Final Report

Project Title: ***Recovery Act: ClearFuels-Rentech Integrated Biorefinery Pilot Project for Diesel and Jet Fuel Production by Thermochemical Conversion of Wood Waste.***

Award Number: DE-EE0002871

Recipient: ClearFuels Technology Inc.
Project Location: 4150 E 60th Avenue, Commerce City, CO 80022

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SECTION 1 INTRODUCTION

The DOE grant was awarded to ClearFuels Technology in December 2009. In June 2009, Rentech acquired 25% interest in ClearFuels Technology and in May 2011 acquired more than 90% of ClearFuels Technology.

1.A Rentech Company Overview

Rentech was founded in 1981 by two engineers at the Solar Energy Research Institute (SERI) that is now known as the National Renewable Energy Laboratory. For much of its history, Rentech was a developer of Fischer-Tropsch technology. The company headquarters are in Los Angeles, CA but with over 35 locations throughout the United States, Canada, Chile, and Uruguay. The company's main business lines include the wood fiber business, production of agricultural fertilizer, and energy technologies. The company has over 750 employees and is publicly traded under the RTK ticker symbol.

1.B ClearFuels Technology Overview

ClearFuels Technology Inc. was founded in 2005. Its founders had evaluated commercially viable cellulosic biofuels conversion technologies since the 1990's under the name of Worldwide Energy. From inception, ClearFuels' core focus has been on the deployment of a flexible thermochemical conversion technology platform to support commercial-scale production of advanced biofuels. After Rentech's review of over 200 different thermochemical conversion technologies, ClearFuels gasification and Silvagas Gasification were selected to be integrated with Rentech's Fischer-Tropsch technology. Rentech acquired Silvagas Corporation for biomass gasification and a 25% interest in ClearFuels Technology in 2009.

Rentech and ClearFuels started working on a project in 2008 to place a pilot demo-scale ClearFuels unit at Rentech's demonstration facility in Commerce City, Colorado. With the passage of ARRA in 2009, ClearFuels and Rentech decided to collaborate on a grant application to the DOE to aid in funding that pilot demonstration integrated with Rentech's gas-to-liquids product demonstration unit (PDU) in Colorado.

1.C Key Team Members Who Contributed to this Final Report

Joshua Pearson – Principal Investigator, Manager of Biorefinery Integration, Rentech
Harold Wright – Senior Vice President and Chief Technology Officer, Rentech
Eric Darmstaedter – President, ClearFuels Technology
Randy Blevins – Director of Engineering, ClearFuels Technology
Mark Robertson – Senior Lead Process Engineer, Rentech
Weibin Jiang – Senior Principal Engineer, Rentech
Mark Still – Process Development Engineer, Rentech
Randy Shearer – Manager Lab Services, Rentech
Josefa Griffith – Senior Analytical Chemist, Rentech
Ernesto Bustamante – Process Development Engineer, Rentech
Matt Greer – Principal Operation Engineer, Rentech
Ray Huang – Manager, Iron Fischer-Tropsch Technology, Rentech
Ute Duvenhage – Data Statistician, Rentech
Eric Elrod – Lead Process Engineer, Rentech

Eric Bemiss – Project Controls Engineer, Rentech
Mark Anselmo – Construction Manager, Rentech
Nick Cozzi – Senior Mechanical Engineer, Rentech
Phil Weathers – Director of Operations, Rentech
Perry Herrick – Operations Manager, Rentech
Rentech Energy Technology Center (RETC) – Analytical and Lab Services
RETC – Operations & Maintenance

1.D Project Partners

National Renewable Energy Laboratory (NREL) for Tar Measurement (TMBMS)
URS for Engineering and Construction Management
Linde HydroChem for design and fabrication of ClearFuels High Efficiency Hydro-Thermal Reformer (HEHTR)

SECTION 2 EXECUTIVE SUMMARY

2.A Overview

ClearFuels Technology and Rentech, Inc. were awarded an ARRA-funded DOE project to integrate ClearFuels' novel, flexible High Efficiency Hydro-Thermal Reformer (HEHTR) technology with Rentech's existing natural gas to liquids Fischer-Tropsch Demonstration Unit for the conversion of high impact woody biomass to renewable diesel as a primary product. The same facility was used to prove the conversion of bagasse and woody biomass/bagasse mixtures to direct substitute renewable diesel and renewable jet fuel (SPK).

The project was awarded to ClearFuels Technology in December 2009. Construction of the additional equipment at Rentech's site was completed in October 2011. Commissioning of the new equipment with the exception of a booster syngas compressor was completed in December 2011 and the booster compressor was commissioned in September 2012.

Operations of the integrated facility and the project were completed in February 2013 with over 2200 hours of HEHTR operations and over 1300 hours of integrated fuels production on various wood and bagasse feedstocks. Data analysis and decommissioning of the facility was completed in May 2013.

On February 28, 2013, Rentech announced the closing of the Commerce City, CO facility and the cessation of all R&D activities. The company will not be pursuing the commercialization of the technology developed with this grant. The company is seeking partners or buyers for its biomass gasification and Fischer-Tropsch technologies. The company is also seeking the most economical disposition for the equipment and site in Commerce City and has been working with the Department of Energy on disposition of the assets acquired as part of this grant.

2.B How the Research Adds to the Understanding of the Area Investigated

ClearFuels and Rentech successfully completed the construction, scale-up, operation and integration of ClearFuels' HEHTR technology at Rentech's site in Commerce City, CO. However, the operation portion of the project was performed at a lower-than-name plate capacity. This project discovered the scale-up issues related to the larger unit, and as a result acquired a deeper understanding of gasification kinetics. At the close of the project, on-spec diesel fuel was created from stream of syngas derived from woody biomass.

There were several steps in the process that prevented from running at nameplate capacity.

- Biomass Grinding - The grinder was not able to process the wet biomass at its intended size distribution. To fix this the unit was fitted with screens containing larger openings to help prevent plugging. The feedstock was also changed to a wood chip from a hog fuel grind.
- Surge Hopper - The feed surge hopper had multiple bridging issues. To fix the hopper, pneumatic assists were installed to keep the biomass moving.
- Rotary Valve – The rotary valve did not create an adequate pressure boundary, allowing steam to enter the dry feed handling system. This plugged (during cold weather, froze) the feed system. Various devices were added to help the issue; however, it continued to be an issue through the close of the project.

- Steam Mixing Vessel – There were concerns that the steam and biomass were not mixing and due to the geometry possibly forcing some of the steam into the feeding system. The Steam Mixing Vessel was modeled, and redesigned. There was some benefit, but it did not completely solve the pressure boundary issue with the Rotary Valve.
- Gasifier Feed Lines – The feed line going into the gasifier was split into two streams. There were uneven flow issues as well as plugging, so the line was redesigned with more emphasis on symmetry which helped the flow issues.
- Gasifier Heat Recovery Boiler – The waste heat boiler would foul on the order of hours during initial operations. A water quench system was installed to cool the syngas, and the waste heat boiler was not put back in service for the duration of the project. It was discovered that a modification of the gasifier operating conditions could produce a syngas with a more favorable tar composition.
- Syngas Cleanup – During start-up and initial operations the tar in the syngas were overloading the primary syngas cleanup system; therefore, multiple changes were made to help relieve the load on the units. A solvent scrubbing system was installed, additional filtration steps were added, and tighter control of unit temperatures was taken to control premature tar condensation.

2.C Technical Effectiveness and Economic Feasibility of the Methods or Techniques Investigated or Demonstrated

A notional 1000 DTPD facility was designed and a heat and material balance was generated for the facility. Using Rentech's cost estimating tools we determined that the approximate cost of a planned biomass-to-liquids facility in Northern Ontario would be over $700 million. The project after-tax levered internal rate of return was estimated at 4.1% where the real diesel price was assumed to be $3.00/gallon. For a 10% after-tax IRR of 10%, a diesel price of $5.16/gallon is necessary.

2.D How the Project is Otherwise of Benefit to the Public

Rentech and ClearFuels demonstrated that renewable drop-in diesel fuel can be produced from woody biomass. The project provides the public some key lessons learned to increase the effectiveness of future projects of this nature. The project ran into numerous feedstock handling issues and the scale-up from small pilot-scale to integrated operation provides some key learning for future project teams.

SECTION 3 PROJECT GOALS, OBJECTIVES AND ACCOMPLISHMENTS

3.A DOE Objectives

The objectives are in line with those of the America Recovery and Reinvestment Act of 2009 (ARRA) and US Department of Energy (DOE) office of Energy Efficiency and Renewable Energy (EERE) for deliberate successful proof of novel advanced biofuels technologies followed by a rapid commercial deployment. To support DOE's goals, it is expected that the pilot-scale projects proposed will be operational within three to four years after applicants are selected. For Topic Area 1, biorefinery technologies and systems are sought that have the capability to proceed rapidly through demonstration. It is expected that the successfully completed projects under this FOA will lead to commercialization after further development at the demonstration stage.

3.B Project Objectives and Targets from Application

Operate the HEHTR to convert biomass to syngas (BTG) and steam at an efficiency based on BTU's in and out at over 80% with a target of 87%.

> ***Accomplishment***: DID NOT ACCOMPLISH. Overall thermal conversion of biomass to syngas was 59% on a biomass to syngas basis.

Control the HEHTR to meet a 1:1 hydrogen to carbon monoxide syngas ratio as measured by National Renewable Energy Lab (NREL) mobile gas laboratory and RTK PDU Facility online analyzers.

> ***Accomplishment:*** ACCOMPLISHED. The project was able to make on-spec syngas for downstream operations.

Vary the operation of the HEHTR to prove flexibility of operation from 0.9:1 hydrogen to carbon monoxide ratio to at least 2:1 hydrogen to carbon monoxide ratio, with an upper target of 3:1. Show control at +/- 0.2:1 increments to match RTK FT and UOP upgrader requirements.

> ***Accomplishment:*** ACCOMPLISHED. Demonstrated hydrogen to CO ratios in the syngas from approximately 1:1 to almost 3:1.

Optimize operating parameters including temperature, pressure, steam flow, and biomass flow, to produce syngas of the target ratios directly from the HEHTR before gas cleanup with total tar contaminants under 50 parts per million (ppm) with a target of less than 25 ppm.

> ***Accomplishment:*** ACCOMPLISHED. Demonstrated the ability to get total tar contaminants to less than a few ppm after syngas conditioning suitable for use in an FT reactor. This required the addition of new project scope, i.e. solvent scrubber and filtration units.

Operate all gas cleanup systems at the integrated CF-RTK IBR to ensure proper removal of all trace contaminants at the appropriate gas clean-up stages in the ppm and parts ppb (parts per billion) range, that may affect the RTK FT process, as measured by NREL mobile gas laboratory at each gas cleanup stage.

> ***Accomplishment:*** ACCOMPLISHED.

Operate the integrated HEHTR and RTK FT process continuously for production runs of renewable diesel and jet fuel for 30 days using wood waste, and an additional 10 days each using bagasse, and mixed feedstock.

Accomplishment: PARTIALLY ACCOMPLISHED. The project accomplished the woody biomass goals but bagasse and mixtures were not operated for the full 10 days each.

Meet ASTM specifications for diesel and jet fuel produced from the CF-RTK IBR as confirmed by RTK, and validated by Hawaii Natural Energy Institute (HNEI) and Hawaiian Electric

Accomplishment: PARTIALLY ACCOMPLISHED. Produced on-spec diesel but did not produce jet fuel during the campaigns. Previous, non-project related work at site demonstrated jet fuel (SPK) production and commercial test flight. HNEI and Hawaiian Electric were not involved in the evaluation.

Complete the CF-RTK IBR pilot project on time and on budget as presented in this proposal and provide sufficient data to validate scale-up designs for the first commercial facility.

Accomplishment: PARTIALLY ACCOMPLISHED. Completed engineering, procurement, and construction of the facility on budget and on time. The commissioning and operations portion of the project were not completed on time or on budget.

3.C Critical Success Factors from Application

Critical success factors for being able to meet the goals and objectives are as follows:

1. Successful on-time engineering, procurement, construction, integration, and mechanical startup of the CF HEHTR platform technology at the RTK PDU by URS.

   Accomplishment: PARTIALLY ACCOMPLISHED. Completed engineering, procurement, and construction on time. Commissioning and operations were longer than scheduled. Based on initial start-up of the gasifier, we had to add a solvent wash system to the syngas cleanup process. Because of feedstock handling issues, we had to add equipment to keep the feedstock from bridging. All of these EPC items added time to the overall commissioning and start-up time line.

2. Controllable biomass drying and grinding to required moisture ranges and sizes of the wood waste and bagasse feedstocks.

   Accomplishment: ACCOMPLISHED. Unit modification was required, did not deviate significantly from original design. Feedstock specification was tightened, and bagasse was more difficult to dry and grind than woody feedstocks. Further details in lessons learned section.

3. Reliable controlled mixing of biomass and steam through the proprietary biomass/steam mixture system.

   Accomplishment: ACCOMPLISHED. Unit modification was required, did not deviate significantly from original design. Re-design focused primarily on nozzle locations on vessel. The system needed to be cleaned periodically. Further details in lessons learned section.

4. Accurate measurement and control of heat recovery systems including syngas and fluegas heat recovery steam generators (HRSGs) for use in dryer and steam transport processes.

   Accomplishment: PARTIALLY ACCOMPLISHED. Syngas heat recovery was not demonstrated. The waste heat boiler design was incapable of handling the tar and char in the syngas during initial operations, a quench system was installed to cool the syngas.

5. Syngas cleanup equipment must correctly remove the contaminants in the appropriate order so trace compounds do not interfere with subsequent gas cleanup processes.

   Accomplishment: ACCOMPLISHED. Naphthalene reduction prior to the compressor still caused problems with the air cooler on the booster compressor.

6. Syngas online measurement of trace syngas contaminants must be accurate to provide measurable data at the ppm and ppb level for appropriate response to vary operations.

   Accomplishment: ACCOMPLISHED.

SECTION 4 PROJECT ACTIVITIES

4.A Schedule Milestone Summary

Table 4-1: Schedule Milestone Summary

Milestone Description	Target	Forecast	Variance
Engineering Completion	6/23/2011	8/5/2011A	30
Procurement Completion	8/18/2011	9/12/2011A	17
Construction Start	4/4/2011	4/4/2011 A	0
Mechanical Completion	9/15/2011	11/08/2011 A	38
Commissioning / Start-up Completion	10/6/2011	2/22/2013 A	460
Data Collection Completion	1/31/2012	3/29/2013	410
Data Analysis & Final Reporting Completion	3/27/2012	6/28/2013	430

4.B EVMS Summary

- CPI is 0.84 PTD
- Cost Variance is $(6,541,035) PTD
- SPI is 0.97 PTD
- Schedule Variance is ($1,031,604) PTD
- EAC Variance is ($6,484,591)

Table 4-2: February Period EVMS Summary

ClearFuels-Rentech Integrated Biorefinery Pilot Project

February Reporting Period EVMS

WBS	Description	Current Budget	Scheduled	Actual	Earned	% Complete	SPI	CPI	Estimate to Complete	Estimate at Completion
1.0	Administration	$878,259	$878,259	$1,108,734	$878,259	100.0%	1.00	0.79	$8,400	$1,117,134
2.0	Project Management	$212,162	$212,162	$112,506	$212,162	100.0%	1.00	1.89	$0	$112,506
3.0	Project Planning	$591,165	$591,165	$514,931	$591,165	100.0%	1.00	1.15	$4,200	$519,131
4.0	OSBL	$3,465,706	$3,465,706	$7,149,772	$3,465,706	100.0%	1.00	0.48	$73,645	$7,223,417
5.0	Engineering	$6,867,606	$6,867,606	$6,836,695	$6,867,605	100.0%	1.00	1.00	$17,681	$6,854,376
6.0	Procurement	$7,957,198	$7,957,198	$8,031,958	$7,957,198	100.0%	1.00	0.99	$228,618	$8,260,576
7.0	Construction	$7,634,750	$7,634,750	$7,635,284	$7,634,750	100.0%	1.00	1.00	$182,508	$7,817,792
8.0	Startup & Operations	$6,672,535	$6,672,535	$9,665,627	$6,672,535	100.0%	1.00	0.69	$0	$9,665,627
9.0	Data Collection	$942,338	$942,338	$275,295	$471,169	50.0%	0.50	1.71	$335,440	$610,735
10.0	Interim Data Evaluation & Validation	$392,214	$392,214	$0	$39,221	10.0%	0.00	0.00	$84,960	$84,960
11.0	Final Report	$203,441	$203,441	$0	$0	0.0%	0.00	0.00	$35,707	$35,707
12.0	Decommissioning Plan	$4,000	$4,000	$0	$0	0.0%	0.00	0.00	$4,000	$4,000
	Total	$35,821,374	$35,821,374	$41,330,802	$34,789,770	97.1%	0.97	0.84	$975,159	$42,305,961

4.C Change Management Summary

Table 4-3: Change Management Summary

Description	CATEGORY Change Order (CO) Trend Notice (TN) Pending (Blank)	Client Appvd Engineering Cost	Client Appvd Capital Cost	Appvd Sch Impact (Days)	Company Approval Status Approved Cancelled	Client Approval Status Pending Potential Approved Cancelled	Included In EAC Cost	Internal Change Budget Transfer or No Action Approved Change Orders Trend Notices Open issues Comments
		$ 3,311,451	$ 1,199,737					
Subtotal URS Approved Change Orders	CO	$ 3,975,663	$ -	0	Approved	Approved	Y	
Subtotal URS Approved Trend Notices	TN	$ 73,884	$ (477,889)	0			Y	
Subtotal URS Pending Change Orders		$ 13,800	$ -	0				
Subtotal HydroChem Approved Change Orders	CO	$ (248,485)	$ -	0	Approved	Approved	Y	
Subtotal Rentech Approved Change Orders	CO	$ 100,000	$ -	0	Approved	Approved	Y	
Subtotal Rentech Approved Trend Notices	TN	$ (603,411)	$ -	0			Y	
Subtotal Ames Approved Change Orders	CO		$ 1,077,026	0	Approved	Approved	Y	
Subtotal Ames Approved Trend Notices	TN		$ 115,300	0			Y	
Subtotal Ames Pending Change Orders		$ -	$ -	0				
Subtotal Piper Approved Change Orders	CO		$ 485,300	0	Approved	Approved	Y	

4.D Safety

Overall, the project had an excellent safety record. A total of 3 first aid cases were reported and no recordable injuries. There were a number of industrial hygiene issues that we had to set up monitoring programs for including the extra tars produced by the process.

Table 4-4: Safety Statistics for Project

First Aid Case	3
Lost Time	0
Incidents / Near Miss	16
Observations	19

4.E Budget / Spend Curve

Total project: $42,305,961
DOE: $23MM
Rentech: 19.3MM
ARRA Funding -100% of Federal Portion

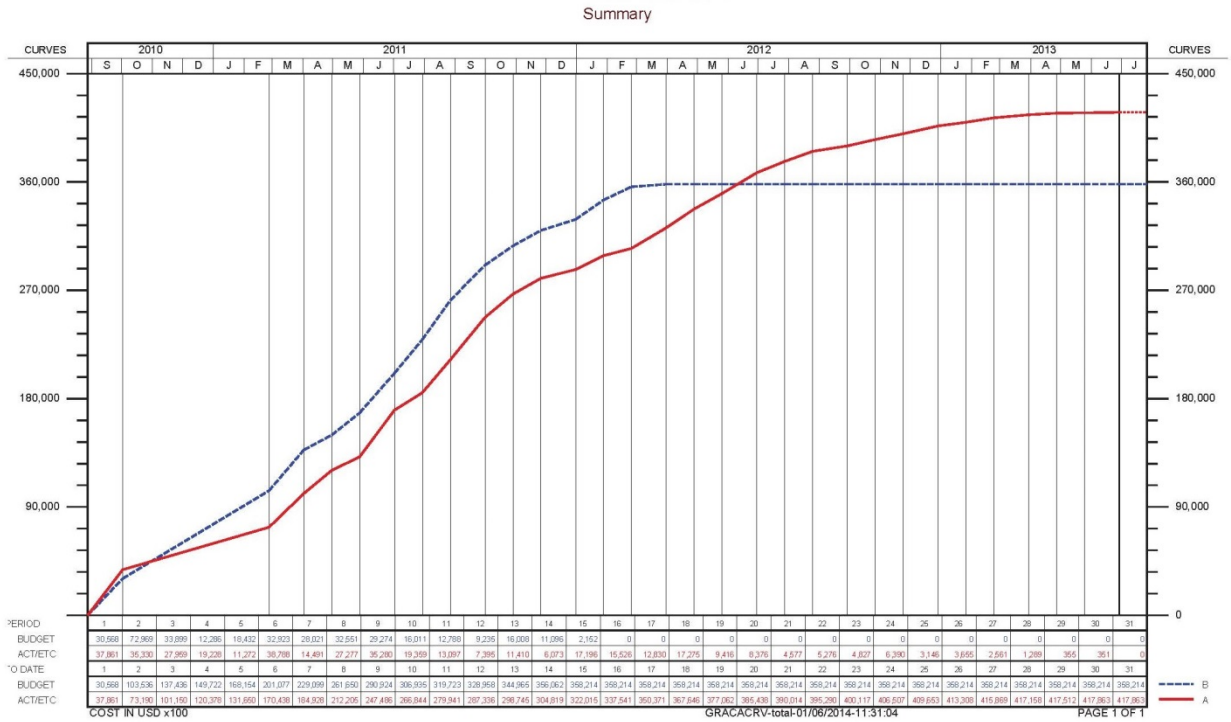


Figure 4-1: ClearFuels-Rentech IBR Spend Curve

4.F Inventions / Patent Applications, Licensing Agreements

No new inventions / patent applications or license agreements resulted from this project.

4.G Approaches Used

G.1 Project Controls, Processes and Procedures

Organization

The Project Controls System uses an integrated hierarchal WBS and Organization Breakdown Structure (OBS) to form the Responsibility Assignment Matrix (RAM) and ensures seamless and complete ownership of the work across all aspects of budgeting, scheduling, cost accumulation and performance reporting that:

- Defines and organizes the authorized project scope in a WBS,
- Identifies which organizations and subcontractors (where applicable) are authorized and responsible for work on the project in an OBS,
- Provides for the integration of the project's planning, scheduling, budgeting, work authorization and cost accumulation process,
- Facilitates the performance measurement of both cost and schedule, and
- Documents the process and organization responsible for the management and control of direct costs.

Planning, Scheduling and Budgeting

Using existing Project Controls processes and procedures to ensure integration of scope, schedule, cost, and technical performance that:

- Establishes an integrated, time-phased schedule/Gantt chart and corresponding budget baseline, at the Control Account level, against which work may be authorized and project performance objectively measured,
- Identifies and sequences authorized work in a resource loaded schedule in a manner that provides visibility of the task interdependencies and critical path of the project,
- Clearly defines project deliverables, milestones, and performance goals,
- Focuses on cost/schedule management and ensures management visibility for work authorization and control of scope, schedule, and cost components,
- Provides timely, valid and traceable baseline performance and trend data,
- Ensures that the budget of the Work Packages and Planning Packages sum to the Control Accounts and WBS structure,
- Identifies Management Reserve and Undistributed Budget, and
- Assesses progress achieved versus progress planned, measured in terms of physical work accomplished.

G.2 Earned Value Management System (EVMS)

The Earned Value Management System (EVMS) project management tool utilizes Gantt charts and resource-based schedules to assess actual cost and schedule versus planned cost and schedule. An invoicing system based on the Code of Accounts is directly linked to the Work Breakdown Structure (WBS) and EVMS. Invoices are based on milestone and/or earned value and generated from the integrated accounting system.

Earned Value is used to evaluate performance for all activities.

1. All Earned Value (EV) methods and techniques include the following characteristics:

- **Stability –** The EV method chosen for a Work Package (WP) will not change after the Work Package is opened, unless approved through formal change control.
- **Objectivity –** For discrete work, completion of an event will be based upon predetermined criteria or a tangible product.
- **Ability to audit –** The procedure and criteria for evaluating physical accomplishment will be auditable.

2. There are three basic methods used for measuring performance. Application of these methods and their various techniques depends on the end product or service to be measured. Objective techniques are used where practicable. Each Work Preformed will utilize one of the following EV methods to track work progress:

- **Discrete Effort –** Discrete tasks are those tasks which are quantifiable to individual work products or predetermined tangible measurement. Techniques utilized for discrete efforts are:
    - **Fixed Formula –** 0/100, 50/50, 25/75 etc.
    - **Units Complete –** physical quantity count.
    - **Milestone –** predetermined percent complete based on internal milestones within the WP.
    - **Percent Complete –** predefined earning methodology based on detailed steps or hours necessary to complete the task.

- **Apportioned Effort –** This method involves the EV for a discrete WP being based upon a defined relationship with related WPs from which progress is measured objectively. For example, Non-Manual Construction Support could be evaluated at 90% of the composite percent complete of all direct construction WPs. The final 10% would be earned when the paperwork closeout at the end of the project is complete (which is generally after the craft is gone).

- **Level of Effort (LOE) –** This method is used for efforts of a general or supportive nature, which does not produce a definite end product. A LOE WP uses only one EV technique – the Budgeted Cost of Work Performed (BCWP) equals the Budgeted Cost of Work Scheduled (BCWS) in each reporting period. LOE tasks are measured through the passage of time rather than through application of a discrete EV technique.

3. Material or subcontract items must utilize an effective performance measurement technique that allows for earned value to be claimed in the same accounting period as actual costs. The earned value techniques will be documented but, in general, material will be earned in the following manner:

- **Engineered Equipment –** Engineered materials receive BCWP and cost for performance measurement reporting purposes when the material is received and accepted, or is based on a verifiable progress payment schedule.
- **Field Materials –** Field materials receive BCWP and cost for performance measurement reporting purposes when the material is withdrawn from stores.
- **Subcontracts –** Subcontracts receive BCWP and cost for performance reporting based on Statement of Work deliverables and using actual invoiced cost plus accrued cost.

G.3 Cost and Schedule Performance Measurement

Cost Performance Index (CPI)

$$CPI = \frac{BCWP}{ACWP}$$

The Cost Performance Index (CPI) gives the efficiency of the utilization of the resources allocated to the project. CPI value above 1 indicates efficiency in utilizing the resources allocated to the project is good. CPI value below 1 indicates efficiency in utilizing the resources allocated to the project is not good.

Schedule Performance Index (SPI)

$$SPI = \frac{BCWP}{BCWS}$$

The Schedule Performance Index (SPI) gives the efficiency of the project team in utilizing the time allocated for the project. SPI value above 1 indicates project team is very efficient in utilizing the time allocated to the project. SPI value below 1 indicates project team is less efficient in utilizing the time allocated to the project.

Cost Variance (CV)

$$CV = BCWP - ACWP$$

The Cost Variance (CV) gives the variance in terms of cost which will indicate how less or more cost has been to complete the work as of date. Positive Cost Variance indicates the project is under budget. Negative Cost Variance indicates the project is over budge

Schedule Variance (SV)

$$SV = BCWP - BCWS$$

The Schedule Variance (SV) gives the variance in terms of cost which will indicate how much cost of the work is yet to be completed as per schedule or how much cost of work has been completed over and

above the scheduled cost. Positive Schedule Variance indicates we are ahead of schedule. Negative Schedule Variance indicates we are behind schedule

Estimate at Completion (EAC) Development

$$\boldsymbol{EAC = ACWP + ETC}$$

The Estimate at Completion (EAC) is a realistic forecast of the final cost of a defined scope of work (lifecycle or contract) when complete or to the end of the fiscal year in the case of fiscal year EACs/spend forecasts. The EAC is calculated as ACWP to date, plus estimate to complete (ETC). The key to preparation of an EAC is accurately forecasting and phasing the ETC for the remaining work scope within the WBS element.

G.4 Variance Management

Variance Analysis

The Project Manager with the support of Project Controls is required to review, analyze, and report on all control accounts with variances exceeding thresholds for current month, cumulative, or at completion. The variance analysis provides the manager a means to communicate scope, schedule, cost, and EAC divergences from their control accounts. Cost and schedule variance explanations are completed each month for control accounts exceeding the variance thresholds.

Variance Analysis Reporting

Control Accounts with cost and schedule variances exceeding thresholds for current month and contract to date are required to submit variance explanations. The manager will provide an accurate description of the problem. The description focuses as much as possible on the root cause, rather than symptoms. This analysis includes identifying the cause of the variance, determining the impact of the variance on milestones, determining the effect on the VAC, and specifying the corrective action(s).

Project Reporting and Contract Performance Report

Project performance meetings are held monthly; more often if it is warranted. Data produced by the EVMS is timely and of sufficient quality providing an effective foundation for management decisions. Performance analysis is a continuous activity. The integrated project scope, schedule, and cost data are gathered and interpreted into project status information. Significant current or potential problems are identified and root causes determined. Alternative courses of action are assessed and corrective action is taken if necessary. The reporting systems for the project were structured to gather project status information for all management levels. The reports were prepared using performance data from established project controls and site business systems to ensure consistent use of approved formats, accuracy, data at the correct level of detail, and commitment to due dates. Data integrity is maintained to accommodate different focus areas and cross-cuts. Contract Performance Reports (CPRs) were provided at least monthly. The reports were:

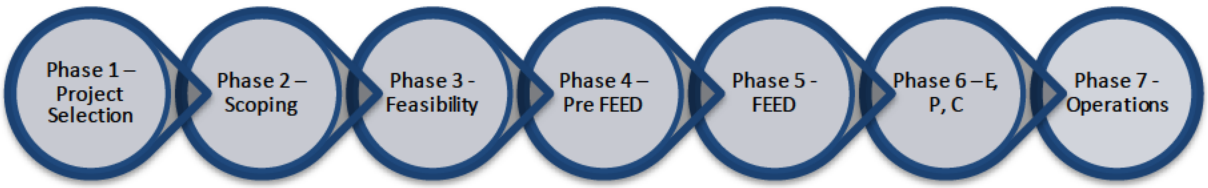
- Cost and schedule performance by summary level WBS,
- Cost and schedule performance data by the responsible organization structure,
- Budget baseline plan against which performance is measured,

- Staffing forecasts for correlation with the budget plan and cost estimates, and
- A narrative report used to explain significant cost and schedule variances and other identified contract problems and topics.

For the purposes of the project, it was assumes that self-certification was the preferred means for EVMS compliance. The Project utilized internal resources to complete EVMS self-certification.

G.5 Phase Gate Process

The project employed a phase gat process. At the time of the DOE solicitation the Project was in Phase 5, FEED. The project phases are defined as follows:



<u>Phase 1 - Project Development</u>

The project is screened from a list of potential projects and identified as a project that meets the corporate requirements. The potential project is given a fatal flaw analysis including siting, feedstock and environmental considerations. The project team compiles a magnitude estimate to further ensure it is within the capabilities of the project. The deliverables from Phase 1 are a scoping budget, pre-scoping study report and a completed pre-scoping checklist. To pass through Gate 1 on to Phase 2, a scoping budget authorization for expenditure (AFE) is completed and a project team is assigned. The go/no go decision point for Phase 1 is based on the successful evaluation of the project meeting the corporate requirements, the project passes the fatal flaw analysis, there is no feedstock or environmental concerns and the project is economically feasible given the magnitude estimate.

<u>Phase 2 - Scoping</u>

Senior management identifies an executive sponsor for the project; it is this sponsor's responsibility to report to the Board of Directors on the project status. A scoping study, and a high-level engineering study, is undertaken and a cost estimate of +/-40% is developed. In this phase the feedstock is identified and commercially available licensed technologies that are required to complete the project are identified. It is in this phase that the proposed site for the project is identified. Environmental permit applications are started along with other federal, state and local permits. A conceptual financing plan is developed. The deliverables from Phase 2 are a feasibility budget, project description, proposed site identified, feedstock identified, product off-take agreements initiated, potential licensors evaluated, and a completed scoping checklist. To pass through Gate 2 on to Phase 3, a feasibility AFE is completed. The go/no go decision point for Phase 2 is based on the successful evaluation of the scoping study, source of feedstock and product off-takes identified, location of the project is identified and the project is economically feasible given the +/- 40% estimate.

Phase 3 - Feasibility Study

A feasibility study is undertaken and a cost estimate of +/-25% is developed. In this phase the required commercially available licensed technologies are selected. Permit applications are completed and solutions to environmental considerations in Phase 1 withdrawn or solved. The selected site is purchased or optioned to lease/purchase, and local zoning modifications initiated. A financing plan is completed, and all engineering assumptions closed out. The deliverables from Phase 3 are return on investment (ROI) calculations, licensed technologies selected, feedstock memorandum of understanding (MOU) obtained, project off-take MOU obtained, site MOU obtained, financial model completed, permitting fatal flaw analysis completed and a completed feasibility checklist. To pass through Gate 3 on to Phase 4 an engineering and construction project manager is assigned, an engineering and construction lead process engineer is assigned and an approved Pre-FEED AFE is completed. The go/no go decision point for phase 3 is based on the successful selection of the commercially available technologies, the project site is secured, and the project is economically feasible given the +/- 25% estimate and the ROI.

Phase 4 - Pre-FEED

This is a fundamental phase for commercial negotiations and optimization studies. Feedstock contracts, product off-take contracts and technology licenses are secured. Permits are submitted and a legal review of the project is completed. The financial model is validated and a bank's engineer is retained to go forward with financing. Request for bids are sent to qualified engineering firms to complete Phase 5 FEED. The deliverables from Phase 4 are signed license agreements, land purchased (leased), feedstock contracts in place, project off-take contracts in place, transportation contracts in place, critical permit applications submitted, ROI and CAPEX confirmations completed, FEED contract and completed Pre-FEED checklist developed. To pass through Gate 4 on to Phase 5 a FEED AFE is completed, an engineering and construction manager is identified and engineering and construction team is assigned. The go/no go decision point for phase 4 is based on securing the feedstock contracts, product off-take contracts, technology licenses, permits are submitted, legal review is competed, and the project is economically feasible given ROI and CAPEX confirmations.

Phase 5 – Front-End Engineering and Design (FEED)

This is the start of engineering design activities for the project. The successful engineering team is selected and the FEED contract is executed. The Phase 6 EP&C contracts are finalized. Permits are issued in this phase. Legal and financial checklists are completed and equity/debt financing is finalized. The operations team is identified. The deliverables from Phase 5 are an EP&C contract, critical permit approvals, site pre-work complete, long-lead equipment pre-ordered and a completed financing checklist. To pass through Gate 5 on to Phase 6 an EPC AFE is completed, an EPC contract is signed, the project is funded and an operations and maintenance (O&M) plant manager is assigned. The go/no go decision point for phase 5 is based on selecting the EPC contractor, permits are issued and the equity/debt financing is finalized.

Phase 6 – Engineering, Procurement, and Construction (EP&C)

During this phase project financing is closed and debt/equity compliance continues. Detailed engineering, procurement, and construction are completed. Operations and maintenance personnel are trained. The operating permits are prepared by the environmental department. After mechanical

completion, pre-start-up safety reviews (PSSR) are completed and the plant is turned over to operations to commence start-up and commissioning.

Phase 7 – Operations

This is the final step in the project where the plant goes through commissioning and start-up activities resulting in operating to produce product, and data for commercialization.

G.6 Change Management Plan

A Change Control Board has been established to provide a consistent and uniform method for the management of both positive and negative impacts to the scope, cost, and schedule of the project. These impacts may result in changes or deviations to the project baseline.

The Project Controls Manager administrated the change control/management process in accordance with the contract, scope of work, existing change control procedures, and project management requirements. The Project Controls Manager was responsible for assisting in training the project team regarding how change control will be administered including forms, approval responsibility for the various steps of the process, and incorporation into the control baseline. Identification of changes is the responsibility of the entire project team.

In order to provide an overall view of the project change health, a **Master Change Management Log** is established. This log identifies, tracks, and reports the status of all project deviations and change categories using the following: PDNs, FPDNs, TNs, CNs, COs, ICs, BTs, and Pending and Potential Changes. To accommodate various internal and external reporting requirements, the Master Change Management Log is sorted and subtotaled by each change category as listed above, (i.e. CN, CO, IC, TN, BT, and Pending and Potential Changes).

There were two types of contract changes resulting from directions or actions:

- Specific "Out-of-Scope" directions that fall outside the project's approved scope of work including changes which involve the quantity of the work, the quality of the work, the calendar time or period required to produce the work, the method of execution, or some combination of these items.
- Specific "In-Scope" directions and actions that are still within the project's approved scope of work (i.e., no quantity growth or design changes, etc.), but involves either failures to perform certain actions as required by contract at a specific time, delays, acts, omissions, or directions that are different than contractual, technical, or procedural requirements, thus impacting the project cost, schedule, or contract terms and conditions.

As changes are identified, an **Engineering Change Instructions (ECI)** is issued to identify changes, answer questions, and instruct or ask for direction to proceed on a particular item. The ECI may or may not lead to a Potential Deviation Notice (see below) and is not a contractual document, but is intended to provide instructions, direction, and act as a historical document for project decisions.

A **project deviation** is an alert raised by any member of the project team (home office or field staff) that something on the project is changing or about to change and, as a result, there may be an impact to the

project cost and/or schedule. Project deviations are to be documented and processed per the following documents:

A **Potential Deviation Notice (PDN)** is the first document issued indicating a possible impact to the project's scope, cost, or schedule. It is initiated by any member of the project management team. PDNs are to be prepared in a sufficient, yet concise, manner that represents the issue at hand, along with clear instructions as to the path forward. PDNs should be for unique items and should not cover different subjects on the same PDN. However, deviations for "like subject matter" may be accumulated and submitted as one PDN to save time and paperwork. For example, multiple design changes after a model review that result in a scope change could potentially roll together and be submitted as a single PDN for processing. But caution and sound judgment must be exercised when combining deviation events on a single PDN.

The formal document issued that initiates "Out-of-Scope" change proceedings per the contract agreement is a **Change Notice (CN)**. A PDN or Field Potential Deviation Notice (FPDN) will precede each CN. CNs require approval of the owner, and requires the response and direction concerning the change notice within a contractual period of time—usually three to five business days. The initial CN must include a rough order of magnitude (ROM) cost estimate, the additional cost of preparing a detail cost estimate for the change, and any schedule impact (in days) is also shown.

If the direction is to proceed with a detailed cost estimate of the change, a completed Summary of **Detail Estimate Form** is attached to the CN.

A **Change Order (CO)** is the formal document that finalizes and dispositions the "Out-of-Scope" project change. The potential Change Order Actions are as follows:

- Change order approved
- Change order approved as noted
- Revise change order and re-submit
- Change order rejected
- Change order preparation cost approved (yes/no)

The associated CN and PDN (or FPDN) precedes the CO and are referenced on the Change Order Form. The CO requires approval of the appropriate Project Manager.

A **Trend Notice (TN)** is normally the vehicle used to adjust the project's EAC cost forecast, but may or may not impact current budget costs. In other words, no deviations to project quantities or project scope have occurred, yet an impact to the EAC cost forecast has occurred as well as a possible impact to the project's baseline schedule. Each TN is listed and tracked on the Master Change Management Log and serves as written notice that an "In-Scope" deviation has occurred or could occur. An example would be the additional cost to the project due to a slippage in the construction schedule caused by below-standard craft performance and productivity. Another example would be an adjustment to the project's EAC cost due to fluctuations in the average wage rate on the project. Note again that such deviations are added to the project's EAC cost without affecting the current budget costs unless reimbursed. A PDN or FPDN precedes a TN.

Each **Internal Change (IC)** is listed on the Master Change Management Log and is used primarily to track "In-Scope" variations in construction quantities that were not accounted for in the "As-Sold Budget." An

IC is usually the result of an estimate error or omission as related to project construction quantities. An example of this is an omitted process equipment item, or under-estimated pipe footages on the project, etc. The IC may also be utilized to track additional engineering costs which are not reimbursed.

Occasionally, there are changes to a project that have no net effect to the project bottom line. These would include changes such as a change in the original project execution strategy from subcontract to direct hire for all or a portion of the work, the amount of engineering given to a vendor, or a request from construction to the engineering and procurement departments to re-align or adjust engineering deliverables and/or field materials in order to save labor or improve schedule per a revised construction execution plan. These deviations are addressed through **Budget Transfers (BT)**, which move budget from one area or cost account to another due to changes in the project's execution plan with no net effect on the current budget. BTs do not require an adjustment to project contingency or fee. A PDN or FPDN precedes a BT.

G.7 Communications Management Plan

The project organization chart established the formal lines of communication for the project. For the purposes of efficient project execution, the team members used direct lines of communication with their respective counterparts across the project organization. It was imperative that intra-project communications not be impeded; however, the respective Project Management, Project Engineering Management, Construction, Procurement, and Financial functions were kept apprised of current technical, schedule, and cost issues. Below is the communication plan.

- Project Management Communication Plan
  - Project Manager(s) Monthly Project Report Engineering Communication Plan
  - Approval of baseline scope
  - Weekly Engineering Team Meetings
  - Weekly Status Reports, with action item list updates
  - Bi-weekly teleconference with all stakeholders, including meeting minutes
  - Monthly Project Status Reports with cost, scope, schedule, quality, safety, and issues update
  - Agendas for all meetings
  - Teleconferences – As needed
  - Web-based Information Exchanges (WebEx) – as needed
  - Hazard analysis
- Construction Communication Plan
  - Weekly Construction Status Meetings
  - Safety (as needed – minimum weekly information report with formal reporting monthly)
    - Incident reporting
    - Near miss reporting
    - Safety observations
    - Morning tailgate meetings
  - QA/QC
    - Status of plans
    - Vendor Surveillance
- Schedule Communication Plan
  - Approval of baseline schedule
  - Bi-weekly schedule updates

- Project Controls Communication Plan
  - Approval of baseline budget
  - Informal Weekly cost reports
  - Formal Monthly cost report
  - Monthly Change control reports
- Procurement Communication Plan
  - Requisition Status (informal biweekly; formal monthly)
  - Purchasing Material Status Report (informal biweekly; formal monthly)

Project correspondence and communications were maintained by the Project Document Control Center (PDCC) in hard copy, Outlook archives, Aconex, or other electronic formats. PDCC is a delineated work area for document control.

- E-mail is a constant. Outlook Archives, stored on a corporate server, provide a near-online retrievable mechanism to capture the day-to-day guidance, direction, discussion, and decisions that are informally determined.
- Aconex is a collaborative, cloud-based portal that allows the sharing of electronic documents. This collaborative tool provides a common location for the exchange of electronic information. It is also the "the filing cabinet." Officially released memos, specifications, drawings, or any other document "of record" is stored and maintained in this online repository.
- Other electronic formats may be required given the location or access to cloud portal. These will be evaluated on a case-by-case basis.
- Project letters are formal communications. Any information that is disseminated, including official letters that pertain to the company, must have prior signature approval by the respective Project Manager within the team prior to release. The Project Manager may choose to delegate their signature authority at their discretion. Formal letters are stored in the PDCC and in Aconex.
- Letters from suppliers or contractors are to be handled similarly to those generated by Project Management, with electronic copies forwarded to the PDCC for filing in Aconex.
- E-mail may be used to document telephone conversation records, and may serve the purpose of transmitting informal information or discussions. Project personnel receiving e-mails are responsible for forwarding the e-mail to the appropriate project personnel and to the PDCC.
- Meetings are to be documented in meeting minutes, which address each subject discussed, the agreements reached, and action items assigned to individuals or parties. Subjects not resolved have an agreed upon future action stated along with date, organization, and individual responsible for resolution. The meeting organizer or senior person in attendance designates primary responsibility for preparing meeting minutes. After review and approval, meeting minutes are distributed to attendees and others, as appropriate, and electronically filed in Aconex. The meeting minutes should be distributed within 5 working days of the meeting held.
- Internal project communications that warrant more formal distribution than an e-mail are documented in memoranda. They can be used to communicate project directives or issue technical information.
- Letters of Transmittal are used to formally transmit drawings, data, or information within the team, to subcontractors, or vendors.

In general, the project team adhered to project-directed confidentiality requirements and the following requirements:

- Access to the project network resources was controlled.
- All project documents, information, drawings, specifications, photographs, and correspondence were treated as confidential and shared only among necessary project, subcontractor, and vendor team members with signed nondisclosure documentation enforced.
- Any articles for publication developed on the project were approved prior to release.
- The Project Team determined distribution requirements based on document types and personnel. Once distribution requirements are established, a document distribution matrix is established. The Document Controller was responsible for the maintenance, implementation, and administration of the document distribution matrix.

In support of project communication control, a Project Contact List was established and maintained for the life of the project. This list documented the assigned personnel working on the project their respective office locations. It includes telephone contacts and e-mail addresses for each of the project personnel.

G.8 Cost Management Plan

Cost Status

The cost process is used to calculate the cost and schedule performance indices, cost and schedule variances, and variances at completion. It is the integration point for the BCWS, ACWP, and BCWP. Cost and Schedule Performance Reports are available for internal and external use. The reports are updated monthly and provide Current Month and Contract to Date reports.

The actual costs are obtained from the accounting system and include both actual costs and accruals. Accruals are submitted on a monthly basis to account for subcontract or progress payment work performed but not yet billed.

Material Status

Material and Equipment earn BCWP and cost for performance measurement reporting purposes when the material or equipment is received and accepted or based on established progress payments. Material and equipment purchases are initiated, tracked and closed through Materials Management System.

All material and equipment procurements are traceable to the WBS via the Cost Account Charge Number (CACN), or Purchase Order Number (PO).

Invoicing System

The use of the current project controls EVMS and accounting system provides the platform for recording project cost information related to the project control accounts planned within the WBS structure. *The Code of Accounts are created directly from the WBS elements managed by the EVMS.* The system collects and reports the project status, performance and expenses, and provides the Project Manager with the

tools and information needed to manage project invoicing against the overall project budget. The invoicing system is integrated with the financial accounting system. Invoicing will be based on milestones or EV as appropriate.

Accounting Considerations

Ensuring the consistent and accurate collection and reporting of the received costs and accruals associated with each Control Account to:

- Establish consistent and accurate project cost collection against the final cost objectives without allocation of a single Control Account to two or more work breakdown structure elements or organizational elements,
- Adhere to accepted accounting principles and Cost Accounting Standards (CAS),
- Allocate indirect costs, in accordance with the CAS disclosure statement, so that all projects benefiting from an indirect service bear their fair share of costs, and
- Ensure that actual costs are collected and compared to the performance in the same manner as planned.

The commitment to financial stewardship and its accounting system is based on accepted accounting principles and cost accounting standards. Efficient, sound management principles are applied to budgeting, cost recording, distribution, and reporting of financial information. Project costs are recorded against a work package level. This establishes consistent and accurate project cost collection against the final cost objectives without allocation to more than one single control account and ensures that actual costs are collected and compared to the performance in a manner as planned. Costs are collected and reported for line items, general plant projects (GPP), capital equipment projects, and operating expense funded projects.

Cost Collection

The project is divided into lower levels of detail, ending with a unique WBS element, within the project WBS structure. All costs are collected through the use of unique control account charge numbers. This allows all cost elements within a project to be rolled up within the WBS structure of the project. The hierarchical WBS structure ensures cost and performance measurement data integrity and that lower level costs cannot be allocated to more than one higher-level WBS element.

Analysis and Management Reports

Reflecting a forward looking approach to cost and schedule control that:

- Provides timely visibility into technical cost and schedule progress,
- Generates planning and performance data at the appropriate level to be used by management in the decision-making process and provides a sound basis for projecting final costs and future funding requirements,
- Develops meaningful performance indicators to provide early warning of potential project problems,
- Identify significant current or potential problems and determine root causes,
- Assess alternative courses of action and take corrective action if necessary, and

- Systems and computerized tools (e.g., web-based application) supply our project managers, control account managers, and DOE with real-time data so they know cost and schedule baselines and expected production status at any given time. Safety and compliance metrics indicate where management emphasis or worker training is needed. This information enables project managers and control account managers to measure their performance, detect variations from expected progress and make corrections early.

The monthly management reporting cycle identifies project performance based on EVMS metrics and variance analyses. The report also recommends corrective actions as appropriate.

G.9 Procurement Management Plan

All purchases that are over $25,000 are sent out for a formal Request for Quote (RFQ). The RFQ is used to request price and delivery for goods, materials, equipment and technical services. Bids are evaluated by various categories: equipment manufacturing process, delivery times and pricing. In parallel with the RFQ, contractors are required to complete a Prequalification Package. The bidders are evaluated on the following items: OSHA Incidents, Experience Modification Rate (EMR) rates, specialty and previous projects, capability and ability to load qualified personnel to the project and financial stability.

A Commercial Bid Evaluation is a detailed comparison of the commercial considerations of the quotation for the goods and services provided by the bidders versus the specified commercial requirements in the RFQ and a comparison between the quotations.

A Technical Bid Evaluation is a detailed comparison of the technical characteristics of the goods and/or services proposed by the bidders versus the specified technical requirements in the RFQ and a comparison between the quotations. A bid analysis summary is generated for summarizing the technical and commercial results of the Bid Evaluation and negotiation process. It is used to make a recommendation and to obtain approval to award a Purchase Order. Not all orders are elected by best pricing; some are selected by best fit for application.

After completing the bidding and prequalification process the successful bidder is issued a Material Requisition. The Material Requisition transmits the quantity and detailed description of goods, materials, equipment and/or services required for a project. The document also transmits all technical and schedule requirements, applicable cost codes, the estimated budget, and provides the authorization to commit the funds. A Purchase Order authorizing the Supplier to engineer, manufacture, ship, provide and invoice for the goods, materials, equipment and technical service representatives as specified in the order. The services provided by the technical service representatives shall be only those that are normally required for installation or start-up of the equipment being ordered based on standard practice in the industry. Purchase Orders shall not be used for any other services. It is a legal document and should clearly and concisely cover the essential elements of the agreement. For this project, services were procured under Cost Reimbursable Fixed Fee contracts, including Davis Bacon Act wage requirements as they applied to the project.

G.10 Material Management Plan

Materials management is the driver between engineering execution and construction completion. All intellectual property and licenses have been obtained.

Expediting will be heavily involved in the front-end expediting of Supplier and subcontractor drawing and data deliverables to ensure that engineering can finalize the technical aspects of the design to support the engineering and construction schedules. Expediting will also ensure that Supplier deliveries are in accordance with construction needs.

The site materials manager administratively takes direction from the materials management manager but will take day-to-day direction regarding site needs from the construction manager. The site material manager will coordinate the activities of material control, engineering, purchasing, equipment, and material compliance as well as coordinate with the project materials management staff to ensure timely resolution of materials management issues affecting construction and turnover.

Materials management responsibilities include:

- Identification of long-lead items and pre-qualified Suppliers and subcontractors. In addition, the group will develop and maintain an approved Supplier and contractor list for project materials and equipment. Our Team places a high emphasis on safety. The safety records of potential subcontractors are an important evaluation factor.
- Updating requisition lists as scope is finalized and/or as changes occur. It will include a requisition number, description, a schedule of milestone events based on the site need dates, and a list of equipment identification associated with each requisition. Requisitions will be generated for each package as the authority to obtain quotes and procure goods and services is received. Each requisition will be pre-approved by project management and will be accompanied by technical specifications, which define the goods, services documentation requirements, and suggested sources of approved Suppliers.
- Issuing Request for Proposals (RFP's) using existing procedures with current commercial terms and conditions.
- Receipt, commercial evaluation, and negotiation of proposals
- Preparation of commercial bid summary and submission with the technical bid summary with recommendation for award
- Preparation and issuance of purchase and contract orders with approval by CF and project management
- Administration of purchase and contract orders
- Maintaining material status report and meet weekly with project management to review vendor/contractor status regarding vendor drawings, material deliveries, fabrication schedule, shipping dates, overdue items, and date arrived at site
- Providing expediting of services, equipment, and materials as required. In addition to the expediting (both internal and external), the expediting team will follow up with all Suppliers on a pre-determined timeframe with the status of all purchase orders relative to the order entry process, manufacturing progress, and delivery to the site.
- Receiving, storage and dispatching materials and equipment
- Maintaining and updating the Overage, Shortage, and Damaged (OS&D) Materials log
- Resolving OS&D issues with the QA/QC manager

Materials management will use the reports listed below to provide current information about the status of procurement status and progress of Suppliers. The frequency of the reports is adjustable to meet the needs of the project.

- Requisition Status. This report provides overview information for each requisition that has been released to procurement. The details include requisition number, description, assigned buyer information, bidders, bid status, technical evaluation status, bid tab status, and recommended bidder selection.
- Purchasing Material Status Report. This report provides detailed information about the status of each purchase order line item and associated item shipments. The details include purchase order number and supplement, Supplier name, purchase order line item, ordered quantity, item description, item shipments, item shipment quantity, received quantity, delivery information, required on-site date, and expected or actual arrival on-site date.

Equipment and materials will be received against a purchase order with the equipment and/or material descriptions, order quantities, received-to-date quantities, and expected quantities. The materials control receiver notes the current quantity received and relevant warehouse and OS&D information in order to post it to inventory. Received equipment and materials will be assigned to a QA/QC warehouse for inspection. Any discrepancies are recorded in the OS&D reports. The Home Office Procurement Group will be notified electronically for immediate action and resolution.

G.11 Quality Management Plan

The Project Quality Assurance Manual is an integral part of the Quality Management System. It identifies the requirements, with respect to quality, that must be integrated into the Project, and defines the responsibilities of each position within the project organization. In addition, the risks that can potentially affect quality results are identified and mitigation actions described, measurements and criteria for quality performance defined, and an implementation plan included that covers the project. The Project Quality Assurance manual will address, but not be limited to:

- Audits
- Continuous Improvement
- Orientations
- Quality Control
- Success Factors
- Reporting
- Technical Reviews

G.12 Risk Management Plan

An extensive Risk Management Plan (RMP) was used to control financial, technical, and environmental risks as well as detail the risk management process, methodology, risk analysis results, and mitigation planning of the whole project from project development through final reporting. The RMP includes the following sequential risk management steps: risk identification, risk impact analysis and quantification, risk mitigation strategies development, risk monitoring, and risk documentation.

The Project Risk Management program will be implemented in keeping with existing project policies, practices, and procedures.

Each function involved in the project shall participate in the identification and assessment of project risks. A disciplined approach is employed, where the project life cycle is divided into assessable elements such as function or scope segment to ensure the entire project is considered. Project risks are categorized in the following 11 project areas:

- Technical
- Cost/Schedule
- Programmatic
- Support
- Safety
- Contracts
- Owner (Client)
- Regulatory/Permitting/Environmental
- Site (Including Location)
- Commissioning and Start-up
- Shut-down, Turnover and Outage

Risk Management is comprised of the following seven steps: Risk Identification, Risk Impact Analysis and Qualification, Risk Grading Matrix, Risk Management Strategy, Risk Documentation, Risk Mitigation Strategies, and Risk Monitoring and Mitigation plans for Post Mechanical Completion.

Risk Identification

A formal risk assessment workshop will be conducted to proactively identify project risks. Risks are identified through discussion by teams of experts, document reviews, and checklists of typical risks based on previous experiences. Other techniques, while not part of the risk management plan, may identify potential risks that require more focused management. This includes HAZOP, constructability, and other project reviews. The risk data from these assessments is used as inputs to the risk registers. The risk workshops for all aspects of project execution will be planned, scheduled and conducted, with the output from risk workshops managed from both a qualitative and quantitative aspect.

Identification of new risks will occur throughout the project life cycle. Risk Management is proactive and risk identification will occur early enough to allow time for risks to be dealt with effectively.

Risk impact analysis and quantification including the potential effect of environmental and other regulatory requirements on the project - Once risks and opportunities have been identified, the project team members categorize the identified risks by probability and severity (consequences) of impact. The project team utilizes judgment and experience to evaluate each risk element and assess its severity and probabilities. For each event, the team must use the Risk Grading Matrix and categorize each risk based on its severity and probability resulting in risk grading from 1 (Very Low Risk) to 5 (Very High Risk).

Table 4-5: Risk Grading Matrix

Severity						
	Category / Criteria	Cost	Schedule	Environmental	Personnel	Public
1	Very Low Risk / Negligible	< $10K	< 2 weeks	Amended Permit Filing < $10K	No increased risk to plant personnel	Potential public forums / Public Relations outreach required
2	Low Risk / Marginal	$10K - $100K	2 - 6 weeks	Repermitting Costs $10K - $100K	Low risk of injury to plant personnel	Nuisance to Public < $10K for remediation
3	Moderate Risk / Significant	$100K– $1MM	6 weeks - 3 Months	Repermitting costs > $100K / Risk of Release	Potential Risk of Injury to Plant Personnel	Nuisance to public Costs for remediation < $100K
4	High Risk / Critical	$1MM - $3MM	3-4 Months	Findings / Permit Violation / Release to Environment	Injury to Plant Personnel	Injury to Public
5	Very High Risk / Crisis	> $3MM	> 4 Months	Violation of Permits / Fines > 1MM Significant Release to Environment	Loss of Life	Possible Public / Bystander Fatality or Injury to Public

Probability		
	Category / Criteria	Frequency
1	Very Unlikely	Annual / NA
2	Unlikely	Monthly
3	Possible	Weekly
4	Likely	Daily
5	Very Likely	Hourly

Risk Category	Risk Strategies	Risk Owner
1 - Very Low Risk	Avoid	Rentech
2 - Low Risk	Transfer	Engineer
3 - Moderate Risk	Mitigate	Supplier / Vendor
4 - High Risk	Accept	
5 - Very High Risk		

Risk Category / Risk Grading Matrix					
Probability/Severity	1) Negligible	2) Marginal	3) Significant	4) Critical	5) Crisis
1) Very Unlikely	1	1	2	3	4
2) Unlikely	1	2	3	3	4
3) Possible	2	3	3	4	4
4) Likely	3	3	4	4	5
5) Very Likely	3	4	4	5	5

Risk Categories

- Very Low Risk: Normal management practices are sufficient
- Low Risk: Normal management practices should be sufficient, but project team awareness should be maintained.
- Moderate Risk: Project team should consider each risk event and should exercise their best judgment. Strong consideration should be given to address the risk elements in the Risk Management Plan with actions deemed appropriate by the project team.
- High Risk: The project team shall perform sufficient analysis to assure the event is understood and appropriate mitigation(s) identified. Risk handling actions are mandatory and shall be addressed in the Risk Management Plan. Continual tracking of these risks and their mitigating actions is appropriate.
- Very High Risk: The project team shall perform sufficient analysis to assure the event is understood and appropriate mitigation(s) identified. Risk handling actions are mandatory and shall be addressed in the Risk Management Plan. Continual tracking of these risks and their mitigating actions is appropriate.

Risk Mitigation Document and Strategies

Risk management strategies are produced with the participation of all project functions utilizing the "what if" approach. The risk management approach is documented in the Project Risk Management Plan. A risk management strategy was developed for each "High" and "Very High" Risk element and for "Moderate" risk elements at the discretion of the Project Manager. For "Low" and "Very Low" risk elements, and "Moderate" risk elements not judged to require documented mitigation plans, the Project Manager assures that they are controlled through the normal management functions and work processes.

The Project Risk Management Detailed Plan is prepared and maintained for the life of the project. The specific contents and level of detail may vary based on the scope of the project, as the project passes through the gated processes. Cost and schedule contingency analyses, when used as mitigation, are required to be addressed separately.

Risk Monitoring

To ensure the Risk Management Plan is being reviewed and the management strategies are assessed on a regular basis, formal risk assessment workshops will be conducted at key project milestones to proactively identify new project risks. Risks can be identified through discussion by teams of experts, document reviews, and checklists of typical risks based on previous experiences. Other techniques while not part of the risk management plan may identify potential risks that require more focused management. This includes HAZOP, safety integrity level assessment, constructability and other reviews. The risk data from these assessments will be used as inputs to the Construction, Checkout, and Start-up risk registers.

Identification of new risks occurred throughout the project life cycle.

G.13 Contingency Planning

It is important to note that contingency, as defined by the team, is separate from management reserve. Contingency, as used herein, is the additional funding or schedule to be used at the discretion of the project leadership to deal with anticipated, but not certain, events in the project. It is not funded or scheduled to address out-of-scope or out-of-project work. Management reserve is a value separate from contingency that is established and controlled by the Project Manager. Management reserve is often created by transferring budget from other direct accounts and targeting an under run. This is a provision made to mitigate project risks.

Rentech certified the minimum 25% contingency as required by DOE in accordance with the terms of the award. The team completed a Line Item Analysis of contingency to establish discrete cash or schedule values by cost element and the risk factors associated with it. The analysis uses a method that examines the quality of the information available for developing the quantity base and pricing included in the estimate. The degree of completion of engineering, the sources and firmness of equipment quotes, and the level of information provided in bids, execution planning, schedule development, third party influences, and commercial/contractual terms affect the level of contingency applied.

The Project Team managed the allotted contingency with a formal planning and reporting process. Each respective team project manager maintains their respective schedule and budget contingency under the overarching philosophy that contingency is a team resource that deserves focused attention and control. The project goal is to execute the engineering, procurement, construction, start-up, and operation without absorbing contingency.

Contingency drawdown was executed in parallel with the Change Control Board Approvals. Contingency was not used until Phase 7, Operations, and was used to support the extended commissioning efforts.

<u>Post Mechanical Completion</u>

Rework to address commissioning and debottlenecking issues was managed as out-of-scope or out-of-project work. There were 12 discrete debottlenecking events that added new scope to the project. These new scope items were managed in accordance with the overall project cost, scope and schedule procedures.

4.H Products Developed Under the Award

H.1 Publications and Presentations

- USDA Biomass Technical Advisory Committee 9/29/10
- Integrated Biorefinery Peer Review in Washington, DC 2/2/11
- Biomass 2011, DOE Annual Conference, National Harbor, MD 7/27/11
- Integrated Biorefinery Peer Review in Washington, DC 5/20/13

H.2 Patents

No project-related intellectual property has been created as part of the DOE funded portion of the ClearFuels – Rentech Integrated Biorefinery project.

H.3 Web Site or Other Internet Sites that Reflect the Results of this Project

None.

H.4 Networks or Collaborations Fostered

Throughout the course of the project, Rentech team members were part of the industrial partners in the Southeastern Partnership for Integrated Biomass Supply Systems (IBSS). This is a partnership between many Southeastern universities including the University of Tennessee, Auburn University, and North Carolina State University. This is a project funded by the United States Department of Agriculture National Institute of Food and Agriculture. Various southeastern woody feedstocks were transported and tested in the Commerce City facility.

SECTION 5 TECHNOLOGIES

5.A Technology Development Overview

A.1 ClearFuels Technology Assessment

The Rentech-ClearFuels High Efficiency Hydro-Thermal Reformer (HEHTR) is an indirectly fired gasifier, which combusts fuel gas(s) in a burner(s), external to helical process coils in which biomass, steam, char and syngas are flowing. This external heating provides the sensible and reaction heat necessary to achieve the desired conversion and gas quality.

This gasification technology is unique, due to the beneficial effects of fast or flash pyrolysis of the biomass, produced as a result of fast particle heating rates due to particle/wall contact, which provides for high carbon conversions. In addition, the unique helical coil geometry results in volatiles released from the biomass and char having to pass through a layer of very hot char, which catalyzes volatile decomposition reactions, and results in a low tar content syngas and in particular very low heavy tar contents. Char catalyzed reactions also allow a high H_2:CO syngas to be produced in the HEHTR, which is a unique feature of this technology.

The technology does suffer from limitations in scale-up potential due to limited surface area being available for fast particle heating, in the early part of the helical coil(s), and ultimately due to potential for coil deposits building up at high biomass feedrates.

This Final Report provides a brief background on the technology, discusses the specific performance features of the technology, discusses issues of importance for scale-up and design of the HEHTR reformer and associated equipment, covers in some detail the design tools that have been developed and then describes critical performance specification of the HEHTR reformer. A simplified diagram of the Commercial HEHTR is provided below:

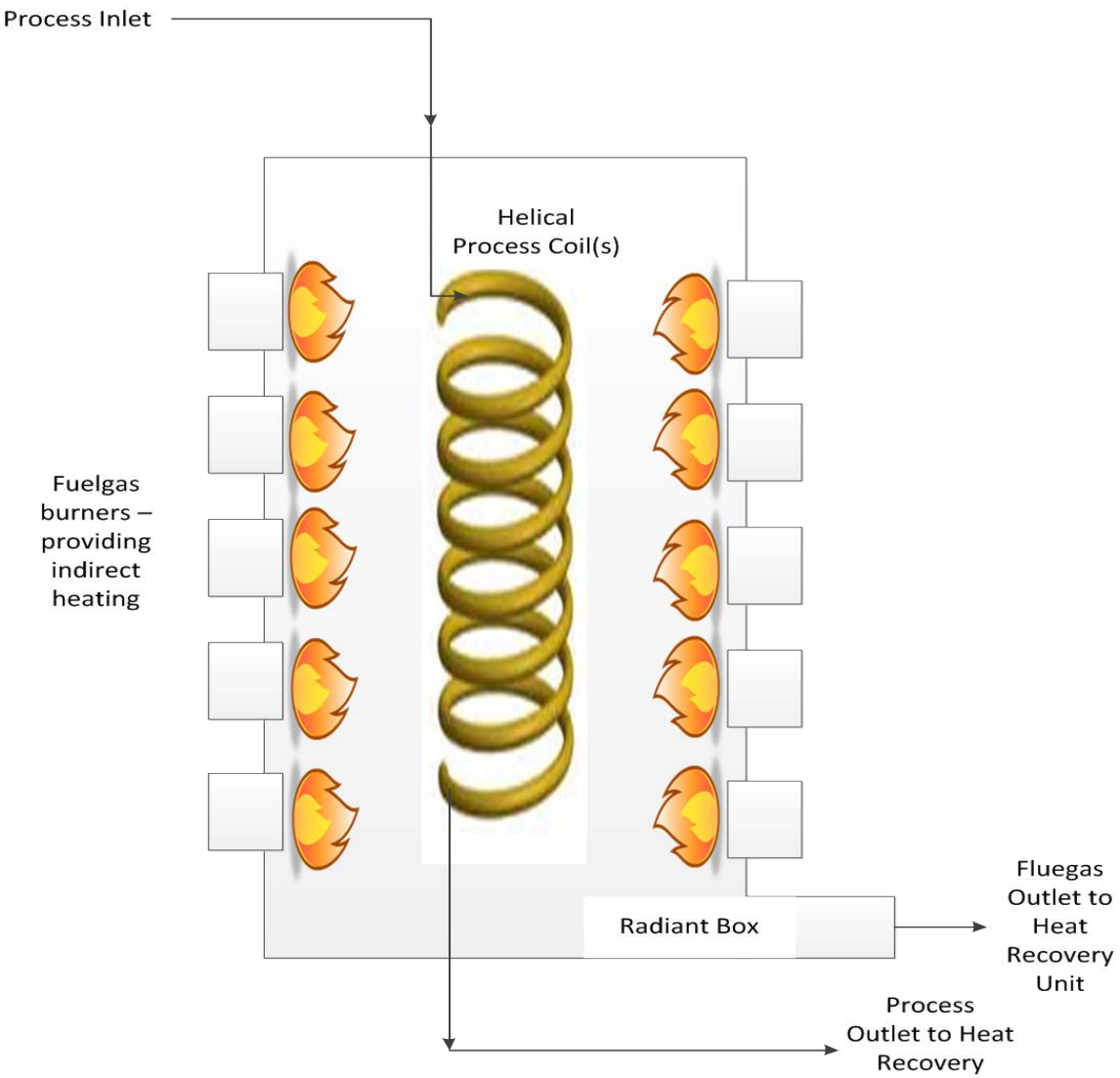


Figure 5-1: Simplified Diagram of Potential Commercial HEHTR Design

The key design features of the commercial HEHTR are:

(i). The ability to control heat flux along the length of the process coil, to achieve the desired skin wall temperature profile.

(ii). Helical coil design which results in fast biomass/char heating and which results in a hot char layer up against the outside of the process coil, which catalyzes specific desirable decomposition reactions.

(iii). A method of steam/Biomass mixing.

(iv). Potential use of limited air injection, upstream of the HEHTR, to increase initial wall temperatures in the Reformer.

A.2 PTI Technology Development

The original basis for the current Rentech-ClearFuels High Efficiency Hydro-Thermal Reformer (HEHTR) technology is a license for technology that was developed at Pearson Technologies Inc. (PTI) between 1986 and 2002. The original PTI 5 tons per day reformer design was tested at multiple pilot plants. The first pilot plant was in Baton Rouge, LA between 1986 and 1989 and operated on lignite feedstock. A second pilot plant in Winona, MS tested wood and other materials between 1990 and 1997 in conjunction with John Brown Engineering. Between 2002 and 2007, PTI operated a pilot plant in Aberdeen, MS to test wood, corn stover, rice straw and several other feedstocks in conjunction with Idaho National Labs and other parties. ClearFuels jointly operated the pilot plant with PTI in conjunction with Hawaii Natural Energy Institute between 2004 and 2007. The unit was subsequently relocated to Livingston, AL. Rentech conducted additional testing at this unit between October 2012 and March 2013.

A.3 Rentech's Product Demonstration Unit (PDU)

ClearFuels was able to secure DOE funding for an Integrated Biorefinery pilot plant project that was deployed at Rentech's Commerce City, CO Product Demonstration Unit (PDU). The plant included a 20 dry ton per day (DTPD) ClearFuels HEHTR reformer, and all of the associated equipment, and was started up in 2012. Although there were physical constraints to operating the reformer at 20 DTPD, there was sufficient capacity to supply the rest of the plant to perform an integrated run. Successful completion of the DOE performance test was conducted in February 2013.

NREL operated their Molecular Beam Mass Spectrometer (MBMS) for syngas tar analysis during the operation of the unit, so Rentech was able to collect detailed information on syngas quality, in addition to other analytical analysis provided by the Commerce City lab.

A.4 Livingston, AL Pilot Plant

As mentioned above, Rentech entered into a contract to operate the PTI 5 TPD pilot plant, located in Livingston, AL, over the period October 2012 to March 2013. Rentech did this work independent of the DOE project to better understand the scale-up issues that we were seeing in the Commerce City PDU unit. Rentech is including the results of that work in this report as it allows the reader a better understanding of the ClearFuels technology scale-up. The data from these tests are marked "LIV" in the following.

During the testing program, Rentech relocated its Wasson tar analyzer from Commerce City, CO to Livingston, AL. The Wasson is an analytical instrument that measures real-time syngas compositions; this analyzer was also funded independently from the DOE Project. In addition, Rentech used a Solid Phase Adsorbent (SPA) method to determine syngas tar analyses.

During the testing program, Rentech replaced the existing 2" NB coil with a 106 ft long 3" NB coil. Skin and in-coil process thermocouples were installed on the new coil. In addition, Rentech installed in-coil gas sample points on the new coil to investigate reaction progress down through the coil.

A.5 HNEI Reports from Aberdeen Pilot Plant

Parametric testing was conducted at the 5 ton per day research and development pilot plant at the Pearson Technology facility site in Aberdeen, MS during 2005 through to 2006. Sugarcane bagasse was the primary feed used for these tests and the testing was primarily concerned with evaluating the ability of the PTI technology to make syngas of variable H_2:CO ratio. Although the testing was conducted on a nominal 5 ton per day pilot plant, the biomass feedrates to the reformer were typically very low at between 9 and 62 lb/hr (0.1 – 0.7 TPD), on a dry basis.

A.6 Brightstar SWERF, Whytes Gully, Australia

During Rentech's commissioning exercise, Brightstar SWERF was contracted to consult and advise on their experiences. Brightstar Environmental was unsuccessful in deploying the PTI technology in Australia. This reformer had 6 x 3" NB coils at a helix diameter of approximately 10 ft. The Reformer was designed similarly to the PDU reformer with a cylindrical can and single floor-mounted burner, although a convective bank was mounted above the radiant section. Although designed for approximately 100 tons per day (1390 dry lbs/coil), the unit had similar operational issues and conversions**.**

5.B Original Hypotheses

The original hypothesis of the project was to use biomass derived syngas from wood and wood-bagasse mixtures to generate drop-in renewable fuels by placing a biomass gasification unit at Rentech's Gas-to-Liquids demonstration facility in Colorado. Rentech selected ClearFuels gasification technology (HEHTR) because there were thousands of hours of operation at a 5 TPD pilot scale which showed syngas with a wide variety of hydrogen to carbon monoxide ratios and low tar. The original technical and commercial hypothesis was that this gasification unit could produce syngas with a high overall thermal efficiency and that tar quantity from previous work could be managed.

The other original hypothesis was that this syngas could be cleaned up and fed to Rentech's Fischer-Tropsch unit. The detailed objectives and accomplishments are listed above. The original hypothesis on project cost was a total project cost of approximately $35 million. Because of some of the design and operational issues described in detail in this report, the total project cost was approximately $42 million.

5.C IBR Operational Periods

The overall project can be broken into four overall time frames for understanding the data better.

PERIOD 1: From December 2009 through October 2011, the major project activities were Engineering, Procurement and Construction of the new equipment at Rentech's existing Gas-to-Liquids (GTL) demonstration facility.

PERIOD 2: From November 2011 through September 2012, the main project activities were commissioning and initial operations of the new equipment. This included the replacement of the WHB with a water quench, the addition of new process equipment, such as the new solvent or oil scrubber unit and filtration equipment to handle the unanticipated tar loading produced by the gasifier (HEHTR).

PERIOD 3: From September 2012 through January 2013, the project produced biomass derived syngas and blended into the natural gas derived syngas. This blend was used to feed to the Rentech Fischer-Tropsch unit and product upgrader to produce diesel fuel. A blend was used to determine if there were any unknown side effects on the FT system. This is also referred to as IBR Run 1 Period.

PERIOD 4: February 2013, during supervision by the DOE Independent Engineering Team, the project completed approximately 200 hours of integrated biorefinery operation using more than 96% of the biomass derived syngas from the HEHTR. Is also called the DOE Run or IBR Run 2. **<u>This report will focus on this period for data presentation.</u>**

5.D Process Block Flow

The overall project block flow diagram is shown in the following graphic. Biomass was prepared and gasified in the HEHTR. The syngas was then conditioned and cleaned up and then sent to the Rentech Fischer-Tropsch Unit. The long chain hydrocarbons produced by the FT Unit were upgraded to final diesel product in a hydroprocessing unit.

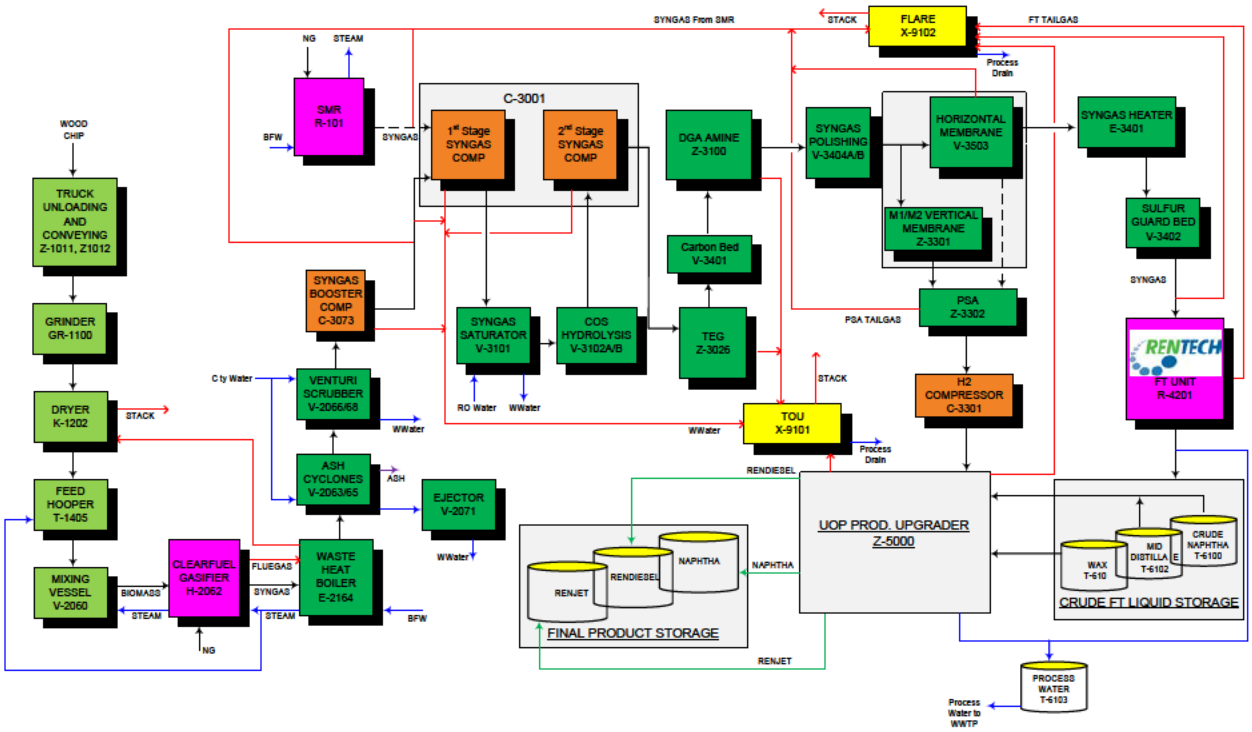


Figure 5-2: Original Block Flow Diagram of Rentech's Integrated Biorefinery. This figure does not show the Solvent Scrubber, FT Recycle, and Quench.

The main focus of this grant was the construction and operation of a large integrated pilot showing the production of renewable fuel from woody biomass. The project was located in Commerce City, CO. The project built and operated a biomass gasification system at Rentech's Gas-to-Liquids demonstration site. The photographs below show the site and some of the new equipment that was added to the site as part of this project.

Figure 5-3: Integrated Biorefinery in Commerce City, CO. The right one-third of the site was built as part of this project

Conveyer

Grinder

Hopper

Reformer & Analyzer

Bag-House

Cyclone

Figure 5-4: IBR Front-End Equipment – Purchased for Project

Figure 5-5: Syngas Cleanup Equipment

Figure 5-6: FT and Upgrading

WWT Building

Membrane

Water Tank

Figure 5-7: IBR Wastewater Treatment Plant – Building and Membrane were purchased for the project. Water Tanks were repurposed for Project

5.E Summary of Performance Test

The DOE performance test performed and was overseen by the project Independent Engineer (IE) during operations PERIOD 4. For this test a feed stream containing more than 96 percent biomass derived syngas from the Rentech-ClearFuels gasifier unit was fed to the Fischer-Tropsch (FT) Reactor for approximately 200 hours. During the run, the Rentech-ClearFuels unit processed a range of biomass feedstocks including wood pellets, wood chips, and 50/50 bagasse/wood mix, and produced syngas with an average H_2:CO ratio of 2.1 at an average syngas productivity of 22.3 SCF/lb dry biomass. Over the course of the performance test, 1096 gallons of product were produced, with an average of 24.9 gal of Diesel / dry ton biomass and a daily best of 34.7 gal of Diesel / dry ton biomass.

Table 5-1: Summary of Performance Run Conversion and Yields

	Unit	PDU DOE Demonstration (avg over test run)	PDU DOE Demonstration (single day)	Commercial Design (pro-forma basis)
Biomass Feed to Gasifier	dry tons	43.9	3.2	1000.0
ClearFuels Reformer CO Yield	SCF CO/lb dry biomass	5.3	6.0	9.1
FT CO Yield	gallons/lbmole CO	0.96	1.17	1.11
Avg Upgrader Yield	gal / gal	0.94	0.94	0.958
Product yield	gal	1095.8	112.2	50997.4
Cumulative yield	gal products / dry ton	24.9	34.7	51.0

5.F Major Lessons Learned

The single most important lesson learned was that more time was needed to commission and start-up the demonstration unit. A more detailed description of specific items that contributed to the delay in operations is available later in the report, as summary is provided below.

- Missed appropriate scale-up parameters from Pilot Plant.
- Re-validate Pilot Plant data.
- Technical Review of other applications of the technology.

5.G Material Handling

Biomass is received at a moisture content of nominally 50% and at varying sizes up to two inches. The material is ground to the desired particle size of less than ¼". It is then dried in a vibratory bed dryer using waste hot fluegas from the Rentech-ClearFuels Reformer (or the High Efficiency Hydro-Thermal Reformer or HEHTR), plus supplemental steam. Fines from the dryer are collected in a Baghouse before the dryer vent is discharged to the atmosphere. The dried biomass is then transported pneumatically to the Feed Hopper. The dried biomass is fed from the Feed Hopper into a proprietary steam/biomass mixer, where it is mixed with superheated steam and injected through externally heated helical coils in the HEHTR.

Feedstock flow rate to the HEHTR is controlled via the speed control on the Reformer Feed Dispensing Screw (FIC-1407). The measured feedstock dried density and moisture content exiting the Dryer are used as inputs to determine the dried biomass bulk density, and this calculated parameter is used to automatically calibrate the output from FIC-1407, for a given measured screw speed (SIC-1407). Although the screw speed is used by Operations to set target feed flow rates and to control the process, this feed flow rate has not been found to always be accurate, so the integrated Weigh Belt Feeder reading (WIC-1013) is used instead to determine the amount of biomass fed to the HEHTR reformer over each 24 hour reporting period. The Weigh Belt Feeder calibration check was run during the DOE Run, and was found to be accurate to within +/- 1%.

To determine the feedstock fed to the HEHTR each 24 hour reporting period, using the Weigh Belt Feeder, the Weigh Belt Feeder output in lb/hr (WIC-1013) is averaged over the 24 hour reporting period. This total x 24 hrs/day provides the total weighed "as received" biomass that is fed to the Grinder & Dryer for the period. The measured "as received" feedstock moisture is used to correct this weight to a bone dry basis. Corrections are then made for the level change in the Feed Hopper for that period, weight of fines collected in the Dryer Baghouse and weighed fines collected at the Dispensing Screw and Rotary Valve vents for that reporting period. These values are also corrected using the measured Dryer product moisture and the measured moisture of the fines, to obtain these weights on a bone dry basis. The bone dry feedrate to the HEHTR is calculated by difference for the reporting period.

As the feedrate using the Weigh Belt Feeder reading is calculated only once a reporting period, whereas the calibrated feed screw feedrate is continuously reported in the DCS and PI systems, the feed screw reading may be shown below on some of the trends, but note that this reading may not equal the feedrate reported in the DOE Run Summary Data (Section 4.0), which is calculated using the Weigh Belt Feeder method described above.

5.H Biomass Gasification

The HEHTR technology is an indirect-fired entrained flow reformer that is heated by combustion of natural gas, or by tailgas from the Rentech FT process (not utilized for the DOE Test Run). Biomass and steam are converted to syngas inside the HEHTR tubes in a rapid, one-step process. By processing the cellulosic feedstocks into a uniform size and moisture content prior to introduction to the HEHTR, the conversion reactions are more easily controlled. By using an indirect-fired design with steam as the transport medium rather than oxygen or air, the Rentech-ClearFuels process reduces the introduction of nitrogen and limits contamination of the syngas by combustion products. A general arrangement of the HEHTR is provided below in Figure 5-8.

After exiting the HEHTR Reformer, the syngas passes through a quench to cool the syngas to a temperature suitable for the downstream non-refractory lined equipment. Previously a Waste Heat Boiler was planned to recover the heat from the syngas. However, fouling problems prevented that boiler from working correctly and it was replaced with a water quench system that was used during the DOE Independent Engineer performance test. Fluegas from the HEHTR is sent through a Steam Superheater, a Heat Recovery Steam Generator (HRSG) to produce steam for biomass transport and process steam, and then the fluegas is used in the Dryer to remove moisture from the biomass prior to exiting from the Dryer Baghouse stack.

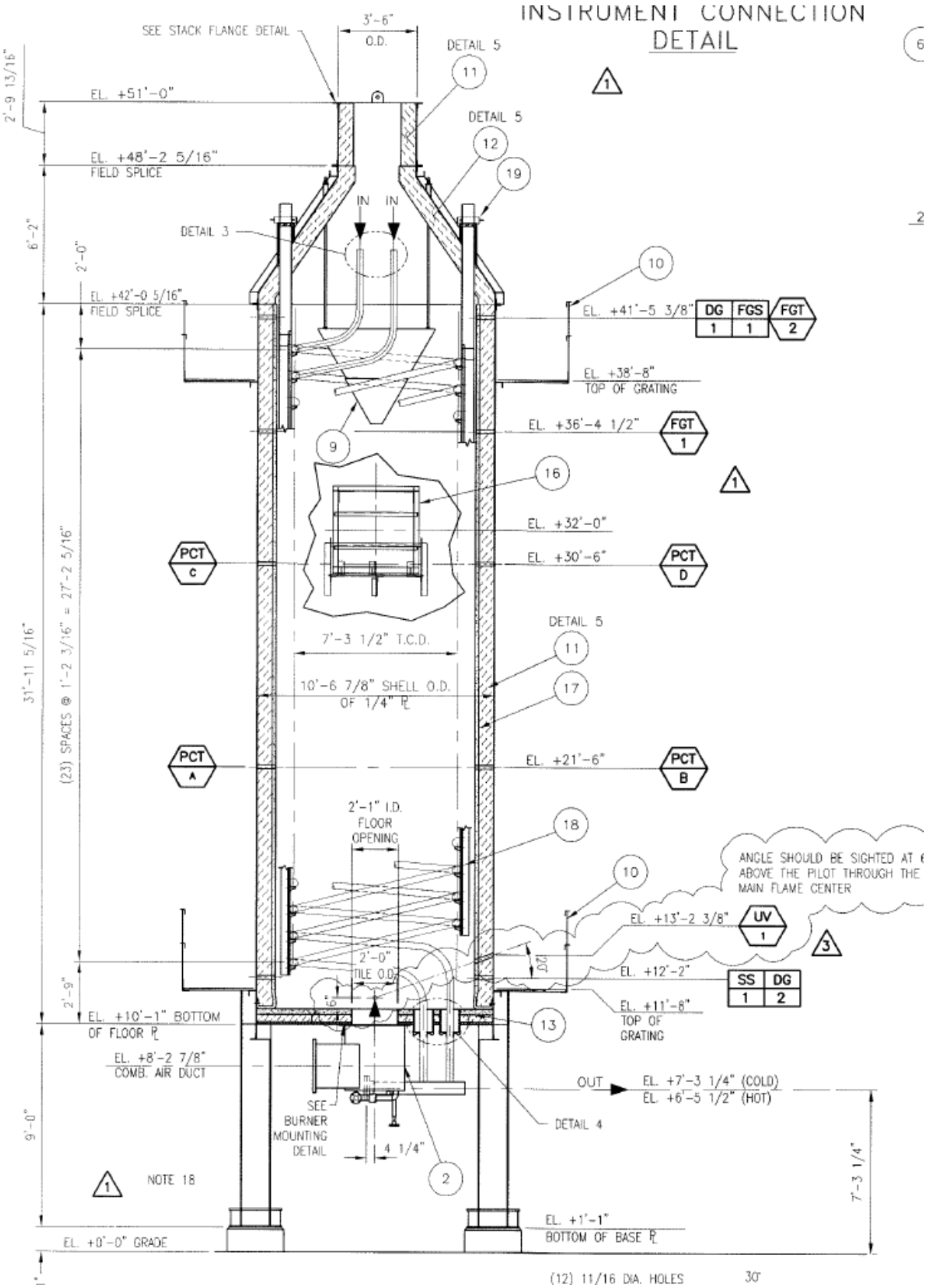


Figure 5-8: Commerce City HEHTR General Arrangement

5.I Primary Syngas Cleanup and Compression

Following the syngas quench, two cyclones in series are used to remove char and ash from the HEHTR syngas. The syngas is then routed to a packed oil scrubber followed by a venturi and packed water scrubber to remove particulates and tars, before the syngas is routed to an additional stage of cooling and liquid knock-out and sock filters, for final particulate removal. The syngas is then compressed in the Booster Compressor, prior to additional compression and contaminant removal steps, as outlined in the Unit 300 DOE Run Report.

5.J Secondary Syngas Conditioning

Figure 5-9 presents the process flow diagram of syngas conditioning unit configuration during DOE IBR run periods. It consists of syngas compression, COS hydrolysis unit, TEG, AMINE, Carbon Bed, Membrane, PSA and ZnO bed.

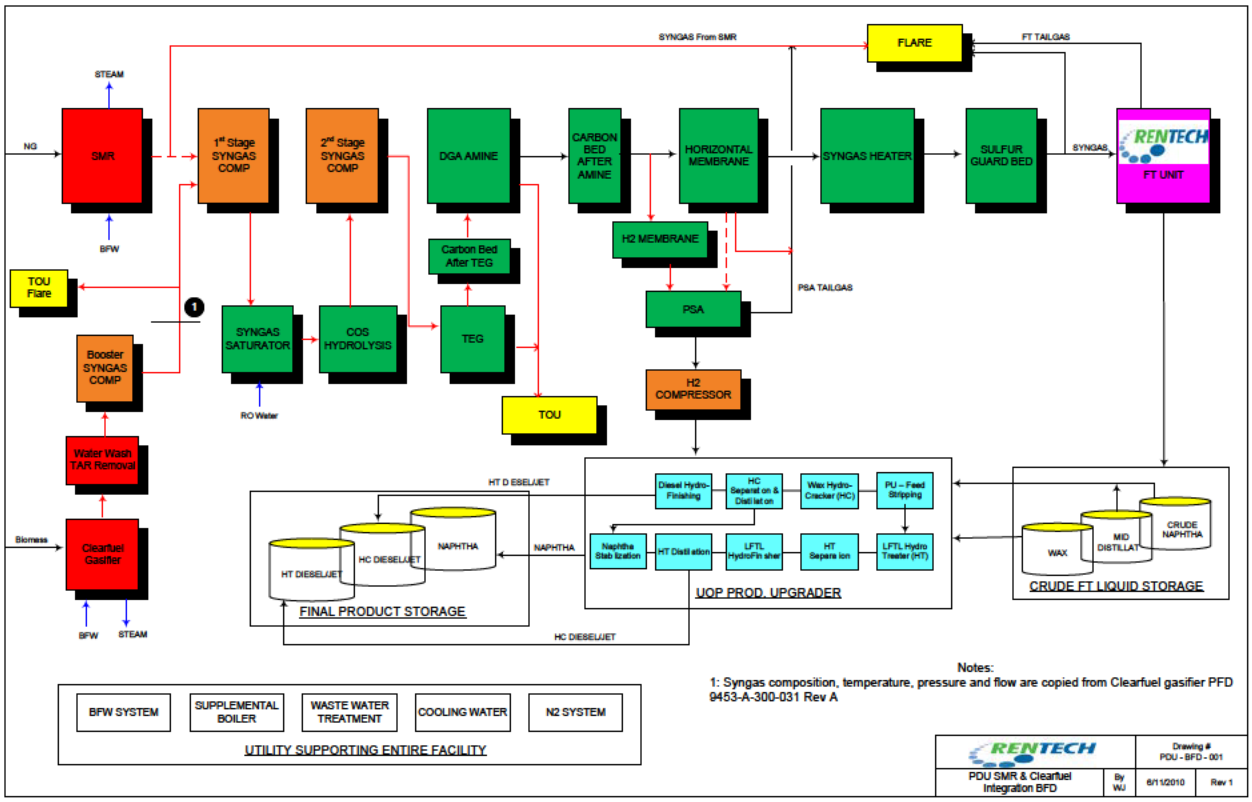


Figure 5-9: Syngas Conditioning Unit Process Flow Diagram

n biomass gasification a variety of trace contaminants are known to be formed and must be accounted for in downstream processing and synthesis gas conditioning. For example, hydrogen sulfide can cause corrosion and many trace species are catalyst poisons. Table 5-2 provides a list of contaminants of concern for FT; however, the use of iron in FT is generally more forgiving because of the higher concentration of active phases in the catalysts. Comprehensive measurements were made for all of the trace contaminants on 2/12/2013 and 2/26/2013. All of the trace contaminants were below detection limits as shown in the last column of Table 5-2. Trace sulfur measurements were made online and more frequently and will be discussed further. Ammonia is often listed in such tables, but experiments in the

PDU CSTR laboratory found no detrimental effect even at high ppm levels. A significant effort is devoted to syngas cleanup and monitoring to prevent catalyst deactivation by poisoning or other detrimental effects. It was planned to use GC/MS in selected ion mode to help monitor trace species, but this proved impractical during the IBR run and a combination of online analyzer, sulfur selective detection and stain tubes were used for monitoring. It was not possible to determine some species in the presence of H_2S because of interferences, so the complete trace analysis was performed on finished FT syngas feed where the gas was the cleanest.

Table 5-2: Typical Syngas Contaminants of Concern as FT Catalyst Poisons

Poison	Maximum Literature* FT (ppmv)	Maximum Rentech Iron FT (ppmv)	@ AE-3420 FT Feed; PDU IBR (ppmv)
COS +H_2S	0.1	0.5	< 0.02
HCN	0.01	1.0	< 0.1
HCl	0.01	0.25	< 0.05
AsH3		0.25	< 0.1
PH3			< 0.1
Metal Carbonyls			< 0.1
NOx	0.1		< 0.04
Total of poisons		1.0	< 1.0

*Review of Technologies for Gasification by E4Tech, NNFCC project 09/008

During the DOE Run, biomass derived syngas from the ClearFuels gasifier was blended with a small amount of SMR-derived syngas in order to maintain the syngas compressor suction pressure. This nearly 100% Biomass derived raw syngas was first sent to the COS hydrolysis unit to convert COS into H_2S and then sent to further compression before reaching TEG unit. The function of TEG unit was primarily to remove BTEX compounds from the biomass derived syngas stream. After the TEG unit, syngas was then sent to the AMINE unit to remove CO_2 and bulk H_2S content in the syngas. After the AMINE unit, Syngas was passed through the membrane unit operation to adjust proper H_2/CO ratio for downstream FT unit operation. The permeated gas H_2 rich stream was sent to the PSA unit for the required hydro-processing demand in the product upgrading unit. Before sending the feed to the FT reactor, a ZnO bed removed the trace amount of sulfur remaining in the syngas.

5.K FT Process Overview

The Fischer-Tropsch reactor utilized by Rentech is a slurry bubble column. Synthesis gas is fed into dual ring gas distributors at the reactor base through a mixture of catalyst and liquid hydrocarbon products (primarily wax). At the start of a run the reactor is pre-filled with a synthetic oil base stock and this inventory of start-up oil is gradually replaced with FT products as the reaction proceeds. The catalyst is an iron based FT catalyst. During a typical run, an initial load of fresh catalyst is added along with the start-up oil and activated as one large batch. During activation the iron in the fresh catalyst is transformed from ferrihydrite to a mixture of iron carbides and magnetite through dehydration, reduction, and carburization. The reactor system also has the capability of online catalyst removal and addition. Small (15-30 lb) batches of fresh catalyst are activated in a small slurry bubble column Catalyst Activation Reactor filled with start-up oil. Following the completion of a CAR activation, the activated

catalyst is pushed to the FT reactor using pressurized nitrogen. Catalyst may be withdrawn from the underflow of the slurry loops below the gas disengaging section. The FT reactor contains two external slurry loops that are described below.

Both external slurry loops are made up of a settler feed line, gas disengaging section, settler, and underflow slurry return. The settler feed line is located part way up the reactor, the degas loop returns near the top of the reactor, and the slurry return re-enters the reactor near the gas distributors at the bottom. The circulation of slurry in the sidearms is driven by the density difference between the degassed slurry and the slurry at the return and the liquid head above each sidearm. Each underflow contains a valve that can be used to regulate the slurry circulation rate. Increased slurry circulation gives improved catalyst fluidization, but increased circulation also puts an increased load on the degassing section.

The settlers in the two loops are different dimensions with one having an 18" diameter and the other a 12" diameter. In addition, the 12" settler is equipped with an electromagnet. In the 12" settler separation of catalyst from wax is achieved by magnetically enhanced settling. The electromagnet contains two independently adjustable electromagnetic coils. The applied axial magnetic field from the coils magnetizes the catalyst particles leading to magnetic agglomeration. These magnetic agglomerates are then swept out of the bottom of the settler by the liquid flow in the cone section. The "clean" wax can be continuously removed from the settler overflow. The "clean" wax goes through an additional cross flow filtration in order to meet the iron content requirements of the upgrading unit. An overview of the 12" slurry loop along with a picture of magnetically enhanced settling is shown in the following figure.

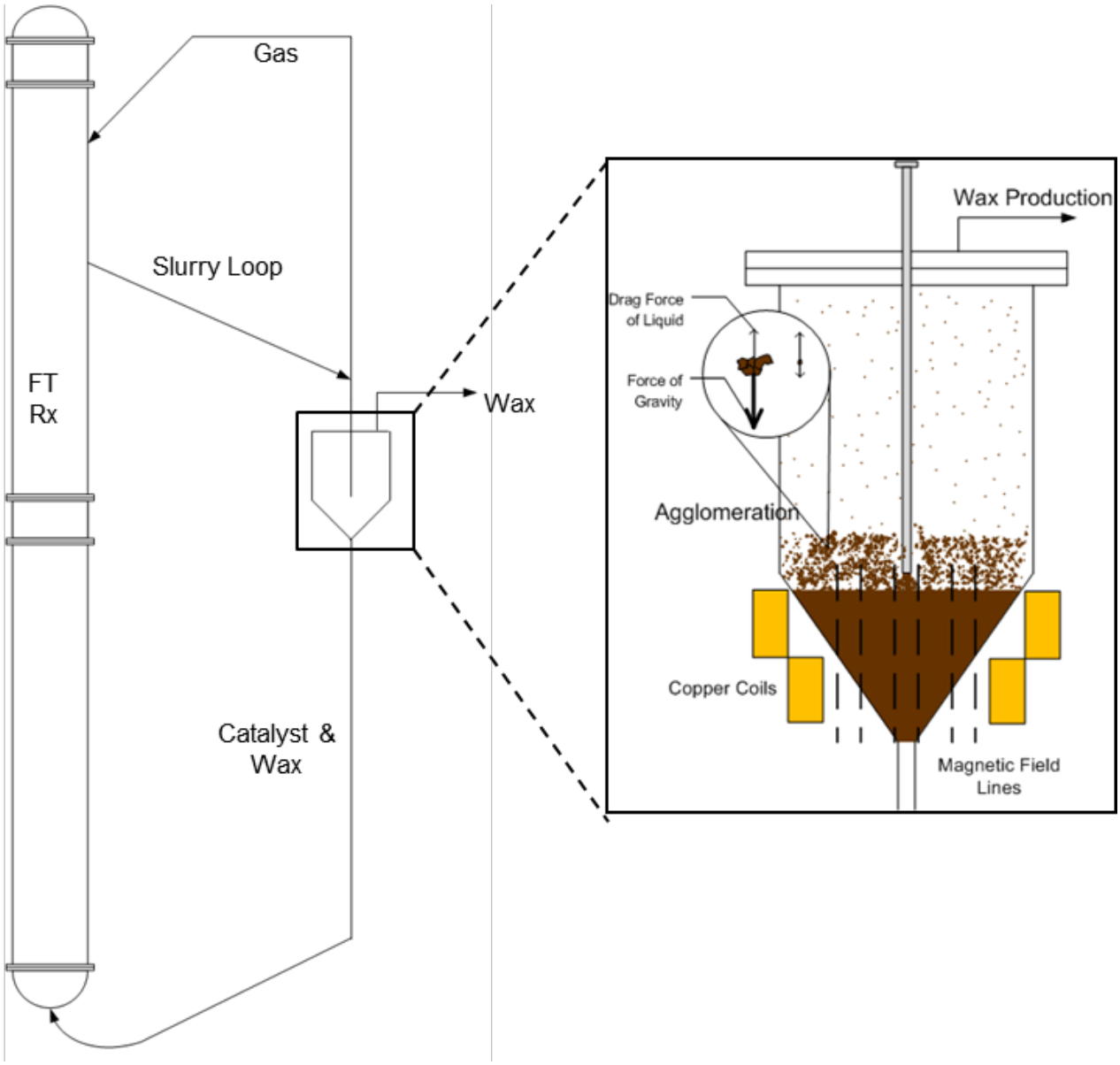


Figure 5-10: Schematic of FT Reactor Sidearm and Magnetically Enhanced Settling

The overhead gaseous products (mid-distillate, naphtha, water) leave the top of the reactor and are cooled and condensed. A portion of the non-condensable gases including unconverted hydrogen and carbon monoxide are fed to a recycle compressor and blended in with the fresh syngas feed to the FT reactor.

The heat from the exothermic reactions in the FT reactor is removed using hot oil flowing through internal cooling coils. The two key reactions Fischer-Tropsch and Water Gas Shift are listed below along with their heats of reaction.

FT Reaction :	$(1+m/2n)H_2 + CO \Rightarrow (1/n)C_nH_m + H_2O$	(165 kJ/mol)
WGS Reaction:	$CO + H_2O \Leftrightarrow H_2 + CO_2$	(41.3 kJ/mol)

Side reactions also occur, producing alcohols and other oxygenates, and the Boudouard reaction produces carbon and CO_2 from CO.

5.L Upgrading / Refining Process Overview

The main operation objective for IBR DOE Run was to achieve on specification ASTM D-975-06b No. 2D S-15 diesel fuel, using low conversion FT liquid products at the same ratio they were produced from the FT reactor. The run was executed while running both the Hydrotreater (HT) and Hydrocracker (HC) with a single vacuum column V-5706. Determine product specifications, product yields and hydrogen consumption.

A drawing of the unit configuration is shown in **Error! Reference source not found.** and the equipment list is included in Figure 5-12. The unit configuration shows stream numbers, sample locations and LIMS reference numbers, mass balance battery limits and major equipment numbers. The equipment list shows the major equipment numbers listed in the unit configuration with referenced descriptions.

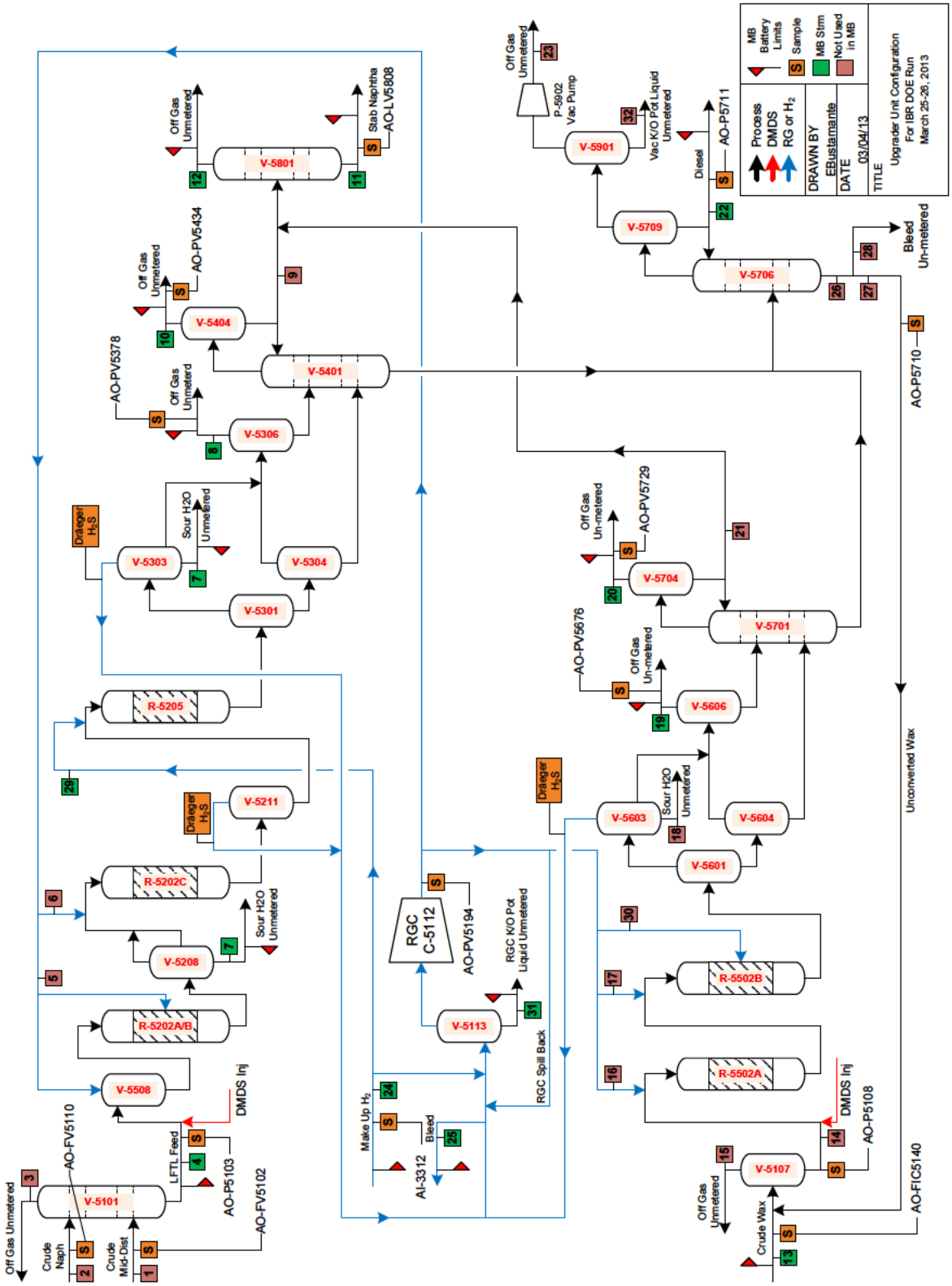


Figure 5-11: Upgrader Unit Configuration for IBR Runs

Equipment List	
Vessel Number	***Vessel Description***
V-5101	Feed Stripper
R-5202B	1st Stage LFTL Hydrotreating Reactor
R-5202C	2nd Stage LFTL Hydrotreating Reactor
V-5208	1st Stage Hydrotreating Separator
V-5301	Hydrotreater HTHP Separator
V-5303	Hydrotreater LTHP Separator
V-5304	Hydrotreater HTLP Separator
V-5306	Hydrotreater LTLP Separator
V-5401	Hydrotreater Naphtha Column
V-5404	Hydrotreater Naphtha Column Reflux Drum
V-5801	Naphtha Stabilizer
V-5601	Hydrocracker HTHP Separator
V-5603	Hydrocracker HPLT Separator
V-5604	Hydrocracker HTLP Separator
V-5606	Hydrocracker LTLP Separator
V-5701	Hydrocracker Naphtha Column
V-5701	Hydrocracker Naphtha Column Reflux Drum
R-5502A	1st Stage Hydrocracking Reactor
R-5502B	2nd Stage Hydrocracking Reactor
V-5107	Hydrocracker Feed Surge Drum
V-5706	Vacuum Column
V-5709	Vacuum Column Reflux Drum
V-5901	Vacuum Pump Suction K/O Pot
V-5211	2nd Stage Hydrotreater Separator
R-5205	Hydrotreater Unisar Reactor
V-5508	Hydrotreater Iron Guard Bed

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Upgrading Unit Equipment List
IBR DOE Run
02/25/13 – 02/26/13

Figure 5-12: Upgrader Unit Equipment List

5.M Analytical

In any process, the tasks of operation, measurement and control are inexorably coupled, and it is often said that in order to control something, it must be measured. This maxim was applied to the processes of the IBR at Rentech's PDU. The purpose of this document is to briefly describe analytical and measurement procedures required by plant operators and plant laboratory personnel for proper operation and control of the IBR and assurance of product quality. A brief summary of describing sample points and measurements of interest is also given.

M.1 General Laboratory and Process Analytical Description

The measurement of composition of various PDU process streams is needed to optimize unit operation and to validate and refine engineering models. In addition, analytical chemistry is used for quality control (QC) to validate product specifications. Most streams and products can be sampled in an offline mode for laboratory analysis; however, process analyzers are used to make online measurements of several streams in which faster turn-around time and more frequent analyses are desired or necessary. Offline samples were designated with a PI "tag" of the form "AO-XXXX," where AO stands for "analysis offline" and "XXXX" would typify a four digit equipment numeric, such as a valve, piece of equipment, etc. Similarly, on-line samples were designated with the prefix "AE," standing for "Analyzer Equipment" that is connected directly to the process, from which samples are taken and analyzed automatically. In many gas sample locations, we can take both online and offline samples, e.g., in a cylinder. PI is the data archival system and platform that is used to consolidate operational, analyzer, instrument, laboratory and engineering data. The laboratory tracks samples with a Laboratory Information Management System (LIMS) from which unique reference numbers are assigned to individual samples for analysis.

Offline samples were typically analyzed in the site laboratory or could be sent outside for contract analysis. The in-house analytical laboratory is well equipped with gas chromatographs, spectrometer, titrimeters and other various analyzers for most plant and operation needs. In some cases, we have used outside laboratories for specialized tests, such as Scanning Electron Microscopy (SEM); XRay Diffraction (XRD) and ultimate and proximate analyses. Two analyzer shelters are used to house the process analyzers for gas analysis. One (the new shelter) is used for NREL's Molecular Beam Mass Spectrometer (MBMS) for tar analysis. The original Rentech shelter houses analyzers for bulk and trace syngas analysis.

A Quality Assurance program is an integral part of delivering consistently good analytical results. Rentech Analytical Services utilizes ASTM D 6792 (Standard Guide for Quality System in Petroleum Products and Lubricant Testing Laboratories) and ASTM D 6299 (Standard Practice for Applying Statistical Quality Assurance Techniques to Evaluate the Analytical Measurement System Performance) as a basis for its Quality Assurance Program. This program includes numerous aspects related to planning, training, calibration, quality control, auditing, reporting, stated quality goals, customer satisfaction and continuous improvement. Many of the analytical methods have established QA/QC procedures, such as the use of Quality Control standards in order to ensure method compliance. Quality management concepts and principles advocated in ANSI/ISO/ASQ Q 9000 standards and ISO Guide 17025 forms the basis of ASTM D 6792. The basic components of this program are as follows:

- Calibration, testing check or QC samples
- Plotting results and looking for trends, problems or errors
- Determining repeatability

- Participation in inter-laboratory cross-checks and studies
- Training and validation
- Documentation: methods; standard operating procedures
- Quality Control procedures for each method and procedure
- Evaluation of laboratory performance

M.2 On-line Analyzers

Two analytical shelters were part of the process. The Analytical Shelter 1 is used to house the PDU process analyzers. Analytical Shelter 2 was installed to house the NREL TMBMS. Air in the shelters is conditioned and the inside temperature is maintained at a comfortable level that is conducive of stable instrument operation and ease of maintenance. Air is taken from above the shelters and used to purge the shelter continuously. Gas monitors are placed inside the shelters to ensure a safe environment. Gases for operation and calibration are located outside the shelters, or provided from plant utilities, along with heated sample conditioning and a stream selection system. Heat traced tubing bundles are used to bring process samples to the analyzer houses to help maintain sample integrity and to avoid condensation issues. Sample conditioning consists of use of membrane and filter devices to protect equipment from contamination. The sample conditioners have a built-in purge system that additionally has fast-loop functionality.

Process analyzers are used to measure gas stream composition and impurities. Table 5-3 describes the online analyzers and their major functions. The MS provides a rapid (seconds timescale) bulk compositional analysis (H2, H_2O, H_2S, CO, CO_2, CH_4, C_2H_6, C_2H_4, N_2, O_2, etc.). Each of the syngas streams will be analyzed approximately every 2 minutes and results will be fed back into the DCS. The GC/MS is used to measure trace species, particularly hydrocarbons and oxygenates and especially for catalyst protection and verification of unit operation. The process GC acts as a refinery gas analyzer, being able to measure permanent gases as well as hydrocarbons, potentially up to C_{12}. Results for the process GC are particularly important for accurate modeling. The total sulfur analyzer is a very sensitive instrument capable of measuring total sulfur down to about the 25 parts per billion concentration range for protecting the FT catalyst. Normal process variability will be observed as noise and drift in the baseline of the analyzer output from ambient plant temperature swings, pressure, and nitrogen content of syngas. So for practical purposes, occasional spike above the detection limit is to be expected. A brief description of the online analyzers is given in Table 5-3.

Table 5-3: Description of Online Analyzers (Rentech Shelter)

Analyzer	Use
MS	Rapid bulk compositional analysis
GC/MS	Trace impurities, hydrocarbons, oxygenates
GC	Refinery gases, bulk fixed and hydrocarbons
Total sulfur (Sola)	Trace total sulfur analysis down to ~ 25 ppb S

M.3 Offline Laboratory Analyzers

The Analytical and Fuels Testing Laboratory is equipped to make chemical and physical property testing to aid Catalyst Development, Engineering, plant operation and quality control of products. The laboratory is able to provide most of the typically needed analytical services. In addition, the laboratory prepares small batches of catalysts and operates microreactors, such as Continuously Stirred Tank Reactors (CSTR), in order to further evaluate FT catalysts. Special samples or samples needing specialized analyses will frequently need to be sent to outside testing facilities.

The Analytical Laboratory has capabilities to measure solids content via gravimetric filtration methods, centrifugation, gravimetric loss on ignition, and thermo-gravimetric analyzers. It has several GC and GC/MS analyzers. MS is useful for detection of species that cannot be detected by other GC detectors, especially well-suited for analysis of unknowns, composition and trace analysis. Supercritical Fluid Chromatography is used for total aromatics in diesel and olefins in gasoline. A specialized GC is used to determine boiling point distribution of materials by way of what is called "Simulated Distillation." This technique is called out in fuel specification practiced as ASDT D2887. It can rapidly determine the boiling point distribution with high accuracy and precision with a small amount of sample (<2 mL) in a largely automated process. A similar high-temperature GC is used for the analysis of wax and is able to speciate hydrocarbons up to and exceeding carbon number 100. Atomic absorption spectroscopy is used for the analysis of metals in fuels, intermediate products, wax, etc. The Analytical Laboratory has the ability to perform the following ASTM tests / methods:

- Viscosity, API Gravity/Density/Relative Density (Anton Paar)
- Ash Content Test, Cloud/Pour/Freeze Point (Phase Technologies 70X)
- Flash Point (Stanhope-Seta Pensky-Martens Closed Cup)
- Sediment and Water (Centrifuge)
- Water Content (Karl Fischer Titration)
- Cetane Index (Calculation Only)
- Copper Corrosion
- Distillation Test
- Acid and Base Numbers
- Bromine Number

In addition, the laboratory was equipped to characterize catalysts and materials using a variety of techniques such as optical microscopy, particle counters, etc. A brief description of our catalyst characterization by BET, TPR, XRD and Mössbauer spectrometry follows.

BET is the primary characterization tool for all types of catalyst. It measures the surface area, pore volume and pore size. BET is performed using a Micromeritics Tri-Star II. Samples are degassed under UHP nitrogen at 50°C for 30 minutes, 75°C for 30 minutes, and 100°C for 4 hours. After degassing, the sample tubes are inserted into the Tri-Star II and the instrument is started. Samples are immersed in a dewar containing liquid nitrogen for the duration of the test. Both adsorption and desorption curves are acquired. Upon completion of the desorption curve, the analysis is completed (usually runs 9-12 hours depending on sample type). The data analysis is done using the MicroActive Data Master software.

Temperature Programmed Reduction (TPR) is performed on all calcined catalysts. The test is performed using a Micromeritics ChemiSorb 2750. Samples are degassed under nitrogen for 1 hour at 100°C. A

furnace is placed around the sample tube and a liquid nitrogen-ICP ice bath is prepared and placed around the cold trap. The furnace is programmed to reach as high as 1000°C. During the test, the catalyst is reduced, and usually there are two reduction peaks. The temperature at which the catalyst is reduced is used to set the parameters for the CSTR runs.

XRD analysis is performed on all types of catalyst samples (filter cake, uncalcined, calcined, washed). XRD is done at the Colorado School of Mines in the Physics Department, using a Siemens Kristalloflex 810 Diffractometer. Samples are either packed into an aluminum sample plate or mounted using double-sided tape. The parameters for most scans are from 20-70 degrees, step size of 0.05, and count time of 2 seconds. For washed catalyst, sample parameters are from 5-100 degrees, step size of 0.05, and count time of 28 seconds. Some samples are prepared with a 10% ceria mixture in order to quantify hematite in the sample. XRD is used to identify whether or not the sample is crystalline or amorphous, and also what types of iron are present in the different stages of the catalyst sample.

SEM, Scanning Electron Microscope, is usually performed on washed catalysts, but has also been done for uncalcined and calcined catalysts. Samples are prepared by covering one side of a sample mount with double-sided SEM tape, and coating the tape with a single layer of catalyst particles. SEM samples are submitted to the Colorado School of Mines, and the instrument used is a JEOL 840 SEM with a PGT X-Ray analyzing system. From this test, the surface of the catalyst can be viewed at several different magnifications (100x, 200x, 1000x).

Mössbauer analysis is performed on wax samples from the CSTR Lab or the PDU. Samples are melted in the oven and homogenized, and a small aliquot is added to a jar of xylene. The wax and xylene are mixed thoroughly and then vacuum filtered to remove the liquid. What is left is the "pre-washed" material, usually with the consistency of a paste. This process removes enough of the wax so that it will not interfere with the Mössbauer analysis, but not so much as to oxidize the iron in the sample. Mössbauer is another way to identify and quantify the iron phases in the catalyst at different stages of the reaction. A small amount of the "pre-washed" material is placed in between layers of non-absorbent tape and the analysis is run at 20K and 30K, usually over a period of 24 hours or longer.

M.4 SYNGAS

Sample points, their descriptions and typical analyses that were performed or could be useful are given in Table 5-4 below. This table includes the bulk and trace components analyzed as described above. In the case of the IBR, the determination of tar was of particular interest and will be described below. Tar was determined principally by NREL's Molecular Beam Mass Spectrometer (MBMS), which was installed in a new analyzer shelter located adjacent to the CF gasifier. Tar measurement by MBMS compares favorably with traditional offline impinger sampling (Carpenter, *et. al., Energy & Fuels*, 2007 (21) pp. 3036-3043).

Table 5-4: Typical Syngas Related Sample Points and Analyses

PI Tag	Sample Description	Analyses
AO-3404C	Between C Bed	NH3, AMINE
AO-NGF1	NG Supply from XCEL	Sulfur, HC Composition,
AO-0612	Mixed NG and H2 Feed Before HX-101	HC, H2, CO, Sulfur Composition
AO-V101	Mixed NG and H2 Feed After V-101 DS unit	HC, H2, CO, Sulfur Composition
AO-V102	Mixed LP Fuel to SMR burner	HC, H2, CO, CO2, N2
AO-3502A	Horizonal membrane V-3502 permeate	CH4, H2, CO, CO2, N2
AO-3502B	Horizonal membrane V-3502 residue	CH4, H2, CO, CO2, N2
AO-3404A	C Bed Inlet	NH3, AMINE
AO-3404B	C bed outlet	NH3, AMINE
AO-3110	AMINE reboiler bottom	pH, water, color, appearance, foaming, heat stable salts
AO-3102	Rich AMINE from sock filter	pH, water, color, appearance, foaming, heat stable salts, loading
AO-3103	Rich AMINE from C filter	pH, water, color, appearance, foaming, heat stable salts, loading
AO-3109A	AMINE reflux from accumulator	pH, water, color, appearance, foaming, heat stable salts, loading
AO-3109B	AMINE reflux from accumulator	pH, water, color, appearance, foaming, heat stable salts, loading
AO-3112	AMINE reclaimer bottom	pH, water, color, appearance, foaming, heat stable salts
AO-V2065	Off-line Sample, Flue Gas after Ash Cyclone	Benzene, H2S, Sulfur Compounds
AO-V2168B	Off-line Sample, Liquid from Quench Chamber	TOC/Aromatics/AnionsIC
AO-E3102	Syngas to COS Hydrolysis	Water content
AO-3102A	Syngas from COS Hydrolysis	H2S/COS
AO-3102B	Syngas from COS Hydrolysis	H2S/COS
AO-V3026	Rich TEG from TEG Contactor	TEG/water
AO-E3037	Lean TEG to Contactor	Benzene/water
AO-V3401	Syngas to Amine	TEG
AE-2062	Syngas from CF Reformer	Tars
AE-2163	Syngas after Steam Generator	Tars
AE-2168A	Syngas from Quench Chamber V-2168	Tars
AE-3026	Syngas to TEG from C-3001	Benzene/water
AE-3400	Syngas from TEG After V-3401	Benzene/TEG
AE-3076	Syngas from CF Reformer Booster Compressor	Gas Comp, poisons (+NO)
AO-2150	Tar/Oil post make-up	Tar, solids, viscosity, density
AO-2150D	Dump Tar/Oil	Tar, solids, viscosity, density
AO-3073	Booster Compressor Lubricating Oil	Visual, viscosity, density

An off-line ECN Solid Phase Absorption (SPA) method and analyzer based on GC/FID from ECE Wasson (Ft. Collins, CO), were used for field work. The SPA method in comparison to impinge sampling has been described in detail elsewhere (Brage, et.al*., Fuel*, (1997) Vol. 76 No. 2, pp. 137-142. The key to successful sampling and analysis is to sample at temperatures of 350°C or preferably hotter and to avoid any cool condensation points, so as to avoid loss of the heaviest aromatic hydrocarbons. In the case of the SPA method, condensation occurs in the SPA cartridge, so a cooler temperature is preferred for the cartridge itself, but not the connective tubing that lead to it. In the case of SPA, if it is too hot, then the opposite problem can occur, such that loss of naphthalene or more volatile species can occur from vaporization.

M.5 FT

FT-related samples, descriptions and typical analysis options are shown in Table 5-5 below.

Table 5-5: FT Related Sample Points and Analyses

PI Tag	Sample Description	Typical Analyses
AO-V4203A	Wax Withdraw from 18" Settler Overflow	% Solids, PSD, Microscope, Sample Wt.
AO-V4203AA	Wax Withdraw from 18" Settler Overflow	% Solids, PSD, Microscope, Sample Wt.
AO-V4203B	Slurry Return from 18" Settler Underflow	% Solids, PSD, Microscope, Sample Wt.
AO-V4202AA	Wax Withdraw from 12" Settler Overflow	%Solids, PSD, Microscope, Sample Wt., High Temp GC
AO-V4202A	Wax Withdraw from 12" Settler Overflow	% Solids, PSD, Microscope, Sample Wt.
AO-V4202B	Slurry Return from 12" Settler Underflow	% Solids, PSD, Microscope, Sample Wt.
AO-4202BB	Slurry from 12" Settler Outlet Line	% Solids, PSD, Microscope, Sample Wt.
AO-V4302A	Mid-distillate from Hot Effluent Separator	NAQ
AO-V4302B	Water from Hot Effluent Separator	AQ
AO-V4304A	Mid-distillate from Warm Effluent Separator	NAQ
AO-V4304B	Water from Warm Effluent Separator	AQ
AO-V4402A	Naphtha From Cold Effluent Separator	NAQ
AO-V4402B	Water From Cold Effluent Separator	AQ
AO-V4403	Naphtha From Naphtha Product Drum	NAQ, M-426(Acid #)
AO-V4501	Mid-distillate from Mid-distillate Prod. Drum	NAQ, M-426(Acid #)
AO-V4501A	Mid-distillate before filter	Metals by AA
AO-V4501B	Mid-distillate after filter	Metals by AA
AO-V4502	Water from Water Prod. Drum	AQ, M-420(Acid #)
AO-V4601	Raw Wax from Wax Product Drum	% Solids, PSD, Composition, Microscope, Sample Wt., Metals AA
AO-V4604	Clean Wax from Clean Wax Product Drum	Metals by AA, Sample Wt.
AO-V4675	Wax from LCI Wax Surge Tank (Skid 1)	% Solids, PSD, Microscope, Sample Wt.
AO-V4681	Wax from LCI Wax Surge Tank (Skid 2)	% Solids, PSD, Microscope, Sample Wt.
AO-F4676	Clean Wax from LCI Membrane (Skid 1)	Metals by AA, Sample Wt.
AO-F4682	Clean Wax from LCI Membrane (Skid 2)	Metals by AA, Sample Wt.
AO-R4201SP1	Slurry Sample from FT Rx	% Solids, PSD, Microscope, Sample Wt., MÖssbauer, XRD, BET
AO-R4201SP2	Slurry Sample from FT Rx	% Solids, PSD, Microscope, Sample Wt.
AO-R4201SP3	Slurry Sample from FT Rx	% Solids, PSD, Microscope, Sample Wt.
AO-R4201SP4	Slurry Sample from FT Rx	% Solids, PSD, Microscope, Sample Wt.
AO-R4201SP5	Slurry Sample from FT Rx	% Solids, PSD, Microscope, Sample Wt.
AO-R4201SP6	Slurry Sample from FT Rx	% Solids, PSD, Microscope, Sample Wt.
AO-R4101SP1	Slurry Sample from FT Makeup Act Rx	% Solids, PSD, Microscope, Sample Wt.
AO-V4202C	Slurry from 12" Settler Degas Line	% Solids, PSD, Microscope, Sample Wt., Viscosity at Diff T
AO-R4101SP2	Slurry from FT MakeUp Reactor	% Solids, PSD, Microscope, Sample Wt.
AO-V4202F	Slurry from 12" Settler Inlet Feed Line	% Solids, PSD, Microscope, Sample Wt.
AO-V3100	Rich Amine	%DGA, Total Acid Gas Loading, Heat Stable Salts (HSS)
AO-P3106	Lean Amine	%DGA, Total Acid Gas Loading, Heat Stable Salts (HSS)
AO-V4104	Mid-dist from drain line	NAQ
AO-V4105	CAR Clean Wax out of F-4101A	Metals by AA, Sample wt.
AO-R4101-Drain	CAR Slurry from Side arm drain line	Metals by AA, Sample wt.
AO-F4696	Permeated wax from Bypass after filtration	Metals by AA, Sample wt.
AO-F4691	Slurry wax from Retentate loop after flow meter	% Solids, PSD, Microscope, Sample Wt.
AO-R4101-dump	CAR slurry	% Solids, PSD, Microscope, Sample Wt.
AO-R4201-dump	FTR slurry	% Solids, PSD, Microscope, Sample Wt.
AO-V4675-dump	LCI surge tank slurry	% Solids, PSD, Microscope, Sample Wt.
AO-V4681-dump	LCI surge tank slurry	% Solids, PSD, Microscope, Sample Wt.

FT-related samples, such as tailgas, aqueous product, raw naphtha, middle distillate and wax are mainly analyzed for chemical and physical properties to determine product distribution to determine catalyst activity and selectivity. Gas chromatography is used extensively for the chemical analysis because of the high degree of complexity of these materials. As discussed previously, high temperature gas chromatography is required to elute the heaviest components of wax.

Slurry samples from the FT reactor are examined to evaluate catalyst integrity, total concentration and distribution within the reactor, for operations and mass balance. Several samples from primary and secondary filtration steps are used to optimize these separations, as well as for mass balance.

M.6 Product Upgrading

Upgrading comprises of the portion of the plant that converts raw products, e.g., naphtha, light Fischer-Tropsch Liquid (LFTL), middle distillate, and wax into finished products, for example chemical grade naphtha, jet and diesel fuels that are suitable for commerce. It does this through a combination of hydrotreating, hydrocracking and distillation. Chemical analysis of products shows whether the proper conversions of oxygenates and olefins in hydrotreating or isomerization of hydrocarbons in hydrocracking has taken place. Analysis of the feeds can help estimate how much hydrogen will be consumed and to help determine how to optimize operations. Chemical and physical properties measurements of feed and products, along with analysis of off-gas and recycle gas feeds, also helps in determining mass balance, specific product yields, hydrogen consumption, etc.

As discussed above, ASTM standards are widely used as the basis for product suitability and certification, as well as to characterize chemical and physical properties of feeds and intermediate products. In particular, ASTM D2887 is used greatly to determinate boiling point distribution of hydrocarbons by GC, so-called simulated distillation. It is able to provide accurate and more precise distillation data than is possible by physical distillation, which forms the basis of many, if not most, fuel properties. A brief summary of upgrader-related sample points and typical analyses that might be performed on those sample points is given below

PI Tag	Sample Description	Typical Analyses
AO-P5103	LFTL Feed @ P5103 Suction	APG Gavity, D2887, Bromine Number, Acid Number, Water, Org Ox, GC, Sulfur, Metals
AO-LV5220A	1st Stage Liq to 2nd Stage	APG Gavity, D2887, Bromine Index, Org Ox
AO-P5212	Hydrotreated LFTL @ P-5212	APG Gavity, D2887, Bromine Index, Acid Number, Water, Org Ox, GC, Pour Point, Cloud Point, Aromatics
AO-FI5476	Distillate from Vacuum Col @ FI-5476	APG Gavity, D2887, GC, Pour Point, Cloud Point, Freeze Point, Aromatics, Sulfur, Copper Strip, Kin Viscosity, Flash Point
AO-P5405	Naphtha from Atm. Column @ P-5405	APG Gavity, D2887, Aromatics, GC
AO-P5108	FT Wax @ P-5108	APG Gavity, HT Sim Dis, Bromine Number, Acid Number, Water, Org Ox, Metals
AO-LV5544	1st Stage Liq to 2nd Stage @ LV-5544	Water, Bromine Index, Org Ox, Metals
AO-E5504	2nd Stage Rx Eff Liq @ T/S O/L of E-5504	HT SimDis
AO-PV5676	Cold LPS Gas @ PV-5676	GC
AO-PV5729	Atmos Col Off-Gas @ PV-5729	GC
AO-P5711	Distillate from Vacuum Col @ P-5711	APG Gavity, D2887, GC, Pour Point, Cloud Point, Freeze Point, Aromatics, Sulfur, Copper Strip, Kinetic Viscosity, Flash Point
AO-P5705	Naphtha from Atm. Column @ P-5705	APG Gavity, D2887, Aromatics, GC
AO-P5710	Vac Col Bottoms @ P-5710 Discharge	APG Gavity, HT Sim Dis, Kin Viscosity @ 100, 210F
AO-LV5577	Distillate from Separator @ LV-5577	APG Gavity, D2887, GC, Pour Point, Cloud Point, Freeze Point, Aromatics, Sulfur, Copper Strip, Kinetic Viscosity, Flash Point
AO-PV5580	Separator Off-gas @ PV-5580	GC
AO-FV5570	Makeup Gas @ FV-5570	GC
AO-LV5807	Stabilized Naphtha @ LV-5808	APG Gavity, D2887, GC
AO-PV5817	Off-gas from Column @ PV-5817	GC
AO-PV5194	Recycle Gas @ PV-5194	GC
AO-FV5193	Recycle Gas @ PV-5193	GC
AO-FV5180	Hydrogen M/U Gas @ FV-5180B	GC

Table 5-6: Upgrader Related Sample Points and Analyses

M.7 Biomass Feed

The biomass feed sample points and typical analyses that were performed are shown below in Table 5-7. Density and moisture determinations were done in-house and used to aid operations and process analysis. The bulk density determination uses a vessel of fixed size in which the sample is placed and shaken to induce some settling and the mass is measured with a balance of sufficient mass range and precision. Particle size distribution was determined using 8" standard sieves, a shaker table and balance. Ultimate and proximate analyses were performed by Huffman Laboratories, Golden, Colorado.

Table 5-7: Upgrader Related Sample Points and Analyses

PI Tag	Sample Description	Typical Analyses
AO-Z1011	Wet Biomass from Truck	Density, Moisture, Ultimate/Proximate
AO-T1425	Ground/dry biomass	Density, Moisture, Ultimate
AO-ME2068	Ash/char from Cyclones	PSD, Ultimate, Moisture, Density

Table 5-8 below is inclusive of the ultimate and proximate analysis of the feeds run during the IBR run.

Table 5-8: Ultimate & Proximate Feed Results Inclusive of CF IBR

		Ultimate Analysis (mass% dry basis)					Proximate Analysis (mass % dry basis)				
Feed Type	**Reference #**	C %	H %	N %	O % (diff)	S %	Ash %	Vol Matter %	Fixed C %	HHV BTU/lb	Tot Moisture % (as recvd)
Oxford Woody Waste - Sx T1	214011-01	45.81	5.48	0.47	38.80	0.08	9.36	70.89	19.8		25.36
Oxford Woody Waste - Sx L1	214011-02	43.60	5 28	0.53	36.43	0.07	14.09	68.05	17.9		26.04
Baggase Sx A	214011-03	44.36	5.47	0.24	39.22	0.05	10.66	72.95	16.4		38.24
Baggase Sx B	214011-04	44.69	5.46	0.23	39.53	0.04	10.05	74.22	15.7		50.98
Baggase Sx C	214011-05	44.88	5 55	0.21	39.89	0.04	9.43	74.16	16.4		41.53
kremling Wood Pellets - AR	112212-01	50.52	6 20	0.05	42.72	0.01	0.50	80.08	19.4	8711	7.10
kremling Wood Pellets - CF DG	41712-01	51.33	6.16	0.05	42.78	0.02	0.37	80.27	19.4	8784	5.89
Alabama Pine Microchips	125712-01	51.34	6.12	0.08	42.05	0.02	0.39	79.54	20.1	8776	59.94
North Carolina Yellow Pine	157212-01	51.40	6.13	0.10	41.94	0.02	0.41	78.49	21.1	8784	17.86
Western Forestry Wood Chips DG	153512-01	50.78	6 38	0.08	41.80	0.02	0.93	79.80	19.3	8791	26.03
Western Forestry Aug-Sept Mix	189112-01	51.83	6 20	0.09	40.97	0.02	0.89	78.86	20.3	8968	31.96
Alabama Aspen	176612-03	49.40	6 00	0.25	42.58	0.05	1.72	78.34	19.9	8508	12.11
Waste Management Sorted Cellulose	176612-02	49.40	6 00	0.25	42.58	0.05	1.72	78.34	19.9	8508	30.74
Bagasse Resampled 9/14/12	189512-01	46.10	5 52	0.20	39.62	0.04	8.52	74.01	17.5	7857	58.88
Upper Penisula Biomass	112413-01	48.99	5 98	0.09	43.58	0.02	1.35	81.43	17.2	8348	36.55
North Carolina Aspen	112413-02	49.19	6 00	0.28	42.61	0.03	1.90	78.78	19 33	8436	17.94
Alabama White Pine	112413-03	50.85	5 92	0.13	42.52	0.01	0.58	78.06	21 36	8675	30.11
Western State Forestry	112413-04	51.67	6 09	0.13	41.26	0.01	0.84	78.40	20.76	8923	46.16
50/50 Bagasse/Western State Forestry	112413-05	46.77	5 61	0.22	39.48	0.02	7.90	74.16	17 94	8034	17.04
Western State Forestry	112413-06	51.31	6.13	0.09	41.81	0.01	0.64	80.78	18 58	8928	54.60

AR As Received, DG Dried and Ground

Plant and utilities

Several sample points on plant utilities, particularly water, are present for taking samples for analyses to aid operations or for environmental reasons, e.g., to determine if process or wastewaters need treatment. These sample points, descriptions and typical analyses are given below in Table 5-9.

Table 5-9: Utility-Related Sample Points and Analyses

PI Tag	Sample Description	Typical Analyses
AO-W8201	Make up Water	Conductivity, M-Alkcalinity, Hardness
AO-WV107	V-107 Blowdown Water	Conductivity, P-Alkalinity, M-Alkalinity, Sulfite, pH
AO-WV106	SMR BoilerFeed Water to (DA)	Conductivity, Hardness
AO-WV104	Soft Water to SMR	Hardness
AO-W8001A	Soft Water to Temp Boiler	Hardness
AO-W8001B	Temp Boiler Blowdown	Conductivity, P-Alkalinity, M-Alkalinity, Sulfite, pH
AO-W8001C	Temp Boiler Water (DA)	Conductivity, Hardness
AO-W8001D	Temp Condensate return	TOC/IC, Conductivity, pH, Chlorides
AO-W8250	Cooling Tower Water	TOC/IC, Conductivity, M-Alkalinity, Hardness, pH, phosphonate, CL, Bacteria, SRB, Skin T
AO-V2168B	Liquid from Quench Chamber	Aromatics and other
AO-W7000	Storm runoff/vault waste water	TOC, pH

5.N Data Collection and Management

There are three types of data collected, of which two types are available in and through the PI historian at the PDU (Process Demonstration Unit). First, the raw data from the PDU is collected by the DCS (Distributed Control System) in the plant and archived in the DCS historian according to compression and exception settings imbedded in the DCS. These archived data are sent to the PI historian and can be retrieved through the PI-DataLink add-in in Excel. The second type of data reflects the analytical results of the samples taken at the PDU. These results are collected in SampleTracker (LIMS – a Laboratory Information Management System) and retrieved by PI using SQL (Structured Query Language) queries. In addition to these two types of data, information (feedstock used, measured weights in the plant, constants used for calculations, and such) as well as calibration data have been shared through communication, email, and in an Excel summary file. This report explains the movement of the data and how it was retrieved for the final reports.

N.1 Process Data to DCS Historian

The data from the process is collected by the DCS system in the plant and archived in the DCS historian located in the control room of the PDU according to the compression and exception settings embedded in the DCS retrieval system. Simultaneously, the raw data is made available on the pre-prepared control display screens in the control room; the values displayed on these screens have not been under compression or exception, but reflect the values directly from the items (thermocouple, pressure controllers, etc.) in the plant.

The archived data that is stored in the DCS historian has undergone compression and exception according to the default settings of the DCS and these settings are only changed per request.

N.2 Process Data in PI Historian

The archived data in the DCS historian is transferred to the PI historian using a PIOPCHDA (PI Object Linking and Embedding for Process Control Historical Data Access) Interface. This archived data does not undergo any further compression or exception (it has been unchecked for all tags). This data is also available through the PI-DataLink add-in in Excel for data retrieval and perusal. This archived data is also displayed in the Process Screens developed for the engineers using PI-ProcessBook.

N.3 Process Data in Summaries

The data in the DOE summary (DOE Feedback.xls) was retrieved using the PI DataLink add-in in Excel and is the hourly averaged filtered value during the time of the DOE run. The filter applied with respect to the percent opening of the syngas flow from the CF gasifier; data was averaged when this opening was larger than 0.95%. The calculated data tab in the PI DataLink add-in was used to retrieve this data.

Similarly, the DOE performance data (DOE Performance Test Base 022713.xls) was also retrieved using the PI DataLink add-in in Excel, but daily average values were calculated using the same filter as for the DOE summary.

N.4 Analytical Results

Analytical results are stored in the LIMS System (SampleTracker) and are stored in the PI historian using embedded SQL queries for each analytical tag (ID Point) through a RDBMSPI interface (rdbodbc) connected to an SQL DBMS (database management system).

The analytical data was retrieved using the compressed data tab in the PI-DataLink add-in in excel and no average or filter was used. Samples were only taken during the periods that the DOE Run was underway, and it is assumed that the value does not change until the next sample is taken.

The total spectrum analysis of the different products is summarized in the following files and is not available through the PI-System:

1.	Component Analysis of Naphtha	:	DOE Naphtha Analysis
2.	Component Analysis of MidDistillate	:	DOE MidDistillate Analysis
3.	Component Analysis of Water Product	:	DOE Water Analysis
4.	Component Analysis of Wax Product	:	DOE Wax Analysis

Samples were taken every other day for analysis and the results for the component analysis is reported per day per sheet in their respective Excel file.

Some samples were sent to outside analytical laboratories for analysis (tar, proximate, ultimate analysis and densities), and these were communicated by means of email and reports.

N.5 Other Data

The constants used, as well as information regarding the biomass feed and weight, are entered in a separate sheet in the Excel file called DOE Performance Test Base 022713.xls which was supplied to SAIC for their evaluations. Most of these constants were retrieved on a daily basis by manual recordings done by the plant personnel.

5.O Wastewater Treatment

As part of the CF-RTK IBR a scope addition was included to build a wastewater treatment plant to treat the wastewaters produced by the project. The wastewater from the ClearFuels gasifier section, Fischer-Tropsch reactor section and other minor process streams in the plant were collected and sent to a Sump/Vault where the dirt and debris is removed. This Vault contains an Oil Skimmer to remove any free oil and grease on the water surface.

The water from the Sump is transferred using a pump to the Equalization Tank which stores and provides hydraulic and load equalization. A pump transfers water from the equalization tank at a constant rate to the Anoxic Tank. A set of internal recirculation pumps recycle Mixed Liquor Suspended Solids (MLSS) from the two Aeration Tanks to the Anoxic tank. Under anoxic conditions, elevated nitrate levels will be converted into Nitrogen and CO_2 in the presence of readily biodegradable COD, phosphoric acid and sodium hydroxide. The pH in the anoxic tank is controlled by a pH analyzer which controls the caustic metering pump.

From the anoxic tank, the MLSS flows by gravity to the two biological treatment tanks (Aeration Tanks) arranged in series, where the oxygen is transferred to the mixed liquor using an aeration system. A dissolved oxygen (DO) concentration of 2 mg/l is maintained by monitoring the DO level and controlling the aeration blowers by variable frequency drives (VFDs).

Aeration tank mixed liquor is pumped to the Membrane Operating System (MOS) tanks. The MOS tanks contain Petro™ UF hollow fiber membrane modules submerged in the mixed liquor. Filtrate from the mixed liquor is withdrawn from the membranes by rotary lobe positive displacement pumps. Air is injected at the bottom of each membrane module for scouring collected solids from the membrane surfaces to maintain "clean" filter surfaces. Concentrated mixed liquor overflows to the outlet of the MOS tanks and discharges to the inlet of the lead aeration tank.

Periodically, Return Activated Sludge (RAS) is wasted (removed) from the biological treatment system. This wasted activated sludge (WAS) is discharged by road tanker for outside disposal. Filtrate from the MBR system is stored in the filtrate storage tank. The Filtrate will be used for internal reuse or pumped to the city sewer (POTW).

After an extended operating time, the trans-membrane pressure (TMP) across the membranes will increase due to fouling and partial plugging of the membrane surfaces and pores, respectively. When this measured and monitored TMP reaches a set-point value, a maintenance clean (MC) cycle is automatically signaled and initiated. A Clean-in-place (CIP) occurs as a planned event as membrane fouling slowly increases as MC cycles fail to restore the clean membrane operating flux at the target TMP operating range.

SECTION 6 DATA ANALYSIS

6.A DOE Run (PERIOD 4) Objectives and Overview

The primary goal of the DOE run was to achieve 240 hours of integrated biorefinery (IBR) operation using biomass-derived syngas to produce on-specification renewable drop-in fuels. Due to concerns of operational stability, a small amount of steam methane reformer (SMR) syngas was blended into the Rentech-ClearFuels produced syngas and 200 hours of integrated operation was achieved, with greater than 95% ClearFuels derived syngas feeding the downstream Rentech Fischer-Tropsch (FT) unit.

During the DOE Run the Rentech-ClearFuels unit was operated at sufficient feedrates in order to enable the FT Reactor to operate above minimum acceptable gas superficial velocity, with the FT tailgas recycle operational. This required an average of 9,040 SCFH of Rentech-ClearFuels syngas, which at an average gas productivity of 22.3 SCF/lb of dry feed, means that biomass feedrates average approximately 405 lb/hr or 4.86 DTPD.

The syngas H_2:CO ratio from the ClearFuels gasifier was controlled at between 1.55 and 2.64 during the DOE Run. Syngas tar contents (excluding benzene) measured by NREL during the DOE run at the HEHTR outlet and at the Booster Compressor suction were 636 ppm and 22 ppm, respectively. See the Syngas Conditioning Unit (Unit 300) DOE Run Report for additional information on syngas quality downstream of the Rentech-ClearFuels unit.

For the FT unit compromises between the desired and actual H_2/CO ratio, fresh feedrate, and recycle ratio had to be made during the run. As a result of these compromises, a higher H_2/CO ratio was fed to the FT Reactor than originally planned and the resulting product slate was shifted to lighter products. There were no adverse effects observed from feeding >95% biomass derived syngas to the FT Reactor. The tailgas recycle performed well during the run and the overall CO conversion increased substantially as a result. Product selectivities were not impacted by recycle.

Product upgrading / refining operated from February 14, 2013 to February 26, 2013, producing a total of 32 barrels of diesel, and 8 barrels of stabilized naphtha. The overall as produced Diesel and Naphtha yield averaged 80 wt% and 14 wt%, respectively. Matching the feed ratio produced from FT for the DOE test, the yields were 74 wt% and 19 wt%.

A.1 DOE Run Start and End

The DOE run (Independent Engineer Run or PERIOD 4) was commenced at 8:00am on February 12, 2013 and was completed by 8:00am on February 27, 2013.

A.2 Downtime

During the DOE IE performance test, there were interruptions in the syngas production that were not significant enough to restart the Performance Test. A short description of the (primary) reason for each downtime period is provided also:

Table 6-1: Explanation of Downtime During DOE IE Run

Date	Approx. Downtime (hrs)	Primary Reason for Downtime
2/12/2013	2	Booster Compressor control problems & Discharge Cooler fouling.
2/13/2013	3	Booster Compressor (cont.) and feed supply.
2/14/2013	8	Pluggage in Dryer Feed Cyclone
2/15/2013	20	Pluggage in Dryer Feed Cyclone and 'Y' in HEHTR feed line
2/16/2013	24	Heat up of HEHTR after Dryer Cyclone & Feed line 'Y' pluggages cleared.
2/17/2013	15	HEHTR trips due to coil thermocouple failures
2/21/2013	20	Steam Mixing Vessel pluggage
2/22/2013	18	Heat-up after Steam Mixing Vessel pluggage cleared
2/25/2013	8	HEHTR coil pluggage and steam-out
2/26/2013	9	Booster Compressor Discharge Cooler plugging

6.B Material Handling

B.1 Biomass Feedstocks

Biomass feedstocks processed during the DOE Run, along with the start time and date for each new feedstock, are included in the table below:

Table 6-2: Feedstocks used During DOE Independent Engineers Run

Feedstock Processed	Start Time & Date
Wood Pellets	8:00am, 2/12/2013
Colorado Soft Wood Chips	7:50am, 2/13/2013
North Carolina Poplar/Birch/Aspen Mix	12:15pm, 2/17/2013
North Carolina Loblolly Pine	3:00pm, 2/18/2013
Alabama Loblolly Pine	7:45am, 2/19/2013
Colorado Soft Wood Chips	3:45pm, 2/19/2013
50/50 Bagasse/wood chip mix	3:30am, 2/23/2013
Bagasse	10:00am, 2/25/2013
Wood Pellets	11:50am, 2/25/2013

The 100% bagasse run was terminated shortly after it started due to problems feeding the bagasse out of the Truck Unloader and due to excessive Dryer fines carryover.

The Feedstock Proximate Analysis for each biomass feedstock is summarized below:

Table 6-3: Feedstock Proximate Analysis

Feedstock	Proximate Analysis (dry, wt%)			Total Moisture (wt% as received)
	Vol Matter %	Fixed C %	HHV BTU/lb	
Wood Pellets	80.27	19.4	8784	5.89
Colorado Soft Wood Chips	80.78	18.58	8928	54.60
North Carolina /Aspen Mix	78.78	19.33	8436	17.94
North Carolina Loblolly Pine	78.49	21.1	8784	17.86
Alabama White Pine	78.06	21.36	8675	30.11
50/50 Bagasse/wood chip mix	74.16	17.94	8034	17.04
Bagasse	74.22	15.7	7522	50.98

The Ultimate Analysis of each biomass feedstock is provided below:

Table 6-4: Feedstock Ultimate Analysis

Feedstock	Ultimate Analysis (dry, wt%)					
	C%	H%	N%	O% (diff)	S%	Ash%
Wood Pellets	51.33	6.16	0.05	42.07	0.02	0.37
Colorado Soft Wood Chips	51.31	6.13	0.09	41.81	0.01	0.64
North Carolina /Aspen Mix	49.19	6.00	0.28	42.61	0.03	1.90
North Carolina Loblolly Pine	51.40	6.13	0.10	41.94	0.02	0.41
Alabama White Pine	50.85	5.92	0.13	42.52	0.01	0.58
50/50 Bagasse/wood chip mix	46.77	5.61	0.22	39.48	0.02	7.90
Bagasse	44.69	5.46	0.23	39.53	0.04	10.05

B.2 Biomass As-Received and Dried Moisture

In order to calculate the dry biomass feedrate to the HEHTR, it is necessary to correct the Weigh Belt Feeder cumulative weight (for each 24 hour reporting period) for moisture. In addition, the dried biomass moisture is monitored to ensure that drier operation is satisfactory. The trend for the as-received and dried biomass moisture is provided below:

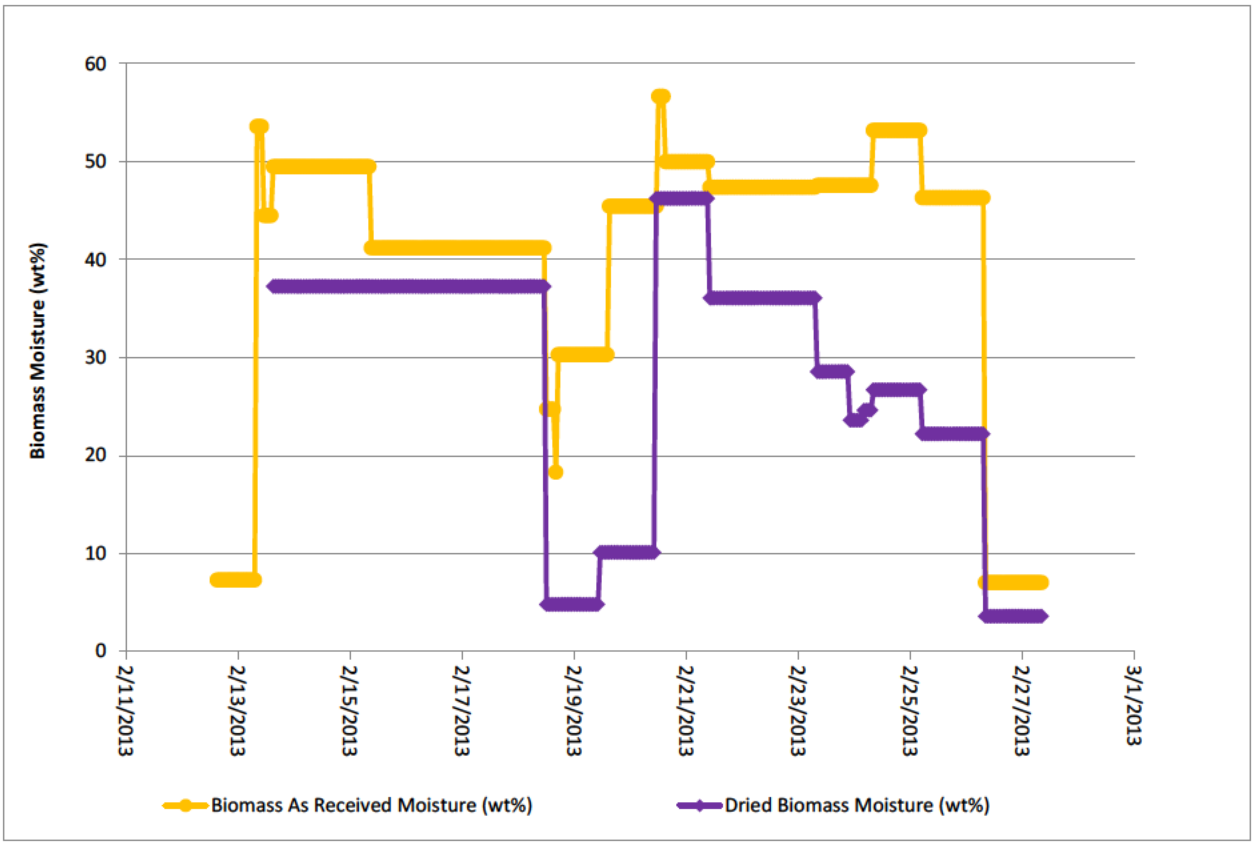


Figure 6-1: Biomass Moisture Trends During DOE IE Run

Steam coil leaks, due to freezing during cold weather, in the supplemental heat section of the Dryer were discovered following the Performance test. This leak resulted in higher dried biomass moisture contents than would otherwise have been the case during the run. This is the source of the relatively high dried biomass moistures in the above chart (> 30 wt. %). The higher than normal dried biomass moistures resulted in lower thermal efficiencies than would normally have been expected, as described below.

B.3 Biomass Drying Heat Supply

Heat from the HEHTR fluegas is used to dry incoming biomass, along with additional steam, as needed. The fluegas flow rate to the Dryer, steam flow to the Dryer and the fluegas temperature exiting the Dryer trend is provided below:

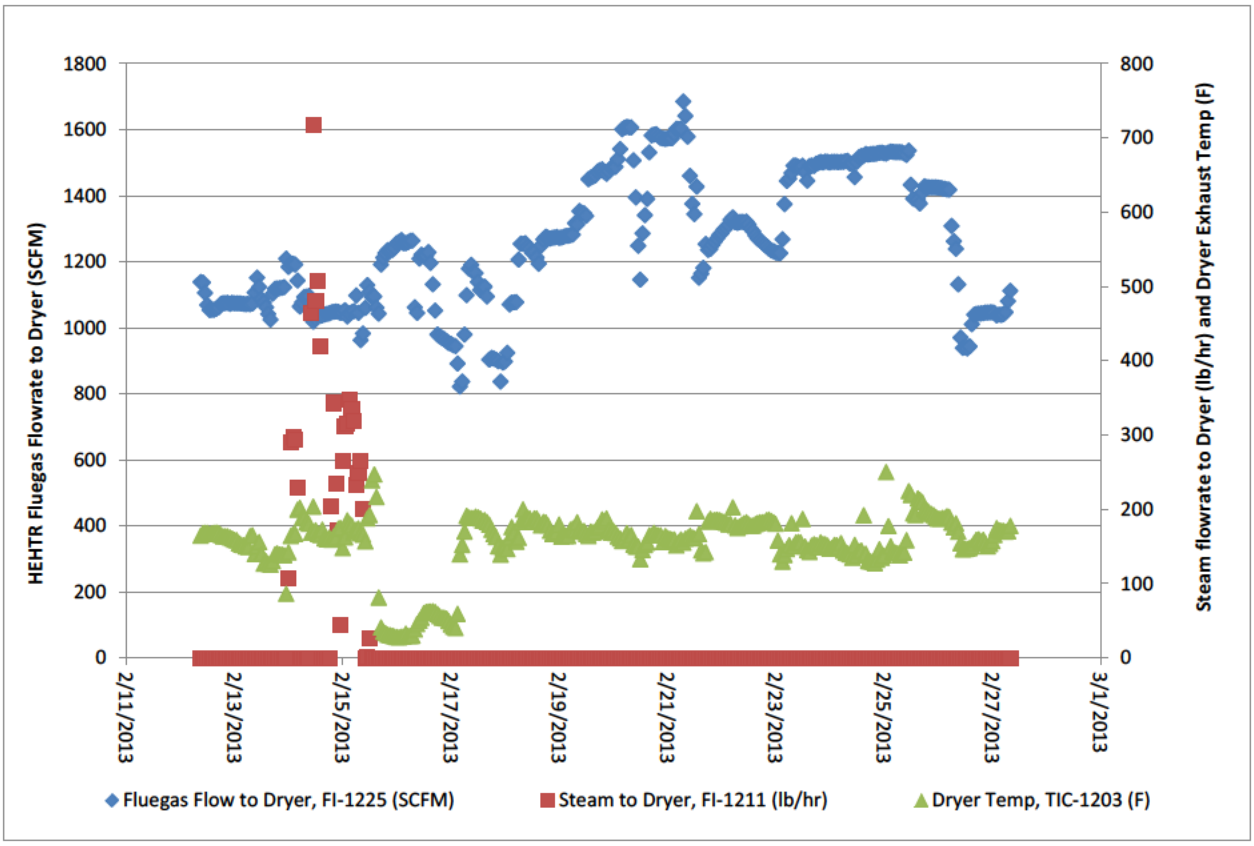


Figure 6-2: Biomass Drier Operating Trends During the DOE IE Run

As described above, multiple steam coil failures prior to the DOE Run resulted in steam being isolated in two of the three steam coils in the Dryer and limited the heating capacity in the Dryer. The steam coils were custom fabrication, and the lead time did not allow for replacement prior to the DOE Run.

B.4 High Moisture Feedstock

Even with the HEHTR being run at higher excess air levels than originally anticipated, in order to maximize fluegas heat available for biomass drying, it is evident from the dried biomass moisture levels in Figure 6-1 above, that the biomass was not being dried adequately for much of the DOE test run. At these higher-than-anticipated dried biomass moisture levels, the firing in the HEHTR has to be increased in order to provide absorbed duty, not just for the required endothermic reforming reactions, but also for the duty required to dry the biomass. It is not thermally efficient to provide this drying duty by additional reformer firing, instead of using lower temperature heat sources (e.g. HEHTR fluegas).

B.5 Biomass Grinding and Drying

This technology is conventional and not necessarily a core part of the Rentech-ClearFuels technology offering. Specific to this technology is the requirement to dry to approximately 15 wt% or less and to reduce the feedstock at least to <1/4".

It may be advantageous, particularly for higher syngas H_2:CO applications, to be able to grind the biomass to smaller particle sizes. The Dryer Fines processed at Livingston is nominally <1/16" material and produced a higher H_2:CO syngas than the larger feedstock. Hence, for applications that require higher syngas H_2:CO, it is recommended that a <1/16" feedstock is prepared. For other applications, a <1/4" feedstock requirement is still acceptable.

The PDU grinder was not able to process high moisture feedstocks (40–50 wt% moisture as received) and grind the particles using the supplied 3/16" outlet screen under the installed configuration. There were problems with screen binding (although it worked fine with dryer feeds). As a result, a ¼" screen was typically used. Both the PDU and the Livingston plant grinder produced stringy feedstock that had difficulties flowing out of the feed hopper. An alternative configuration using screens and recycle to the grinder is recommended to produce a more uniform and tighter size distribution material.

During initial commissioning runs, foreign material was present in the feedstock (still within specification) which caused premature wear to the knives in the grinder. Knife materials need to be selected and reviewed properly to ensure adequate knife life/sharpness.

B.6 Biomass Feed Storage

Problems were experienced both at the PDU and at the Livingston pilot plant with steady feeding of biomass out of the conical bottom hoppers employed at both plants. It is a technology requirement that a live bottom feed hopper is employed to store the required biomass feed inventory upstream of the reformer. Determining the flow and controlling at a steady mass flow to the reformer was a constant problem at both the Livingston plant and at the PDU. This needs to be considered in feed system redesign efforts.

B.7 Pressure Boundary System

The rotary valves utilized at the Livingston Pilot plant and the rotary valve installed at the Commerce City PDU both suffered from steam backflow. To minimize backflow of steam the reformer was limited to an operating pressure less than 20 psig at the reformer inlet. The steam backflow caused plugin in the feed system and reduced the achievable on-stream factor for both units due to the need to intermittently clear plugging in the feed screw.

In general, the operating experiences gained with sealing pressure rotary valves, feeding a dry/fine feed, was not favorable.

B.8 Feeding Multiple Coils

During commissioning the feed splitter plugged multiple times. The system was modified, with more emphasis on flow modeling and symmetry, with reasonable results. Larger units will need a multiple configuration; there are two recommendations to solve this step.

First is further design of a biomass splitter, relying on mechanical design or symmetry and mot moving parts to accomplish feed separation.

The second is to evaluate a single controlled feed to each HEHTR coil. It is necessary to provide for multiple feeds out of a single feed surge vessel. Given this is the case, it is considered preferable from a

cost and operability/reliability perspective to make this surge vessel pressurized and to utilize a (redundant) lock hopper system to feed into this pressurized surge vessel/charging vessel, from the bulk feed storage hopper (live bottom bin), versus providing for multiple pressure boundaries (one pressure sealing rotary valve for each coil).

This is the design described in the commercial design below. This is essentially the design employed at the FERCO Silvagas plant a Burlington, VT, but only a single outlet was provided for that pressurized vessel, as there was only a single gasifier feed.

Utilizing compressed fluegas (cooled and moisture trapped) as a sealing gas was successfully demonstrated at the Livingston pilot plant, and should be included in the design of any commercial unit (e.g. compressed fluegas can be used as pressurizing gas in lock-hoppers above the surge vessel).

The vented gas from the lock-hoppers would need to be passed through a dust collector, but could then be vented directly to atmosphere.

The lock-hoppers could be pressure vessels or could be fabricated as piping spools, depending on the feed requirements, but excessive cycling should be avoided to prevent maintenance problems with the lock-hopper valves.

Each pressurized feed from the Surge Vessel will be controlled via a variable speed auger, on speed control. Each feed screw will provide feed to a separate steam/mixing vessel, feeding a single downstream reformer coil.

A separate slide valve will be provided to isolate the feed to each coil on a shut-down or trip. Compressed fluegas can be utilized to provide a small constant purge from the Surge Vessel, in normal operation.

6.C Gasification

C.1 Rentech-ClearFuels Process Schematic

The following schematic shows the Rentech-ClearFuels unit configuration, downstream of the Feed Hopper, during the DOE Run.

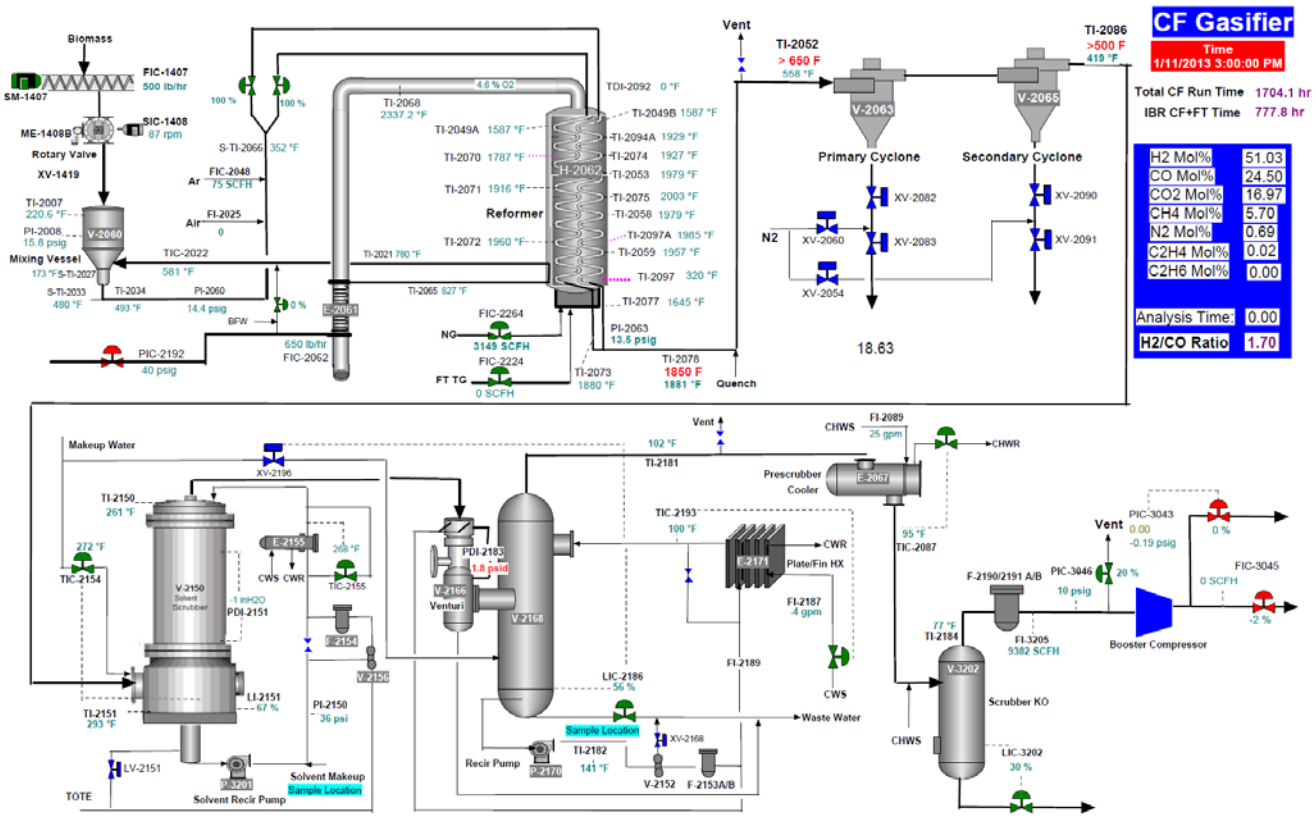


Figure 6-3: Rentech-ClearFuels Unit Configuration

C.2 Rentech-ClearFuels DOE Run Summary Data

Table 6-5: Data on HEHTR Operations during DOE IE Run (Also see Table 5-4)

2/12/13 8:00 AM		FILTER			0	1	2	3	4	5	6	7
		'FIC-3045/PID1/OUT.CV' > 1		hours run in 24 hour period	22.9	20.6	16.3	3.9	0.0	8.8	24.0	24.0
PDU DOE					22.9	43.5	59.8	63.7	63.8	72.6	96.6	120.6
		Start Time		Unit	2/12/13 8:00	2/13/13 8:00	2/14/13 8:00	2/15/13 8:00	2/16/13 8:00	2/17/13 8:00	2/18/13 8:00	2/19/13 8:00
		End Time			2/13/13 8:00	2/14/13 8:00	2/15/13 8:00	2/16/13 8:00	2/17/13 8:00	2/18/13 8:00	2/19/13 8:00	2/20/13 8:00
CF Gasifier Conditions	Biomass Feed to Gasifier	calc (F95 CF Calcs)		DTPD	4.31	3.31	3.41	1.07		2.06	4.61	5.73
	SH Steam Feed Rate	FIC-2062/PID1/PV.CV	E-2061 Steam flow to the Steam Superheater at the Gasifier	lbs/hr	662.86	637.58	595.51	538.12		635.53	650.00	605.43
	NG Fuel Usage	FIC-2264/PID1/PV.CV	Natural Gas Fuel to Gasifier Flow Rate	SCFH	3296.80	3415.88	3098.59	3116.95		3315.67	3400.18	3758.59
	Reformer Process Temperature	TI-2078/AI1/PV.CV	Combined Process temp Exit coils -Thermowell in 6" header of the Gasifier	F	1857.60	1857.63	1845.08	1830.07		1832.36	1833.87	1848.56
	Reformer Process Pressure	PI-2063/AI1/PV.CV	Gasifier Outlet Pressure	psig	13.94	14.37	13.96	13.90		13.77	16.19	17.55
	Total CF Syngas to FT per day	calc		scf	229418	193914	134634	27654		74943	210408	212494
	Syngas Flow From Gasifier	FI-3205/AI1/PV.CV	Syngas Flow from scrubber to booster compressor	SCFH	10037.02	9406.43	8235.38	7039.96		8547.61	8766.99	8853.93
		FIC-3045/PID1/PV.CV	ClearFuels Syngas Flow	SCFH	10325.06	10245.61	8882.83	7729.66		8929.68	9628.59	9827.76
	Ash Content in Char/Ash	AO-ME2068-ASH	Percent Ash in a sample of the ash/char from the Cyclones (Proximate Analysis)	wt%	%	12.51	12.37	13.40		18.08	21.61	25.15
CF Syngas	Syngas H2%	AI-3076_RGA/AI-3076_RGA_E.CV	H2 in the Gasifier Gas product to the FT Reactor using RGA analysis	mol%	49.94	50.05	52.30	49.93		51.30	50.35	47.68
	Syngas CO%	AI-3076_RGA/AI-3076_RGA_H.CV	CO in the Gasifier Gas product to the FT Reactor using RGA analysis	mol%	23.97	22.83	23.38	23.22		19.46	20.24	25.77
	Syngas CH4%	AI-3076_RGA/AI-3076_RGA_F.CV	CH4 in the Gasifier Gas product to the FT Reactor using RGA analysis	mol%	6.49	6.74	5.29	7.10		6.16	7.25	7.77
	Syngas CO2%	AI-3076_RGA/AI-3076_RGA_L.CV	CO2 in the Gasifier Gas product to the FT Reactor using RGA analysis	mol%	15.93	18.41	17.56	18.46		19.72	20.30	16.94
	H2:CO Ratio in CF Syngas	calc			2.08	2.19	2.24	2.15		2.64	2.49	1.85
	Syngas Pressure	PI-3048/AI1/PV.CV	V-3072 SUCT K-O DRUM RECIRC PRESS XMTR	psig	10.11	9.80	9.34	8.97		9.78	9.21	8.39
	Syngas Temperature	TI-3049/AI1/PV.CV	V-3072 SUCT K-O DRUM OUT THRMCPL	F	48.57	52.63	40.97	46.53		65.03	47.26	47.66
CF Performance	Carbon Conversion (Ash Balance)	calc		%	89.69	83.77	92.18	92.65	94.10	85.89	88.42	90.51
	Fuel Consumption @ 3%O2	calc (F54 CF Calcs)		SCFH	2962.24	3074.90	2744.33	2686.85		2784.10	2826.66	3019.55
	Gas Yield	calc (F73 CF Calcs)		SCF/lb dry Biomass	27.69	29.18	19.55	12.88		17.99	22.78	18.55
	CO Yield	calc (F79 CF Calcs)		SCF/lb dry biomass	6.80	6.81	4.66	3.06		3.58	4.72	4.92

2/12/13 8:00 AM		FILTER			8	9	10	11	12	13	14
		'FIC-3045/PID1/OUT.CV' > 1		hours run in 24 hour period	24.0	3.8	6.6	24.0	24.0	15.7	17.4
PDU DOE					144.6	148.4	154.9	178.9	202.9	218.7	236.1
		Start Time		Unit	2/20/13 8:00	2/21/13 8:00	2/22/13 8:00	2/23/13 8:00	2/24/13 8:00	2/25/13 8:00	2/26/13 8:00
		End Time			2/21/13 8:00	2/22/13 8:00	2/23/13 8:00	2/24/13 8:00	2/25/13 8:00	2/26/13 8:00	2/27/13 8:00
CF Gasifier Conditions	Biomass Feed to Gasifier	calc (F95 CF Calcs)		DTPD	4.24	0.86	1.42	5.02	4.40	3.23	4.59
	SH Steam Feed Rate	FIC-2062/PID1/PV.CV	E-2061 Steam flow to the Steam Superheater at the Gasifier	lbs/hr	600.00	600.09	604.08	600.15	570.99	639.75	685.83
	NG Fuel Usage	FIC-2264/PID1/PV.CV	Natural Gas Fuel to Gasifier Flow Rate	SCFH	3965.76	3766.98	3738.20	3725.18	3818.61	3588.98	3330.28
	Reformer Process Temperature	TI-2078/AI1/PV.CV	Combined Process temp Exit coils -Thermowell in 6" header of the Gasifier	F	1862.08	1860.50	1845.22	1841.83	1850.14	1843.70	1862.13
	Reformer Process Pressure	PI-2063/AI1/PV.CV	Gasifier Outlet Pressure	psig	15.95	16.41	15.62	15.06	13.00	12.14	13.55
	Total CF Syngas to FT per day	calc		scf	222945	33423	62475	186951	201677	140682	202891
	Syngas Flow From Gasifier	FI-3205/AI1/PV.CV	Syngas Flow from scrubber to booster compressor	SCFH	9289.36	8781.97	9528.57	7789.62	8403.22	8941.67	11650.89
		FIC-3045/PID1/PV.CV	ClearFuels Syngas Flow	SCFH	9800.72	8706.86	9883.46	8480.60	8486.72	8794.27	9470.14
	Ash Content in Char/Ash	AO-ME2068-ASH	Percent Ash in a sample of the ash/char from the Cyclones (Proximate Analysis)	wt%	7.41	9.42	10.23	16.20	22.43	28.65	10.19
CF Syngas	Syngas H2%	AI-3076_RGA/AI-3076_RGA_E.CV	H2 in the Gasifier Gas product to the FT Reactor using RGA analysis	mol%	49.41	49.00	49.70	48.77	45.10	50.23	44.57
	Syngas CO%	AI-3076_RGA/AI-3076_RGA_H.CV	CO in the Gasifier Gas product to the FT Reactor using RGA analysis	mol%	22.89	22.30	24.90	24.59	25.76	23.00	28.81
	Syngas CH4%	AI-3076_RGA/AI-3076_RGA_F.CV	CH4 in the Gasifier Gas product to the FT Reactor using RGA analysis	mol%	7.59	7.31	6.28	6.72	7.53	5.97	8.88
	Syngas CO2%	AI-3076_RGA/AI-3076_RGA_L.CV	CO2 in the Gasifier Gas product to the FT Reactor using RGA analysis	mol%	17.81	18.40	15.67	16.14	15.55	10.79	14.98
	H2:CO Ratio in CF Syngas	calc			2.16	2.20	2.00	1.98	1.75	2.18	1.55
	Syngas Pressure	PI-3048/AI1/PV.CV	V-3072 SUCT K-O DRUM RECIRC PRESS XMTR	psig	8.08	7.98	8.68	8.00	8.02	8.19	8.47
	Syngas Temperature	TI-3049/AI1/PV.CV	V-3072 SUCT K-O DRUM OUT THRMCPL	F	41.16	43.28	38.80	51.05	65.10	67.98	74.36
CF Performance	Carbon Conversion (Ash Balance)	calc		%	83.49	84.92	68.01	78.61	84.60	93.65	93.17
	Fuel Consumption @ 3%O2	calc (F54 CF Calcs)		SCFH	3343.05	3206.58	3211.64	2945.39	3056.26	2909.85	3062.65
	Gas Yield	calc (F73 CF Calcs)		SCF/lb dry Biomass	26.05	19.33	21.49	18.38	22.54	18.81	22.22
	CO Yield	calc (F79 CF Calcs)		SCF/lb dry biomass	6.12	4.45	5.53	4.65	6.13	4.46	6.57

C.3 HEHTR Operating Conditions

The primary HEHTR operating conditions monitored during the DOE Run, excluding the biomass feedrate, were the transport steam flow (FIC-2062), HEHTR process outlet temperature (TI-2078) and the firing in the HEHTR (i.e. Natural Gas fuel consumption, FIC-2264). These operating parameters are plotted in the Chart below:

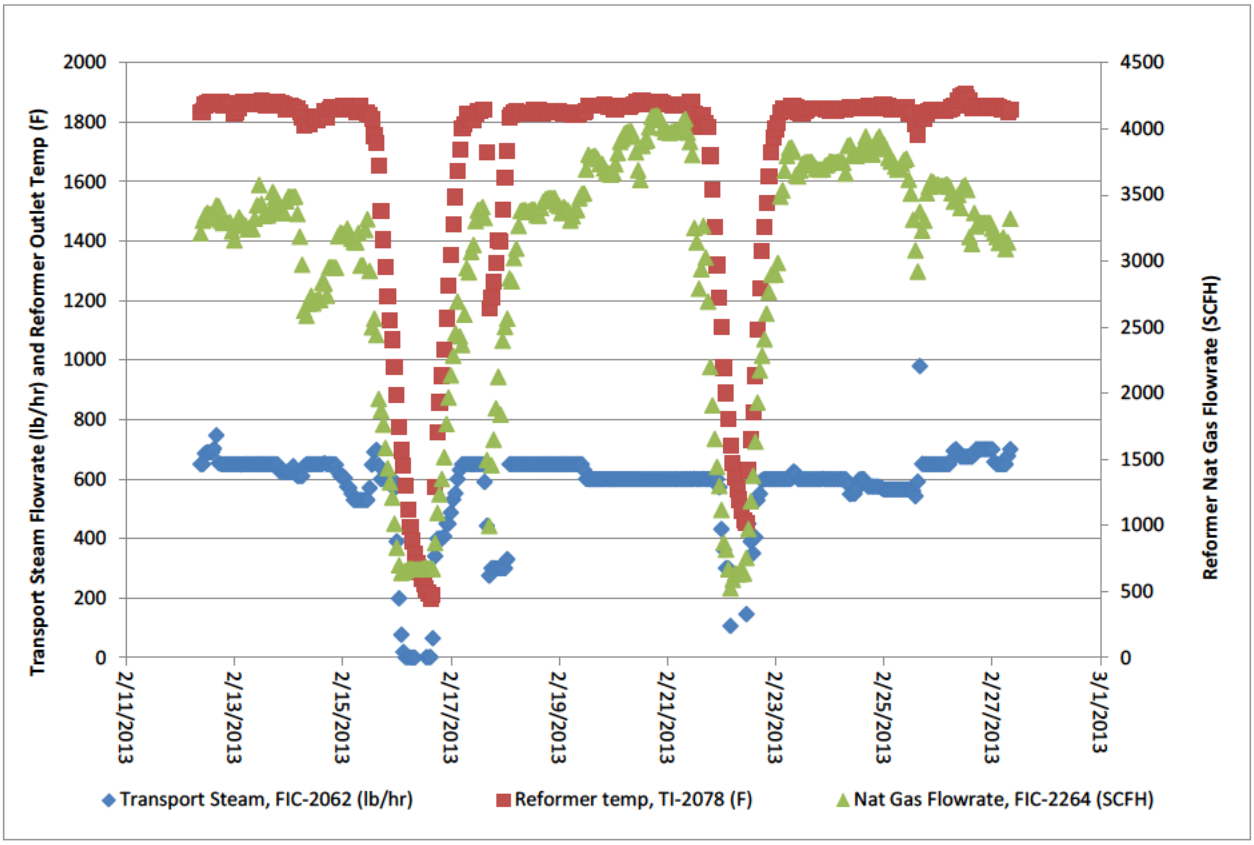


Figure 6-4: HEHTR Operating Conditions Trends During DOE IE Run

C.4 Feedrate and Syngas Production

As described earlier, the HEHTR was operated at lower-than-design rates, sufficient to demonstrate the integrated IBR operation, with tailgas recycle. As a Research and Development project, the HEHTR was intentionally designed with excess capacity. The unit was operated at a capacity to match the needs of the FT section. Operation at HEHTR turndown conditions is not as efficient as operation at increased biomass feedrates as, for example, heat losses are a higher percentage of the incoming biomass heating value and the transport steam to biomass ratio is higher at lower biomass feedrates.

The chart below shows the HEHTR biomass feedrate (via calibrated feed screw indication FIC-1407) and the Rentech-ClearFuels syngas production as measured at the Booster Compressor suction (FI-3205) and discharge (FIC-3045) trended over the duration of the DOE Run.

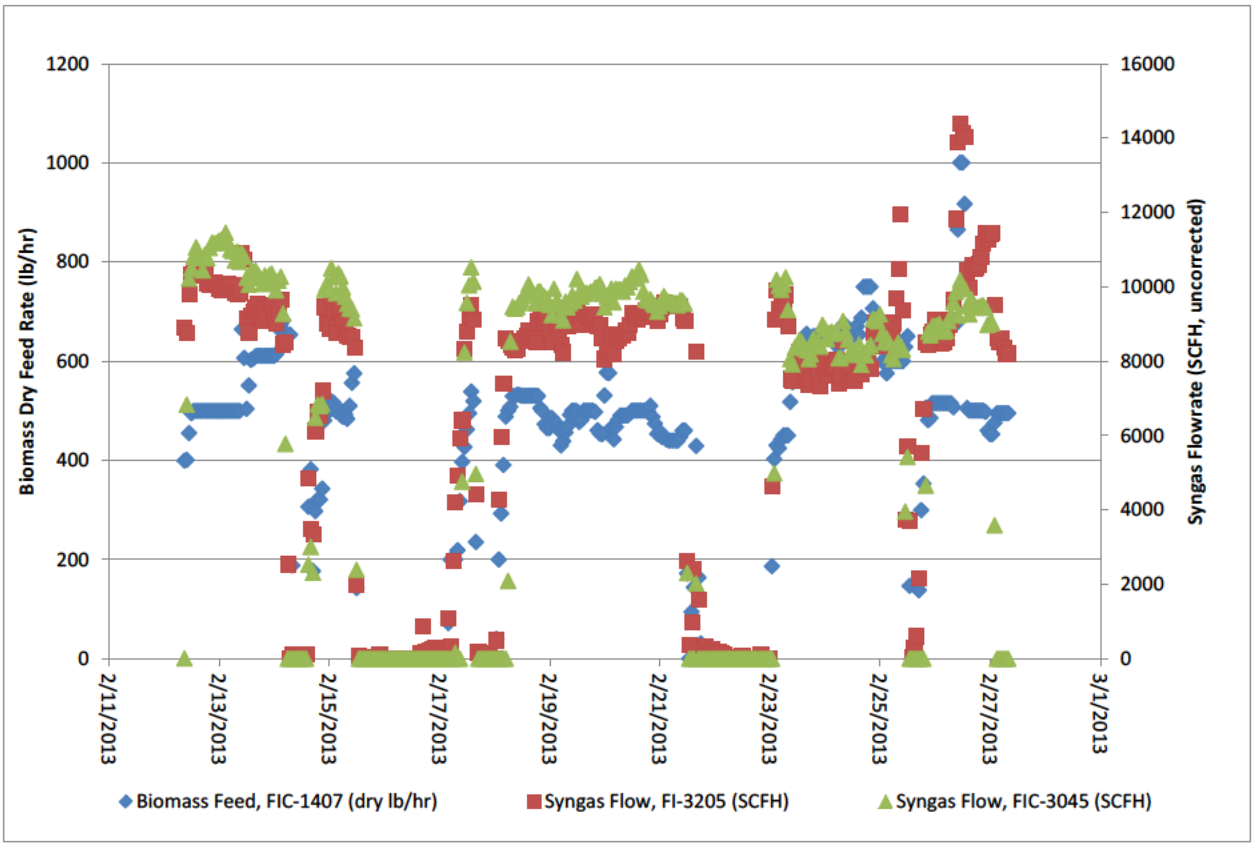


Figure 6-5: Biomass Feedrate & Syngas Production Trends

C.5 Syngas Flow Meter Calibration

The Rentech-ClearFuels syngas productivity is determined using the syngas flow meter at the suction of the Booster Compressor (FI-3205). This flow meter is automatically temperature and pressure compensated and the calibration on the meter was checked prior to commencement of the DOE test Run, using an assumed gas molecular weight of 16.5. To calculate the reported syngas productivity, the FI-3205 reading is corrected for the measured gas molecular weight, using the online RGA syngas analysis, and then further correcting for the nitrogen and water content of the syngas, to obtain a dry and N_2-free syngas production rate.

C.6 Syngas Composition

The trend data for the Rentech-ClearFuels online syngas analyzer, permanent gas analysis (AI-3076), is provided in the chart below.

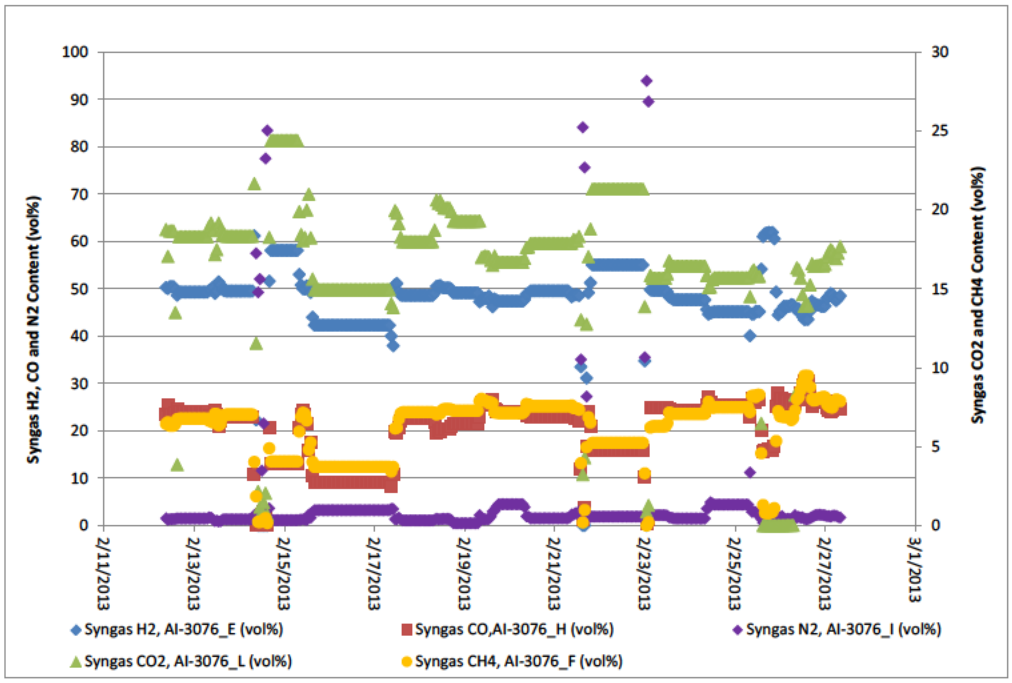


Figure 6-6: Syngas Composition Trends During DOE IE Run

C.7 Syngas Tar Analysis

NREL provided analysis for tars exiting the HEHTR and the ClearFuels Gas Cleanup system, using their Molecular Beam Mass Spectrometer (MBMS) analyzer, installed at the site during the DOE Run. The February 13th results from this analysis, while running on the Colorado sourced wood chips, are summarized below:

Table 6-6: Tar Speciation and Content at HEHTR Outlet and Booster Compressor Suction

Tar Species	HEHTR Outlet (sampled 2/13, 9:30-10:30 am)	Booster Compressor Suction (sampled 2/13, 12:00-12:30 pm)
	ppm (dry basis)	ppm (dry basis)
Benzene	3199	4732
Toluene	nd	nd
Phenol	nd	nd
Naphthalene	411	18
Phenanthrene	44	nd
Pyrene	68	4
Other tars (78<MW<202)	80	nd
Other tars (MW>202)	33	nd
Total (including BTX)	3835	4754
Total (Excluding BTX)	636	22

nd: non-detectable

The tar analysis exiting the HEHTR at 636 ppm (dry basis, excluding BTX) is higher than the target of 50 ppm for the DOE Run, but is consistent with the data collected from previous operation of the Rentech-ClearFuels unit at the PDU, at similar conditions.

As the HEHTR was operated during the DOE Run at higher-than-normal excess air levels, in order to maximize the fluegas heat available for biomass drying, it was not possible to operate the HEHTR at higher skin metal temperatures at the top of the coils, which has been observed to reduce the syngas tar levels, at the PDU.

C.8 Syngas Component Flows

The table below compares the measured DOE Run maximum gas component flows (lbmol/hr) with those stated in the target "Syngas Composition Criteria" for the project:

Table 6-7: Comparison of Measured Syngas Component Flows vs. Composition Criteria

Syngas Component	Units	Criteria Max	Criteria Min	DOE Run Max
Hydrogen	lbmols/hr	93.9	29.0	13.7
Carbon Monoxide	lbmols/hr	37.4	29.0	8.8
Carbon Dioxide	lbmols/hr	26.5		4.7
Nitrogen	lbmols/hr	1.7		0.96
Methane	lbmols/hr	13.7		2.7
C_2^+ (incl. tars)	lbmols/hr	0.2		0.19
H_2:CO Ratio	-	2	1	1.55 – 2.64

As discussed above, the Rentech-ClearFuels reformer was only operated during the DOE Run at biomass feedrates necessary to provide sufficient syngas flow rate to the Fischer-Tropsch (FT) reactor, to meet minimum acceptable fluidization velocity criteria for the reactor, with tailgas recycle also operational. This resulted in lower syngas flow requirements and resultant component flow rates than anticipated when the criteria for the run were established (above). As a result, the hydrogen and carbon monoxide component flows achieved were less than the minimum criteria in the above table.

The syngas H_2:CO ratio was varied between a range of 1.55 and 2.64 during the DOE test. The control of this ratio was achieved primarily by adjustments to the HEHTR transport steam flow rate and firing, demonstrating successfully that this ratio could be adjusted and controlled and that suitable steam-biomass mixing could be reliably achieved.

C.9 HEHTR Thermal Efficiency

The nominal thermal efficiency (calculated on a higher heating value (HHV) basis) of the HEHTR is calculated by summing the following cumulative stream enthalpies, totalized over the entire DOE Run:

Table 6-8: HEHTR Thermal Efficiency Measured During DOE IE Run

Stream	Units	Output	Input
Biomass	MMBtu (HHV)		831.4
Natural Gas Usage	MMBtu (HHV)		847.5
Syngas (excluding tars)	MMBtu(HHV)	651.7	
Syngas Tars	MMBtu (HHV)	34.4	
Net Steam export	MMBtu (HHV)	156.7	
HEHTR Fluegas Dryer Heat	MMBtu (HHV)	113.0	
Steam Superheating	MMBtu (HHV)	35.6	
Totals	MMBtu (HHV)	991.4	1678.9
Thermal Efficiency	%	59.05	

Notes:

(1). Biomass HHV obtained using the cumulative biomass dry feed flow from the DOE Run Summary Data (Section 4.0) and the average biomass HHV data from Section 3.2.

(2). Natural Gas HHV obtained using cumulative natural gas flow to the HEHTR burner from the DOE Run Summary Data (Section 4.0) and assuming a natural gas specific HHV of 1010 BTU/SCF.

(3). Syngas HHV obtained using the syngas yield (SCF/lb dry biomass), cumulative biomass dry feed flow and syngas composition, excluding tars (to calculated syngas BTU/SCF) from the DOE Run Summary Data (Section 4.0).

(4). Syngas tars HHV obtained using the syngas yield (SCF/lb dry biomass), cumulative biomass dry feed flow, an average syngas tar composition, including benzene, of 3835 ppm (dry) and an average tar specific HHV of 4250 BTU/SCF.

(5). Net steam export HHV calculated by summing export steam flow rate from ClearFuels unit (FI-2162) for periods during the DOE Run while biomass was being fed to the HEHTR and using calculated enthalpies for BFW and saturated steam export.

(6). HEHTR Fluegas Dryer Heat HHV calculated by summing the fluegas flow rate from HEHTR (FI-1225) for periods during the DOE Run while biomass was being fed to the HEHTR and using average measured fluegas temperature to and from the Dryer (TI-2166 & TIC-1203), with an estimate of fluegas average specific heat.

(7). Steam superheating HHV calculated by summing transport steam flow rate (FIC-2062) for periods during the DOE Run while biomass was being fed to the HEHTR and using calculated enthalpies for saturated steam and superheated steam at average measured superheat temperature (TI-2021).

The average thermal efficiency obtained for the HEHTR is less than originally anticipated and targeted as a performance criteria for the DOE Test Run (80%) for a number of reasons, which are discussed below:

C.10 High HEHTR Excess O_2

Due to the failed steam coils in the Biomass Dryer, it was necessary to provide as much heat as possible to the Dryer from the HEHTR fluegas heating, which resulted in the HEHTR being operated at higher-than-normal excess air levels (average HEHTR fluegas O_2 content during the DOE Test Run at 6.0 vol%, versus 3.0 vol% expected for normal HEHTR operation). Operation at these high excess air levels results in lower thermal efficiency.

For comparison purposes only, the natural gas consumption calculated for operation at 3 vol% O_2 in the fluegas, for the DOE Run conditions, is 715 MMBtu/hr versus the measured value of 847.5 MMBtu/hr. The theoretical thermal efficiency would increase to 64%.

C.11 Syngas Cooler

The Syngas Cooler was bypassed due to fouling of the tubes, and replaced with a BFW injection/direct quench system to cool the syngas prior to the syngas being routed to the Primary and Secondary Cyclones. Hence, the sensible heat content of the syngas exiting the reformer was not being utilized to raise steam, as the unit was originally configured, which lowers the overall thermal efficiency of the unit.

C.12 HEHTR Performance

To analyze the performance of the HEHTR, it is necessary to understand aspects of two-phase gas/solids flow in the transport piping, transitional piping, as well as in the helical coils. These issues are discussed in more detail below, in the discussion regarding CFD modeling.

Pneumatic transport of solids in horizontal piping requires that the bulk velocity exceeds both a saltation velocity (required to keep solids dispersed in the flowing gas stream), as well as a pick-up velocity (required to re-entrain solids that may have separated out of the bulk gas stream at an elbow or transition). If the gas velocity exceeds these lower limits, the solids will typically be travelling only slightly slower than the bulk gas flow, with the resultant drag acting on the particles, exceeding the gravitational forces acting on the particles. Solids can separate out at elbows or other transitions, which results in their velocity dropping at the transition, and after normal flow is re-established after the transition, the gas velocity (which exceeds the pick-up velocity) can generate sufficient drag on the slowed particles, to re-accelerate them back up to something close to the bulk gas velocity.

The gas/solids flowing in the transport line to the HEHTR will behave as described above, and the particles in the transport line will normally be traveling at something close to the transport line bulk velocity, as the stream enters the HEHTR. The degree to which the solids will be decelerated at the transition into the HEHTR helical coil will depend on the geometry of the transition. A long radius elbow, or an even more gentle transition, will tend to retain more of the particle velocity at the entry to the helical coil. A short radius elbow or a piping expansion will result in solids being significantly decelerated as they enter the HEHTR helical coil.

Once the gas/solids stream enters the HEHTR helical coil proper, and after the transition from the transport line, biomass particles will still retain some portion of their momentum from the transport line. If the particles are still moving at a velocity close to the bulk gas velocity at the start of the helical coil (i.e. the transition did not result in significant particle slowing), the drag acting on the particles will be relatively

low, and the momentum of the particles will be a more significant factor, in the trajectory the particles will take in the first part of the coil. This particle momentum will result in the particles bouncing off of the coil walls at multiple points in the first coil turn.

This particle bouncing, or wall contact, is a very significant feature of the HEHTR reformer, as it is believed that this particle/wall contact is the primary mechanism for very fast particle heating and pyrolysis in the first part of the coil. This fast pyrolysis results in higher carbon conversion and more active char, for secondary gas phase reactions, as discussed below.

As the particles bounce off of the coil walls, they lose some of the momentum they were carrying from the transport line, although the gas velocity will increase quickly, as it heats. In addition, the particles are shrinking due to mass loss from pyrolysis. These smaller particles have less momentum and eventually they begin to move exclusively along the outside of the coil wall. The velocity of these solids is significantly less than the bulk gas velocity, at any particular point in the coil, and the slip between the solids and gas is such that the net drag generated on any single particle balances with the centrifugal force acting on that particle. Depending on the helix diameter, the particles can be moving at velocities of anywhere from 25 to 50% of the bulk gas velocity. This phenomenon is also very significant for the HEHTR performance, as it results in a layer of slower moving char, which is being heated against a hot coil wall. This hot char layer can act as a catalyst for various secondary gas reactions as is described below.

An interesting feature of the bouncing trajectory of the biomass particles, as they enter the helical coil, is that the number of bounces the particles make to complete a full turn in the helical coil is not a strong function of the transport gas velocity or the coil helix diameter. So it takes approximately the same number of bounces for a particle to transverse a complete turn in the helix. This phenomenon is illustrated below in Figure 6-7, and Figure 6-8 which shows particle trajectories for two different helical coil geometries at significantly different inlet gas velocities.

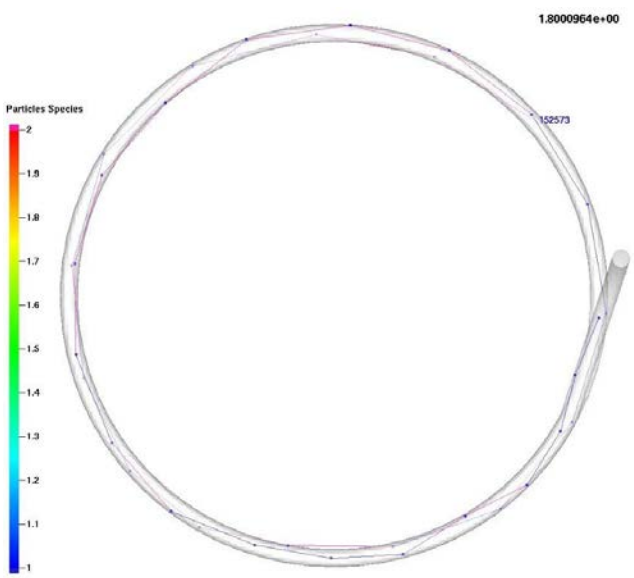


Figure 6-7: Particle Trajectory for IBR – 3”pipe dia. 7.3 ft helix diameter for 1/12" particle diameter at a coil inlet velocity of 72 ft/s (Left);

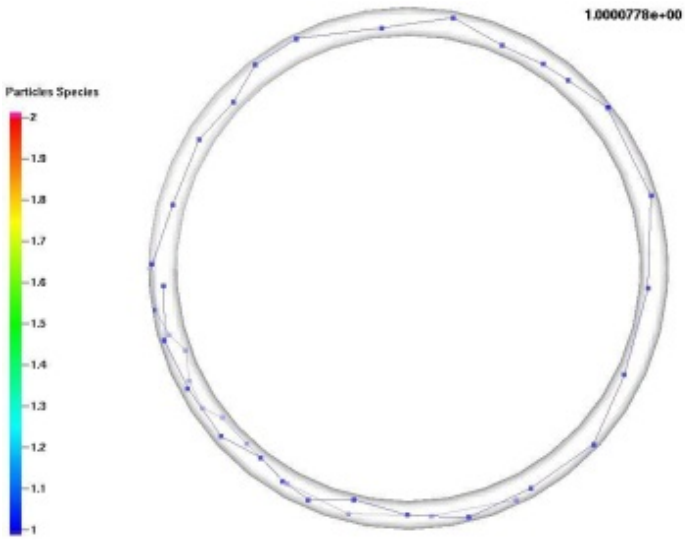


Figure 6-8: Particle Trajectory for Small Pilot PTI 3" pipe dia. 3 ft helix diameter for 1/12" particle diameter at coil inlet velocity of 18 ft/s

The fact that particles take approximately the same number of wall bounces to traverse a complete coil turn is a significant observation, as it means that individual particles heat and begin to pyrolyze in approximately the same number of coil turns, irrespective of the coil inlet velocity, transport steam flow or helix diameter, if the coil metal temperature in the first part of the coil is the same. Of course, the particles may achieve those number of bounces in less time, if they are moving more quickly as they enter the coil, but most importantly, the relevant particle heating rate is the rate of particle heating, while the particle is in contact with the wall, and this is not impacted by the velocity that the particle is traveling at, but is a function primarily of the wall temperature.

As described below, initial fast heating of the biomass is achieved in the Rentech-ClearFuels HEHTR, which results in several significant performance benefits. The above discussion allows the performance of the HEHTR to be modeled using primarily the tube metal temperatures in the first turn(s) of the coil. Much of the performance data can be fitted reasonably using this operating variable, along with the coil biomass feedrate, as will be discussed more fully in subsequent sections. Somewhat arbitrarily, the skin temperature at ¾ of a full coil turn is used in subsequent analysis as a primary operating variable, and a "hot zone" of one and a half coil turns is assumed in much of the following analysis. This hot zone is defined as the coil length required to achieve initial fast or flash particle heating and pyrolysis. The fact that reasonable performance data correlations can be achieved using this simple parameter and simplistic reaction models confirms that fast initial particle heating is a key part of this technology.

C.13 Carbon Conversion

Although there are multiple pathways for particle heating in the first part of the coil, including radiant heat transfer directly from the coil wall to the particles and convective heating from the coil wall to the particle via the gas, the primary pathway for very rapid heating of the biomass particles is the direct contact between the particles and the coil wall as a result of the particle bouncing described above.

At these successive contacts, the particles are heated and commence to rapidly pyrolyze. Volatile gases are released from the biomass particle, due to the pyrolysis, and remain close to the wall (i.e. once released,

the volatile gases don't travel with the particle), whereas the particles move down the coil quickly, headed for their next wall bounce.

As noted later, our understanding of the process is that particles are heated and flash/fast pyrolyzed at the outside coil wall, and that this mechanism drives the carbon conversion. As such, the following rate equation for carbon conversion is proposed:

$$-r_c = \frac{1}{A}\,\frac{d\,N_c}{dt} = k\left(\frac{N_c}{A}\right)^n$$

Where: $-r_c$ = rate of carbon reaction in the fast pyrolysis zone (kmol/m^{2}s)
A = Wall surface area in the fast pyrolysis zone (m^2)
N_c = Carbon in fast pyrolysis zone (kmol)
k = Rate constant (kmol/m^{2}s/(kmol/m^2)^n)

As we don't know the actual solids (and hence carbon) content at the hot pipe wall, we can assume that the solids hold-up and/or the frequency of particle/wall contacts is proportional to the solids feedrate (i.e. $N_c = K'\,\dot{N}_c$), where $\dot{N}_c$ is the carbon flowrate (kmol/s) exit the hot pyrolysis zone.

The above rate equation can then be re-arranged to:

$$\log r_c = (\log k + n \log K') + n \log\left(\frac{\dot{N}_c}{A}\right)$$

and plotted as per the following chart (see Figure 6-9 below):

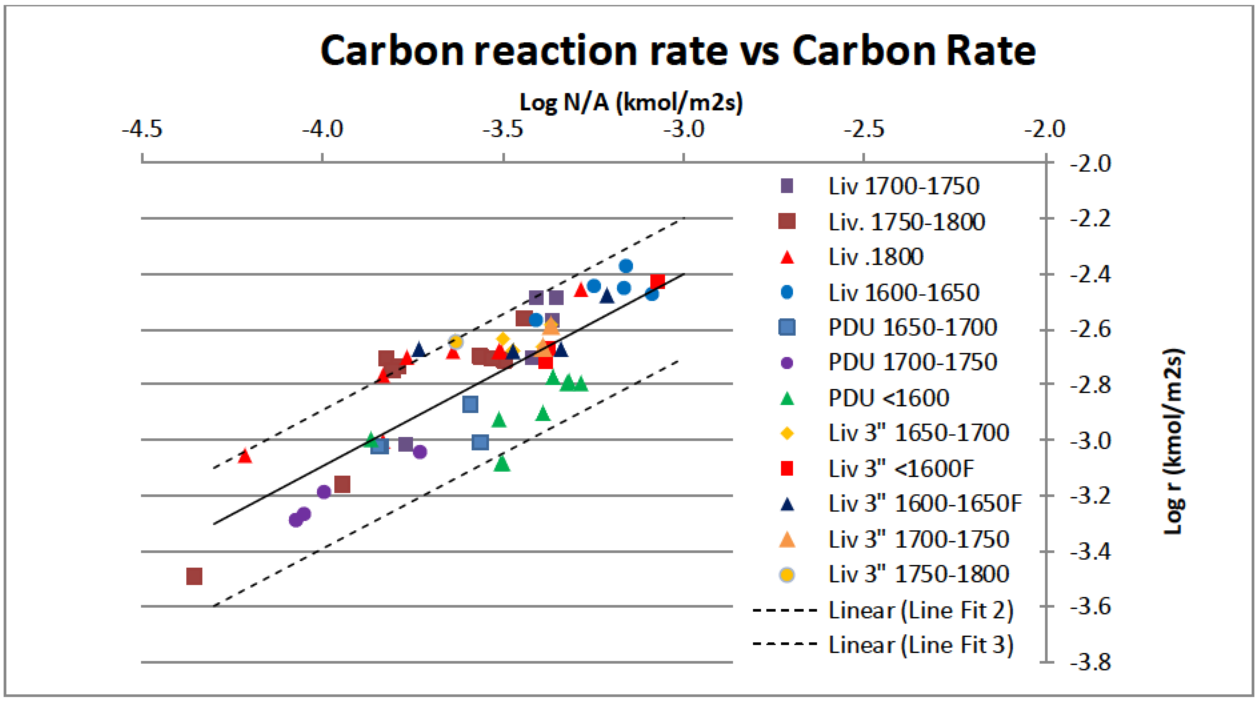


Figure 6-9: Carbon Reaction Rate Data Plotted vs Carbon Flowrate per unit area in the Fast Pyrolysis Zone

The line fit to this data in this case has a slope (=n) of approximately 0.69, which may indicate that the inherent reaction is 1st order with respect to carbon concentration; however, particle crowding at higher carbon concentrations (and flowrates) is resulting in slower particle heating and hence lower carbon conversion rates.
The intercept of the above (center) line, for data at a skin temperature 1700-1750°F (average 1213°K) is $(\log k + n \log K')$ and is equal to -0.32, in this case.

The rate constant is defined as:

$$k = k_o \, e^{\left(\frac{-E_a}{RT}\right)}$$

The natural log of the modified rate constant $\left(k' = k\,(K')^n\right)$ can be plotted versus the inverse temperature (initial wall temperature, as defined above). From this analysis the activation energy is determined to be approximately 17,550 J/molK and the intercept in this case $(\ln(k_o\,(K')^n))$ is equal to 1.37.

The average of the data showed only a 1.7% increase in carbon conversion per 100°F increase in the initial wall temperature.

The preceding relationships involving k, k_o and K' can be solved for K' = 0.34 sec (approx.) and k_o = 5.0 $kmol^{0.31}/m^{0.62}s$.

A K' value of 0.34 sec is equivalent to a solids hold-up in the pyrolysis zone of approximately 0.34 seconds. This is in the right order, considering the initial particle velocities entering the coils and potential accelerations due to gas heating and production.

Hence, the above analysis results in a simple model for carbon conversion, which has been used to check against actual plant data. The correlation between the model predicted and actual carbon conversions is shown in Figure 6-10 below:

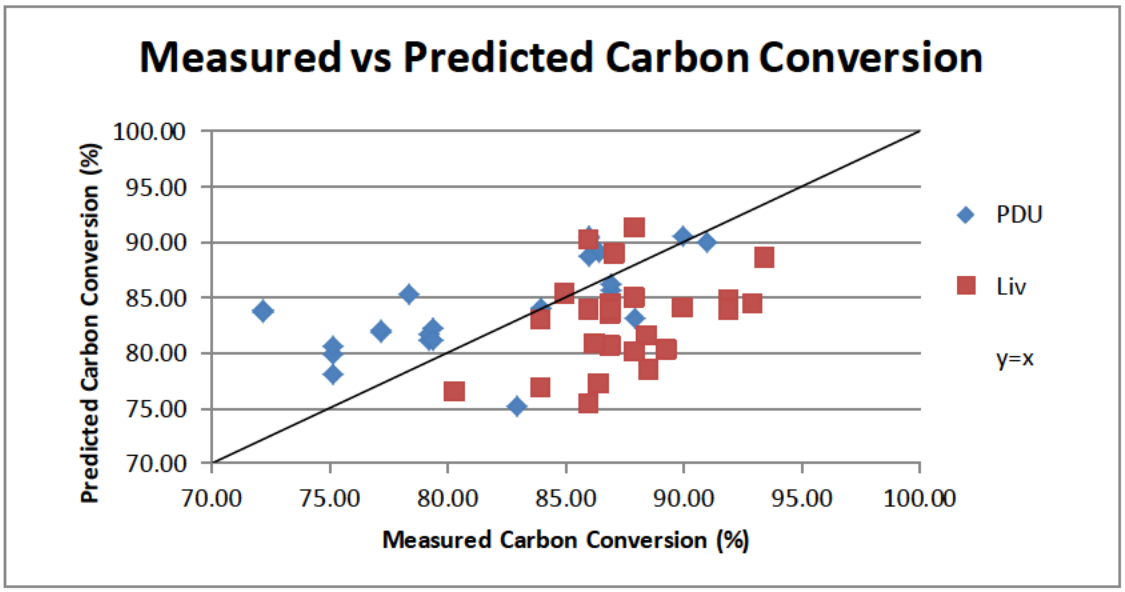


Figure 6-10: Model Predicted Carbon Conversion vs Measured Carbon Conversion

The model tends to under-predict the Livingston carbon conversion and over-predict the PDU conversion. This may mean that the additional hot zone length available for the PDU coil, due to the larger coil helix diameter (7.3 ft versus 3 ft at Livingston plant), may not be totally available, and that regardless of the calculated hot zone length, particle crowding in the early part of the coil and coil inlet can effect performance. A more rigorous model could be developed that accounts for this. Significant inaccuracies are also inherent in the measurement of carbon conversion in both the PDU and at the Livingston pilot plant, when using a simple ash balance method.

Specific testing was conducted at the Livingston plant, isolating the effects of the initial wall temperature on carbon conversion. These results indicated that, on average a 100°F increase in the initial wall temperature of the reformer produced a 1.5 to 2% improvement in carbon conversion, and this is consistent with the model described above. Also, carbon conversion at Livingston, the PDU and the HNEI testing at Aberdeen can also be plotted versus feed capacity (dry basis) through a single coil (See Figure 6-11 below):

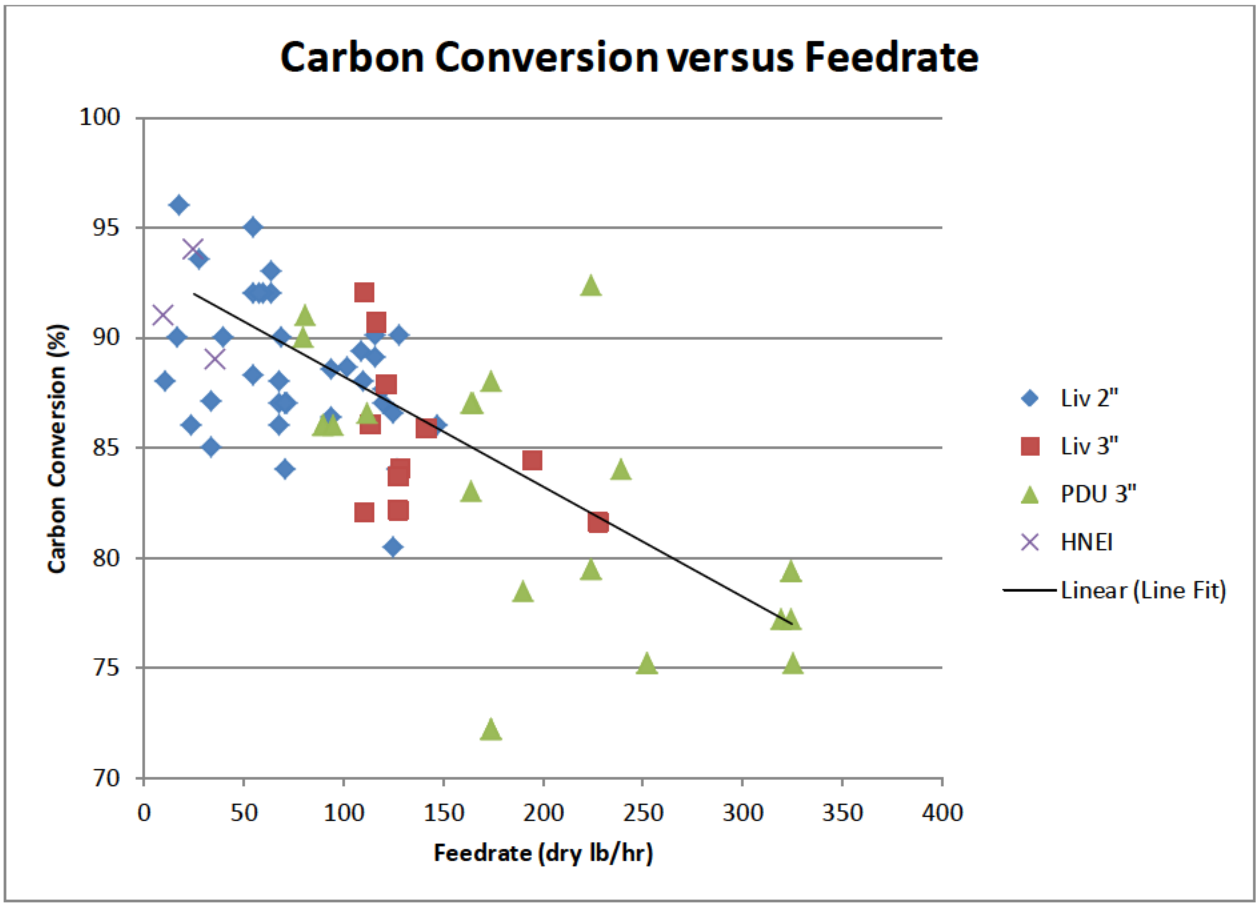


Figure 6-11: Carbon Conversion vs Feedrate per Coil. Data taken from PDU and Livingston Pilot Plant at Various Coil Diameters

The model described above (with n=0.69) is consistent with the reductions in carbon conversions observed at these plants, as feedrates to each coil is increased.

The model described above, and the data collected on the impact of coil temperature and feedrate on carbon conversions, has significant implications when it comes to scale-up of the Rentech-ClearFuels technology. Even with initial wall temperatures maximized (say at 1800°F for a commercial design, utilizing an incoloy 800HT coil metallurgy), with 10 DTPD through a single 3" coil (for a 7.3 ft helix diameter, per the PDU), the carbon conversion predicted is only 78%. At 20 DTPD feedrate to a single 3" coil, the conversion predicted would drop to 73%. This would improve to 75% with a 4" coil, but as indicated in Figure 6-11 above, the benefits of larger coil diameter assumed in the model may not all be realized.

The carbon conversion may not be as impacted by coil diameter, as predicted by the model, as the model assumes that the entire outside 50% of the coil internal surface area is available for particle heating, whereas in fact many of the particles will tend to migrate to the extreme outside point on the coil due to the effect of centrifugal force. In this regard a formed tube with a less than circular cross section could be beneficial for the technology, as is discussed later in this report.

As a minimum, it would appear that char recycle will be required for a commercial plant design in order to boost the carbon conversion at higher solids mass fluxes in the coils. Single pass carbon conversion for 100% char flow was demonstrated at 60% during testing at Livingston.

The above findings are consistent with an Analysis Of Variance (ANOVA) of the PDU carbon conversion data, which indicated that only the coil biomass feedrate is significant (P-value < 0.05) with regards to the carbon conversion. An ANOVA is a statistical tool to determine if the variation between data is significant.

As an additional reference on carbon conversion, the Brightstar reformer deployed in Australia around the year 2000 was eventually shut down, but published information on that unit stated that it achieved very low carbon conversions (char yield as high as 40 wt% of gasifier feed reported). A separate char gasifier was added to the plant to further reform the Char.

C.14 Carbon Conversion Calculation Method

The carbon conversion numbers described above are generated using an ash balance (i.e. all of the biomass ash is assumed to be partitioned to the char/ash byproduct stream and the ash content of this byproduct stream is used to infer the carbon content of the char (carbon content assumed to be 100%-ash content). Carbon conversions were also calculated at the PDU and at Livingston using the syngas flowrate and analysis. In general, the carbon conversion using the syngas balance is lower. For example, at Livingston, this is believed to be due to syngas losses in the syngas train, including the cyclone blowdown losses, flange leaks, etc. This is best illustrated in Figure 6-12 below, which shows the difference in the two carbon conversion calculation methods as a function of feedrate. At higher feedrates, the differences are significant, due presumably to greater backpressure in the piping downstream of the reformer but at lower feedrates the two methods give similar results.

$$\textbf{Carbon Conversion (\%)} = \frac{\left[\%\,C\ in\ feed - \left(\frac{\%\ Ash\ in\ feed}{\%\ Ash\ in\ Char}\right) x\,(100 - \%\ Ash\ in\ Char)\right]}{\%\,C\ in\ feed}\ x\ 100\%$$

Another potential reason for the discrepancy in carbon conversion calculation methods is that fine soot particles represent a loss in carbon conversion, but some portion of these fines particles are not collected in the cyclone or gas filters, and hence will not be accounted for using the ash balance method. Soot formation is discussed below.

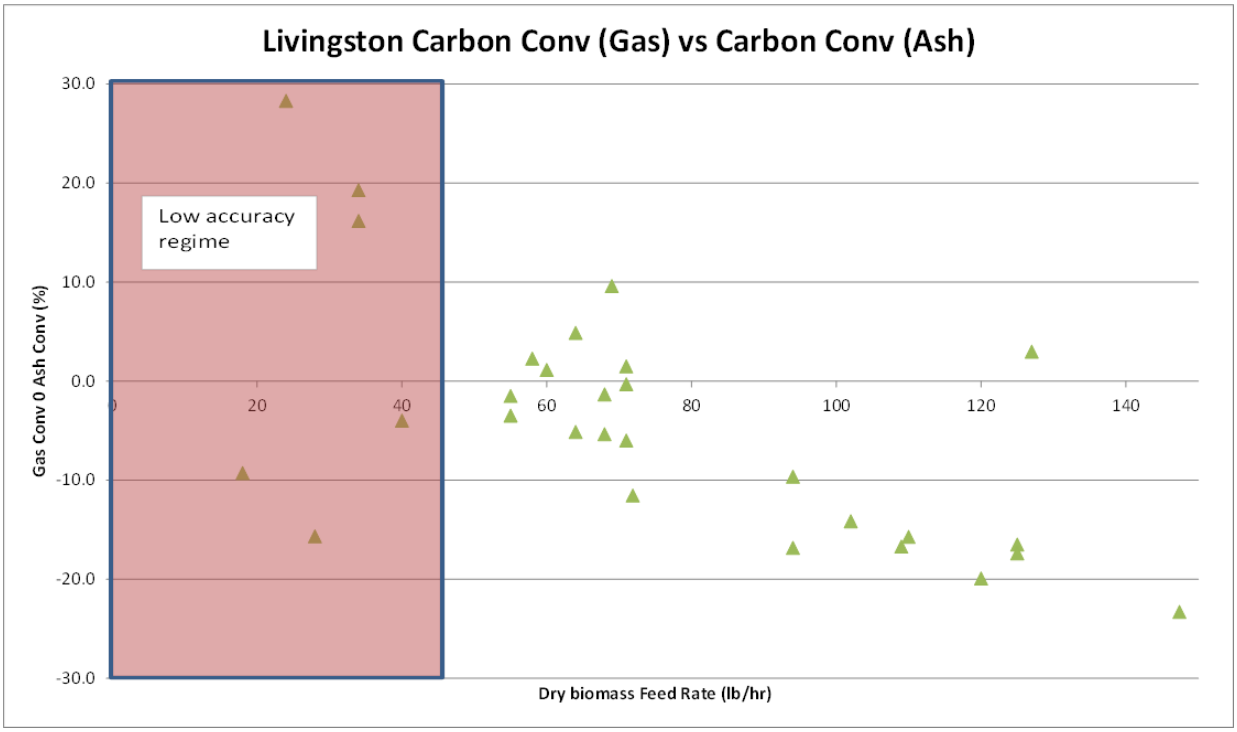
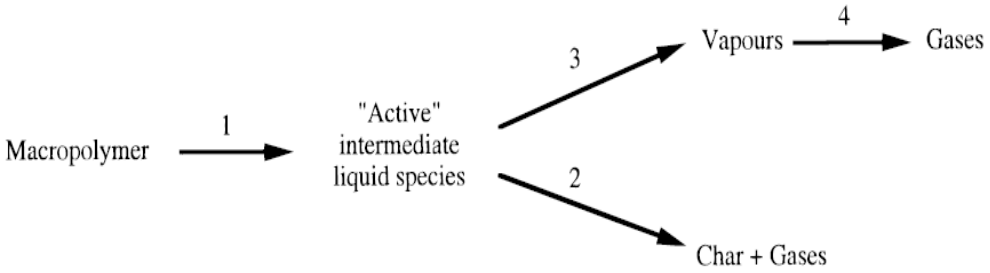


Figure 6-12: Difference between the Livingston Carbon Conversion Calculated by Ash Balance and Gas Analysis

C.15 Tar Production

When biomass particles are heated, against the hot walls in the HEHTR, volatile gases are released. These volatile vapors are cracked to permanent gases as per reaction #4, in the Broido-Shafizadeh reaction scheme illustrated below:



CFD modeling of particle flow in helical coils show how relatively large biomass particles bounce thru the helical coil and intermittently make contact with the hot coil walls. At these successive contacts, volatile gases are released from the biomass particle and remain close to the wall (i.e. once released, the volatile gases don't travel with the particle).

Lede[(1)] describes reaction #3 being more than 1000 times faster than reaction #4, so vapor cracking rates are not limited by vaporization of the liquid intermediate species. He also describes reaction #4 as occurring in a thin hot boundary layer, located along the wall (in a vortex/cyclone reactor, for his work, but

this situation is in many respects similar to flow through the HEHTR helical coil), at a temperature close to the skin metal temperature.

A simple CSTR model for this tar cracking reaction has been derived, assuming a first order reaction with regards to the volatile concentration, for the reaction #4 above. In this model, the CSTR volume is assumed to be the thickness of a single particle, on the outside half of the coil only, for the hot zone coil length defined previously.

First order kinetics in a CSTR reactor:

$$k_4 = \frac{\chi\,(1+\varepsilon_A\chi)\,\upsilon}{(1-\chi)\,V}$$

Where:

χ =	volatile fractional conversion
$\varepsilon_A =$	ratio of mols of gas before and after cracking rxns (estimated = 6.5 as MW of levoglucosan is 162 and average cracked products MW is assumed to be ~25)
$\upsilon =$	volumetric flowrate
V =	reactor volume
k_4 =	rate constant for reaction #4 (volatiles cracking to gases)

The volatile conversion in this model is defined as:

$$\text{Volatile Conversion (\%)} = \frac{\left[\frac{(Ult.\,Carbon\,content - Prox.\,Fixed\,carbon)}{Ult\,carbon\,content}\right] x\,50\% - \%\,carbon\,converted\,to\,tars}{\left[\frac{(Ult.\,Carbon\,content - Prox.\,Fixed\,carbon)}{Ult\,carbon\,content}\right] x\,50\%}\;x\,100\%$$

The denominator in this equation is the nominal volatile carbon content of the biomass (per the proximate analysis), but a 50% correction factor is included to account for the fact that some devolatization products are permanent gases, moisture, etc. that won't crack any further, or don't crack to the extent that the larger volatile species do.

The temperature of the CSTR is the initial wall temperature in the coil, as previously defined. In addition, the reaction rate of the volatiles is observed to be approximately proportional to the carbon (char) concentration in the hot zone, to an n=0.9 power. The results from this analysis, for Western State Forestry (WSF) Colorado Soft Wood chips only are presented in Figure 6-13 below.

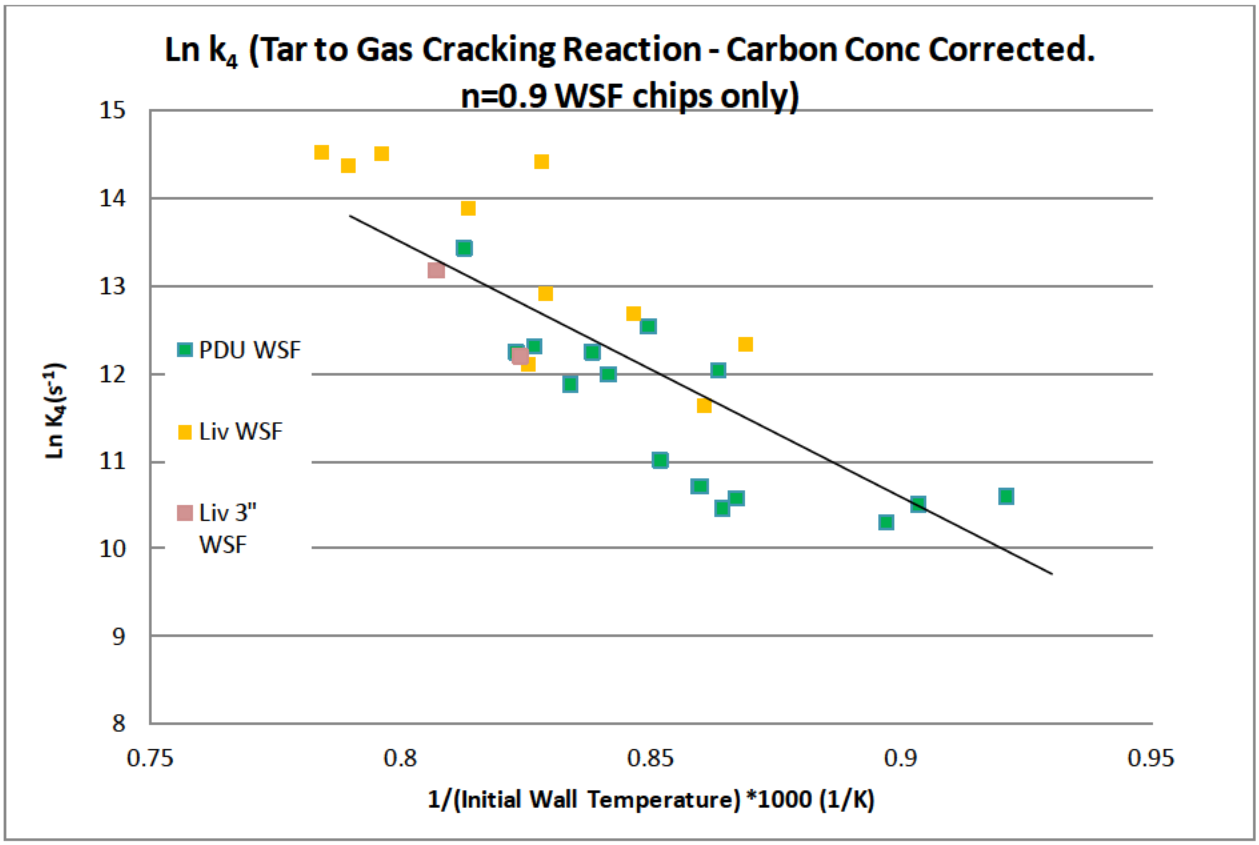


Figure 6-13: Arrhenius Plot for Tar Cracking Model. Carbon Concentration corrected; n=0.9; WSF Wood Chips Only

An activation energy of 243,481 J/molK and a pre-exponential constant of 1.099×10^{16} fit the data.

Tar levels in syngas were not able to be correlated statistically with other reformer primary operating variables such as steam/biomass ratio, coil residence time or reformer outlet temperature, which were expected to be significant. This seems to support the simplistic model described above, which has initial skin temperature as a primary operating variable, with biomass feedrate as a secondary variable.

In this proposed model, the volatiles would be released from the biomass/char particles in a thin hot layer, close to the coil wall, and would be exposed to a temperature approximating the wall temperature at that location (not the bulk gas temperature). After the volatiles are cracked in this hot zone, they will pass into the colder bulk gas phase, where some limited additional tar reactions may occur (limited by lower temperature and reactant dilution). The volatiles in this hot zone will be concentrated, as steam and syngas from the bulk gas phase will be excluded from this boundary layer, by net gas flow out of this zone.

The fact that the rate equation fits the data best using a n=0.9 order carbon concentration term, seems to support the argument that the tar cracking reaction is facilitated by the char meaning that the char is providing active catalytic sites, and the number of active sites is proportional to the feedrate and char concentration in the defined hot zone.

This theory is also supported by the limited testing conducted at NREL, passing pyrolysis gas generated from our WSF biomass, through a bed of char, using char produced at the PDU. In this case, the char bed is

controlled at approximately 1500°F, and the type and quantities of volatile species changes significantly across this char bed, resulting in mainly aromatic tars (naphthalene, benzene, anthracene, etc.) but significantly reduced heavy polyaromatics (PAHs), oxygenates, phenolics, non-aromatics and methylated tars exit the char bed (see Figure 6-14 below):

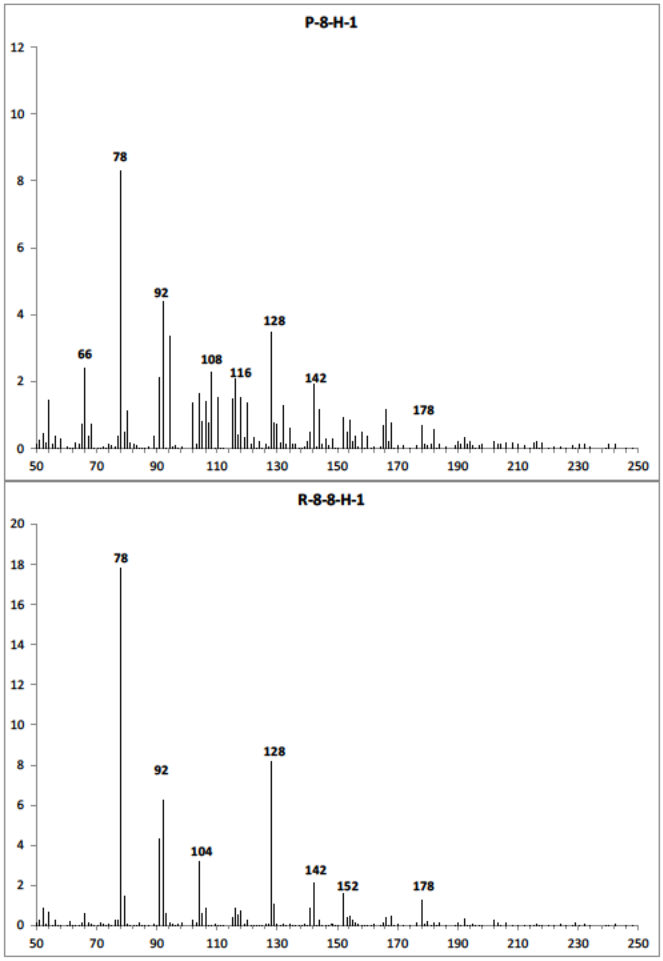


Figure 6-14: Product Spectra of Vapor Cracking (i.e. no char, top) and high temperature char (bottom) from Rentech (90 mg) at 800C in Steam (Y-axis represents % of total tars, X-axis is species molecular weight

These findings are consistent with other literature on the effectiveness of biomass derived char as a tar cracking catalyst. Data from one paper by Wang et al [(2)] is included in Figure 6-15 below:

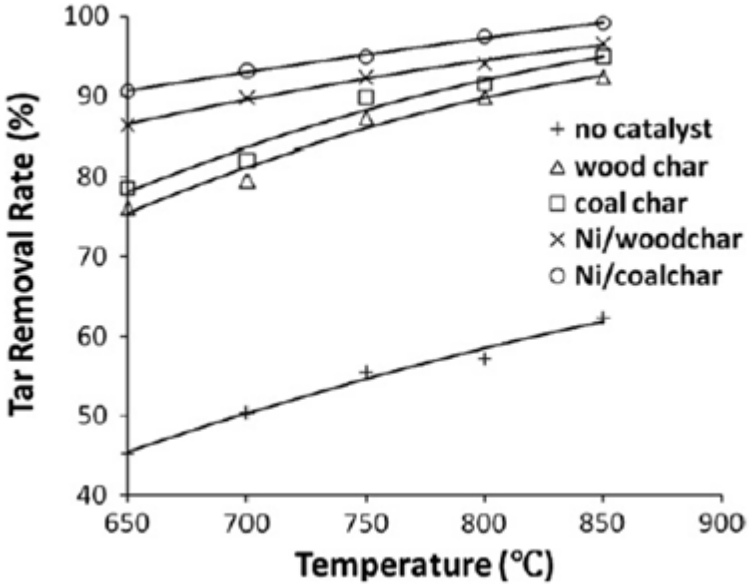


Figure 6-15: Effect of Catalytic Tar Cracking Temperature on Char Catalyzed Tar Cracking

The above CSTR tar reaction model suggests that the particles should fit into a viscous sub-layer (boundary layer) adjacent to the wall for maximum performance; otherwise, volatiles may be more easily swept or released into the bulk gas flow before having adequate opportunity to react at the pipe wall. For fully developed turbulent flow in a pipe, this layer may be as large as 0.15" at typical Livingston operating conditions, but will reduce significantly at higher pipe velocities (e.g. as experienced at the PDU). This issue may have some bearing on acceptable particle sizes (and initial pipe flow conditions) for Rentech-Clear Fuels reformers. Without additional testing, it is best to assume that the feed particle size should be equal to or less than the boundary layer thickness expected at the inlet to the HEHTR coil, as a precaution, pending additional testing on particle size.

The impact of feedstock on tar content in the syngas has not been studied extensively, but the Arrhenius chart from Figure 6-13 above, is reproduced in Figure 6-16 below with multiple feedstocks types (straight line fit for WSF feed as a reference):

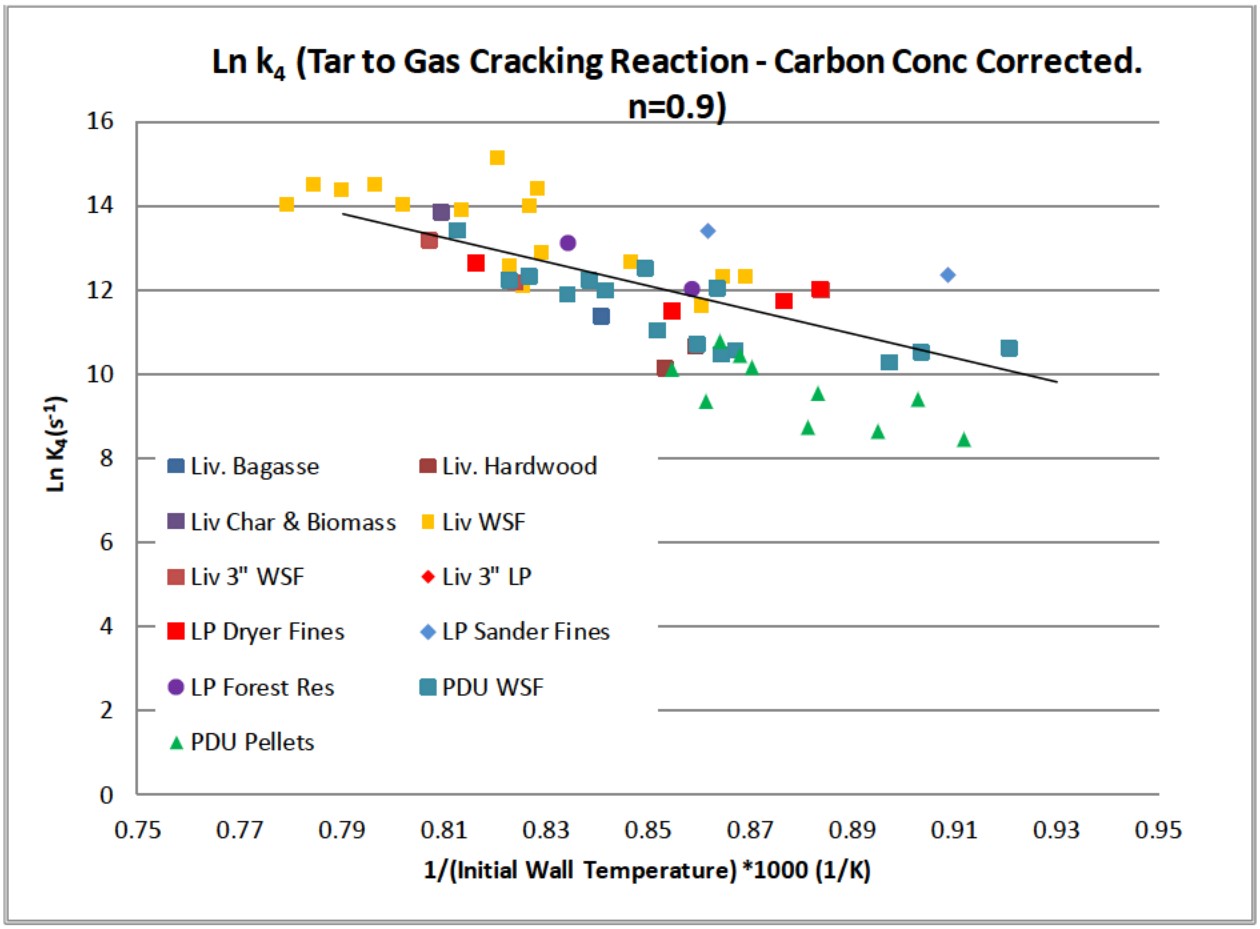


Figure 6-16: Arrhenius Plot for Tar Cracking Model. Carbon Conc. corrected, n=0.9, Multiple Feedstocks

The data might indicate that syngas tar contents with bagasse, pellets and hardwoods may be higher than for softwoods (mainly WSF material) and that feedstocks such as sander fines may produce less tars relatively. More extensive testing would be required to improve the tar modeling and make it feedstock-specific.

Obviously, this simple first order model doesn't capture the complexity of what tar/volatile reactions are occurring in reality, and as such it isn't able to predict a detailed tar analysis. This issue is discussed later.

In terms of scale-up the model described above can be used to estimate tar production in a commercial-scale gasifier. Due to the high order (n=0.9) carbon concentration term used in the rate equation, the syngas tar level can be maintained at a relatively low level, even at increased coil feedrates, as long as the initial wall temperature can be maintained at a high value. This is confirmed by ANOVA of the PDU and Livingston Tar analysis (after the Wasson was installed), which indicated that only initial skin temperature is significant (P-value < 0.05), with regards to the syngas tar content.

C.16 Tar Species

For the total tars (excluding benzene), the breakdown of the tar species can be modeled using the following criteria:

Assume toluene at 3 mol% of total tars

Use the following equation to determine the total syngas light tar (MW< 202) content as a % of the total tars:

Lt tars (%) = 81.1 – 0.037 x Initial wall temperature (^{o}F)

Use the following equation to determine the total syngas heavy tar (MW ≥ 202) content as a % of the total tars:

Hvy tars (%) = 174.6 – 0.097 x Initial wall temperature (^{o}F)

(Note: for initial wall temps > 1800°F, set Hvy tar % =0).

Assume the balance of the total tars are naphthalene (e.g. the % naphthalene in tars will increase as the initial wall temperature increases, but the total syngas tars and total syngas naphthalene content should reduce, as the initial wall temperature is increased).

For the light tars assume the following mix of components:

Acenaphthalene	50%
Phenanthrene	30%
Anthracene	20%

For heavy tars assume the following mix of components:

Pyrene	50%
Fluoranthene	44%
Benzofluoranthene	3%
Benzoperylene	2%
Benzopyrene	1%

C.17 Syngas Methane Content

Published reaction kinetics for non-catalyzed steam-methane reforming would indicate that very little methane reforming would be expected, at the low residence times experienced in the HEHTR. In fact, the methane content of the syngas can be reduced significantly, when operating at high initial skin temperatures, which seems to indicate that, as per the tars, methane reforming can be catalyzed by the hot char also (i.e. when increasing initial wall temperatures to reduce tars, the methane content of the syngas will also tend to reduce).

In fact, there is published data indicating that char/carbon can act to catalyze methane reforming, including the Figure 6-17 below, reproduced from Lee et al [(3)], which shows the extent of conversion of methane in the presence of steam and an activated carbon, at increasing temperatures.

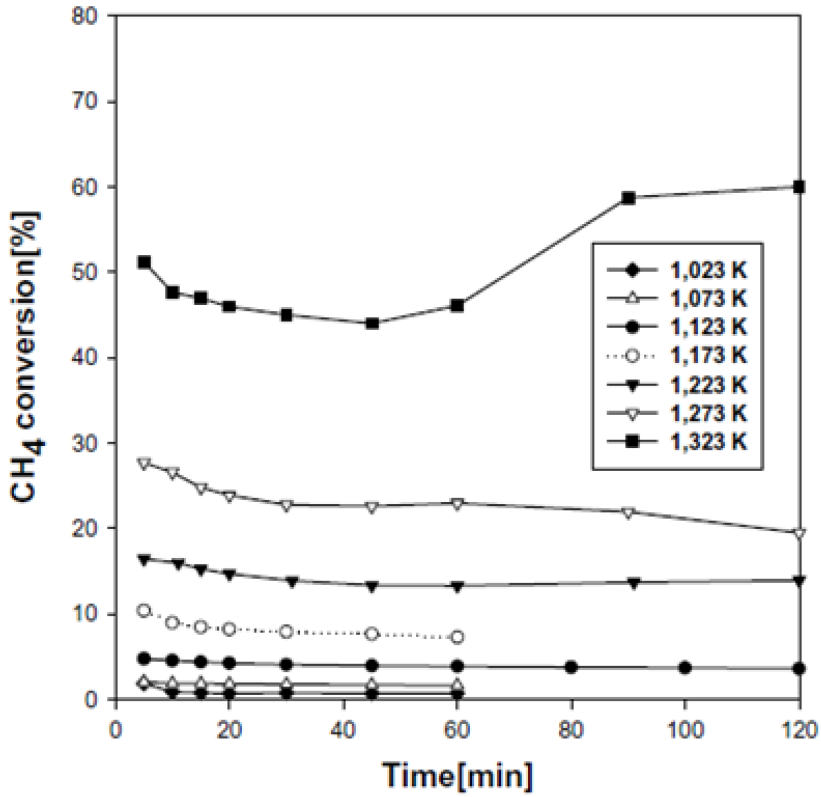


Figure 6-17: Methane Conversion vs. Time over BP-2000 at Different Temperatures.

A similar "hot zone" CSTR model to that constructed for tar cracking, and described above, has been constructed for methane decomposition, including a carbon concentration term (in this case using an ε_A value of 2.0 (instead of 6.5)). Also, in this case, the order for the carbon concentration term is best fitted by an order of 0.7 (n=0.7). The Arrhenius plot for the plant data is presented in Figure 6-18 below:

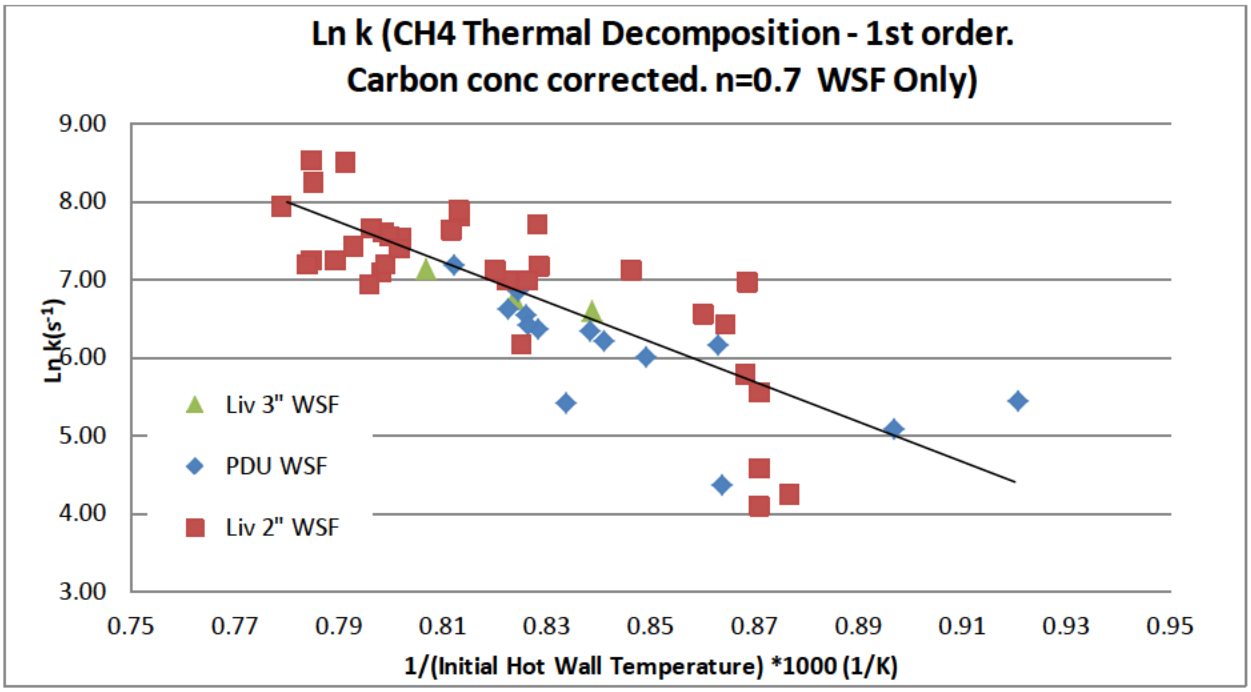


Figure 6-18: Arrhenius Plot of CH4 Decomposition/Reforming. Carbon Conc Corrected (n=0.7). WSF Only

An activation energy of 213,788 J/molK and a pre-exponential constant of 1.531×10^{12} fits the data.

The impact of feedstock on syngas methane content in the syngas has not been studied extensively, but the Arrhenius chart from Figure 6-18 above is reproduced in Figure 6-19 below with multiple feedstock types (straight line fit for WSF feed as a reference):

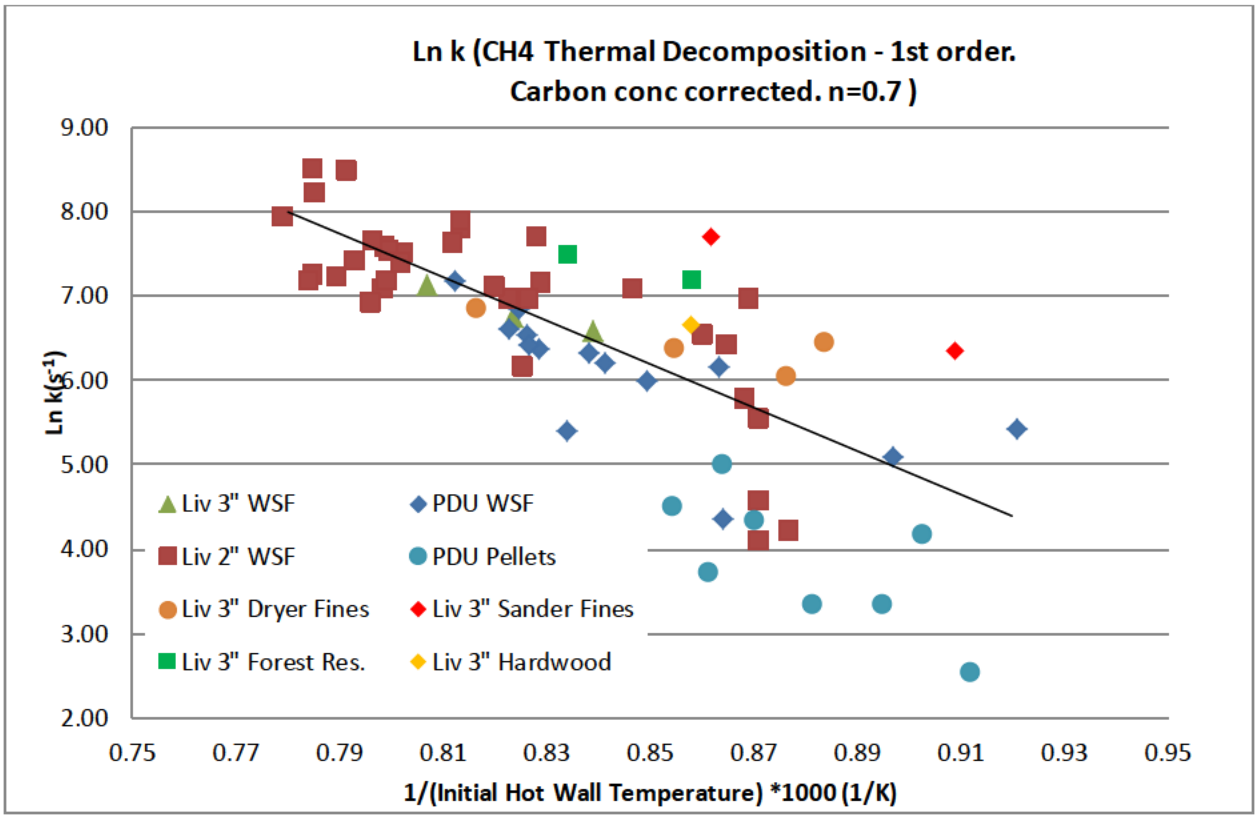


Figure 6-19: Arrhenius Plot for Methane Decomposition/Reforming. Carbon Conc Corrected (n=0.7). All Feeds

Similar feedstock trends with regards to syngas methane content, to those indicated for tars seem to exist.

It's important to note that there is some significant variability around the first order model fit and the plant data for this Arrhenius plot, as for many of the plots included in this report. This is believed to be due, in part, to the variability in catalytic activity of the char, which depends on feedstock properties, ash contents, heating rates, and many other parameters. This variability makes it literally impossible to accurately estimate the gas analysis from the HEHTR, although the parametric and fundamental models developed attempt to provide an estimated gas analysis. In this regard, it is probably prudent to establish error bars with the estimated gas analysis for future work.

At low initial wall temperatures, some of the data falls well below the Arrhenius curve. This is believed to be a result of there literally being no CH_4 decomposition reactions occurring at these low initial wall temperatures. Hence an initial wall temperature of approximately 1600°F might be considered a minimum "strike" temperature for these reactions.

It's also worth mentioning that methane is believed to be formed via initial biomass pyrolysis, but also is subsequently formed, in secondary gas phase reactions, as methane groups break off of methylated tar species.

The simple first order model described above predicts syngas methane contents as low as 4-5 vol% at low feedrates and high initial wall temperatures or as high as 12 vol% (the assumed methane content of the syngas after devolatization (i.e. with no methane decomposition). This largely matches the range of syngas

methane contents measured at the PDU and at the Livingston plant. The point being that the methane content of the syngas can be reduced significantly, by appropriate reformer design, which may be desirable (i.e. BtL applications for the technology). Another point that needs to be recognized is that this methane reforming comes at significant thermal cost. The methane reforming reaction is highly endothermic and driving the CH_4 content of the syngas down significantly increases the absorbed duty of the coils, and hence increases the required fired duty for the HEHTR.

C.18 Syngas H_2:CO Ratio

Plots of the syngas H_2:CO ratio versus initial wall temperature for the Livingston 2" coil, the Livingston 3" coil and the PDU are included in the figures below:

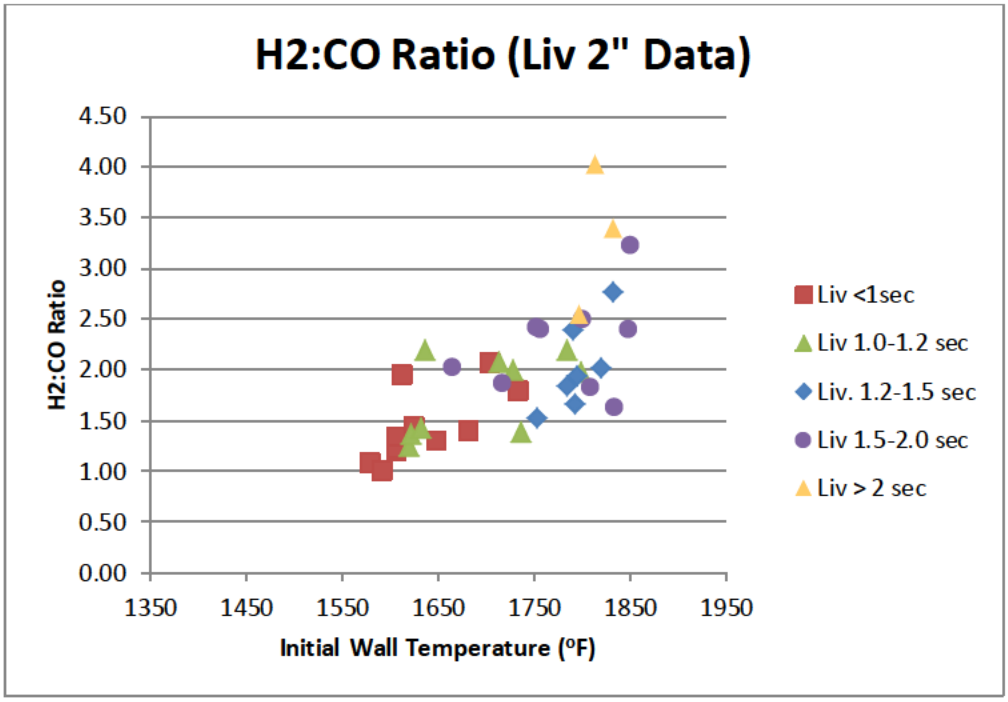


Figure 6-20: Syngas Hydrogen to CO Ratio Data for Livingston 2" Coil

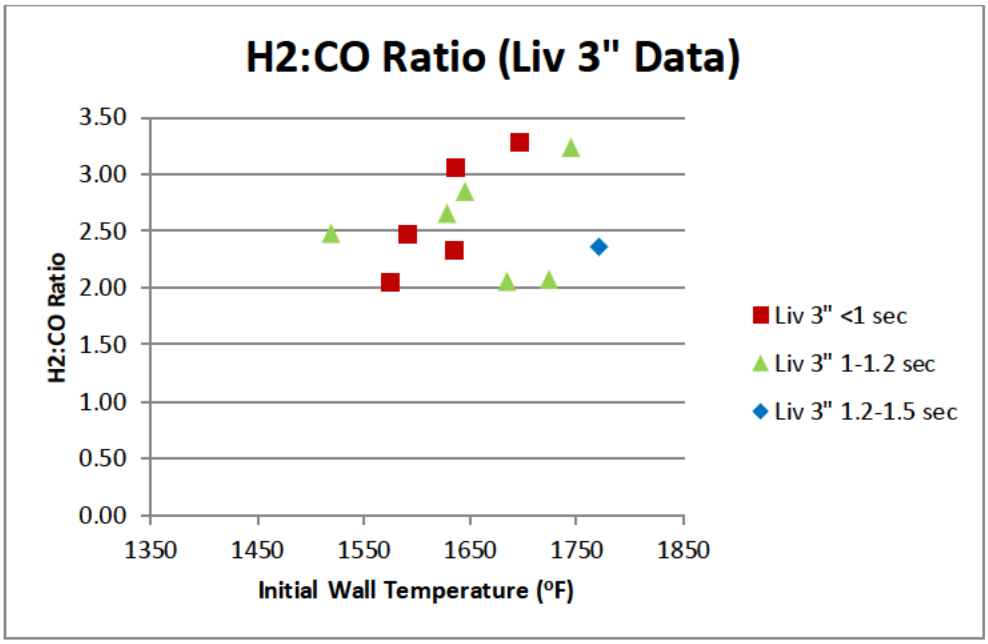


Figure 6-21: Syngas Hydrogen to CO Ratio for Livingston 3" Coil

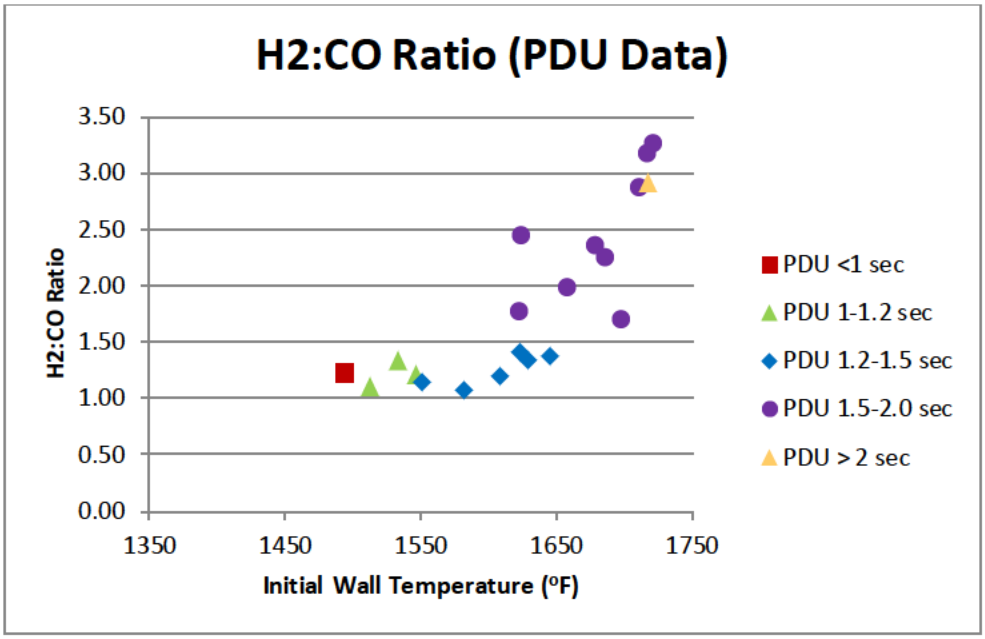


Figure 6-22: Syngas Hydrogen to CO Ratio for PDU HEHTR

The 2" coil Livingston data presented above would seem to indicate that coil residence time does not have a significant impact on syngas H_2:CO ratio at lower initial skin temperatures, but that at higher skin temperatures, the higher residence time does appear to impact the H_2:CO ratio. This is less clear with the PDU data plotted, probably primarily due to there being less overlap of the data at similar initial wall temperatures (i.e. less comparative data at similar skin temperature and different coil residence times).

It would appear that the Livingston 3" coil produced higher syngas H_2:CO ratio for the same gas residence times (up to residence times of 1.2 sec) and equivalent initial wall temperatures, as the 2" coil. Above initial wall temperatures of 1700°F at least the syngas H_2:CO achieved in the 3" PDU coil also appeared to be higher than was achieved with the Livingston 2" coil. This is explained, at least partially, below.

Given all of the above data, it is not a simple task to model the syngas H_2:CO ratio and provide a predictive tool. Although it is possible to construct a more rigorous model, it appears that a simple correlation with the syngas methane content provides a useful correlation. This correlation is represented in the figure below:

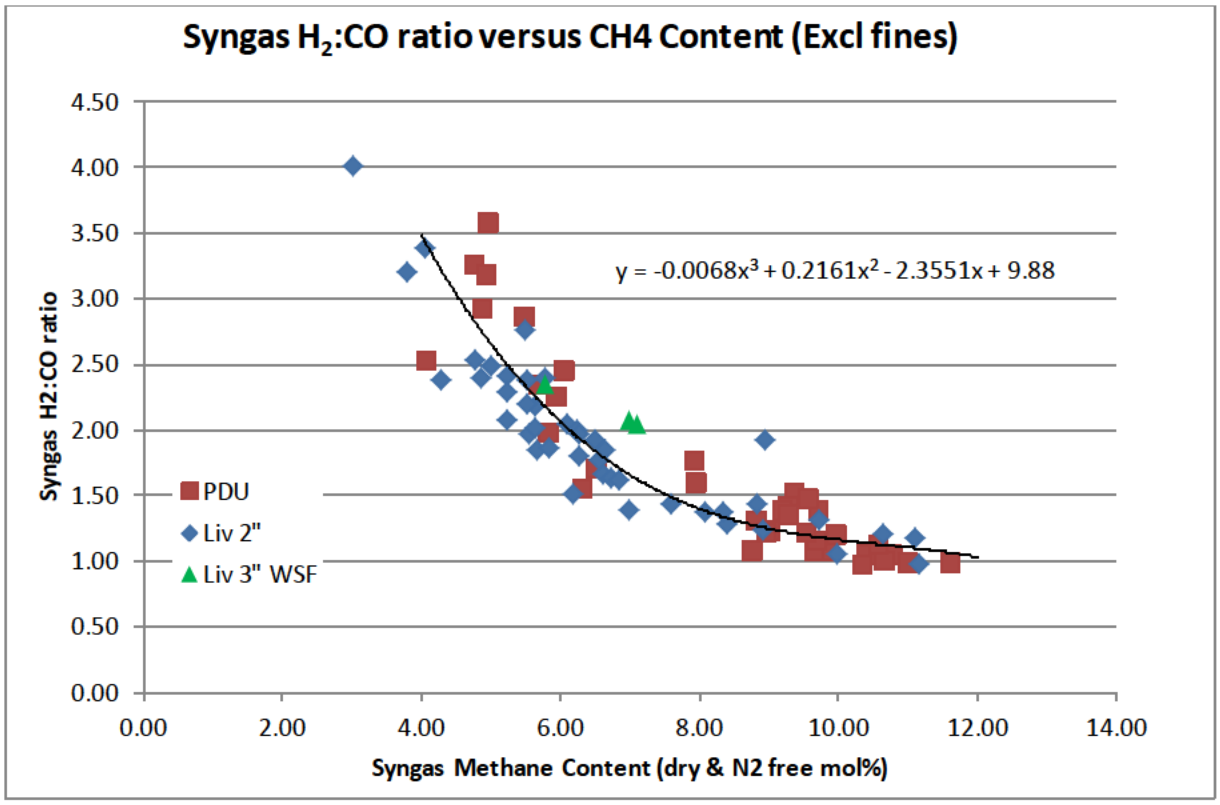


Figure 6-23: Syngas Hydrogen to CO Ratio vs Methane Content (excluding dryer and sander fines)

The correlation that fits the curve approximates:

$$H_2\text{:CO ratio} = 9.88 - 2.355 \times CH_4\ \text{mol\%} + 0.216 \times (CH_4\ \text{mol\%})^2 - 0.0068\,(CH_4\ \text{mol\%})^3$$

The reason that dryer and sander fines were not included in the above chart, is that these finer feeds did seem to result in higher syngas H_2:CO ratios, for the same syngas methane contents than the regular Livingston ground (and reground) materials, including the bagasse and hardwoods that were run at Livingston. The particle size distributions are shown in the following table:

Table 6-9: Particle Size Distributions for Various Feedstocks

	> 2 mm (%)	1-2 mm (%)	0.5-1 mm (%)	< 0.5 mm (%)
Double Ground WSF Feed 12/12/2012	**3.5**	**36**	**32**	**29**
Ground WSF Feed	**28.0**	**47**	**22.2**	**2.7**
WSF PDU Ground November 2012	**37**	**39**	**18**	**5**
Double Ground WSF Feed 1/14/2013	**9.2**	**26**	**28**	**37**
Dryer Fines	**4.0**	**12.7**	**43.1**	**40.2**
Sander Fines	**0.04**	**1**	**18**	**81**

For reference the Dryer Fines and the Sander Fines are shown below, and are significantly finer and somewhat drier than the normal WSF feeds:

Figure 6-24: Finer Feedstocks

So even though the re-ground Livingston WSF feeds produced syngas H_2:CO ratios that fall on the proposed correlation curve, the smaller Dryer and Sander Fines resulted in data, as plotted in the figure below:

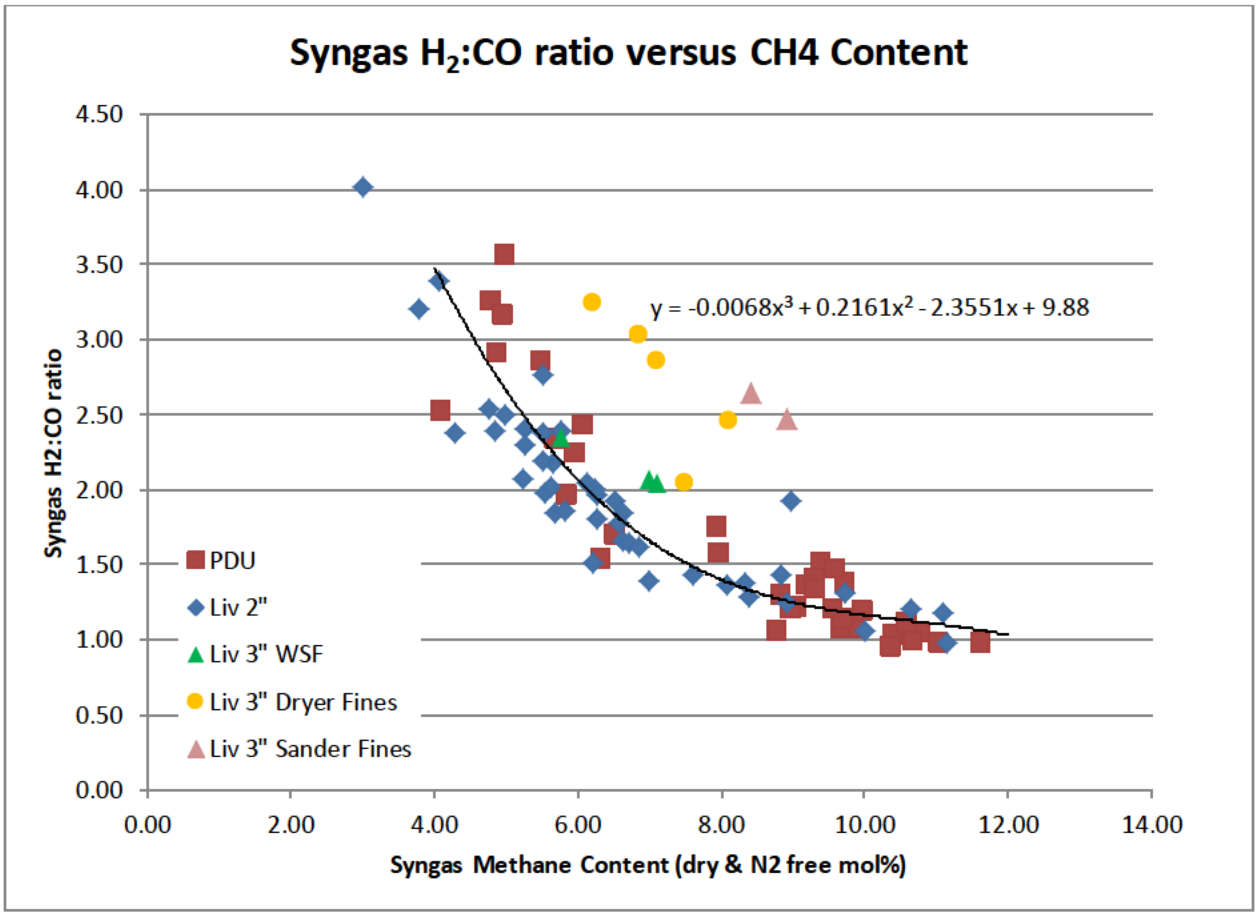


Figure 6-25: Syngas Hydrogen to CO Ratio vs. Methane Content (Finer Feedstocks Included).

C.19 Syngas Benzene Content

A similar "hot zone" CSTR model to that constructed for tar cracking, and described above, has been constructed for benzene decomposition, including a carbon concentration term (in this case using an ε_A value of 3.0 (instead of 6.5) and the order for the carbon concentration term is best fitted by an order of 0.1 (n=0.1)). The Arrhenius plot for the plant data is presented in Figure 6-26 below:

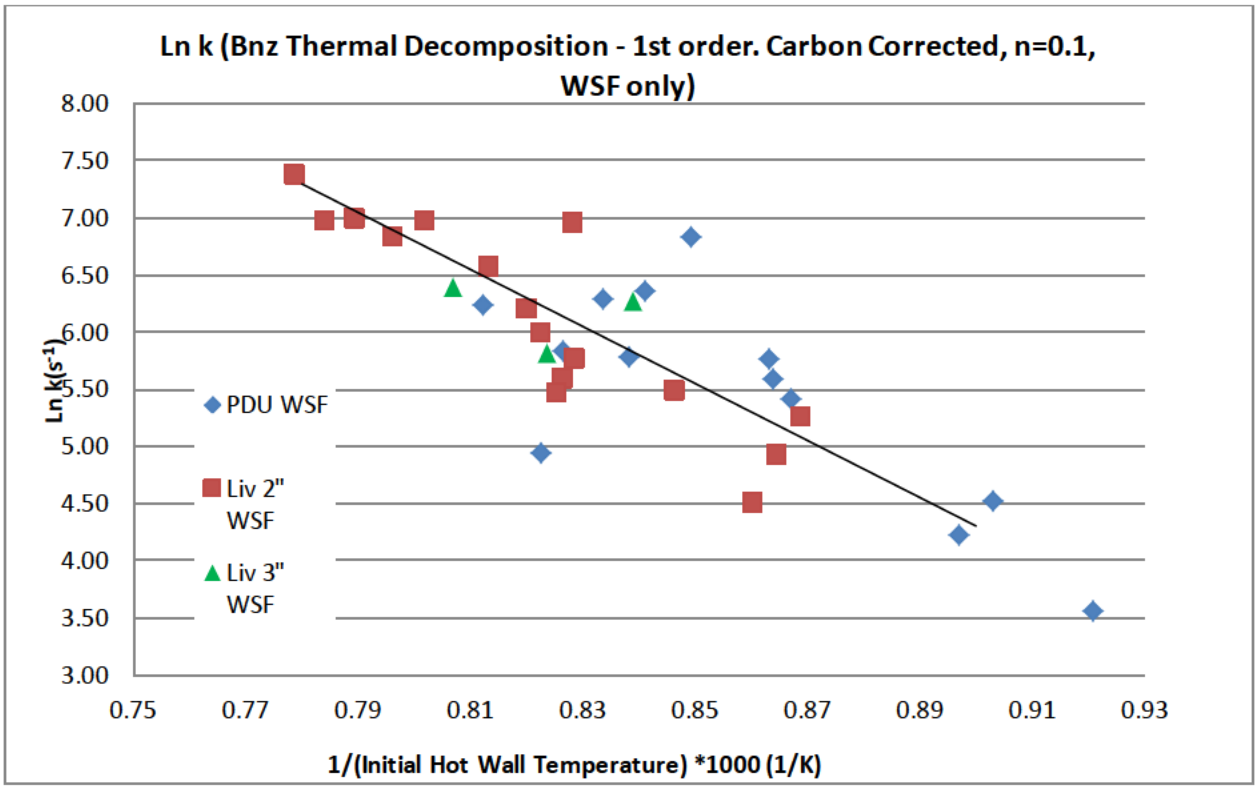


Figure 6-26: Arrhenius Plot for Benzene Decomposition/Reforming. Carbon Conc Corrected (n=0.1). WSF Only.

An activation energy of 207,850 J/molK and a pre-exponential constant of 4.356×10^{11} fit the data.

The impact of feedstock on benzene content in the syngas has not been studied extensively, but the Arrhenius chart from Figure 6-26 above is reproduced in Figure 6-27 below with multiple feedstocks types (straight line fit for WSF feed as a reference):

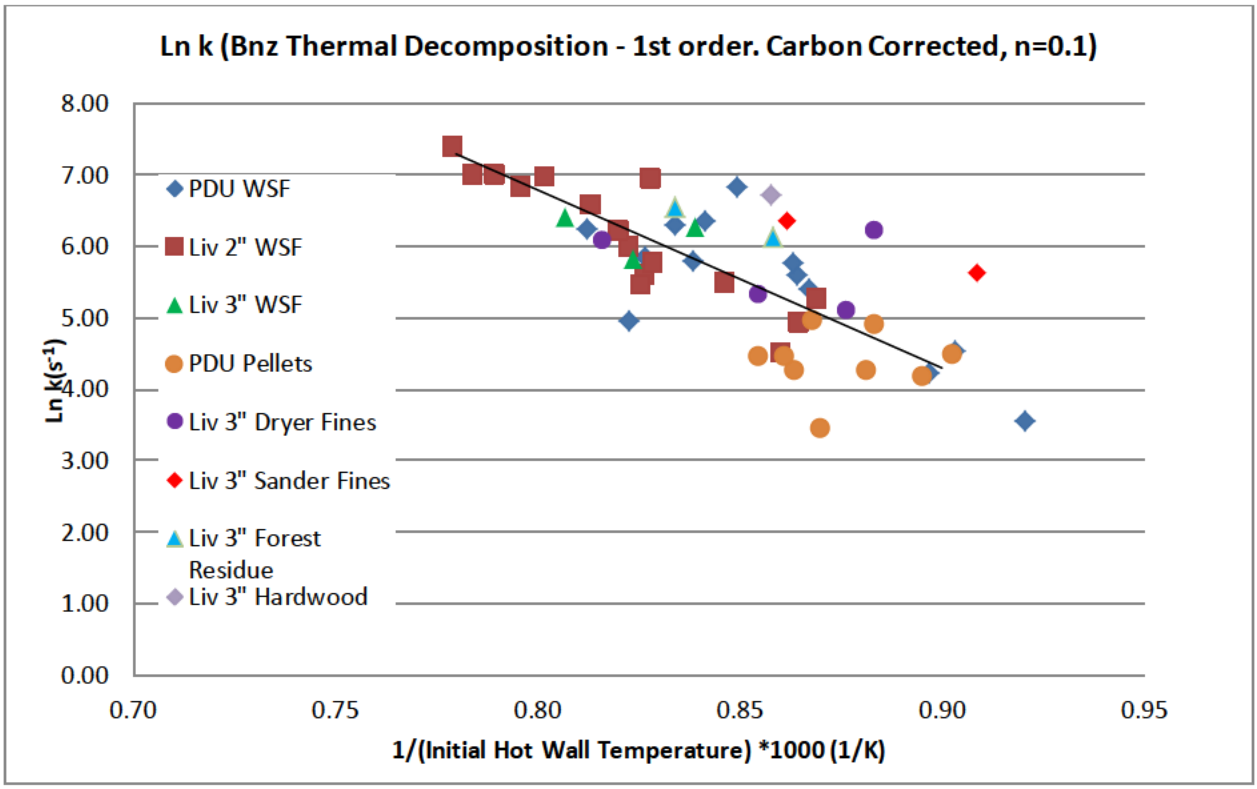


Figure 6-27: Arrhenius Plot Decomposition/Reforming. Carbon Conc corrected (n=0.1). All Feeds

Similar feedstock trends with regards to syngas benzene content, to those indicated for tars seem to exist.

Benzene is produced in initial biomass pyrolysis, but also is the product of gas phase decomposition of heavier, polyaromatic tar species. This may partially explain why the reaction model is fitted best, with only a low order (n=0.1) for the carbon concentration term (i.e. char catalyzed reactions at initial pyrolysis are not as critical).

C.20 Syngas Ethylene Content

A similar "hot zone" CSTR model to that constructed for tar cracking, and described above, has been constructed for ethylene decomposition, including a carbon concentration term (in this case using an ε_A value of 2.0 (instead of 6.5) and the order for the carbon concentration term is best fitted by an order of 0.9 (n=0.9)). The Arrhenius plot for the plant data is presented in Figure 6-28 below:

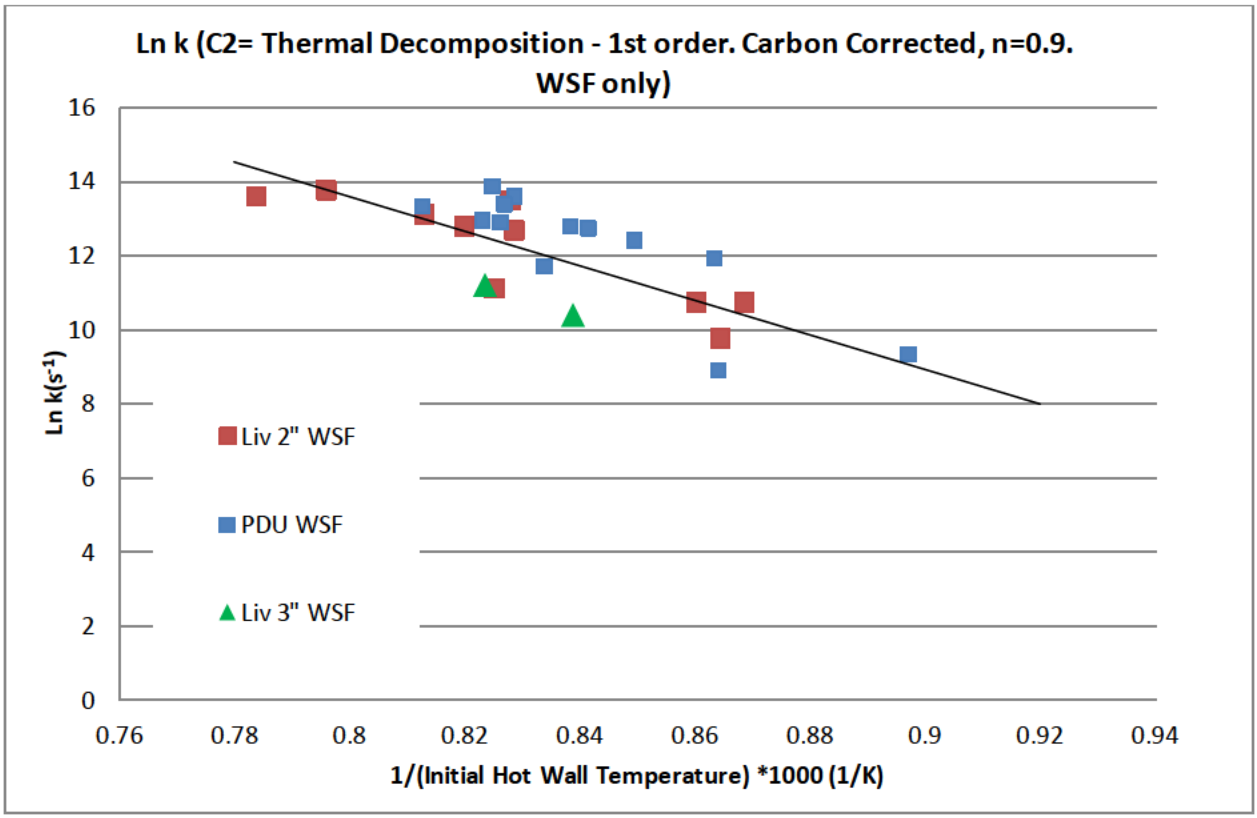


Figure 6-28: Arrhenius Plot for Ethylene Decomposition/Reforming. Carbon Conc corrected (n=0.9). WSF Only.

An activation energy of 386,007 J/molK and a pre-exponential constant of 1.059×10^{22} fit the data.

The impact of feedstock on syngas ethylene content in the syngas has not been studied extensively, but the Arrhenius chart from Figure 6-28 above is reproduced in Figure 6-29 below with multiple feedstocks types (straight line fit for WSF feed as a reference):

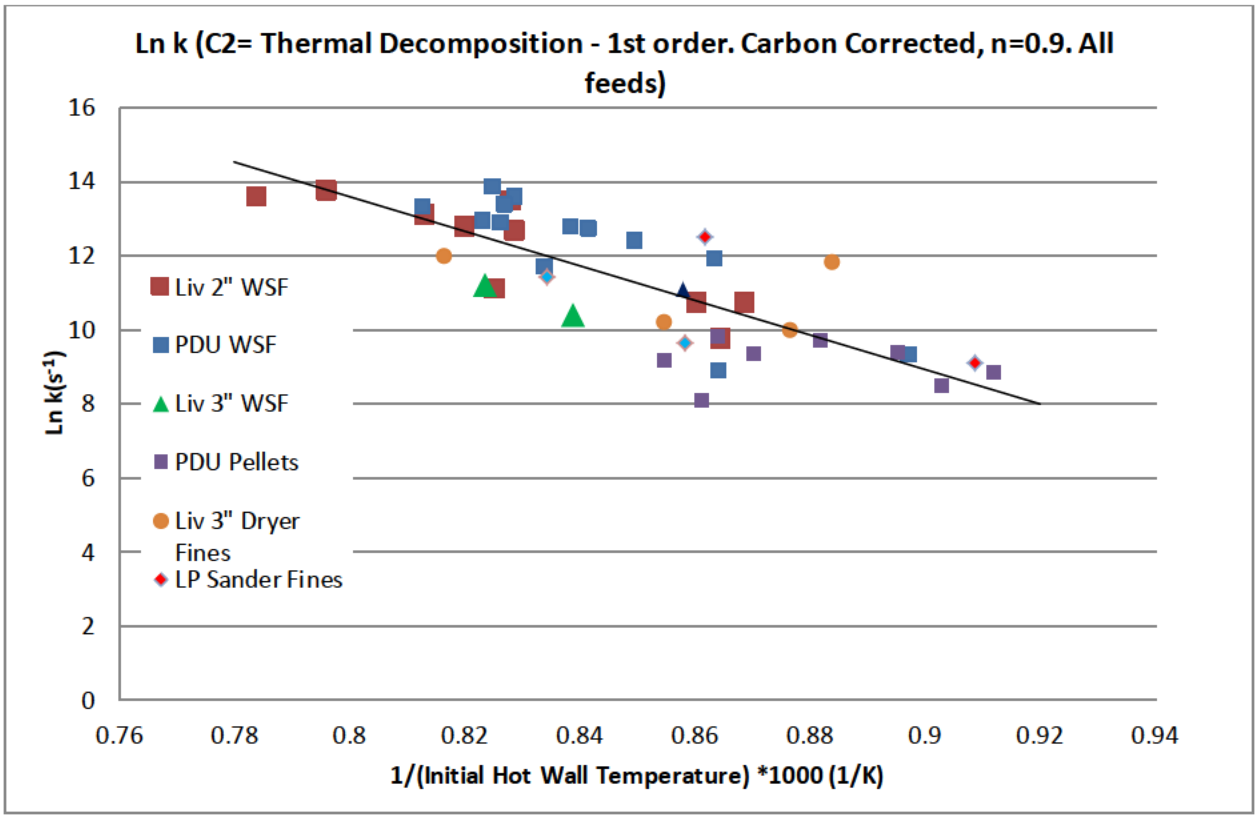


Figure 6-29: Arrhenius Plot for Ethylene Decomposition/Reforming. Carbon Conc Corrected. (n=0.9). All Feeds.

In addition to the kinetic reaction model described above, it is also possible to correlate the ethylene and methane concentrations, as indicated in the figure below:

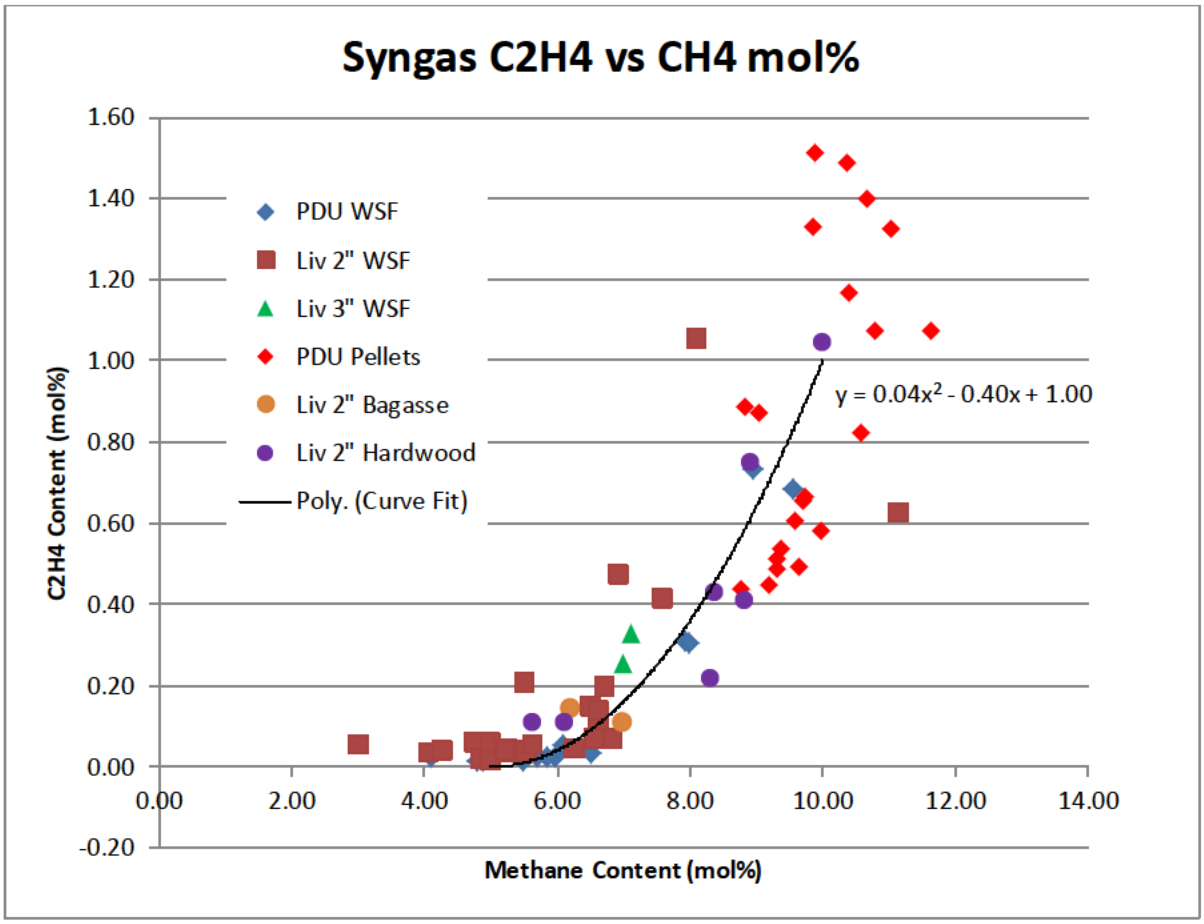


Figure 6-30: Syngas Methane Content vs. Ethylene Content

C.21 Biomass Devolatization

In order to be able to estimate the absorbed duty-temperature relationship for the steam/biomass stream, it is necessary to estimate the degree of devolatization of the biomass as a function of the stream temperature and/or the distance down the coil(s). In-coil gas analysis data collected on the 3" coil installed at the Livingston pilot plant allows the extent of gas production at specific points in the coil to be assessed, using a nitrogen and/or argon balance, as well as the actual gas analysis. The results of this analysis are summarized in the charts below:

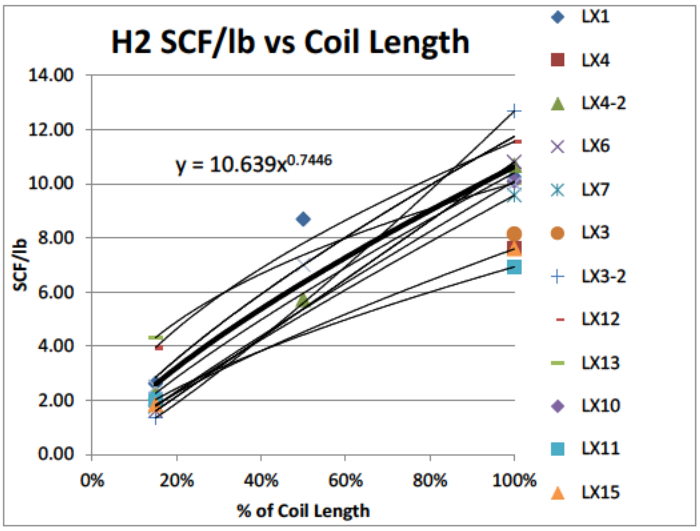


Figure 6-31: Hydrogen Yield vs. Coil Length

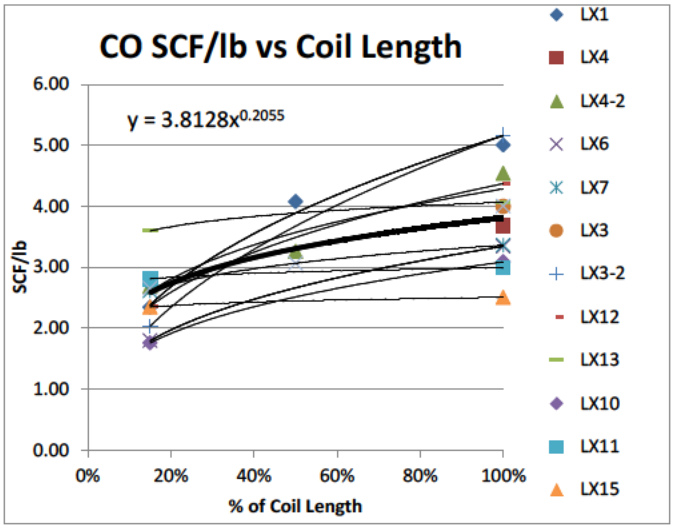


Figure 6-32: CO Yield vs. Coil Length

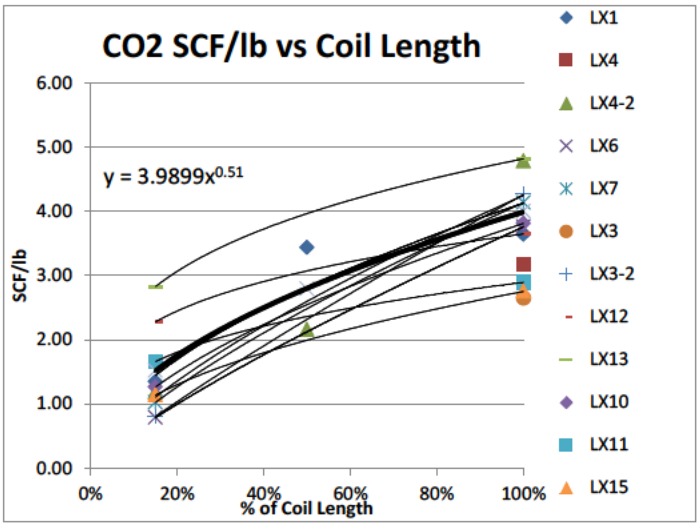


Figure 6-33: CO_2 Yield vs. Coil Length

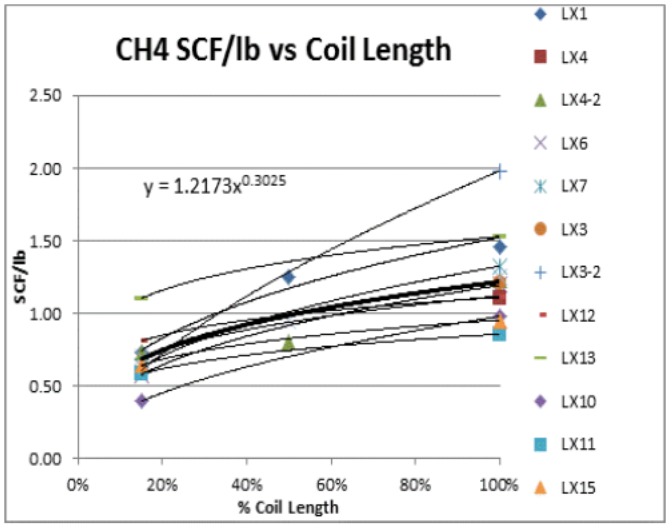


Figure 6-34: Methane Yield vs. Coil Length

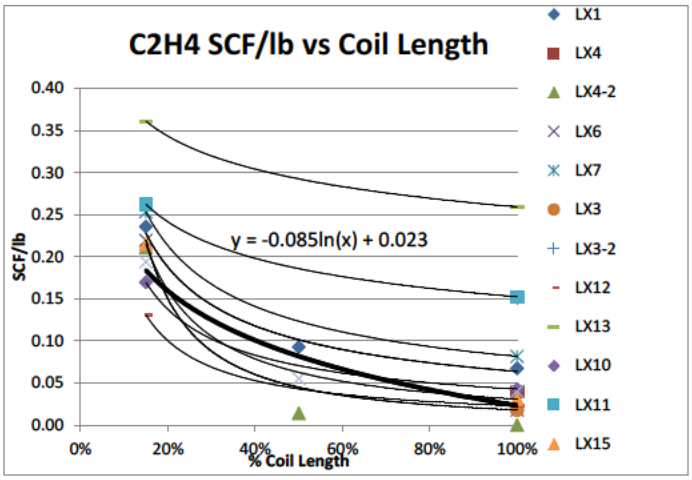


Figure 6-35: Ethylene Yield vs. Coil Length

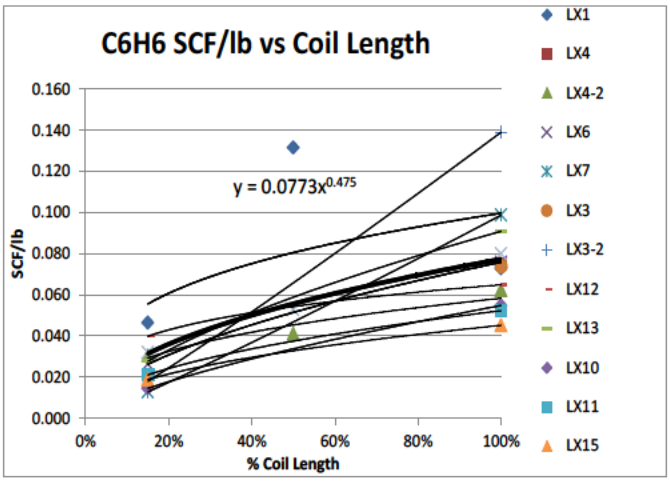


Figure 6-36: Benzene Yield vs Coil Length

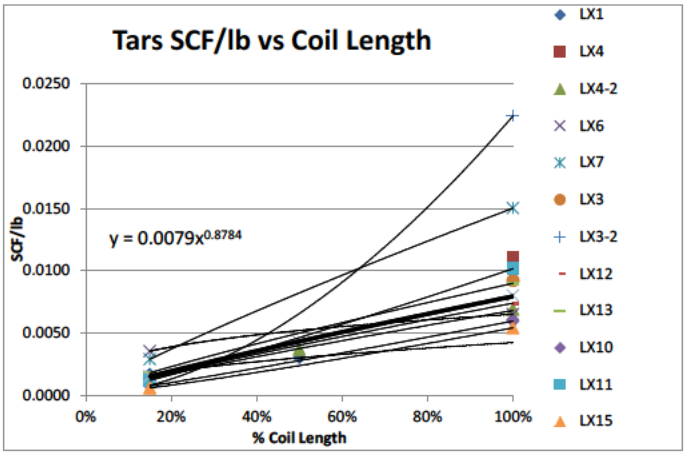


Figure 6-37: Tar Yield vs. Coil Length

C.22 Air Injection

Air injection upstream of the HEHTR coil(s) was tested at both the PDU and at Livingston to determine if this could be used as a way to minimize tar production, as well as a way to reduce the required coil absorbed duty.

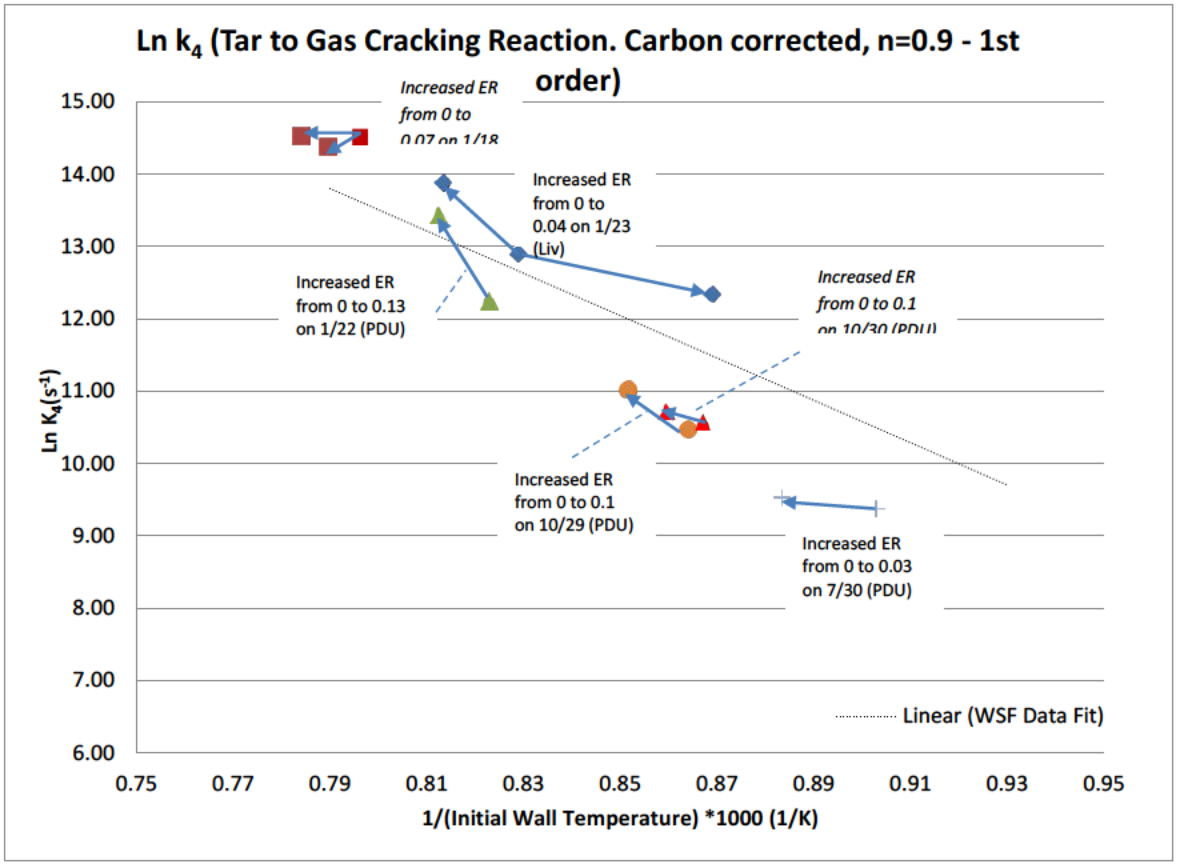


Figure 6-38: Impact of Air Injection

In terms of tar reduction, the following curve indicates that air injection, per se, does not tend to reduce syngas tar content (i.e. the ln k4 value does not seem to increase more rapidly than would be expected purely as a result of increased coil skin temperature, for most of the air injection test conducted).

However, it does appear that in several cases, the air injection did in fact reduce the syngas tars significantly by virtue of the fact that it increased the initial wall temperature. Hence, air injection may still be a valid tar reduction feature that can be employed, in addition to simply reducing the absorbed duty requirement, by internal heat generation in the coil.

A rough approximation for the reactions produced by air injection into the coil is approximately 70% of the oxygen reacting with H_2, 15% with carbon monoxide and 15% partially oxidizing methane to $CO + 2\ H_2$. As well as being consistent with PDU and Livingston plant observations, this stoichiometry is consistent also with the data in Reference 10.

C.23 Coke and Soot Production

Scanning electron microscopy of char produced at the PDU showed evidence of fine particles, with high carbon concentration, adhering to larger char particles. Results of this SEM are provided below:

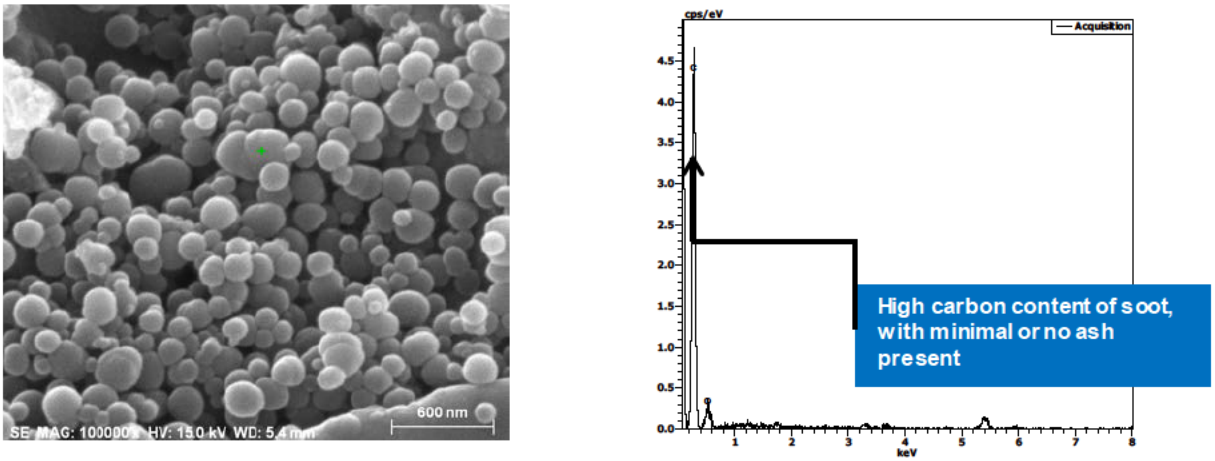


Figure 6-39: Scanning Electron Micrograph of Char from PDU HEHTR

Also, the bimodal nature of the particle size distribution of sampled venturi water (See figure below), suggests that there is some amount of very fine particulate, that is passing through the cyclones and oil scrubber, and is being collected in the downstream water wash tower, or the downstream filters.

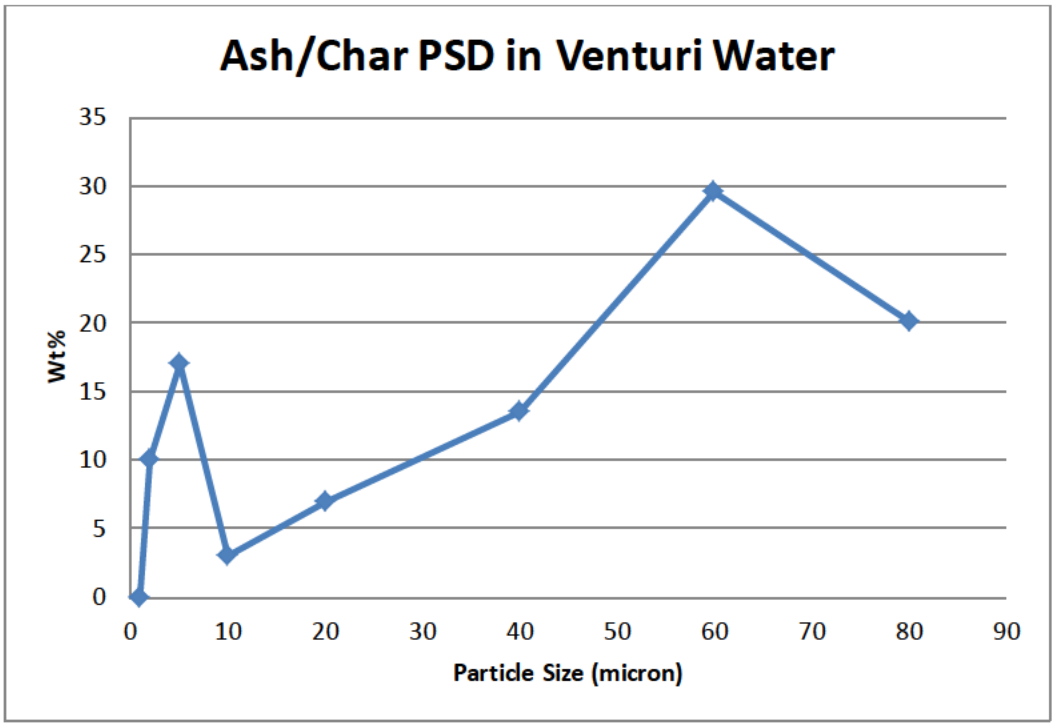


Figure 6-40: Ash/Char Particle Size Distribution in PDU Venturi Water

Additional planned testing on char and carbonaceous solids collected at the PDU, to determine what % of these materials may be generated from soot forming reactions, is currently on hold.

Without additional soot analysis being able to be conducted at the PDU, it is suggested that an allowance equal to 2% of the biomass feed (approximately 4% of the feed carbon content) for soot production, which is present primarily as very fine particulate material, that is able to pass through primary and secondary cyclones, is sufficient. This is consistent with data presented in Reference 11 also.

C.24 Char Recycle

Char could be recycled in a separate coil or it could be recycled back, with the fresh biomass, in the same coil. The argument for recycling it back with biomass would potentially be that the additional catalytic effect of the char tends to enhance one or more of the favorable char catalyzed reactions.

A test was conducted at Livingston, using a mixture of biomass (77 wt%) and char (23 wt%). The figures below illustrate the apparent impact of the char recycle on several secondary reaction rates.

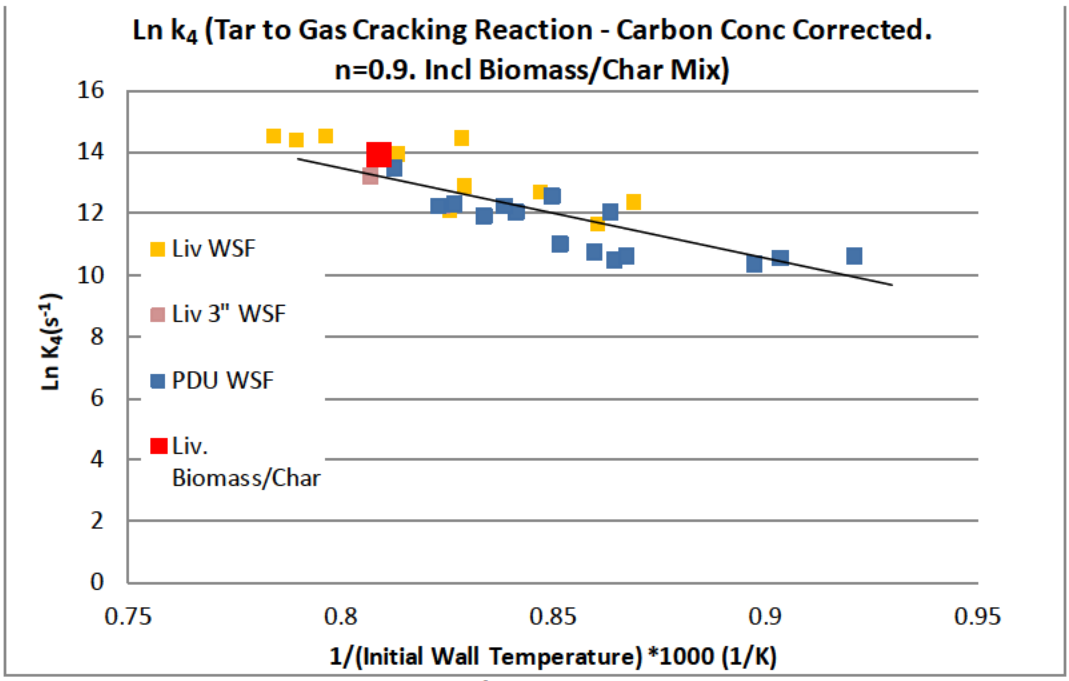


Figure 6-41: Tar Cracking Kinetics for Biomass/Char Mixture

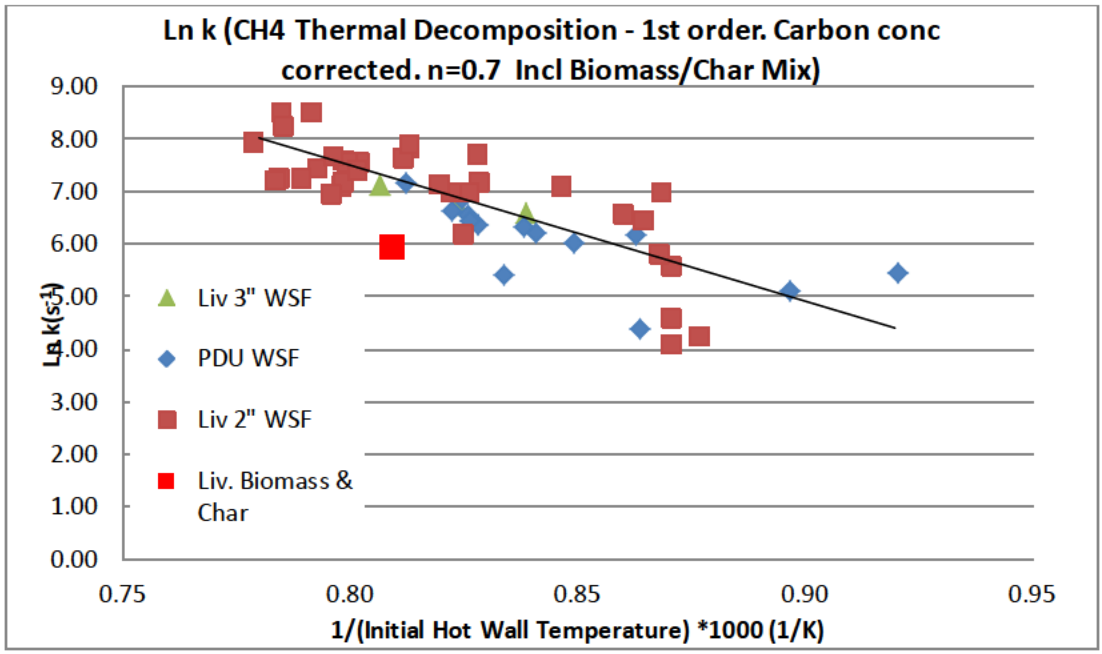


Figure 6-42: Methane Decomposition Kinetics for Biomass/Char Mixtures

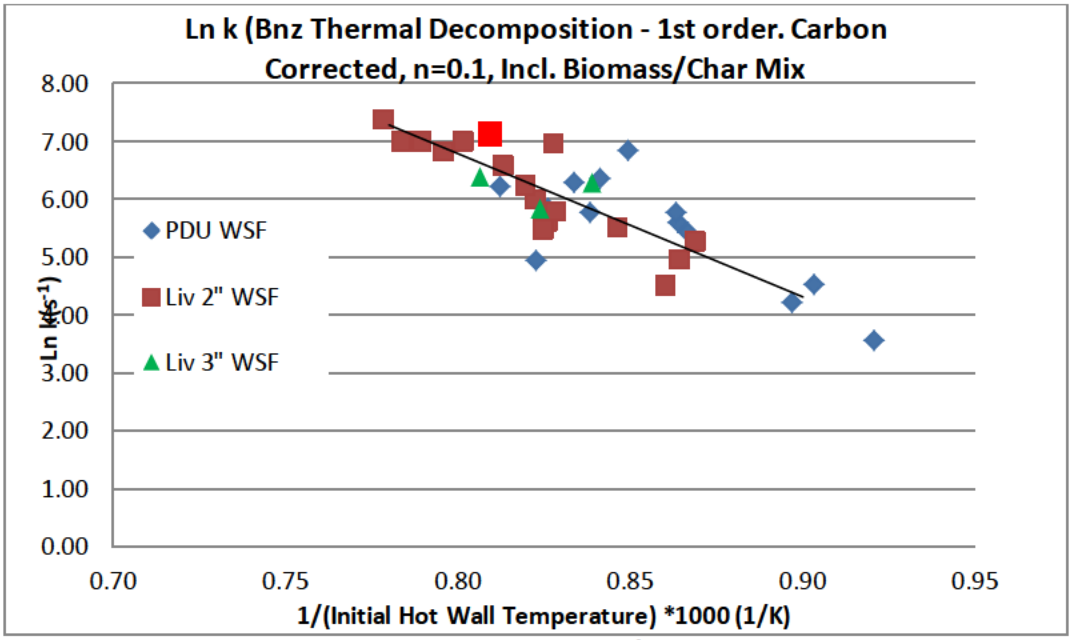


Figure 6-43: Benzene Decomposition Kinetics for Biomass/Char Mixtures

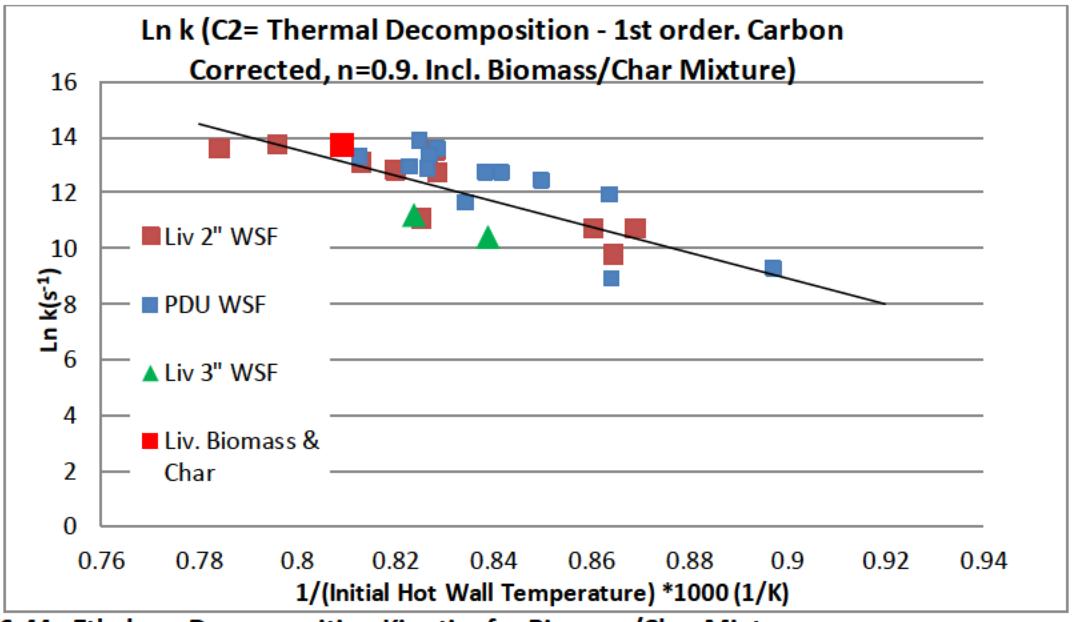


Figure 6-44: Ethylene Decomposition Kinetics for Biomass/Char Mixtures

In addition, the syngas H_2:CO ratio may have increased marginally, for the 77% biomass/23% char run, but the original relationship still seems to be largely applicable.

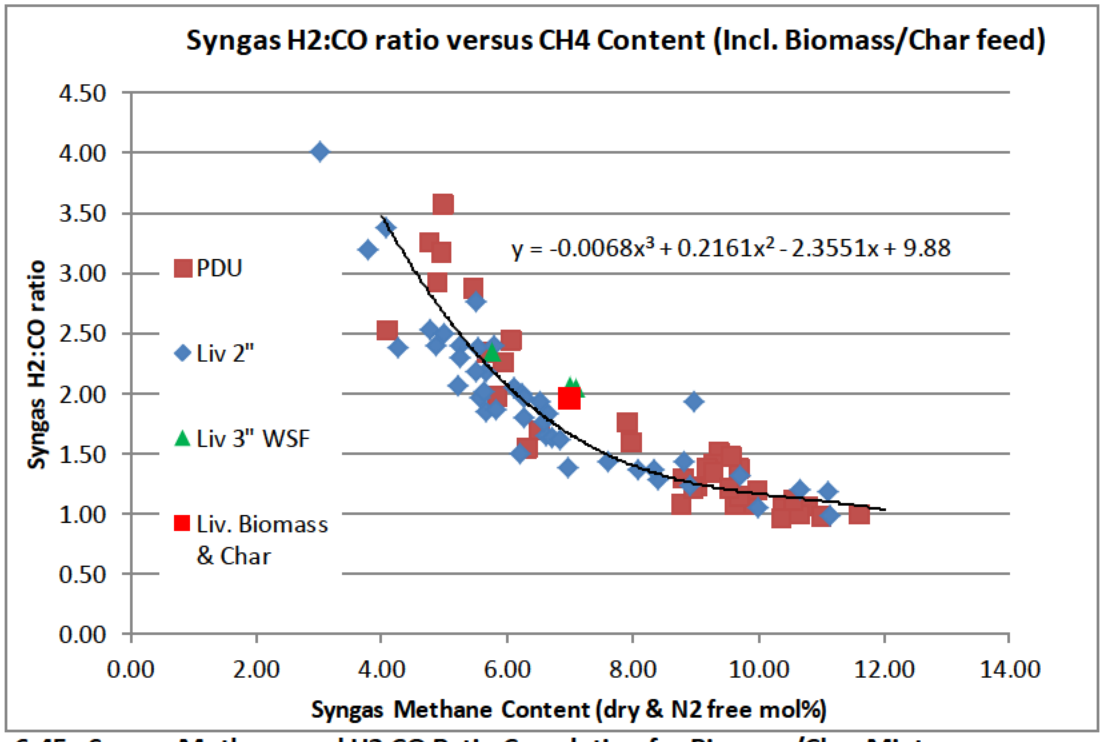


Figure 6-45: Syngas Methane and H2:CO Ratio Correlation for Biomass/Char Mixtures

In the case of char recycle, there is additional carbon present in the reformer pyrolysis zone, and this is expected to increase the reaction rates, to some extent, as a result of the carbon concentration term in each of the species gas kinetic models. It appears that at least for tar, benzene and ethylene decomposition reactions, additional char recycle has the expected effect, in that these decomposition reactions appear to proceed at roughly the rate calculated by the model (i.e. taking into account the higher carbon concentrations). In the case of methane decomposition, the actual reaction rate is slower than would be anticipated, as a result of the increased carbon content.

Hence, char recycle, in particular for syngas tar control may be a valid approach, although the capacity limits described below may effectively limit the extent to which this control can be employed. In addition, there is the impact on overall carbon conversion that needs to be considered.

The Livingston test with combined WSF biomass (55 lb/hr @ 52% C) and char (16 lb/hr @ 83% C) was run with a calculated overall carbon conversion of 72%. The carbon conversion model described above would predict a conversion of 82% with biomass only feed (assuming no interaction with the char, but accounting for the combined feed flow to the coil). Hence, if the biomass conversion was actually 82%, the conversion of the char only could be estimated at approximately 50%, which is not significantly different to the carbon conversion achieved for 100% char only recycle testing conducted at Livingston, which was 60%, at similar conditions.

Hence, the presence of the biomass and more importantly the higher syngas species concentrations in the coil, didn't appear to significantly inhibit the char reactions.

Hence, char recycle could be employed either in a separate (dedicated) coil or it could be employed by simply pre-mixing char with the biomass feed. A 50% carbon conversion per pass of the char can be assumed in either situation.

C.25 Trace Analysis

Sulfur

From syngas and water analyses, the sulfur in the biomass partitions such that approximately 10% of the biomass sulfur is retained in the char, 50% to the wash water and 40% in the scrubbed syngas, essentially all as hydrogen sulfide, depending on the water wash conditions (e.g. pH, temp, etc.).

Nitrogen

Approximately only 10% of the biomass nitrogen is released as ammonia and hydrogen cyanide in the syngas, with only 1% or less of the nitrogen remaining in the char and the balance being released as diatomic nitrogen, in the syngas. The low conversion of biomass nitrogen to ammonia and hydrogen cyanide is believed to be related to the fast pyrolysis conditions that exist in the HEHTR. This issue would probably warrant additional testing, at a later date, if possible. Of the nitrogen released as ammonia and hydrogen cyanide, approximately 12% is in the form of hydrogen cyanide, with the balance (88%) being present as ammonia. Almost all of the ammonia and hydrogen cyanide is removed in the water scrubber.

Chlorine

For design purposes, assume that 100% of the biomass derived chlorine is volatized into the syngas stream. All of this should be recovered in the water scrubber.

C.26 Ash Constituents

By and large, the major ash constituents in the biomass remain in the char. Exceptions to this are chloride, described above, which can be assumed to be almost 100% volatized into the syngas and potassium and manganese, which are likely released as KCl and $MnCl_2$ respectively. If 100% of the chlorine present is volatized either with potassium or manganese, which should set the upper limit for the expected volatization of these two ash constituents, KCl will be the primary form of the chloride. Ash analysis at the PDU indicated that approximately 25% of the potassium present in the feedstock was volatized into the syngas.

C.27 Feedstock Particle Size

As described above, the finer feeds (dryer fines and sander fines) did produce syngas with a higher H_2:CO ratio, relative to the syngas methane content, than the other feedstocks processed at Livingston or at the PDU.

The carbon conversion rate data for these finer feeds overplayed on Figure 6-9, and are highlighted on the carbon reaction rate plot below:

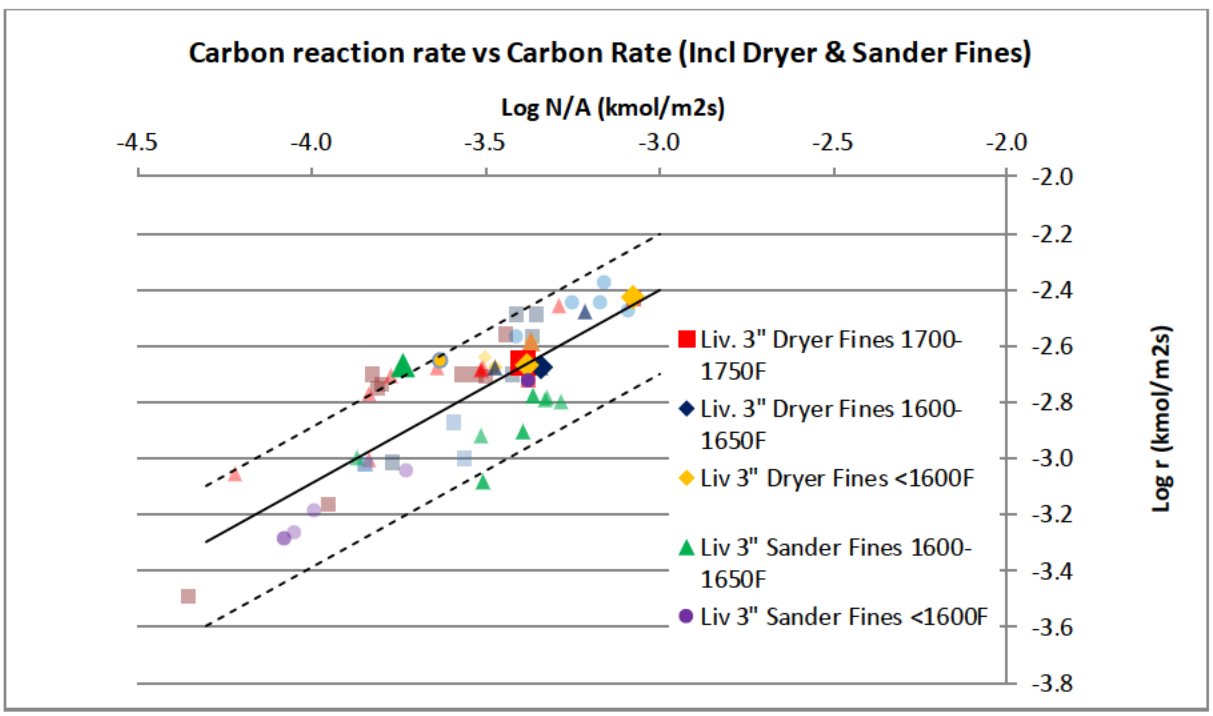


Figure 6-46: Carbon Reaction Rate Data for Finer Feedstocks

This data would seem to indicate a somewhat higher relative reaction rate, for relatively low initial wall temperatures, for both materials, but particularly for the sander fines.

Data for tar, methane, benzene and ethylene decomposition reaction rates are included in the earlier sections and also seem to indicate that these finer feeds are more reactive at lower initial wall temperatures.

C.28 Feedstock Moisture

Most of the feedstocks processed at the Commerce City PDU and the Livingston pilot plant were generally relatively dry (5-15 wt% moisture), so extensive parametric testing at a wide range of feedstock moistures was not able to be conducted. Data was collected at the PDU, at low feedrates (330 lb/hr) on WSF material and at similar initial wall temperatures for a range of feedstock moistures, from 25 wt% to 12 wt%. In this case, the syngas composition, gas yield and conversion were not substantially different and the syngas total tar content was slightly higher in tars for the high moisture feedstock, but in particular the heavy tar content was significantly higher for the high moisture feedstock. This data would suggest that it is preferable to maintain a feedstock moisture at 15 wt% or less, for the HEHTR feedstock. Additional testing is warranted (later) to provide more data on the impacts of higher moisture feedstocks.

C.29 Coil Maximum Capacity

Neither the PDU or the Livingston plant were able to be run continuously at sufficiently high feedrates, to ascertain definitively the ultimate capacity limits of the HEHTR reformer itself. There was, however, some limited operations at higher rates, which provide some data, as discussed below, and there is literature on the capacity limits determined for the vortex reactors as determined by Lede and by Diebold

Both Lede and Diebold described the maximum capacity of the vortex reactor systems they operated and both determined that the ultimate capacity limit to be approximately 6.5 lb/hr per ft^2 of vortex reactor internal surface area. For the PDU, this limit would equate to an approximate feedrate of 650 lb/hr per coil (using only the outside area of the helical coil). For the 3" coil installed at Livingston, the limit would equate to a feedrate of 280 lb/hr. In both cases, we were not able to operate either unit at these feedrates continuously, to be able to test these limits.

Lede[1] reports rapid metal temperature increases as the vortex reactor began to plug at higher feedrates. Data collected from Livingston, at high feedrates, show that the skin thermocouple at point A increased significantly, relative to the downstream skin thermocouples. Some of these temperature trends are provided in the figures below, as well as a skin temperature trend at lower feedrates, for comparison:

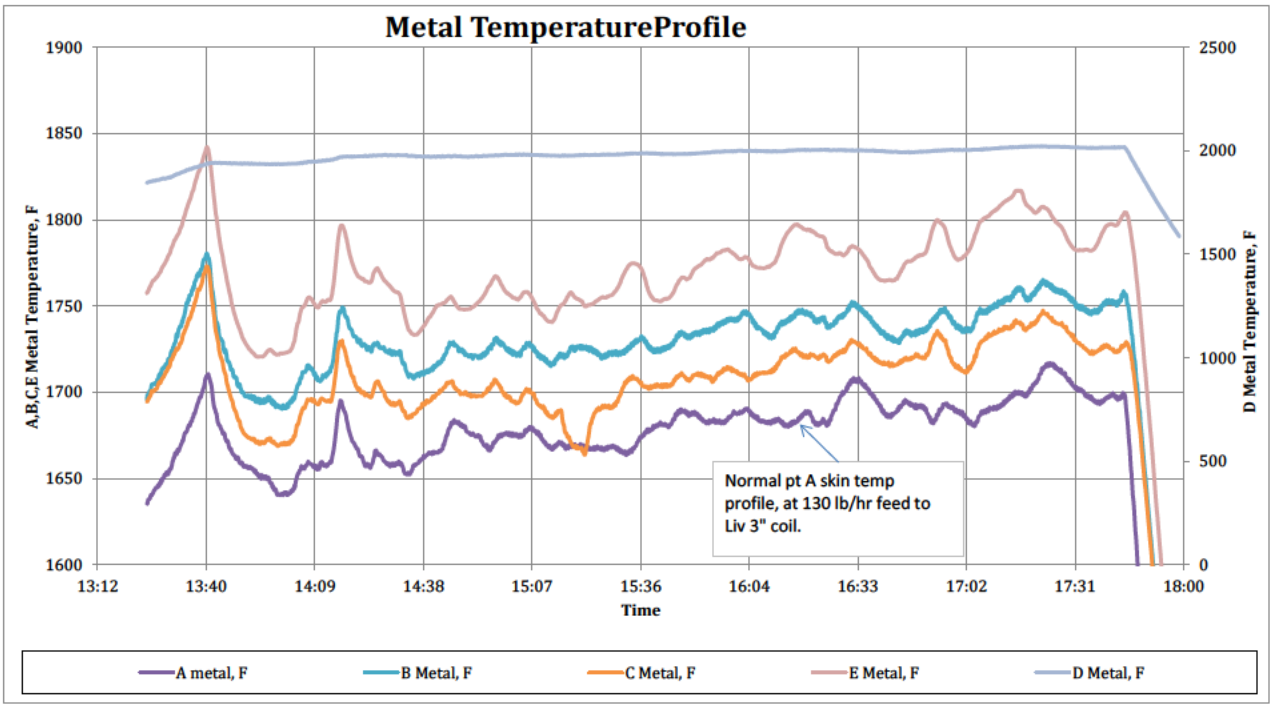


Figure 6-47: Normal Skin Temperature Profiles at 130 lb/hr Biomass Feedrate for Livingston 3" Coil. (Run LX6)

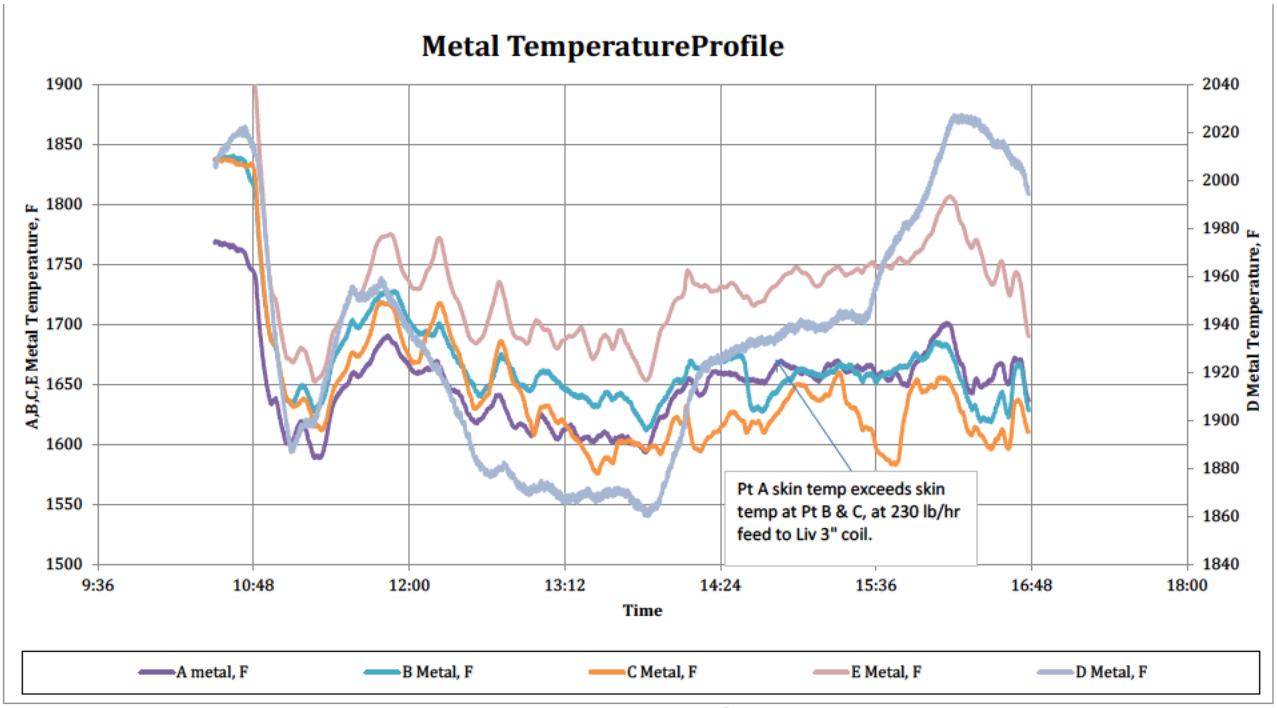


Figure 6-48: Abnormal Skin Temperature Profile at 230 lb/hr biomass feed for Livingston 3" Coil (Run LX3)

This abnormal skin temperature profile, at increased biomass feedrates, is postulated to be a result of build-up of material on the inside coil at point A, as similarly described by Lede and Diebold. The solids flux at this condition was approximately 5.3 lb/hr ft^2.

The only time the PDU was operate at something close to the predicted capacity limit (above) of 650 lb/hr per coil, was in May 2012, when a feedrate of 1400 lb/hr (700 lb/hr per coil) was achieved for a short period (~1 hour). The HEHTR was not operating at the optimum design conditions, resulting in undesirable tar / char production. Due to sticky "deposits" accumulating downstream of the reformer and because of the high char loading (low carbon conversion) experienced at these higher feedrates, the cyclones and venturi system plugged off. When the downstream equipment plugged off, the upstream feed system followed suit. Some photos of the feed line control valve and cyclone piping accumulation after this high capacity operation are provided below:

Figure 6-49: Accumulation on Piping Exit Primary Cyclone (top) and Wood Plug at Temperature Control Valve (TV-2092) after High Capacity Operation on 5-11-2012

Although we don't know from this test what the capacity limit in the HEHTR might be, there is certainly evidence of very low carbon conversion, overloading the downstream cyclones, and possibly solids back-up in the HEHTR inlet piping (resulting in wood plug at the upstream temperature control valve). Hence, it is not unrealistic to assume that we had reached a practical HEHTR capacity limit at these conditions.

Based on the limited information we currently have on maximum coil capacity, it is recommended to design for less than the 5 lb/hr per ft^2 of coil surface area (using only outside 50% of coil). This would equate to a capacity of 650 lb/hr for a 250 ft long 3" coil, and approx. 850 lb/hr for a 4" NB coil x 250 ft long. The optimal feed capacity per coil may also be determined by consideration of the achievable carbon conversion at higher mass fluxes, as described above.

Also, as we were not able to operate either Livingston or the PDU steadily at rates close to these stated limits, there is significant uncertainty as to what the appropriate capacity limits for this technology are, and this would only be able to be resolved with additional pilot plant testing, which is not an option at this point. Hence, the capacity limits stated above are conservative.

As an additional reference point, the Brightstar reformer deployed in Australia around the year 2000 was eventually shut down. The unit only achieved 75% of the name plate capacity of around 3800 lb/hr, or less than 2800 lb/hr feedrate achieved. That unit had six (6) 3" NB incoloy 800HT coils, which equates to around 500 dry lb/hr per coil.

C.30 Coil Velocity Limits

No coil erosion was detected in the PDU coil during the 2240 hrs of ClearFuels operation, although cracks did develop in the outlet piping, as a result of piping stress. Some impingement/erosion was evident where the two PDU coils enter the outlet header, opposite the coil entry points to the header and severe erosion of the thermowell that was located in the outlet header was experienced at one time, before installing an impingement pad on the well.

Livingston testing durations were much shorter and although a number of cracks did develop during the testing at the coil inlet, outlet and the WHB inlet, the coil and piping did not generally appear to be thinned as a result of erosion. The exception was a crack that developed at the outlet of the HEHTR coil, that did show signs of thinning due to erosion at the upstream elbow, but this was an original coil component, with many operating hours.

[redacted]

The 180 degree return bend on the WHB did fail during the Livingston testing, apparently due to thinning, so 180 degree bends need to be avoided. Likewise short radius elbows should be avoided in the piping transitions to and from the reformer and associated equipment.

As ethylene cracking furnaces operate with coil velocities up to 500 ft/s, have elbow fittings, but have coil lives in the order of years, HEHTR coil velocities up to this value should be acceptable, but ideally normal operating velocities are somewhat less.

Specific impingement points like HEHTR coil entry points into an outlet header, etc. should be assessed, and if necessary, erosion pads provided.

The thickness of piping elbows/transitions and the HEHTR coil "back wall" should be assessed to determine what corrosion allowance is available, at system operating and design conditions.

C.31 Maximum Coil Metal Temperatures

The maximum coil metal temperatures at the PDU and at the Livingston plant were higher than would be acceptable in a commercial plant design, where coil life would need to be 50,000 to 100,000 hours. Using API-530 calculations for Incoloy 800HT material, and assuming a coil life of 100,000 hours at a nominal

design pressure of 50 psig, a Schedule 40 coil material could be utilized and achieve the desired coil life at a maximum skin metal temperature of 1800°F, with some allowance for corrosion/erosion.

Hence, 1800°F is suggested as the maximum skin metal temperature in the commercial unit design. As it is necessary to attain a high skin temperature (1700 – 1750°F) early in the coil, it is then necessary to design a HEHTR radiant box that allows the heat flux and resultant coil temperature profile to be controlled accurately to achieve the desired goals of high initial skin temperatures without exceeding the specified maximum skin metal temperature. This is the primary driver in the commercial unit design described below.

C.32 Transport Steam Flow

The first requirement of the transport steam is to ensure that the biomass is transported via the Steam Mixing Vessel and the HEHTR feed piping, into the HEHTR without saltation of the biomass particles anywhere in the system.

It is recommended that the transport steam flow is set at least at a minimum of 2x this reaction steam extent, to ensure that sufficient steam partial pressure is maintained in the coil, to drive the required reforming reactions. Typically the extent of steam reaction is 0.2 x the dry biomass flow, so a minimum steam to dry biomass ratio of 0.4 is typically required.

Increased transport steam will increase the coil mass flux and hence the coil inside heat transfer coefficient, and so will make it more difficult to maintain the necessary high initial wall temperatures for fast pyrolysis. It is recommended that the transport steam rate is set high enough for satisfactory transport of biomass into and through the HEHTR coil, but that excessive transport steam flows don't result in a requirement for excessive radiant box temperatures, to achieve the required initial wall temperature.

In practice, radiant box temperatures as high as 2200°F, or more, are employed in ethylene cracking furnaces, but it is recommended to keep the HEHTR commercial design radiant box temperature below 2100°F, to minimize high temperature material carburization and oxidation of burner and coil support materials. At these high radiant temperatures, it will still be necessary to consult with heater vendor(s) to ensure that materials are selected that satisfy the required service life and to assess impacts on the NOx emissions for the burner. A more detailed discussion regarding high temperature burners is provided by McAdams et al [19]

C.33 Coil Feed temperature

Coil feed temperatures of more than 350°F should be maintained, certainly no less than 300°F, to ensure that biomass is maintained in a dry, clump-free state, in the feed piping. Coil feed temperatures of less than 450°F are recommended, certainly no more than 550°F to prevent premature devolatization of the biomass in the feed system, which can result in tar and solid deposits in the Steam Mixing Vessel and feed piping, which can cause feed system plugging.

C.34 Operating Pressure

All of the PDU and Livingston plant testing was conducted at reformer outlet pressures of less than 25 psig. This is the recommended maximum reformer outlet pressure for future designs.

C.35 Air Injection Design

Air injection to the HEHTR coils, if employed, should be done in the biomass/steam inlet piping, just upstream of the HEHTR, to avoid potential accumulation of oxygen/volatiles in the feed system and piping.

C.36 Stream Splitting

Feed stream splitting was a challenge at the PDU (c.f. Livingston only had one coil). The issue at the PDU was that the unit would intermittently experience coil temperature deviations (i.e. different coil temperature profiles in the two coils). This phenomena was due to partial laydown of material in one coil, typically at higher biomass feedrates and lower transport steam flows, which resulted in some increased gas flow resistance in that coil. Once this laydown started in one coil, the gas flow would preferentially flow to the clear coil, further reducing the gas velocity in the partially plugged coil, which would very quickly result in a total pluggage in the one coil, unless feed was cut or the individual coil temperature valves were adjusted quickly, in response to the initial coil temperature deviations.

Feed stream splitting is discussed in more detail in the CFD modeling discussions below. For the 20 DTPD modular (commercial) design described below, a single feed screw is recommended for each coil, to avoid this problem.

C.37 Waste Heat Recovery

The operating experiences with syngas waste heat recovery on the PDU and at the Livingston pilot plant were very different. During initial operations the PDU syngas cooler plugged very quickly and was eventually replaced with a water quench system, whereas the Livingston pilot plant WHB appeared to operate without significant fouling during the duration of the Livingston testing. The waste heat recovery was not re-tested before the close of the project. A comparison of the design features for each cooler is provided in the table below:

Table 6-10: Comparison of PDU [redacted] Syngas Cooler Arrangement

	PDU Syngas Cooler	[redacted]
Heat Exchanger Design	**Firetube boiler, Fixed tube-sheet (98 tubes x 10 ft long)**	[redacted]
Process Inlet temperature (°F)	**1750**	[redacted]
Process Outlet temperature (°F)	**450 - 550**	[redacted]
Steam generation temperature (°F)	**429**	[redacted]
Estimated syngas tar dew point (°F)	**375 – 525, depending on operation**	[redacted]
Tube ID (in)	**1.012**	[redacted]
Tubeside velocity (ft/s)	**25 – 35 at tube outlet**	[redacted]
Estimated fouling factor (°F ft^2 hr/Btu)	**0.12 (in 24 hours of operation)**	[redacted]

The Livingston pilot plant fouling factor was stable at 0.02 – 0.04°F ft^2 hr/Btu during the testing, which was confirmed via visual observation of the WHB tube surface, which did not seem to show increased fouling over the test period.

For the commercial unit design, the tar dew point should be determined and the syngas cooler tube metal temperatures should be maintained at least 50°F above this dew point temperature. Large diameter tubes should be utilized (1.5 in minimum) to prevent cake build-up on the tube surface partially plugging the tubes. A target tubeside velocity of 60 ft/s in the tubes, at the cooler outlet, should be employed as a compromise to ensure that fine particulates are fully dispersed in the gas stream, while minimizing tube erosion.

It is recommended that the tar dew point is calculated using the www.thersites.nl web site, and that the calculated dew point is corrected for elevated system pressure.

A design process side fouling factor of 0.05°F ft^2 hr/Btu should be utilized.

C.38 Char Particle Size Distribution

Particle size distribution data collected for raw biomass, char and soot exit the HEHTR is summarized in the table below. Soot is assumed to be 100% smaller than 5 micron. For smaller or larger feed particles, it is suggested that the char PSD is ratioed to the biomass feed PSD:

Table 6-11: Biomass, Char, and Soot Particle Size Distributions

Particle Micron Size	Biomass Feed (wt% retained)	Char (wt% retained)	Soot (wt% retained)
1500	22	0	0
1000	13	0	0
800	14	3.8	0
400	14	16.7	0
200	24	13.6	0
100	13	6.8	0
80	0	13.2	0
60	0	18.4	0
40	0	11.8	0
20	0	6.2	0
10	0	2.5	0
5	0	4.5	0
2	0	2.4	33
1	0	0	33
<1	0	0	33

C.39 Absorbed Duty

The HEHTR coil absorbed duty is modeled using a heat of formation and enthalpy balance calculation, which is embedded in the ClearFuels HYSYS model template. The model has been validated using Aspen Plus.

C.40 Coil Metallurgy

Incoloy 800HT is recommended as the HEHTR coil material as it is a readily available wrought (not centrifugally cast) material that is able to be formed into the helical shape required for the ClearFuels reformer, and it has the necessary high temperature creep resistance required for the service.

Another higher temperature material was identified (Haynes HR-160) as an alternate alloy, but it is preferable to design a unit that can operate satisfactorily with 800HT coil metallurgy due to material cost and delivery, if at all possible.

C.41 Coil Diameter

As described above, scaling up to a 4" coil, from 3" NB provides only a limited increase in achievable coil capacity (approximately 30%) and it is uncertain, from the available performance data, if the same carbon conversion could be achieved at this scale-up in feedrate (30%), with the larger tube. For these reasons, it is recommended that the coil diameter is limited to 3" NB for any scale-up or commercial design proposals.

Particle heating against the outside wall of the coil is the primary mechanism for the fast/flash pyrolysis required to achieve the performance benefits this technology can provide. That heating might be

accomplished more easily in a coil with a somewhat elliptical cross section (longer axis in vertical) versus a purely circular cross section. In fact, it is believed that this non-circular profile can be readily achieved in the process of forming the coil.

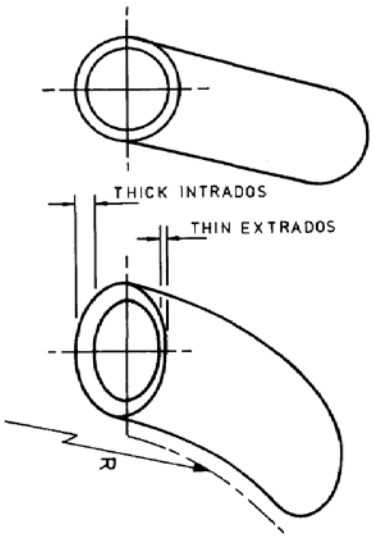


Figure 6-51: Coil Cross Section in Bending

This oval pipe cross section would reduce particle crowding at the extreme outside (i.e. at point of largest distance from the helix centerline) and should provide improved performance. Of course potential increased stresses in the pipe due to this non-circular profile would need to be assessed in the pipe stress analysis as well as the potential wall thickness reduction at the outside of the coil.

C.42 Coil Length

Using a plug flow model developed by Rentech for the HEHTR technology to model the gas analysis (wet basis) through the HEHTR coils, for the 20 DTPD commercial reformer design, with an assumed 200 ft coil length, results in the following profile:

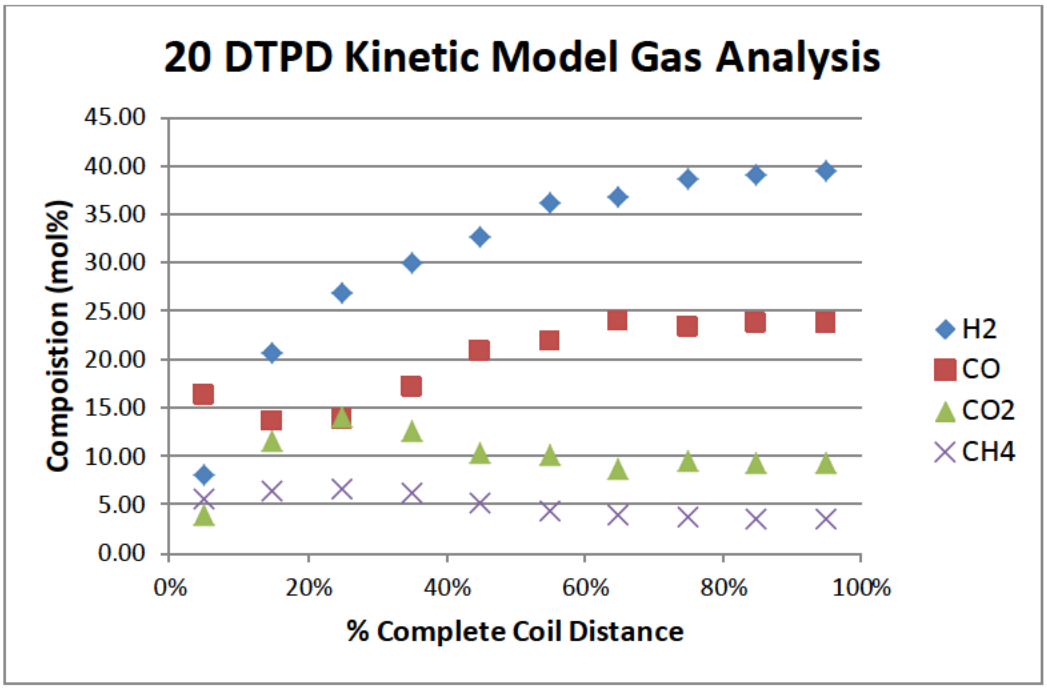


Figure 6-52: 20 DTPD HEHTR Coil Gas Analysis (Wet Basis) Profile

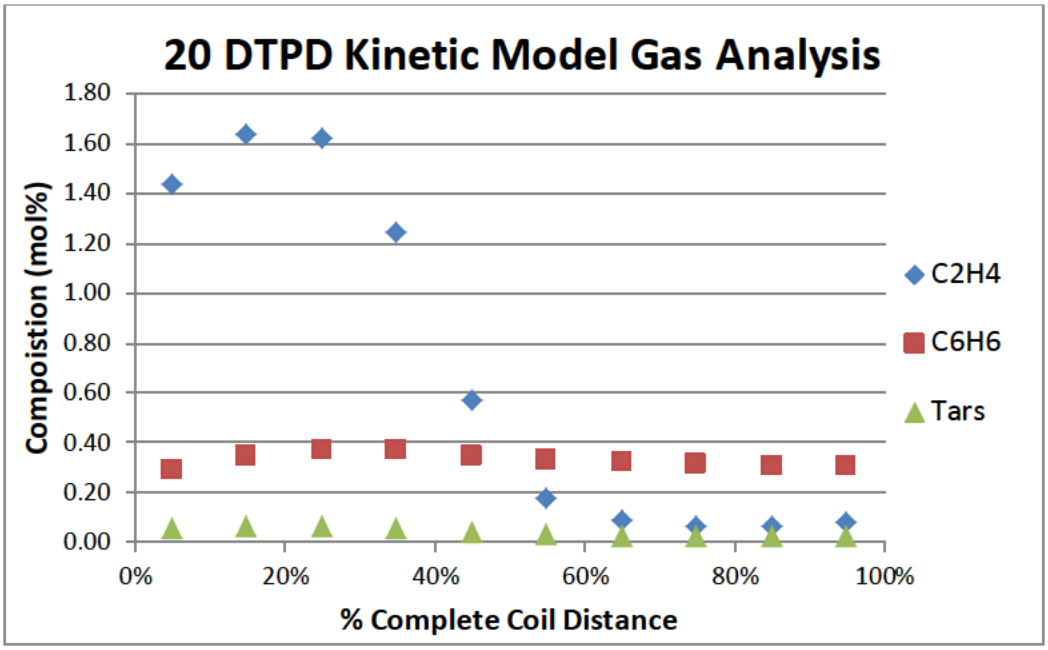


Figure 6-53: 20 DTPD HEHTR Coil Gas Analysis (Wet Basis) Profile (Continued)

This preliminary analysis would indicate that the coil length could potentially be shortened, to as little as 50% of the 200 ft assumed coil length, depending on the syngas compositional requirements. For example, in the case of a 20 DTPD modular unit for hydrogen production, the requirement to maximize the H_2:CO

ratio may dictate that the coil length be retained at 200 ft, to ensure that sufficient time is provided for the maximum amount of shift reaction to occur.

For a combined heat and power CHP application, this may not be necessary, and the coil may be able to be significantly shortened. Further development of the fundamental kinetic model is required to be able to estimate accurately the required coil length.

The gas analysis profile in the charts above are not entirely consistent with the in-coil gas analysis conducted at Livingston, the results of which are provided above, and where the gas analysis and production is shown to be less stable close to the reformer outlet. Unfortunately, there wasn't enough gas analysis at the 50% of coil length sample point (point "D") collected at Livingston, due to failures of the sample point connections early in the testing, so most of the in-coil gas analysis data collected at Livingston was only at the 15% of coil length sample point (point "C+1"), and whatever data we have from the point "D" sample point is somewhat inconsistent.

C.43 Coil Helix Diameter

The Livingston pilot plant reformer had a helix diameter of 3 ft and the PDU coil helix diameter was 7.3 ft.

A larger diameter helix reduces the centrifugal forces acting on the particles, and this force holds the particles up against the outside wall of the coil, and provides a mechanism for increased particle heating. It also changes the slip between the particles and the gas (particle slow down relative to the bulk gas velocity for smaller coil helix diameters), which increases the particle residence time in the coil. So there might be an argument made for minimizing the helix diameter.

As described above, the trajectory of the particle in the initial part of the coil is not a strong function of the helix diameter (or the inlet velocity), but a larger helix provides more coil surface area in the initial hot pyrolysis zone, as it is defined in this section, and this should be beneficial with regards to the ultimate coil capacity and the gas quality. In this regard, it might be more accurate to define the capacity limit per coil as a function of coil helix diameter instead of using a coil surface flux as described above.

Based on the (limited) high feedrate testing at Livingston and the PDU, this relationship would be represented by the figure below, with the coil capacity being roughly proportional to the coil helix diameter:

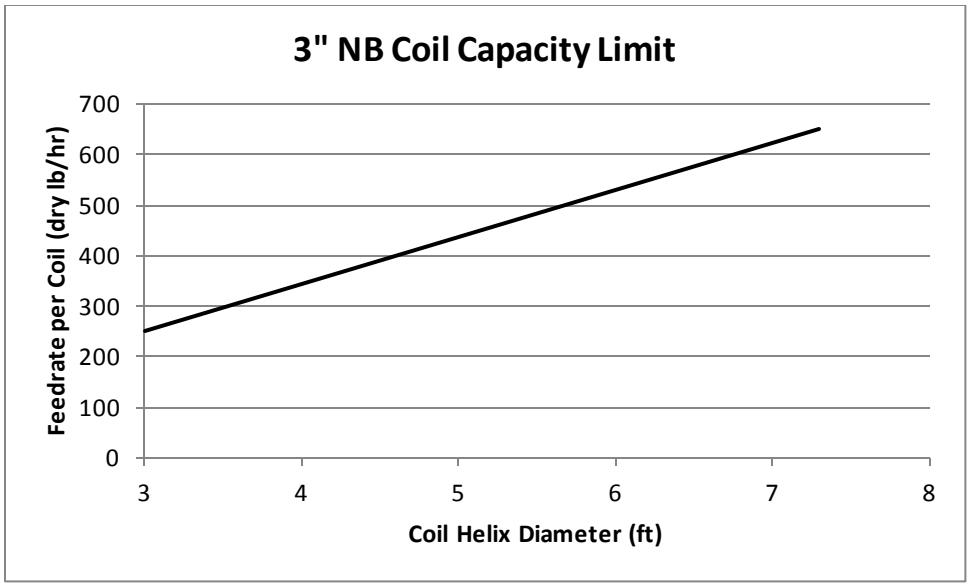


Figure 6-54: 3" Coil Capacity Limit Vs. Helix Diameter

As minimizing particle-particle interactions and crowding in the coil hot pyrolysis zone appears to be a key driver for successful performance of the technology, future HEHTR reformers should err on the side of using relatively large coil helix diameters, to try and extend this hot zone length, but not at the expense of being able to maintain a compact HEHTR design with good ability to control the heat flux and coil skin temperature profiles.

With the concept of commercial HEHTR design using a refractory box and wall mounted burners, limiting the coil helix diameter to approximately 5 ft provides a design which achieves even controllable flux through the coil. In this case, the coil feedrate 420 lb/hr per coil, was chosen to achieve a desired carbon conversion, but this feedrate is also approximately equal to the coil capacity limit, as defined in Figure 6-54 above, for a 5 ft coil helix diameter.

C.44 Re-radiating Cone Design

The radiant box and re-radiating cone design for the Livingston pilot plant reformer was much more conducive to fast initial heating of the top coil rows than the Commerce City PDU [redacted]

[redacted]

For the commercial HEHTR design described below, heat flux to the coils will be controlled by an array of wall mounted radiant burners, in a rectangular radiant box, which avoids the need for a re-radiating cone altogether, but if a cylindrical, bottom fired HEHTR needs to be constructed, potentially for a smaller application of the technology, the beneficial features of the Livingston plant radiant box and re-radiating cone design should be incorporated.

C.45 Coil Heat Transfer

Using the Livingston plant radiant box temperature, the measured skin temperatures at various points and the measured in-coil process temperatures (corrected for conductive and radiant heat effects in the coil), it is possible to calculate the coil inside heat transfer coefficient at various points in the coil. This can be compared to calculated coil heat transfer coefficients using established correlations. The results of this analysis are summarized in the chart below:

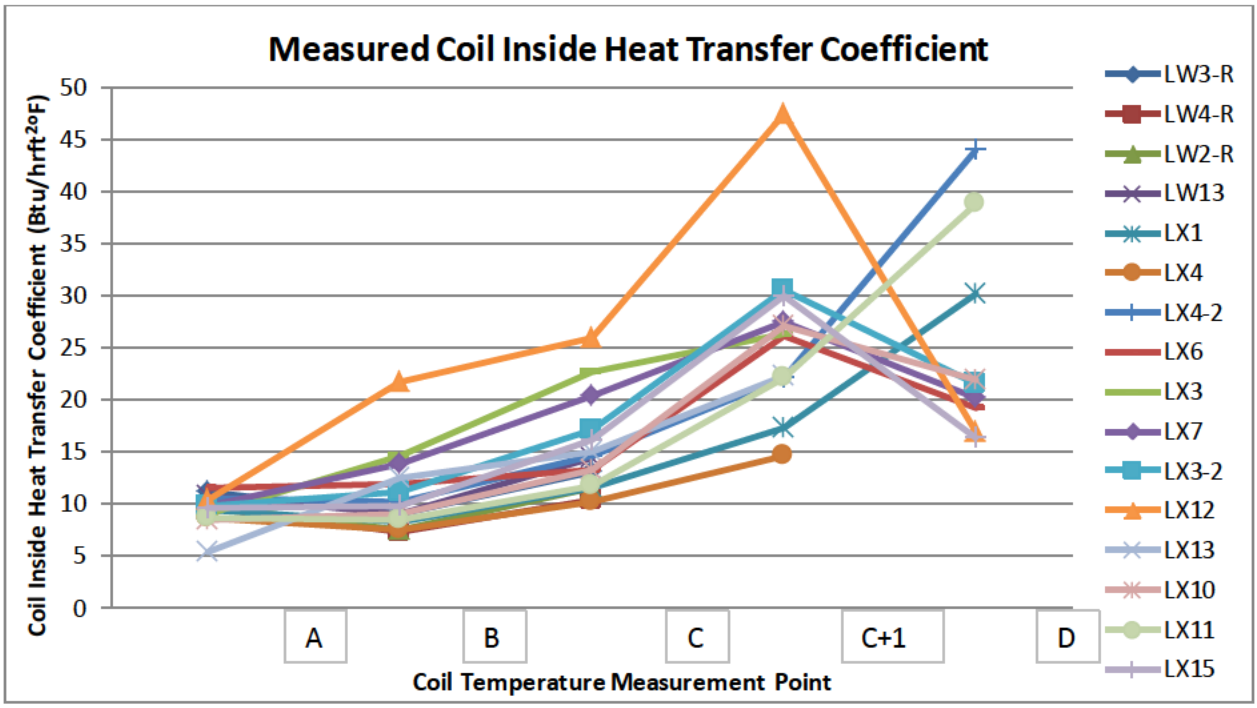


Figure 6-56: Coil Inside Heat Transfer Coefficient

The average measured heat transfer coefficients equates to 70 to 120% of the calculated inside heat transfer coefficient, using the Dittus-Boelter Correlation for the gas only flow.

C.46 Coil Deposits

The fast pyrolysis which provides much of performance benefits provided by this technology is achieved in part by ablative pyrolysis, in which particles literally melt as they contact the coil metal surface. This ablative pyrolysis leaves a molten residue on the coil surface, which over a short period of time is largely volatized, steam gasified and eroded off by other biomass and char particles. In most cases, the residue is not able to accumulate and build-up due to these effects.

The capacity limits described above are largely a result of this residue being able to accumulate, as the rate of erosion and gasification can't keep up with the deposition rate.

The operating experience at the PDU has been that deposits can be removed very effectively by a short duration (10-15 minutes) steam-only purge at normal transport steam flows, while operating still at temperature, which appears to allow sufficient time for the residue to steam gasify away.

Hence, it is recommended that some form of online steam-out provisions are made for future HEHTR designs. For the 20 DTPD commercial unit design, described below, the four separate feeds should allow a single coil to be taken out of service and steamed, while the other 3 coils remain operating.

This steam-out operation should be considered in the design of downstream equipment and utilities. The coil steam-out could also be programmed to occur at regular intervals.

The PDU coil inlet area was boroscoped after a shut-down and a small amount of build-up of material on the bottom of the coil was visible, in one coil only, after the elbow which transitions from the vertical coil drop and into the helical coil. Otherwise there was no evidence that, apart from the coil temperature deviation incidents discussed elsewhere, the PDU coils were accumulating deposits as a normal course. That's probably explained by the typically low biomass feedrates and high operating velocities that the PDU coil was operated at which averaged 50 ft/s at the coil inlet and 200 ft/s at the outlet.

The 2" coil at Livingston, when removed to install the 3" coil, didn't show evidence of internal coil deposits. The average inlet and outlet velocities the 2" coil was operated at were 30 and 110 ft/s respectively.

After completing the Livingston pilot plant testing, there was evidence of laydown of material on the inside of the 3" coil, as depicted in the photo below:

Figure 6-57: Coil Build-up after Livingston Testing (Reformer Coil Outlet)

The deposit was tested and found to contain only 5 wt% organic matter with the balance being primarily ash, iron and possibly nickel (deposits were slightly ferromagnetic). This average inlet and outlet coil velocities for the 3" coil at Livingston 23 ft/s and 100 ft/s, respectively, marginally less than the Livingston 2" coil velocities.

The material processed in the 3" coil included sander fines, which contains wax and resin. We suspect that the resins included in the sander fines produced the coil build-up, although it is not clear why this material is not readily gasified. So, in general, feedstocks with some resin, wax, pitches and/or glues should be further tested.

It would be preferable to operate with inlet and outlet coil velocities of 30 ft/s and 120 ft/s, respectively (i.e. higher than operating velocities for the Livingston 3" coil), to assist in erosion of potential coil deposits, as they may build up.

C.47 Coil Thermal Growth and Supports

The expansion loop design for the Commerce City HEHTR outlet piping was not optimum and required continual maintenance and operations attention. Due to repeated start-up and shut-down cycles, the piping creeped and eventually suffered a failure (at a weld upstream of the BFW quench cracked) during the plant operations.

The Livingston plant also experienced a crack at the piping weld, upstream of the WHB as well as at the inlet and outlet of the reformer coil. Hence, the design of an operable, maintainable piping system that addresses piping thermal growth and satisfies the piping allowable stresses not just for normal operation but also for start-up, shut-down and abnormal operating conditions, is absolutely critical for this technology to be successfully deployed.

The PDU coil supports were fixed at the top of the reformer, and as the height of the coil was ~28 ft coil height and 40 ft total heated height, the resultant coil movement at the bottom of the reformer was also ~8" from cold to operating temperature. The coil bank height and the total heated height should instead be minimized, in order to minimize the vertical thermal growth. For example, the 20 DTPD commercial design, described in Section 5, employs a heated coil bank height of only 13 ft. Rather than dropping the coil feeds vertically down into the box, it is preferable from a performance and thermal growth perspective to bring the coil feeds into the box horizontally, and with a (very) large sweeping radius transition into the coil helix. This will maximize the coil capacity while at the same time minimizing the piping heated height and hence the vertical thermal growth.

If the resultant thermal growth is taken up entirely in the outlet piping (to the fixed inlet to the Syngas Cooler), there should be adequate space provisions made for the required expansion loop. For the PDU, the space for the loop was constrained and this resulted in an overly complex loop design, which ended up being difficult to operate and maintain.

If at all possible or practical, it is recommended that most or all of the piping thermal movement is taken up on the inlet (cold) end of the reformer. This could be achieved by a counterweighted support above the reformer box, much as is practiced on conventional Steam Methane reformers. Due to the helical coil design, however, it would be necessary to support the coil(s) in an assembly, which is separately supported from above, with the counterweighted support system.

6.D CFD Modeling

Computational Fluid Dynamics (CFD) modeling of Rentech fluidized bed technologies has been an ongoing effort in the Process Development and Reactor Design team since the acquisition of the Silvagas gasification technology brought with it a suite of CFD models using a precursor to the current Barracuda software package offered by CPFD Software LLC.

Currently, the primary focus of Rentech CFD modeling is to further its understanding of biomass-steam systems in its ClearFuels technology package. The specific areas of interest which have been analyzed using CFD modeling include:

Biomass transport (transport line from steam mixing vessel to HEHTR)
Biomass feed splitting
Biomass – Steam mixing (steam mixing vessel design)
Flow and heat transfer in helical coils.

There are many considerations to be made when modeling systems using CFD, especially those involving complex two-phase solids-gas flow patterns. Currently, Barracuda is one of the only commercially available software packages that can be used to model such complex systems; however, the software is more designed for use in fluidized bed reactor systems of much larger geometries and lower gas velocities than Rentech is using in its simulation work. As such, it is pertinent to test these systems using cold flow type setups prior to implementing any design which is solely based on CFD work. A full analysis of each simulation should be conducted before recommending any findings from the system and it is important to look for uncharacteristic particle flow and to ensure steady state operation has been achieved. Additionally, laboratory bench scale systems should be designed to further understand the heat transfer complexities which occur in these processes.

One of the limitations of the Barracuda software for ClearFuels technology applications is the geometry of the system. Barracuda uses a Cartesian coordinate system to define its calculation grid while almost all flow is conducted in a cylindrical coordinate system. It is important to maintain a high enough resolution in the simulation to both solve the fundamental equations accurately as well as maintain a high enough resolution of the CAD geometry that is input into the software. This can cause extremely large grids to be implored for transport line calculations as well as helical coil calculations as there is a tremendous amount of void space which causes a large percentage of excess cells to be rendered which the grid generator is unable to remove. The user must balance the need for a high enough resolution with the need to complete a simulation in a reasonable amount of time. In general, simulations need to be performed on truncated geometries of key importance and may take several weeks to solve at a desirable resolution.

D.1 CFD Modeling – Biomass Transport

Transport of biomass particles within the ClearFuels technology generally falls under a dilute phase pneumatic conveying flow regime. Particles are fluidized as long as the bulk gas velocity is maintained above the saltation velocity where particles are maintain in dispersed flow and the pickup velocity where the gas velocity is high enough to pick up any particles that may drop out of the bulk phase at high friction points. The volume fraction of biomass as a function of steam to wood ratio is shown below in Figure 6-58 and is a key operating parameter for CFD simulations as the software sets the amount of particles that can enter a space based on the closed pack volume fraction. The volume fraction (ϑ) is defined below as a function of the steam to wood ratio (x).

$$\vartheta = 1 - \frac{\rho_s}{\rho_s + \frac{\rho_{H2O}}{x}} \qquad x = \frac{\dot{m}_{H2O}}{\dot{m}_s}$$

ϑ - Solids volume fraction,
ρ_f - Gas density,
ρ_{H2O} – Steam density ;
ρ_s – solids density;
$\dot{m}_{H2O}$ – steam flow (lb/hr);
$\dot{m}_s$ – biomass flow (lb/hr)

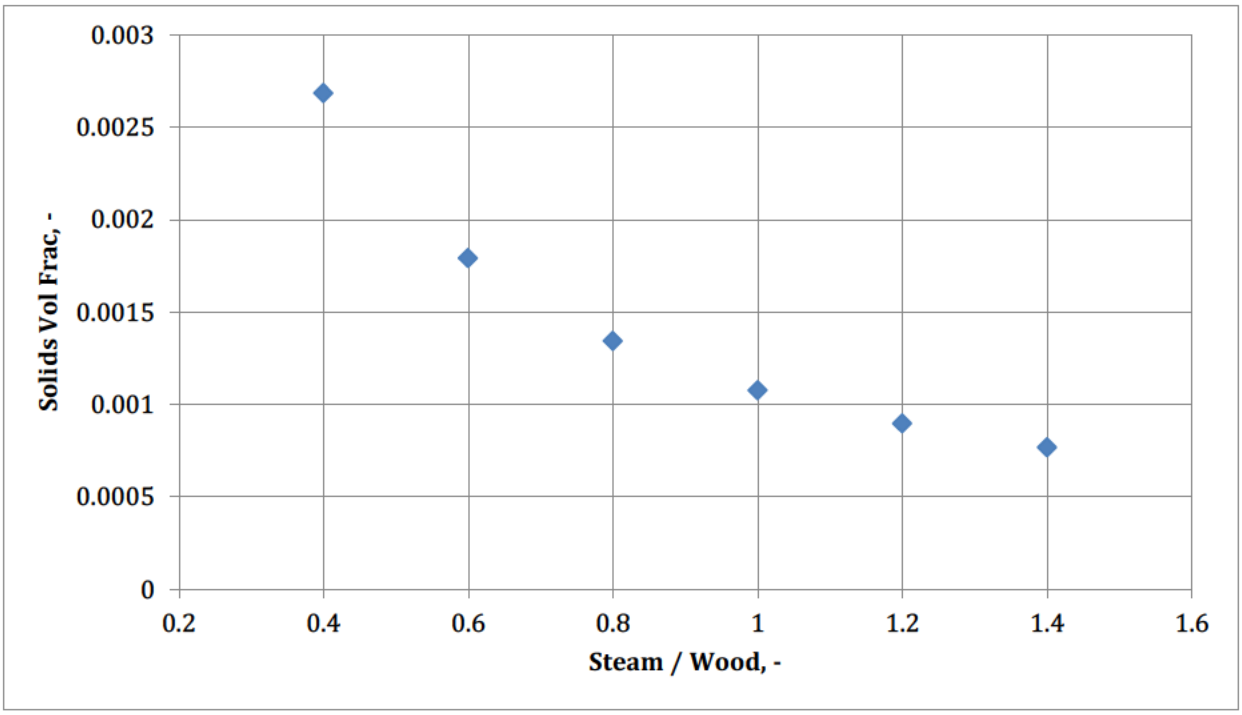


Figure 6-58: Solids Volume Fraction as a Function of Steam to Wood Ratio

Zenz studied the flow of many different particles (glass beads, FCC catalyst, biomass, coal) in horizontal pneumatic conveying systems. The figure below shows the comparison of the drag coefficient to the Reynolds number of the pipe such that the findings are presented simply as a function of the fluid and particle properties. As expected, his findings show the decrease in saltation velocity with particle size and were used for calculation of the saltation velocity along with those from PSRI. (Zenz, 1964)

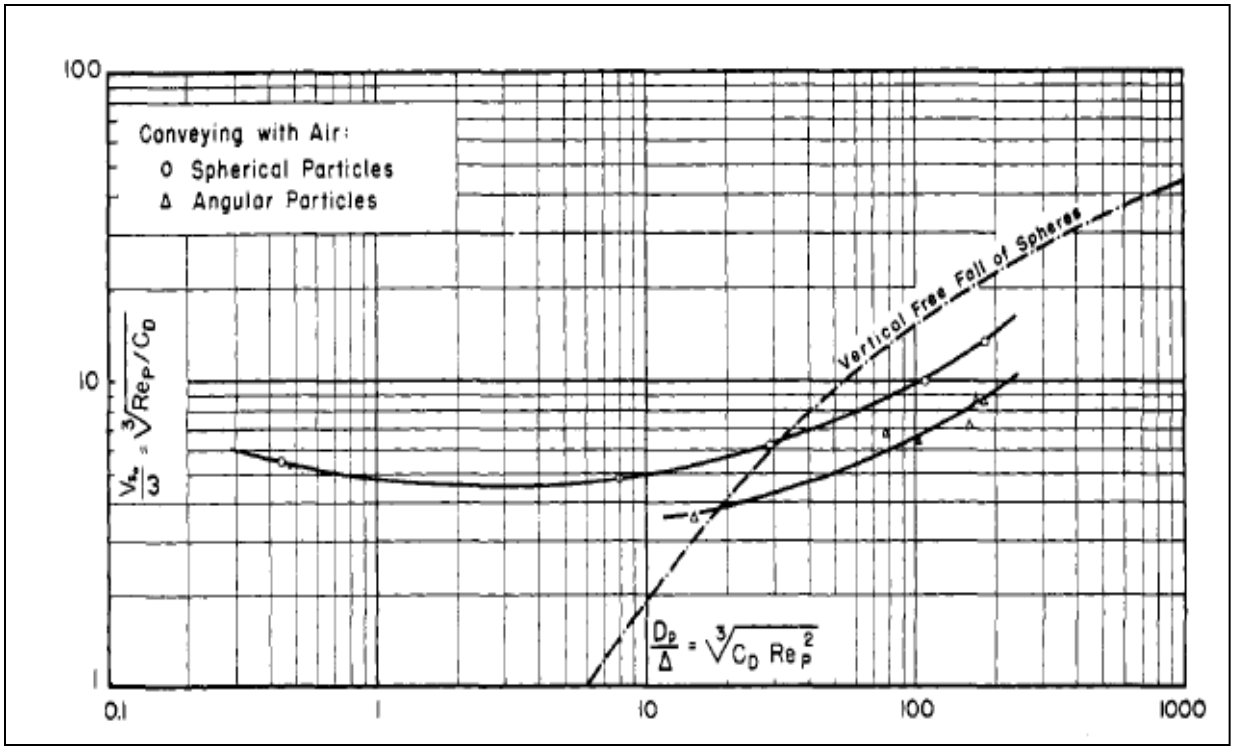


Figure 6-59: Relationship of Drag Coefficient to Reynolds Number for Spherical and Angular Particles in a 2.5" ID Tube, From Zenz.

Additionally, biomass particles add a complexity to the system not usually addressed in the literature. Its low particle density (compared to conventional testing materials, i.e. sand), elastic nature (ability to absorb significant amounts of momentum at the wall), irregular shape and stickiness during devolatilization add numerous variables that conventional CFD software packages (including Barracuda) are not able to process. For example, a key parameter in solving the momentum balance around a particle is how its momentum is absorbed when it contacts another solids surface. The below Figure 6-60 represents two different simulations in Barracuda where tangential momentum retention is varied from 0.99 (the default) to 0.9 in a helical coil.

As one can see, there is significantly more particle crowding (as expected) in the simulation where 90% of the tangential momentum is retained. This is a complex issue in the HEHTR as this would most likely be dependent on the biomass particle's physical makeup (i.e. is it a piece of bark, green biomass, bagasse, wood, etc.) as well as if it is hitting a pipe wall or another biomass particle.

The stickiness of biomass particles during devolatilization is completely lost in the Barracuda simulations and may play an important factor in particle heating pathways if it enhances the contact time between the particle and pipe wall.

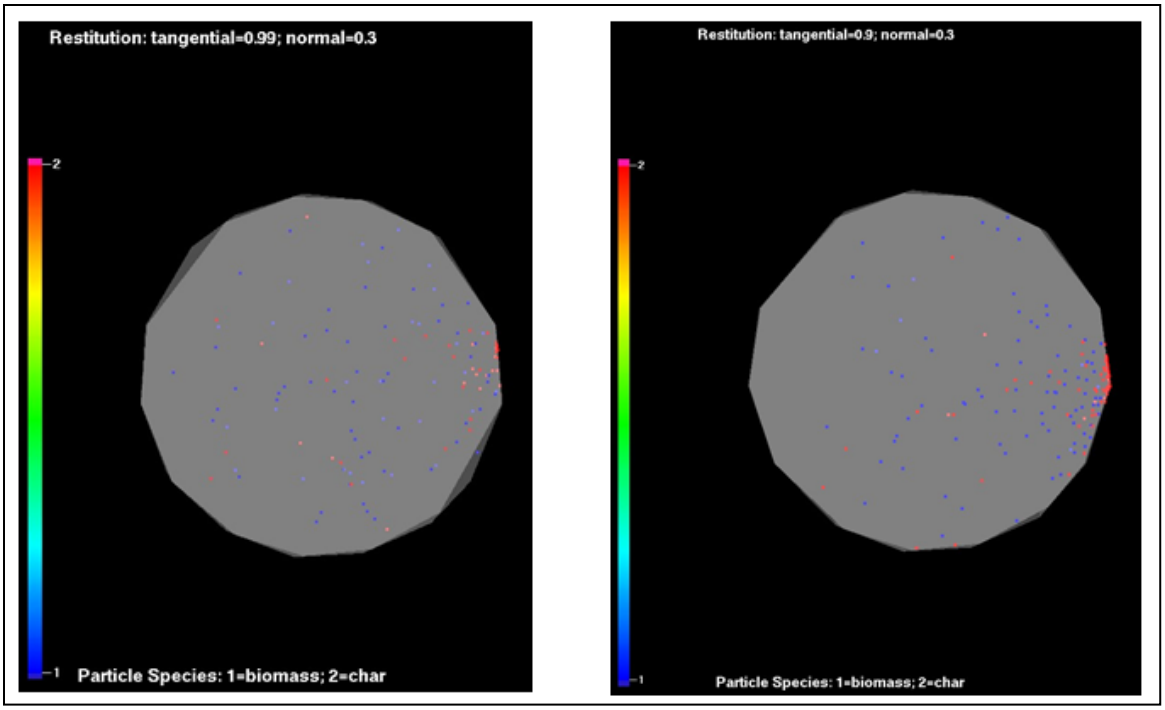


Figure 6-60: Effect of Momentum Retention Parameters in a 3" NB, 7.5 ft Diameter Helix

The minimum fluidization velocity was compared in Barracuda to those calculated using the below correlation from PSRI (Ted Knowlton, S.B. Karri, 2012).

$$U_s = 11.5\sqrt{gD}\left(\frac{G_s}{U_s\rho_f}\right)^{0.3}\phi(\theta)$$
$$\phi(\theta) = 1 + 0.002\, d_p^{0.9}\sin\theta$$

As it is generally more desirable to operate at a low steam to wood ratio to minimize the amount of adsorbed duty in the reformer due to the transport gas as well as maintain a higher skin metal temperature in the reformer. This need can clash with operational limits as one must operate in excess of the minimum fluidization and saltation velocity to ensure dispersed flow prior to any feed splitting (i.e., the "Y" splitter at the PDU) or entrance into the reformer. Additionally, operational observations at the PDU indicate that at times biomass particles were not distributed evenly between the reformer coils, at time, this was correlated to the biomass feedrate and the amount of transport steam in the system. Lastly, by minimizing the amount of transport steam the gas residence time is increased for the fixed volume at the PDU and minimizes the amount of reactor volume needed for future designs.

In the PDU, the minimum transport steam was often limited by a need to operate in large excess of the saltation velocity of the biomass particles due to operational limits. The saltation velocity as a function of wood flow rate for a horizontal 3 inch pipe is show below.

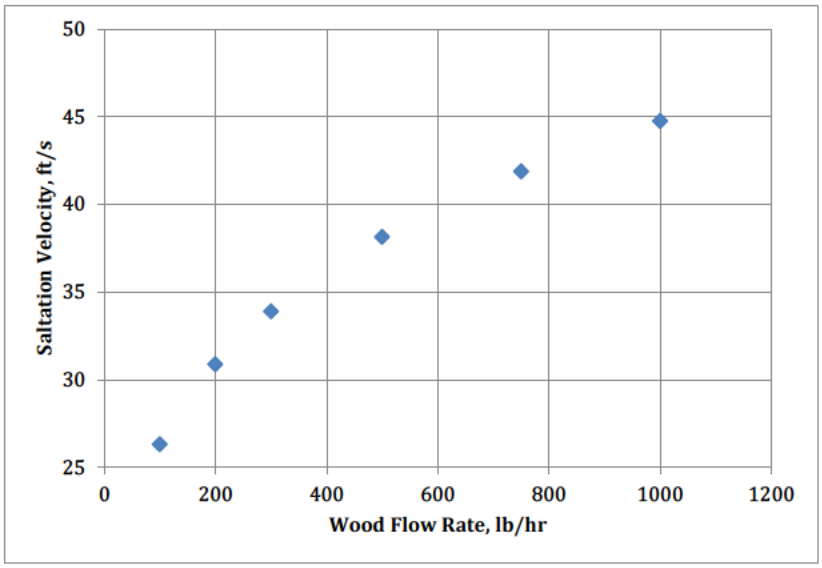


Figure 6-61: Saltation Velocity of Biomass Particles as a Function of Solids Flow Rate in a 3" Pipe

A simulation was performed in Barracuda varying the gas velocity in a section of feed pipe representing the transition from horizontal to vertical flow at the PDU. The outlet solids flow rate is plotted along with the gas velocity as a function of time in the simulation in
Figure 6-62. As can be seen, there is uniform solids flow until approximately 12 seconds where the gas velocity is roughly 40 feet per second. This represents the beginning of saltation as particles begin to lay down in the pipe. After 17 seconds as the gas velocity drops below 30 feet per second, another shift in solids flow occurs as particles begin to heavily lay down in the pipe. Figure 6-63 below shows snapshots of the particle flow at the elbow transition from horizontal to vertical flow at the PDU. Particle laydown is observed at the beginning of the elbow where the PSRI correlation would predict the saltation velocity to be greatest.

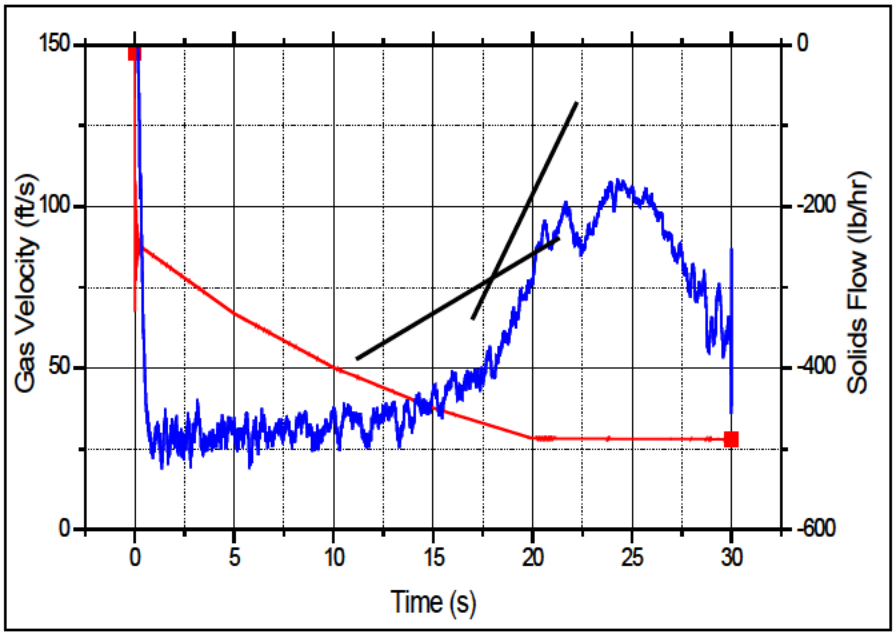


Figure 6-62: Outlet Solids Flow and Gas Linear Velocity

Overall, the computational results agree well with those predicted by the PSRI correlation. It is important to note that the PSRI correlation was developed using sandy type particles and may have increased uncertainty when used with biomass particles. Additionally, the computational results from Barracuda use a more idealized particle flow system and should compare with experimental results from future cold flow or operational data.

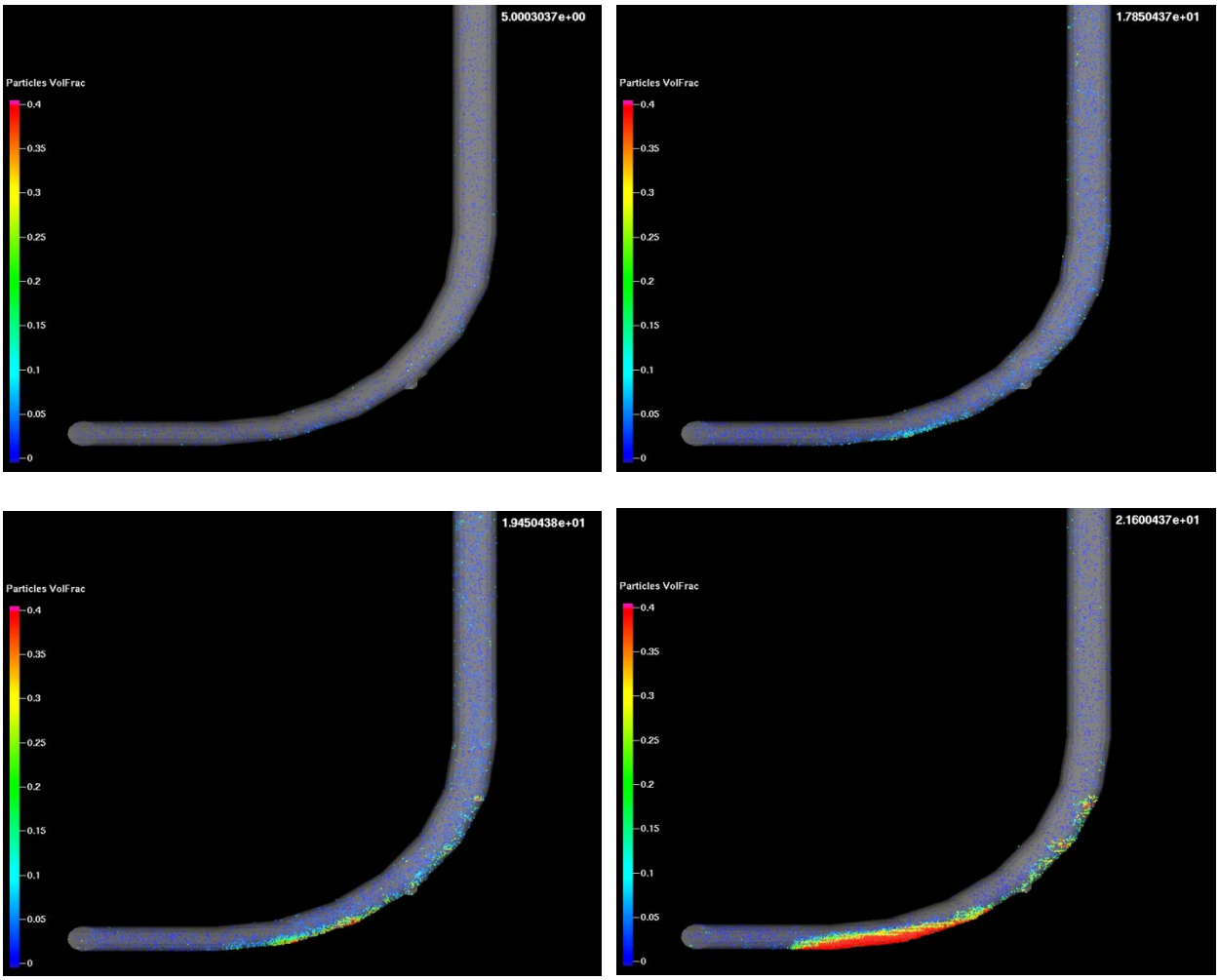


Figure 6-63: Solids Flow in a 3" Pipe at a 90 degree Elbow Representing Horizontal and Vertical Flow

D.2 CFD Modeling – Biomass Feed Splitting

Biomass feed splitting in the transport line from the steam mixing vessel to the reformer is an important aspect to the ClearFuels technology as it can greatly impact the commercial design and capital cost of the process. Additionally, uneven feed splitting can lead to differences in the performance of an individual coil in the reformer which can lead to both unsatisfactory performance and operational issues.

Typical operational observations at the ClearFuels PDU in Commerce City recorded temperature deviations of 10-50°F between the "A" and "B" reformer coils. It is thought that uneven feed splitting at

the “Y” splitter could have exacerbated any downstream issues. Figure 6-64 below shows a CAD representation of the original “Y” splitter following a 90° elbow to vertical flow.

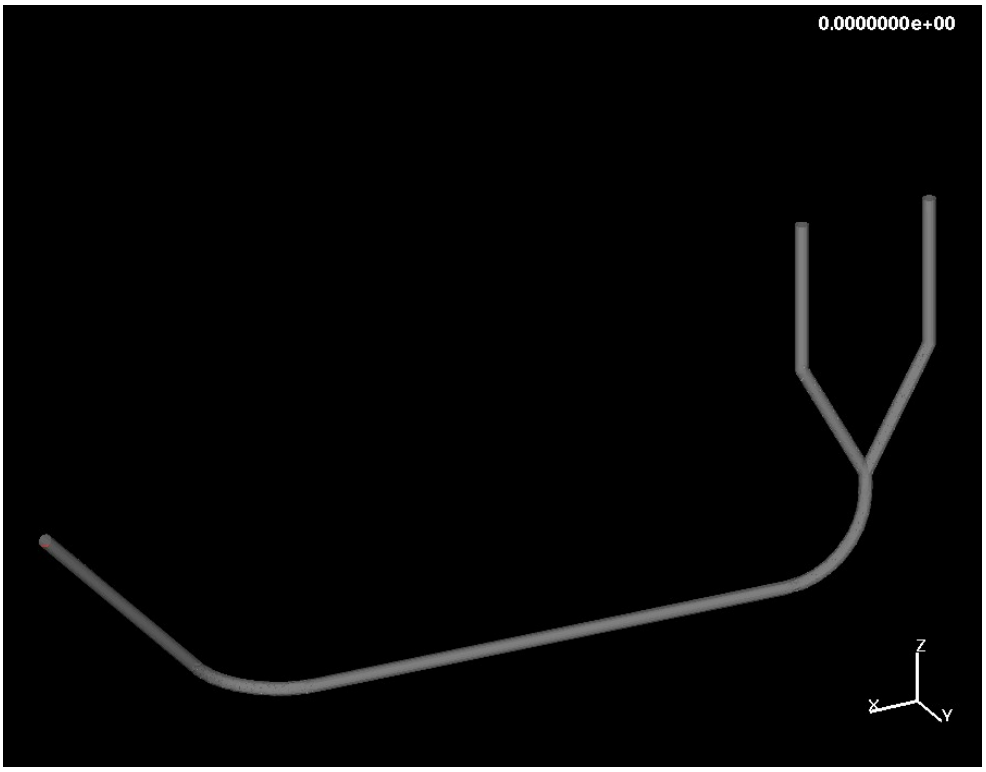


Figure 6-64: Pipe Orientation Entering the Original "Y" Splitter Configuration at the PDU

A Barracuda simulation was performed on the original PDU configuration of the “Y” splitter using the following operating conditions:

Temperature_steam – 750 F
Temperature_biomass – 80 F
Pressure_inlet – 24 psia
Steam Flow – 737 lb/hr
Biomass Flow – 500 lb/hr

Results from Barracuda simulations show a preferential amount of gas and solids flow on the “right” arm of the “Y” splitter. Results of the simulation using the original configuration of the splitter are shown below in Figure 6-65.

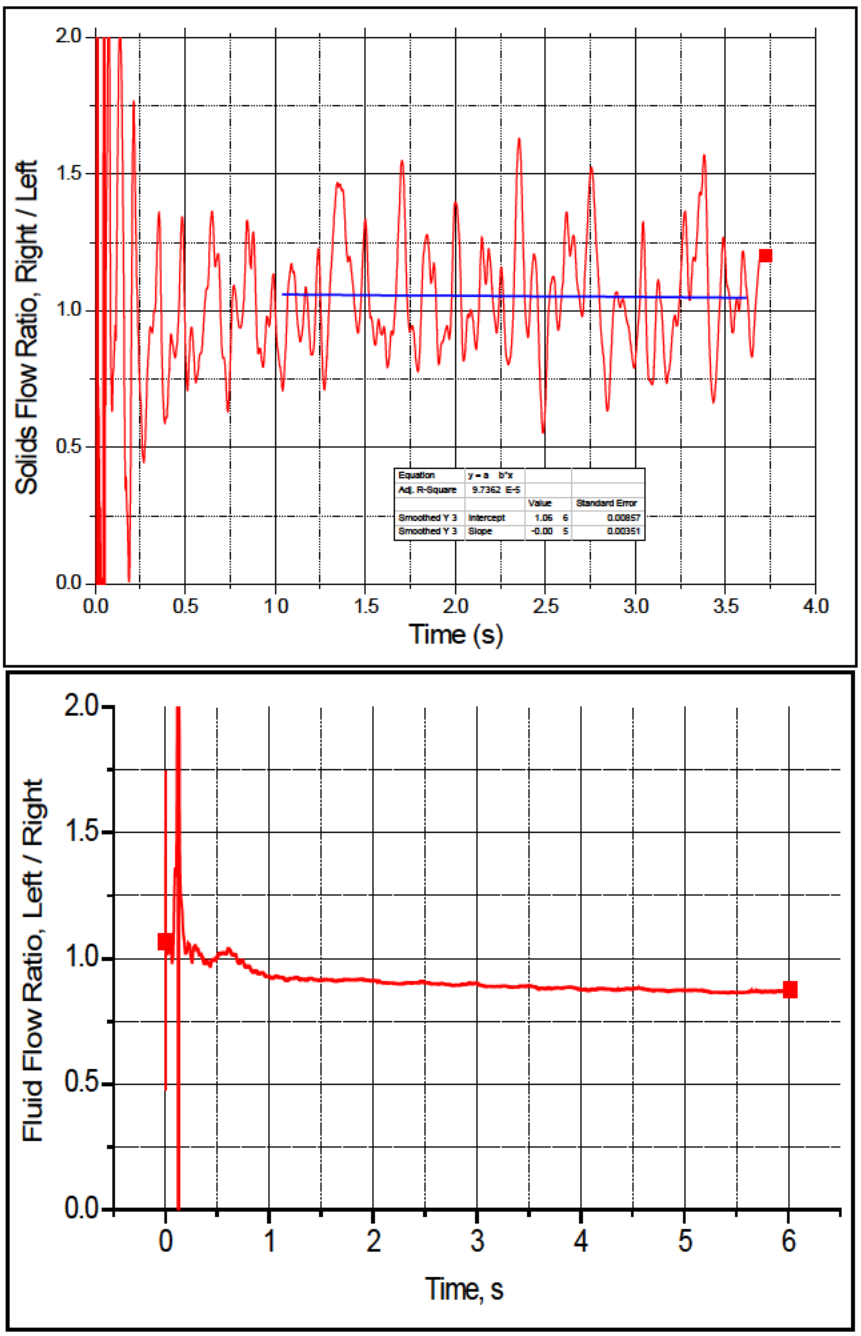


Figure 6-65: Solids Flow Ratio and Fluid Flow Ratio of the Original PDU *Y*

These results suggest that inertial forces may be large enough to cause preferential flow of solids and steam through the right arm which can lead to uneven performance between the two reformer coils. Potential evidence of this at the PDU was evident at times by a skin metal temperature difference between coils "A" and "B" (A = left, B = right in the simulation legend) representing different amounts of heat flux through either coil.

A proposed modification was also simulated in Barracuda in attempts to alleviate the misdistribution problems at the PDU. Figure 6-66 below shows the proposed configuration. Briefly, instead of the

splitter immediately following the 90 degree elbow, additional piping would be used to make the inlet to the splitter orthogonal instead of planar to the "Y".

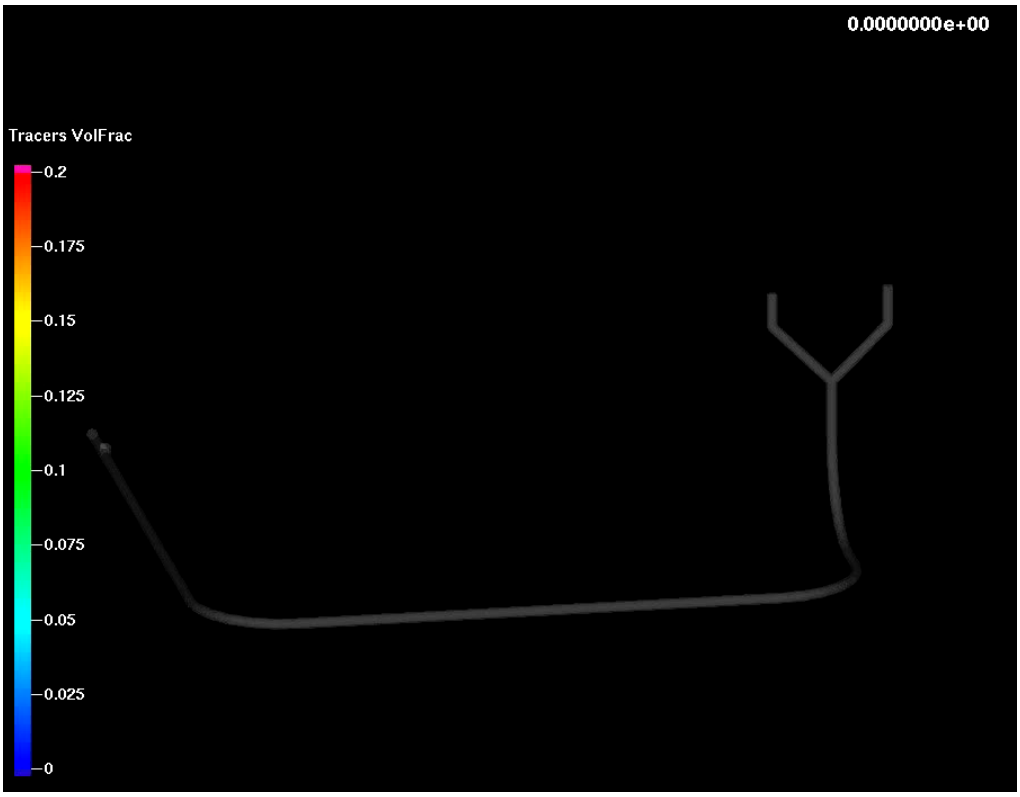


Figure 6-66: Proposed Re-Orientation of the Inlet Piping to the Original Feed Splitter at the PDU

Barracuda simulations performed on this arrangement generated more similar results to the original simulation with preferential separation on the right arm of the splitter. As these results were similar to those observed in the original configuration, the above design was abandoned. The feed splitter at the PDU was instead moved upwards to approximately two thirds of the distance up the reformer box to allow for more than sufficient pipe length for fully developed dispersed flow to form. Due to priorities in Barracuda simulations, the final orientation was never simulated with the software; however, operational issues were minimized after the move.

Lastly, a commercial feed splitter design was proposed and simulated using an 80 DTPD basis in Barracuda. The design is shown below in Figure 6-68 with solids flux exiting the splitter in Figure 6-69. It incorporates a concentric reducer within a pipe to ensure equal flow between the outlet pipes. Results were favorable with this design versus those used at the PDU; however, the simulations were done incorporating a straight pipe prior to the beginning of the splitter and any possible deleterious inertial forces were eliminated. Nevertheless, this design provides for a simplistic solution for feed splitting issues where greater than 3 reformer coils are required and may be followed up with cold flow testing to determine its utility in practice.

This Report also describes an alternative 20 DTPD modular design where individual steam mixing vessels are used in order to provide a more flexible commercial solution. This design may have more utility for a first of kind commercial facility in order to alleviate the operational issues experienced at the PDU.

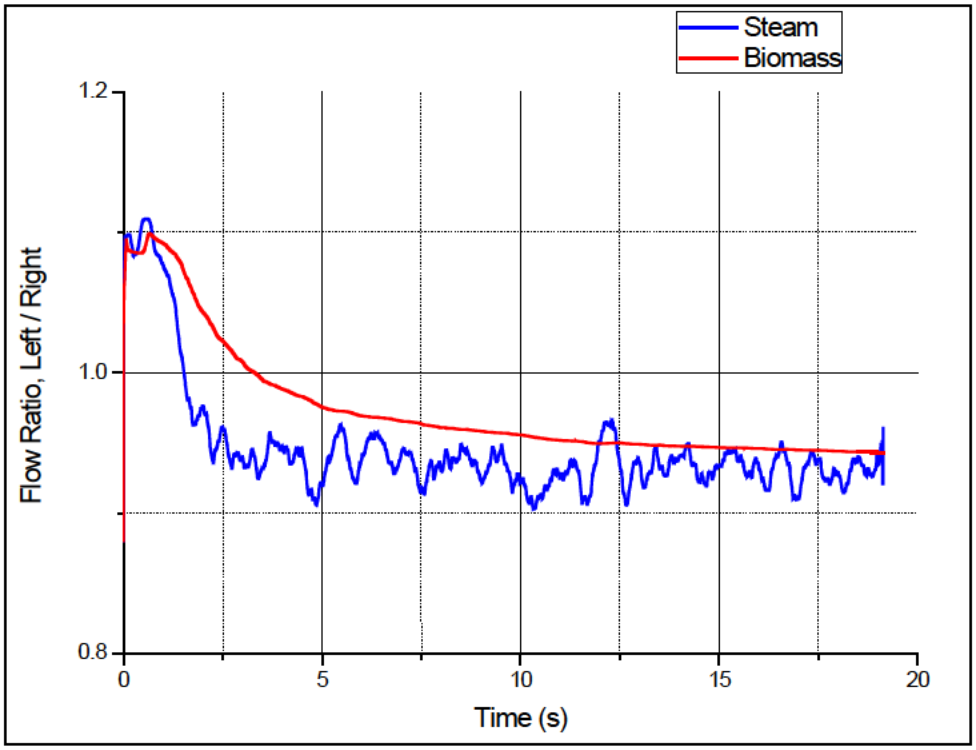


Figure 6-67: Flow Split Ratios from the Proposed Re-Orientation of the Feed Splitter

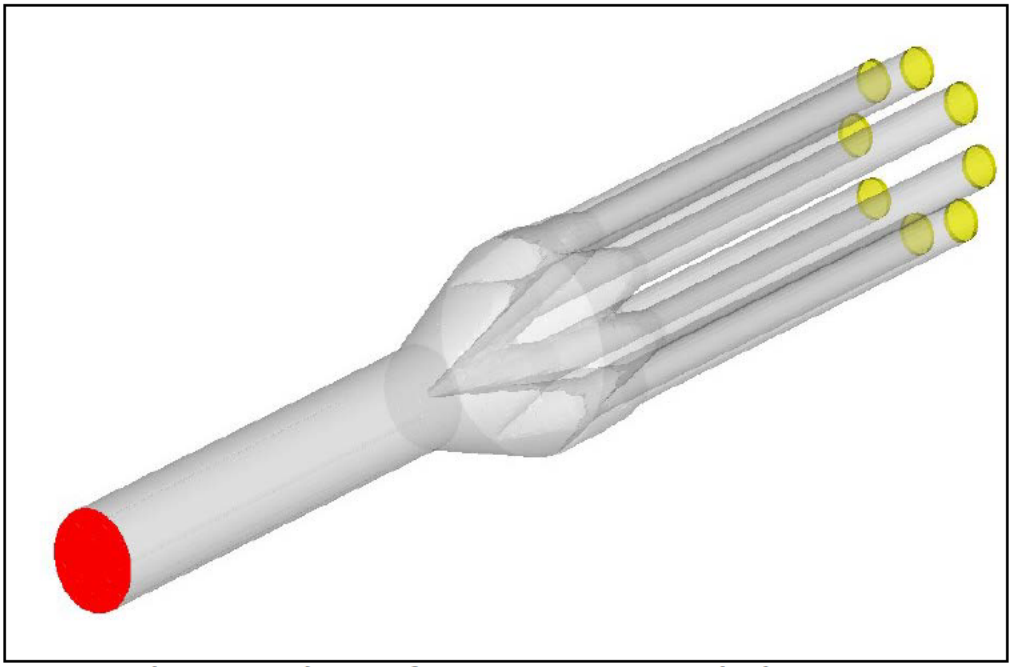


Figure 6-68: Proposed Commercial Design for 80 DTPD Biomass Feed Splitter

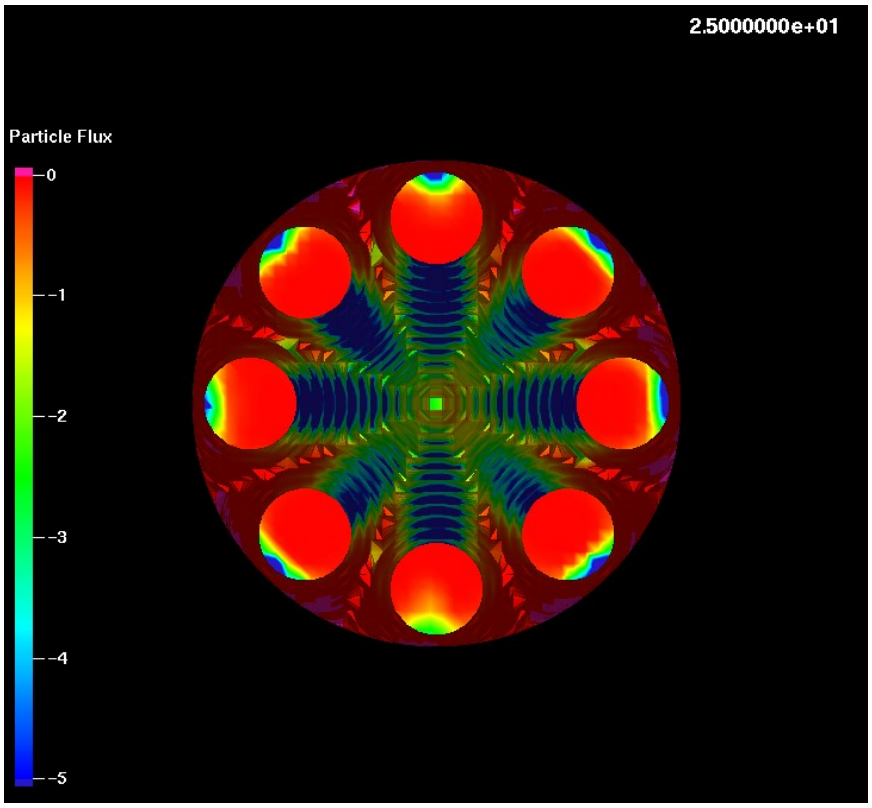


Figure 6-69: Solids Flux Exit a Commercial Feed Splitter Design; Solids Leaving the System have a Negative Flux Value

D.3 CFD Modeling – Biomass Steam Mixing

A proprietary design of the ClearFuels biomass gasification system is the method in which the biomass and steam are mixed inside of a steam mixing vessel or SMV. Operational experiences at the steam mixing vessel during operation at the PDU prompted the need to evaluate the validity of the design of the SMV further. Deleterious observations around the steam mixing vessel included:

Steam leakage back through the rotary valve caused the biomass from the screw feeder to wet resulting in inconsistent feeding from bridging, etc.

Solids hold up inside of the steam mixing vessel as evident by chary materials, causing blockages in the mixing vessel which would plug the feed line

Potential to exacerbate feed splitting issues for a downstream "Y" type splitter

High thermal stress regions where high temperature steam is mixed with biomass but metal temperatures must be kept cool to prevent steam leakage backwards

Large demand for purge gas to either cool the metal surfaces and/or provide a pressure barrier to prevent steam from leaking through the rotary valve

Inability to operate at pressure in excess of 15 psig without steam leakage (may be more rotary valve related)

The PDU design for the SMV is shown below in Figure 6-70. Briefly, it consists of a vessel with a conical bottom where steam is introduced in a near tangential manner near the top of the conical section. Biomass is introduced by dropping into the vessel by means of a rotary valve immediately on top of the vessel itself. The biomass travels down a dip tube inside of the vessel and in the annular region around the dip tube an inert purge gas (N_2 at the PDU) is used to maintain low metal temperatures in attempts to condense steam and prevent any leakage backwards. As designed, the biomass and steam will mix in the conical section and leave the vessel through a 90 degree elbow attached at the bottom of the cone.

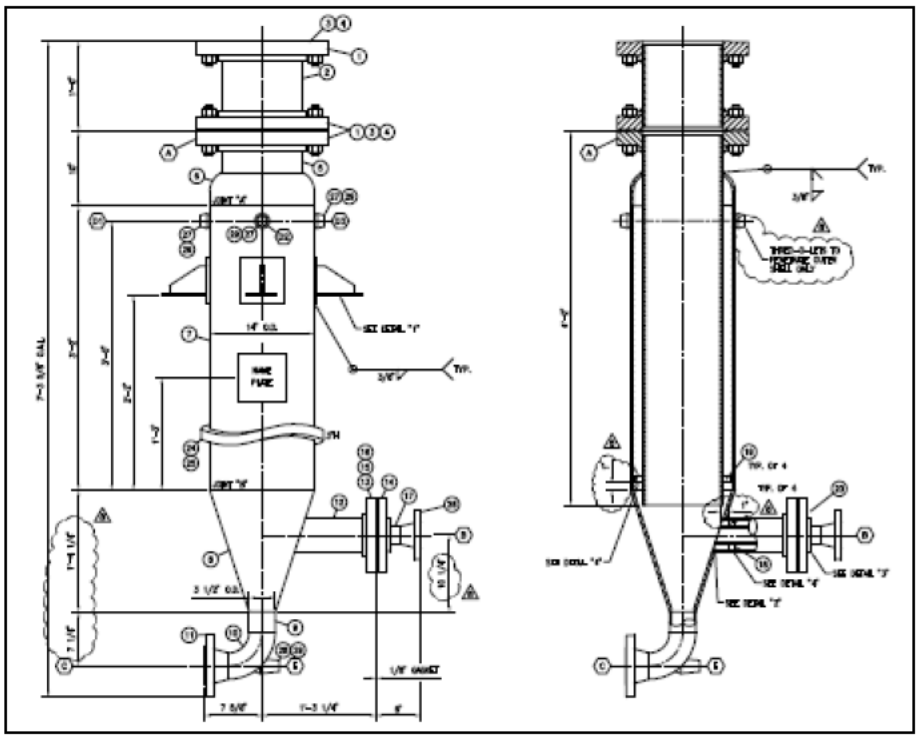


Figure 6-70: Original Design of the PDU HEHTR Steam Mixing Vessel

Simulations were performed to determine the utility of the SMV to produce an even flow of steam and biomass exit the 90 degree elbow. Additionally, the holdup and flow profile of both the biomass particles and steam were looked at to further understand the operation of the SMV. The simulation setup and operating conditions are summarized below in Table 6-12.

Table 6-12: Simulation Setup and Operating Conditions

	N_2 Boundary	Biomass Boundary	Steam Boundary	Outlet Pressure Boundary
Pressure, psig	35	11.1	40	10
Temperature, F	80	200	900	580
Flowrate, lb/hr	88.6	500	750	NA

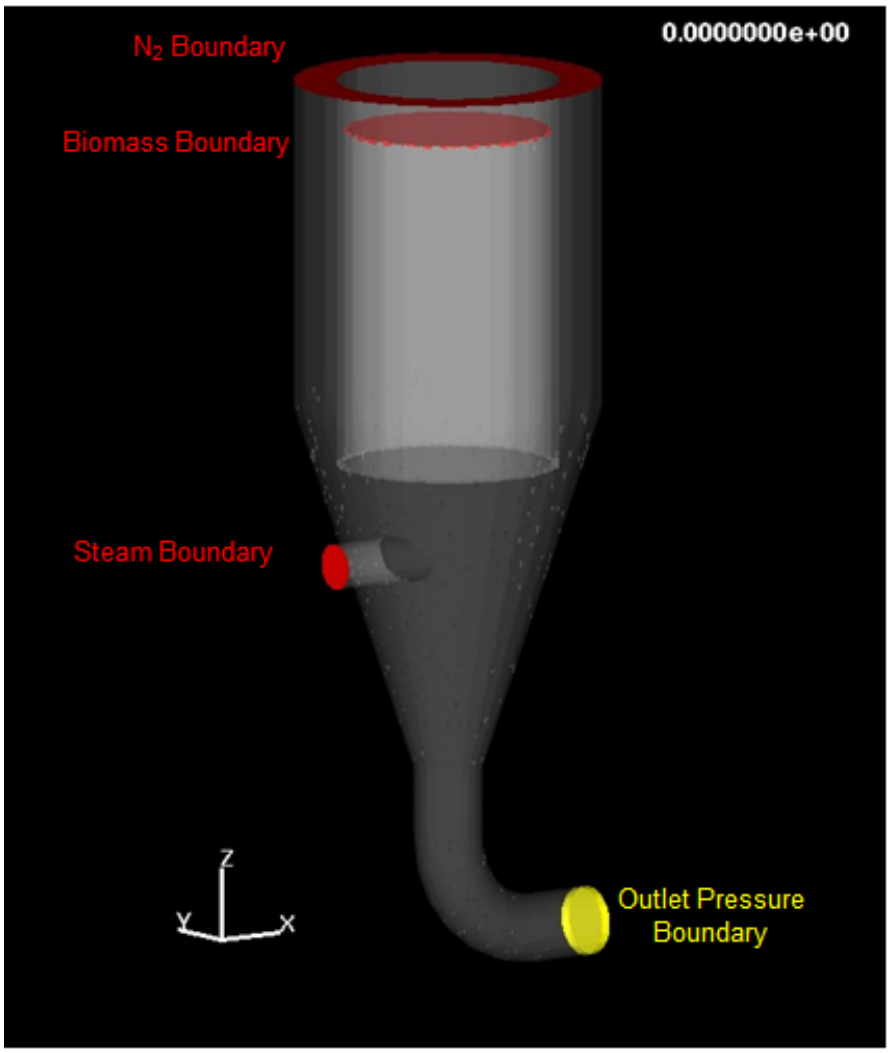


Figure 6-71: Steam Mixing Vessel for PDU HEHTR

Results from the original PDU SMV are presented in the figures below. Figure 6-72 below shows the fluid flow profile in the conical section and shows a significant amount of steam crosses the conical section and is deflected upwards on the opposite wall. This is reiterated in Figure 6-73 where a fluid temperature profile is shown depicting a "jet" of steam crossing across the conical section and hitting the opposite wall. This should be considered for design of future vessels as local metal temperatures opposite the steam inlet may be higher than expected.

Figure 6-74 shows a slice of the fluid flow profile along the entirety of the mixing vessel. Turbulent regions are evident in the figure and depicted using yellow circles in the figure and would inhibit the even down flow of biomass particles in the dip tube, especially due to the lack of gas flow in the dip tube region. Additionally, it was found that in the annular region surrounding the biomass dip tube, there was significant amount of fluid recirculation and swirling in this region. This flow pattern is contrary to the design of the SMV where the purge gas introduced in the annular region should have sufficient momentum versus the steam to be able to prevent any backflow. The swirling motion is depicted by a

circular "X" denoting flow traveling into the picture and "+" denoting flow traveling out of the picture frame.

Particle flow was also studied in the simulation of the SMV and is shown below in Figure 6-72, Figure 6-73 and Figure 6-74. Visible particle channeling is marked and can be seen in Figure 6-74 below. This phenomenon goes against the design of the mixing vessel where the biomass is expected to swirl along with the steam in the conical section before leaving the vessel via the 90 degree elbow at the bottom. The cause of the channeling may be linked to the upward momentum that a large percentage of the steam has following the jetting effect across the conical void resulting in a large amount of turbulence and upward forces. The particles can then be carried up into the annular space where the swirling motion limits the mixing between the two phases and results in a large percentage of particles channeling along the walls.

Figure 6-75 below shows the solids flux exiting the 90 degree elbow to measure the efficacy of the mixing vessel. As can be seen, there is a large amount of flux on the bottom portion of the pipe and the exit of the elbow compared to the center and upper portions of the pipe. This would represent an uneven mixing exit the mixing vessel boundary limits and questions the efficacy of the design in itself.

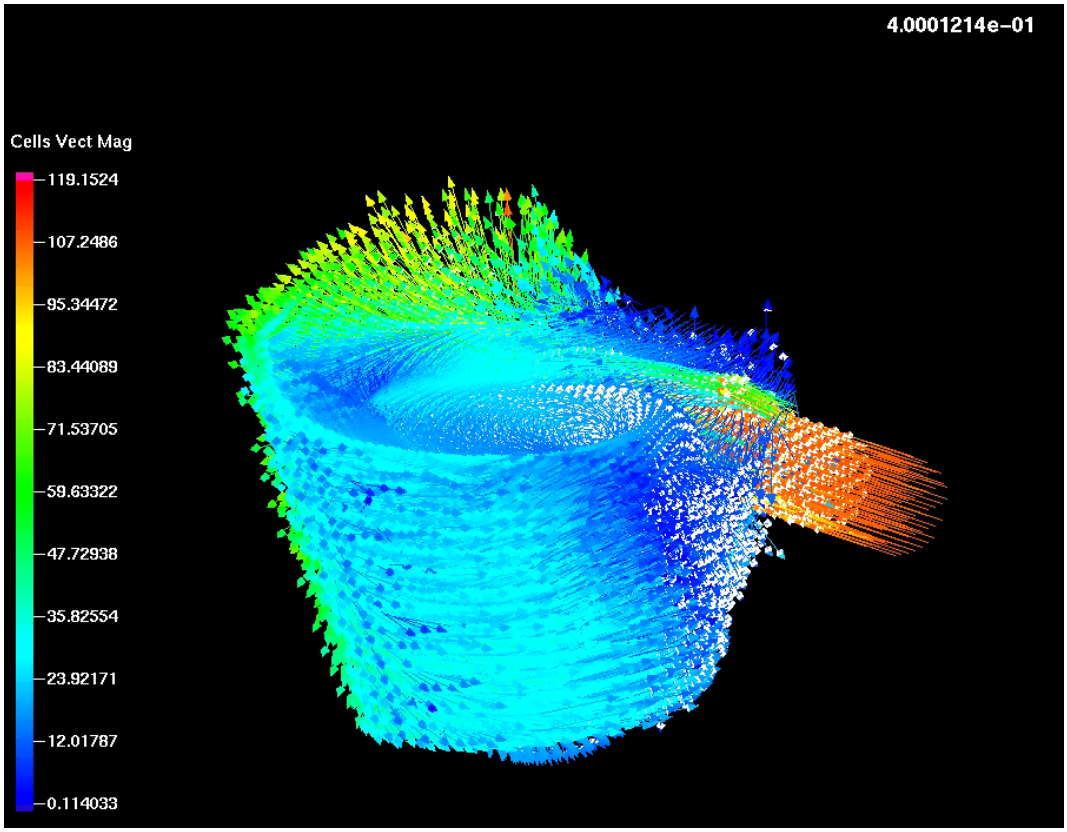


Figure 6-72: Fluid Velocity Profile in the Conical Section of the SMV

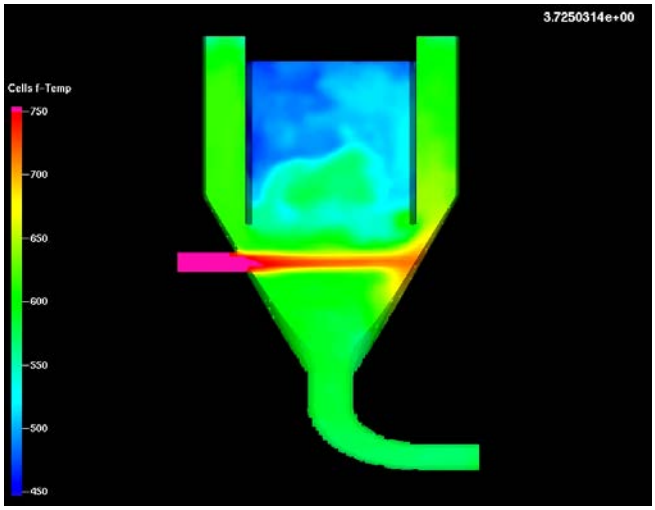


Figure 6-73: Fluid Temperature Profile of the SMV

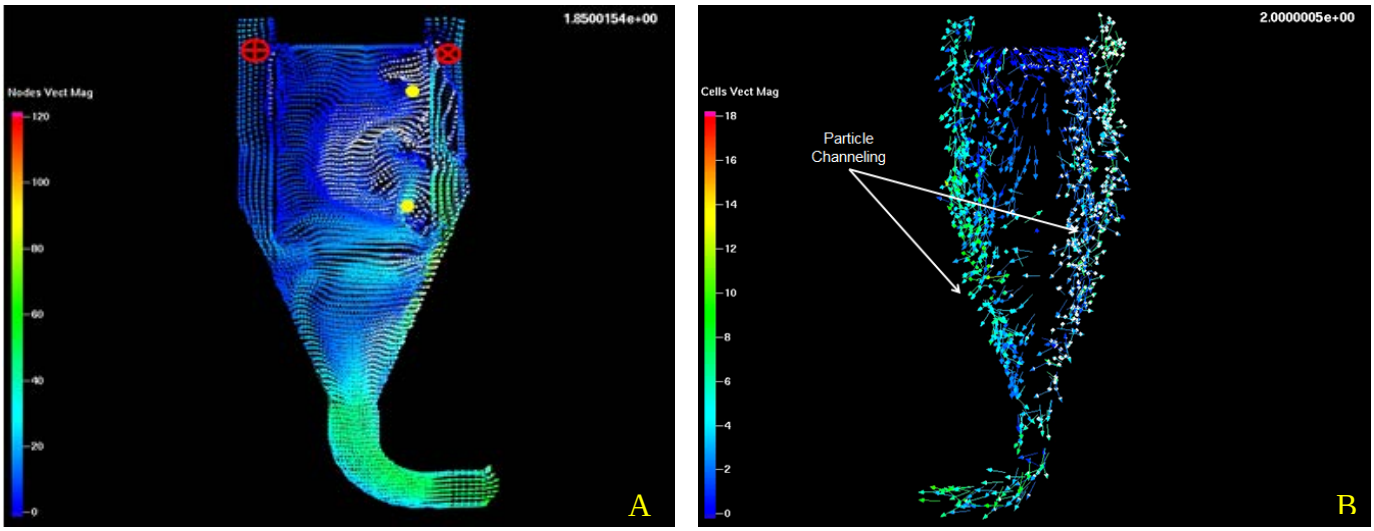


Figure 6-74: A- Fluid flow profile in the entirety of the SMV, B – Particle channeling in the SMV

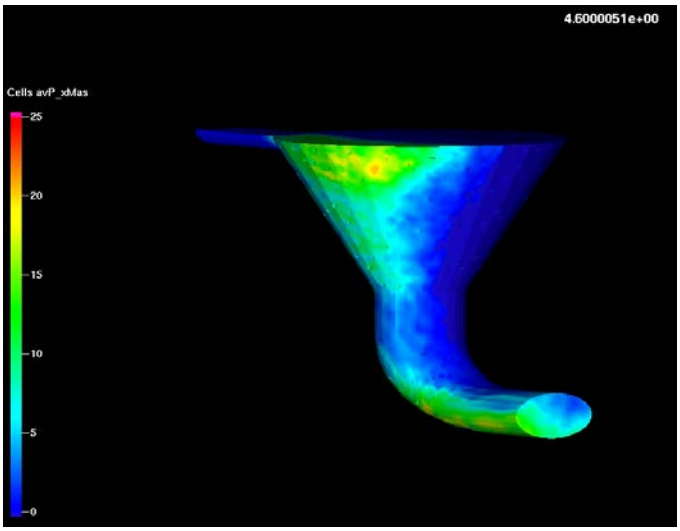


Figure 6-75: Solids flux exiting the SMV

The PDU steam mixing vessel was refabricated [redacted]

Results from the simulations are shown below in Figure 6-77, Figure 6-78, and Figure 6-79, using the same operating conditions as the original simulation to keep consistency despite the different operating conditions at the PDU over time.

Fluid flow profiles are shown in two separate ways beginning in Figure 6-77-A. The first depicts the temperature profile of the fluid phase after the redesign of the mixing vessel and can be compared above. As can be seen, there is still a significant amount of hot zones opposite the steam inlet piping, however, this may be slightly reduced in the redesigned vessel.
Figure 6-77-B below shows the fluid flow profile in the conical section and may be compared above. While there is still significant amount of fluid crossing the conical zone, the close proximity of the outlet piping in the direction of the fluid flow appears to offer a reduced resistance to the fluid leaving, thus causing less holdup and "swirling" than in the original design. This would theoretically in turn cause less biomass holdup and prevent potential problems in solids accumulation, premature devolatilization, and condensation.

Lastly, a comprehensive slice of the fluid flow is shown in Figure 6-78-A and can be compared above. There is a significant reduction in the amount of turbulent regions in the biomass dip tube which results in a more even flow distribution of particles when they contact the steam stream and minimize the amount of particle holdup inside of the mixing vessel.

Additionally, particle flow was studied in the redesigned mixing vessel and compared with that of the original. There is still significant amount of particle flow in the annular region as evident in Figure 6-78-B below; however, the particle channeling that was evident in the original design is no longer apparent in the simulation of the redesigned vessel. Lastly, the particle flux exit the mixing vessel is presented in Figure 6-79 and there is an even distribution of the flux around the exit of the pipe.

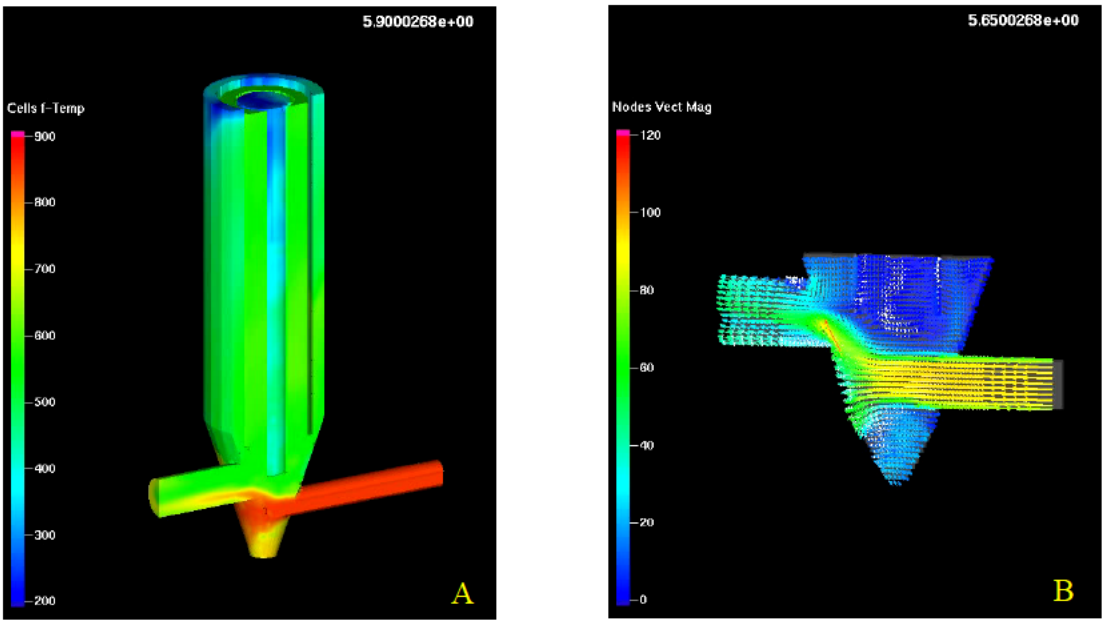


Figure 6-77: A – Fluid temperature profile; B – Fluid vector profile in the conical section

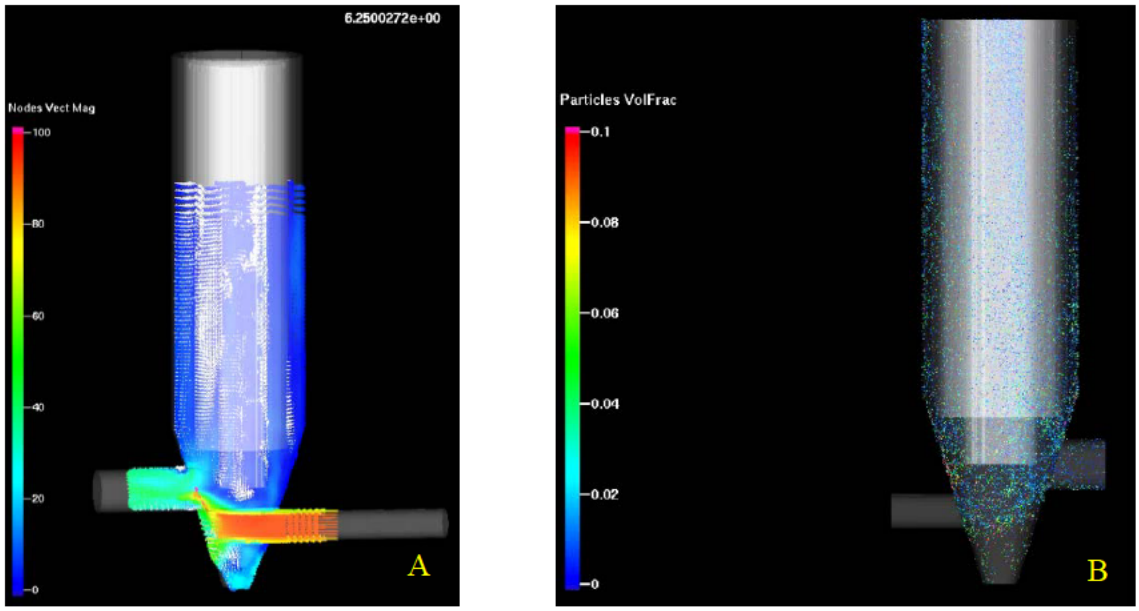


Figure 6-78: A – Fluid vector profile in the entirety of the SMV; B – Particle location and holdup in the SMV

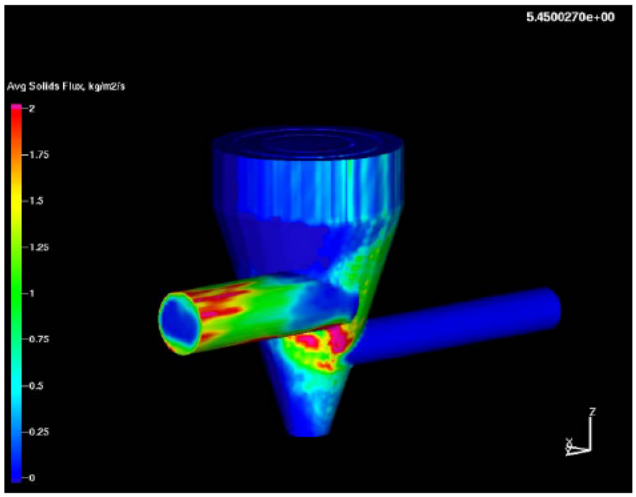


Figure 6-79: Solids flux exit the SMV

D.4 CFD Modeling – Biomass Particle Flow and Heat Transfer in Helical Coils

Flow of biomass particles in helical coils is an area of special interest within the ClearFuels technology as the HEHTR's helical coil design provides sufficient centrifugal forces to enhance particle contact with the outer wall; this facilitates the rapid heat transfer via conduction to the particle which is needed to obtain higher heating rates required for fast / flash pyrolysis, thus improving the performance of the HEHTR. Particle flow in helical coils is different from conventional straight line conveying due to the significant amount of centrifugal forces that are exerted upon the particles compared to strictly drag and gravitational forces such as in straight line pipes. Shu et al explains this phenomenon well:

"…in the helical system an increase in gas velocity does not move beyond saltation velocity, regardless of its magnitude and the lifting force is balanced by the centrifugal force on the particles. As a result, for a given gas velocity, the particle velocity 'self-adjusts' to yield balancing centrifugal and lifting forces." (Ming-tsai Shu, 1986)

Of particular importance is the particle slip (i.e. particle velocity / fluid velocity) in helical coils in order to estimate the particle residence time in a specific zone (i.e. reaction zone) of the HEHTR. Shu et al conducted bench-scale testing to determine the effect operating conditions and various coil parameters have on the particle slip for lignite and coal char. (Ming-tsai Shu, 1986) Their findings show that helix diameter (albeit much smaller diameter than the ClearFuels unit) has one of the strongest relationships to the particle slip with increasing helix diameter decreasing the particle slip (i.e. higher particle velocity / fluid velocity) as well as the decreasing with decreasing solids flow and decreasing particle size.

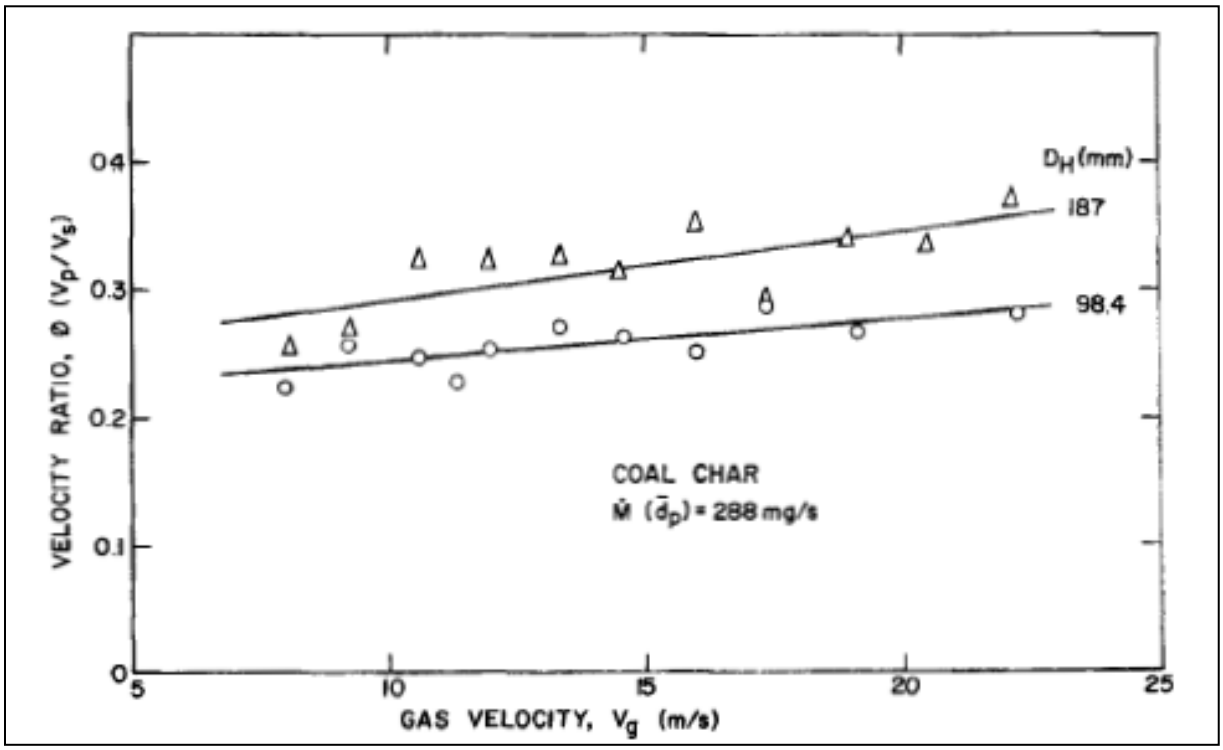


Figure 6-80: Effect of helix diameter on velocity ratio for coal char, from Shu et al

Using correlations developed from Shu et al, the particle slip can be estimated for the PDU and Livingston coils at varying operating conditions. For the systems investigated here, the major factors for the particle slip are the coil diameter and gas velocity. When solids flow is varied keeping other variables constant in the Livingston pilot plant, the particle slip does not change significantly; however, for the different gas velocities exhibited from the 2" to the 3" coil at Livingston the particle slip changes dramatically. At the PDU, varying the operating conditions can significantly affect the particle slip and needs to be considered in commercial operation and design. In general, one may estimate the particle to gas velocity ratio to be between 0.25 and 0.50 for systems of interest in the ClearFuels technology.

Table 6-13: Particle velocity vs gas velocity at Livingston and the PDU

Unit	Gas Flow*, lb/hr	Solids Flow*, lb/hr	Vp/Vg
Livingston, 2in	100	65	0.30
	100	110	0.30
Livingston, 3in	140	110	0.53
	140	180	0.53
PDU	300	250	0.40
	500	125	0.24
* Gas and solids flow are per coil for PDU			

Last, several key assumptions were made in the CFD simulations for both the Livingston and PDU HEHTR coils.

(i) No devolatilization of biomass particles
(ii) Biomass and char particles are non-spherical with a sphericity of 0.4 used for drag force calculations
(iii) Tangential momentum retention is 0.99 and normal momentum retention is 0.3
(iv) Particles do not squish, flex or stick at wall contact points
(v) All systems are modeled in a Cartesian coordinate system and the resolution of the result is no finer than the coarseness of the grid.

Particle flow was investigated in the PDU HEHTR coils as well as the Livingston reformer coils with the main goal of understanding the nature of the particle flow inside of the helix. Observations from initial simulation results (Figure 6-81 below) of the PDU coils show char particles preferentially travel along the outer wall indicating centrifugal forces greatly dominating the particle flow; whilst the biomass particles are observed to "bounce" around the outer and inner walls of the coil. This is in agreement with Shu's findings about particle flow and most likely is due to the much smaller particle size the char particles have in the simulation compared to the biomass particles allowing centrifugal forces to dominate. (Ming-tsai Shu, 1986) Nevertheless, this provides two key observations which may play of special importance to understanding the performance of the HEHTR.

The first is that along with the radiant heat transfer from the hot wall to the particles and convective heat transfer from the transport media (steam) to the particles, particle-wall direct conduction may be a significant source of heat transfer to the particles. This direct contact and subsequent rapid heat transfer via conduction between the hot wall and colder biomass particles would facilitate the higher heating rate necessary to achieve the fast and/or flash pyrolysis at a high heating rate which is necessary to achieve the desired carbon conversion and syngas composition. (Lede, 2000) Secondly, the smaller char particles which appear to transverse along the wall (Figure 6-81-A) would provide an "activated char layer" which when a biomass particle comes in contact with the wall where pyrolysis of a portion of the particle occurs. The subsequent volatile gases would then pass through this char layer which is known to have catalytic effects of secondary reforming and/or cracking reactions thus significantly reducing the amount of heavy tars and other hydrocarbons in the bio-derived syngas. (Duo Wang, 2011)

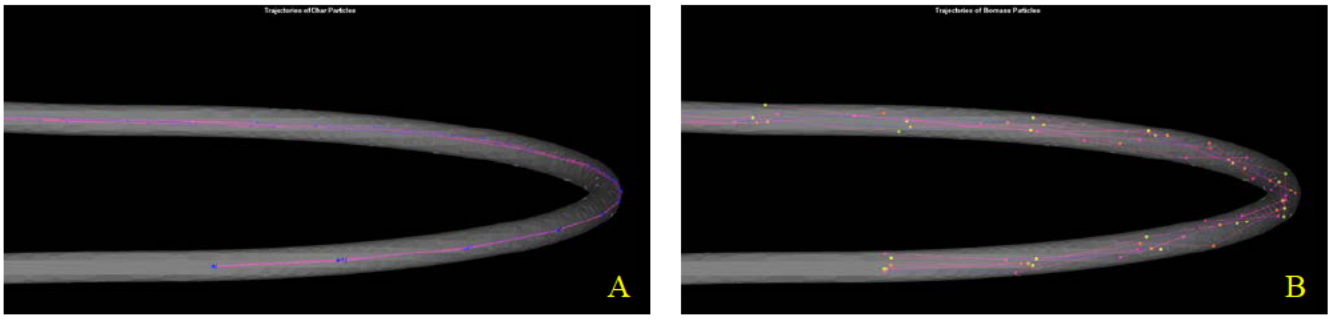


Figure 6-81: A – Char particle flow tracers; B – Biomass particle flow tracers

The particle bouncing that occurs in Figure 6-81-B is of special importance in the design and performance of the ClearFuels HEHTR as this is believed to be where the majority of heat is transferred to the particle (via conduction) resulting in a high heating rate which is necessary to achieve the desired performance of the HEHTR.

Figure 6-82 below shows a comparison of particle trajectories with different coil geometries, operating conditions and particle sizes. A key observation here is that the number of bounces appears to be independent from operating and design parameters (i.e. coil diameter, steam flow, etc.) with the only potentially significant variable being particle size. This is a very important observation as this would indicate that the heating rate (which is presumed to be dominated here by particle/wall contact, hence bounces) is independent of operating conditions (i.e. gas / particle velocity) and may be written as a function of the metal temperature of the first turn of the HEHTR. Subsequent analysis of the PDU and Livingston performance data has confirmed the significance of the first coil turn metal temperature as a predictor of HEHTR performance.

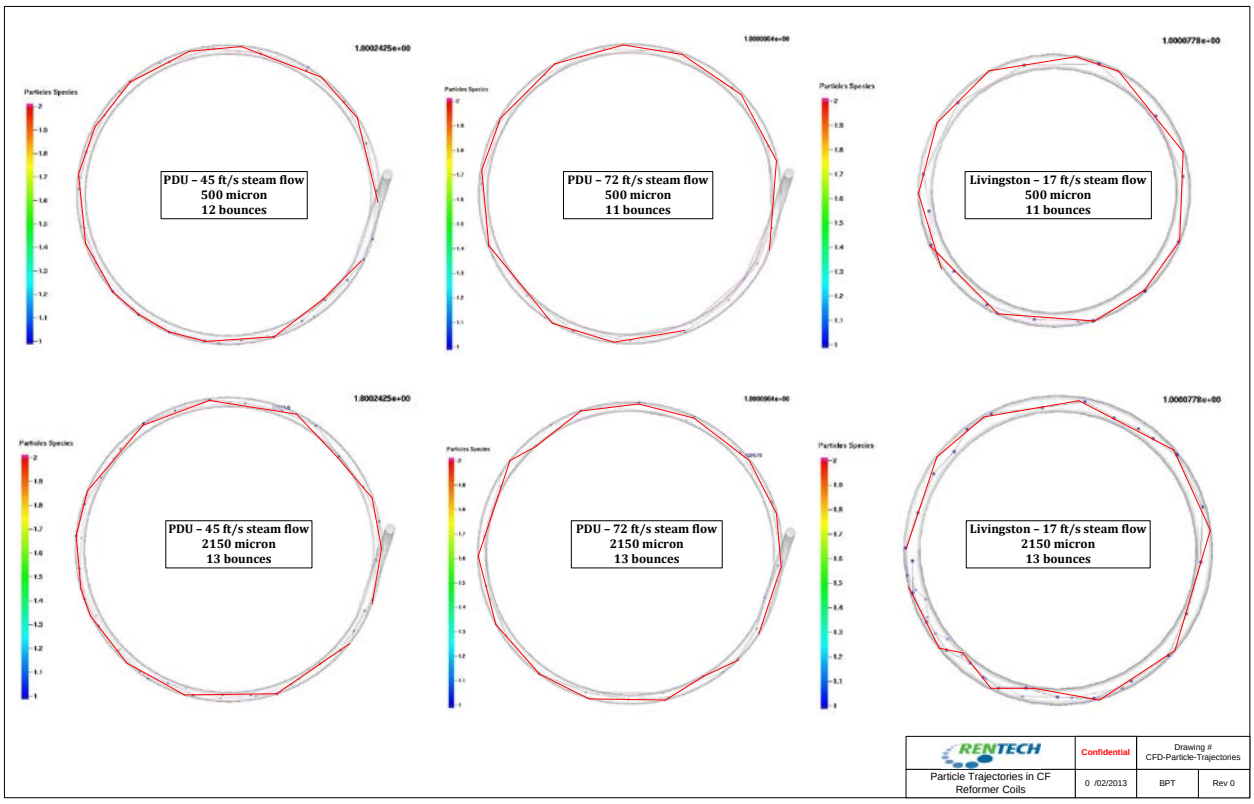
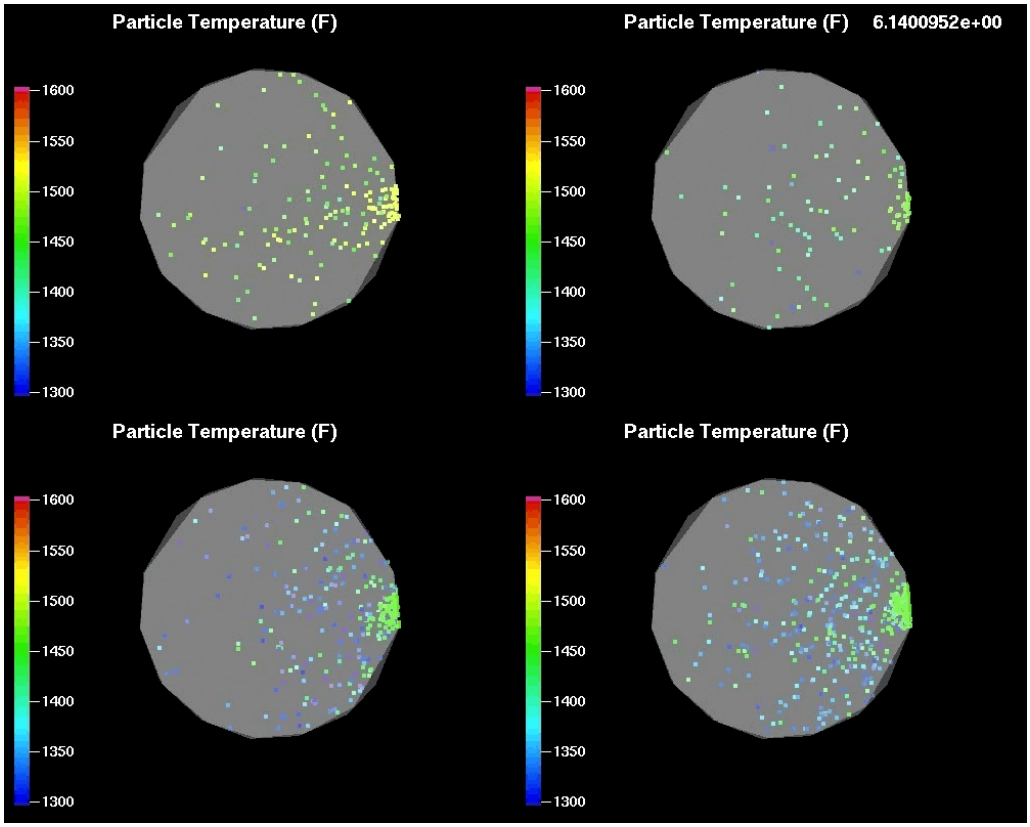


Figure 6-82: Particle bounce trajectories in various geometries and operating conditions

Figure 6-83 below shows a cross section of particles at a point in the second turn of the ClearFuels PDU coil (see subset). The simulation results show a significantly higher temperature (~50 – 100°F) of particles near the wall edge for four different simulations which were conducted on the ClearFuels coil. This grouping of particles primarily consists of the smaller particle size char particles which tend to travel along the outer edge of the helix as centrifugal forces greatly dominate its flow since the particle has little mass and thus momentum. This could lead one to design a system with a smaller particle size in the feed in order to maximize the centrifugal force effects on the particle; thus keeping the particle in close proximity to the wall for maximum heat transfer. More than likely, there will be practical limitations in practice to both the operability of processing very small particle size biomass particles as well as significant economic implications in order to reduce the particle to a size small enough where centrifugal forces dominate. A second observation from the below figure is that this char layer is significantly hotter than the dispersed biomass particles in the bulk gas. This could strengthen the argument in favor of having a catalytic char layer in close proximity to the wall which volatile gases must travel after pyrolysis as well as confirming the validity in using the metal wall temperature as a key design factor for the HEHTR.



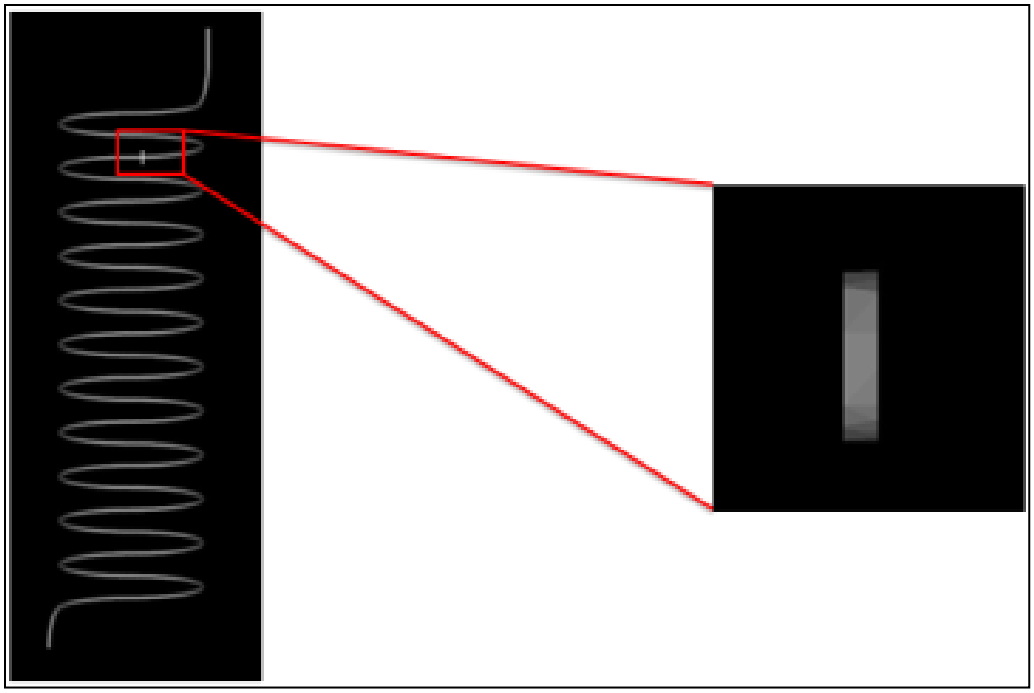


Figure 6-83: Cross-section of PDU HEHTR coil showing greater increase in temperature of particles located nearest the wall

Particle flow was investigated thoroughly between the Livingston coil and the PDU coil to determine if there are any significant differences between the flow profiles in the two coils. A summary of the conditions are below. It is important to note that at the time of the simulation design for the Livingston coil, the exact geometry and operating conditions of the Livingston coil were unknown and taken from verbal recollection from Stan Pearson. Upon Rentech operating the Gulf Coast Energy pilot facility, the coil geometry was a very close match to what Stan Pearson had recalled with slight differences in the length and pitch versus those conducted in the simulation; however, Rentech was unable to ever operate near the conditions specified and dramatically decreased the biomass flow to 30-75 lb/hr in most testing conditions.

[redacted]

In the proposed simulation, particle flow is qualified using an average solids volume fraction to determine the location of the majority of particles in the simulations. **Figure 6-84** below presents the volume fraction for both simulations side by side for clarity. A key observation here is that as the gas velocity increases along the coil in **Figure 6-84**-A due to the increase in wall temperature and time in the coil, the particle velocity increases and the centrifugal forces begin to dominate some of the larger particles. This is evident as the increasing volume fraction of particles along the outer wall as the particles travel further down the coil. Conversely, in the Livingston coil (Figure 6-84-B), there does not appear to be any significant differences in the particle flow down the coil. One important factor here to consider is the temperature profile along the coil wall. For the PDU simulation, data from operations was used to define a temperature profile along the vertical of the coil but for the Livingston operations, a constant wall temperature was used because of the lack of data at the time the simulation was conducted.

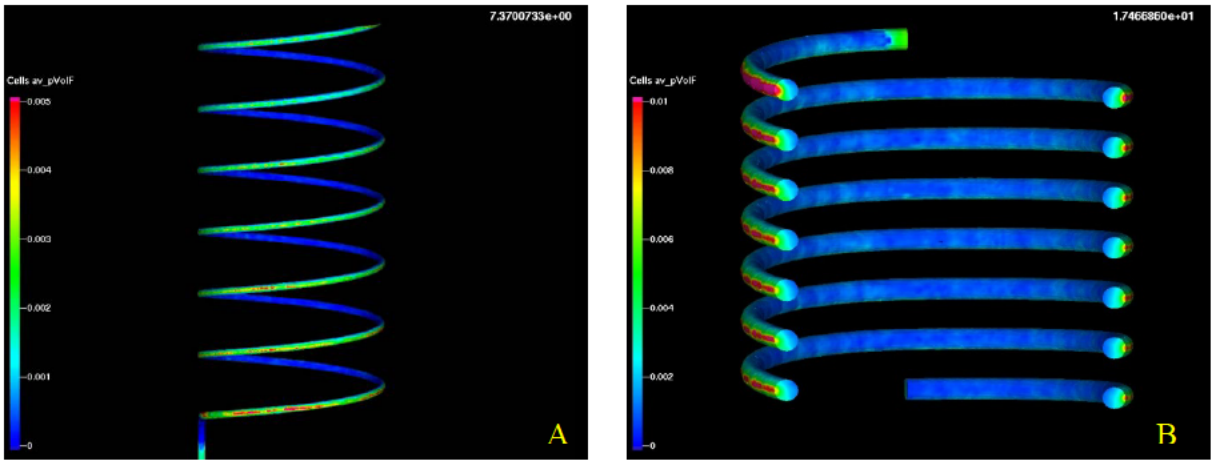


Figure 6-84: Solids volume fraction comparison in the PDU (A) and Livingston (B) coils.

From the particle flow profiles observed in both the Livingston and PDU coils it is expected to have enhanced heat transfer to particles versus conventional dilute phase solids transport in a straight pipe. There is minimum literature available on the heat transfer characteristics of helical coils for a gas-solids system; literature is available for single phase gas or liquid and two phase gas-liquid fluid systems. For a single phase fluid system, the advantage of a helical coil system is presented by Acharya et al where different coil arrangements are compared to a straight pipe. (Narasimha Acharya, 1992) The relevant results are shown at right where a constant axis (CA) helix, alternating axis (AA) and straight pipe (STR) heat transfer abilities are compared via the Nusselt number ratio. Their findings conclude that a constant axis helix (such as that in the HEHTR) has a roughly 2.5 times higher Nusselt number compared to a straight pipe. This would result in higher convective heat transfer coefficients for the fluid phase in the helix compared to conventional straight pipes.

Since there is negligible literature available in the public domain on heat transfer to particles in a helix, CFD experiments were conducted with the main objective of determining the benefits of the helix over a conventional straight pipe. Operating conditions were chosen as 200 lb/hr of biomass flow and 600 lb/hr of steam flow for both simulations with a constant wall temperature of 2015 F for all metal surfaces in the simulation. Barracuda software is able to calculate the total surface area available for heat transfer and for the straight pipe is 7.39 ft^2 and for the single turn coil is 14.27 ft^2, these numbers are used for flux calculations. Additionally, flux planes were placed along the single turn coil simulation at points where a quarter and half of the available area has been passed by the particles. The simulation setups are shown below in Figure 6-85 and Figure 6-86.

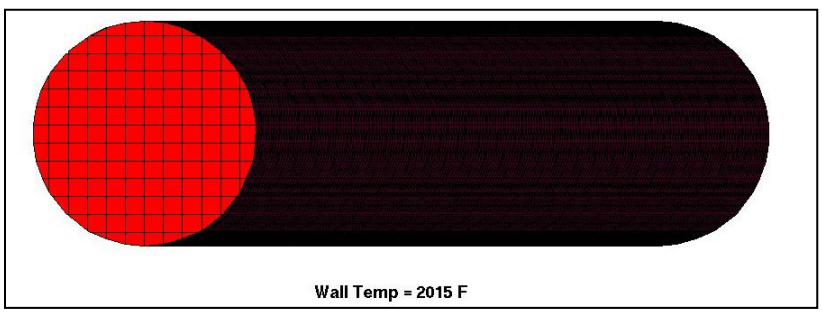


Figure 6-85: Grid setup for straight pipe calculations

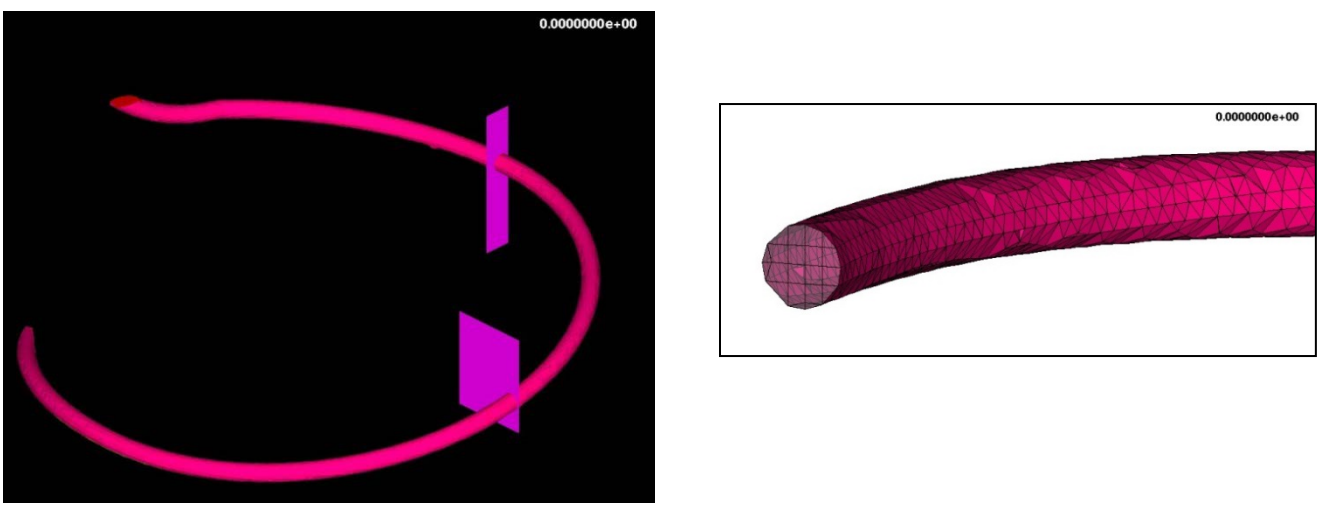


Figure 6-86: Grid and flux plane setup for a single turn in the PDU HEHTR coil

Particle residence time is shown in Figure 6-87 to show the different amounts of time that the particles are in the system. For the straight pipe surface the particles have an average residence time of 0.13 s upon exiting the system while for the single turn of the coil the average residence time is 0.31 s. This is primarily a function of the longer length of pipe that was needed in order to model roughly one turn of the PDU coil.

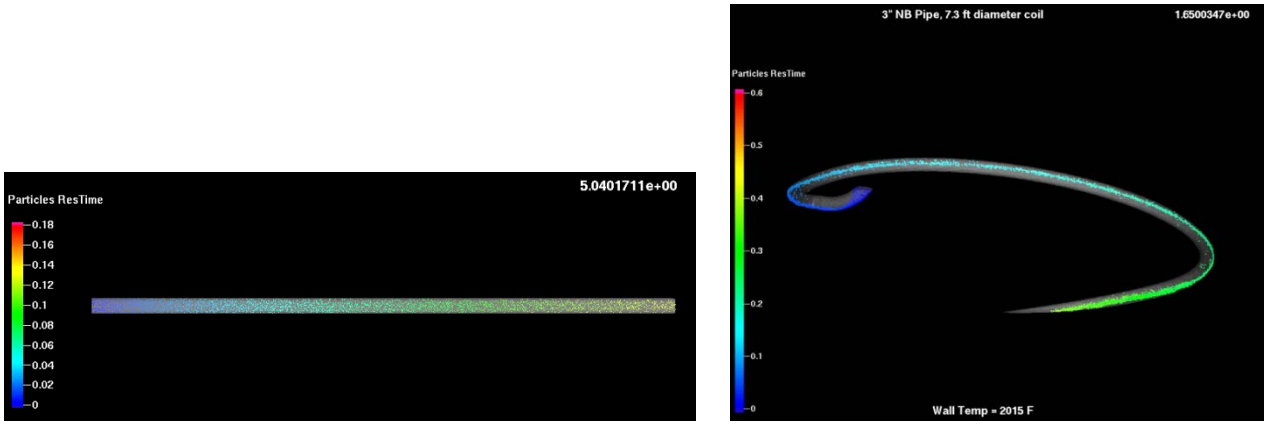


Figure 6-87: Particle residence time in the straight pipe and PDU coil

Particle and fluid temperature are presented for the straight pipe below in Figure 6-88 and Figure 6-89. There is a distinct fluid temperature profile in the straight pipe indicating that heat transfer due to convection from the fluid may play a small role in heating the particles in a straight pipe, radiation from the wall to the particles may be the dominant driver. Further analysis using Barracuda's ability to turn radiation off may be warranted if future studies are done. The exit particle temperature is scattered with an average value of roughly 600°F.

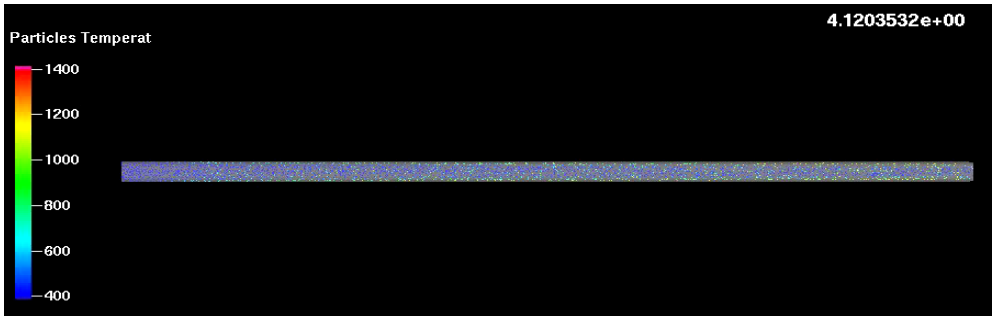


Figure 6-88: Particle temperature in the straight pipe

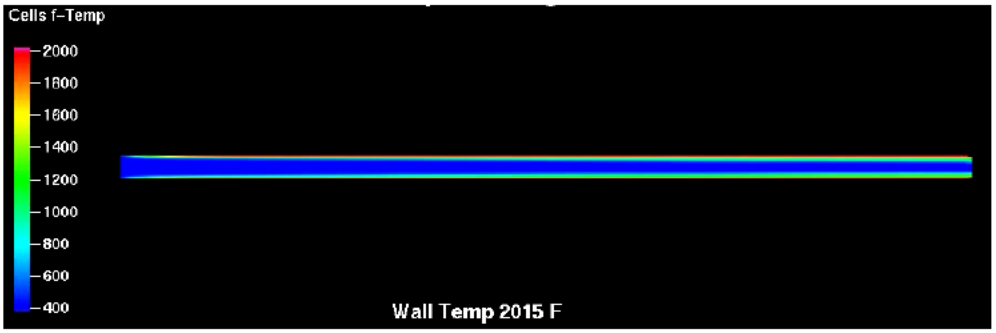
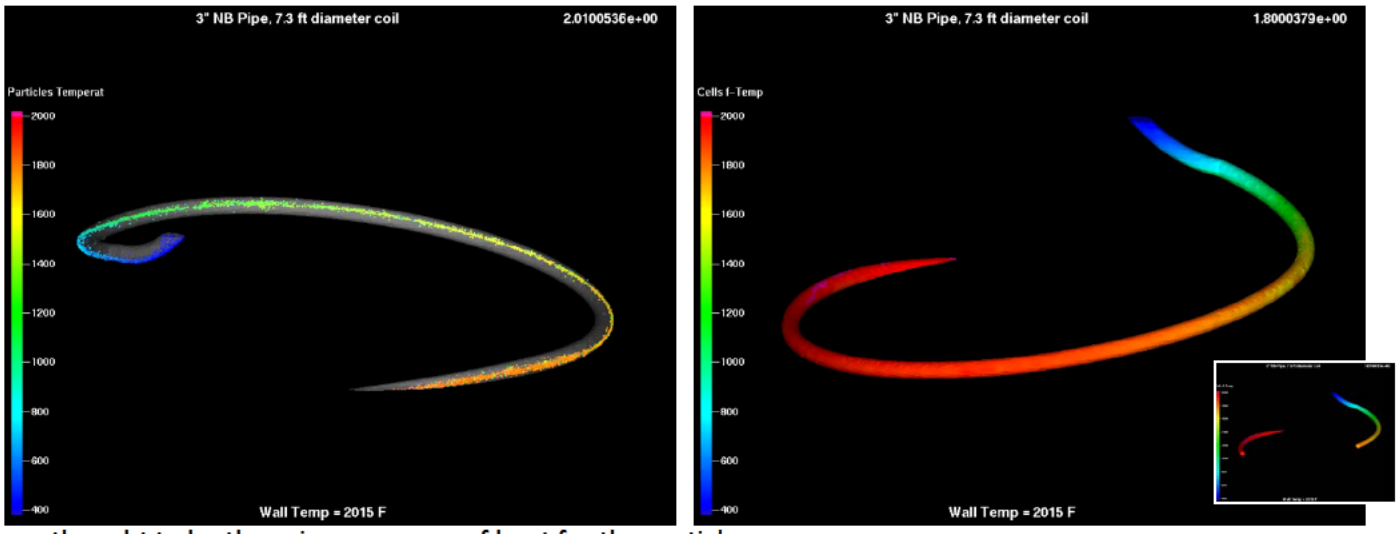


Figure 6-89: Fluid temperature profile in the straight pipe

Particle and fluid temperatures are shown in Figure 6-90 for the single coil turn simulation. There are noticeable differences in the fluid temperatures profile along the length of the coil compared to the straight pipe; there is no noticeable radial temperature gradient in the single turn coil as opposed to the very large gradient that is seen in the straight pipe. Additionally, the particles tend to increase in a more homogeneous manner than in the straight pipe. This is presumably due to both the centrifugal forces maintaining the particles in close proximity to the hot wall as well as the even fluid temperature that is steadily increasing along the length of the coil. It is important to question the significance of the grid resolution here impacting the solution of the problem. The coarser grid that is necessary in the coil simulation in order to maintain a reasonable amount of simulation time could impact the solution as Barracuda is unable to solve for the eulerian field (fluid) at a resolution that is smaller than the grid. This large grid size may impact the heat transfer since the grid cell closest to the wall covers approximately 20% of the distance across the pipe wall where in the straight pipe solution a grid cell covers approximately 8% of the distance. This could factor into how the heat is transferred across the radial direction of the pipe and should be investigated further. Presumably, this would not have significant impact on how heat is transferred to the particles as they are in very close proximity to the wall which is



thought to be the primary source of heat for the particles.

Figure 6-90: Particle and fluid temperature in the single turn PDU coil

The total enthalpy which crosses a flux plane (flow or pressure boundary and manual flux planes) is computed by Barracuda in both the solids and fluid phases. From this one can compute the heat flow that is transferred to the solid particles by taking the difference between the two values and then calculating the derivative to obtain a heat flow. From an energy balance around the system, one can obtain the energy accumulation term and by taking the derivative and dividing by the area the resulting flux can be calculated.

$$Q_{accum} = Q_{out} - Q_in \qquad \dot{Q} = \frac{1}{A} * \frac{dQ_{accum}}{dt}$$

For this system, a cross flow exchanger surface is used to calculate the heat transfer and obtain an overall heat transfer coefficient for the particles in the system. The following defines the heat transfer and temperature differences used for the calculations.

$$Q = U * A * \Delta T \qquad \Delta T = \frac{T(p,out + T_{p,in})}{2} - T_{wall}$$

As Barracuda is not able to discretely export the average particle temperature that crosses a flux plane, particles were individually counted and multiple time stamps as they cross the boundary. When a satisfactory sample size was achieved (>250 particles) the average was computed and used for the calculations. The heat flux and heat transfer coefficients for the boundary conditions defined in the straight pipe and coil are presented below in Figure 6-91. The key difference between the two figures is the basis in which the flux and heat transfer is calculated in the coil. Figure 6-91 uses a calculation starting at the inlet of the coil and going to each flux plane along for its basis while Figure 6-92 calculates each section of the coil individually. Both the heat flux and the heat transfer in the straight pipe are roughly 10 times smaller than in the coil using either basis, suggesting significant enhancements in heat transfer to particles in the helix. Unfortunately, this method of calculation does not deconvolute whether the majority of the heat is transferred via conduction, convection or radiation but it is presumable that conduction and enhanced convection and radiation near the particle wall would obviously play a significant factor.

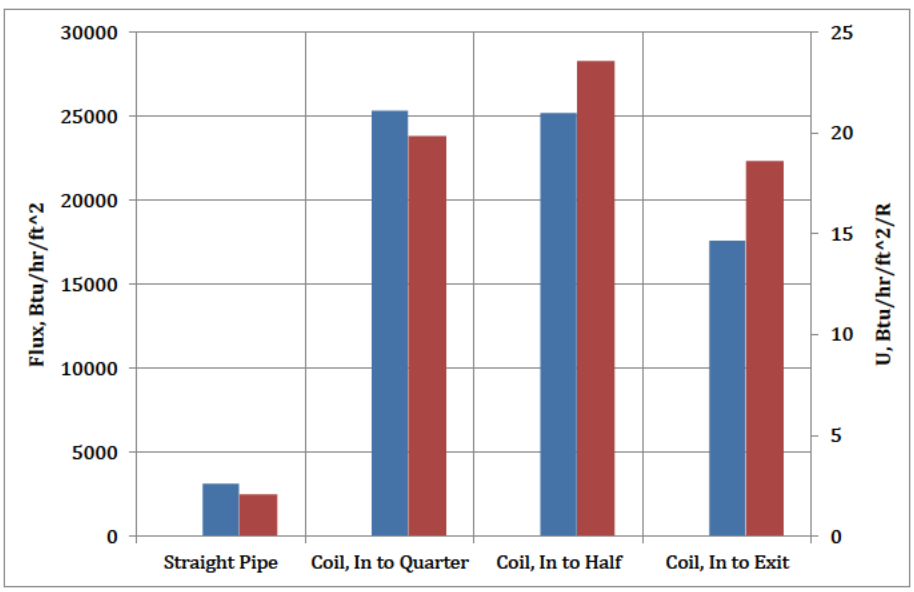


Figure 6-91: Heat flux and overall heat transfer coefficient in the two systems, calculations are from the inlet to the flux planes

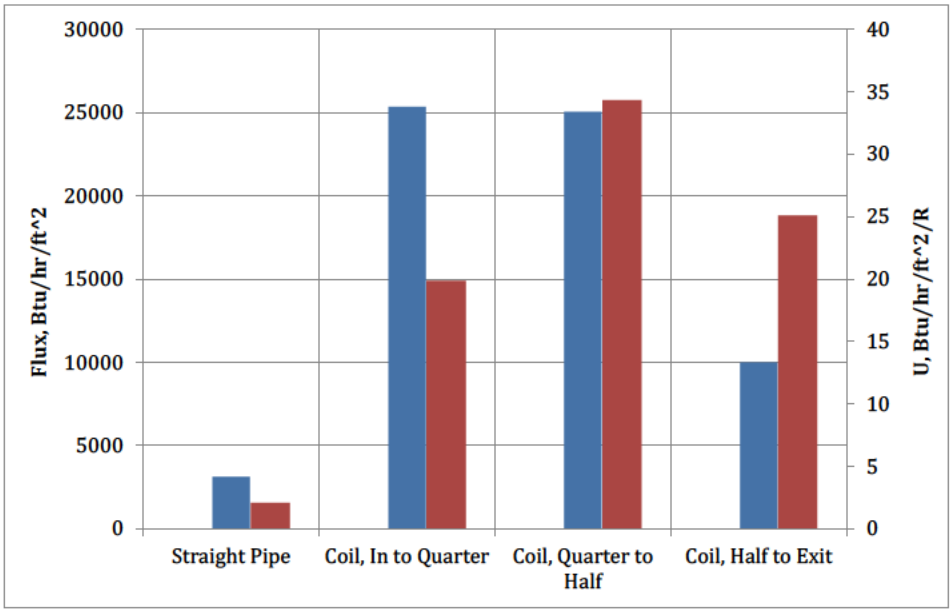


Figure 6-92: Heat flux and overall heat transfer coefficient in the two systems, calculations are for each section of pipe

6.E Primary Syngas Cleanup

E.1 Syngas Cleanup Operating Conditions

Syngas from the HEHTR is quenched, particulates are removed in two cyclones in series, and the syngas is scrubbed in a Solvent Scrubber followed by a water wash system, before it is compressed in the Booster Compressor for delivery to the main Syngas Compressor. The primary operating variables monitored in the Rentech-ClearFuels syngas cleanup system, during the DOE Run were the Solvent Scrubber overhead temperature, the Quench Chamber recirculating water temperature and the Booster Compressor suction and discharge pressures. These parameters are trended in the following chart.

During the DOE IE Run (PERIOD 4), the solvent addition to the solvent scrubber was approximately 8 gallons per hour. The solvent used was Raffene 1200L which is the trade name for a refined heavy naphthenic distillate. As mentioned below in the Lessons Learned section, tar reforming using Rentech's NiDFB technology would probably be preferred to the use of a solvent system.

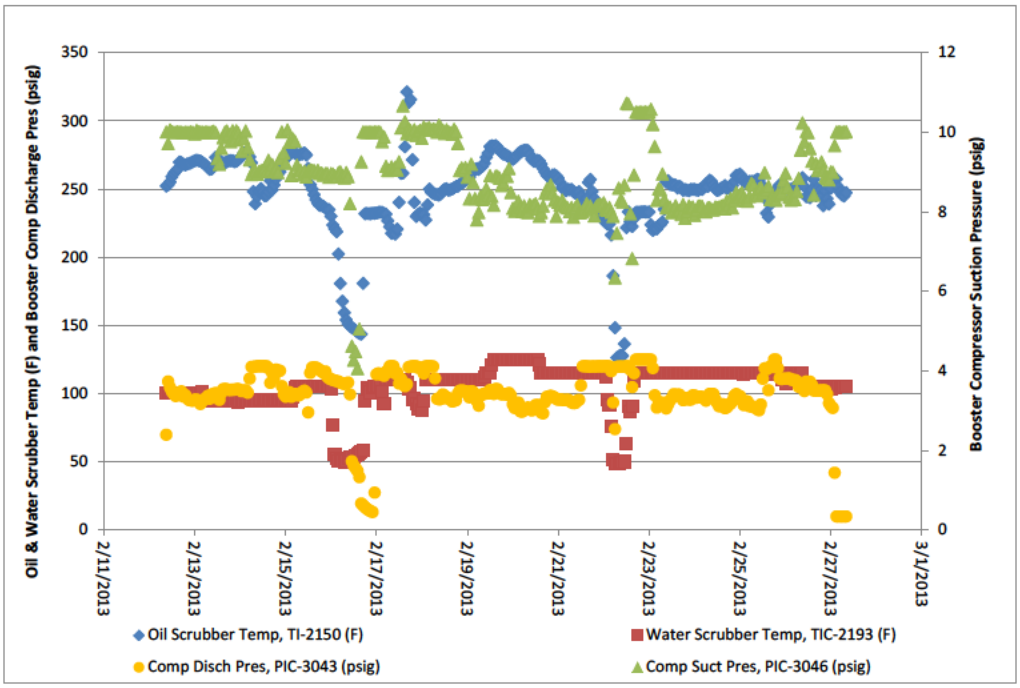


Figure 6-93: Syngas Cleanup Operating Condition Trends During DOE IE Run

E.2 Particulate Removal

Both the Livingston and Commerce City plants employed cyclones for particulate recovery after the syngas cooler. The PDU had two cyclones installed in series (primary and secondary cyclones), which recovered 90%+ of the particulates exiting the Reformer, once the inlets were modified to provide sufficient inlet velocity at the low operating rates the unit was normally run at.

If char recycle is employed in a future design, the char from the primary cyclone could be routed to a separate steam/solids feed mixer or solids eductor, and fed back to either a separate coil in the HEHTR, or combined with the biomass/steam feed to a coil.

An adequate lock-hopper system, with sufficient solids hold-up would need to be provided to allow for steady feedback to the HEHTR. In this case, the char/ash from the secondary cyclone, plus some portion of the primary cyclone char, would be recovered as a separate byproduct stream.

The Livingston plant employed a particulate filter (cartridge) upstream of the wash tower. For a commercial unit design, either a hot gas filter (pulse jet type) should be included upstream of the venturi/water wash column, to remove the bulk of the <5 micron particulate material before it gets into the water wash system, or continuous filtration equipment will be required on the venturi/wash column pumped circulation, to remove solids that build up in that water over time.

Sock filters were employed at the PDU, but frequent sock filter change-outs (particularly at higher feedrates) is not considered acceptable for a commercial unit design. As a result, an automated (self-cleaning) hot gas filter system, upstream of the water wash system, is highly recommended.

After the water wash system, it may be necessary to provide fine duplex sock/cartridge filters or alternately a WESP to remove very fine particulates (< 1 micron) and condensed tar fumes. These were found to be necessary at the PDU. Prior to the sock filter installation, the compressor suction strainers plugged prematurely and naphthalene carryover would crystalize in the compressor discharge air cooler, requiring cleaning.

E.3 Gas Cleanup

The Livingston plant operated acceptably during the test campaign, without a heavy oil scrubber upstream of the venturi/water wash column, apart from some accumulation of naphthalene in the column packing, probably as a result of significant on-purpose operating hours at low initial skin temperatures, as part of the test matrix conditions (plugging primarily observed during these low firing runs, and was typically rectified by steam out of the packing). Apart from these occurrences, the low heavy tar content of the syngas is believed to be the primary reason for the water wash column operating without apparent problems.

The experience at the Commerce City PDU was very different, however, as the much higher heavy tar content of the syngas caused the water wash piping, heat exchangers, packing in the scrubber, etc. to plug severely with tars that were not able to be steamed out, requiring intermittent shut-downs and very messy cleanout operations. The solution implemented at the PDU was to install a heavy oil scrubber upstream of the Water Wash system to remove these heavy tars. The oil scrubber initially used a soy oil scrubbing solution, which appeared to work best, but this soy oil was later replaced with highly aromatic base oil, due to soy oil availability problems. The oil scrubber had operational challenges including temperature control, oil/water emulsion formations, carry-over of entrained solvent, spent solvent disposal issues, and filtration of the hot solvent.

The key is to make very little or no heavy tars (MW>202) in the HEHTR and this is the reason for targeting the high initial skin temperature in the commercial unit design. If this is done, it is anticipated that heavy tar production will be minimal, and the syngas from the cyclones/hot gas filter should be able to be routed directly to the Venturi/water wash system, as is practiced at Livingston. The syngas after the hot gas filter should be able to be flared to allow it to be diverted away from the water wash column, during periods of abnormal operation, when the syngas composition may not be optimal.

As there may still be some light and heavy tars collected in the water wash system, it is recommended that carefully designed light tar (less dense than water)/solids skimming and heavy tar (more dense than water)/solids bottom draw-offs be provided. Particulate filters will still be required on the Wash system circulating water, but the upstream Hot Gas Filter (operating above the tar dew point) should minimize the filter element replacement frequency.

A plate and frame heat exchanger specifically designed for fouling/plugging service (e.g. larger plate spacing, higher velocities, etc.) was installed on the PDU Wash system circulating fluid (after the original generic plate and frame heat exchanger had a poor operating history), and this operated well. Make provisions to gas purge the heat exchanger (e.g. using nitrogen or pressurized fluegas) while it is online.

Both the PDU and the Livingston pilot plant employed a light oil scrubber downstream of the water scrubber (either directly downstream or after the gas compression) to remove residual light tars, including benzene (both units had downstream catalytic reaction units prone to deactivation). Both units worked satisfactorily [redacted]

[redacted] the PDU utilized a TEG solvent, with a regenerator. Be very careful about potential personnel exposure to benzene accumulation in these systems. This gas cleanup step may need to be employed depending on the specific gas compositional requirements.

E.4 Gas Compression

An oil flooded screw Booster Compressor was employed at the PDU to compress the ClearFuels syngas from ~ 5 – 10 psig up to 100 psig (approx.), prior to the main Syngas compressor. With over 1000 hours of operating time on the compressor, the compressor oil did not show excessive degradation. The major operating problems were initially plugging of the suction strainers, which was largely solved by installing upstream duplex sock filters and accumulation of naphthalene in the compressor discharge cooler. Operation at higher HEHTR initial skin temperatures should significantly reduce the downstream cooler fouling problems.

6.F Secondary Syngas Cleanup

F.1 Syngas Compressor

Raw syngas from the booster compressor enters the first stage knockout of the Syngas Compressor after which it is compressed from ~110 psig and 88°F to 260 psig and 218°F. Once compressed the gas is sent to the COS Hydrolysis (refer to COS Hydrolysis Process Description) where the sulfur is converted from COS to H_2S. The gas is then cooled to 120°F before entering the second stage scrubber and then being compressed in the second stage to 510 psig and 257°F. The gas is then cooled one last time and sent through the last knockout before entering the TEG Wash.

The liquids from the scrubbers and the pulsation bottles are sent to the onsite wastewater treatment plant.

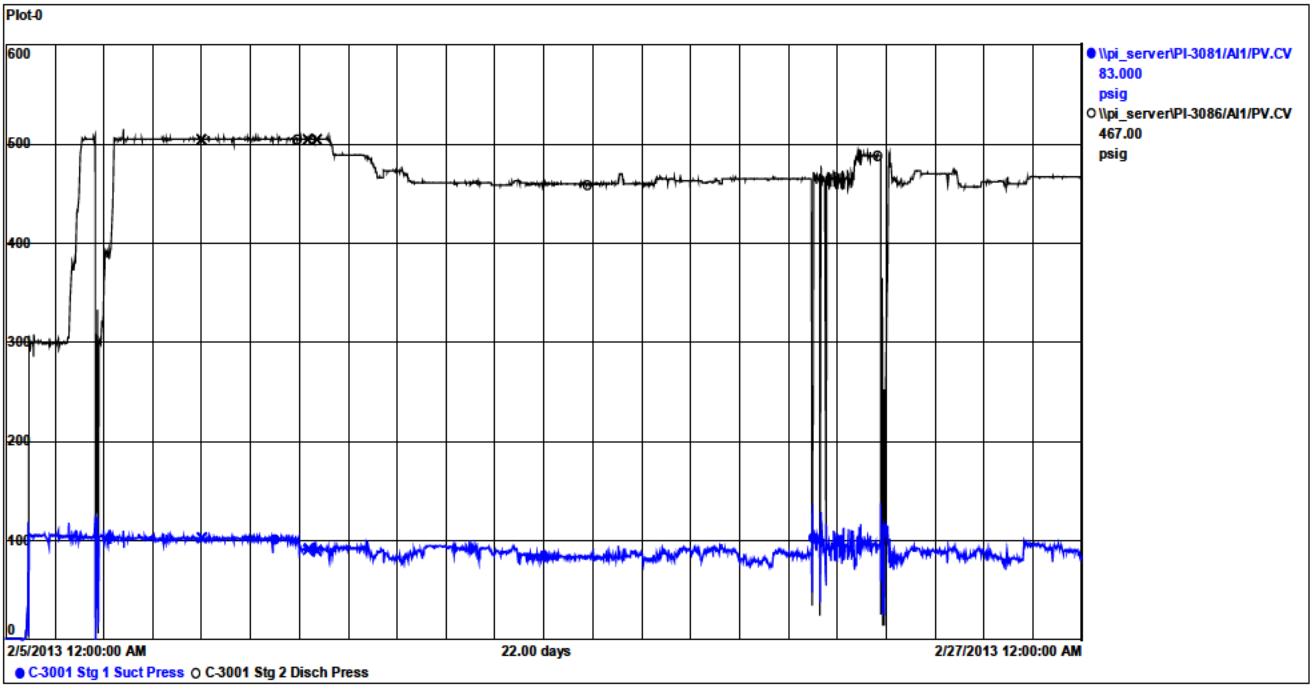


Figure 6-94: Syngas Compressor Performance during DOE Run

Over the period of IBR performance run, the Syngas Compressor ran stably with exit pressure ~ 450 and 490 psig.

F.2 COS Hydrolysis Unit

Syngas enters into the dual bed hydrolysis vessels that contain a high-purity activated alumina catalyst which reacts as follows:

$$COS + xH_2O \rightarrow H_2S + CO_2 + (x\text{-}1)H_2O$$

The hydrolysis products H_2S and CO_2 pass through the dual hydrolysis beds to be removed downstream. The hydrolysis unit is most effective at COS concentrations up to approximately 100 ppmv. Most of the sulfur in the syngas produced by the gasifier was H_2S and < 100 ppmv (~ 100 ppm with bagasse feed and average ~ 50 ppmv with other feeds). This level is dependent on the sulfur content of the feed and reformer conditions, such as feedrates, steam to feed ratio, temperature and pressure. The concentration of COS produced in the gasifier was only ~ 5-10 ppmv when measured but more study is desired. A speciated sulfur analysis is given below in
Table 6-15. It is not certain whether operating conditions could be adjusted to lower the COS concentration from the reformer, thus eliminating the need for COS hydrolysis; however, other than H_2S, the concentration of other sulfur species were insignificant.

Table 6-15: Trace Sulfur Speciation of Biomass Derived Syngas @ AE-3076

Sulfur Species in Syngas @ Booster Compressor AE-3076 (ppmv) AM 2/26/2013	
Hydrogen sulfide	35
Carbonyl sulfide	6
Carbon disulfide	0.04
Thiophene	0.08

F.3 TEG (Tri-Ethylene Glycol) Unit

The inlet gas is contacted with 12 gpm of 90 wt% TEG. The treated gas exits the top of the tower containing < 10 ppmv of benzene. TEG Contactor V-3026 has 4 theoretical trays of structured packing. The inlet gas enters below the packing, traveling up contactor contacting with the TEG travelling down through the packing. The treated gas exits the top of the tower and the TEG containing the Benzene exits the bottom of the contactor on level control.

The rich TEG is routed to the TEG flash tank. Liquid hydrocarbons flow into a bucket and are removed manually. The TEG flows under the bucket and over a weir and exits the flash tank on level control. Any flashed gases exit the flash tank through a back pressure regulator and are sent to the flare. The rich TEG is then filtered first in the TEG sock filter to remove solids and then in the TEG carbon filter to remove trace amounts of hydrocarbons. The rich TEG is then heated to ~ 300 F in the Lean/Rich Exchanger. The flash tank level valve is located downstream of the lean/rich exchanger to prevent any vapor breakout in the filters and the exchanger. The hot, rich TEG is then routed to the TEG Still Column, which is a packed tower using random packing. The rich TEG travels down through the packing and is stripped using steam

generated in the TEG Reboiler, which heats the TEG solution to approximately 397 F. The Reboiler is direct fired using natural gas as fuel. The benzene and water vapor exits the top and is routed to the TEG Still Condenser. Most of the water vapor and some of the benzene is condensed and the mixture is routed to the benzene/water separator V-3055 which is a three-phase separator.

The water is removed from a boot on the separator by level control. Benzene and other hydrocarbons flow over a weir and are removed on level control also. Any vapors are removed and flow out the top of the vessel on back pressure control. The operating pressure of the three phase separator is 3 psig. The water is pumped back to the top with the still Reflux pumps as reflux. The TEG and water fall into the TEG Reboiler where steam is generated and sent up the TEG still. The regenerated TEG flows over a weir in the Reboiler into an integral surge tank. The TEG flows out of the surge tank to the lean/Rich exchanger where the lean TEG solution to cooler to 202 F. The lean TEG is pumped up to contactor pressure in the lean TEG pumps and is routed to the lean TEG cooler. The lean TEG is cooled with cooling water to approximately 88 F. The lean TEG is then routed back to the contactor. The treated syngas is then routed to the TEG Guard Bed to clean any residual TEG from the Syngas stream.

In order to measure benzene removal efficiency, its concentration was determined by GC with FID (Flame Ionization Detection). Results are given in Table 6-16. The TEG unit was found to reduce the benzene concentration of the syngas by ~98% as shown below. In the syngas to FT at AE-3420, with recycle, benzene was found to be present at less than 50 ppm. This low level should have no impact on FT operation.

Table 6-16: Concentration of Benzene Before and After TEG Unit

	AE-3076 Syngas at Booster Compressor	AO-3400 TEG Outlet
Benzene Conc. (ppmv)	5400	105

F.4 Amine Unit

The sour syngas enters the absorber at the bottom and rises through the column, interacting with the amine solution on the trays. The H_2S and CO_2 and small amounts of hydrocarbon are absorbed into the amine. The solution is then flashed to a lower pressure to evolve the absorbed hydrocarbon. The rich amine solution is heated and filtered before being fed to the stripping column. At higher temperatures, the reactions holding the acid gases in solution are shifted to release the gases which exit the top of the stripper to the atmosphere or an additional treatment plant. The hot amine solution is collected in the surge drum. The amine solution is then pumped up to the absorber pressure and cooled before returning to the absorber.

Over the period of DOE performance run operation, Amine unit ran stably. Product gas flow from Amine unit was stable ~ 250 lbs/hr average.

As shown in Figure 6-95, there was no CO_2 slip detected for product gas after Amine unit. This indicates that CO_2 recovery is almost 100%. During the operation period, DGA content was closely monitored by the operations team. Amine samples at various locations were taken and analyzed by Analytical Service team for color, foaming tendency, DGA wt% and iron content etc. For the duration of the run, amine

concentration was the most critical parameter to monitor for operational control and was targeted at about 40-50%.

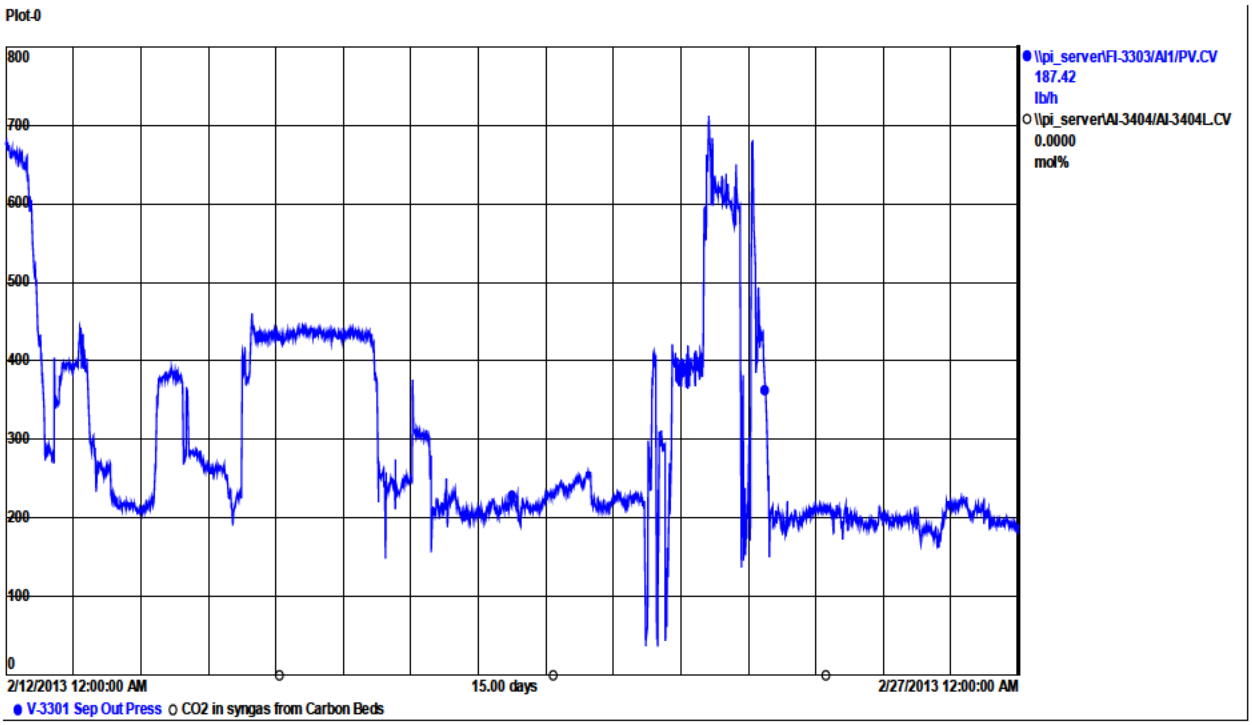


Figure 6-95: CO_2 Content & product gas flow from Amine unit

Color, foaming tendency, and iron content are analyzed during shut-downs or operational upsets and were not needed during this run. Relevant measurement of amine concentration, acid gas loading and heat stable salts for the rich and lean amine streams are given in Table 6-17

Table 6-17: Rich and Lean Amine Analysis during DOE IE Run

Date	Rich Amine concentration (mass %)	Acid Gas Loading (%)	Heat Stable Salts (%)
2/12/2013	42.45	0.09	0.05
2/19/2013	42.5	0.14	0.05
2/22/2013	41.72	0.12	0.05
2/26/2013	42.6	0.11	0.05
2/26/2013	42.6	0.11	0.05
Date	Lean Amine Concentration (mass %)	Acid Gas Loading (%)	Heat Stable Salts (%)
16-Jan	45.35	0.05	0.05
19-Feb	41.87	0.04	0.05
22-Feb	42.22	0.12	0.05
26-Feb	42.41	0.07	0.05

F.5 Carbon Guard Beds

Syngas leaving the Amine knockout enters the top of carbon guard bed and exits the bottom; the beds are set up in a lead lag configuration. There is an analyzer on the outflow of each vessel. Once breakthrough is detected on the first vessel, the second is placed in the primary service. The carbon is replaced on the depleted vessel and it is put back in service in the number two position. The skid is valved so either vessel can operate in the lead position.

In the carbon guard beds, SULFUSORB is used. SULFUSORB® 12 is a copper oxide (CuO) impregnated product specifically designed to remove hydrogen sulfide and low molecular weight organic sulfur compounds from gas streams. Hydrogen sulfide is physically adsorbed into the pores of the activated carbon. It then comes in contact with the CuO, resulting in a chemical reaction which increases the adsorption capacity over non-impregnated activated carbons.

The current design objective of Carbon bed system (two towers in series) is to remove trace DGA in the vapor phase from Amine unit and function as a guard bed during the event of Amine system upset (i.e. liquid carryover) for downstream membrane unit protection.

As shown in Table 6-18, the carbon beds were very effective in removing trace DGA in the vapor gas stream. Less than 1 PPM level DGA content was within equipment tolerance of downstream membrane unit.

Table 6-18: DGA and Water Content

	Inter-bed Concentration	After C Bed
DGA Content using Gastec stain tubes	0.3 ppmv 2/12/2013	ND. <0.1 PPM 2/12/13; ND. <0.1 PPM 2/26/2013
Water mol%	Saturated at 130 F	0.13%

F.6 Membrane Performance

The H_2 Membrane System has been designed to adjust the H_2/CO ratio of a syngas feed to a range of 0.77 to 3 H_2/CO, and produces H_2 as a permeate at high purity levels. The Membrane System consists of two different membrane vessels (large and small) that operate in parallel with one another.

The syngas feed to the H_2 Membrane System initially passes through a gas/liquid separator and is then heated to approximately 120°F in an electric heater. After being heated the syngas feed passes through a particulate filter, at which point it is ready to enter the membrane vessels at inlet conditions of 474 psig and 120°F.

The larger membrane vessel is responsible for producing the adjusted H_2/CO ratio that feeds a series of heaters and is then used in conjunction with a catalyst inside the FT reactor in order to produce long chain hydrocarbons. The larger membrane vessel also produces a waste H_2 stream at a purity level greater than 90% by volume. The waste H_2 stream is used as a fuel feed to the SMR burner unit.

The smaller membrane vessel is responsible for producing a H_2 stream at a purity level of approximately 80% by volume. The H_2 from the membrane feeds a H_2 PSA system in order to further purify the H_2 and is then used as a feed to various vessels on the upgrade system. The smaller membrane vessel also produces a waste syngas stream that relieves to the TOU system.

During the DOE performance run, since there was sufficient syngas permeated from larger membrane vessel, which met the downstream PSA feed requirement, the smaller membrane vessel was effectively bypassed. Figure 6-96 below shows the general trends of feedrate, feed temperature and H_2/CO ratio from residue side of the membrane unit.

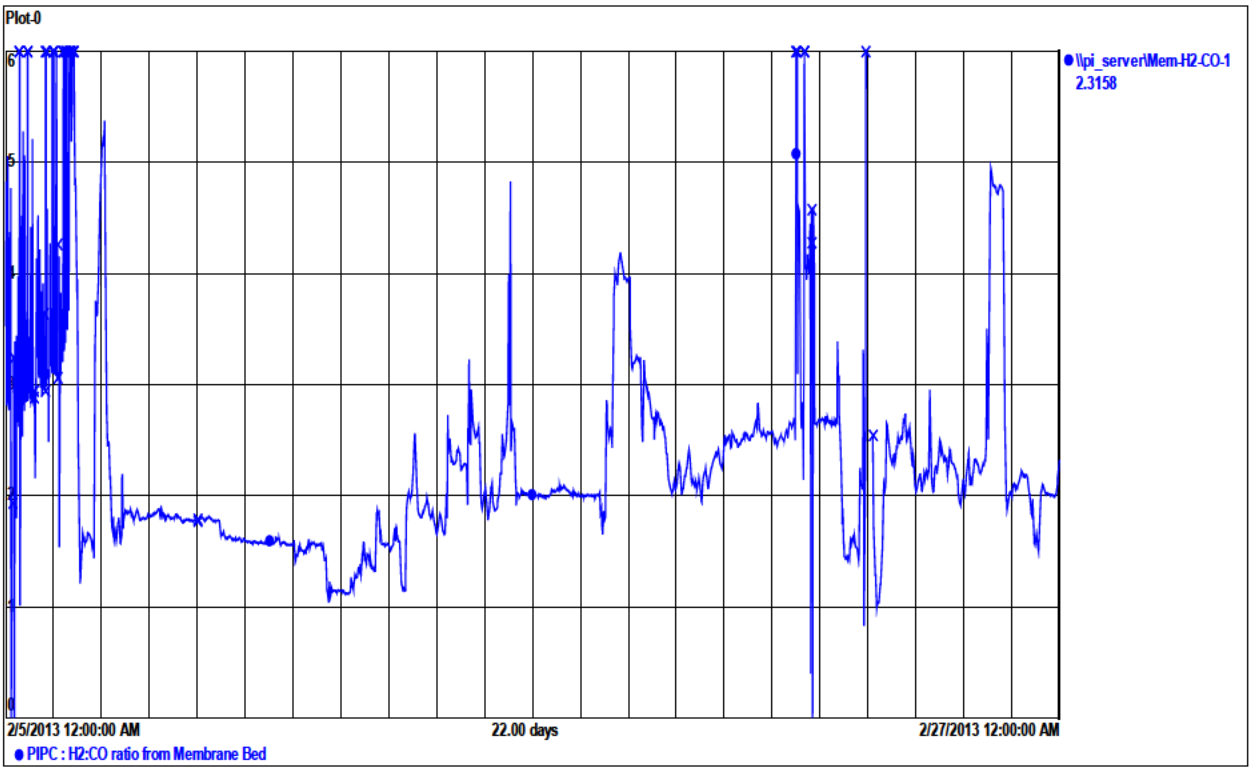


Figure 6-96: H_2/CO ratio during DOE IE Run operation.

F.7 H_2 PSA Performance

The PSA gas separation system is designed to separate gas mixtures by means of the Pressure Swing Adsorption (PSA) process. This process takes advantage of the selective adsorption characteristics of different gases by zeolite adsorbents when subjected to varying pressures. The gas mixture (Feed Gas) is made to flow vertically upwards through a tall column of adsorbent material at high pressure. The easily adsorbed components of the mixture ('heavy' components) are retained by the adsorbent while the less easily adsorbed gases ('light' components) are released from the top of the column as purified (product) gas. Before the adsorbent material becomes saturated in the 'heavy' gas components, product delivery is halted and the pressure is released from the bottom of the adsorbent column ('bed'). The lower

pressure releases the heavy gases from the zeolite and they are made to flow out from the system as waste (exhaust) gases. The adsorbent bed is then re-pressurized and is ready to repeat the cycle.

The product, feed, and exhaust lines transport gas through the required valves and control equipment to the rotary valves. The PSA equipment comes with instrumentation for process management as well as for shut-down and start-up duties. These devices are easily connected to a supervisory and control PLC. A product receiver tank is used to aid separation performance and to minimize flow and pressure surges.

Due to the lack of reliable flow meter upstream and downstream of H_2 PSA system, we were unable to predict the H_2 recovery percentage of PSA. However, the product purity (99+% H_2, <100 PPM CO) and flowrate (~8 lbs/hr pure H_2) met the requirement of product upgrading unit. The feed pressure to PSA was ~ 140 psig. Figure 6-97 shows the general trend of H_2 purity on spec over DOE IBR performance period.

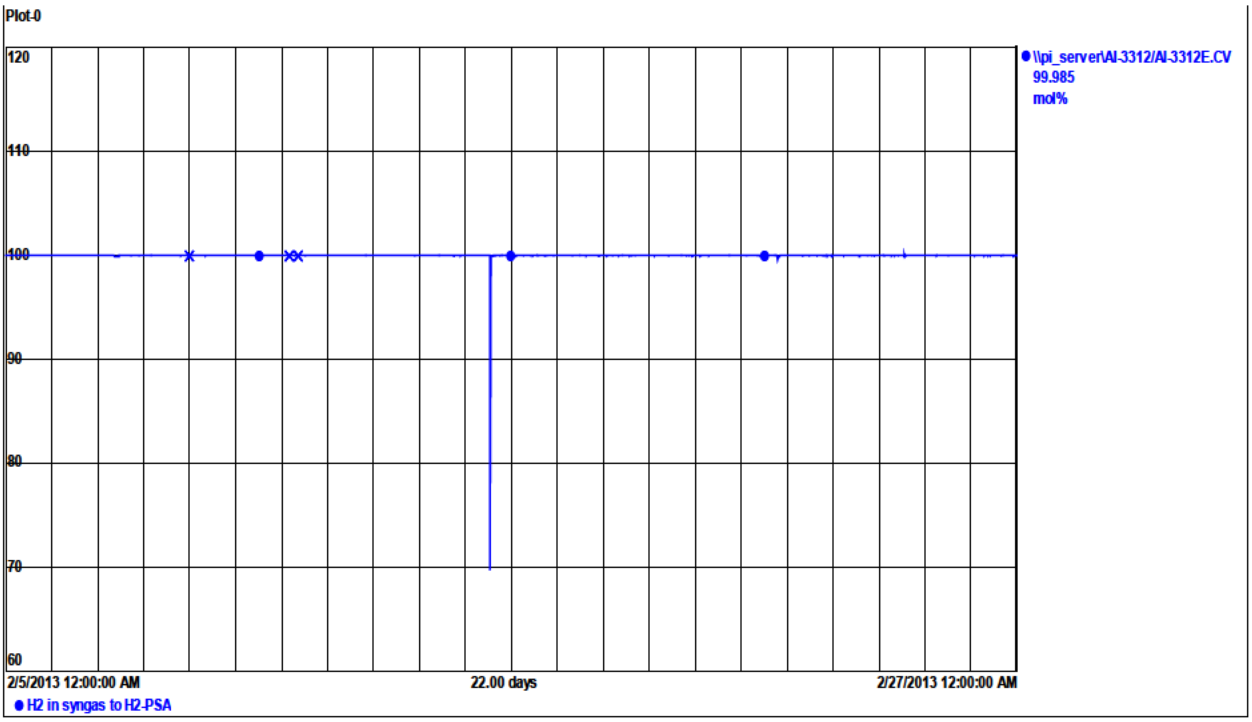


Figure 6-97: H_2 Purity out of PSA

F.8 ZnO Bed

The preheat and Sulfur guard systems (ZnO Bed) receive syngas from the hydrogen membranes. The syngas flows through a 5 stage electric syngas heater and then through the sulfur guard bed. The sulfur guard bed removes the remaining trace amounts of sulfur.

According to the analytical report, sulfur in the syngas was not a problem during the DOE Run. The operating temperature of ZnO bed was ~ 400°F with pressure ~ 450 psig. As shown in Figure 6-98, S content is less than 50 ppb.

Sulfur compounds in general and carbonyl sulfide in particular are representative surrogates for removal of other trace contaminants of concern. Some sulfur is present in biomass feeds and at least a portion will be converted to gas phase species. Removal of these species is based on volatility, reactivity, polarity or solubility, etc. Carbonyl sulfide is a good surrogate to monitor because it is difficult to remove, owing to its high volatility, low reactivity and polarity.

Although its boiling point is only slightly higher than that of hydrogen sulfide (-50°C for COS vs -60°C for H_2S), it is much less reactive than hydrogen sulfide. That is why a COS hydrolysis unit is used to convert carbonyl sulfide to hydrogen sulfide to aid its downstream removal, e.g., in an amine scrubber (and carbon beds and ZnO bed for any amount that breaks through).

Total sulfur was monitored by an online Thermo Solar analyzer that is based on combustion of sulfur compounds to sulfur dioxide, SO_2, followed by pulsed UV fluorescence. This method is cable of detecting total sulfur at low levels with a detection limit of approximately 25 ppbv (parts per billion by volume). However, unfortunately at this low level of analysis, normal process instabilities will be observed as noise and drift in the baseline of the analyzer output. For instance, ambient plant temperature swings will result in some condensation of water and sulfur species, and nitrogen is a known interference in the analyzer. During the normal operation of the gasifier and addition of nitrogen to maintain fluid velocities, some variability is expected and is normal. The output of the analyzer as shown in Figure 6-98, obtained over the course of the run, shows that for practical purposes that sulfur content was very low, less than 25-50 ppb for the great majority of time.

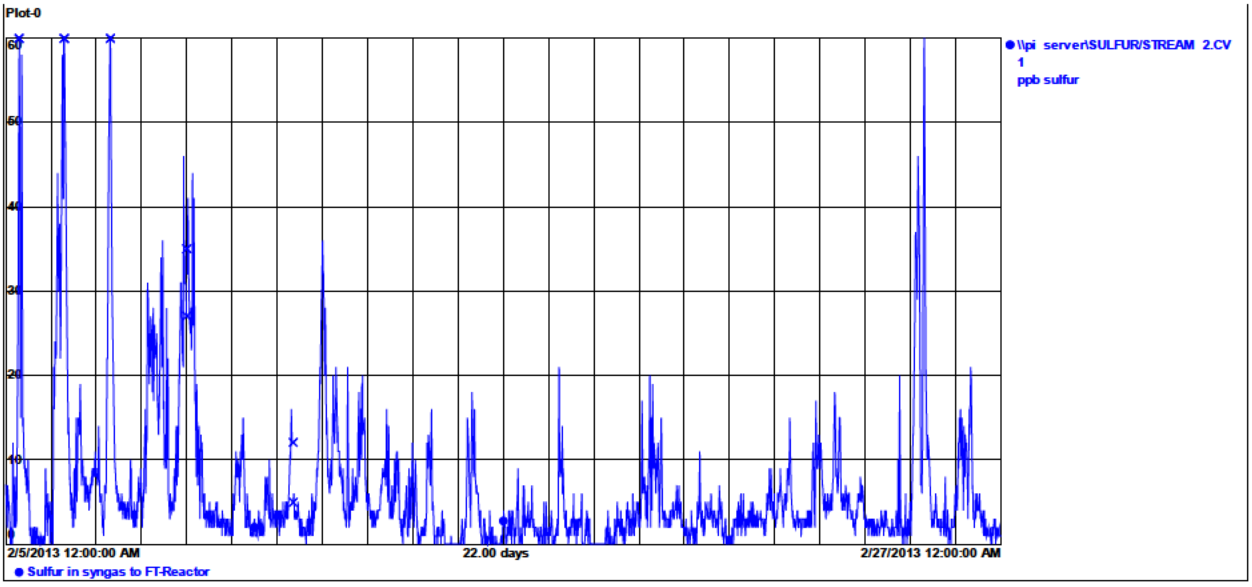


Figure 6-98: S from ZnO Bed during DOE Run by Combustion UV Fluorescence

In order to more accurately monitor sulfur at sample point AE-3420, which is point of most critical importance, gas chromatography (GC) with Sulfur Chemiluminescence Detection (SCD) was used for the analysis per ASTM D-5504 (Annual Book of Standards, Volume 05.06, ASTM International, West Conshocken, PA, USA.) This method is capable of detecting individual volatile sulfur compounds, such as COS, down to single digit ppbv levels. A relatively large volume injection, 2 CC and low split ratio are

used for the analysis, and the Agilent FID adapter was used for allowing simultaneous FID detection. Figure 6-99 illustrates overlaid representative chromatograms for a calibration mixture of 455 ppbv COS in nitrogen (Matheson) and a sample taken from AE-3420. A pressure pulse is observed at the beginning of the run and baseline returns to normal prior to elution of the earliest sulfur components, H_2S, COS. It is not possible to baseline resolve H_2S and COS without the use of cryogenics. For the purpose of monitoring COS, it was not necessary to do this. The carbon disulfide present occurred as a contaminant in the standard at ~ 9 ppbv.

A refinery gas analyzer (RGA) based on an Agilent 7890 GC and configured by ECE Wasson was used to measure bulk syngas concentrations automatically and semi-continuously, roughly every 20-25 minutes depending on which other streams were being analyzed. The analyzer uses multiple columns and for determination of fixed gases with Thermo Conductivity Detection (TCD) and FID detection for hydrocarbons. Nitrogen and hydrogen are used for carrier gases (nitrogen for the hydrogen determination). This analyzer outputted results to our PI data historian *via* our DCS. For illustrative analysis an example analysis is shown in Table 6-20.

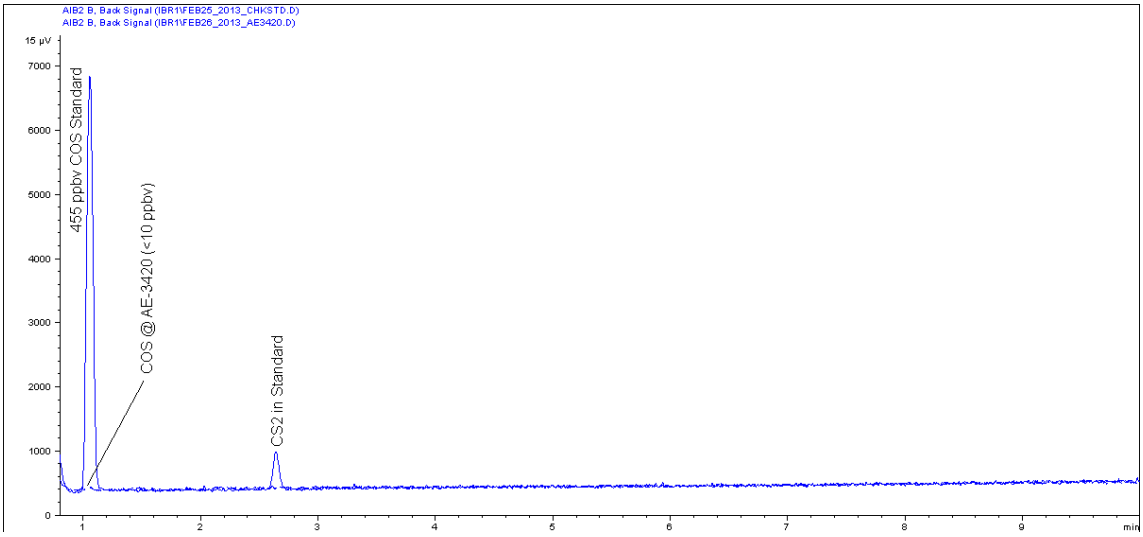


Figure 6-99: Representative Chromatogram of COS Standard and FT Syngas Feed by ASTM FD-5504.

Table 6-19: COS Content @ AE-3420 – Syngas to FT During Run

Date	10-Feb-13	11-Feb-13	12-Feb-13	17-Feb-13	23-Feb-13	24-Feb-13	25-Feb-13	26-Feb-13
COS @ AE-3420 (ppbv)	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10

Table 6-20: Illustrative Analysis of Bulk Syngas Composition @ AE-3076 Booster Compressor

Component	**Retention Time (min)**	**Concentration (mol %)**
Hydrogen	1.59	52.07

Carbon dioxide	3.46	22.46
Argon/Oxygen	4.89	0.08
Nitrogen	5.58	6.31
Methane	7.10	4.25
Carbon monoxide	8.19	14.44
Ethane	2.64	0.001
Ethylene	2.84	0.016

6.G Fischer-Tropsch / Syngas Conversion

G.1 Catalyst Preparation

[redacted]

G.2 Catalyst Physical and Chemical Properties

[redacted]

[redacted]

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G.3 Fischer-Tropsch (FT)

The FT reactor was transitioned to biomass syngas on February 10th. The initial intent of the run was to feed 100% biomass-derived syngas to the FT reactor, but a small amount of SMR syngas was left in the FT feed because of insufficient suction pressure on the syngas compressor. The ClearFuels/SMR blended syngas feed had a high H_2/CO ratio and a compromise between fresh feed flowrate, recycle rate, and H_2/CO ratio had to be made. Because of the high H_2/CO ratio of the fresh feed and the need to

maintain high recycle ratios in order to maintain sufficient gas flow to the FT reactor, the H_2/CO ratio of the combined FT feed was higher than desired (2.5 - 4 instead of 1.5 – 2).

Around 200 hours of integrated ClearFuels/FT run time were achieved from February 12th to 26th with only a small amount of SMR syngas being added. Several gasifier-related upsets occurred during the course of the DOE Run, plugging in the feed system and gasifier entry piping, but all of the disruptions were overcome in a timely manner. The FT section was able to handle the upsets and maintain operation for the entire period. The tailgas recycle compressor operated smoothly for the entire duration of the test and also made feed gas disruptions easier to handle.

G.4 Tailgas Recycle

A process flow diagram for the syngas in the FT section including the tailgas recycle loop is shown in the following figure. The recycle loop used during the DOE Run involved taking syngas from upstream of the FT reactor pressure control valve (PIC-4405) through the recycle suction compressor control valve (PIC-4450). Pressure in the loop was controlled with a pressure control valve (PIC-4453) on the spillback and the vent (PIC-4455). A valve on the discharge flow to the FT feed (FIC-4454) was used to control the recycle flow rate. The recycled tailgas mixed with the FT feed at a point between the first two syngas heaters. With this configuration, CO_2 was not removed from the recycled gas.

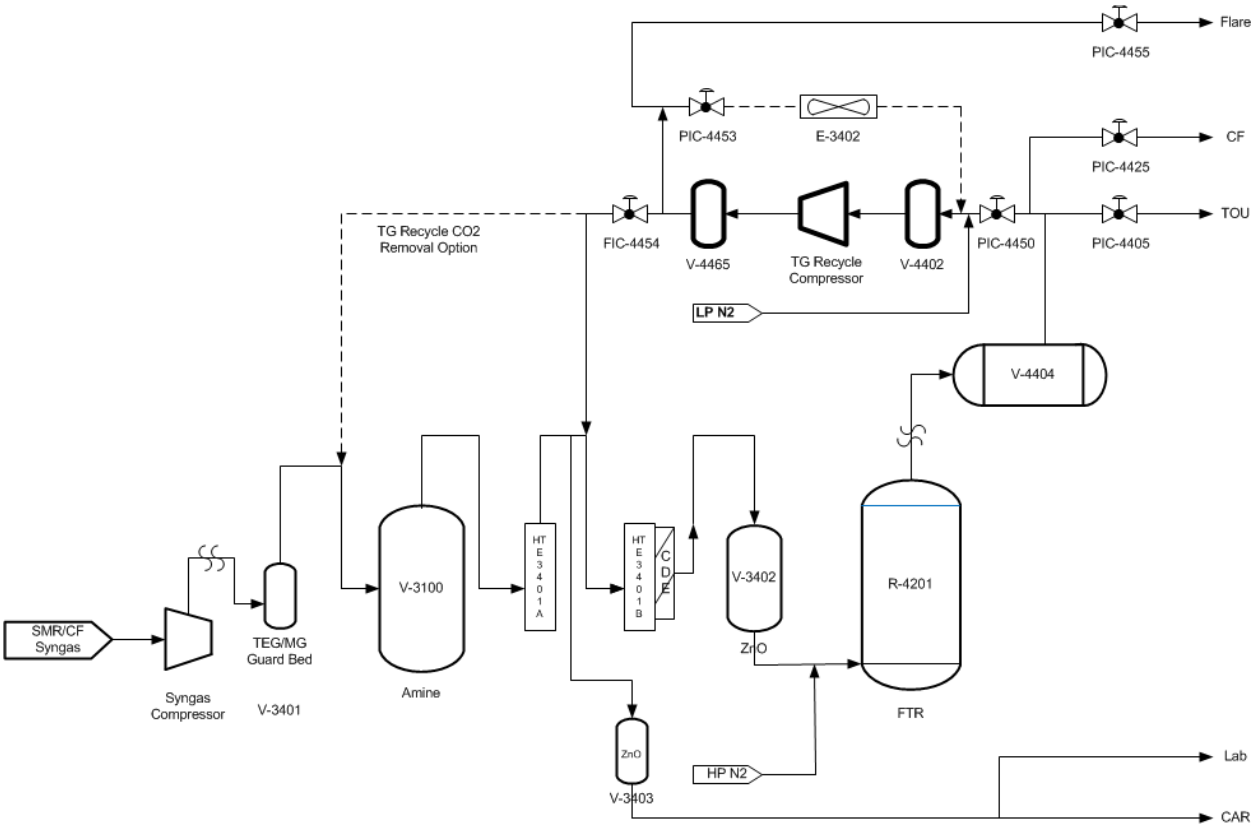


Figure 6-103: Process Flow Diagram of FT Syngas Including Tailgas Recycle Loop

The pressure in the tailgas recycle loop was operated 25 to 50 psi above the pressure at which it mixed with the fresh feed. The recycle flow was controlled by manually setting the valve opening of FIC-4454. The fresh feed flow rate was controlled by adjusting pressures downstream of a hydrogen separation membrane between the amine system and syngas heaters. For the DOE Run, efforts were made to try and maximize the fresh syngas flow and avoid venting syngas from the FT feed. The recycle ratio was also reduced when sufficient fresh feed flow was available. The following figure shows the fresh feed and recycle flow rate as well as the recycle ratio during the DOE Run. The fresh syngas feed to the FT reactor was between 50 and 100 scfm for the majority of the run. Recycle ratios between 1 and 2.5 were used during the run.

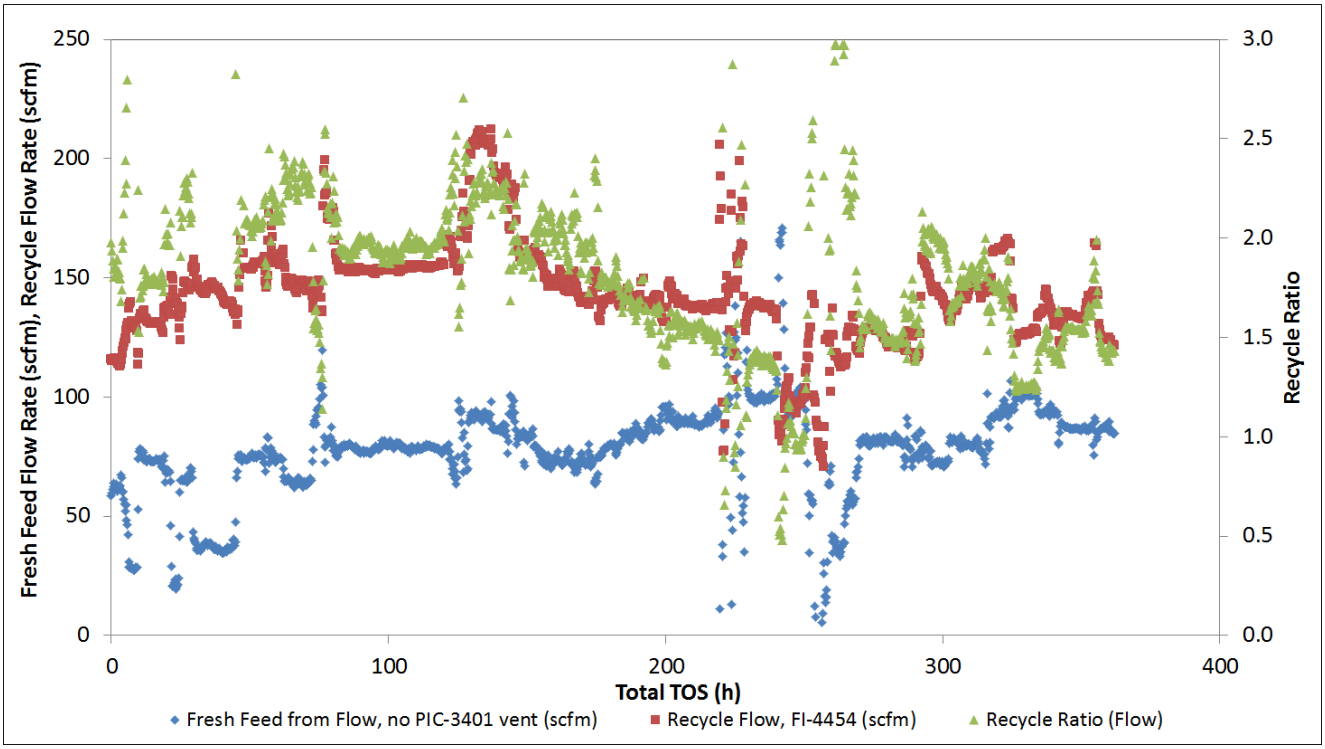


Figure 6-104: Fresh Syngas Feed, Recycle Flow Rate, and Recycle Ratio during the DOE IBR Run

The following figure shows the fresh feed to FT and the blended feed (recycle and fresh feed) to FT over the course of the DOE IBR Run. The H_2/CO ratio of syngas utilized in the synthesis was consistently lower than the H_2/CO ratio of the fresh feed so recycling the tailgas led to an increase of the H_2/CO ratio of the FT feed during the run. The H_2/CO ratio of the fresh syngas was between 1.5 and 2.5 for the majority of the run while the blended syngas ranged from 2 to 3.5. There were two short periods around 140 h and 320 h where pure SMR syngas was fed without membrane adjustment and the H_2/CO ratio of the fresh feed was as high as 5 leading to a blended H_2/CO ratio as high as 7.5.

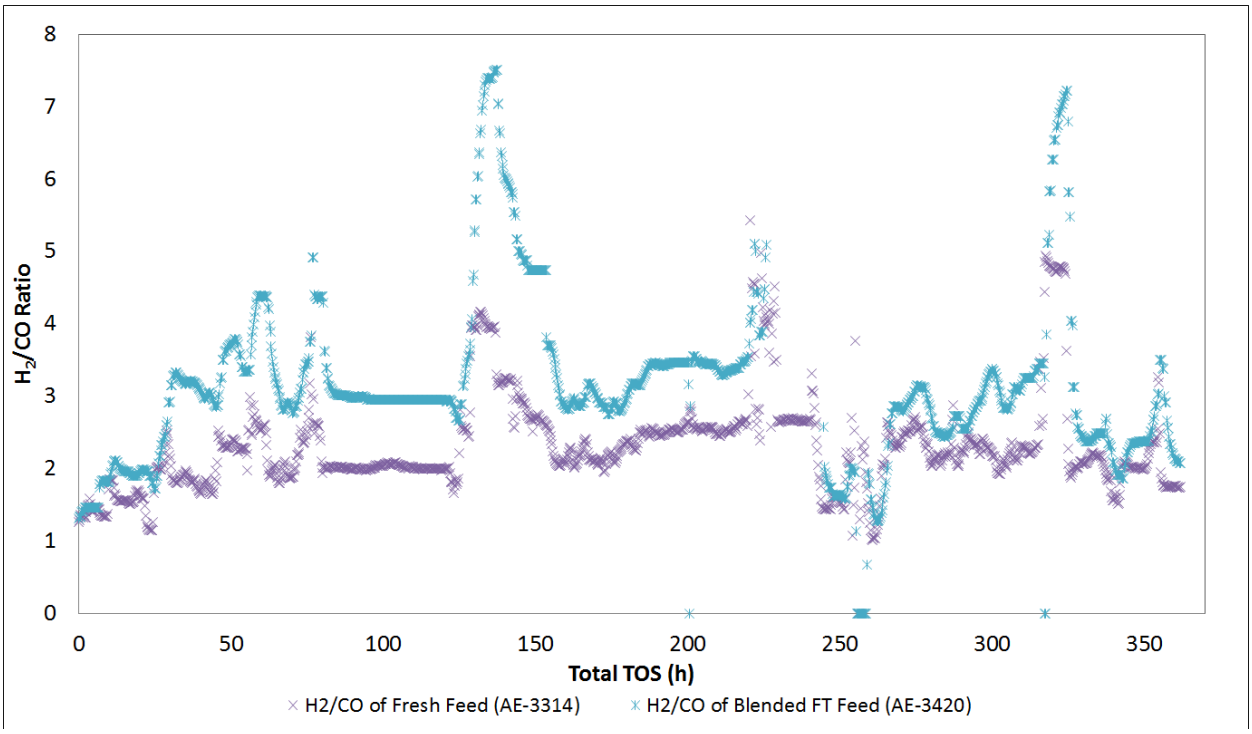


Figure 6-105: H_2/CO Ratio in Fresh and Blended FT Feed

G.5 General Performance Highlights

There were several variations in the process that were present during the DOE Run that made the system more dynamic and made it more difficult to collect representative performance data in short time periods. One of the variations was the fresh feed composition. The fresh feed composition was dependent on the composition of the syngas from the gasifier, the membrane pressures, and the amount of SMR gas being blended into the feed. Another source of variation was the recycle. Any change to the recycle flow caused compositional changes in the blended FT feed that took several hours to stabilize. A third source of variation in the FT reactor was the temperature control. It proved difficult at times to maintain temperatures in the reactor. The most likely reason for the problem was the relatively low syngas feedrates and low CO content in the feed to the reactor. This combination produced insufficient reaction heat to maintain the desired temperature of 460°F. The following figure shows the FT performance during a relatively stable period during the DOE Run including the reactor temperature, single pass CO conversion, and single pass CO_2 and hydrocarbon selectivity. The temperature variation during this period was as much as 10°F. The single pass CO conversion ranged from 45 to 55 mol%, the CO_2 selectivity was 20 to 30 mol%, and the C_{5+} selectivity based on online gas analysis and flow meters was 50 to 70 mol% of the converted carbon.

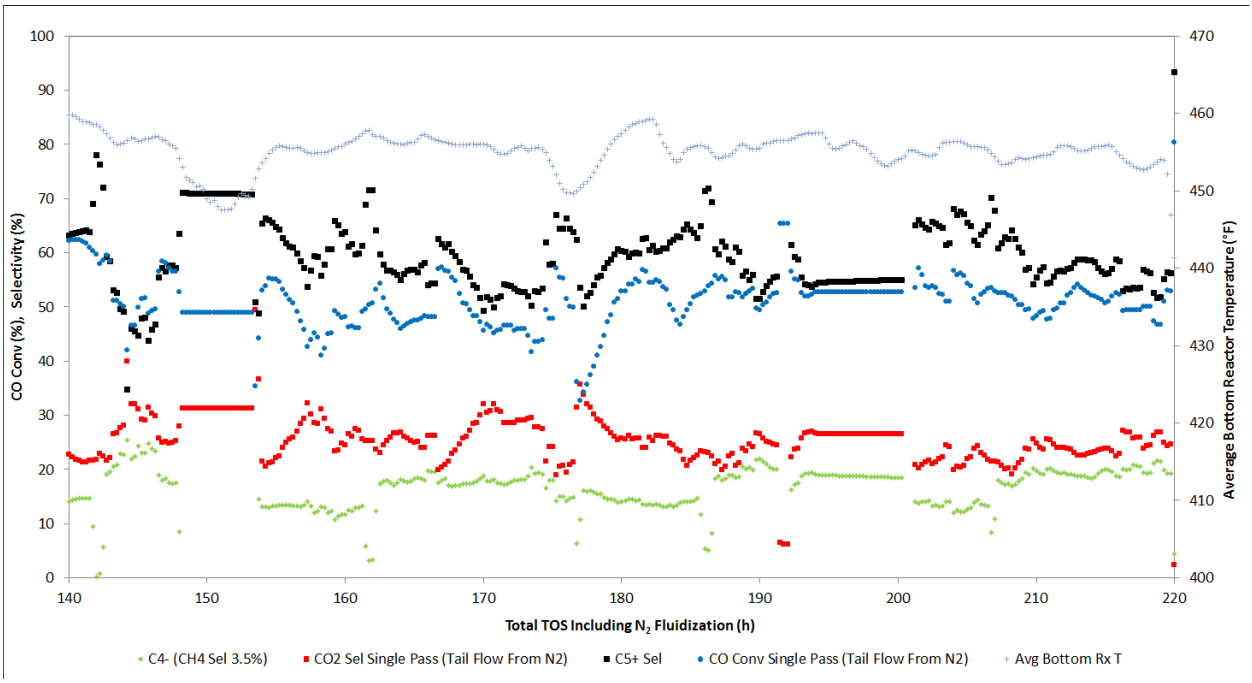


Figure 6-106: FT Performance during DOE Run Including Reactor Temperature, Single Pass CO Conversion, and Selectivities (RGA and Flow meters)

The following figure shows the reactor temperature, overall CO conversion, and overall CO_2 selectivity for the entire DOE Run period. Considerable variations can be noted in all three values. The overall CO conversion ranged from 60 to 85 mol% over the run. The overall CO_2 selectivity varied from 40 to 20 mol%.

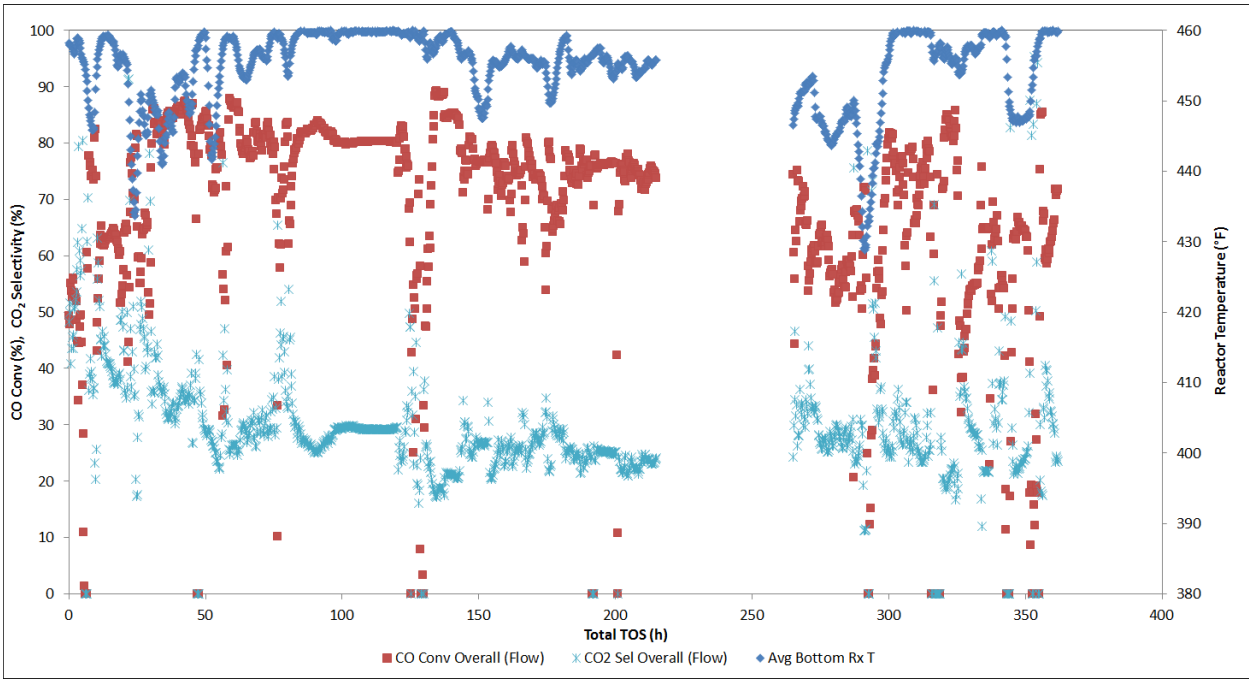


Figure 6-107: Average FT Reactor Temperature and Overall CO Conversion and CO_2 Selectivity during DOE IBR Run

G.6 Performance and Product Distribution

The following table gives a summary of the stable periods during the DOE IBR Run. Given the dynamic nature of the process as described in the previous section, the upsets experienced on the gasifier, and the relatively low production rates, it was a challenge to obtain representative data in the given time periods. The wax production rates shown in the table are an average of the entire run period. An average value was used because the combination of low wax production and a large reactor volume made accurate determination of wax production challenging for short time intervals. The single pass CO conversion of the stable conditions ranged from 38 to 59 mol% while the overall CO conversions were 52 to 85 mol%. In comparing the single pass and overall CO conversions of the stable conditions during the DOE IBR Run, it can be seen that the relative increase in CO conversion from recycle was 31 to 52%. One thing to note in the table is the high content of inert, 30 to 56 mol%, present in the blended FT feed. Inert contents this high reduce the syngas partial pressure substantially negatively affecting the FT performance. Much of the inert during the DOE Run was nitrogen which was added for fluidization stability and reduced over the course of the run as the dynamic operation of the system became more clearly understood. The CO yield (gallons of liquid products per pound mole of CO) ranged from 0.6 to 1.09 during the run. The catalyst productivities shown in the table are low ranging from 0.06 to 0.09 pounds of wax and FT liquids per pound of catalyst per hour. This is not unexpected considering the relatively low feedrates (200 to 245 scfm) and low CO concentration (10 to 21 mol%) fed to the reactor.

Table 6-24: Performance Summary for Stable Biomass Derived Syngas Periods during DOE IBR Run

TOS	h	20	45	73	194	216	291	317	352
T	°F	459	455	457	458	457	452	460	455
P	psig	303	304	304	309	311	312	299	310
Fresh Feed	scfm	72	39	70	77	90	81	80	89
H_2 in Fresh Feed	mol %	56	57	64	63	66	64	63	59
CO in Fresh Feed	mol %	35	32	29	28	26	28	28	31
Total Feed	lb/h	760	615	614	598	568	658	539	538
	scfm	245	197	240	237	245	242	231	226
MW Feed		19.6	19.7	16.2	16.0	14.7	17.2	14.8	15.0
H_2 in Feed	mol %	31	30	45	44	49	39	49	46
CO in Feed	mol %	16	10	13	14	14	14	16	21
Feed H_2/CO		1.95	3.08	3.43	3.06	3.42	2.73	3.13	2.20
N2,CH4,CO2 in Feed	mol %	50	56	39	39	34	44	33	30
Catalyst Concentration	wt %	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
SV	nlph/g-cat	3.6	2.9	3.5	3.5	3.6	3.6	3.4	3.3
Single Pass CO Conv	%	41	59	58	49	52	41	55	38
Single Pass CO_2 Sel	%	41	34	26	26	23	25	26	28
Recycle Ratio		1.8	3.9	2.2	1.9	1.4	1.5	1.8	1.5
Overall CO Conv	%	61	85	77	74	74	59	73	52
Overall CO2 Sel	%	41	34	29	26	23	28	28	28
C_{5+} Sel (Tail C_{4-} and CO2)	%	45	51	59	60	62	59	60	61
Overall C_{5+} Sel (Tail C_{4-} and CO2)	%	45	52	53	59	61	60	59	61
Wax (4601 Level)	lb/h	6	6	6	6	6	6	6	6
Mid Distillate	lb/h	5	5	6	6	6	5	6	7
Naphtha	lb/h	5	3	6	6	7	4	7	6
Liquid Production Volume	gal/h	2	2	3	3	3	2	3	3
Water	lb/h	21	15	28	27	29	21	30	29
Wax %	wt %	36	42	42	31	30	38	30	31
Mid Distillate %	wt %	35	35	29	35	34	37	34	36
Naphtha %	wt %	29	23	29	33	36	25	36	33
Relative CO Conv Increase from Recycle	%	51	45	34	50	43	43	32	37
CO Conv*C_{5+} Sel		0.18	0.30	0.34	0.29	0.32	0.24	0.32	0.31
Syngas Yield	g C_{5+}/m^3 H2+CO fed	66.4	99.8	80.5	83.0	80.2	66.4	81.8	67.3
CO Yield	g Wax+LFTL/g CO	0.137	0.254	0.211	0.181	0.213	0.155	0.199	0.150
	gal/lbmol CO	0.61	1.09	0.87	0.80	0.81	0.65	0.85	0.66
Cat Productivity	lb Wax+LFTL/lb cat/h	0.066	0.058	0.089	0.073	0.079	0.062	0.079	0.076
Start	2/12/13 8:00	2/12/13 20:50	2/13/13 19:00	2/14/13 12:15	2/18/13 19:00	2/20/13 17:00	2/23/13 17:45	2/24/13 22:50	2/26/13 10:05
End		2/13/13 4:10	2/14/13 5:00	2/15/13 9:00	2/20/13 10:00	2/21/13 8:00	2/24/13 10:40	2/25/13 12:42	2/26/13 23:40

The following table shows a breakdown of the hydrocarbon product selectivities for the stable operating period starting on February 18th and ending on the 20th. The light hydrocarbon selectivity (C_{4-}) is 21% meaning that 21% of the converted carbon went to products containing four or fewer carbon atoms. This value is relatively high but understandable given the high H_2/CO ratio of the FT feed. The C_{4-} selectivity at similar conditions during IBR Run 1, other than H_2/CO ratio, was 14 to 17%.

The C_{5+} selectivity obtained by adding up the product groupings from the table is 49%. The C_{5+} selectivity from for this time period is 59%. The value in the table was obtained by subtracting the CO_2 selectivity and C_{4-} selectivity as determined using GC tailgas analysis from 100%. If the C_{4-} in the naphtha, water, and GC-MS analysis is taken into account, the C_{5+} by difference becomes 55%. It should also be noted that the high temp GC method used for wax analysis does not detect hydrocarbons heavier than about C_{85}. This may explain the remaining 6% gap in C_{5+} selectivity as determined by difference and by summing the products.

Table 6-25: Hydrocarbon Product Selectivities from Feb. 18th – 20th (DOE IBR Run)

Selectivity	C mol%
C_{4-}	21
C_{5-11}	18
C_{12-18}	10
C_{18-23}	5
C_{23+}	16

An Anderson-Schulz-Flory (ASF) polymerization model is often used to describe the product distribution from Fischer-Tropsch synthesis. The ASF product distribution is described by

$$m_n = (1 - \alpha)\alpha^{n-1}$$

where α is the chain growth probability factor and m_n is the mole fraction of hydrocarbon with chain length n. The model is not representative of the entire FT product slate as deviations from the model are known to occur in the lighter hydrocarbons. The ASF equation can be rearranged to linear form giving

$$log(m_n) = n\, log\, \alpha + \log\left(\frac{1-\alpha}{\alpha}\right)$$

A plot of the log of the mole fraction of each carbon number versus carbon number should produce a straight line whose slope is log α. The following figure shows a plot of mole fraction versus carbon number for the stable period from February 18th to 20th during the DOE IBR Run. A chain growth probability (α) was obtained for the linear portion of the plot ranging from C_{15} to C_{85}. The alpha value was 0.928.

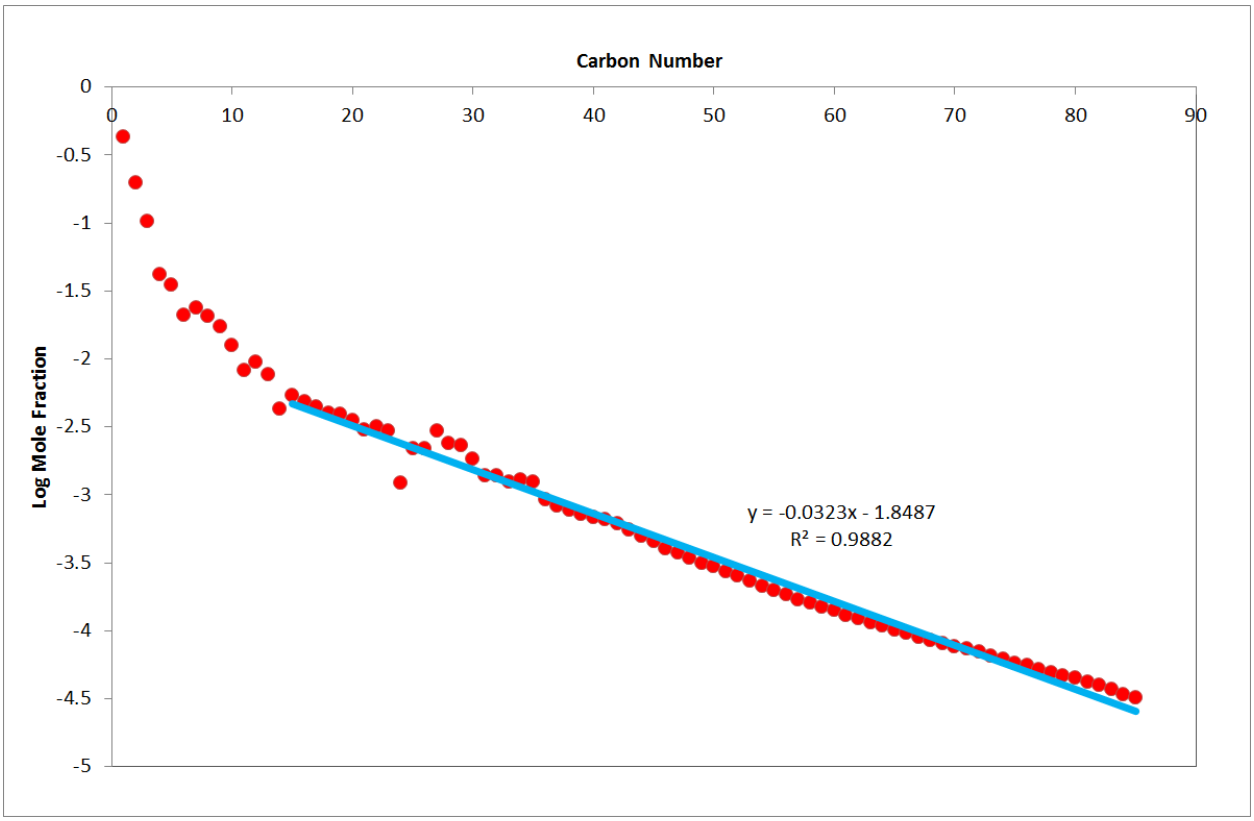


Figure 6-108: Anderson-Schulz-Flory Plot for Stable Operating Period during DOE IBR Run

G.7 CAR Reactor Activation Summary

The following table lists the activation conditions used for the three 25 pound catalyst additions from the Catalyst Activation Reactor prior to the DOE Run.

[redacted]

G.8 Gas Holdup in the FT Reactor

The following figure shows the gas holdup along with the temperature, pressure, and superficial gas velocity (Ug) in the FT Reactor during the DOE IBR Run. There were spikes in the bottom reactor pressure reading that are believed to be related to some kind of interference or problems with the sensor. The top reactor pressure did not display the same issues. The pressure drop on February 23rd was the result of a syngas compressor trip. The Ug is calculated based on the bottom reactor pressure reading, so it displayed the same spikes. The temperature displayed some fluctuation as discussed previously. The gas holdup was fairly noisy during the run ranging from 0.50 to 0.65.

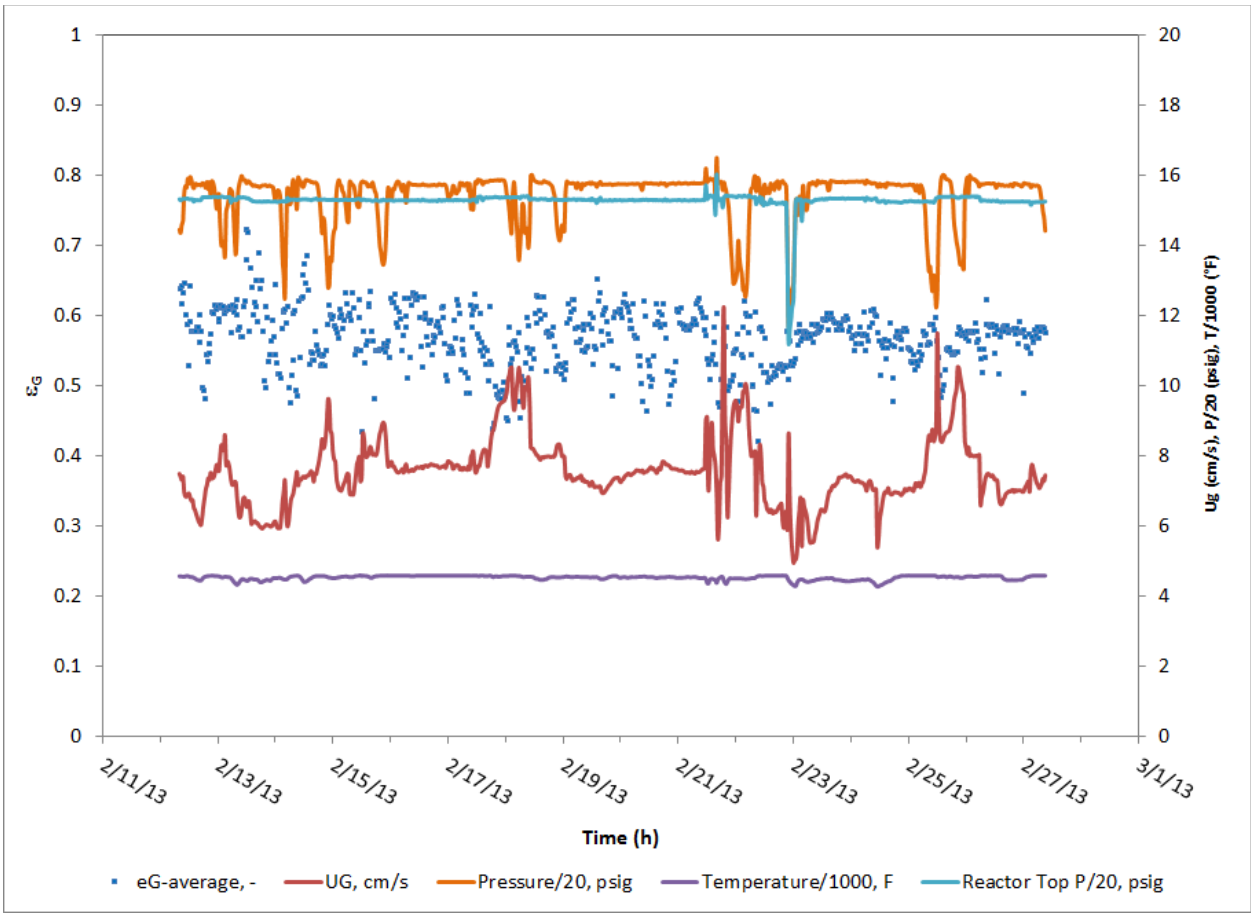


Figure 6-109: Gas Holdup, Temperature, Pressure, and Superficial Gas Velocity in the FT Reactor for the DOE IBR Run

6.H Upgrading / Refining

H.1 Feed Properties

Feed to the unit consisted of crude mid-distillate, crude naphtha and crude wax, and at times off-spec liquid.

Table 6-27 and Table 6-28 average the feed properties.

Table 6-27: Crude Mid-distillate, Naphtha, and LFTL Feed Properties

	Density @ 15˚C, g/cc	D-2887/6352 IBP, ˚C	D-2887/6352 5%, ˚C	D-2887/6352 10%, ˚C	D-2887/6352 30%, ˚C	D-2887/6352 50%, ˚C	D-2887/6352 70%, ˚C	D-2887/6352 90%, ˚C	D-2887/6352 95%, ˚C	D-2887/6352 FBP, ˚C	Bromine No., gBr/100g	Acid No., mgKOH/g	Organic Oxygen, wt%	Iron, wppm
IBR DOE Run														
Crude Mid-Distillate[1]		209	216	229	271	314	360	432	494	681	20.1	4.28	-	139
Crude Naphtha		53	66	75	99	129	170	222	245	395	74	6.7	-	151
Hydrotreater (LFTL)		66	79	98	172	244	311	399	429	498	42	6.5	-	185

Table 6-28: Hydrocracker Crude Wax Feed Properties

	Wt% Spectrasyn 4	D-6352 IBP, ˚C	D-6352 5%, ˚C	D-6352 10%, ˚C	D-6352 30%, ˚C	D-6352 50%, ˚C	D-6352 70%, ˚C	D-6352 90%, ˚C	D-6352 95%, ˚C	Iron, wppm
Crude Wax	**IBR DOE Run**									
	-	270	326	371	453	522	589	656	675	70

From

Table 6-27 for the IBR DOE Run can be observed that the bromine number from the naphtha was significantly high. That concentration which indicates the amount of olefins in the stream, triggered exothermic reactions in the hydrotreating bed of the reactor R-5202A which hindered achieving the feed ratio needed to match the FT crude liquid productions for the study of the DOE Run. The flow rate of naphtha should be decreased after seen a temperature excursion in the reactor R-5202A Top bed.

[1] MidDistillate produced from FT was heavy, so high temperature gas chromatography for simulated distillation was used, ASTM D-6352.

H.2 Operating Conditions

The tables below show the average reactor operating conditions that were maintained in both runs.

Table 6-29: Hydrotreater Reactor Average Operating Conditions

Description	Stream No.	UOM	IBR DOE Run
HT Rx Charge Rate	4	lbs/hr	30
Crude Mid-Dist Charge	1	lbs/hr	16
Crude Naphtha Charge	2	lbs/hr	12
R-5202A ABT HC-DM		°F	532
R-5202C ABT HC-T		°F	477
R-5205 ABT AS-200LT (Unisar)		°F	Offline
R-5202A LHSV HC-DM	4 ÷ Cat Volume	hr^{-1}	2
R-5202C LHSV HC-T	4 ÷ Cat Volume	hr^{-1}	2
R-5205 LHSV AS-200LT (Unisar)	4 ÷ Cat Volume	hr^{-1}	Offline
Gas to Oil Ratio @ R-5202A	5 ÷ 4	SCF/BBL	3692
Gas to Oil Ratio @ R-5202C I/L	(5 + 6) ÷ 4	SCF/BBL	3994
Gas to Oil Ratio @ R-5205 I/L	29 ÷ 4	SCF/BBL	Offline
R-5202A/B Pressure	@ Rx Inlet	psig	885
R-5202C Pressure	@ V-5211	psig	852
R-5205 Pressure	@ V-5303	psig	Offline
Recycle Gas H_2S Concentration	@ V-5211	vppm	Offline
Recycle Gas H_2S Concentration	@ V-5303[2]	vppm	400-600

After the parameters were maintained in the IBR DOE Run, the sample taken after the reactor R-5202A showed very low bromine index, indicating that most of the olefins were reacted in that reactor. Since most of the reactions were accomplished in the reactor R-5202A, there was no need to increase temperature in the reactor R-5202C to hydro-finish any remaining reactants.

[2] Recycle Gas H_2S Concentration was controlled by injecting DMDS downstream of the reactor charge pump, P-5103.

Table 6-30: Hydrocracker Reactor Average Operating Conditions

Description	Stream No.	UOM	IBR DOE Run
HC Rx Charge Rate	14	lbs/hr	56
HC Crude Wax Feedrate	13	lbs/hr	19
UCO (Unconverted Wax Recycle)	26	lbs/hr	36
UCO Bleed Rate	28	lbs/hr	0
CFR Mass basis	(13 + 26) ÷ 13	Unitless	2.9
R-5502A ABT HC-DM/HC-T		°F	546
R-5502B ABT Top Bed HC-205LT		°F	647
R-5502B ABT Bot Bed HC-205LT		°F	635
R-5502A HC-DM LHSV	14 ÷ Cat Vol	hr^{-1}	2.5
R-5502A HC-T LHSV	14 ÷ Cat Vol	hr^{-1}	1.25
R-5502B DHC-2 Top Bed LHSV	14 ÷ Cat Vol	hr^{-1}	0.45
R-5502B DHC-2 Bottom Bed LHSV	14 ÷ Cat Vol	hr^{-1}	0.45
Gas to Oil Ratio @ R-5502A I/L	16 ÷ 14	SCF/BBL	9154
Rx Pressure	@ V-5603	psig	950
Recycle Gas H2S Concentration	@ V-5603[3]	vppm	200-300

H.3 Product Properties and Production Rates

Table 6-31 shows the average diesel product properties during the runs. For both runs the product properties show outstanding cold properties. However, there still was room for improvement.

Table 6-32 shows the average stabilized naphtha product properties. The vapor pressure could not be reported because of the turnaround of the sample result, which could not be reported for the time this report was submitted.

[3] Recycle Gas H_2S Concentration was controlled by injecting DMDS downstream of the reactor charge pump, P-5108.

Table 6-33 shows the simulated distillation of the Unconverted Wax by HTGC. No bleed rate of unconverted wax was established due to the visual absence of Heavy Polynuclear Aromatics (HPNAs). No jet fuel was produced during any of the runs, which trigger the production of HPNA.

Table 6-31: Diesel and Jet Product Properties (Stream 22) AO-P5711

Main Product	Production Rate BBL/Day	Density @ 15˚C, g/cc	D-2887 IBP, ˚C	D-2887 5%, ˚C	D-2887 10%, ˚C	D-2887 30%, ˚C	D-2887 50%, ˚C	D-2887 70%, ˚C	D-2887 90%, ˚C	D-2887 95%, ˚C	D-2887 FBP, ˚C	Aromatics, wt%	Cloud Point °C	Flash Point, °C	KVisc @ 40°C, mm2/s	Sulfur, wppm
Target per: ASTM 975-06b, for No. 2D S15 Diesel	**Min**	**0.76**							**300**					**52**	**1.9**	
	Max	**0.80**							**356**			**5**	**<0**		**4.1**	**15**
IBR DOE Run	3.28	0.77	130	152	159	218	264	309	351	361	375	-	-8.1	69	2.05	NA

Table 6-32: Average Stabilized Naphtha Properties (Stream 11) AO-LV5808

Main Product	Production Rate, BBL/Day	Density @ 15˚C, g/cc	D-2887 IBP, ˚C	D-2887 5%, ˚C	D-2887 10%, ˚C	D-2887 30%, ˚C	D-2887 50%, ˚C	D-2887 70%, ˚C	D-2887 90%, ˚C	D-2887 95%, ˚C	D-2887 FBP, ˚C	Vapor Pressure D-5191, psi@100
IBR DOE Run	1.24	-	55	63	68	79	100	119	131	133	151	-

Table 6-33: Unconverted Wax Distillation (Stream 26) AO-P5711

Main Product	D-6352 IBP, ˚C	D-6352 5%, ˚C	D-6352 10%, ˚C	D-6352 30%, ˚C	D-6352 50%, ˚C	D-6352 70%, ˚C	D-6352 90%, ˚C	D-6352 95%, ˚C
IBR DOE Run	278	345	359	387	419	467	588	635

H.4 Mass Balance

During the IBR DOE Run the mass balance was between 95-97 wt% but the flow meter again showed some issues of accuracy which, together with the hydrogen makeup flow meter errors FI-5180B, reported incorrect results of mass balance.

H.5 Product Yields

Figure 6-110 show the diesel yields during the DOE Run. The diesel yields decreased substantially after matching the ratio of FT products production. With the two days of operation for the DOE Run, it is estimated after prorating the results, that for the total of 4714 lb of crude FT liquids produced, the PU would have produced, if fed that amount to PU, a total of 3704 lb of on-spec No. 2 diesel product.

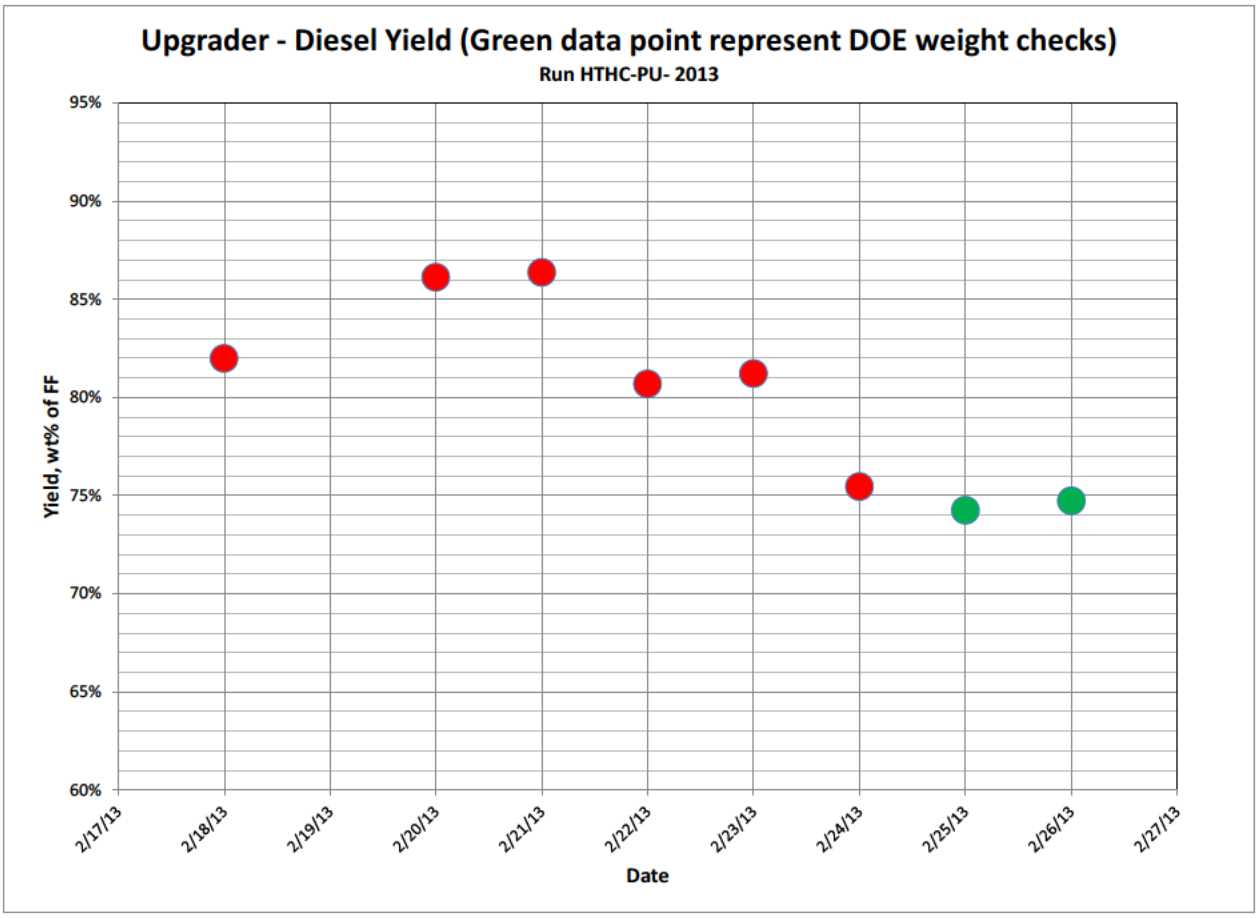


Figure 6-110: Diesel Yield during IBR DOE Run

Analyzing the results from the lab, observe the values highlighted in yellow in Table 6-31 and

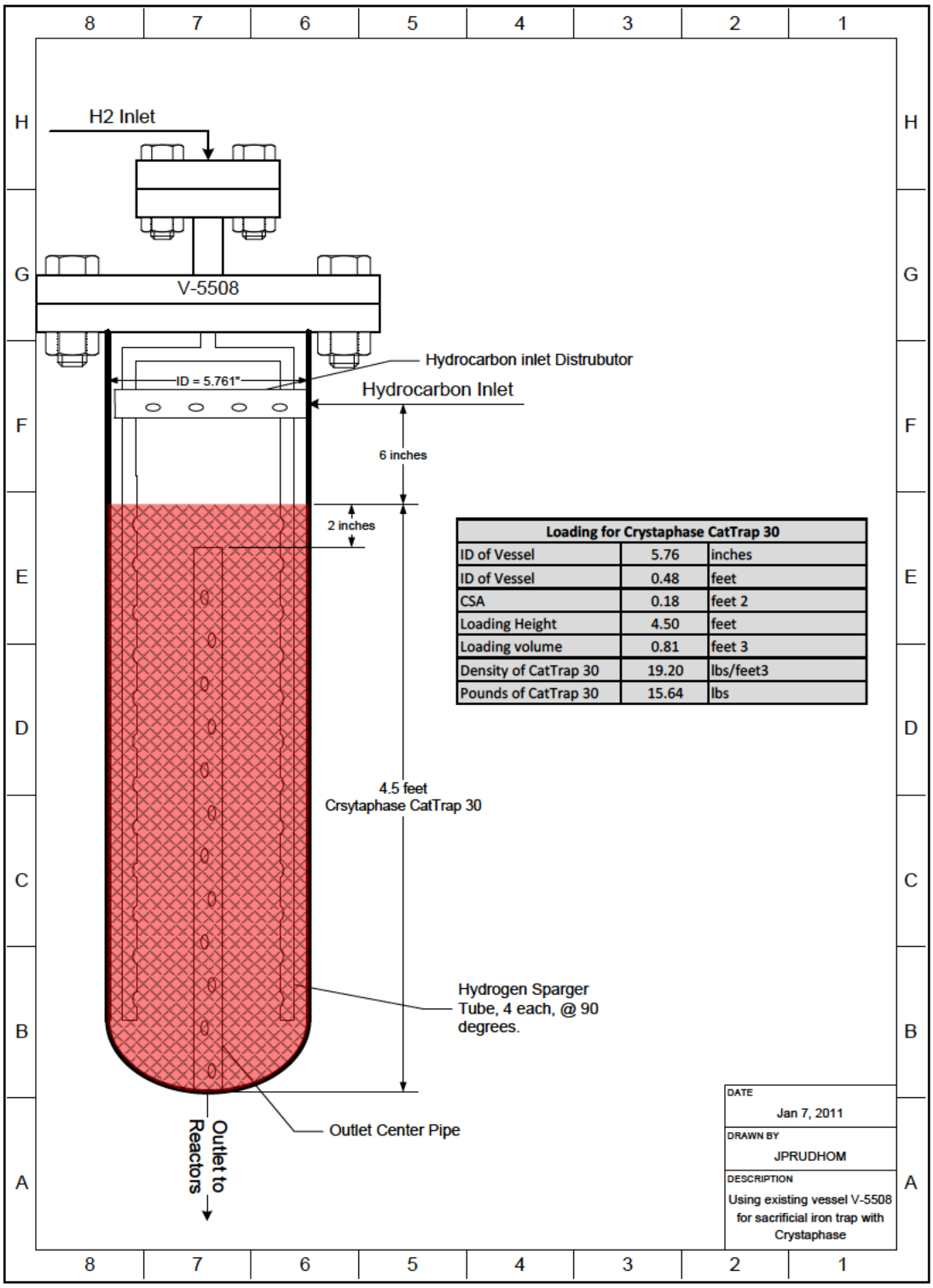
Table 6-33 for diesel production. The difference between these numbers shows the overlap in the boiling points where the quality of the main product (diesel) could be affected. Although the diesel produced was on specification, this overlap (-20°C) between the 5 vol% of the unconverted wax minus the 95 vol% of the diesel product, is an indication of poor separating power. See Figure 5-12 for reference of the principal equipment in PU. If the feed temperature to the columns fluctuates, maintaining a constant overhead temperature, the separation of the components will vary. That is, the boiling cut will entrain more or less heavy components in the lighter product, and more or less lighter component in heavier product. The fluctuation in feed temperature varies the reflux ratio which affects the components separation.

H.6 Hydrogen Consumption and Gas-to-Oil Ratio

In IBR DOE Run, efforts were made to understand and report more accurate hydrogen consumption after adjusting and re-zeroing the flow meter FIC-5193. Low pressure gas samples were taken and analyzed in the Mass Spectrometer (instead of the RGA since the RGA needed more sample volume and the sample bomb in the field is not sufficiently big for the requirements for RGA to get the analysis done); however, after analyzed the results showed oxygen content, when the gas samples from the low pressure section of the unit should not entrain any oxygen. It is indicated that the MS has issues of accuracy when heavy hydrocarbons are present. Therefore, the study including the off-gases in the hydrogen consumption estimation could not be executed. It is necessary to purchase a higher volume sample bomb in order to run the compositional analysis in the RGA analyzer.

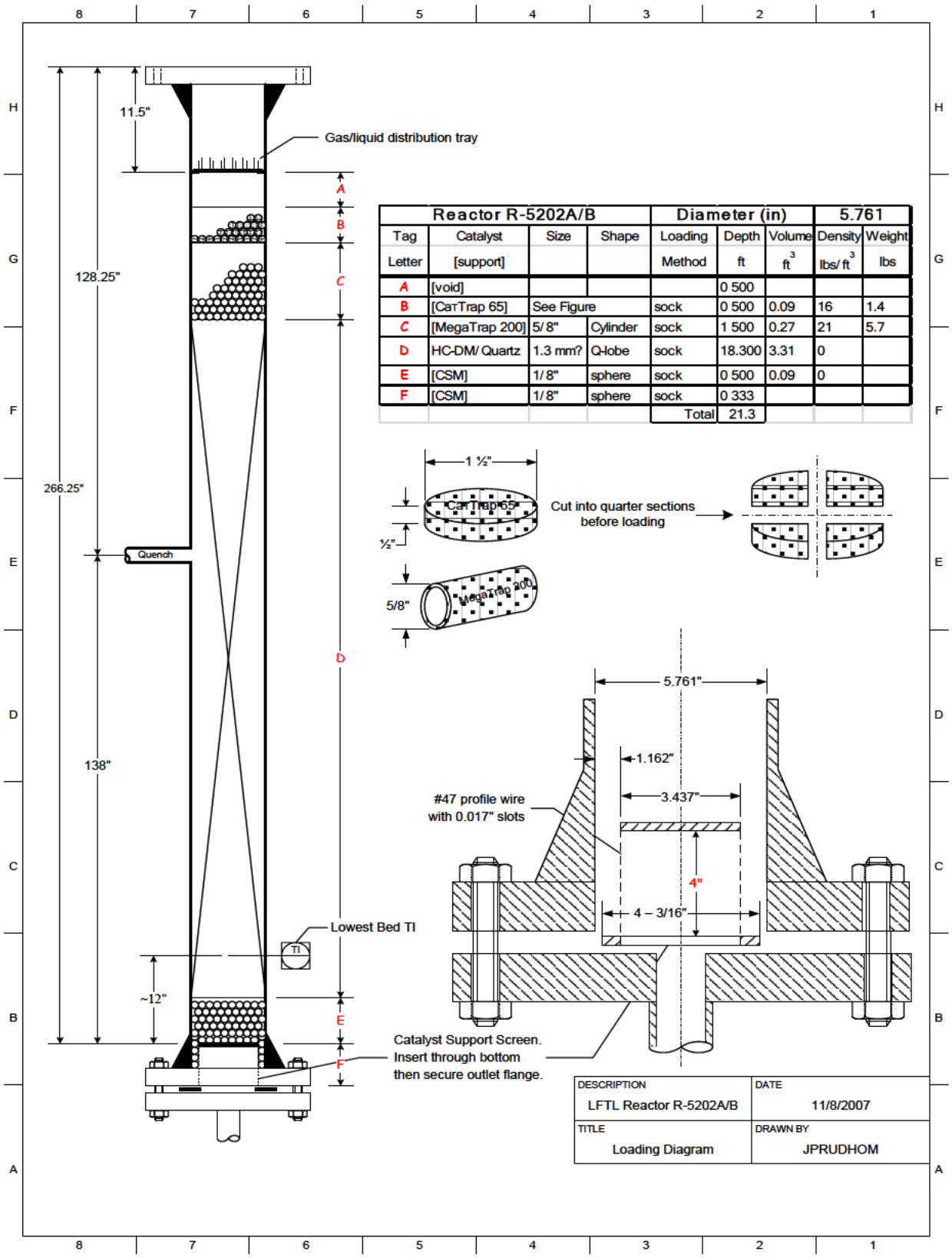
The flow meter FE-5193, from the recycle hydrogen purge, started to indicate faulty numbers after being re-zeroed. It is suggested to calibrate and re-zero the meter in the factory together with the transmitter. On the other hand, the flow meter FI-5180B from the fresh hydrogen compressor has also been fluctuating. This flow meter is not sized for such low hydrogen flow rate; the accuracy of the meter is compromised at the hydrogen flow rate available for PU in the IBR DOE Run. The supply from the hydrogen membrane to the hydrogen makeup compressor was not enough for the flow meter to pick up an accurate reading. It is suggested to size lower range flow meters for the PU hydrogen makeup and the recycle gas compressor in order to accurately indicate flow rate due to lower hydrogen makeup availability and for the bled recycled gas.

The Gas-to-Oil ratio showed for both runs, are sufficiently higher than design which is favorable in maintaining the catalyst life. However, for IBR DOE Run the gas-to-oil ratio showed a decrease in the parameter, indicating that the hydrogen recycle purity was affected. This reduction in the parameter is mainly because of the lower availability of hydrogen makeup from the hydrogen membranes.



Loading for Crystaphase CatTrap 30		
ID of Vessel	5.76	inches
ID of Vessel	0.48	feet
CSA	0.18	feet 2
Loading Height	4.50	feet
Loading volume	0.81	feet 3
Density of CatTrap 30	19.20	lbs/feet3
Pounds of CatTrap 30	15.64	lbs

Figure 6-111: V-5508 Hydrotreater Iron Guard Bed



Reactor R-5202A/B				Diameter (in)			5.761	
Tag Letter	Catalyst [support]	Size	Shape	Loading Method	Depth ft	Volume ft^3	Density lbs/ft^3	Weight lbs
A	[void]				0 500			
B	[CaTTrap 65]	See Figure		sock	0 500	0.09	16	1.4
C	[MegaTrap 200]	5/8"	Cylinder	sock	1 500	0.27	21	5.7
D	HC-DM/ Quartz	1.3 mm?	Q-lobe	sock	18.300	3.31	0	
E	[CSM]	1/8"	sphere	sock	0 500	0.09	0	
F	[CSM]	1/8"	sphere	sock	0 333			
				Total	21.3			

Figure 6-113: R-5202A/B Catalyst Loading

6.I Wastewater Treatment

I.1 Wastewater Influent

The collected wastewater from the PDU operations was collected and equalized prior to being fed to the wastewater treatment plant.

The wastewater comprised of the following:

- ClearFuels Venturi Water
- FT Process Water
- Flare KO Water
- Boiler Blowdown
- Contact Water from washdown
- Incidental stormwater collected on skid

I.2 Influent/Effluent Characteristics/Permit Max Monthly Average for POTW

This sample was collected from the equalization tank and effluent sample was taken from the wastewater treatment plant filtrate storage tank. Per the Wastewater permit filtrate water was batch discharged after compliance testing and approval from the local authority.

The effluent was discharged to the South Adams County sanitary sewer and met all of the categorical and prohibitive standards.

Table 6-34: WWTP Influent and Effluent Analytical Results

Constituent	Influent	Effluent	Max Avg for One Month
(all concentration in mg/L)			
Benzene	7.030	*ND	0.057
Ethyl Alcohol	81.90	0.313	--
Phenol	0.106	*ND	--
Acenaphthene	0.114	*ND	0.019
Acenaphthylene	3.160	*ND	--
Anthracene	0.217	*ND	0.019
Chrysene	0.104	*ND	--
Fluoranthene	1.350	*ND	0.022
Fluorene	0.164	*ND	0.019
Naphthalene	9.860	*ND	0.019
Phenanthrene	2.370	*ND	0.019
Pyrene	1.660	*ND	0.020
Zinc	0.167	*ND	1.050
BOD5	334	*ND	--
COD	893	18.9	--
Cyanide	1.2	0.018	0.420
Oil and Grease	163	*ND	**387
Total Suspended Solids	109	*ND	**264

Total Organic Carbon	232	6.9	--
pH	6.60	8.49	**5 to 10
Phosphorus	0.11	0.38	--
Sulfate	85.4	86.2	--
Total Dissolved Solids	600	1270	--

*ND – Non Detect, analysis below analytical detection limit

**Not regulated with Categorical Pretreatment Standards, regulated with POTW prohibitive standards

SECTION 7 COMMERCIAL

7.A Design

A.1 20 DTPD Commercial HEHTR Design

A 4 x 3" coil HEHTR could be designed for a 20 TPD ClearFuels unit, which would result in an acceptable feedrate of 420 dry lb/hr per coil. The carbon conversion would be relatively low (76 wt%), and recycle of char (in a separate coil) would be required to achieve an overall carbon conversion approaching 90 wt%.

If the radiant box is designed for an initial wall temperature of approximately 1750°F, the syngas composition will be approximately:

Table 7-1: 20 DTPD Commercial Unit Performance Data (Estimated from PDU HEHTR)

	20 DTPD Syngas Analysis
Hydrogen (vol%)	56.1
Carbon monoxide (vol%)	18.2
Carbon dioxide (vol%)	20.8
Methane (vol%)	4.5
Ethylene (vol%)	0.02
Benzene (ppmv)	4200
Total Tars (ppmv)	160
Naphthalene (ppmv)	106
Toluene (ppmv)	5
Acenaphthalene (ppmv)	21
Phenanthrene (ppmv)	13
Anthracene (ppmv)	8
Pyrene (ppmv)	3.5
Fluoranthene (ppmv)	3.1
Benzo-fluoranthene (ppmv)	0.2
Benzo-perylene (ppmv)	0.2
Benzo-pyrene (ppmv)	0.1
Syngas H2:CO Ratio	3.08
Carbon Conversion (%)	76
Syngas Yield (SCF/dry lb)	26.8
Tar Dew point (°F)	302

In this case, a syngas cooler generating 150 psig would satisfy the requirement to operate the cooler metal temperatures at least 50°F above the tar dew point.

At this capacity and number of coils, it is prudent to avoid flow splitting after the steam mixing vessel(s) as this was problematic at the PDU. This would allow the unit to operate at low steam/biomass ratios and

also should be configured to allow a single coil to be intermittently steamed out, to remove built-up carbon deposits. Feeding four coils out of a single pressurized feed hopper can be achieved in a feed hopper, as illustrated in the figure below:

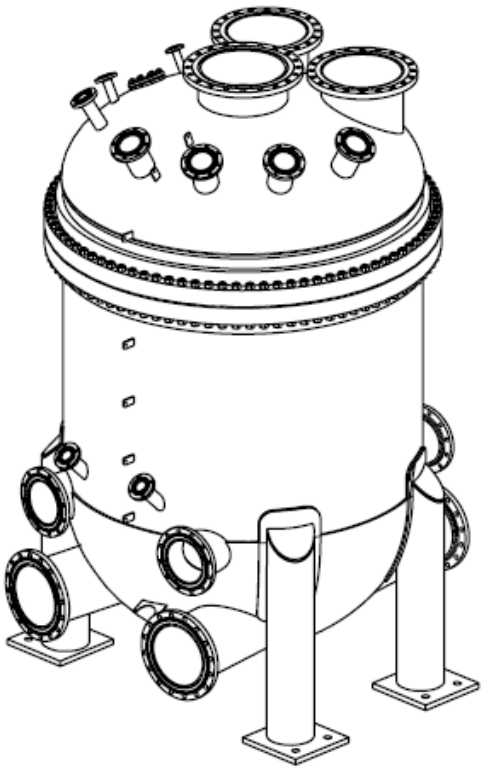


Figure 7-1: Pressurized Feed Hopper with 4 Individual Bottom Outlets

In order to maintain initial wall temperature, as described above, with the 4-coil arrangement, a box type reformer with 2 sets of 2 coil banks (2 coils per bank) would be required. A box reformer design would facilitate multiple rows (3 min) of wall mounted burners that can be installed, which importantly allows the heat flux profile and the initial wall temperature to be controlled independently of the lower skin temperatures and process outlet temperature.

An overall conceptual layout for the 20 DTPD HEHTR is provided below:

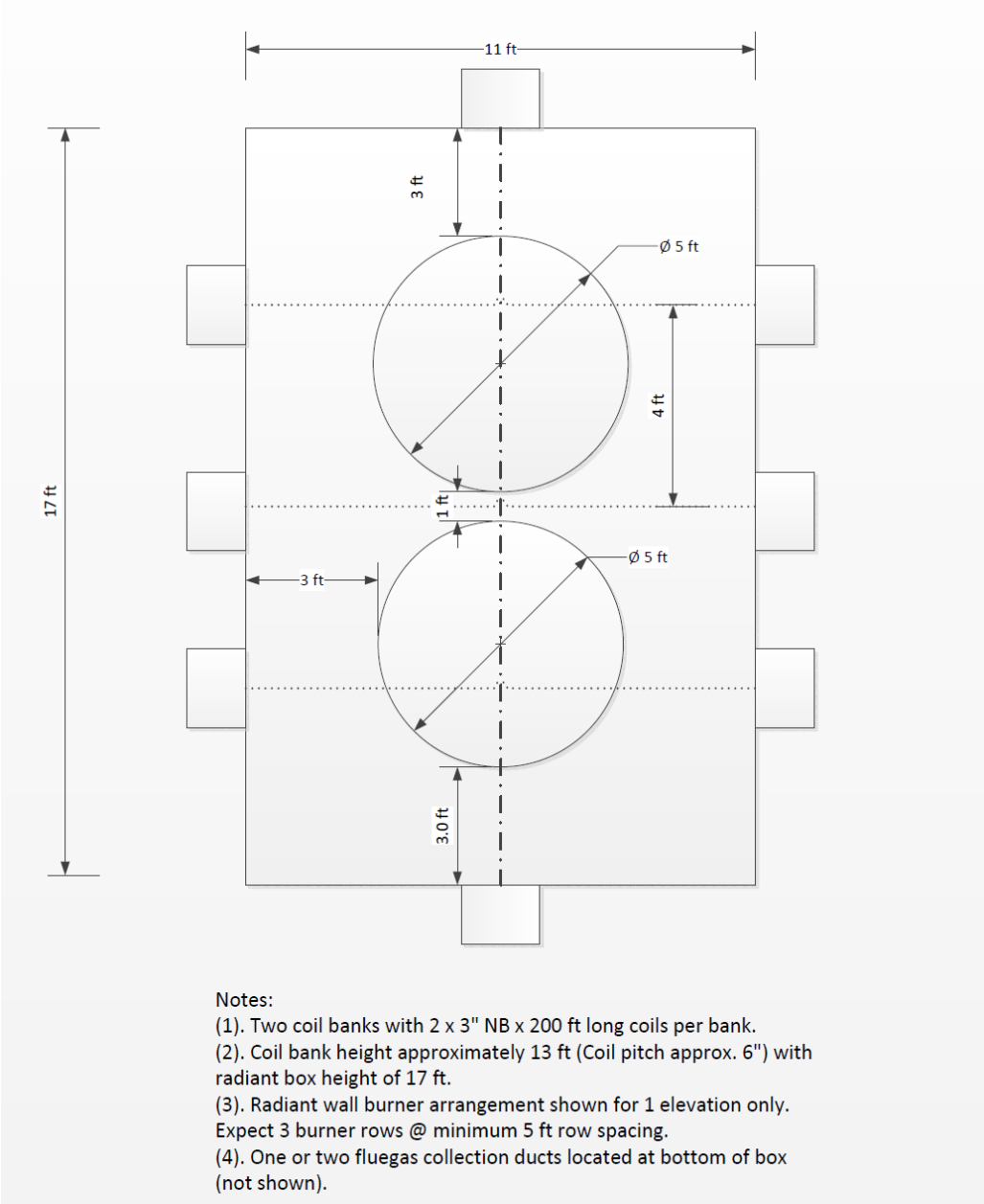


Figure 7-2: 20 DTPD HEHTR Conceptual Layout

An isometric sketch of the conceptual box layout is provided in the figure below, showing the arrangement of the rows of radiant wall burners:

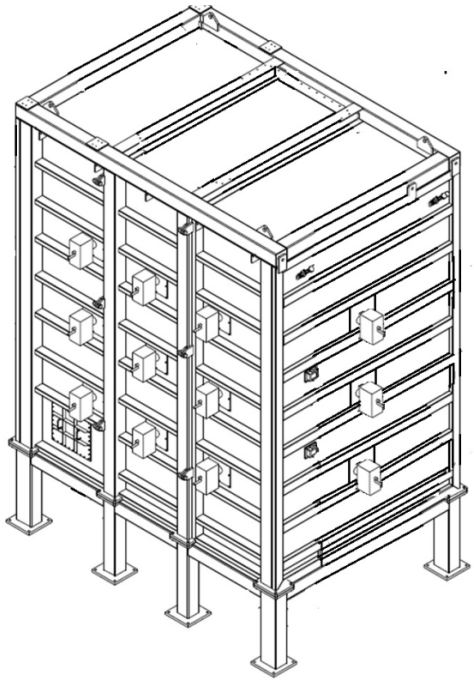


Figure 7-3: Isometric Sketch of 20 DTPD HEHTR Reformer Box

Multiple wall mounted radiant burners, such as burner Zeeco RW burner, shown below, will be mounted on the walls as shown above. Forced draft radiant wall burners could also be selected, at additional cost.

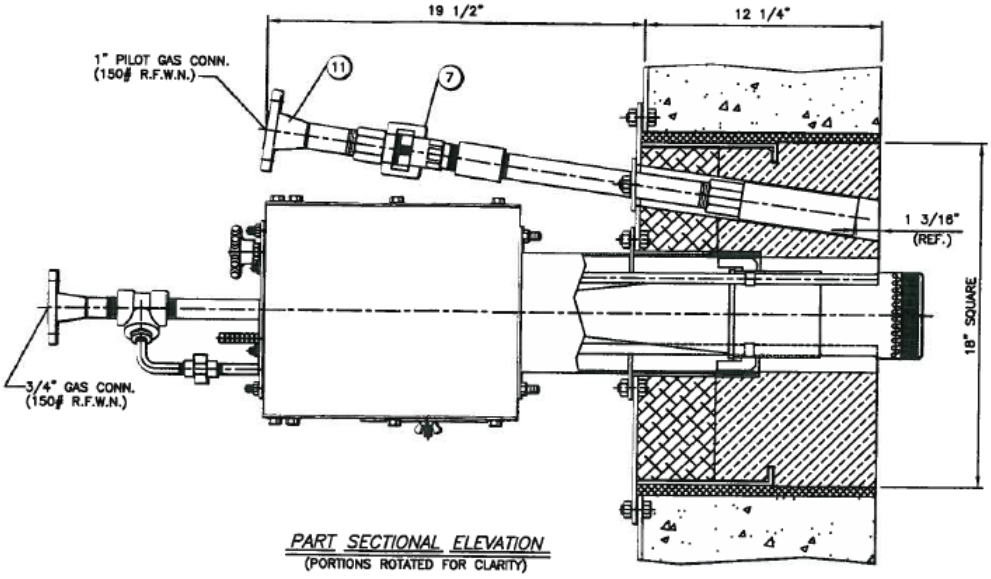


Figure 7-4: Radiant Wall Burners General Arrangement

A.2 40 DTPD Commercial HEHTR Design

For a 40 DTPD HEHTR the design would consist of either two separate 20 DTPD HEHTR units, as described below, or a single HEHTR box, twice as long as the 20 DTPD box, could be fabricated with 4 coil banks.

A.3 250 DTPD Commercial HEHTR Design (or larger)

In order to achieve a 250 DTPD, the original concept for a commercial unit, a configuration of 25 two coil banks with 2x3" NB x 200 ft long would be used. If this is done in one box, or divided into multiple boxes, needs further evaluation.

A.4 20 DTPD Commercial HEHTR Design Cost estimate

A 20 DTPD HEHTR module contract value is expected to be approximately $2.7 MM (+/- 40%). The approximate cost breakdown is provided below:

Table 7-2: 20 DTPD Conceptual Design Cost Summary (US Gulf Coast basis)

HEHTR Equipment Costs	**$k**
Coils	**214.5**
Box	**896.4**
Burners	**120**
Ducting	**447.552**
Structure, Platform & ladders	**149.184**
Total HEHTR Equipment Cost	**1,827.636**
Associated Equipment Costs:	
Fluegas HRSG	**252.5**
Syngas Cooler	**159.03**
Air Preheater	**109.483**
Fans	**53.935**
Stack	**56.4**
HEHTR Subcontract piping	**123**
HEHTR Subcontract instruments	**123**
Total HEHTR Subcontract Value	**2,704.984**

Note: This cost does not include the cost of downstream particulate removal systems, gas cleanup, biomass feed system, pressure boundary feed system, steam-biomass mixing, etc. and it is a contract price not an installed cost.

A.5 ClearFuels Technology Applications

The table below summarizes the potentially applicable markets for the Rentech-ClearFuels gasifier, with comments on the suitability of the technology for these markets:

Table 7-3: Rentech-ClearFuels Potential Markets

Technology Basis	Suitability
Feedrate (DTPD)	More suitable for smaller feedrates, can be multiplied to reach higher capacities for larger markets.
Combined Heat & Power Market	Currently a developed market, niche applications might make sense.
Hydrogen Market (BtH)	20 – 40 DTPD small modular hydrogen market (can produce high H2:CO syngas directly from the reformer, without need for downstream shift reactor and associated equipment, producing 0.6-1.2 MMSCFD H2. Low olefin content of syngas reduces pretreatment required upstream of the PSA unit).
Biomass to SNG	20 – 40 TPD (CF Gasifier can make 3:1 syngas required for methanation step, without water gas shift reactor and associated equipment)
Other Markets	BtL, BIGCC and other markets need scale, individual economic evaluation required.

A.6 Small Modular Biomass-to-Hydrogen (BtH) Plant Design

The performance summary for a modular 20 DTPD Rentech-ClearFuels BtH plant is provided below:

Table 7-7-4: Performance Summary for Conceptual 20 DTPD Biomass to Hydrogen (BTH) Plant

Design Parameter	Value
Feedrate (DTPD)	20
Feedstock Moisture (wt%)	15
Hydrogen Produced (MMSCFD @ 99.9%+)[(1)(2)]	0.60
Char/Ash byproduct (tons/day)	2.5
Power Consumption (HP)	310
Cooling Water Demand (gpm)	200
BFW makeup (gpm)	7
300 psig sat Export Steam (lb/hr)	1500

Notes: (1). Does not include recycle of char to HEHTR.
(2). Excludes heat requirement for biomass drying.

The project economics for this size BtH application are summarized in the following table:

Table 7-5: Cost of Production of Hydrogen from Biomass

	Units	
Hydrogen Production	**MMSCFD**	**0.6**
Biomass Feedrate	**DTPD**	**20**
Biomass HHV	**MMBtu/hr**	**15.4**
Unit Productivity (SCF H2/ Feed Btu)	**SCF/MMBtu**	**1624**
Nett steam export (Saturated 400 psig)	**t/hr**	**0.84**
Total Power Requirement	**kW/hr**	**232**
Raw Water make-up	**gpm**	**11**
Wastewater Discharged	**gpm**	**14**
Availability	**%**	**90**
Total Installed Cost	**$MM**	**$16.3**
O&M Labor	**$MM/yr**	**$0.8**
O&M Expenses	**$MM/yr**	**$0.7**
O&M power	**$MM/yr**	**$0.1**
Steam Credit	**$MM/yr**	**$0.1**
Subtotal		**$1.51**
O&M Costs per day		**$4,577**
O&M cost ($/kg H2)		
Feedstock cost ($/kg H2) @ $50/DT		**$3.17**
Capital cost over 15 yrs ($/kg H2)		**$0.69**
		$3.42
All-in H2 production Cost ($/kg)		**$7.27**

At over $7/kg, it is unlikely that small modular biomass to hydrogen plants of this type would ever compete with pipelined or on-purpose produced hydrogen from Natural Gas, at any foreseeable natural gas price. The DOE's 2012 report on "Hydrogen Production Costs using Low Cost Natural Gas" also clearly indicates that hydrogen at $7/kg will not be economic in the US for the foreseeable future.

The delivered cost for hydrogen trucks in the US, excluding refueling, is approximately $4-12/kg according to the Department of Energy's 2004 report, "Hydrogen Delivery Options and Issues." Tube trailers only have a capacity of 300 kg of hydrogen, so the 1445 kg/day of hydrogen produced by the 20 TPD modular

BtH plant may meet a demand that is not practically provided for via tube trailers. Liquid hydrogen tank trucks (LH2) can provide up to 4,000 kg per truck, but are only available in limited geographic locations.

7.B Commercial ProForma

Rentech has made the strategic decision to not pursue the commercialization of the technology that we developed. This decision was made based on the return profiles and the time to cash flow. Rentech's shareholders directed us to look at projects with a shorter time horizon. However, prior to the strategic decision, Rentech was developing a number a possible projects. The proforma described here is based on a project we were pursuing in Ontario called the Olympiad project.

Rentech developed a commercial-scale heat and material balance around a notional facility in Northern Ontario. The project was designed to convert 1000 dry tons per day of Ontario hard wood to 839 BPD of diesel and 372 BPD of naphtha. The project was essentially a direct scale-up of the table below which shows the key commercial proforma metrics for the project. The heat and material balance was completed using data from the pilot demonstration and a HYSYS simulation of the notional facility.

Table 7-6: Key Commercial Project Proforma Metrics

	Units		Comments
Biomass feedrate	DTPD	1000	
Diesel	bbl/d	839	
Naphtha	bbl/d	372	
Power Import(-ve)/Export(+ve)	kW	-8250	Max Fuel Case chosen with slight power import
Aux power demand	kW	20730	
Total Power generation	kW	12480	
Liquid Product yield	gal/DT	50.9	
Heat rate (HHV basis)	BTU/gal	377012	
Electrical (Nett) Demand	kWhr/gal	3.9	
Electrical (Total) Demand	kWhr/gal	9.8	
% fuel usage, fossil based	%	3.5	
Gate-to-Gate efficiency (LHV)	%	36.6	
Water usage per gallon product	gal/gal	20	1.3 gal/gal process water; remainder primarily cooling tower, boiler blow down, Lower water consumption possible if water costs are high.

After the completion of the heat and material balance using HYSYS, Rentech developed a cost estimate of the facility. This cost estimate was developed from a proprietary costing model based on a number of commercial Front-End Engineering and Design (FEED) that Rentech had done in support of other projects. For example, Rentech completed a FEED package for a biomass-to-fuel and power project with Fluor in 2010. We used that and other information to estimate this project cost on an equipment cost basis. We also used our best indications on the cost of labor, freight, and taxes for the Northern Ontario location. This costing analysis was done outside the scope of the DOE project. In fact, the entire proforma analysis was NOT billed to the DOE project.

The Table below shows the cost inputs that went into the proforma calculations.

Table 7-7: Project Cost Inputs to Proforma Analysis

Sources ($MM)	Total	%
Equity		
Project Equity Funding	$572.3	74.1%
Total	**$572.3**	**74.1%**
Debt		
Construction Loan	$0.0	0.0%
SDTC Loan	$200.0	25.9
Total Debt	**$200.0**	**25.9%**
Total Sources	**$772.3**	**100.0%**

Uses ($MM)	Total	%
Project Capital Costs		
Scoping Period	$0.0	0.0%
Feasibility Cost	0.0	0.0
FEED Costs	22.5	2.9
Final Design Costs	50.6	6.6
Construction Direct Costs	348.6	45.1
Construction Indirect/Other Costs	161.8	20.9
Contingency	113.3	14.7
Owner's Costs	34.2	4.4
Start-up Costs	20.2	2.6
Extra Working Capital Cash	2.0	0.3
Initial Inventory	3.4	0.4
Total	**$756.6**	**98.0%**
Financing Costs		
Interest During Construction	$0.0	0.0%
SDTC Interest During Construction	$0.0	0.0%
Debt Service Reserve	0.0	0.0
Operating Reserve	15.7	2.0
Debt Placement Fees	0.0	0.0
Equity Placement Fees	0.0	0.0
Total	**$15.7**	**2.0%**
Total Uses	**$772.3**	**100.0%**

For the project, we assumed that the project would be eligible and obtain up to CAD $200 million from Sustainable Development Technology Canada (SDTC) Next Gen Biofuels Fund. Rentech had passed due diligence on that process before the decision to not proceed.

The next table shows the assumptions that went into the proforma analysis.

Table 7-8: Financing and Economic Input Parameters to Proforma Analysis

Assumptions	
TIC ($MM) - RTK Internal (15% Contingency)	$699.2
Output and Usage	
Diesel Fuel Output (bbls/d)	839.0
Naphtha Output (bbls/d)	372.0
Power Sold (MWh)	12.5
Power Purchased (MWh)	20.7
Biomass Usage (wtpd)	1,818.2
Pricing	
Biomass Cost ($/wt)	$30.00
Sold Power Price ($/MWh)	$134.60
Purchase Power Price ($/MWh)	$69.28
Green Attributes ($/bbl transportation fuel)	$97.44
Diesel Fuel ($/bbl)	$126.00
Naphtha ($/bbl)	$115.50
Total Construction Debt	$0.0
SDTC Funding	$200.0
Equity Funding	$572.3
Total Funding ($MM)	**$772.3**

Based on our analysis of wood costs determined in concert with the Province of Ontario, we believe that biomass could be delivered to the project at approximately $30 per wet ton with approximately 45% moisture. The project would also be able to produce green power and sell to the grid at Green Power Pricing while purchasing brown power off the grid. This idea was confirmed by the Province as well. The Feed In Tariff for green power was assumed to be $134.60 per MWh while brown power pricing bought by the project was lower. The diesel fuel price was assumed to be $3.00/gallon while naphtha pricing was assumed to be $2.75/gallon. The green attributes of the fuel are based on the ability to receive 1.6 RIN's for every gallon produced with a price of approximately $1.45/gallon. Essentially, even though the project is producing in Canada, Canadian renewable fuel prices are set by US pricing so the RIN estimation is consistent with that assumption. We assumed that all product pricing escalated at 3% per year and all project costs increased at 2.5% per year.

Based on these cost and pricing assumptions, the table below shows an example of a 10-year proforma income statement for the project.

Table 7-9: Example of 10-Year Proforma Income Statement

Financial Summary (USD in Millions)												
	2012	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**	**2020**	**2021**	**2022**	**2023**
Operating Efficiency			0%	0%	56%	68%	79%	89%	89%	89%	89%	89%
Total Production												
Transportation (bbl)			0	0	143,768	207,430	241,920	272,543	272,543	272,543	272,543	272,543
Naphtha (bbl)			0	0	63,749	91,978	107,272	120,850	120,850	120,850	120,850	120,850
Total Production (bbl)			0	0	207,517	299,408	349,192	393,393	393,393	393,393	393,393	393,393
Revenue												
Production Revenue			$0.0	$0.0	$31.9	$46.6	$52.9	$61.3	$63.2	$65.1	$67.0	$69.0
Green Benefit Revenue			0.0	0.0	16.0	23.8	28.9	33.6	34.6	35.6	36.7	37.8
Other Revenue			0.0	0.0	7.9	11.7	14.3	16.6	17.1	17.6	18.1	18.7
Total Revenue			**$0.0**	**$0.0**	**$55.8**	**$82.1**	**$96.1**	**$111.5**	**$114.8**	**$118.3**	**$121.8**	**$125.5**
Growth Rate				*NA*	*NA*	*47.1%*	*17.1%*	*16.0%*	*3.0%*	*3.0%*	*3.0%*	*3.0%*
COGS			$0.0	$0.0	$17.3	$25.6	$31.1	$36.0	$37.0	$38.0	$39.1	$40.2
Gross Profit			$0.0	$0.0	$38.5	$56.5	$65.0	$75.5	$77.8	$80.2	$82.7	$85.3
Operating Expenses			$0.0	$0.0	$29.7	$36.5	$37.6	$38.6	$39.6	$40.6	$41.6	$42.7
EBITDA			**$0.0**	**$0.0**	**$8.9**	**$20.0**	**$27.5**	**$36.9**	**$38.2**	**$39.6**	**$41.1**	**$42.6**
EBTIDA Margin			*NA*	*NA*	*15.9%*	*24.3%*	*28.6%*	*33.1%*	*33.3%*	*33.5%*	*33.7%*	*34.0%*
Free Cash Flow			**$0.0**	**$0.0**	**$8.9**	**$19.3**	**$27.2**	**$36.4**	**$38.1**	**$39.5**	**$41.0**	**$42.5**
Distribution Equity Holders	**$0.0**	**($51.4)**	**($481.6)**	**($225.3)**	**($10.1)**	**$19.3**	**$27.2**	**$36.4**	**$38.1**	**$39.5**	**$41.0**	**$42.5**

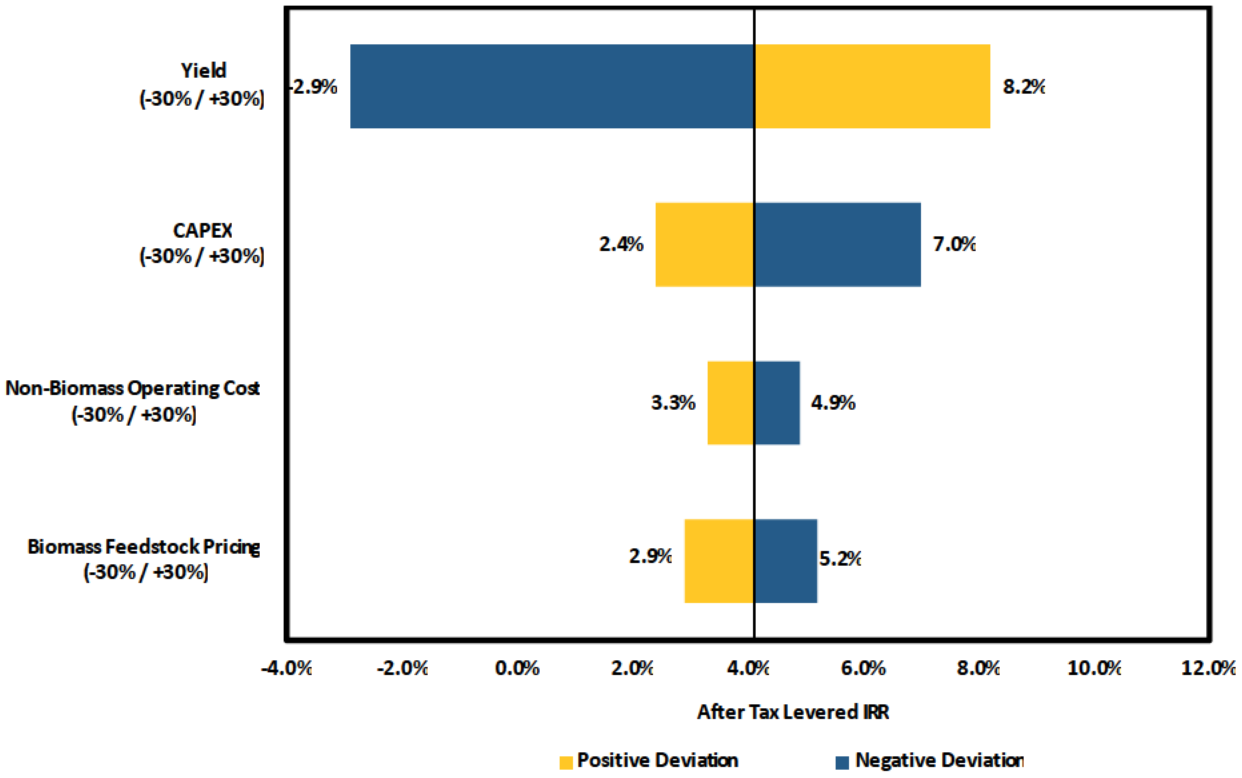
Tax rate was assumed to be 35% and the After-Tax Leveraged IRR is calculated as 4.1%. We did do a sensitivity analysis on product pricing to determine what fuel product pricing would be required to obtain a 10% IRR. The diesel price necessary for a 10% after-tax leveraged return is $5.16/gallon.

Table 7-10: Diesel and Naphtha Pricing Required for 10% IRR

Diesel & Naphtha Pricing / IRR		
	Base Case	**Indicative**
	4.1% IRR	**10% IRR**
Diesel Price ($/gal)	$3.00	$5.16
Diesel Production (MM gal)	11.4	11.4
Naphtha Price ($/gal)	$2.75	$4.73
Naphtha Production (MM gal)	5.1	5.1
IRR	4.1%	10.0%

Sensitivity analysis was done on the primary economic variables of yield (gallons per ton), capital costs, non-biomass operating costs, and biomass feedstock costs. The following table shows the Tornado Chart on +/-30% sensitivity on those variables

Table 7-11: Sensitivity Analysis - Tornado Diagram



SECTION 8 LESSONS LEARNED

8.A General Technology Lessons Learned and Recommendations

Rentech chose the ClearFuels Technology because of the belief that the small pilot work at the 1-5 TPD level that was completed meant that the technology was de-risked to allow a larger scale unit to be built. Tens of thousands of hours of small-scale data had been collected. The data was not available in a comprehensive format and was held very closely by the inventor of the technology. Rentech failed to understand the scale-up issues at an early stage. When the issues with the IBR HETR unit became clear, Rentech did go back, armed with more advanced engineering tools and analytical equipment, and obtained new pilot data at the Unit in Livingston, AL. However, it did take over 1 year from initial data to start to obtain new pilot-scale data.

It is quite expensive for a technology development company such as Rentech to operate a fully integrated demonstration-scale biorefinery. Although going through the demonstration scale is necessary, one recommendation for future teams is to build a demo large enough so that a portion of the operating costs could be covered by the sale of any products from the site.

8.B ClearFuels Technology – Lessons Learned

Scale-up of process technologies is not always straight forward. This was the case with the deployment of the ClearFuels gasification technology, as deployed at the PDU. In this case, much of the 20 TPD PDU demo unit design was based primarily on testing conducted at Pearson Technology's name plate 5 TPD pilot unit. Although the scale-up capacity factor (4:1) did not seem to be large, there were fundamental differences in the geometries and design features of the two units, which resulted in fundamental performance differences.

- The demo unit scale-up relied solely on maintenance of a similar coil residence time between the demo and pilot units, and later demo unit testing found that this parameter was not a primary variable in the scaled-up unit's performance.
- Although the pilot unit had a name plate capacity of 5 dry tons per day, testing done to set the design basis for the demo unit was done at lower biomass feedrates. The upper limits of the unit's capacity was not evaluated.
- Analytical equipment and resources were limited during the PTI data collection events. Data collected on syngas tar levels for the pilot plant was more qualitative and less quantitative. Expectations about syngas tar levels for the demo unit were understated.
- The demo unit basis for carbon conversion was not based on data collected at the pilot unit and, specifically, not at the higher solids fluxes at which the demo unit was designed to operate.
- Experiences from previous attempts to scale up the technology (e.g. the Brightstar Environmental SWERF, installed in Australia) were not adequately investigated.
- The pilot plant was resource limited and not adequately instrumented (e.g. with multiple skin temperature measurements) and hence key process variables were not understood. (hindsight)

- Drawings and specifications from the pilot plant were not available during detailed engineering. Some aspects of the design of the demo unit were not accurately scaled up.

- The pilot plant used a single coil, whereas the demo unit used two coils with an upstream 'Y' splitter. The challenges with stream splitting on the demo unit were not adequately understood.

- The responsibility for the design of the demo unit reformer and associated equipment was largely based on natural gas reformation based on the supplier's experience. Additional complexities of biomass gasification were not understood.

8.C Commercialization Lessons Learned and Recommendations

Rentech started down the path of development and production of renewable fuels at the PDU in 2007 when it seemed clear that some sort of carbon legislation would be enacted. When this did not occur in 2009 or 2010, this decision was brought into question at the corporate level. Rentech continued to move down the same path with a number of projects in the DOE Loan Guarantee Program as well. When this path became unworkable, re-evaluation of corporate strategy was eventually completed which resulted in Rentech ending R&D activities in alternative energy.

The uncertainty in future regulation makes any project that depends on government incentives highly speculative in Rentech's current opinion. Renewable diesel, using the FT process, for example, requires the use of RIN credits in all circumstances at current energy prices. The uncertainty in those RIN prices makes financial project returns uncertain and the ability to raise equity in most circumstances very difficult.

8.D Engineering, Procurement, and Construction Lessons Learned and Recommendation

In general, this project utilized cost reimbursable fixed fee contracting. Engineering and Construction Management were performed with the assistance of an engineering contractor. Procurement was completed as a joint effort between the engineering contractor and Rentech (Rentech performed the final procurements). Two separate primary construction contractors were used to construct the plant. This was a benefit to the project because it reduced risk, and associated risk money from contractor proposals. It also minimized the number and magnitude of disputes over included scope.

As a result, the change order process was also streamlined which was very helpful in preventing the project from getting bogged down due to the multiple scope additions required for modifications during the start-up and operations phases. This EPC structure allowed the project to be constructed under budget. It was not until after mechanical completion of the original project scope, during the extended commissioning exercise, that cost over-runs in the project occurred.

This E,P,CM, C structure allowed for agility reacting to the nebulous scope that can occur in an R&D setting. We recommend that future projects use such a structure for the E,P,CM, C portion of the project.

8.E Operations Lessons Learned and Recommendations

E.1 Biomass Processing and Feed Systems

Loading Dock (EcoDock) to the Grinder Inlet:

The augers feeding the material from the EcoDock to the pocket-belt conveyor worked very well on wood chips and pellets. They had difficulty feeding the bagasse material especially the material processed in Hawaii. When running the Hawaiian Bagasse, the augers lifted and the auger motors showed signs of motor loading.

> ***Recommendation:*** *To be able to handle a variety of biomass materials, the interaction between the format of the feedstock and the process design must be understood.*

Biomass Mass Balance:

The weigh belt was calibrated during the DOE Performance Run and was shown to be accurate. However, this is not the best relationship between the feedrate to the grinder and the feedrate to the Feed Hopper or to the Steam Mixing Vessel due to the biomass losses to the Bag House. The loss of material was greater on the lower density bagasse than on the wood. The metering screw was intended to be mass flow control device, but with the steam backflow problems this was not accurate; material would hold up and not flow evenly.

> ***Recommendation:*** *A method to measure the feedrate much closer to the feed screw is necessary to have an accurate mass balance for the process.*

Grinder:

The blades showed a degree of wear even during the DOE Performance Run using the specified blade material. Although rocks and stone caused chipping of the knives, there were patterns of uneven wear across the blades causing variable spacing between the blades and the cutting bar.

> ***Recommendation:*** *Additional work is needed to better understand blade wear and the material of construction across a wider variety of biomass materials. For commercial projects, an engineering study should be performed, after feedstock selections completed, comparing a knife grinder with other grinding techniques (hammer mill, jet grinder, etc.) to determine which grinding process is more robust.*

The grinder setup was sensitive to the moisture content of the feed and would create a fibrous mass that would plug the screen. In the project the size reduction was to be completed in a single pass. Alternative design would use a larger opening in the grinder and a series of screens and recycle. In addition to avoiding the fibrous mass, it will also tighten up the particle distribution, making the product more uniform.

> ***Recommendation:*** *It was found that grinding a pre-dried material produced a grind that would flow better, but it did create more dust. Recommendation is to continue performing wet size reduction in multiple passes and dry grind, if necessary, last.*

Dryer/Cyclones/Baghouse:

The three primary operational considerations are as follows. As the moisture of the feed increased, the dryer inlet cyclone would plug, the supplemental hat steam radiators in the dryer were prone to freezing and rupture, and the Fluegas used as the primary drying medium did not have a bypass.

> ***Recommendation****: The project designed the feed handling system to process a large variety of feedstocks, which inheritably meant some feedstocks would be more difficult to process. Recommendations for commercial design are to freeze the feedstock specifications and perform testing on the actual feedstock. These tests should include, at a minimum, material characteristics (arching , bridging), and explosivity / ignitability.*

Feed Hopper:

The diamond back hopper design was an experimental design from the vendor. In order to get reliable flow to the feed screw, 9 air cannons were added and the level in the hopper was maintained at 25%. The performance was also sensitive to the material grind.

> ***Recommendation:*** *Commercial designs and perhaps even the demonstration unit should use a live bottom feeder or other alternative to the diamond back hopper.*

Feed Screw through Rotary Valve:

The section from the inlet of the feed screw to the inlet of the steam mixing vessel was problematic during most of its operation. The primary cause was steam leaking past the rotary valve into the feed screw. A number of modifications were made to this area to provide additional venting which improved, but did not solve, the issues. When "chunks" of moist biomass dropped into the Steam Mixing Vessel, it would many times cause plugging between the SMV and the inlet of the HEHTR coil. The equipment also lacked "clean out ports" between the Feed Screw and the outlet of the Rotary Valve.

> ***Recommendation:*** *Both plug screw feeders and rotary valves were considered during engineering. An alternative design would be to use pressurized lock hoppers.*

Overall Recommendation to the Feed System:

The current design and installation was operated for relatively short periods of time (up to 2 weeks) with constant operator attention and intervention. In order to make extended verification runs (2000-4000 hours) using a wider range of feedstock (both type and moisture content), the Demonstration Unit would need some modifications, many of which are described above. It is believed that the feed system can be made capable of handling a wide variety of materials and moisture contents with the proper sequencing and design of the equipment.

E.2 HEHTR Sections

Steam Mixing Vessel:

The Steam Mixing Vessel was prone to plugging and uneven steam/feed distribution resulting in plugging of the feed distribution pipe exiting the SMV as well as the vertical section where the pipe divided into a "Y" which then connected to each of the two coils. Based on first-hand observations of the Pilot Plant in Livingston, AL, the design was modified which had some improvement to the unit's operation. This arrangement resulted in a more uniform mixture exiting the SMV. However, the SMV still would accumulate wet biomass which would periodically drop off in chunks and cause plugging in the feed distribution pipe, causing the outlet to plug and biomass to build up in the SMV.

> ***Recommendation:*** *Further design modifications are needed to ensure steady, uniform flow of the steam/biomass mixture exiting the Steam Mixing Vessel. This might include a plenum around the areas where the wet biomass builds up that would periodically pulse or continuously emit a low volume of air or fluegas. The other option would be to use an eductor in lieu of the SMV.*

Feed Distribution Pipes:

A single steam/biomass feed pipe exited the SMV but had to be split prior to entry into the Reformer box in order to feed the two coils. The point of the split ("Y") proved to be critical in getting good flow. The insulation of the pipe also proved to be critical in keeping the mixture above dew point and at a prescribed temperature when entering the reformer.

> ***Recommendation:*** *Future designs should look at getting the outlet of the SMV positioned closer to the entry point into the reformer and the connection points to the coils.*

Reformer:

The coil-to-coil spacing was greater on the Demonstration Unit than on the Pilot Unit in Livingston. Consequently, the flame pattern was insufficient to provide the temperature at the top of the coils which was later determined to be necessary to get "fast pyrolysis" at the top of the coil. A Reed Wall was also added at the bottom of the reformer to better direct the burner flame inside the reformer can.

> ***Recommendation:*** *The next step (which was underway prior to the conclusion of the research effort) was to add lance burners near the top of the coil, providing hotter coil surface temperature in the initial heating zone of the reformer coils. If the hypothesis was verified using the lance burners, further redesign of both the burner and coils would have been the next steps. With some of these possible modifications, the height of the reformer could have been decreased.*

Overall Recommendation for the HEHTR Section:

From an operational and reliability perspective, future work should focus on the Steam Mixing technology and the design of the feed system from the SMV into the Reformer.

E.3 Syngas Conditioning Sections

Expansion Loop:

The coil was hung from the top of the reformer. The outlets at the bottom of the Reformer would grow down while at the higher temperatures and contract when cooling down. Many times the coils would not return to the same position in a "cold" state. Frequent heat-up and cool-down needed during the commissioning and operating phases caused cracks in the welds. As the pipe "relaxed" during the heating/cooling cycles, the geometry of the pipe changed. Due to the resulting change in geometry, the spring cans on the expansion loop were inadequate to keep the loop level, resulting in twisting of the loop. Weight boxes were substituted for the spring cans in two locations to allow for a more manual adjustment as needed.

> ***Recommendation****: A large part of the configuration of the exit to the reformer was space constrained. Commercial design should allow adequate space to optimize piping. Alternative designs for the support of the coils in the Reformer may also help in the configuration.*

Waste Heat Boiler, De-Superheater:

During initial runs the outlet syngas contained higher and different levels of tar and char than had been anticipated, causing material to condense on the inside of the Waste Heat Boiler tubes which would plug after only a few hours of operation. After three unsuccessful tries, the Syngas section of the WHB was by-passed and a "De-Superheater" was installed in the expansion loop piping. The "De-Superheater" consisted of a water nozzle spraying into a larger diameter pipe section that was welded into the lower leg of the expansion loop. To assist with syngas water contact, a static mixer was inserted into the De-Superheater section of the piping.

> ***Recommendation****: Concluding the learnings from Livingston, the tar composition and concentrations improved, although the project did not have an opportunity to put the waste heat boiler back in service to re-test. Beyond the normal required heat exchanger design inputs, tube wall temperature and tar dew points need to be included.*

Cyclones and Ash Hood System:

The performance of the cyclones was impacted by the problems with the WHB removal and use of the "De-Superheater." The temperature at the inlet of the Cyclones coming from the De-Superheater was initially too low, resulting in tar condensation and plugging. Operating at low syngas velocities relative to the cyclone design also impacted the performance. To improve performance due to the low velocities, inserts were ordered which allowed the velocity to increase at the same syngas flow. Due to the operational changes, the Ash Dump Valves also saw higher operating temperature and increased frequency of actuation. This resulted in premature wear and Syngas leakage, requiring frequent repair and re-packing of the valves.

> ***Recommendation****: The importance of setting the design basis is key. This unit underperformed due to its operating outside the design parameters to which it was built.*

Solvent and Venturi Scrubbers:

The Solvent Scrubber was not part of the original installation. It was added during the start-up phase of this project due to the unexpectedly high level of heavy tars. Problems were encountered with solids as well as a solvent/water emulsion carrying over into the Venturi Scrubber. Temperature control of the solvent scrubber was performed by water injection and solvent recirculation through an in-line heat exchanger.

The Venturi Scrubber experienced plugging from solids carryover before the Solvent Scrubber was added and from a solvent/water/tar emulsion after the addition of the Solvent Scrubber. Additional sock filtration was added after the Venturi Scrubber to further remove the Naphthalene from the Syngas.

> ***Recommendation:*** *Tar removal needs an optimized design based on the performance data gathered from this project.*

Overall Recommendation for the Syngas Conditioning Section:

The Syngas Conditioning was designed under the assumption that the char and tar content in the Syngas would be extremely low. The scale-up of the HEHTR from 5 to 20 Dry Tons per Day resulted much higher levels of tar and char than expected. Consequently, the Syngas Conditioning design was inadequate to handle the higher levels without frequent interruptions to clean the packing and additional labor to maintain the filters and cyclones

Alternatively, the use of Tar Reforming technology should be considered to convert tars to useful syngas. Rentech is developing a dual fluidized tar reforming technology using a nickel catalyst. A reforming step would then eliminate a waste stream and introduce the reformed tars back into the process as syngas. We call this technology NiDFB. It is described in detail in U.S. Patent number 8,241,523 issued on August 14, 2012.

E.4 Summary

The 200-hour DOE Performance Run using nearly 100% Bio-derived Syngas with tailgas recycle was successfully completed. However, the current design of the Syngas process (input of biomass feed to the outlet of the Booster Compressor) is not yet optimized, and required operational attendance and maintenance intervention. To achieve the increased reliability and lower operational cost needed for the process to be considered pre-commercial, continued experimentation and process design is required. With modifications to all sections of the process, the necessary reliability and operational costs are achievable.

SECTION 9 REFERENCES

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