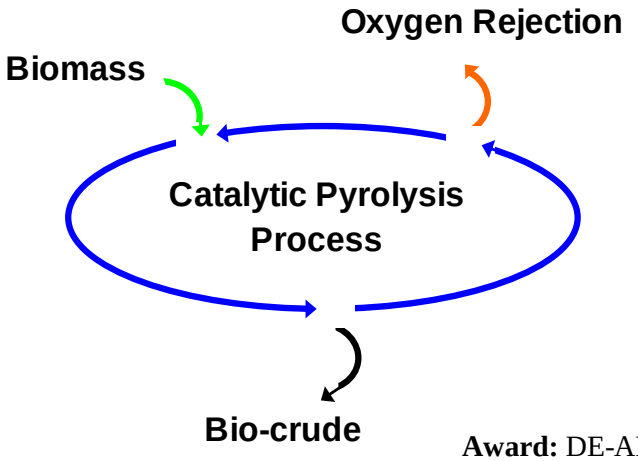
ARPA-E Final Project Report
Catalytic Bio-crude Production in a Novel, Short-Contact Time Reactor



Award: DE-AR0000021
Recipient: RTI International

Project Title: Catalytic Bio-crude Production in a Novel, Short-Contact Time Reactor

Principal Investigator:
David C. Dayton
RTI International
3040 Cornwallis Road
Research Triangle Park, NC 27709
Phone: 919-541-7202
Fax: 919-541-8002
e-mail: ddayton@rti.org

Program Director:
Dr. Mark Hartney, Advanced Research Projects Agency - Energy (ARPA-E)

Contract POC:
David Faucette

Date of Report: December 22, 2014
Project Period of Performance: January 1, 2010 – September 30, 2013

This document contains protected data that was produced under agreement DE-AR000021 with the U.S. Department of Energy that may not be published, disseminated, or disclosed to others outside the Government until five years after development of such data, unless express written authorization is obtained from recipient. All paragraphs/sections containing protected data are marked with the symbol ╬. Upon expiration of the period of protection set forth in this Notice, the Government shall have unlimited rights in this data, including the right to publish the data. This Notice shall be marked on any reproduction of this data, in whole or in part, during the applicable period of protection.

Public Executive Summary

RTI is developing a catalytic fast pyrolysis (CFP) process to produce biomass-based hydrocarbon replacement fuels. From a technology perspective, this advanced biofuels process produces liquid transportation fuels that can leverage capital expenditures in the existing petroleum distribution infrastructure. From a business perspective, this technology does not face potential market limitations caused by oxygenate blend limitations for light-duty-vehicle applications.

A promising catalyst has been developed with excellent potential for deoxygenation to produce a hydrocarbon-rich bio-crude that is more suitable for upgrading with traditional hydroprocessing technology. The role of the catalyst is to control the chemistry during biomass pyrolysis to produce a bio-crude in a single step that has lower oxygen content and is more thermally stable than conventional biomass fast pyrolysis oil. Catalyst properties are optimized to minimize gas and coke production and improve catalytic deoxygenation and bio-crude yields.

Results from this project have demonstrated that bio-crudes from catalytic fast pyrolysis contain < 20 wt% oxygen, with the organic fraction as low as 12% oxygen. These oxygen numbers are > 50% lower compared to traditional fast pyrolysis oils. The bio-crude produced from our CFP process can be upgraded to gasoline range hydrocarbons. A very conservative approach for upgrading included a preliminary stabilization step followed by a hydroprocessing step. The oxygen content in the upgraded product was decreased by 97% (to less than 3wt %) from the oxygen content of the bio-crude sample. Additionally the acid content was reduced by 99% from the acid content of the bio-crude sample. In an optimized integrated process, the CFP step and the hydroprocessing (upgrading) step need to be carefully balanced to maximize the input biomass energy that is recovered in the finished biofuels. Hydrogen utilization and carbon recovery during both catalytic biomass pyrolysis and bio-crude upgrading need to be optimized to maximize energy recovery in the finished biofuel.

A nominal 1 ton per day (TPD) catalytic biomass pyrolysis system was designed based on the laboratory experimental data. The system was designed to achieve the short residence times (0.5–2 sec) and high heat transfer rates required for maximum liquid bio-crude yields while optimizing process integration to maintain catalyst activity by continuous regeneration. The catalytic biomass pyrolysis reactor is a continuously circulating single-loop transport reactor design that is flexible enough to allow sensitivity studies around temperature, residence time, biomass feed rate, and catalyst-to-biomass ratio (i.e., catalyst circulation rate) for process optimization. For a nominal 100 lb/hr feed rate of dry biomass, the products include ~25 lb/hr char and coke, ~20 lb/hr permanent gases, and ~55 lb/hr condensable vapors. Pyrolysis temperatures are 350–600°C, and the system is operated close to ambient pressure.

Production of the catalyst developed within the project was scaled-up to provide enough material (200-kg) for bench-scale testing. The 1-TPD bench-scale unit was fabricated, installed and commissioned with this project. Bio-crude samples from wood were produced in this unit with the CFP catalyst with material balance > 90%. The intermediate bio-crude yields and chemical composition compare well with previous laboratory results and a hydroprocessing strategy for upgrading the resulting bio-crude was developed.

The experimental results obtained within this project were used to develop a process model for a 2000 TPD commercial facility. Detailed flow sheets were developed for all major unit operations in the process and provided a basis for an economic analysis to develop capital and operating costs. Estimates of the biofuel production costs were used to develop internal rates of return for the yields and compositions measured for the current state of technology at the end of this project and for the yields anticipated for an optimized (nth plant) scenario as additional process improvements are made.

Acknowledgements

RTI International would like to thank the generous financial support from the U.S. Department of Energy's Advanced Research Projects Agency – Energy (ARPA-E) and our cost share partners at Archer Daniels Midland Company (ADM) and Phillips 66 Company. Technical guidance from our ARPA-E Program Managers, Dr. Mark Hartney and Dr. Karma Sawyer is greatly acknowledged as is the technical guidance and project oversight provided from Dr. Daniel Matuszak (Booz Allen Hamilton). Contracting support from Ryan Randall, Sim Stokes, and Kristen Ivey (ARPA-E) is also acknowledged.

The technical contributions from Dr. Todd Werpy (ADM) and Dr. Kristi Fjare (Phillips 66), and their respective research teams, had a significant impact on the success of this project. We were very fortunate to be able to leverage their collective R&D experience and biofuels market awareness to continually keep this project focused on commercially-relevant and scaleable technology development.

Contents

Public Executive Summary 2
Acknowledgements 3
List of Figures 5
List of Tables 6
Accomplishments and Objectives - Quarterly Milestone Summary 7
Project Activities - Descriptive Narrative of Completed Tasks 11
Task 1: Biomass Feedstock Preparation, Handling, and Analysis 11
Biomass Feed System Design and Operation 11
Task 2: Catalyst Development 12
Catalyst Preparation and Characterization 13
Catalyst screening with Model Compounds 13
Long-term Catalyst Cycle Test 16
Catalyst Testing with Biomass 18
Go/No Decision Point 21
Supporting Information 23
Bio-crude Production and Long-Term Catalyst Testing 24
Task 3: Process Development 28
Bench-Scale System Design Basis and Process Design 28
Cold Flow Catalyst Circulation Test 31
Hot Flow Testing and Catalytic Fast Pyrolysis with FCC catalyst 34
Catalytic Fast Pyrolysis with RTI-A9 catalyst 38
Task 4: Bio-Oil Analysis and Upgrading 41
Catalytic Biocrude Sample Quality 41
Upgrading Strategy Overview 42
Upgraded Product Analysis 42
Conclusion 43
Task 5: Process Modeling and Economic Analysis 44
Capital Cost Estimate 47
Fuel Production 47
Utility Summary 48
Economic Analysis 50
Project Output 51
Follow-On Funding 53

List of Figures

Figure 1. Loblolly biomass conveying rate based on M120 motor setting. 12
Figure 2. Biomass feed rates to the reactor based on the M160 or M170motor setting. 12
Figure 3. Picture of automated system 14
Figure 4. MS data for 6 days (75 reaction/regeneration cycles) of guaiacol deoxygenation with RTI-A9 at 450°C. 17
Figure 5. Single cycle MS data from extended 100 reaction/regeneration cycles for guaiacol deoxygenation with RTI-A9 at 450°C. 17
Figure 6. Guaiacol Converison for each cycle during extended testing of guaiacol deoxygenation with RTI-A9 at 450°C. 18
Figure 7: Process flow diagram of RTI's bench-top 1″-diameter fluidized bed system. 18
Figure 7. Energy efficiency of the bio-crude (in terms of % of feedstock energy) compared with the oxygen content of the bio-crude. 22
Figure 8. Revaporization efficiency of bio-crudes based on their oxygen content 23
Figure 9. Comparison of Measured HHV and Calculated HHV 24
Figure 10. Process Flow Diagram of 2" Fluid Bed Reactor for catalytic fast pyrolysis. 25
Figure 11. 2" fluid bed reactor that replaced the entreained flow pryrolsis reactor. 25
Figure 12. Permanent product gas composition as a function of the number of cycles run. 27
Figure 13: Process block flow diagram for the catalytic biomass pyrolysis demonstration unit 29
Figure 14: Schematic of the catalyst circulation loop along with differentialpressure transmitter tap locations numbered and aeration points identified by the green arrows 32
Figure 15: Feed and effluent gas flow rates during 07-16-2013 cold flow test 33
Figure 16: PDT and pressure transmitter readings during 07-16-2013 cold flow test 34
Figure 17. Temperature profiles from catalytic fast pyrolysis with FCC catalysts. TE 201 and TE 202 are pyrolysis reactor temperatures and TE 300 and TE 302 are regenerator bed temperatures. 35
Figure 18. Differential pressure profiles from catalytic fast pyrolysis with FCC catalysts. 36
Figure 19. Product gas concentrations in the pyrolysis off-gas. (Volume percent of total off-gas including nitrogen.) 37
Figure 20. CO and CO_2 concentrations in the regenerator off-gas. (Volume percent of total off-gas including nitrogen.) 38
Figure 21. Temperature profiles in the pyrolysis mixing zone (TE201) and in the regenerator bed (TE302). 39
Figure 22. Differential Pressure measurements in the regnerator leg of the system. PDT303 measures the diufferential pressure across the top of the bed and PDT302 measures across the bottom of the bed. 40
Figure 23. Differential pressure measurements from the pyrolysis leg of the reactor. PDT202 is the differential pressure across the riser. PDT204 is the differential pressure across the elbow at the top of the riser. (PDT204 is maximum reading of 10 inches of water column 40
Figure 24. 1L catalytic biocrude sample C and product after 2-stage upgrading. 42
Figure 25. SIMDIS result for upgraded hydrocarbon product. 43
Figure 26: Block flow diagram of the integrated catalytic biomass pyrolysis hydroprocessing process. 44
Figure 27: Distribution of equipment material cost based on plant area 47
Figure 28. Integrated catalytic biomass pyrolysis hydroprocessing process. 49
Figure 29: Percentage distribution of various operating cost components 51

List of Tables

Table 1. Guaiacol Deoxygenation Results with RTI-A9 (7ul/min feed, 100sccm dilutant) 16
Table 2. Fast Pyrolysis White oak characterization of feedstock, liquid products, and char. 19
Table 3. Product distribution from white oak fast pyrolysis and catalytic fast pyrolysis with RTI-A9. 20
Table 4. Compistional comparison of liquid products from fast pyrolysis andRTI-A9 catalytic fast pyrolysis of white oak by GCxGC-TOFMS analysis 20
Table 5. Progress towards Go/No Go milestone targets..... 21
Table 6. Product distribution from catalytic fast pyrolysis with RTI-A9 at selected cycles 26
Table 7: Pyrolysis reaction product yields on dry basis of biomass..... 28
Table 8: Design basis for the biomass pyrolysis demonstration unit 28
Table 9: Mass and carbon balance from catalytic biomass pyrolysis in the 1 TPD pilot unit with FCC catalyst. 36
Table 10. Bio-crude composition from operation of pilot unit with FCC catalyst. 37
Table 11. Mass and carbon balance from operation of the 1TPD pilot unit with RTI-A9 catalyst. 41
Table 12. Bio-crude composition from operation of the 1TPD pilot unit with RTI-A9 catalyst. 41
Table 13. Gas product compositions from operation of the 1TPD pilot unit with RTI-A9 catalyst. .. 41
Table 14. A comparison of the chemical structures and thermal properties of the RTI biocrudes sent to Phillips 66. Sample A is a conventional biocrude and samples B and C are catalytic biocrudes. 42
Table 15. A comparison of the chemical structures and thermal properties of the RTI biocrude and the resulting deoxygenated hydrocarbon phase (denoted as upgraded HC in the table)..... 43
Table 16: Estimates for various categories of total plant cost 47
Table 17: Summary of utility requirements..... 48
Table 18: Summary of electricity consumption 48
Table 19: Summary of items included in production cost..... 50

Accomplishments and Objectives - Quarterly Milestone Summary

Month	Milestone	Description
3 (Q1) Mar 2010	Catalytic deoxygenation with model compounds	Proof-of-concept experiments to validate iron-based catalyst performance for deoxygenation of selected model compounds. Selective removal of oxygen containing functional forms (hydroxyl, methoxy, carboxyl, aldehyde, and ether) with requisite 80% carbon efficiency. **RESCOPED to focus on energy efficiency instead of 80% carbon efficiency, based on lessons learned during performance of award. Model compound experiments are**
6 (Q2) Jun 2010	Develop methodology for high throughput screening	Determine appropriate measurements or test protocols for evaluating catalyst performance in high throughput screening systems. Correlate benchmark results with proof-of-concept experiment results to develop catalyst screening parameters. **Refer to Q8 milestone. RESCOPED to focus on medium throughput (MTP) catalyst microreactor built at RTI. MTP is now an integral part of catalyst screening, testing, and development.**
8 (Q3) Sep 2010	Deliver Corn stover and lignin for bench-scale testing	Prepare and analyze composition of 2-kg batches of corn stover and lignin separated from corn stover. Deliver to RTI for bench-scale testing. **Materials were used for catalytic biomass pyrolysis studies in 1" fluidized bed reactor system.**
18 (Q6) Jul 2011	Develop Bio-crude Stability Metric	Develop a measurement of bio-crude stability based on residual solids remaining after distillation at 350°C. Correlate oxygen content with residual solids. Current bio-oils have >35% oxygen and > 50% residual solids after distillation. Target <20% oxygen with < 20wt% residual solids. **Thermal stability measurement based on residual solids remaining after batch distillation of bio-crude product at a 10°C/minute temperature increase up to 350°C.**
20 Sep 2011	Go/NoGo	Achieve 42% energy efficiency for a bio-crude with less than 20 wt% oxygen content and better thermal stability than bio-oils produced from fast pyrolysis. • Energy efficiency is defined as the ratio of energy content in the bio-crude product to the sum of energy inputs. Energy inputs include the energy content in the biomass feedstock and in other input streams if used (e.g. hydrogen), and the electricity that would be required if the char yield falls below the range of having an energetically self-contained process from raw feedstock to biocrude. Energy content is defined extensively as a product of stream mass and higher heating value. • Thermal stability is defined as less than 20% residual solids after distillation to 350°C • Sum of char and coke yields is 15-20%. Mass balance closure exceeds 90% for all reported process data. Additional information to report (but is excluded from the Go/NoGo decision): solids content (ethanol insolubles using 0.1-micron filter), verification of above-used HHV correlation for RTI oils. **ACHIEVED with RTI-A9 catalysts in 1" fluidized bed reactor system. Provided the basis for the 1 ton/day reactor design.**
21 (Q7)	Catalytic Biomass	Develop a process model to simulate the catalytic pyrolysis of corn stover to produce a bio-crude that is upgraded to fuel in a stand-alone process. This will

Oct 2011	Pyrolysis Process Model	serve as the base case. The heat and material balance will determine energy efficiency and biofuels yields, plus equipment lists and sizing will provide the basis for capital and operating costs. Milestone: External validation of commercial design based on this process model. Review capital and operating cost assumptions and cost of bio-crude production. **Detailed flow sheets of identified unit operations in a 2000 tpd catalytic biomass pyrolysis process with upgrading (hydroprocessing) were developed to estimate capital costs for the integrated process. Laboratory data for the catalytic biomass pyrolysis process were used to develop heat and material balances for the process. Minimum fuel selling price based on estimated hydroprocessing yields were calculated and verified with Phillips 66 and ADM.**
24 Jan 2012	Complete 1 TPD-scale Circulating Fluid Bed Reactor System Design	Complete process design and detailed engineering for a 1 ton/day-scale Circulating Fluid Bed reactor system (reactor feed is 100 lbs/hr biomass). Compile process flow diagram, approved set of P&IDs, instrument and equipment lists, and heat and material balances into a design package for fabrication. Process model and updated results for latest catalysts reinforce that the Q10 target still is feasible (i.e. >50% energy recovery and <20wt% oxygen in bio-crude). **Process Design and HMB completed Dec. 2011. Fabrication completed, unit delivered on April 9-10, 2013**
24 (Q8) Jan 2012	Catalyst optimization	Based on test plan for screening catalysts in the MTP reactor system: 1) optimize metal loading and in the RTI-A9 catalyst, and 2) optimize effect of promoters in RTI-A2 and RTI-A9 to understand and minimize coke formation with model compounds. • Screen modified RTI-A9 catalysts that have: three different active metal loadings with at least 6 different promoters. • Screen promoted RTI-A2 catalysts • Evaluate long term deoxygenation activity of most promising catalysts for at least 100 cycles (reaction/regeneration) in the MTP reactor system. Milestone: Selected catalyst shows less than 0.5% steady-state activity loss per day over 100 cycles (approximately 10 days) with at least 60% residual activity. **Optimum metal loading validated with model compound screening and 1" FBR testing. Activity unchanged over 100 cycles in MTP testing.**
27 (Q9) Apr 2012	HAZOPS for 1 TPD unit	Complete a HAZOPs review of the designing and operating philosophy for the 1TPD catalytic biomass pyrolysis unit. Incorporate any findings or issues into a revised process design. **Completed March 2012.**
30 (Q10) July 2012	Detailed engineering and fabrication package for 1 TPD catalytic biomass pyrolysis unit.	Finalize all P&IDs, instrument lists, I/O list, mechanical vessel drawings, system layout, and control philosophy for 1 TPD catalytic biomass pyrolysis unit and submit for fabrication. **Detailed engineering completed June 1, 2012.**

33 (Q11) Oct 2012	Produce 1-L of RTI-A9 bio-crude for preliminary upgrading tests	Utilize available laboratory reactors at RTI to produce 1-L of the organic bio-crude fraction for preliminary upgrading by Phillips 66. Total mass closure for the process should be 90% and intermediate bio-crude product should contain less than 20 wt% oxygen and >42% energy efficiency as defined above. **Completed 350 reaction/regeneration cycles in 2" FBR system to produce 1.5-L of bio-crude with < 20 wt% oxygen.**
35 (Q12) Jan 2013	Define strategy for upgrading 1 TPD bio-crude samples	GO/NO-GO: Complete one preliminary upgrading test for the 1-L sample using a two-step upgrading strategy of stabilization followed by hydroprocessing with best conditions possible to determine potential upgradability of 1TPD catalytic pyrolysis oil samples. The sample is considered unsuitable for upgrading using a two stage hydroprocessing pathway if the following conditions are not met. 1) Stabilization catalyst leaching rate < 0.05 wt% per day for 100 hours on stream. 2) Stabilized products pass in-house thermal stability test up to 350°C for 2 h. 3) Pressure drop less than 10% of hydroprocessing pressure during a 50 h hydroprocessing run 4) Oxygen content in hydroprocessing product is consistently less than 3 wt% over time on stream. **RTI-A9 bio-crude successfully upgraded to gasoline and diesel range hydrocarbons using a 2-step stabilization plus hydroprocessing process.**
36 (Q13) Jan 2013	Complete vessel fabrication	Machining and fabrication of all vessels in the 1TPD catalytic biomass pyrolysis unit will be completed and delivered to the fabricator for final assembly. **Fabrication of all 10 pressure vessels completed per code in December 2012 and delivered to the fabricator in early January 2013.**
38 (Q14) Apr 2013	1 TPD catalyst charge	Complete batch activity testing for scaled-up materials and take delivery of a 400-kg of catalyst for the 1 TPD catalytic biomass pyrolysis unit. <5% variation from the expected RTI-A9 energy recovery (>42%), measured in the small laboratory reactor, and oxygen content (< 20 wt%) as defined above. **Batch samples of RTI-A9 were tested for activity in the 1" FBR system and 400-kg of the final RTI-A9 catalyst was delivered to RTI June 2013**
39 (Q14) May 2013	Circulating Fluid Bed Reactor Commissioning	Complete installation and commissioning of a 1TPD-scale Circulating Fluid Bed reactor system. Produce at least 10-L of bio-crude with less than 20 wt% oxygen content with mass closure greater than 85% as part of shakedown. **COMPLETE - Fabrication completed and unit delivered on April 9-10, 2013, installation and commissioning occurred during June – July 2013.** • **Biomass feeder calibrated with 2 mm loblolly pine sawdust – up to 200 lbs/hr** • **FCC Catalyst used for cold flow and hot flow testing to verify solids circulation rates - ~1000 lbs/hr** • **Biomass feeding demonstrated with diesel and water injection in regenerator** • **First bio-oil produced on August 9, 2013** • **Pyrolysis catalyst (RTI-A9) loaded August 12, 2013 – solids circulated at ~2000 lbs/hr** • **First bio-crude produced August 21, 2013**

41 (Q15) Jul 2013	Bio-crude production	Produce at least two 25-L bio-crude samples in the Circulating Fluid Bed reactor system for upgrading that meet the following stability requirements (also outlined in the Month 36 milestone). One sample will be produced from corn stover and the second will be produced from woody biomass. Target metrics: ≥ 50% energy recovery and ≤ 20 wt% oxygen in the bio-crude. Greater than 90% mass closure in 1 TPD scale experiments. **Bio-oil produced from loblolly pine; however, poor catalyst physical properties prevented extensive production.**
44 (Q15) Aug 2013	Process Economics	Integrate experimental results from circulating fluid bed reactor system and preliminary bio-crude hydroprocessing to update process economic model; including updated capital and operating expenses. A revised detailed cash flow analysis will be used to determine annualized biofuels production costs and internal rates of return. Updated pro forma analysis to evaluate the economic competitiveness of the catalytic biomass pyrolysis/hydroprocessing technology. Sensitivity analysis will be used to identify the most important technical and economic factors that will lead to a commercially-viable technology. **RTI's initial technoeconomic analysis updated based on experimental results (catalytic pyrolysis and bio-crude upgrading). Hydrotreating process updated to include bench-scale upgrading results and sensitivity on overall process economics ws evaluated**
45 (Q15) Sept 2013	Upgraded bio-crude fuel properties	Bio-crude samples produced in the Circulating Fluid Bed reactor system will be hydrotreated and resulting fuels will be characterized. The sample is considered unsuitable for upgrading using a two stage hydroprocessing pathway if the following conditions are not met. 1) Stabilization catalyst leaching rate < 0.05 wt.% per day for 100 hours on stream. 2) Stabilized products pass in-house thermal stability test up to 350 oC for 2 h. 3) Pressure drop less than 10% of hydroprocessing pressure during a 50 h hydroprocessing run 4) Oxygen content in hydrotreated product is consistently less than 2 wt.% over time on stream. Key fuel properties include octane number, vapor pressure, density, and boiling point ranges. Threshold criteria that must be met for consideration are oxidative stability (>960 minutes), miscibility with diesel or gasoline and a total acid number <10. **1.5-L sample upgraded to gasoline and diesel range hydrocarbons. SIMDIST and NOISE analysis completed on the product.**

Project Activities - Descriptive Narrative of Completed Tasks

Task 1: Biomass Feedstock Preparation, Handling, and Analysis

ADM prepared 4 tons of corn stover that was chopped to 0.5" top size and bagged in supersacks. Twenty sacks of corn stover were delivered to RTI and stored in the covered outdoor biomass storage area. ADM also provided ~1,500-g of lignin-rich material derived from corn stover for microreactor testing.

An additional 4 tons of loblolly pine sawdust was procured from Iowa State University who are partners with us in the DOE/EERE National Advanced Biofuels Consortium being managed by NREL and PNNL. This material was delivered on June 17, 2013. The feed system (bulk bag discharge unit and biomass feeder) was successfully tested and commissioned with the pine sawdust.

Biomass Feed System Design and Operation

The biomass feeder for the 1 ton/day catalytic biomass pyrolysis unit was designed by T.R. Miles Technical Consultants, Inc. They have a long history designing biomass feed systems for pilot- and demonstration-scale biomass combustion, gasification, and pyrolysis systems. The feeder is a dual lock hopper system that will be used to continuously feed purged biomass into the mixing zone of the catalytic biomass pyrolysis reactor.

Biomass is continuously loaded into the top section of the feeder at a rate of up to 100 lbs/hour through a flexible screw that connects the bulk bag discharger to the feeder. On demand, the top valve opens to fill the intermediate hopper. Nitrogen is used to purge this biomass charge before it is dropped into the 1.8 cu. ft. feed chamber. The volumetric feed rate is controlled by adjusting a set of dosing screws that meter the biomass onto a water-cooled constant speed transfer screw. The transfer screw delivers the biomass to the center of the mixing zone where it contacts the hot catalyst solids and pyrolyzes. Based on the volume of the bottom bin and a projected biomass density of 15-30 lbs/cu. ft. each biomass load can last up to 15-20 min. A cooling water jacket surrounding the screw feeder will be used to limit temperature increase.

Feeder testing was performed to correlate motor settings to feed rates for both filling the feeder system and feeding biomass to the reactor. A 1/8" top-size loblolly pine material was used for initial feeder testing and catalyst testing. The material has a nominal bulk density of 17 lb/ft^3. Two motor systems are used to convey biomass from the ground into the reactor. First a conveyor motor (M120) lifts biomass from a ground level hopper to the loading bin on the top of the feeder system. At the bottom of the feeder two motors M160 and M170 controls screws that deliver biomass to the reactor.

The feed rate to load the feed system using the M120 conveyor motor was determined by loading the ground floor hopper and running the M120 motor at a set output for 5 minutes. The screw was prefilled with biomass before testing by running the M120 motor at 50% output till a steady output of biomass at the top of the screw was achieved. Each motor setting was tested multiple to consistent measurements. Measurements at specific settings varied by no more than 2%. Figure 1 shows the linearity of the conveying rate of the screw based on the M120 motor setting. Operating the M120 motor at 75% requires a 3 minute cycle to fill the loading bin of the feeder system. When different biomass feed stocks are used it is anticipated that these correlations can be adapted based on the differences in material bulk density and will be validated.

The biomass feed rate to the reactor was determined by removing the bottom flange to the reactor and collecting biomass feed to the reactor from the feeder system. Two screws control the feed from the bottom feed bin of the feeder system to the reactor inlet. M170 controls 4 screws that drop biomass from the bin on to a single screw controlled by M160 that delivers biomass to the reactor. 2 ft^3 of biomass was loaded into the feed bin and M 160 and M170 were operated at 25% till a steady stream of biomass was being fed to the reactor indicating the screw was filled. The feed rate from various M160 and M170 settings combinations was determined with repeats as done for the conveyor motor. Figure 2 shows the determined feed rates as a function of each motor setting. Figure 2 indicates that the feed rate of the 1/8"

loblolly pine is controlled by the M160 motor setting as at the same M160 motor setting little variation is observed with different M170 setting. A 100 lb/hr feed rate can be achieved with the 1/8" loblolly pine at an M160 setting of 22%. While the M170 setting did not significantly change the feed rate operating at a M170 setting greater than the M160 setting on occasion lead to binding around the screw. Operational procedure will be to operate both at the same setting.

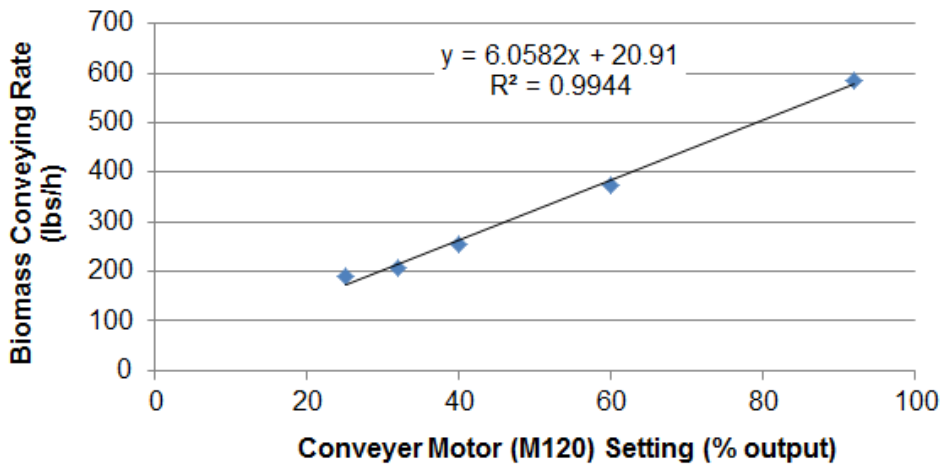


Figure 1. Loblolly biomass conveying rate based on M120 motor setting.

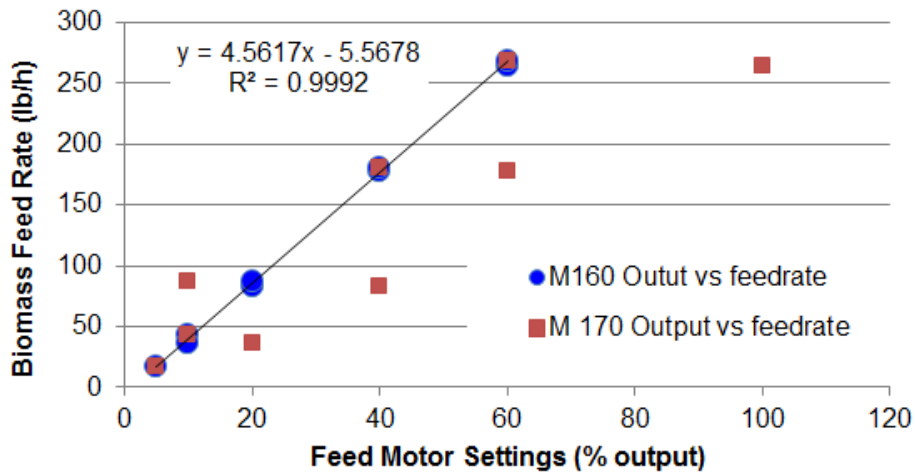


Figure 2. Biomass feed rates to the reactor based on the M160 or M170motor setting.

Task 2: Catalyst Development

A key goal of the catalyst development is to identify important functions that are needed to produce a stable bio-crude via catalytic biomass pyrolysis. These catalyst functions are as follows:

Hydrogen production from steam, WGS, and oxygen storage: Catalytic redox was a key function of the proposed catalytic biomass pyrolysis concept. Pyrolysis vapors contain significant amounts of water and carbon monoxide. These byproducts could be converted into hydrogen via water oxidation and water gas shift (WGS) reactions. This additional hydrogen could be used for hydrodeoxygenation or hydrogenolysis leading to increased overall deoxygenation by increasing the C/H ratio in the product and avoiding the need for an additional mild hydrotreatment step. It will lead to increased energy efficiency and liquid yield. Iron oxides and iron oxide solid solutions are the primary materials under consideration for the redox function.

Decarboxylation, dehydration and cracking: Acidic, high surface area catalysts have been used for hydrocarbon cracking and the recent literature suggests that such solid acids catalyze both C-C and C-O bond breaking. As in fluid catalytic cracking (FCC) processing, strong acid catalysts tend to produce coke precursors that lead to carbon deposition on the catalyst. Catalyst regeneration is achieved by using oxygen/air to oxidize surface carbon.

Hydrogenolysis: Hydrogenation activity is likely to be an important function in catalytic biomass pyrolysis. Hydrogenation can take the two forms: (1) hydrogenolysis of oxygenates to water and (2) hydrogenation of unsaturated carbon-carbon bonds in the pyrolysis vapor to prevent coke formation. The latter selectivity is desired if deoxygenation can be accomplished by cracking catalysis, redox catalytic action, or other direct deoxygenation reactions that eventually lead to production of carbon oxides.

A total of 33 different catalysts were prepared and tested as part of this task. Results for the best performing catalyst, designated RTI-A9, will be presented as representative to illustrate the methods and techniques developed to screen and test materials. The RTI-A9 catalyst achieved the desired activity and efficiency goals for catalytic fast pyrolysis. Consequently, the RTI-A9 catalyst has been identified as the catalyst for scale-up testing in the 1 ton per day (TPD) catalytic fast pyrolysis unit designed, fabricated, and installed as part of this project.

Catalyst Preparation and Characterization

Catalyst development efforts were devoted to understand the relationship between deoxygenation activity and acid properties of the catalyst. It is well known from the literature that the acidic properties of metal oxide based solid acid catalysts can be tailored by changing the active component loading, calcination temperature, support oxide and by adding different metal and metal oxide promoters. Catalyst acidity is defined by acid strength, acid site density and nature (Bronsted/Lewis). In this task, a series of metal oxide promoted catalysts on various supports were synthesized. The objective was to systematically vary the active metal loadings and preparation methods (incipient wetness, co-precipitation, binders, and calcination temperature) to determine if the deoxygenation activity could be controlled and optimized. Deoxygenation activity of these catalysts was evaluated in an automated model compound screening reactor and a microfluidized bed catalytic pyrolysis reactor.

The catalysts prepared within this task were characterized by powder XRD for elemental composition, BET for surface area, and NH_3-TPD and pyridine FT-IR for acid strength and site density. Both fresh and spent samples of catalysts were analyzed to understand changes in the catalyst properties during operation and the nature of the steady-state catalyst.

The details of the catalyst formulations, characterization, and deoxygenation activity are proprietary and are currently being captured in several patents. Key findings from the catalyst characterization suggest that optimizing dispersion of the active metals is critical for deoxygenation activity and acid strength is correlated to coke formation, as expected. The pyridine-FTIR results also confirm that the Bronsted acid sites have higher acid strength compared to the Lewis acid sites and are consistent with the ammonia-TPD results. Low coke formation on the best performing catalyst could be attributed to moderately strong Lewis acid sites.

Catalyst screening with Model Compounds

Model compound studies are a convenient way to simplify complex chemistries and provide insight into deoxygenation mechanisms/pathways on selected catalysts under controlled conditions. Guaiacol is a compound from biomass pyrolysis with functional groups similar to those present in a many of products from biomass pyrolysis oils. These model compound studies are used to screen catalysts and facilitate the development of new catalysts and optimum catalyst formulations. In addition, understanding transient behavior of deoxygenated product formation and coke generation rate is critical for the design of a continuously circulating lab-scale catalytic pyrolysis unit.

An automated microreactor system was developed at RTI for catalyst screening under variable process conditions relevant for cayalytic biomass pyrolysis. The automated microreactor system is self-contained in a cabinet style enclosure with a touch-screen user interface. The major components including the reactor hotbox enclosure, mass flow controllers, and controller hardware are all housed in the mobile cabinet. A command sequencer allows the system to be programmed to run many reduction, reaction, and oxidation steps at different conditions. The system can also be programmed to run many reaction/regeneration cycles to evaluate the long-term catalyst activity and stability. A picture of the automated system is shown in Figure 3.

A vaporized bio-oil model compound and hydrogen are co-fed over a fixed bed reactor containing hydrodeoxygenation catalyst at elevated pressures and temperatures. Guaiacol and anisole were selected as model compounds for the hydrodeoxygenation reaction because both are thermally-stable liquids that vaporize under hydropyrolysis conditions and contain oxygen in the form of methoxy and hydroxyl functional groups that commonly occur in pyrolysis vapor compounds.

Liquid feed is pumped at 7 to 20 µL per minute with a syringe pump to a vaporizer and mixed with hydrogen co-feed, nitrogen as a diluent, and argon as an internal standard to make up the reactant mixture with a total flow rate of 50 – 400 SCCM. The reactant mixture is directed to a fixed bed reactor with 0.4 to 2.0 g of catalyst pellets maintained at bed temperatures between 300 – 500 °C. These conditions correspond to a ratio W/F of 0.3 to 4.3 h where, W/F is defined as the ratio of catalyst mass (g) to mass flow rate of liquid feed (g/h).

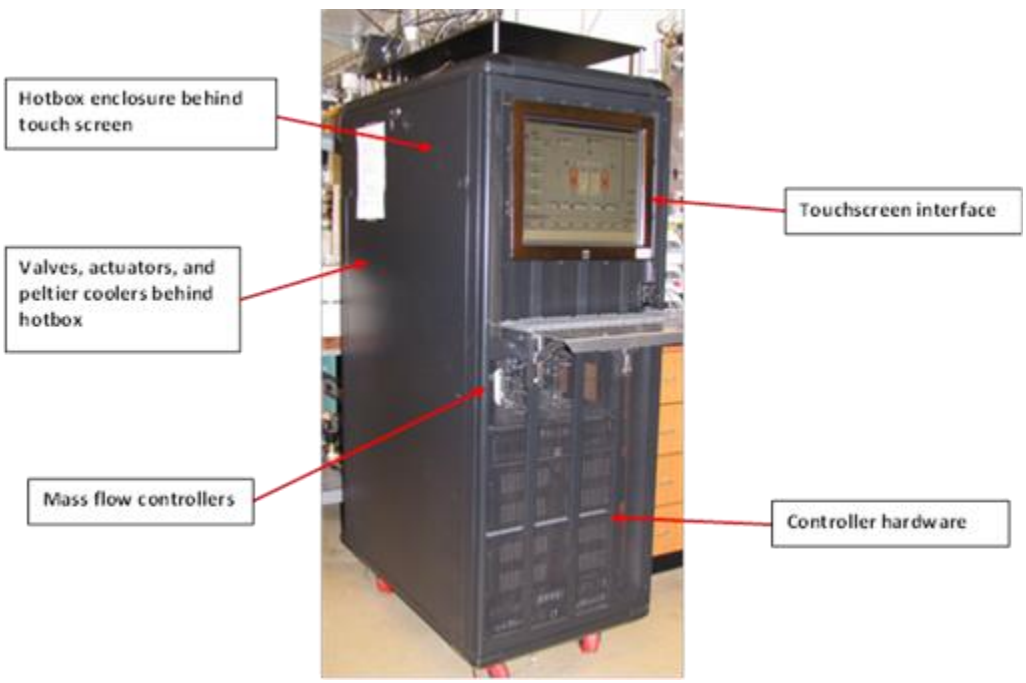


Figure 3. Picture of automated system

A slipstream of the reactor effluent, maintained at elevated temperatures to prevent product condensation, is sampled directly after the reaction by an online residual gas analyzer (RGA). The RGA is equipped with a quadrupole mass filter and an open ion source that allow it to detect ppm level concentrations at 1E-06 mbar. Selected mass/charge (m/z) ratios from each chemical compound in the reaction system were calibrated for mole % using argon as an internal standard with known calibration standards. The remaining product stream is sent to a peltier cooler to collect condensable liquids, and permanent gases are directed to a back pressure regulator before vented.

A standard test program has been developed for this system to screen the catalysts described above. The test program will include testing each catalyst over varying conditions to evaluate deoxygenation

activity and understand the coking behavior of the catalyst. A standard test protocol that is being considered includes the following steps:

1) Any required preconditioning of the catalyst
2) Testing at 400°C and a GSHV of 5000hr^{-1} for 1 hr followed by oxidative removal of the coke and reduction if required.
3) Testing at 450°C and a GSHV of 5000hr^{-1} for 1 hr followed by oxidative removal of the coke and reduction if required.
4) Testing at 500°C and a GSHV of 5000hr^{-1} for 1 hr followed by oxidative removal of the coke and reduction if required.
5) Testing at 450°C and a GSHV of 3000hr^{-1} for 1 hr followed by oxidative removal of the coke and reduction if required.
6) Testing at 450°C and a GSHV of 5000hr^{-1} for 1 min followed by oxidative removal of the coke and reduction if required.
7) Testing at 450°C and a GSHV of 5000hr^{-1} for 5 min followed by oxidative removal of the coke and reduction if required.
8) Testing at 450°C and a GSHV of 5000hr^{-1} for 10 min followed by oxidative removal of the coke and reduction if required.
9) Testing at 450°C and a GSHV of 5000hr^{-1} for 30 min followed by oxidative removal of the coke and reduction if required.
10) Testing at 450°C and a GSHV of 5000hr^{-1} for 1 hr with no oxidation in order to recover a spent catalyst for analysis.

In this sequence, steps 2-4 explore the effect of reaction temperature while steps 3 and 5 compare the effect of gas hourly space velocity. Steps 3 and 6 through 9 will be used to measure coke formation as a function of time. The final step will serve to understand any changes in the catalyst behavior through the series of cycles by comparison with step 3. The catalyst will be left in a spent state for analysis. Other parameters may be added as warranted. The automated operation of the new medium throughput screening will make it possible to complete this catalyst testing sequence in 1 day compared to over a week of effort with the manual test system that has been used. Results from medium throughput screening in the automated microreactor will be validated and correlated with catalyst performance in the fluid bed catalytic biomass pyrolysis reactor system.

To illustrate the effectiveness of RTI-A9 for deoxygenation of biomass pyrolysis vapors, guaiacol (2-methoxy phenol) was introduced into a fixed bed microreactor packed with the catalyst. Reactions were carried out at 400-500 °C with a LHSV of 0.3 h^{-1}. Nitrogen was used as a carrier gas with a flow rate of 100 sccm. Products were determined by online mass spectrometer. Coke was determined by products during an oxidation step to regenerate the catalyst. Products during the oxidation step were also monitored by an online mass spectrometer. Table 1indicates the product yield from the deoxygenation of guaiacol with RTI-A9 at varying temperatures. Product monitoring by mass spectrometer gave no indication of additional products.

As can be seen in Table 1, reaction temperature had an effect on guaiacol conversion and deoxygenated product distribution. Conversion increased from 79% (at 400 ºC) to >99% (at 500 ºC). Water content in the product also increased with increasing temperature, indicating that the dehydration activity of the catalyst is increasing with temperature. Phenol is a major product at all reaction temperatures, along with other deoxygenated products.

Removing the methoxy group from guaiacol is the most facile deoxygenation pathway. At lower temperatures and conversion phenol is the dominate product indicating loss of the methoxy group from guaiacol. The other main products are coke deposits and water. At more severe conditions, the guaiacol conversion increases, additional oxygen is removed as CO2, and the benzene/toluene yields increase significantly. Formation of benzene and toluene may result from the deoxygenation of the phenol product. This is observed when the temperature is increased to 500°C and benzene and toluene yields

increase at the expense of the phenol. The production of water, CO, and CO2 indicate RTI-A9 is able to catalyze deoxygenation through multiple pathways, dehydration, decarboxylation, or decarbonylation.

Table 1. Guaiacol Deoxygenation Results with RTI-A9 (7ul/min feed, 100sccm diluent)

Temp (°C)	Conv. (%)	Product Yield (Weight %)										Mass Balance
		H_2O	CO_2	Benzene	Toluene	Phenol	Cresol	CO	CH_4	H_2	Coke	
400	78.9	15.5	0.7	1.4	2.7	17.0	8.9	0.0	0.3	0.1	29.6	99.0
450	96.2	21.0	1.6	8.0	4.9	22.2	6.1	0.0	0.7	0.2	35.3	104.1
500	99.3	22.5	3.0	17.3	3.5	14.2	2.6	2.5	1.6	0.4	38.2	106.5

Long-term Catalyst Cycle Test

During catalytic fast pyrolysis, coke deposits on the catalyst surface need to be periodically removed in an oxidation step to regenerate the catalyst and recover deoxygenation activity. Over time, catalyst deactivation can occur if the carbon deposits cannot be effectively removed or if local hot spots form during repeated regeneration that causes catalyst sintering. The automated microreactor system was utilized to evaluate long term catalyst stability with respect to repeated deoxygenation and regeneration steps. Guaiacol conversion over the RTI-A9 catalyst was measured over 100 reaction/regeneration cycles. 2-g of catalyst was loaded into the fixed bed reactor that was maintained at 450°C. During the reaction step, 7µl/min of guaiacol was fed with 100 sccm of 20% Ar in N_2 over the catalyst for 60 minutes. The regeneration step followed with 50 sccm of air and 50 sccm of N_2 flowing over the catalyst for 35 minutes to oxidize any coke formed on the catalyst. These reaction conditions established a high initial activity (>90% conversion) without reaching complete conversion. This cycle was repeated 101 times with the same catalyst loading. The testing was completed over 12 days where the last 6 days were continuous automated operation of the MTP system with only periodic checks by the operator.

Figure 4 shows a screen shot of the MS data from 6 days of testing covering 75 cycles. Figure 5 shows the detail of a single cycle from the extended testing. The change in the argon (40) signal, caused by valve switching, provides a time stamp in the data to indicate the beginning of new reaction and regeneration segments. Guaiacol conversion is determined from the integrated areas of the MS signal areas as shown in the following equation:

$$\text{Guaiacol Conversion} = 100\% * \left(1 - \frac{\text{Area of Guaiacol during Reaction} * \text{Guaiacol MS Response Factor}}{\text{Area of Guaiacol in baseline for equal reaction time} * \text{Guaiacol MS Response Factor}}\right)$$

High guaiacol conversion was maintained for the duration of the extended testing indicating no observable loss of initial activity after repeated catalyst regeneration. The conversion data are plotted in Figure 6. Over the first ten cycles, the average conversion was 91.9 % and over the last 10 cycles, the average conversion was 91.6%. 10 cycles corresponds to approximately 1 day. The standard deviation of guaiacol conversion during the extended testing was 1.5% meaning the difference between conversion on the first and on the last day is insignificant. If catalyst deactivation caused a decrease in guaiacol conversion of 0.5% per day over the 10 day period, the conversion would have dropped 4%.

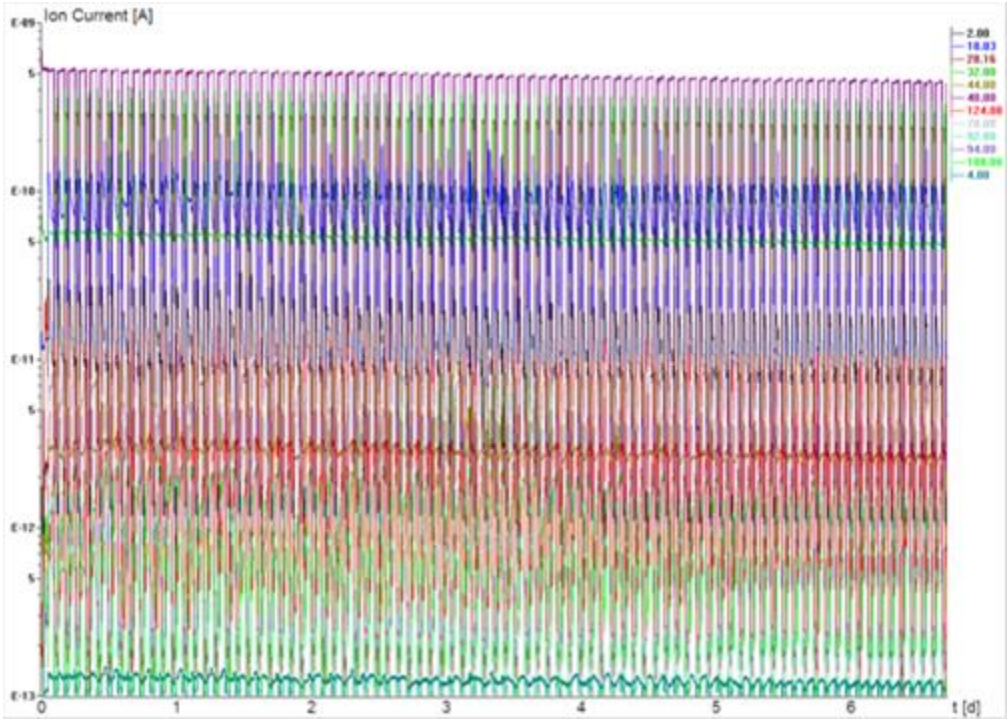


Figure 4. MS data for 6 days (75 reaction/regeneration cycles) of guaiacol deoxygenation with RTI-A9 at 450°C.

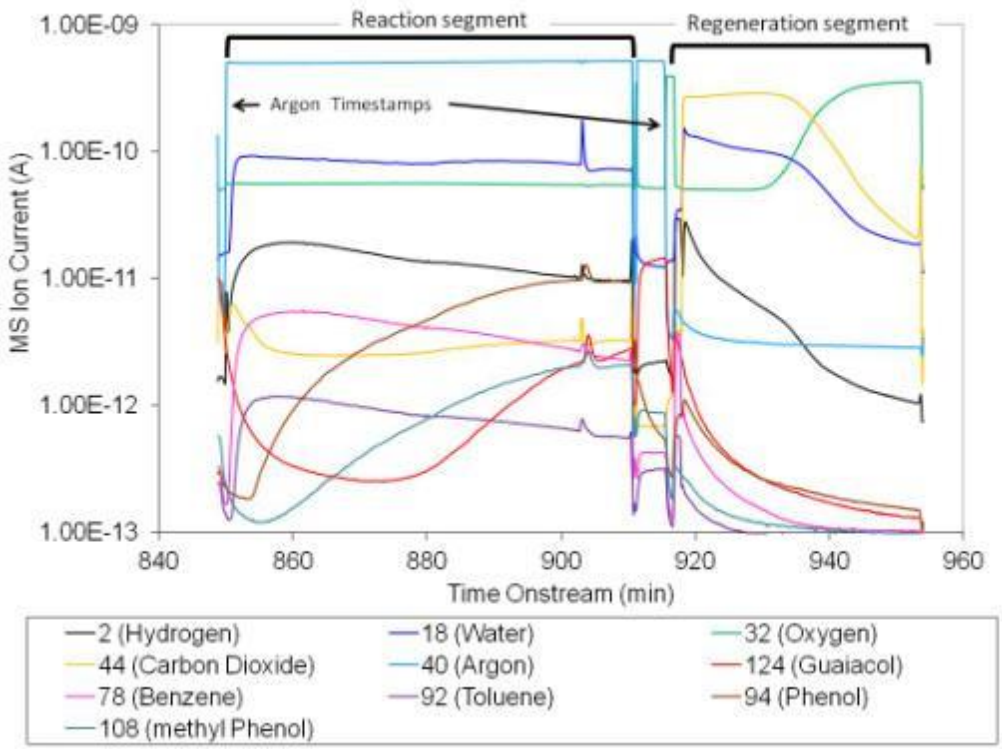


Figure 5. Single cycle MS data from extended 100 reaction/regeneration cycles for guaiacol deoxygenation with RTI-A9 at 450°C.

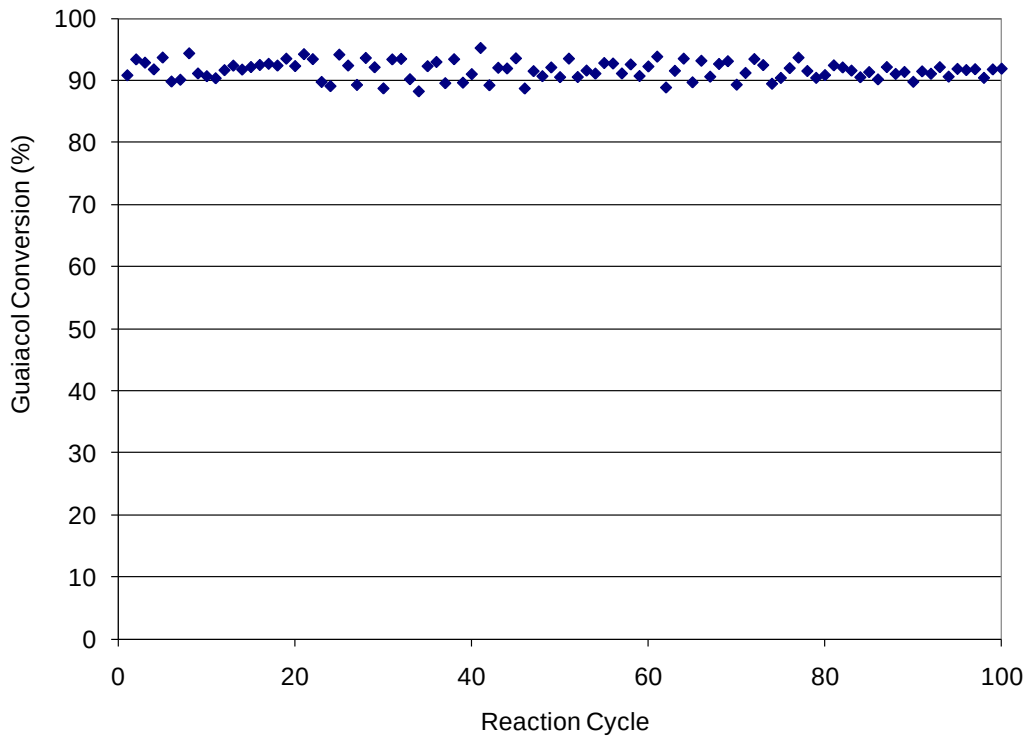


Figure 6. Guaiacol Conversion for each cycle during extended testing of guaiacol deoxygenation with RTI-A9 at 450°C.

Catalyst Testing with Biomass

A bench-top fluidized bed reactor system for investigating catalytic biomass pyrolysis is shown in Figure 7. The fluidized-bed reactor is a 1″-diameter quartz tube reactor externally heated in a furnace. An inert bed of silicon carbide acts as a support for the catalyst bed through which a ¼″-diameter tube injects the solid feed into the bottom of the catalyst bed. The exit of the reactor has a disengagement zone for solids collection and a condensation train for liquids collection. An online micro GC system is used to measure permanent gas composition.

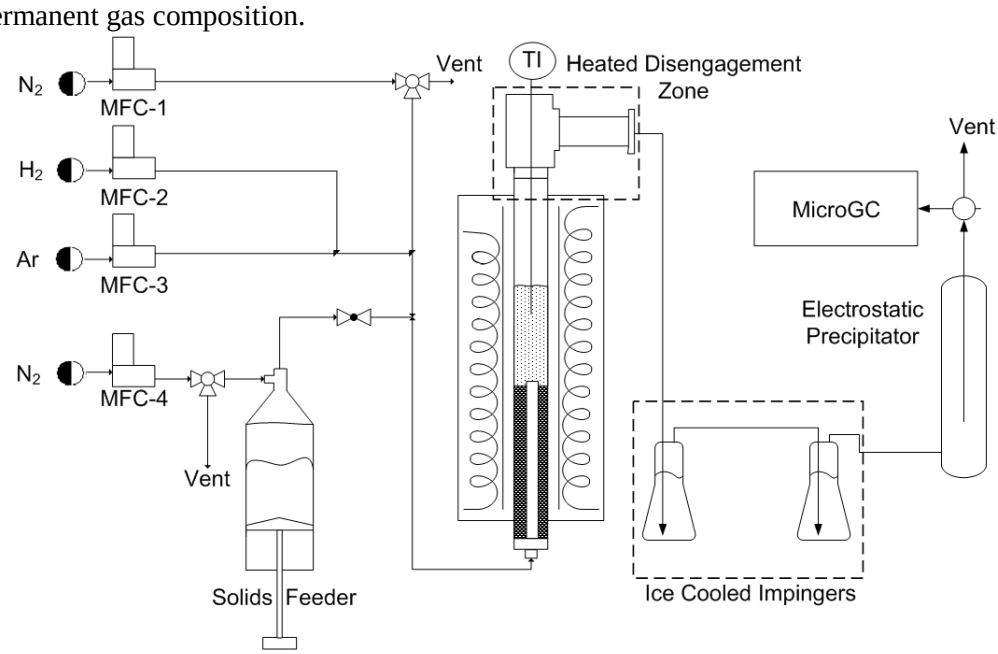


Figure 7: Process flow diagram of RTI's bench-top 1″-diameter fluidized bed system.

In the feed system, the biomass is loaded in a syringe modified with an adapter that injects a sweep-gas and allows the exit of an entrained-biomass stream. The biomass feed rate is controlled by adjusting the sweep-gas feed rate and the head space in the syringe. The reactor operates at temperatures between 350 and 600°C, with 1 to 2 SLPM gas feed rate and a 0.5 to 1.5g/min biomass federate. The reactor holds 25 to 60 g of catalyst that provides a total residence time in the reactor between 1 to 2 sec. Biomass is fed directly into the catalyst bed where pyrolysis takes place in the presence of the catalyst. The condensation system consists of an impinger cooled in an ice bath followed by an electrostatic precipitator and a second impinger cooled in a dry ice/acetone bath. Mass closures are consistently around 92 to 95% in this system. The product yields from biomass catalytic pyrolysis with numerous catalysts at a wide range of process conditions have been measured in this system.

Fast pyrolysis generates a bio-oil with an oxygen content similar to the initial feedstock. Table 2 details the characterization of a white oak feedstock and the liquid product and char from fast pyrolysis of the white oak. Table 3 details the product distribution for the fast pyrolysis of white oak and catalytic fat pyrolysis with RTI-A9. The liquid product is a mixture of the water and organic liquids. In fast pyrolysis this typically remains a single phase for white oak but in catalytic fast pyrolysis separates into an aqueous phase and organic phase. Each phase contains a fraction of both the water and organic liquid yields.

Table 2. Fast Pyrolysis White oak characterization of feedstock, liquid products, and char.

	Baseline Bio-Oil	Biomass (White Oak)	Baseline Char
Proximate Analysis (wt%)			
Volatile Matter	65.9	75.2	25.5
Fixed Carbon	8.1	17.4	68.0
Ash	0.07	0.39	4.32
LOD	26.00	7.0	2.3
Higher Heating Value (BTU/lb,dry)	9570	8250	12200
Ultimate Analysis (wt%, dry)			
Carbon	55.64	49.82	77.11
Hydrogen	6.18	5.86	3.07
Oxygen (by difference)	37.97	43.81	15.22
Nitrogen	0.12	0.10	0.27
Sulfur	0.01	0.01	0.02
Ash	0.07	0.39	4.32

Catalytic fast pyrolysis in the 1” fluidized bed reactor with RTI-A9 produced a liquid product whose dry oxygen content is below 20 wt% a significant reduction from the fast pyrolysis bio-oil. The catalytic fast pyrolysis results were consistent with the model compound testing in that evidence of dehydration, decarbonylation, and decarboxylation are all presented by increases in the yields of H_2O, CO, and CO_2. The organic product also has improved properties by a greater than 60% reduction in the total acid number indicating a reduction in acids and less corrosive nature of the product than fast pyrolysis oil.

Table 3. Product distribution from white oak fast pyrolysis and catalytic fast pyrolysis with RTI-A9.

	Baseline	RTI-A9
Solids (wt%)	14.3	19.8
Gas (wt%)	11.6	23.9
Water (wt%)	18.4	28.7
Organic liquids, dry (wt%)	49.4	24.8
Bio-crude Composition (wt%)		
C	55.6	72.8
H	6.2	7.2
O	**38.0**	**19.9**
Gas composition (vol%)		
H_2	1.5	7.7
CO	25.4	37.1
CO_2	42.1	32.6
CH_4	3.5	10.6
C_{2+}	27.4	12.0

Table 4. Compositional comparison of liquid products from fast pyrolysis andRTI-A9 catalytic fast pyrolysis of white oak by GCxGC-TOFMS analysis

	Fast Pyrolysis	Catalytic Fast Pyrolysis
Catalyst	None	RTI-A9
Compound classes expresses in spectra area percent		
Acids	1.8	2
Furans	5.4	6.3
Ketones	11.7	11.5
Phenols	4.7	14.1
Methoxyphenols	8	14.1
Dimethoxyphenols	33.1	12.6
Polyoxygen compounds	5.3	ND
Sugars	14.4	0.6
Hydroxy-PAHs	ND	15.7
Paraffins	0.2	0.8
monoaromatics	0.8	1.5
Fluorenes	ND	1.9
Phenanthrenes	ND	2.8
Pyrenes	ND	2.2
Higher PAHs	ND	4.9
Unknown	11.1	4.2

The chemical composition of the bio-crudes from fast pyrolysis and catalytic fast pyrolysis were characterized using GCxGC-ToFMS (Gas chromatography x gas chromatography - Time of Flight Mass Spectrometer) analysis. Table 4 details the chemical composition differences between the two bio-crudes. Significant reduction in sugars, dimethoxyphenols, and polyoxygen compounds are observed. Conversely, the amount of phenols and deoxygenated aromatic products increased significantly compared to the baseline bio-oil compositions. Catalytic pyrolysis with the RTI-A9 catalyst clearly produces a bio-crude that has higher concentration of deoxygenated products.

Catalytic fast pyrolysis with RTI-A9 produces a bio-oil with lower oxygen content that has improved properties such as better thermal stability and lower acid content however the mass yield is lower. Baseline bio-oil has poor processability because the residual from reheating leads to significant carbon, and therefore energy, loss during upgrading to fuels. While the energy recovery in the bio-oil from the biomass feedstock is high, when it is hydroprocessed a significant energy loss occurs. Catalytic fast pyrolysis may have lower energy recovery in the bio-crudes but these intermediates appear actually easier to process. The goal is to optimize energy recovery throughout the entire process from bio-crude production by catalytic fast pyrolysis through hydroprocessing to finished fuel.

Go/No Decision Point

A series of targets were defined for the catalytic biomass fast pyrolysis process to demonstrate the technical potential of this technology. These targets form the basis the Go/NoGo decision point for the 7th project quarter. The milestone targets and the experimentally measured parameters are shown in Table 5. The results in Table 5 were determined from catalytic oak pyrolysis with the RTI-A9 catalyst in the micro-fluidized bed reactor. The reported results are the average of three repeated tests. The standard deviation in the results is presented in parenthesis. These targets were achieved through a combination of improved catalyst performance and process optimization of the micro-fluidized bed reactor system. Repeated experimentation revealed an inverse relationship between oxygen content and bio-crude yield and a correlation between lower oxygen content and thermal stability. Consequently, process optimization involves maximizing yields while minimizing oxygen content to improve bio-crude thermal stability.

Table 5. Progress towards Go/No Go milestone targets

Criteria	Go/No Go Targets	Experimental Results
Energy efficiency	42% of input energy	44.8% (2.7)*
Oxygen content	<20 wt%	19.9 wt% (1.6)*
Thermal stability	<20 wt% residuals	18.3 wt% residuals
Solids yield	15-20 wt%	19.8 wt% (1.0)*
Mass closure	>90 wt%	96.7 wt% (1.7)*
**std. dev. in measurements from 3 trials*		

Improved bio-crude properties were also the focus of continued catalyst development. The goal was to lower bio-crude oxygen content while maintaining the energy efficiency. Several modifications to the RTI-A9 catalyst were tested. The RTI-A9-3 catalyst demonstrated the highest deoxygenation activity. Catalyst improvements included:

- A reduction in the amount of binder used in the formulation. This increased the number of active sites for deoxygenation evidenced by the fact that the bio-crude oxygen content was reduced from 24 wt% to 19wt% while maintaining >40% energy efficiency.
- An initial deactivation to yield an equilibrium catalyst. A catalyst break-in period was observed for the RTI-A9 catalyst in which coking and gas yield decreased while bio-crude yield increased over the first couple trials with a fresh catalyst batch. Using an equilibrated catalyst increased bio-crude yield by 2 wt% and the improved deoxygenation so the resulting energy efficiency was 44.8%.

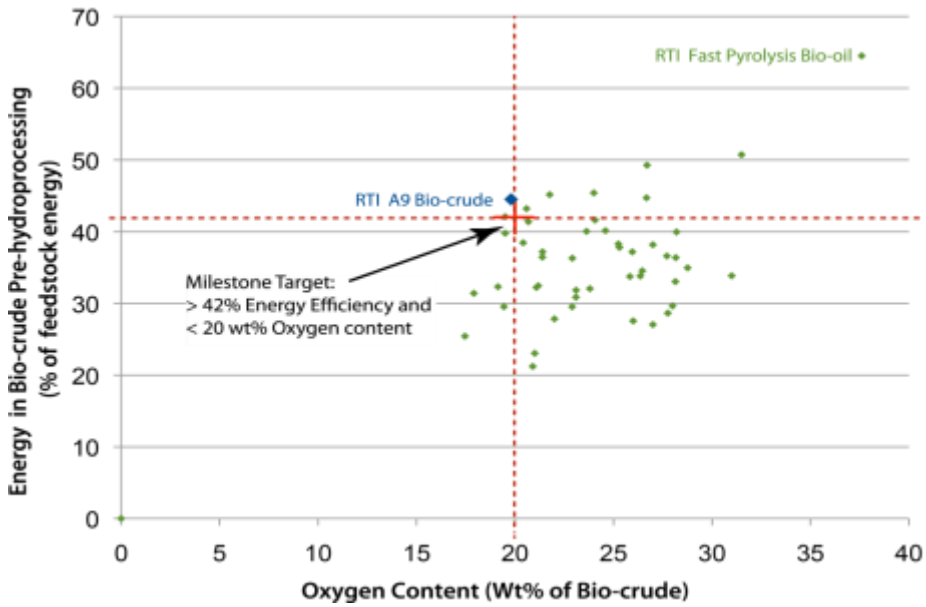


Figure 8. Energy efficiency of the bio-crude (in terms of % of feedstock energy) compared with the oxygen content of the bio-crude

Figure 8 shows the results from several months of catalyst screening and process optimization that allowed the production of several bio-crudes that met or exceeded the target oxygen content while still maintaining over 42% of the feedstock energy. Clearly, lower oxygen containing bio-crudes can be produced at the expense of yield and energy efficiency. The objective of future efforts is to continue to improve the catalyst to increase deoxygenation activity while minimizing char and coke formation. Current solids yield (char and coke) for the target case is 19.8 wt%. Maintaining a larger percentage of that carbon in the bio-crude product has the potential to improve energy efficiency significantly. The future bench-scale (~ 5-10 kg/hr) catalytic biomass pyrolysis system (currently being designed) will have lower surface to volume ratio so wall effects will be reduced and heat transfer can be optimized to better control the catalytic biomass pyrolysis process to lower char yields. Optimizing the catalyst to biomass ratio in the bench-scale system is another strategy for reducing coke formation.

Bio-crude stability is a well-documented technical challenge for upgrading these liquid intermediates into biofuels. The oxygen containing compounds (acids, aldehydes, ketones, and phenolics) in bio-crude tend to be very reactive and can polymerize as bio-crude is reheated for upgrading. At the very least, as bio-crude viscosity increases, process operability is adversely affected. Ultimately, solids form and conversion efficiency of bio-crude to biofuels is significantly reduced.

A thermal stability metric based on residual losses after batch distillation of bio-crude was introduced last quarter. One role of the catalyst in catalytic biomass pyrolysis is to reduce the concentration of the reactive oxygen containing compounds in bio-crude. This lowers the oxygen content of bio-crude and also improves the bio-crude thermal stability. Figure 9 shows the measured residual losses as a function of bio-crude oxygen content based on results from screening a series of different catalysts under varying conditions. There is a definite trend for higher revaporization efficiency at lower bio-crude oxygen content. Bio-crude produced with the RTI-A9 catalyst has less than 20 wt% oxygen and greater than 80% revaporization efficiency while maintaining high energy efficiency.

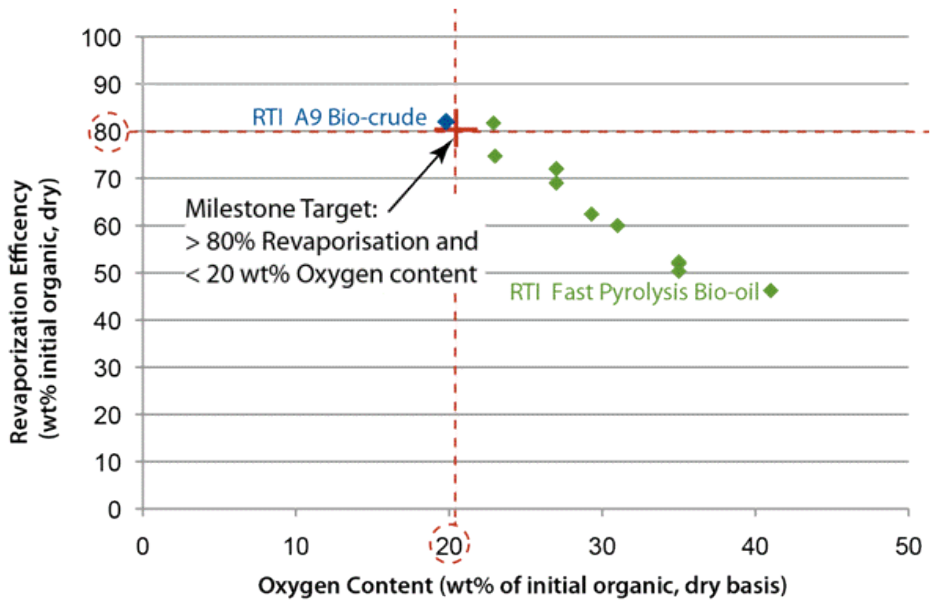


Figure 9. Revaporization efficiency of bio-crudes based on their oxygen content

Supporting Information

Solids content is an important physical parameter for using bio-crude in stationary power applications such as compression ignition (diesel) engines and turbines. The solids content of the bio-crudes produced in the microfluidized bed reactor were measured based on the ethanol insoluble content of the material recovered with a 0.2µm filter. 1.3g of liquid product from catalytic fast pyrolysis with the RTI-A9 catalyst was dissolved in 25 ml of ethanol and filtered. The beaker was then rinsed with another 25ml of ethanol which was also passed through the filter. The filter was dried and weighed. The bio-oil solids content was determined by the mass increase of the filter. Duplicate samples were tested. The solids content of the bio-oil from catalytic fast pyrolysis with the RTI-A9 was determined to be 0.11 wt% of the total liquid product.

The energy content of the bio-crudes produced in this project were not measured directly but determined from a published correlation between the elemental composition of a material, on a wt% basis, and the higher heating value (HHV). [S.A. Channiwala and P.P. Parikh, A unified correlation for estimating HHV of solid, liquid and gaseous fuels, Fuel 81 (2002), pp.1051-1063] given as Equation 1. This correlation was derived from over 200 different samples and had an absolute average error of 1.45%.

Equation 1:

$$HHV(\text{in Btu/lb}) = 429.9*(0.3491*C + 1.1783*H - 0.1034*O - 0.0151*N + 0.1005*S - 0.0211*Ash)$$

Figure 10 compares calculated HHV's with experimentally measured values for a wide selection of materials used in RTI's biomass testing. Values for 27 materials including biomass, chars, fast pyrolysis bio-oils, and catalytic fast pyrolysis bio-crudes were compared. Similar to the published results, a good agreement between the predict HHV from ultimate analysis and measured HHV of several RTI bio-oils was observed. The absolute average error for this comparison was 1.5% which is equal to ~ 150 Btu/lb similar to the ASTM reproducibility limit of the HHV measurement which is ~100 Btu/lb.

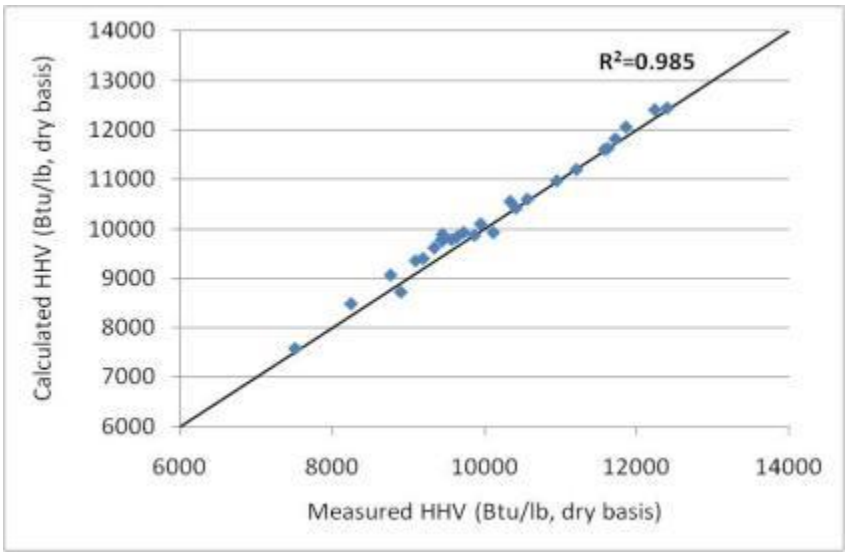


Figure 10. Comparison of Measured HHV and Calculated HHV

Bio-crude Production and Long-Term Catalyst Testing

Preliminary characterization of the bio-crude produced with the RTI-A9 catalyst in the 1" diameter fluid bed reactor indicated improvements in thermal stability, viscosity, and acid content that warranted further hydroprocessing testing. Phillips 66 requires at least 10-L of bio-crude to operate a lab-scale hydroprocessing reactor for a week, long enough to achieve steady-state catalyst activity, to complete their upgrading evaluation planned near the end of the project period of performance. These quantities of bio-crude can easily be produced in the 1 TPD system once it is fabricated and commissioned; however, the project team decided that it would be useful to perform preliminary hydroprocessing tests with blends of bio-crude and petroleum-based hydrocarbons (kerosene or dodecane) to inform the later upgrading tests. Preliminary hydroprocessing of 10% blends would require 1-L of bio-crude.

RTI's bench-scale 1"fluidized bed reactor was not suited for in-situ regeneration and has very limited production capacity. Consequently, RTI converted the entrained flow pyrolysis unit into a 2" fluidized bed system to allow for in situ regeneration and increase bio-crude production capacity by a factor of 4.

The system was designed to behave like the 1" fluid bed by maintaining parameters such as catalyst to biomass ratio, bed height, disengagement area, and linear velocity of the gases. A process flow diagram of the system is shown in Figure 11. The reactor, shown in Figure 12, was fabricated out of 2" tubing using compression fittings. The fluidized bed is designed to hold approximately of 150g of catalyst that produces a static bed height of 2.25" that expands to about 5" during operation. This catalyst loading is compromise between higher total biomass throughput and RTI's catalyst production capabilities. The reactor was also designed with a 20" disengagement zone to minimize catalyst loss by entrainment out of the reactor.

Biomass is delivered from a feed hopper by a dual screw feeder into the inlet gas line where it is pneumatically conveyed into the reactor at a rate of 2 to 4 g/min. The downstream separations are the same as in the entrained flow system and consist of a heated cyclone for char separation, followed by a water cooled condenser, ice cooled impinger, ESP, and a dry ice impinger. Gases are analyzed on stream using an Agilent MicroGC with samples taken every 4 minutes.

Long-term catalyst testing and bio-crude production involved cycles alternating between feeding biomass in an inert carrier gas (nitrogen) and regenerating the catalyst with air to oxidize catalyst coke and char that builds up in the bed. Initially, 150 g of RTI-A9 catalyst was added to the reactor and additional catalyst was added to the bed to make up for catalyst losses due to attrition that formed small particles that entrained out of the bed and captured in the cyclone catch. About 5-10 g of catalyst was recovered and returned to the bed every 65-80 cycles. Biomass was typically fed for 12-15 minutes at an average feed rate of 2.5 to 3.5 g/min. Gas phase products were monitored to determine steady-state

biomass feed and catalyst deactivation. Catalyst deactivation was determined by the change in the CO/CO_2 ratio. The catalyst deactivates as coke deposits on the surface and this is removed by adding dilute air to the fluid bed after the biomass feed is stopped. Up to 8 cycles a day could be completed.

Water generated during the regeneration was not collected and carbon oxide products were quantified by GC analysis to determine coke yields. Liquid and solid products were collected, weighed, and characterized by CHON analysis. The water content of the liquid samples was determined by Karl-Fischer titration.

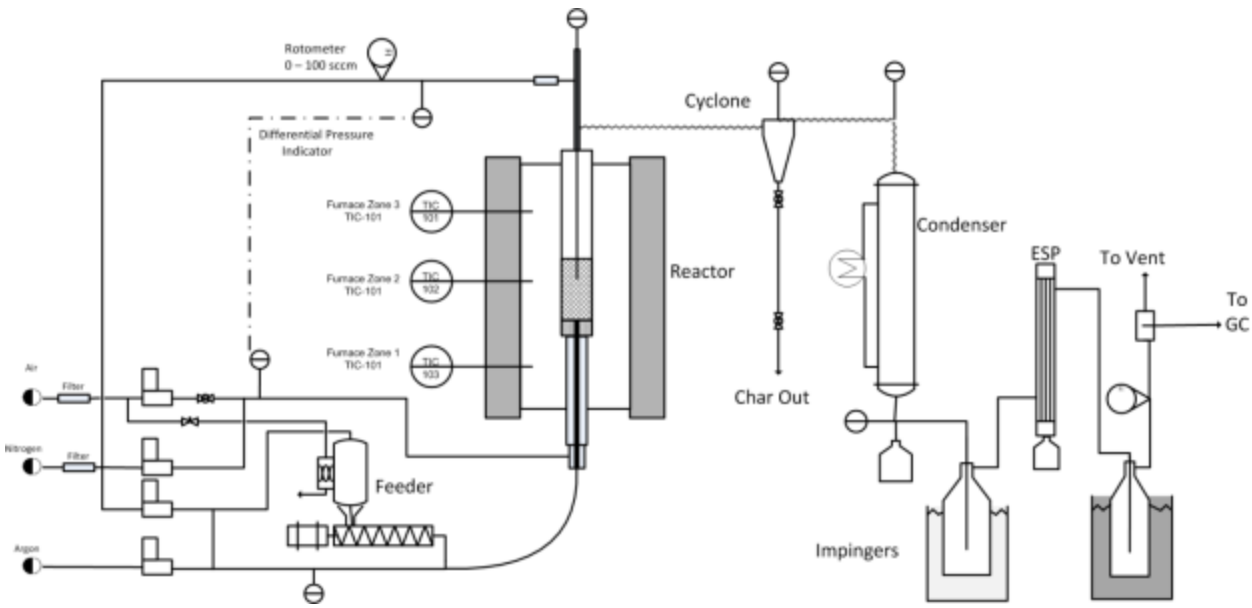


Figure 11. Process Flow Diagram of 2" Fluid Bed Reactor for catalytic fast pyrolysis.

Figure 12. 2" fluid bed reactor that replaced the entrained flow pyrolysis reactor.

Overall, 1.5-L of bio-crude was produced from 14-kg of white oak in 345 reaction/regeneration cycles for a total biomass/catalyst contact time of 87 hours time on stream. A 1-L sample was sent to Phillips 66 for upgrading. The additional 0.5-L was either off-spec material or used for sample analysis. Some product was also lost during post process separation.

Mass balance for the bio-crude production was typically 90% and product quality, as defined by the oxygen content was very consistent over all cycles. The process data at four different cycles during the production are presented in Table 6. The mass balances for this system were slightly lower than in the 1" fluid bed as the products are more dilute in the gas stream increasing the challenge of collecting the condensable liquids such as benzene and phenol.

Table 6. Product distribution from catalytic fast pyrolysis with RTI-A9 at selected cycles

Cycle number	Cycle 15	Cycle 100	Cycle 200	Cycle 345
Product Distribution (wt% of biomass as fed)				
Liquid	41	37.4	35.4	27
Gas	21.9	24.7	30.7	31
Char	8	4.4	3.12	8
Coke	18.4	22.4	20.9	22
Mass Balance	89.3	88.9	90.12	88
Bio-oil Characterization				
C (wt% of bio-oil, dry basis)	74	72	72	75
H (wt% of bio-oil, dry basis)	7	7	7	7
O (wt% of bio-oil, dry basis)	19	21	21	17
Bio-oil water content (wt% of bio-oil)	11	6	5	7
Gas Yield (wt% of biomass as fed)				
H_2	0.05	0.09	0.19	0.24
CO	10.4	8.8	6.0	6.1
CO_2	9.6	13.7	21.8	22.0
CH_4	1.0	1.4	2.0	1.9
C_{2+}	0.9	0.6	0.7	0.7

The liquid yield tended to decrease with time on stream and this correlates with a lower aqueous phase (and water) yield. The organic phase yield, however, was consistent and elemental composition of the organic phase was essentially unchanged over the length of the production. However, a slight shift in chemical composition was observed. In the early cycles, a two phase product was observed while at longer times on stream a third phase was collected in the dry ice impinger after the ESP. This liquid fraction was mostly benzene, toluene, and xylenes. This third phase was miscible with the other organic phase so that when the separate liquid fractions were combined the liquid product resulted in only two phases, a single organic fraction and a single aqueous fraction.

Analysis of the gas composition suggests that the lower water yield may be indicative of increasing water-gas shift activity. A distinct shift in the gas phase products CO to CO_2 is observed with an accompanying increase in the hydrogen concentration as seen in Figure 13. The cause of this is still being investigated as potential ash buildup downstream of the reactor could catalyze the water-gas-shift reaction.

The precise breakdown between char and coke was difficult to determine. The char is about 3-4 times less dense than the RTI-A9 catalyst so char is expected to entrain in the product vapors and readily exit the reactor. Vapors and solids are separated in the cyclone so everything collected from the cyclone catch is assumed to be char. Any carbon remaining in the bed is assumed to be coke and quantified by the CO_2 released during regeneration. However, if char remains in the bed and is also oxidized, the coke yields will be higher than expected. Similarly, the higher char yields at cycles 15 and 345 were caused by a small amount of catalyst that entrained out of the reactor.

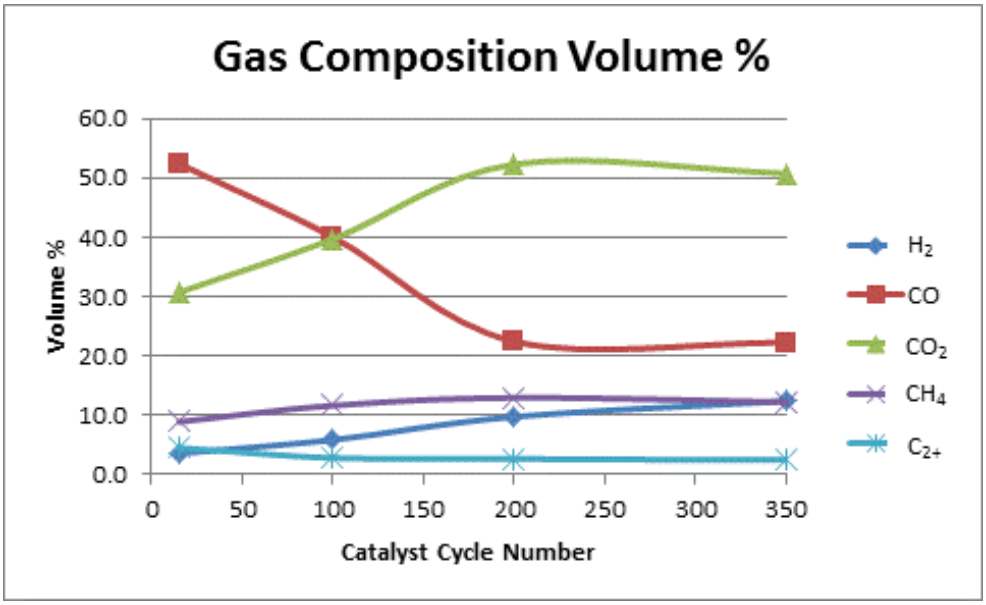


Figure 13. Permanent product gas composition as a function of the number of cycles run.

Catalyst Scale-up

RTI-A9 has been chosen as the catalyst for scale-up and utilization in the 1 TPD catalytic biomass pyrolysis reactor system based on the deoxygenation activity demonstrated in the laboratory. RTI has worked with two suppliers to obtain materials for scale-up and determine the most cost effective option for procuring a catalyst. In this respect, the catalyst is defined as an attrition resistant, fluidizable material that has the same chemical composition as RTI-A9 and comparable performance for catalytic biomass pyrolysis.

Three materials from our scale-up partners were tested by RTI for catalytic fast pyrolysis performance. The final scaled-up material had the desired chemical composition and acidity. However, the desired physical parameters posed a significant challenge. For use in the circulating pyrolysis reactor system, the desired particle size of the catalyst is 50-100 microns with a Davison Attrition Index < 20. To maximize catalyst activity, the desired BET surface area should be > $50 m^2/g$, but surface area and attrition resistance (catalyst hardness) are inversely related so a trade-off between activity and hardness is required. The final catalyst material had a smaller particle size and weaker attrition resistance than desired. Nevertheless, cold flow testing demonstrated good fluidization could be achieved, even at the small particle size, and attrition tended to decrease after initial catalyst wear. Our catalyst scale-up partner completed production of 400 kg of the selected material for pilot-plant testing. The material met chemical formulations and surface area specifications but contained a significant fraction of fines (particles below 30 µm).

Task 3: Process Development

Bench-Scale System Design Basis and Process Design

The bench-scale reactor system was sized for a biomass feed rate of 100 lb/hr. Biomass pyrolysis will be conducted at 350-600˚C and 0-10 psig. Product yields observed during laboratory tests of white oak catalytic pyrolysis at 500˚C are shown in Table 7. These results are used as the basis for sizing the bench-scale unit. Char, coke and ash are collectively represented as solids in Table 7. Individual estimates of char (which includes the ash from biomass) and coke yields are 20.5wt% and 5wt% respectively.

Table 7: Pyrolysis reaction product yields on dry basis of biomass

Product	Product Yield, wt% (dry basis)
Bio-crude	23.7
Water	30.8
Gas	20.0
Solids	25.5

The design basis used for the sizing of the bench-scale unit is shown in Table 8. However, to understand the effect of all the design basis parameters, pyrolysis will be conducted at various operating conditions. The range for each design basis parameter is also shown in Table 8. Catalyst circulation rate is determined by the catalyst to biomass ratio required to maintain desired activity in the mixing zone and to supply sufficient heat with catalyst to 1) heat biomass up to 500˚C and 2) support endothermic heat of pyrolysis. Based on reaction data from laboratory experiments and preliminary heat calculations, it is expected that a catalyst to biomass ratio of 10:1 will be necessary.

Table 8: Design basis for the biomass pyrolysis demonstration unit

	Design Basis	Range
Pyrolysis temperature, ˚C	500	350-600
Regeneration temperature, ˚C	700	500-700
System pressure, psia	20	20-25
Biomass feed rate, lb/hr	100	10-120
Catalyst circulation rate, Catalyst:Biomass	10	5:50
Pyrolysis reaction residence time, s	0.75	0.4-1.2

The catalytic biomass pyrolysis reactor is a continuously circulating single loop transport reactor design that is flexible enough to allow sensitivity studies around temperature, residence time, biomass feed rate, and catalyst-to-biomass ratio (i.e. catalyst circulation rate) for process optimization as outlined in Table 8. One of the design challenges for this technology is heat management within the regenerator. Catalyst coke and char will be oxidized in the regenerator to provide heat to drive the endothermic biomass pyrolysis process. Ideally, the heat of combustion balances with the heat required for biomass pyrolysis and any heat losses in the system. Electrical heating can be used to overcome minor heat losses. Additional fuel (like diesel) can be added to overcome excessive heat losses, if necessary. Conversely, water can be added to the regenerator to remove excess heat. The reactor design must be able to control the temperature to maximize conversion and avoid damaging the catalyst. Additionally, effective control of the solids circulation rate can only be achieved if the pressure between the pyrolysis reactor and regeneration vessels can be balanced. The catalyst circulation rate is anticipated to be about 1000 lb/hr. The actual rate of catalyst circulation between the pyrolysis and the regenerator section will be determined by the:

a) rate of catalyst deactivation
b) regenerated catalyst to biomass ratio
c) rate of heat transfer supplied by the hot catalyst to sustain pyrolysis at a given biomass feedrate

The process flow diagram of the bench-scale reactor system is shown in Figure 14. Biomass is injected into the mixing zone using a screw feeder. The feed hopper can be refilled during operation to accommodate continuous 24/7 operation into the bottom of the mixing zone where it is mixed with regenerated catalyst. Nitrogen is added as fluidization gas to maintain a well fluidized bed in this section. Biomass interacts and mixes with hot catalyst and undergoes pyrolysis at the bottom of the mixing zone. Bed temperature will be maintained by controlling the temperature and circulation rate of the regenerated catalyst and, if necessary with external electric heating of the reactor. Pyrolysis product gases and vapors flow upwards in the mixing zone and continue to interact with the catalyst to produce the final product stream.

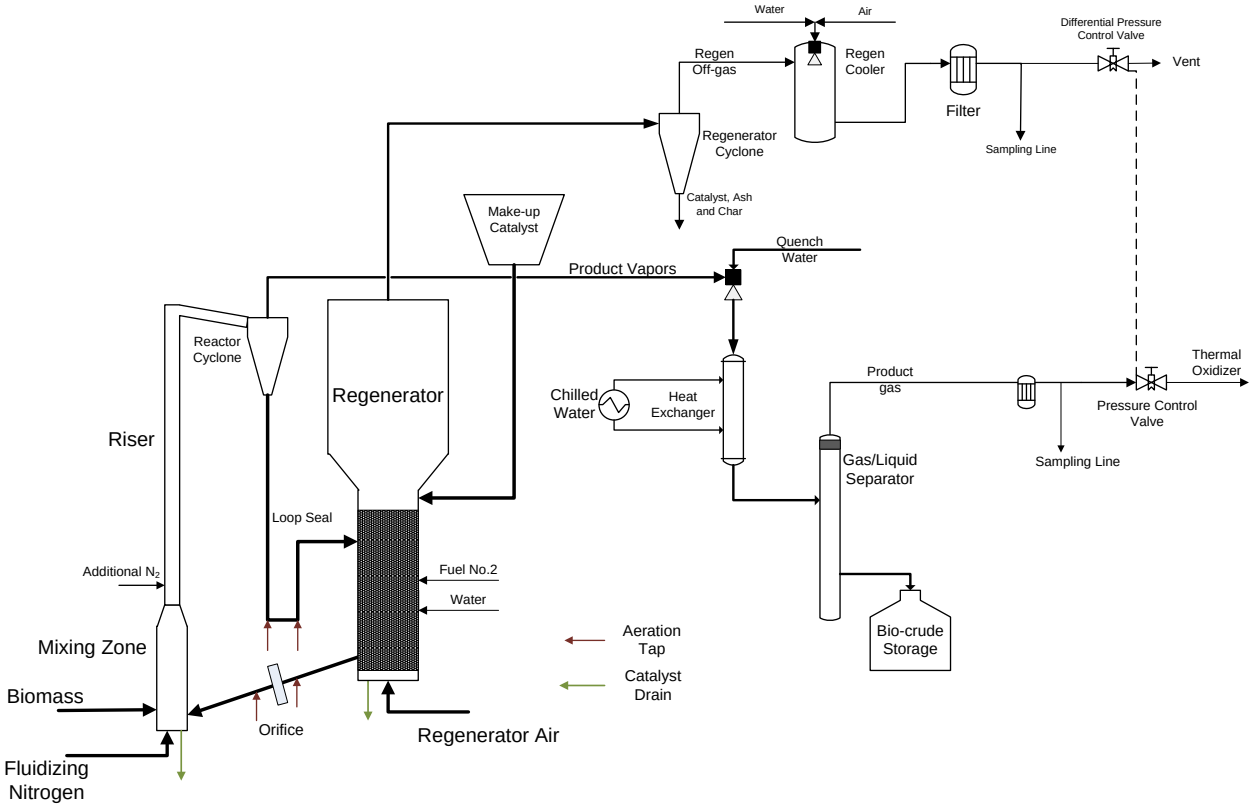


Figure 14: Process block flow diagram for the catalytic biomass pyrolysis demonstration unit

The combination of the biomass pyrolysis product and the fluidization gas leaving the mixing zone entrains the solids mixture (catalyst, char, ash and unconverted biomass) through the riser section at a rate of >20 ft/sec. The entrained char and catalyst is separated from the product vapors and gases in the reactor cyclone, maintained at temperature equal to or lower than the mixing zone/riser reactor but higher than 350˚C to prevent condensation.

The vapor phase products are condensed in a quench system that includes a water spray quench with a heat exchanger to cool the product vapors and gases. The condensed products will be collected in a gas/liquid separator and distributed to product storage tanks. The product gas exiting the scrubber is sent through a particulate filter and exist gas control valve before it is sent to a thermal oxidizer.

Coke deposited catalyst, char and ash captured in the reactor cyclone are transferred to the regenerator through a loop seal that separates the oxidizing regeneration from the inert pyrolysis process. The used catalyst is regenerated by burning off coke using air. Char that ends up in the regenerator

catalyst bed will also be oxidized. At the designed superficial gas velocity, the catalyst is retained in the bed but the unburned char and ash is entrain in the gas flow that exits the regenerator. The regenerator cyclone is used to capture the ash before the off-gas is cooled, filtered, and vented. Finally, hot regenerated catalyst leaves the regenerator bottom and is transferred back to the mixing zone through an= orifice to control solids flow.

Installation and Commissioning

The installation of the 1 TPD catalytic biomass pyrolysis unit was completed this quarter. The task list below shows the schedule for assembling the unit and integrating the unit with all utilities and the control system.

Installation Tasks and Schedule

- Riggers to unload trucks and stack skids. Large equipment and vessels will be off loaded and installed. COMPLETED April 19th
- Deliver the control cabinet – COMPLETED April 8th
- Offload bulk bag discharger – COMPLETED April 9th
- Locate and connect the control cabinet – COMPLETE April 26th
- Mechanical interconnections between the skids (swagelock and pipe connections) – COMPLETED and leak checked May 10th
- After control cabinet is powered, run conduit and pull wires for interconnections between cabinet and skid junction boxes – COMPLETED June 7th
- Heat tracing by fabricator – COMPLETED May 13-17
- Insulation - COMPLETE
- Take delivery of corn stover feedstock from ADM – June 12th 4000 lbs in 20 supersacks arrived
- 4 tons (2-5 mm) loblolly pine delivered June 17th
- Thermal Oxidizer installation– COMPLETED June 21st
- Chilled water unit installed – COMPELTED June 14th
- Installation of Controls, connection to control room, hardware connections in box, validation – COMPLETED June 28th
- All Utilities connections made to Unit (water, air, nitrogen, and electricity) - COMPLETE

The control system commissioning was started on June 24th. Communication has been established with all instruments and mass flow controllers, differential pressure transmitters, level transmitters, and pressure transmitters have been checked and calibrated. All connections have been tested and verified in the control system with the exception of the level sensors in the feed system.

- All pneumatically actuated valves have been checked and pressure control valves work.
- All heat tracing has been tested and all thermocouples have been validated.

The liquid collection system has been tested by flowing water into the quench/heat exchanger, through the filter manifold, and into the collection tanks.

The feed conveyer hopper was filled with loblolly pine sawdust (0.125” top size) and the Flexicon system has been tested and calibrated. The screw conveyer can be controlled through the control system software and the screw speed has been calibrated with the biomass feedrate. The maximum transfer rate is 600 lbs/hr at 100% motor speed. Feed system testing was initiated at the end of this quarter. The mechanical components are all functional and we have been able to calibrate the feedrate of the feeder system by varying the dosing screw and feed injector screw speeds independently. The 7 level sensors in the feed hoppers are not working properly and are in the process of being replaced. As a result, the feeder can be manually operated by transferring biomass from one hopper to the next at fixed time intervals. The bottom most level sensor is working properly and signals when there is 1 cu. ft. of biomass remaining in

the main feeder hopper. There is a 9 minute interval with the feeder operating at 100 lbs/hr before the bottom hopper empties. There is ample time to convey biomass from the bulk bag discharger to the top of the feeder, transfer it to the lock hopper and purge the feed, and drop it into bottom hopper and repeat this cycle. The non-working level sensors will be replaced, wired into the control system, and tested by July 19th. Once these sensors are operational the automated feed system logic and control can be verified.

Cold Flow Catalyst Circulation Test

The objective of the cold flow tests was to validate the catalyst circulation and system operation at ambient temperature and pressure conditions using inert gases. The cold flow tests were also helpful in identifying process variables that can be used to change the rate of catalyst circulation. Some of these process variables are identified as below:

- Set point for differential pressure between regenerator and reactor effluent
- Conveying gas flow rate through mixing zone
- Aeration across orifice plate

A schematic of the catalyst circulation loop is shown in Figure 1. Air is fed to the regenerator to fluidize the catalyst and as the oxidizing medium during pyrolysis experiments. Fluidized catalyst from the regenerator is transferred to the reactor mixing zone through the orifice standpipe. Nitrogen is fed at the bottom of the mixing zone to maintain fluidization of the catalyst. In the absence of pyrolysis product vapors, additional nitrogen is added as lifting gas which conveys solids through the mixing zone and riser sections of the reactor and feeds into the reactor cyclone. The catalyst separated in the cyclone is returned back to the regenerator through the loop seal. Catalyst in the orifice standpipe and loop seal legs is fluidized by adding aeration nitrogen, as shown by the green arrows in Figure 15. The circulation loop is sufficiently instrumented with differential pressure transmitters, as numbered in the figure, which are continuously recorded and displayed in the control system.

The cold flow test was conducted using fresh FCC catalyst. It has similar physical properties, namely appropriate particle density, particle size, and attrition resistance compared to our pyrolysis catalyst and it was readily available in larger quantities at RTI. About 160-kg of fresh FCC catalyst was added to the unit through the catalyst make-up bin and transferred to the regenerator vessel. Most of the catalyst inventory stays in the regenerator but some flows down through the orifice into the mixing zone. The bed height above the regenerator gas distributor is estimated using the pressure drop measured by pressure differential transmitter PDT-303. This measurement is a direct indicator of the solids inventory in the system. This differential pressure was at ~13 inches of water (in.H_2O) at the start of the test.

Qualitative measure of the catalyst circulation rate can be obtained using the pressure drop measured across the orifice plate (PDT-211). Prior to initiating catalyst circulation, pressure drop across the orifice plate was approximately -10 in.H_2O. As catalyst circulation commences, pressure drop across the orifice increases and the extent of increase in pressure drop is proportional to the rate of catalyst circulation. It is observed that PDT-211 pressure drop was -10 in.H_2O before and after the cold flow test when catalyst was not circulating.

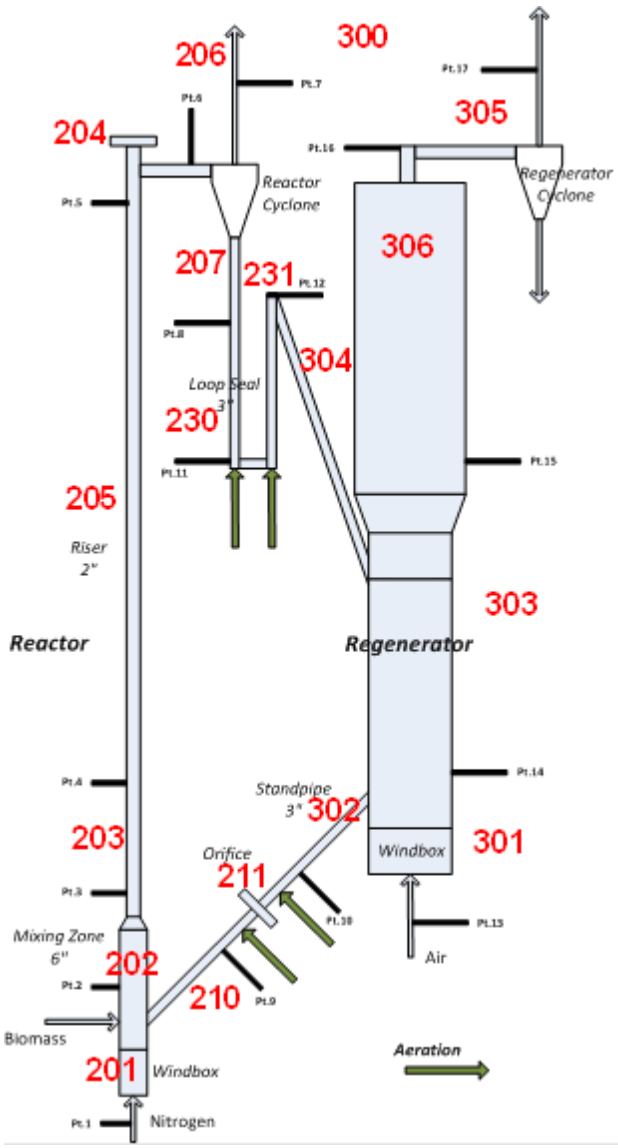


Figure 15: Schematic of the catalyst circulation loop along with differential pressure transmitter tap locations numbered and aeration points identified by the green arrows

A plot of the feed and effluent gas flow rates measured during the cold flow tests is shown in Figure 16. The reactor effluent flow rate will always be higher than N_2 feed to the reactor due to the addition of purge gas through pressure taps and biomass feeder screw. The pressure drop (in.H_2O) measured by some of the pressure differential transmitters is shown in Figure 17.

Initial Start-up

During start-up, air feed to the regenerator and nitrogen feed to the reactor were increased while simultaneously increasing overall system pressure to 4 psig. The differential pressure set point between the reactor and regenerator effluent gases (shown as GasDP-SP in Figure 16) was set at -5 in.H_2O. At first, when air feed rate was increased an error on the air compressor caused the compressor to switch to standby mode which resulted in loss of air feed flow as well as instrument air and thus resulting in loss in communication with instruments. Once the compressor was brought online, air feed was steadily increased to 2835 scfh, equivalent to superficial gas velocity of 0.86 ft/s through the catalyst bed and 0.38 ft/s through the freeboard. As nitrogen feed to reactor was increased, catalyst circulation commenced when N_2 feed flow was above 425 scfh (equivalent to ~5 ft/s through the riser). The rate of catalyst

circulation, as measured by increase in pressure drop across the orifice plate, increased with increase in N_2 feed flow. Once the N_2 feed flow crossed 1100 scfh (equivalent to 12 ft/s through the riser), no further increase in circulation rate was observed. Nitrogen feed flow was further increased to 1250 scfh to ensure pneumatic conveying was not operating under choked flow mode, which tends to be erratic and difficult to control. As seen in Figure 3, pressure drop across the orifice plate (PT-211) increased from -10 to -2.5 in.H_2O. During startup, N_2 aeration flow across the orifice was set at 10 scfh.

Performance

During the cold flow test, catalyst circulation was maintained for ~6 hours. For the entire runtime, except for the last 40 minutes, the solids inventory in the system (measured using regenerator bed pressure drop, shown in Figure 17 as RegenBed) stayed steady indicating minimal catalyst losses during the run through the reactor cyclone or due to catalyst entrainment out of the regenerator. During the initial 2.5 hours of catalyst circulation, aeration flow across the orifice plate was increased from 10 to 30 scfh. However, there was no effect on the catalyst circulation rate. Similarly, aeration feed to the loop seal was also changed but did not affect the circulation rate.

Finally, the effect of changing the differential pressure set point was studied. The PDIC-300 set point was changed from -5 to -12 to -20 in.H_2O (in steps), As the differential pressure set point was lowered, pressure drop across the orifice decreased which indicates decrease in catalyst circulation rate. During this time, pressure drop across the riser elbow, riser, and reactor cyclone also decreased. The decrease in catalyst circulation rate was expected as lowering the differential pressure set point lowers the pressure on the regenerator side relative to the reactor side. As the driving force for catalyst circulation is the pressure head on the regenerator side, lowering the pressure on the regenerator side reduced the driving force for catalyst circulation. Subsequently, the rate of catalyst circulation was increased by increasing the differential pressure set point from -20 to 0 in.H_2O. However, a sudden drop in regenerator bed pressure drop from 13 in.H_2O to 10 in.H_2O was observed indicating loss of catalyst. Further increase in differential pressure set point only increased the rate of loss of catalyst.

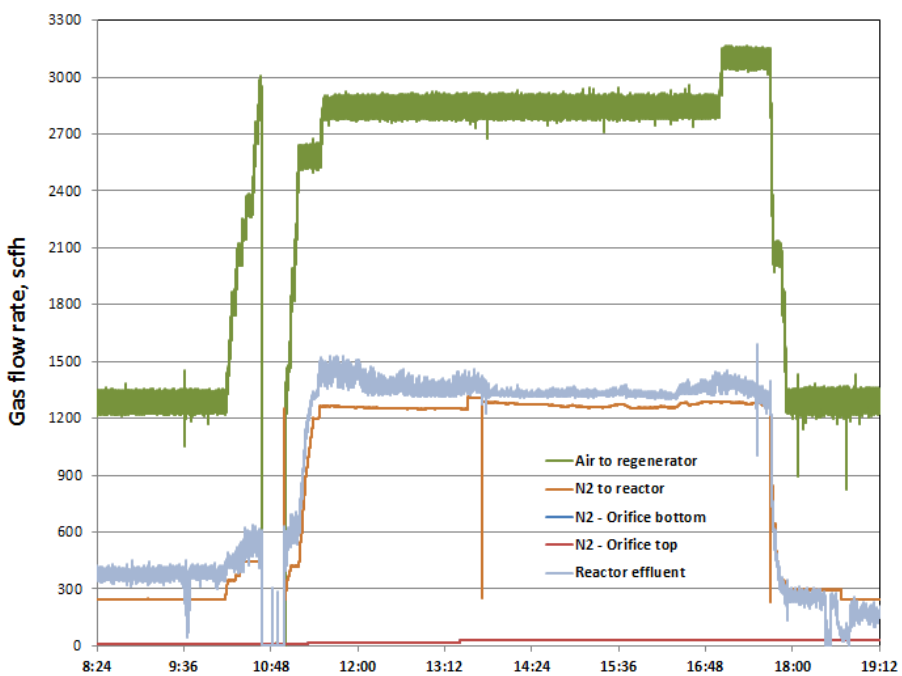


Figure 16: Feed and effluent gas flow rates during 07-16-2013 cold flow test

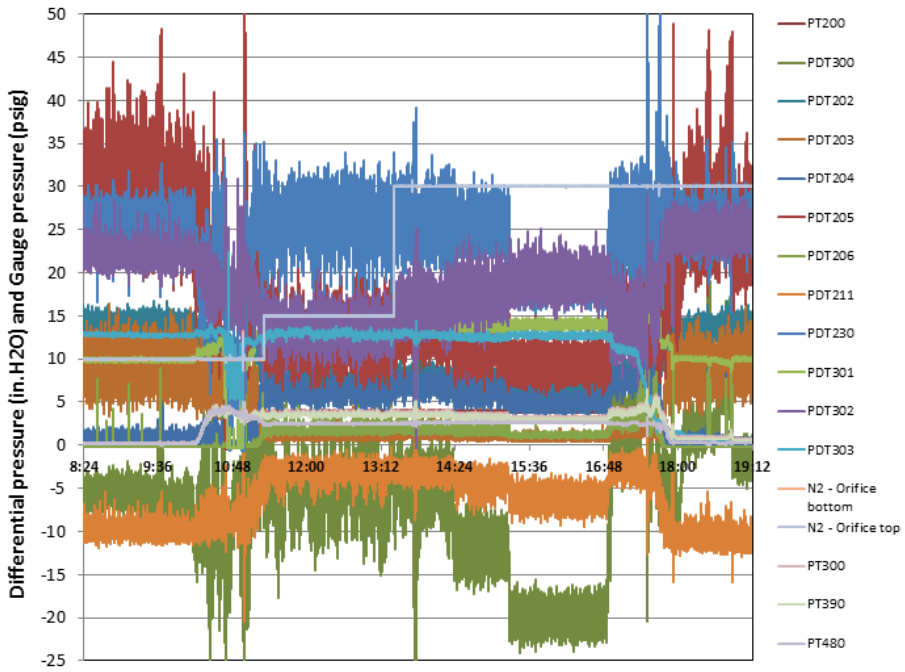


Figure 17: PDT and pressure transmitter readings during 07-16-2013 cold flow test

Toward the end of the cold flow test, the catalyst escaped the circulation loop through the reactor cyclone and ended up in the gas-liquid separator. The total amount of catalyst recovered from the separator vessel was ~56 kg (~35% of the catalyst inventory). Further investigation concluded that at higher differential pressure set point the solids height in the cyclone dipleg was very close to the cyclone bottom and fluctuations in the differential pressure led to solids backing up in the cyclone and adversely affecting its collection efficiency.

Hot Flow Testing and Catalytic Fast Pyrolysis with FCC catalyst

The FCC catalyst used for cold circulation testing was also used for catalytic fast pyrolysis testing to shakedown biomass addition under reaction conditions. These tests indicate of the behavior of product streams and were used to develop normal operation procedures.

The catalyst inventory in the system was refreshed to approximately 150-kg by adding additional fresh FCC to compensate for the losses in the cold flow tests. The entire system was electrically heated to between 250°C to 300°C with the heat tracing. Both the reactor and regenerator were operated as static bubbling fluid beds during the initial heating. The water was added to quench system through the spray nozzle at a rate of 10-13 gal/h. Gas flow rates and system pressure settings are adjusted to initiate catalyst circulation once desired temperatures were achieved.

Diesel fuel was injected into the regenerator once the catalyst was circulating through the system to increase the system temperature to achieve 500°C in the mixing zone. As diesel was injected into the regenerator, the coke deposition on the FCC catalyst increased quite substantially and created a large inventory of carbon in the regenerator as the system temperature increased. Consequently, as biomass was introduced into the system, the regenerator increased faster than expected to a higher temperature than anticipated. Water was added to the regenerator to limit and control the regenerator temperature. After biomass feeding was stopped, carbon oxidation continued in the regenerator for an additional 4 hours.

One of the key design concerns for such a small pilot plant was potentially excessive heat losses that would limit the conversion efficiency for the endothermic biomass pyrolysis process. This initial hot flow test demonstrated that the supplementary diesel fuel is not needed to maintain desired process

temperatures and that there is more than enough energy in the char produced during the catalytic biomass pyrolysis process to provide all of the required process heat, and more. As a result, diesel addition during initial heating was deemed unnecessary. The revised startup procedure now uses only biomass to increase process temperatures.

Electrical heating is still used to increase the system temperature to 300°C but a single charge of biomass (1 ft^3 – or about 17 lbs of loblolly pine sawdust) is added to the mixing zone. The low pyrolysis temperature initially limits conversion of the biomass increasing the biomass solids to the regenerator where it is burned. The temperature slowly increases over 45 min until the regenerator temperature is 625°C. Water can be added to the regenerator to control the temperature in this range. The resulting pyrolysis temperature in the mixing zone is ~500°C. Pyrolysis temperature can be adjusted by changing the temperature in the regenerator and varying the biomass feed rate. Continuous biomass feeding starts after the temperatures are stabilized at the desired operating conditions.

Figure 18 shows the temperature profiles from the two sides of the reactor system for the length of a run with the FCC catalyst including the heating from biomass addition. For the duration of the test, 300 lbs. of biomass was fed over 5 hours with additional time for start-up and shutdown. Temperatures TE201 and TE202 are bed temperatures from the mixing zone of the pyrolysis reactor and TE300 and TE302 are bed temperatures from the regenerator. A 150°C temperature differential between the regenerator and pyrolysis sides of the reactor system was needed during sustained biomass feeding to achieve the desired pyrolysis temperature. The temperature differential between the two sides decreased when biomass feeding was stopped as the pyrolysis reactor temperature rose in the absence of the endothermic pyrolysis reactions.

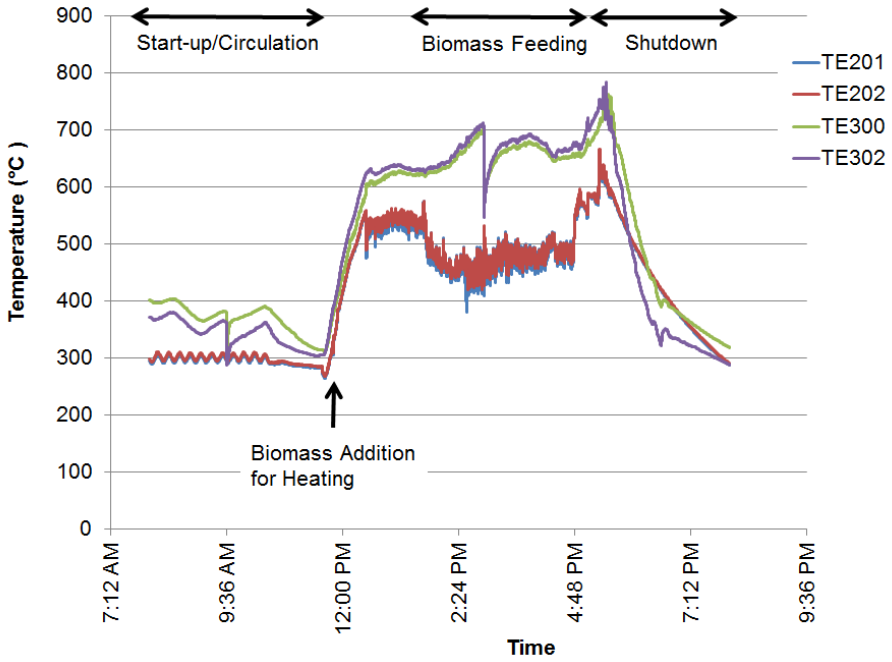


Figure 18. Temperature profiles from catalytic fast pyrolysis with FCC catalysts. TE 201 and TE 202 are pyrolysis reactor temperatures and TE 300 and TE 302 are regenerator bed temperatures.

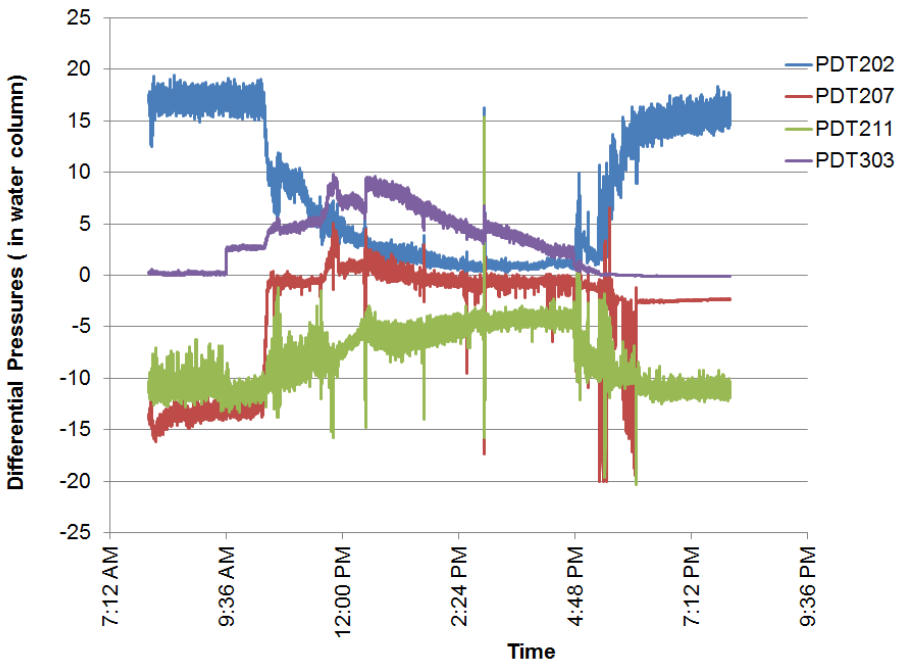


Figure 19. Differential pressure profiles from catalytic fast pyrolysis with FCC catalysts.

Differential pressures are measured throughout the system to monitor solids circulation behavior. Figure 19 shows several key differential pressure measurements from catalytic fast pyrolysis with FCC. PDT 202 indicates the differential pressure across the riser of the pyrolysis reactor. The higher the differential pressure the higher the density of solids in the riser section. Under static conditions the differential pressure is high at 17 in. H_2O and decreases as circulation begins. PDT207 is the differential pressure at the top of the down leg on the loop seal. PDT211 is the pressure drop across the orifice that is related to the catalyst circulation rate and PDT303 is the pressure drop in the regenerator bed that is related to the catalyst inventory.

Table 9: Mass and carbon balance from catalytic biomass pyrolysis in the 1 TPD pilot unit with FCC catalyst.

Inputs		Outputs		
Stream	**Mass (lbs)**	**Stream**	**Mass (lbs)**	**% on input C**
Pine	304	bio-oil/organics	33	15.8 %
Water	922	Water/aqueous	1044	7.6 %
Oxygen	169	char	41	18.1 %
		Pyrolysis Gases	48	13.3 %
		Regen Gases	147	34.6 %
Total	1395	Total	1313	
		Balance	94 %	89.5 %

The material balance and the carbon closure for the catalytic biomass pyrolysis test with the FCC catalyst is show in Table 9. The total inputs include biomass, water in the spray quench and the regenerator, and oxygen in the air into the regenerator. The initial charge of catalyst and nitrogen into the pyrolysis reactor are measured but not included in the mass balance calculation. The outputs include the bio-oil organic product, aqueous bio-oil fraction and water, char and catalyst fines from the regenerator cyclone, pyrolysis product gases that are treated in the thermal oxidizer, and regenerator off-gases produced during char oxidation. Catalyst fines collected from the regenerator cyclone are measured but

not included in the mass balance calculation. For this experiment the overall mass closure was 94% and the carbon balance was nearly 90%. The char content was determined by measuring the carbon content of the solids collected in the regenerator cyclone and assuming the remaining ash material was catalyst fines ejected from the regenerator. Pyrolysis product gas composition was measured with an on-line microGC and the regenerator CO and CO_2 products were monitored with a Continuous Gas Analyzer (NDIR).

The pyrolysis product gas composition shown in Figure 20 is consistent with catalytic cracking of biomass pyrolysis vapors and is similar to the laboratory-scale catalytic biomass pyrolysis results measured in a 1”-diameter fluidized bed reactor. The most abundant pyrolysis product gas is CO followed by CO_2. A small amount of methane and higher hydrocarbons were also measured. The CO_2 and CO concentrations measured in the regenerator off-gas are shown in Figure 21. The elemental composition of the bio-oil product from catalytic biomass pyrolysis with the FCC catalyst is shown in Table 10. The oxygen content is quite a bit lower than conventional bio-oil from biomass fast pyrolysis but the yields are low, only about 11 wt% of the total biomass input. Excessive cracking of the biomass pyrolysis vapors with the FCC catalyst produced high char yields considering the solid char collected (13 wt%) and the high regenerator off-gas yield (48 wt%). Nearly 50% of the carbon is lost through the regenerator side of the system and only 16% of the carbon is recovered in the bio-oil product.

Table 10. Bio-crude composition from operation of pilot unit with FCC catalyst.

Bio-crude Average Elemental Composition (dry basis)	
C	71 wt%
H	7 wt%
O	22 wt%
Moisture Content	
Water Content	6 wt%

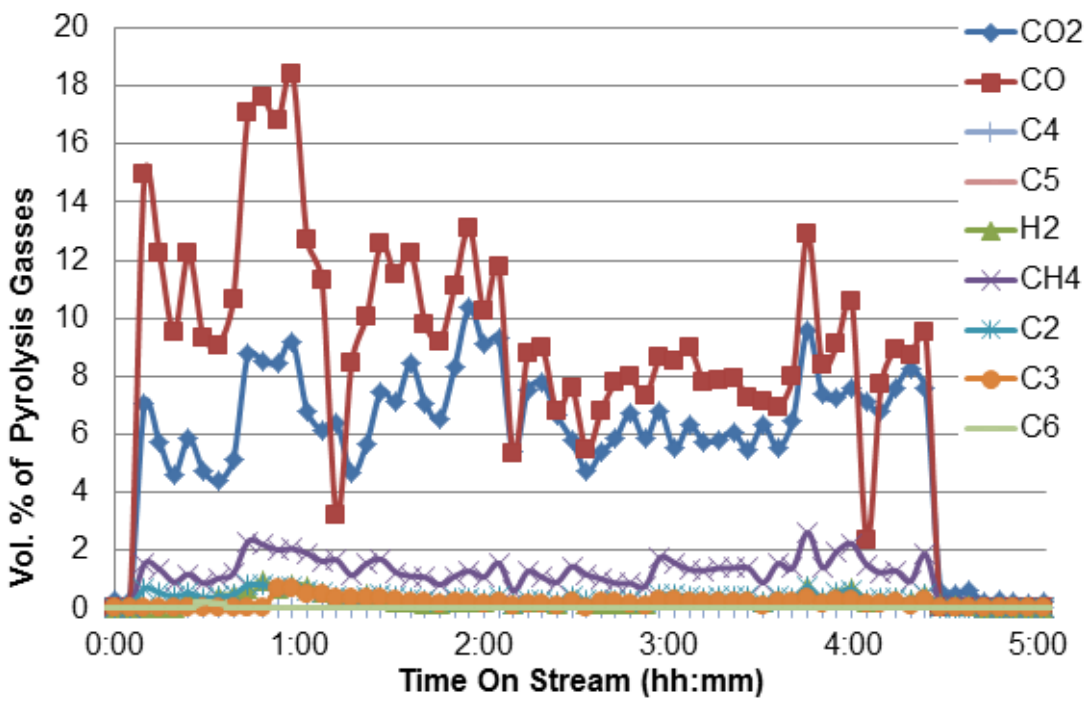


Figure 20. Product gas concentrations in the pyrolysis off-gas. (Volume percent of total off-gas including nitrogen.)

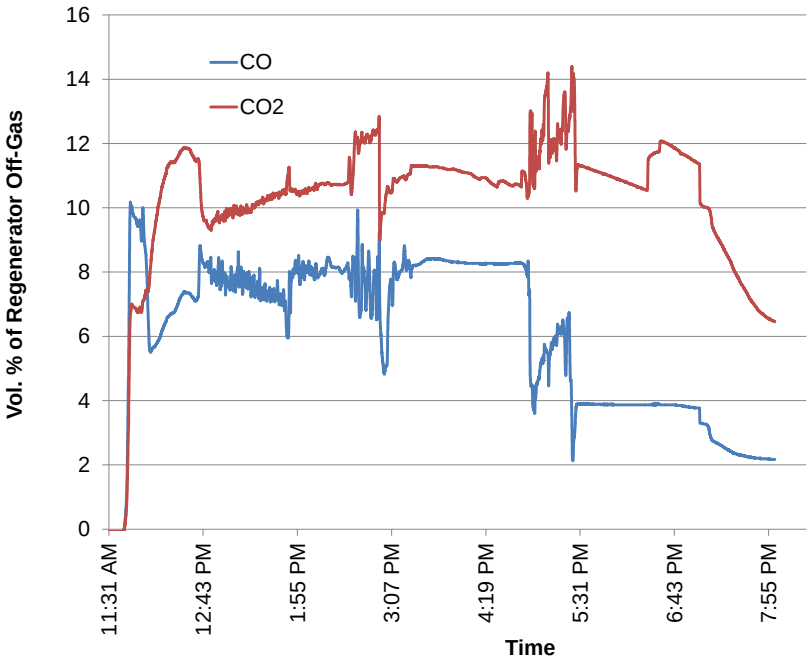


Figure 21. CO and CO_2 concentrations in the regenerator off-gas. (Volume percent of total off-gas including nitrogen.)

Catalytic Fast Pyrolysis with RTI-A9 catalyst

Roughly 150-kg of the RTI-A9 pyrolysis catalyst was loaded into the 1 TPD system on August 12, 2013. The system was electrically heated to 300°C and the gas flows in the mixing zone and in the regenerator were increased as the control valves on the pyrolysis side and the regenerator side were slowly manually closed until catalyst circulation was achieved. Circulation was adjusted by controlling the pressure drop across the orifice plate (PDT – 211). The RTI-A9 material is denser than the FCC material so consequently, the circulation rates were higher and closer to ~2000 lbs/hr.

Once the system temperature reached 300°C and stable circulation was received, a charge of 17lbs of biomass was fed to the system to raise the system temperatures to 500°C in the pyrolysis mixing zone and 600°C in the regenerator bed. Figure 1Figure 22 shows the temperature profile on each side of the reactor system for the length of the run. The initial charge of biomass to raise the system temperature was fed at 13:00 and the system was allowed to stabilize till 15:00. Between 15:00 and 19:00 continuous feeding was achieved. The expected temperature drop in the pyrolysis mixing zone is seen at around 15:00 when continuous feeding began. The regenerator temperature was allowed to rise to compensate and increase the mixing zone temperature. When biomass feeding concluded at 19:00 the pyrolysis mixing zone temperature begins to approach the regenerator bed temperature because the endothermic biomass pyrolysis process ceases.

Figure 23 and Figure 24 depict the differential pressures across the regenerator bed and in the pyrolysis riser and elbow. In Figure 23 the differential pressure across the top of the bed remains constant however the differential pressure across the bottom of the bed begins to decrease when continuous feeding begins. These trends are likely caused by an increasing char content in the regenerator. Catalyst losses were observed over time both out of the regenerator and out of the quench system through collected at the bottom of the gas liquid separator. Increasing the char in the reactor bed would not affect the differential pressure across the top of the bed because the volume of solids remains constant. However, lower in the bed as the less dense char would lower the overall bed density and decrease PDT302. Similarly the differential pressures across the riser (PDT202) and across the elbow (PDT204) on the pyrolysis leg of the reactor system begin to decrease over time during continuous biomass feeding. Increased char content and catalyst loss causes the regenerator bed to decrease density resulting in a lower

solids circulation rate. In Figure 23, PDT303 drops rapidly after continuous feeding ends as the volume of solids in the regenerator bed decreases as the char is consumed without replacement.

During the test 374lbs of loblolly pine was fed over a 4 hour period. Overall, the mass balance for this 4-hour campaign was 89%. A summary of the inputs and outputs used to calculate the mass balance is shown in Table 11. A water spray was used to quench pyrolysis vapors entering the heat exchanger at approximately 13 gal/hour of water. The quench system was successfully used to capture the aqueous fraction of the bio-crude produced plus the added water. The collection efficiency of the organic fraction in the gas liquid separator was quite low. Much of the bio-crude product passed through the quench vessel as aerosols that ultimately coalesced in the gas filters (F-480A/B) in line to protect the pyrolysis gas control valve (PV-200). The filters were periodically drained and approximately 2 gallons of bio-crude product collected in this manner. The flow of pyrolysis gas and off-gas from the regenerator were continuously measured to account for all of the gas phase products.

The average elemental composition of the collected bio-crude is shown in Table 12. The oxygen content of the bio-crude (23 wt%) is slightly higher than what was measured from the products of the smaller laboratory scale experiments (20 wt%). The oxygen content of the bio-crude initially produced was likely less than 20 wt% but as the catalyst was continually lost out of the regenerator, the deoxygenation activity of the solids in the reactor likely decreased. Consequently, the bio-crude oxygen content increased over time such that the average oxygen content was 23 wt%.

The pyrolysis gases were continuously analyzed with an on-line microGC and the average composition is shown in Table 13. The average CO/CO_2 ratio was ~1 compared to 0.6 that was measured in the 1”-diameter laboratory scale reactor. This is consistent with the slightly lower deoxygenation activity assumed in the 1 TPD system. The CO and CO_2 concentration in the off-gas from the regenerator was measured continuously with an on-line NDIR gas analyzer and is also shown in Table 13. Collectively, the compositions of the inputs and the outputs supported the carbon balance also presented in Table 11.

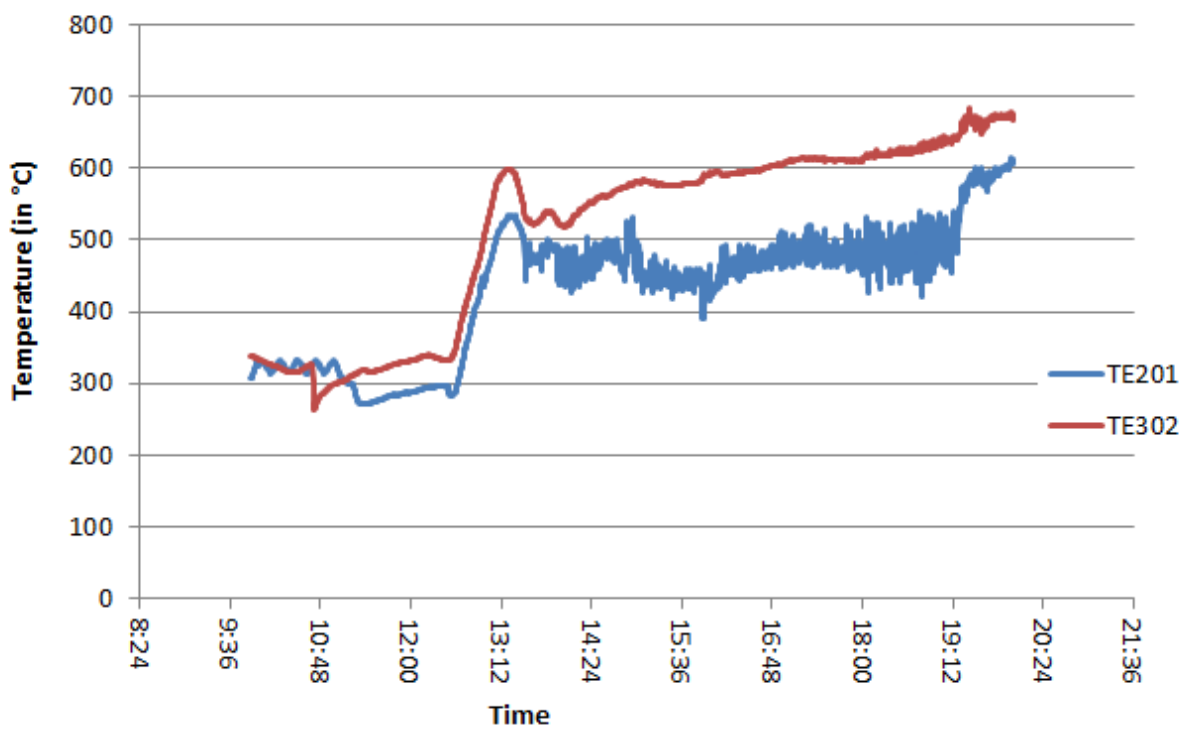


Figure 22. Temperature profiles in the pyrolysis mixing zone (TE201) and in the regenerator bed (TE302).

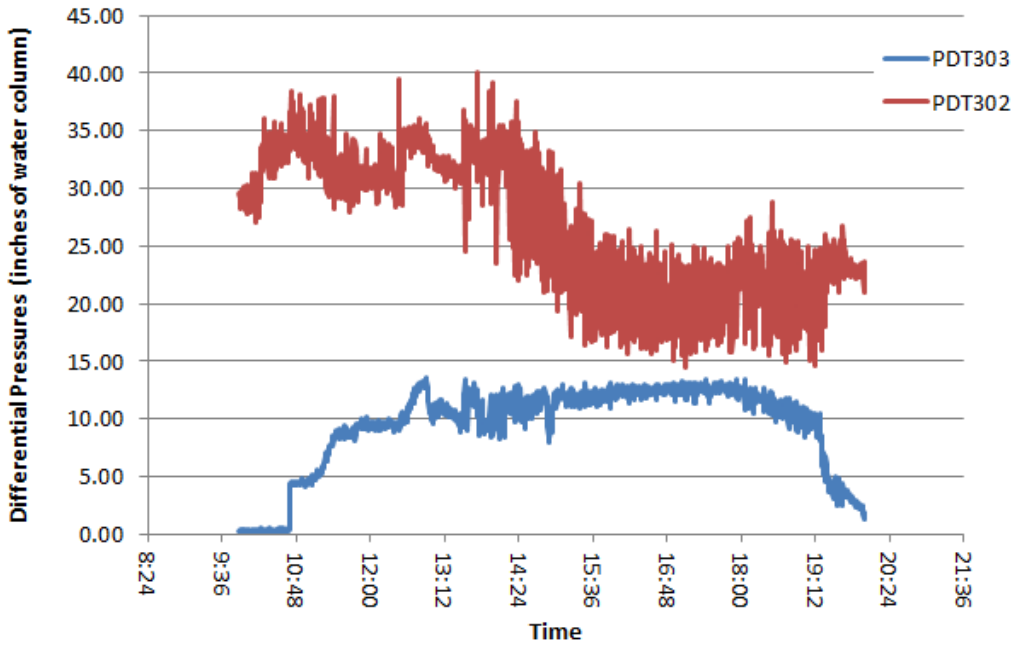


Figure 23. Differential Pressure measurements in the regenerator leg of the system. PDT303 measures the differential pressure across the top of the bed and PDT302 measures across the bottom of the bed.

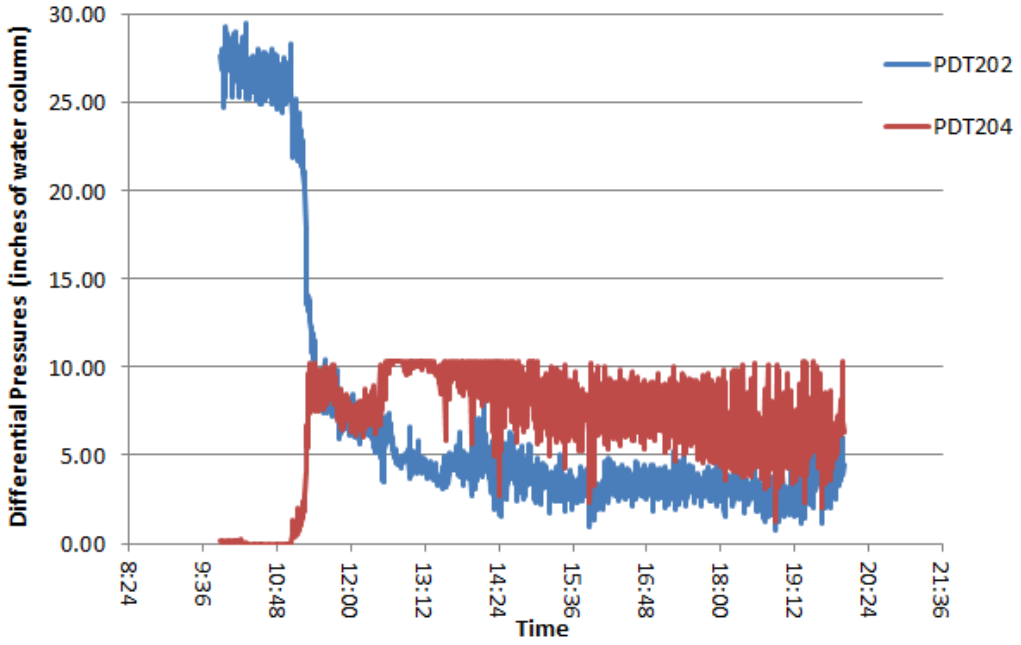


Figure 24. Differential pressure measurements from the pyrolysis leg of the reactor. PDT202 is the differential pressure across the riser. PDT204 is the differential pressure across the elbow at the top of the riser. (PDT204 is maximum reading of 10 inches of water column

Table 11. Mass and carbon balance from operation of the 1TPD pilot unit with RTI-A9 catalyst.

Inputs			Outputs		
Stream	**Mass (lbs)**		**Stream**	**Mass (lbs)**	**% on input C**
Pine	374		bio-oil/organics	18	7.2%
Water	922		Water/aqueous	919	2.7%
Oxygen	169		char	53	18.8%
			Pyrolysis Gases	98	21.5%
			Regen Gases	209	38.9%
Total	1465		Total	1297	
			Balance	88.6%	89.2%

Table 12. Bio-crude composition from operation of the 1TPD pilot unit with RTI-A9 catalyst.

Average Elemental Composition (wt% dry basis)	
C	70.9
H	6.0
O	23.1
Moisture Content	
Water Content	24.3

Table 13. Gas product compositions from operation of the 1TPD pilot unit with RTI-A9 catalyst.

Pyrolysis Gas Composition (wt% of biomass fed)	
CO	13.6
CO_2	12.6
H_2	0.06
CH_4	0.5
C_{2+}	0.6
Regenerator Off-Gas (vol.% of 2500 scfh flow)	
CO	6
CO_2	11

Task 4: Bio-Oil Analysis and Upgrading

Phillips 66 evaluated the upgradability of the catalytic biocrude produced by RTI. A total of three samples were evaluated, 1) conventional biocrude, 2) catalytic biocrude 125B, and 3) catalytic biocrude 161B, and are labeled as Sample A, B, C respectively. A very conservative two-stage bio-crude upgrading strategy consisting of stabilization followed by hydroprocessing was evaluated for proof-of-concept. Given the amount of Sample C that was received, an upgrading experiment was conducted for less than 100 h. In order to fully identify challenges facing commercialization, larger samples are required to demonstrate the upgrading process for at least 1000 hours.

Catalytic Biocrude Sample Quality

The biocrude samples were analyzed to determine the chemical structures present and the thermal properties. This information was used to qualitatively predict the upgradability of the sample and determine the upgrading strategy. Table 14 shows the differences between Samples A, B, and C as received from RTI.

Table 14. A comparison of the chemical structures and thermal properties of the RTI biocrudes sent to Phillips 66. Sample A is a conventional biocrude and samples B and C are catalytic biocrudes.

	Sample A	Sample B	Sample C
Composition (wt% - dry basis)			
C	56.5	68.9	76.9
H	5.5	6.1	6.6
O	38.0	25.0	16.5
Organic Acids, wt%	8.0	7.5	2.6

The most significant change in the elemental composition of sample C is that the oxygen content dropped to 16.5 wt% from 38 wt% for conventional biocrude (sample A) and 25 wt% for the first catalytic biocrude (sample B). The chemical transformation contributing to this change was revealed by a breakdown of the carbon functional groups measured with a Nuclear Magnetic Resonance (NMR) technique. The carbonyl content and ether content in the catalytic biocrude (samples B and C) were much lower than that of the conventional biocrude (sample A). Consequently, the aromatic/olefin content in catalytic biocrudes (samples B and C) increased by around 100%. During the catalytic pyrolysis process, C=O may undergo a decarbonylation reaction to expel oxygen as carbon monoxide and C-O may take a route of dehydrogenation followed by decarbonylation or a path of dehydration to form water and unsaturated C=C. Alternatively, C=C may derive from cracking/dehydrogenation of aliphatics or aromatization of olefins depending on catalyst. It is worth noting that the carboxylic acid content of the sample C was significantly reduced from 4.4% to 0.9%. As a result, the total organic acid of the latest biocrude (sample C) was the lowest among the three samples.

Upgrading Strategy Overview

A two-stage stabilization-hydroprocessing upgrading strategy was applied to catalytic biocrude sample C since it was still thermally unstable. The biocrude was first stabilized at 150 ºC~200°C using a commercial hydrogenation catalyst and the intermediate was hydrodeoxygenated at a higher temperature (300ºC~350ºC) using an off-the-shelf hydroprocessing catalyst. The volume of sample C received provided enough material to complete a 96 h stabilization test followed by a 50 h hydroprocessing test.

Upgraded Product Analysis

Using the 2-stage upgrading process, sample C was upgraded to a product with a hydrocarbon phase (upper layer) and aqueous phase (bottom layer) as shown in Figure 25. An elemental analysis of the product showed that over 99% of the produced carbon was located in the hydrocarbon phase. Chemical composition and thermal property data are listed in Table 15 for the upgraded hydrocarbon phase. The data shown in Table 15 indicates that hydrodeoxygenation occurred during the two-stage upgrading process as the resulting oxygen content is 2.3 wt%. Similarly, the organic acid content was lowered to 0.03 wt%.

Figure 25. 1L catalytic bio-crude sample C and product after 2-stage upgrading.

Table 15. A comparison of the chemical structures and thermal properties of the RTI biocrude and the resulting deoxygenated hydrocarbon phase (denoted as upgraded HC in the table).

	Sample C	Upgraded Sample
Composition (wt% - dry basis)		
C	76.9	86.8
H	6.6	10.9
O	16.5	2.3
Organic Acids, wt%	2.6	0.03

The upgraded hydrocarbon phase is fully distillable with 100% recovery measured by Simulated Distillation (SIMDIS) technique as shown in Figure 26. In sharp contrast, the conventional biocrude (sample A) only recovered around 40%. The upgraded product contains an equal amount of gasoline and diesel range hydrocarbons. When compared to typical petroleum crude as shown in Figure 26, the upgraded product contains more hydrocarbons with lower boiling point. In other words, fractionation of the upgraded product would generate more gasoline product than regular crude.

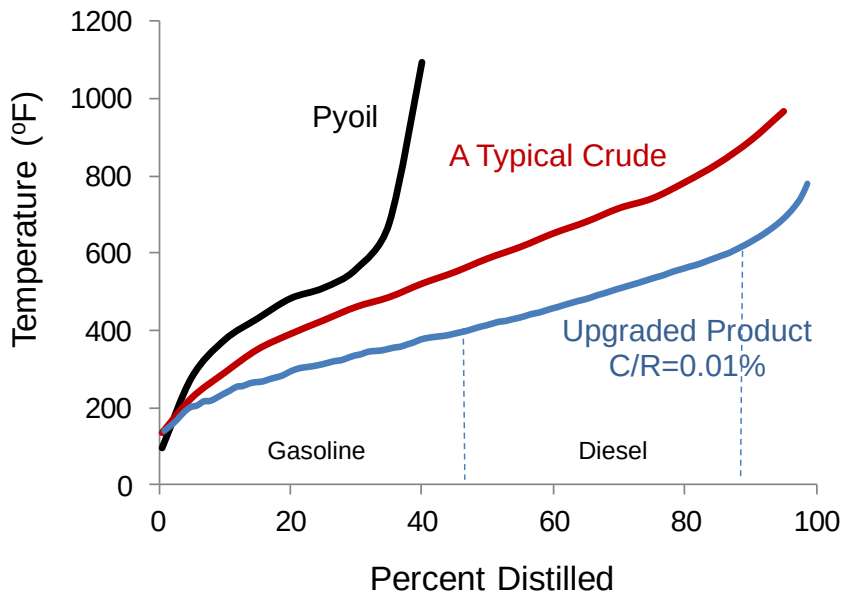


Figure 26. SIMDIS result for upgraded hydrocarbon product.

Conclusion

A catalytic biocrude (sample C) was upgraded using a two-stage stabilization-hydroprocessing process where over 99% of the produced carbon resided in the hydrocarbon phase. The upgraded hydrocarbon phase contained nearly equal amounts of gasoline and diesel (around 45 wt% respectively) and a small amount of gas oil. The gasoline fraction for the upgraded product is higher than regular crude. The produced hydrocarbons are mainly cyclanes and aromatics. The DHA shows that the RON for the gasoline range product is comparable to a premium gasoline sample. In summary, the quality of the upgraded product makes it possible to blend the product with a regular hydrocarbon blend stock or to co-process it in a hydroprocessing unit.

Despite the demonstration of upgrading feasibility, the longevity of the upgrading operation could be negatively impacted by leaching of stabilization catalyst due to acids in the biocrude. Therefore, further reduction of the acid content is recommended for future samples. Since the recent upgrading experiment was run for only a few days, it is impossible to capture most of the challenges that could impede commercial

operation. As a result, a larger sample will be required to demonstrate the continuous operation of the upgrading process for at least 1000 h.

Task 5: Process Modeling and Economic Analysis

Techno-economic analysis of a commercial-scale 2000 dry tons of biomass per day stand-alone integrated bio-refinery to convert biomass to gasoline was performed to compare RTI's catalytic biomass pyrolysis technology with other biofuels technology options. A preliminary process flow diagram for a commercial-scale (2,000 tpd) biorefinery based has been developed. The commercial process integrates RTI's catalytic biomass pyrolysis process with bio-crude hydroprocessing unit to produce gasoline from biomass. A block flow diagram of the process is shown in Figure 27 and a process flow diagram of the integrated process is shown in Figure 27.

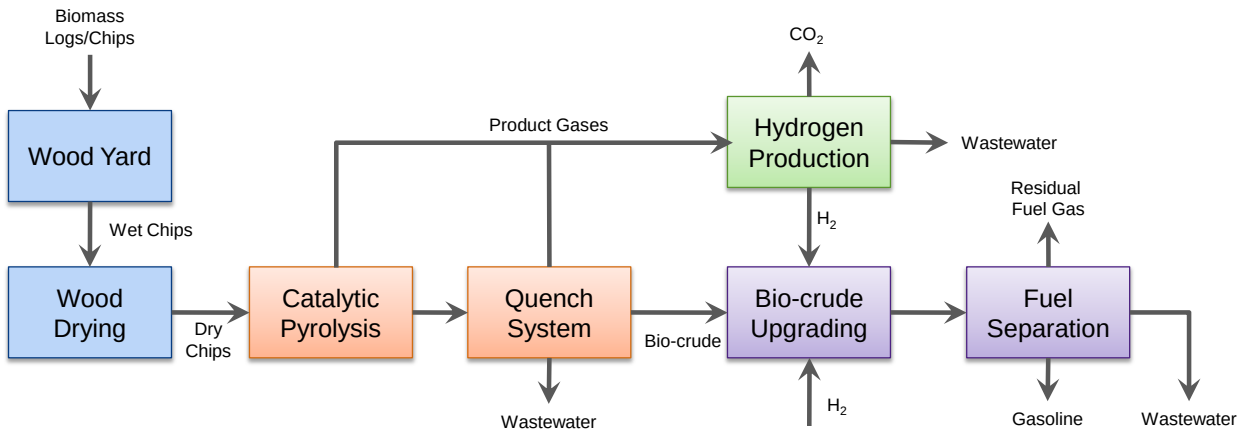


Figure 27: Block flow diagram of the integrated catalytic biomass pyrolysis hydroprocessing process.

The plant is designed to process biomass logs or chips with ~50 wt% moisture content (as received). The process is flexible towards the type of biomass received but is focused on woody biomass for the present analysis. Biomass is pyrolyzed at 450-550 °C in presence of a catalyst developed at RTI. The catalyst deactivates during the process due to coke deposition. Spent catalyst is continuously regenerated in a single loop transport reactor system in which the catalyst is transferred from the pyrolysis mixing zone to the regenerator where air is used to burn off coke and oxidize char. Pyrolysis vapors from the reactor are condensed in the quench system to recover bio-crude. A fraction of the pyrolysis product gas is recycled to the catalytic pyrolysis unit as fluidization gas and the rest is processed to produce hydrogen which is used for bio-crude upgrading in the hydroprocessing unit. Bio-crude is upgraded to gasoline in the hydroprocessing unit by removing oxygen as water and improving the H:C ratio to 2.1. Gasoline and water are separated from residual fuel gas by condensing the liquids. Finally, gasoline is separated from water in a gravity separator and stored. The details of the individual sections of the commercial-scale biorefinery are provided below.

Feed Handling. The plant is designed to process both logs and chips. Logs are received and stored in log storage whereas a chip dump is used to receive biomass chips. Logs are fed to a chipper to produce biomass chips of desired size which are screened in a disk screener. Larger chips from the disk screener are size reduced in an overs hog. Similarly, biomass received as chips is conveyed directly to a disk screener to separate chips of desired size and transfer the rest to an overs hog to reduce their size. Finally, chips from either the logs chipper or chip storage are collected in a chip stacker and reclaimer and then transferred to a feed dryer surge bin.

The moisture content of as received biomass (both logs and chips) is assumed to be 50wt%. The wood yard is sized to process 4000 TPD of as received biomass (equivalent to 2000 TPD of dry biomass) on a 12 hr/day operation basis. The conveyors, chippers, disc screener are thus sized for 334 tons/hr capacity. The log storage and chip dump bin are both sized for 8000 tons which is sufficient to support 2

day's capacity. The chip truck dump has a holding capacity of 28,000 tons, equivalent to an inventory of 7 days. The feed dryer surge bin, used to store wet wood chips, is sized for 8,000 tons, equivalent to 2 days inventory.

Wood chips from the feed dryer surge bin are fed in to a high pressure wood dryer using an auger-conveyor assembly. The wood dryer is operated at 50 psia and biomass is dried by indirect contact with superheated steam at 400 psia and 526°F. Biomass is dried to a moisture content of 10wt% and the moisture leaves the dryer as steam at 50 psia and is used for steam reforming, water gas shift and regeneration of CO_2 rich solvent in the amine plant. The dried biomass is stored in a dry chip day bin sized for 2 days capacity (4000 dry tones).

Catalytic Biomass Pyrolysis. A single loop transport reactor is used for catalytic biomass pyrolysis. Dried biomass chips are fed to the catalytic fast pyrolysis unit at the bottom of the mixing zone where it is mixed with regenerated catalyst at 700°C (1292 °F). Hot catalyst supplies the heat required to 1) preheat biomass up to reaction temperature, and 2) supply the endothermic heat of pyrolysis reaction. Recycled pyrolysis product gas is used to fluidize and mix the catalyst and biomass mixture. The catalytic fast pyrolysis reactor is operated at 500°C (932 °F) with a residence time of ~1.0 s. The resulting biomass pyrolysis products transport the used catalyst and solid products (char and ash) through the riser reactor.

The product yields for catalytic fast pyrolysis are extrapolated from the experimental results from bench-scale testing of white oak catalytic fast pyrolysis with RTI-A9 catalyst. Liquid, solid, and gas yields of 41 wt%, 20 wt%, and 39 wt%, respectively, are assumed. The liquid products contain 29 wt% bio-crude and 12 wt% water. The catalytic fast pyrolysis bio-crude is estimated to have an oxygen content of 23 wt%. The product gas composition contains 25 vol% H_2, 24 vol% CO, 40 vol% CO_2, 9 vol% CH_4 and 2 vol% light hydrocarbons, based on laboratory experimental results. The preliminary design assumes that hydrocarbons in the tail gas from the pyrolysis reactor are reformed and the product gas is shifted to produce hydrogen and carbon dioxide.

Catalyst, char and ash are separated from the product stream in a cyclone and returned to the regenerator. The regenerator is a bubbling fluidized bed reactor where air is introduced at the bottom to accomplish complete oxidation of coke and char while simultaneously reactivating and reheating the catalyst. Char and coke combustion in the regenerator provides heat in excess of the heat required to reheat the catalyst from 500 °C (932°F) to 700°C (1292°F). The excess heat in the regenerator is removed by generating steam which is used elsewhere in the plant for 1) drying the biomass to 10 wt% moisture, and 2) reheating the bio-crude at the inlet of the hydroprocessing unit. Ash is entrained out of the regenerator with the exhaust gas and is separated in a cyclone and transferred to ash cooler. Hot regenerator exhaust gas from the cyclone is cooled to generate usable steam. A portion of the cooled N_2/CO_2 combustion exhaust is used as inert gas for aeration in the transport reactor while the rest is vented. Regenerated catalyst exits the regenerator at the bottom and is transferred to the reactor mixing zone bottom through a J-leg.

Quench System. The pyrolysis product vapors and gases from the cyclone of the catalytic pyrolysis unit are cooled to recover bio-oil while extracting energy. A two-stage product cooling philosophy is used. In the first heat exchanger, pyrolysis product vapors are cooled down to 220°F by pre-heating boiler feed water (used in regenerator to produce steam). Pyrolysis product vapors at 220°F are then sent to a spray column where they are cooled down to 100°F. Approximately 80wt% of bio-oil is condensed in this step. A portion of the aqueous fraction of the bio-crude is cooled and recirculated as the spray liquid in the quench vessel. Circulating cooling water, condensed bio-crude, and water from the pyrolysis product stream leave the bottom of the spray column. The objective of the spray column is to 1) cool the product vapors down to 100°F, and 2) coalesce bio-crude aerosol droplets. The cooled pyrolysis product gas from the spray column consists of aerosols of pyrolysis liquid products and is sent to an electrostatic precipitator (ESP) where it is assumed that the rest of the bio-crude is removed. Liquid streams from the spray column and ESP are combined and sent to a decanter vessel. It is assumed that all the bio-crude separates from water by gravity and accumulates at the bottom of the decanter vessel. Water, which forms the top liquid fraction, is sent to wastewater treatment plant and bio-crude is sent to the hydroprocessing section. Product gases from the ESP are sent to hydrogen production section.

Hydrogen Production. Hydrogen required for bio-crude hydroprocessing is produced from the pyrolysis product gas using steam reforming and water gas shift. About half of the gas from the ESP is recycled back as fluidization gas to the pyrolysis reactor mixing zone, while the remaining product gas stream is used for hydrogen production. This stream is first preheated to reforming temperature using steam generated in the regenerator. The preheated pyrolysis product stream is then mixed with steam from the biomass dryer. This reformer feed mixture is then heated up to 2000°F in a thermal oxidizer using heat from combustion of hydrotreater product gas (also known as residual fuel gas). The hot reformer feed gas is then reformed in the adibatically-operated steam reforming unit. A space velocity of 10,000 hr^{-1} is used to size the steam reformer. Product gas leaves the steam reforming unit at 1350°F and is cooled down to 596°F by generating steam. The cooled product gas is then mixed with steam (at 300°F) from biomass dryer and is sent to shift reactor. Approximately, 90% CO conversion is assumed in the shift reactor. A space velocity of 5,000 hr^{-1} is used to size the shift reaction vessel. Finally, the product stream from the shift reactor, consisting predominantly of H_2 and CO_2, is sent to an amine plant where 95% of CO_2 is removed using aqueous methyl diethanolamine (MDEA) solution. This decreases the CO_2 concentration from 40 mol% to 7 mol% in hydrogen stream. The rich MDEA solution is regenerated using steam from biomass dryer and recycled back to the absorber. Regeneration energy demand of 1100 Btu/lb-CO_2 is assumed for the aqueous MDEA process. The enriched hydrogen stream is then compressed to 765 psi in a 6-stage compressor with 5 intercoolers. Gas leaving the final compression stage is not cooled as it is to be heated prior to entering the hydrotreater. Concentration of hydrogen in the compressed stream is 87.5%.

Bio-crude Upgrading. Bio-crude produced during catalytic pyrolysis of biomass consists of 23wt% of oxygen. Additionally, the H:C ratio in bio-crude is 1.15. Thus, hydroprocessing is used to remove oxygen from bio-crude and upgrade its H:C ratio to 2.1, similar to gasoline. With successful catalyst and process development for biomass conversion to bio-crude, it is optimistically assumed that all the oxygen in bio-crude is removed as water and the H:C ratio is upgraded to 2.1 during one-step hydroprocessing resulting in production of gasoline which does not require additional upgrading or conditioning. The hydrotreater is operated at 740 psia and 662°F. A space velocity of 1.5 hr^{-1} is used to size the hydroprocessing reaction vessel. Bio-crude from the water/bio-crude separation tank is pumped to 746 psi and heated from 100°F to 452°F using hydrotreater product stream. Bio-crude vapors are then combined with hydrogen and heated up to 662°F using steam. The bio-crude hydrogen mixture then enters the hydroprocessing unit where hydrogen reacts with oxygen in bio-crude to produce water and additional hydrogen is added to bio-crude to upgrade its H:C ratio to 2.1. The hot product stream from the hydrotreater exchanges heat with bio-oil feed to hydrotreater during which the product stream cools to 448°F. Finally, the product stream is cooled to 148°F using cooling water. At this point, water and gasoline are separated from gas stream in a flash vessel and sent to a decanter where water and gasoline are separated by difference in gravity. Water will be sent to wastewater treatment plant and gasoline will be sent to storage tank. The product gas from the flash vessel is combusted in a thermal oxidizer to pre-heat steam reformer feed stream up to 2000°F.

Product Storage. The product storage capacity is estimated for 1.2 million gallons of product, equivalent to 1 week of production.

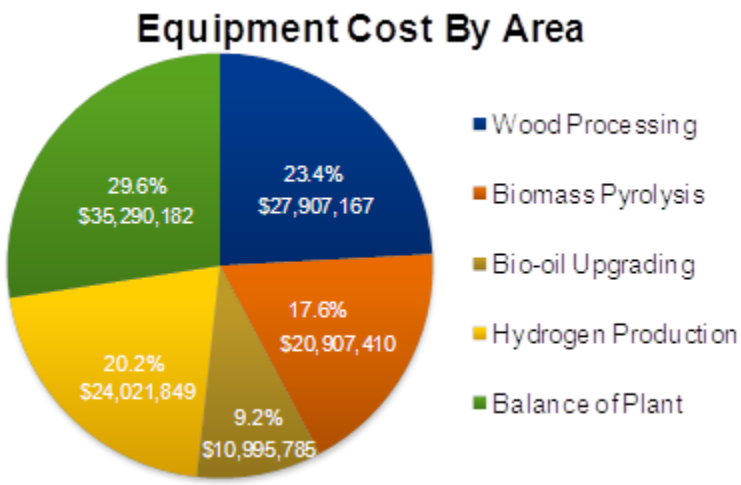


Figure 28: Distribution of equipment material cost based on plant area

Capital Cost Estimate

Process flow diagrams providing details of the pyrolysis process and required utilities were prepared for each unit operation. The heat and mass balance for the entire plant was generated by simulating the design case in Aspen Plus® and was used to size individual equipment. These results are summarized in a list of sized equipment. The equipment costs were estimated using Aspen Icarus® and factors were applied to estimate the bulk (e.g., pipe, steel, electrical, I&C, civil) costs for individual equipment items. Once the bulk costs were derived, factors to determine the breakdown between material and labor costs were applied. The applied factors are based on industry standards used in capital projects.

The total equipment cost of the commercial-scale plant is $121 million with a breakdown of $119 million in the material cost and $2 million is fabrication labor cost. The distribution of the equipment costs in various areas of the plant is given in Figure 28. The feed processing area (wood receiving, storage, chipping, and drying) contributes to 23.4% of the total capital equipment cost. Biomass pyrolysis makes up 17.6% of the total capital cost and includes the transport reactor, quench system and bio-crude/water separation unit. The multi-stage hydrogen compressor, bio-crude and hydrogen preheating, hydroprocessing and gasoline separation and storage are included in the bio-crude upgrading area that contributes 9.2% of the total capital equipment costs. Hydrogen production includes steam reforming pyrolysis product gases, the water-gas-shift reactor, and amine scrubber for CO_2 removal. The total equipment cost for hydrogen production is $24 million and is 20.2% of the total. The balance of plant includes the cooling tower, thermal oxidizer, steam turbine, generator, wastewater treatment, make-up water pretreatment, liquid storage, foam generation package, fire protection system, etc. The balance of plan cost is $35 million.

Table 16: Estimates for various categories of total plant cost

	Percentage	Amount, million $
Engineering	12%	31
Home office	5%	13
Commissioning	5%	13
Escalation	3%	8
Contingency	25%	64

The total project cost is estimated based on the total capital equipment cost. As mentioned earlier, installed cost is estimated based on industry standards to estimate the costs associated with pipe, steel, electrical, I&C, civil, etc. for each piece of equipment. The installation cost is estimated as $145 million. Thus, the total installed cost is $266 million. Other categories included in the project cost, in addition to

the installed capital cost, are listed in Table 16. These costs are estimated as a percentage of the installed cost. The estimated total project cost (TPC) is $395 million.

Fuel Production

For this preliminary design, the product yields for catalytic fast pyrolysis are extrapolated from the experimental results from bench-scale testing of white oak catalytic fast pyrolysis with the RTI-A9 catalyst. Bio-crude yield of 29 wt% during the catalytic pyrolysis process was assumed. Additionally, no loss of carbon was assumed during reheating of bio-crude and in the hydroprocessing step. As a result, a commercial-scale plant processing 2000 dry tons/day of biomass produces 3,984 barrels per day of gasoline at full plant capacity assuming a gasoline yield of 83.6 gal/dry-ton of biomass. A plant capacity factor of 80% for the first year, 85% for the second year, 90% for the third year and 95% for the remaining 20 year term was assumed. Thus, the annualized gasoline production rate, an average of gasoline production rate over the 20 year term of plant, is 1,359,618 barrels per year. Carbon dioxide is captured in the amine plant to enrich the purity of hydrogen produced from pyrolysis product gases. The amine plant CO_2 capture rate is 874 tons/day. Since this CO_2 is a product of biomass, no credit is assumed.

Table 17: Summary of utility requirements

	Units	Amount	Consumption/gal of gasoline
Make-up water	gpm	387	3.3 gal/gal
Electricity	MWe	8.4	1.21 kWh/gal
Natural Gas	MMBtu/hr	60	0.009 MMBtu/gal
Wastewater treatment	gpm	562	
Ash disposal	tons/yr	758	

Utility Summary

A summary of the utility requirements is presented in Table 17. The make-up water consumption rate is 387 gpm. The cooling water make-up requirement is 380 gpm and is directly used from the well. The remaining 7 gpm of make-up water is used as boiler feed make-up water that needs to be demineralized. The total electricity consumption of the plant is 28.9 MWe. A summary of some major electricity consuming unit operations is provided in Table 18. The compressor used to compress the air fed to the regenerator is the largest consumer of electricity (9.7 MWe). The multi-stage compressor used to compress hydrogen for bio-crude hydroprocessing consumes 5.6 MWe. Steam is generated at several locations of the plant as a means of recovering energy. This steam is eventually expanded in a steam turbine to generate electricity. Approximately 20.5 MWe are generated in the plant. Thus the net electricity requirement of the plant is 8.4 MWe. Natural gas is used in the plant to operate the plant flare, gasoline loading flare and supplement residual fuel gas from hydrotreater to supply energy to preheat steam reformer feed gas. The two main waste streams in the plant are wastewater generated at 562 gpm and ash produced at 758 tons/year.

Table 18: Summary of electricity consumption

	Consumption, MWe
Chipper	1.9
Air Compressor	9.7
Electrostatic precipitator	1.5
Hydrogen compressor	5.6

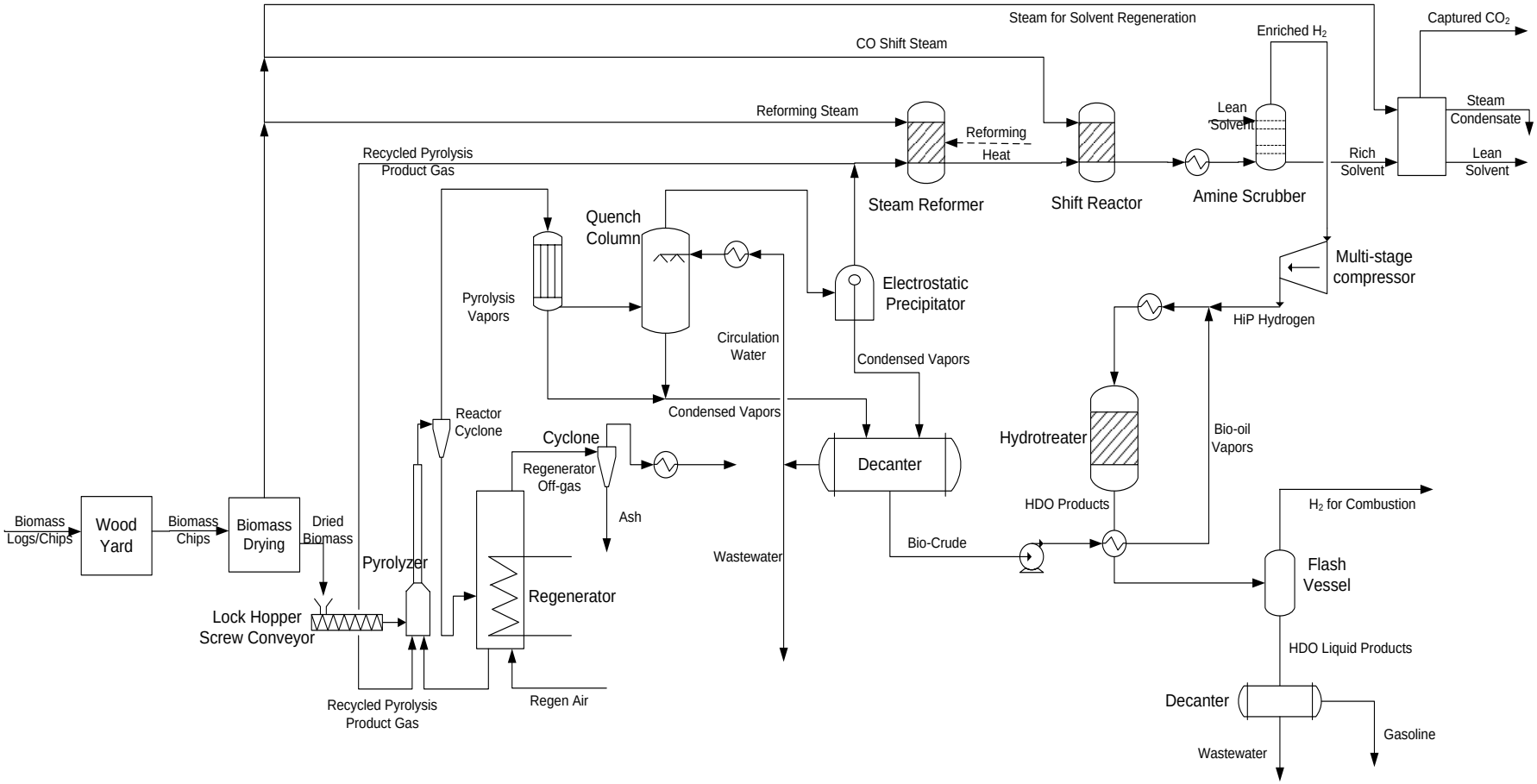


Figure 29. Integrated catalytic biomass pyrolysis hydroprocessing process.

Economic Analysis

The total project capital cost is estimated to be $395 million. For a 20 year term of plant, the annualized capital cost is $19.7 million and the product normalized capital cost is $6.90/(gal/yr). It is assumed that 60% of the capital cost is leveraged and the total financed debt is $237 million. The debt term for the project is assumed to be 20 years. Assuming the debt is made available at an interest rate of 7.5% paid over the debt term of 20 years, monthly payments on the loan are $2,191,338.

The total annualized operating expense was estimated to be $105,486,435. A summary of the demand, price and expenses of the individual items included in the operating expenses is given in Table 19. All the parameters are annualized averages over the 20 year plant term. The biomass feedstock price used for the analysis was $65/dry ton. This estimate was provided by Price BioStock. An escalation of 2%/year was assumed in the price of biomass feedstock. The price of spray dried RTI-A9 catalyst was assumed to be $15,000/ton (for comparison, price of fresh FCC catalyst is $3,000/ton). The catalyst loss rate for FCC material is usually around 50 lb/MMlb-circulated. Although spray dried RTI-A9 is stronger than FCC catalyst, it is not a highly developed technology. Thus, make-up catalyst demand was calculated using a very conservative catalyst loss rate of 100 lb/MMlb-circulated. This leads to an annualized make-up catalyst demand of 758 tons/yr. Natural gas and electricity price and escalation were obtained from US Energy Information Administration's (EIA) 2010 Annual Energy Outlook (www.eia.doe.gov). Make-up cooling and boiler feed water cost estimates, and ash disposal and wastewater treatment costs were derived from industrial standards.

Table 19: Summary of items included in production cost

	Base price	Escalation	Annualized demand	Annualized cost
Biomass	$65/dry ton	2.0%	682,550 dry tons/yr	$54,041,947/yr
Make-up catalyst	$15,000/ton	0.0%	758 tons/yr	$11,375,832/yr
Electricity	$0.06/kWh	2.1%	68,844,139 kWh/yr	$5,082,581/yr
Ash disposal	$25/ton	0.0%	159,719 tons.yr	$3,992,979/yr
Wastewater treatment	$0.01/gal	0.0%	275,752,042	$3,358,937/yr
Natural gas	$4.5/MMBtu	1.6%	491,436 MMBtu/yr	$2,587,753/yr
Make-up cooling water	$0.01/gal	2.0%	186,731,663 gal/yr	$301,169/yr
Make-up boiler feed water	$0.02/gal	2.0%	3,456,344 gal/yr	$84,203/yr
OPEX	$15.8 MM/yr	0.5%		$14,550,581/yr
Personnel	$5.8MM/yr	3.0%		7,835,873/yr

The OPEX costs cover maintenance, ES&H, insurance, operations, property taxes, etc., and is a percentage of the total project cost based on industry standards. The personnel expense covers salaries for a total staff of 71 employees with an average estimated base salary of $54,138. Finally, the total production cost is calculated by combining operating expenses and payments made on loan. Thus, the total annual gasoline production cost is $128,394,968/yr for the 57.1 million gallon per year facility resulting in a production cost of $2.25/gal of gasoline.

A percentage distribution of the individual items towards the total operating expenses is given in Figure 30. Biomass feedstock contributes 42.1% to the operating expenses followed by debt payments and OPEX at 17.8% and 11.3%, respectively. The annualized cost of make-up catalyst is the fourth major operating expense at 8.9% of the total. Ash and wastewater disposal costs contribute to 3.1% and 2.6%, respectively, whereas the cost of all the utilities is ~4.1%.

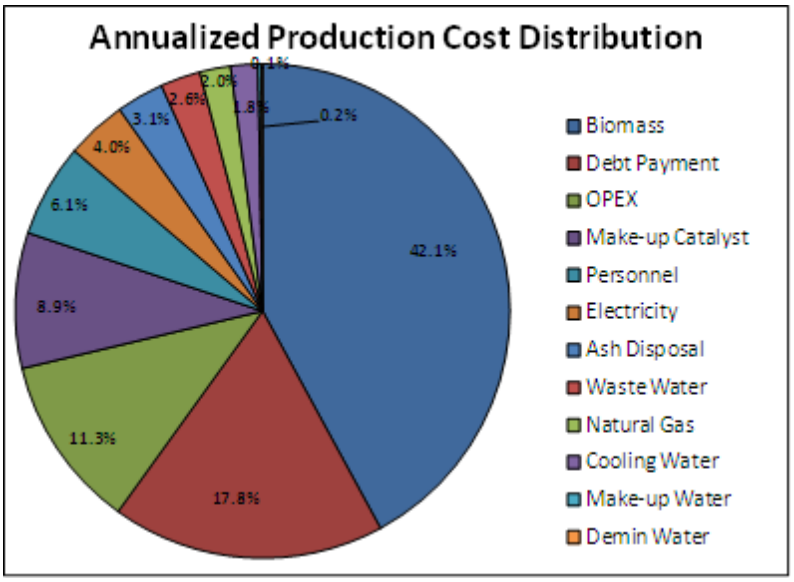


Figure 30: Percentage distribution of various operating cost components

Revenue

The annualized gasoline production rate, over the 20 year term of plant, is 1,359,618 barrels per year. Gasoline price estimates and forecasts were obtained from EIA's Annual Energy Outlook. A gasoline price of $3.13/gal was used for the first year with an escalation factor of 0.95%. Average gasoline prices over a 20 year period are $3.43/gal. Additionally, two government subsidies were assumed: 1) production tax credit of $0.45/gal and 2) blender credit of $0.46/gal. Thus, the total government subsidy was $1.01/gal. This results in an annualized revenue of $253,754,943 per year.

Project Output

Journal Articles:

None

ARPA-E teleconferences and meetings:

- D. Dayton and R. Gupta provided a project update and discussed milestones with M. Hartney and D. Matuszak by teleconference on April 6, 2011.
- D. Dayton and R. Gupta provided a project update and discussed milestones with M. Hartney and D. Matuszak by teleconference on April 28, 2011.
- D. Dayton and R. Gupta provided a project update to M. Hartney at RTI International with D. Matuszak joining by teleconference on May 20, 2011.
- R. Gupta and J. Carpenter provided a project update and discussed milestones with M. Hartney and D. Matuszak by teleconference on June 29, 2011.
- D. Dayton, J. Carpenter, and R. Gupta revised milestone discussion with D. Matuszak on July 15, 2011.
- D. Dayton and J. Carpenter. Revised milestone discussion with D. Matuszak on August 9, 2011.
- D. Dayton, B. Gardner and R. Gupta met with K. Sawyer, D. Matuszak, S. Mirmira, R. Conrado, and M. Hartney at ARPA-E headquarters on September 23, 2011 to provide an update on the

technical progress made in the project and discuss the preliminary economics and scale-up opportunities for the proposed technology.

- K. Sawyer, D. Matuszak, and M. Hartney visited RTI on October 28, 2011 for a project update and review of the Go/NoGo decision point.
- K. Sawyer and D. Matuszak visited RTI on April 3, 2012 for a project update. Bryna Berendzen also attended the meeting and Melissa Klembara was on teleconference both from the Office of Energy Efficiency and Renewable Energy's (EERE's) Biomass Program.
- K. Sawyer and D. Matuszak visited RTI on November 2, 2012 for a project update.
- K. Sawyer and Kristyn Ivey visited RTI on April 11, 2013 for a project update.

Presentations:

A paper entitled "Understanding Catalytic Deoxgenation in Biomass Pyrolysis: A Model Compounds Approach" was presented at the Thermochemical Sciences 2010 meeting at Iowa State University, Sept 21-23, 2010. Co-authors are M. Pavani, P. Sharma, M. Cooper, D. Dayton and R. Gupta.

One oral presentation and two posters were presented at the TCBiomass 2011 conference held September 28-30, 2011 in Chicago, IL. The titles are:

1. D. C. Dayton, J. Carpenter, M. Pavani, M. von Holle, and R. Gupta. "Catalytic Biomass Pyrolysis for Bio-Crude Production: Catalyst Screening and Process Development" (Oral Presentation)
2. J. Carpenter, M. Pavani, M. von Holle, D.C. Dayton, and R. Gupta. "Catalytic Fast Pyrolysis of Biomass in a Bench-top Fluidized Bed" (Poster Presentation)
3. M. Pavani, J. Carpenter, M. von Holle, D.C. Dayton, and R. Gupta. "Understanding Catalytic Deoxygenation Mechanisms for Bio-crude Production Using Model Compounds." (Poster Presentation)

A poster entitled "Catalytic Bio-crude Production in a Novel, Short-Contact Time Reactor" was presented at the 2012 ARPA-E Energy Innovation Summit in Washington, D.C., February 27-29, 2012.

D.C. Dayton was invited to present "Catalytic Biomass Pyrolysis Technology Development for Advanced Biofuels Production" at the NSF Sponsored Workshop on Lignocellulosic Biofuels Using Thermochemical Conversion at Auburn University, June 14-15, 2012.

D.C. Dayton was invited to present "Catalytic Biomass Pyrolysis Technology Development for Advanced Biofuels Production" at the Thermochemical Conversion of Biomass-2012 Symposium, at North Carolina State University, October, 24, 2012

A poster entitled "Catalytic Bio-crude Production in a Novel, Short-Contact Time Reactor" was presented at the 2013 ARPA-E Energy Innovation Summit in Washington, D.C., February 26-27, 2013.

D.C. Dayton, "Catalytic Biomass Pyrolysis Technology Development for Advanced Biofuels." Oral Presentation, TCBiomass 2013 September 3-6, 2013 Chicago, IL.

M. Von Holle, "Small Scale Catalyst Testing with Biomass for Advanced Biofuels Technology Development." Poster Presentation, TCBiomass 2013 September 3-6, 2013 Chicago, IL.

J. Hlebak, "Experimental Capabilities at RTI International to Support R&D for Direct Biomass Liquefaction Pathways." Poster Presentation, TCBiomass 2013 September 3-6, 2013 Chicago, IL.

J. Peters, "Deoxygenation Chemistry of Bio-oil Model Compounds with Selected Catalysts." Poster Presentation, TCBiomass 2013 September 3-6, 2013 Chicago, IL.

Status Reports:

ARPA-E Q1 Quarterly Status Report – April 30, 2010
ARPA-E Q2 Quarterly Status Report – July 20, 2010
ARPA-E Q3 Quarterly Status Report – October 20, 2010
ARPA-E Q4 Quarterly Status Report – January 20, 2011
ARPA-E Q5 Quarterly Status Report – April 15, 2011

ARPA-E Q6 Quarterly Status Report – July 25, 2011
ARPA-E Q7 Quarterly Status Report – October 17, 2011
ARPA-E Q8 Quarterly Status Report – January 23, 2012
ARPA-E Q9 Quarterly Status Report – April 20, 2012
ARPA-E Q10 Quarterly Status Report – July 15, 2012
ARPA-E Q11 Quarterly Status Report – October 15, 2012
ARPA-E Q12 Quarterly Status Report –January 30, 2013
ARPA-E Q13 Quarterly Status Report –July 30, 2013
ARPA-E Q14 Quarterly Status Report – November 6, 2013

Press Reports:

RTI International – Internal News Release - 10.27.2009 "RTI International to Develop Alternative Fuels from Biomass to Reduce Greenhouse Gas Emissions"

Lane, James. Biofuels Digest, October 27, 2009. "ARPE-E awards $151 million in advanced energy R&D – pyrolysis, algae, butanol, CO_2 capture among hot technologies funded"

SyncTM Weekly Highlights from the North Carolina Department of Commerce, November 3, 2009. "RTI to develop biomass fuel"

Green Car Congress, October 26, 2009, "ARPA-E Awards $151M to 37 Projects for Transformative Energy Research"

Biorefining Magazine, August 22, 2011."High Risk, High Reward - The U.S. DOE's Advanced Research Projects Agency-Energy targets the "white space" of existing energy research" by Erin Voegele

DOE Press News Item (www.energy.gov) "Move Over Flash Pyrolysis, There's a New Bioenergy Sheriff in Town" by April Sawyer December 16, 2011.

"A World of Knowledge" article in the November 2012 edition of Business North Carolina highlighting RTI's biofuels activities.

Patents:

International Application No. PCT/US2013/029379; filed March 6, 2013 Entitled Catalytic Biomass Pyrolysis Process Claims Priority to Appl. No. 61/607,866; Filed March 7, 2012

International Patent Application No. PCT/US13/72948 Claiming Priority to U.S. Patent Application No. 61/733,142; filed December 4, 2013 entitled CATALYST COMPOSITIONS AND USE THEREOF IN CATALYTIC BIOMASS PYROLYSIS

Licensed Technologies:

None

Follow-On Funding

USDOE/EERE - DE-FOA-0000467. "EE-0005358 - Catalytic Upgrading of Thermochemical Intermediates to Hydrocarbons." 2011-2015. Funding: $4,000,000