppmv parts per million by volume
PSI Pounds per Square Inch (pressure measurement)
PSIG Pounds per Square Inch Gage (pressure measurement)
PTIO Permit-to-Install and Operate (PTIO)
REII Renewable Energy Institute International
RFS2 Renewable Fuels Standard 2
RGB Reformulated Gasoline Blendstock
RLB Red Lion Bio-Energy
RMP Risk Mitigation Plan
ROI Return on Investment
SCADA Supervisory Control and Data Acquisition
Scf Standard cubic feet (at 70°F, 14.7 psig)
SO$_2$ Sulfur Dioxide
ST Solar Turbines
SRM Standard Reference Material
SVOC Semi-Volatile Organic Compounds
T Temperature
TEA Techno-economic Analysis
TCC Thermochemical Conversion System
TCD Thermal Conductivity Detector
TDS Thermal Desorption System

TMBMS Transportable Molecular Beam Mass Spectrometer
TOC Total Organic Carbon
TOR Thermal Optical Reflectance
TOT Thermal Optical Transmittance
TPD tons per day
TPM Total Particulate Matter
UHP Ultra-High Purity
UT University of Toledo
VE Value Engineering
VOC Volatile Organic Compounds
Vol% Percent by volume
WP WorleyParsons
Wt % Percent by weight
WtW Well-to-Wheels
XRF X-Ray Fluorescence spectrometry