2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

WBS 3.3.1.9 - Catalytic Upgrading of Thermochemical Intermediates to Hydrocarbons

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Bio-Oil Technology Area Review

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RTI International

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Goals and Objectives

Objective: Demonstrate an advanced biofuels technology that integrates a catalytic biomass pyrolysis step and a hydroprocessing step to produce infrastructure compatible biofuels.

Directly supports *in-situ* bio-oil pathway from liquefaction through bio-oil upgrading and fuel processing

DE-FOA-0000467: Catalytic Upgrading of Thermochemical Intermediates to Hydrocarbons

- Develop technology and processes that yield a finished fuel (blendstock), infrastructure-ready hydrocarbon, and/or biofuel-enabling chemical product.
- Design and operate fully integrated processes capable of reaching steady state and generating long term, continuous data sufficient to validate the process.
- Demonstrate the upgrading step(s) in a continuous, integrated process with the ability to monitor key parameters of the process operating conditions.
- Comprehensive characterization of the selected catalysts for upgrading process and full chemical and physical characterization of the resulting hydrocarbon products.
- Estimate the cost of the final hydrocarbon product stream that meet advanced biofuels specifications
- Long term thermochemical intermediate upgrading bringing the technology to a process development unit (PDU) or pilot ready status at the end of the project.

Quad Chart Overview

Timeline

- Project selected: 8/31/2011
- Conditional award date: 9/22/2011
- Contract award date: 8/16/2012
- Project kick-off: 11/6/2012
- Project end date: 9/30/2015

Budget

- $5MM Total project funding
  - $4MM DOE share
  - $1MM Cost share
- $1,808,380 received in FY12
- $1,256,000 received in FY13

Barriers Addressed

- Tt-E Liquefaction of Biomass and Bio-Oil Stabilization
- Tt-G Fuel Synthesis and Upgrading
- Tt-K Bio-Oil Pathways Process Integration

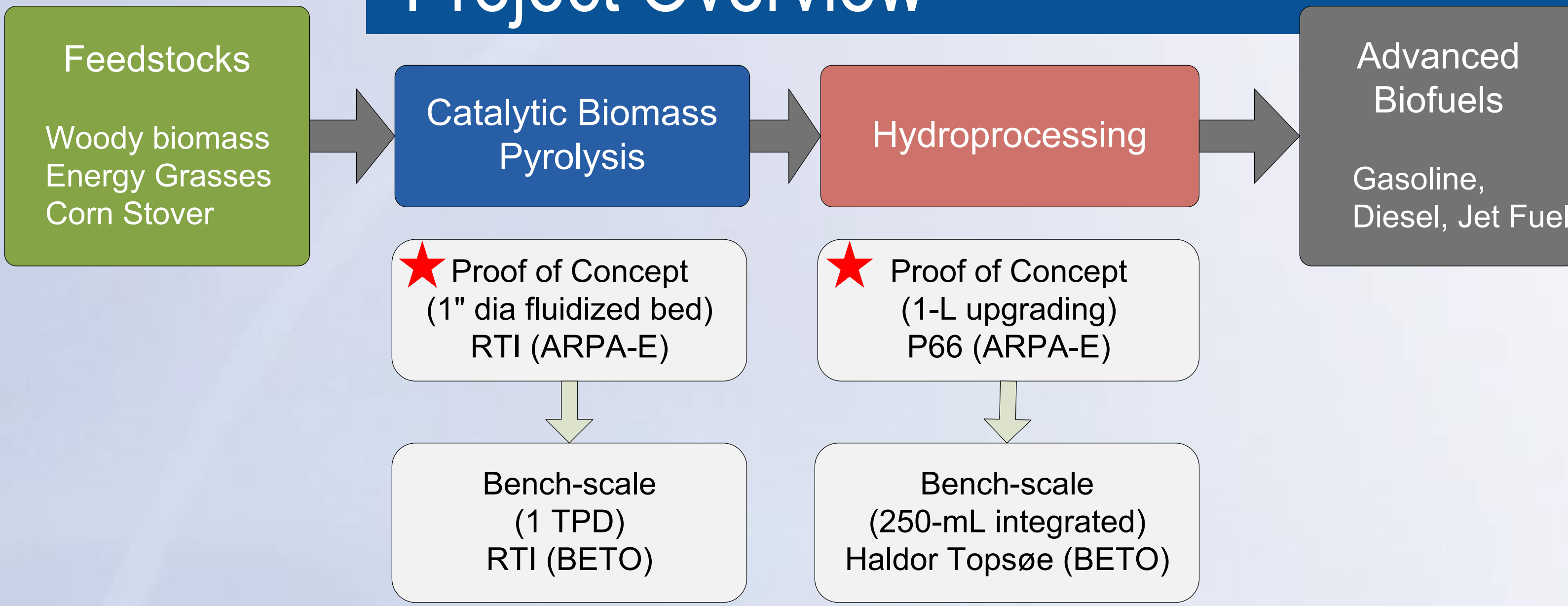
Partners

- RTI – project lead, catalytic biomass pyrolysis technology development, Engineering Design and Scale-up, project management
- Haldor Topsøe A/S (HTAS) - Hydroprocessing Development and Process Modeling

High impact feedstock providers

- Archer Daniels Midland Corporation (corn stover)
- Biofuels Center of North Carolina (woody biomass and switchgrass)

Project Overview



The technical goals are to:

1) Optimize the catalytic biomass pyrolysis process to achieve high degree of deoxygenation, while maximizing the bio-crude production
2) Improve bio-crude thermal stability
3) Evaluate the impact of bio-crude quality in the hydroprocessing step
4) Minimize hydrogen demand of the integrated process
5) Maximize biofuels yields

★ **Catalytic Bio-crude Production in a Novel, Short Residence Time Reactor (DOE/ARPA-E/DE- AR0000021)**

Project Scope

Task Structure

Task 1.0: Parametric Catalytic Biomass Pyrolysis Optimization (RTI)
Task 2.0: Hydroprocessing Evaluation and Optimization (HTAS)
- **2.1 Bio-crude Upgrading and Analysis**
- **2.2 Bio-crude Hydroprocessing Model Development**

Task 3.0: Integrated Process Development (RTI and HTAS)
Task 4.0: Integrated Process Operation (RTI)
- 2000 total hours of integrated operation with woody biomass, corn stover, and switchgrass

Task 5.0: Process Modeling and Refinery Integration (RTI and HTAS)
- **5.1 Process Modeling**
- **5.2 Life-Cycle Assessment**
- **5.3 Refinery Integration**

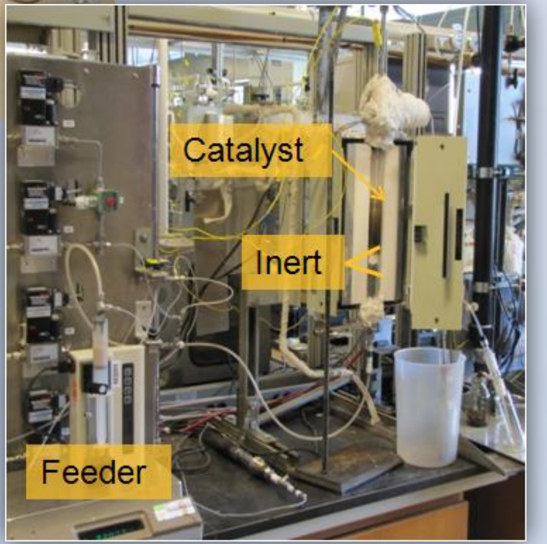
Task 6.0: Project Management and Reporting (RTI)

Technical Approach

Scale-up RTI's catalytic biomass pyrolysis process, integrate a hydroprocessing unit, and demonstrate the long-term operation and performance of the integrated process.

Month	Milestone Description
3	Hydroprocessing unit design basis
6	Process operating conditions optimized for stable bio-crude production
8	Deliverable: 10-L of wood bio-crude
9	Hydroprocessing Unit Design Package
10	Deliverable: 10-L of switchgrass bio-crude
12	Deliverable: 10-L of corn stover bio-crude
15	Hydroprocessing conditions for 3 bio-crude samples
24	Technical evaluation of bio-crude/refinery intermediate blends
25	Complete 1,000 hours integrated operation with woody feedstock
30	Complete 500 hours integrated operation with switchgrass
31	Refinery integration options for catalytic biomass pyrolysis technology
34	Complete 500 hours integrated operation with corn stover
35	Design package for a 2,000 tpd integrated process for TEA and LCA
36	Final Report

Catalyst Development (ARPA-E Project)



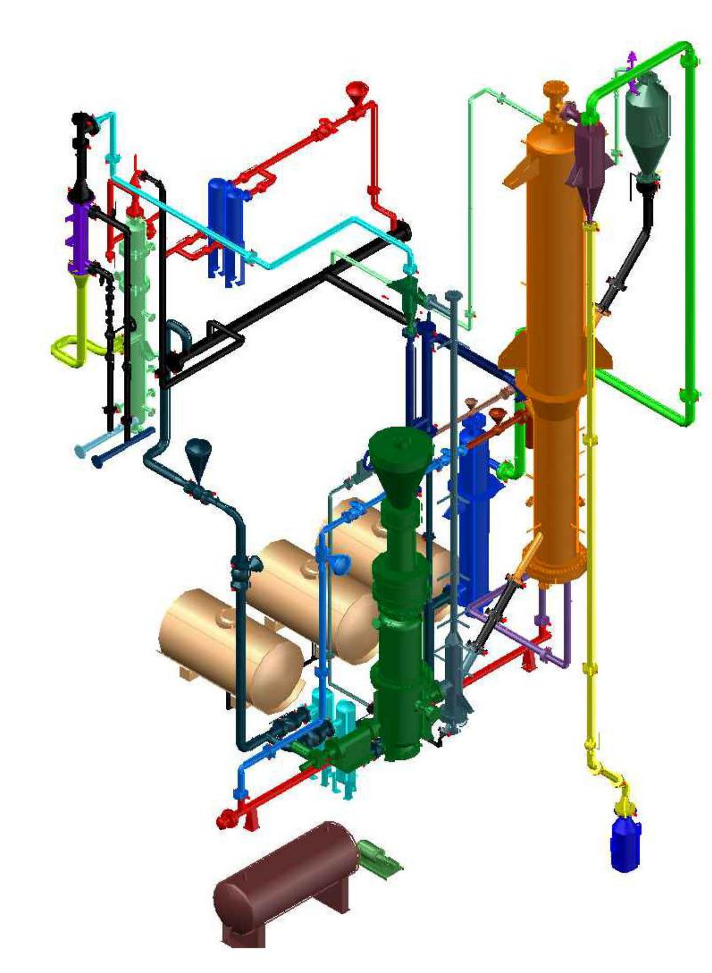
- Screened catalyst formulations for deoxygenation activity in multiple reactor systems
- Automated Medium Throughput Microreactor (MTP)
  - Programmed reaction sequence for unattended operation
  - Rapid screening to evaluate deoxygenation activity with model compounds
  - Quantitative real-time product analysis
  - Measure regeneration products for coke yield
- Bench-top fluidized bed reactor for catalytic biomass pyrolysis
  - Correlate deoxygenation activity with bio-crude oxygen content
  - On-line gas analysis
  - Liquid and solid product collection and analysis
  - > 95% mass closure for bio-crude yield and energy recovery
  - Over 100+ trials of catalytic fast pyrolysis in the bench-top fluidized bed reactor

Bio-crude Properties

	Baseline	RTI-A9
Solids (wt%)	14.3	19.8
Gas (wt%)	11.6	23.9
Water (wt%)	18.4	28.7
Bio-crude, dry (wt%)	49.4	24.8
Bio-crude Composition (wt%)		
C	56.6	72.8
H	5.8	7.2
O	37.7	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

Bio-crude Properties	Baseline	RTI-A9
TAN (mg KOH/g bio-crude)	105	25
KF water Content (wt%)	27	10
Kinematic Viscosity at 40°C (cSt)	53.2	56
Revaporization Efficiency at 350°C	48%	82%

1 TPD Catalytic Biomass Pyrolysis Unit Overview



Objectives:

- Demonstrate RTI's catalytic biomass pyrolysis process at pilot-scale with a biomass feed rate of 100 lb/hr
  - Bio-crude with less than 20 wt% oxygen
  - At least 50% energy recovery
  - Mass closure at least 90%
- Understand the effect of operating parameters on product yields and quality
  - Pyrolysis temperature (350-500 ºC)
  - Residence time (0.5-1.0 s)
  - Regenerator temperature (500-700 ºC)
  - Catalyst circulation rate
  - Type of biomass

Design based on single-loop transport reactor system

- Catalyst undergoes continuous reaction and regeneration
- System can be operated autothermally with heat of regeneration (and char combustion) carried over by the catalyst to the reaction zone

Design Basis and System Overview

	Design Basis	Range
Pyrolysis temperature, ˚C	500	350-500
Regeneration temperature, ˚C	700	500-700
System pressure, psia	20	20-30
Biomass feed rate, lb/hr	100	25-110
Residence time, s	0.5	0.4-1.2

Process Sub-systems

Biomass Feeder

- Bulk bag discharge system
- Double lock hopper – T.R. Miles design

Reactor System

- Transport reactor
- Make-up catalyst storage
- Quench system for pyrolysis products recovery
  - Spray column
  - Separation vessel
  - Heat exchanger

Product Collection and Storage

Regenerator Off-gas Cooler

Thermal Oxidizer and Vent

Installation

RTI's 1 TPD Biomass Unit

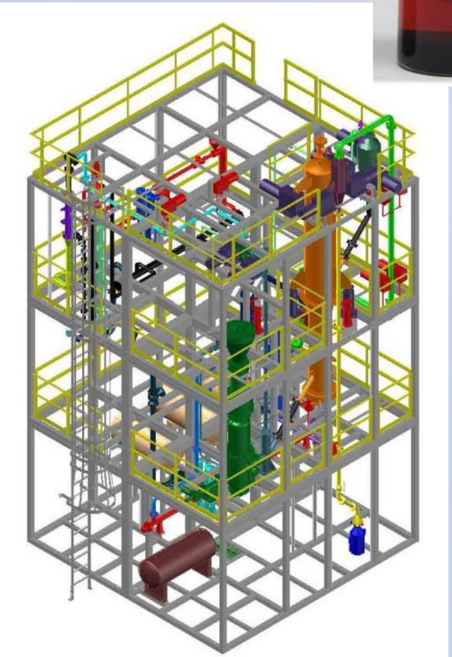
RTI's Energy Technology Development Facility

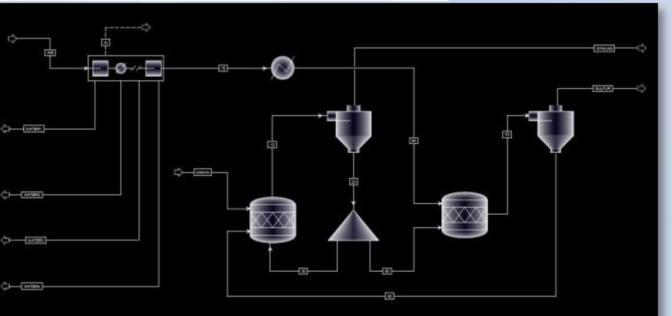
Critical Validation Matrices

- Pilot plant representative of a commercial engineering design
- Pilot plant operated for long-enough duration to get design data for a commercial plant and operational experience
- Multiple biomass feedstocks tested
- Catalyst scaled-up and physical/chemical properties confirmed
- Long-term durability of the catalyst demonstrated
- Oil yields and oil quality validated
- Final product certified as a “drop-in” fuel

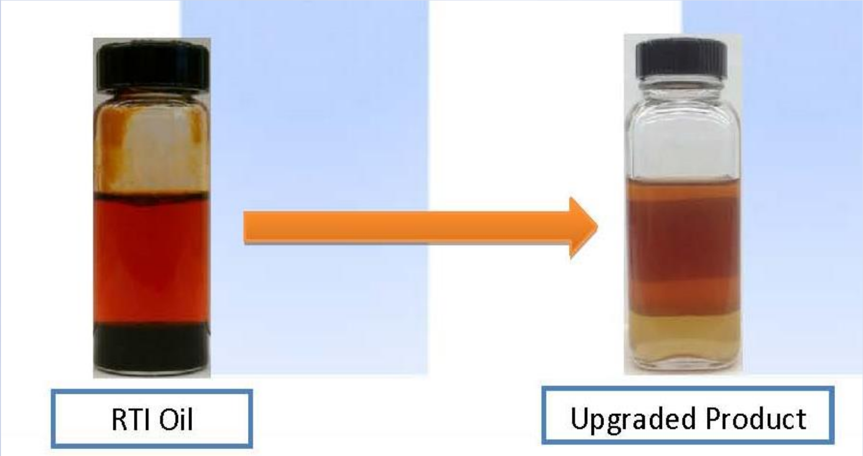
Summary of Technology Status

- Catalyst development included model compound screening and bench-top (~ 1 g/hr) biomass conversion
  - Suitable catalyst identified for scale-up
  - Working with catalyst partners for bench-scale batches
- Catalytic biomass pyrolysis in a 1”-dia fluidized bed reactor
  - Organic and aqueous phases
  - 20 wt% oxygen content
  - 42% energy recovery
- Laboratory data provided the basis for a 1 TPD bench-scale unit
  - HMB and process design complete
  - Detailed engineering completed June 1, 2012
  - Fabrication completed, delivery April 9-10, 2013
  - Installation and commissioning May-June 2013
- Catalyst Scale-up to 400-kg batch
- Preliminary Techno-Economic Analysis
- Bio-crude Upgrading proof-of-concept complete





Bio-crude Upgrading - Hydroprocessing



Proof-of-Principle (ARPA-E)

- Bio-crude can be upgraded to hydrocarbons
- Product is mainly in gasoline range
- Product is rich in cyclic alkanes and monoaromatics

Hydroprocessing reactions:

- Decarbonylation
- Decarboxylation
- Hydrodeoxygenation (HDO)

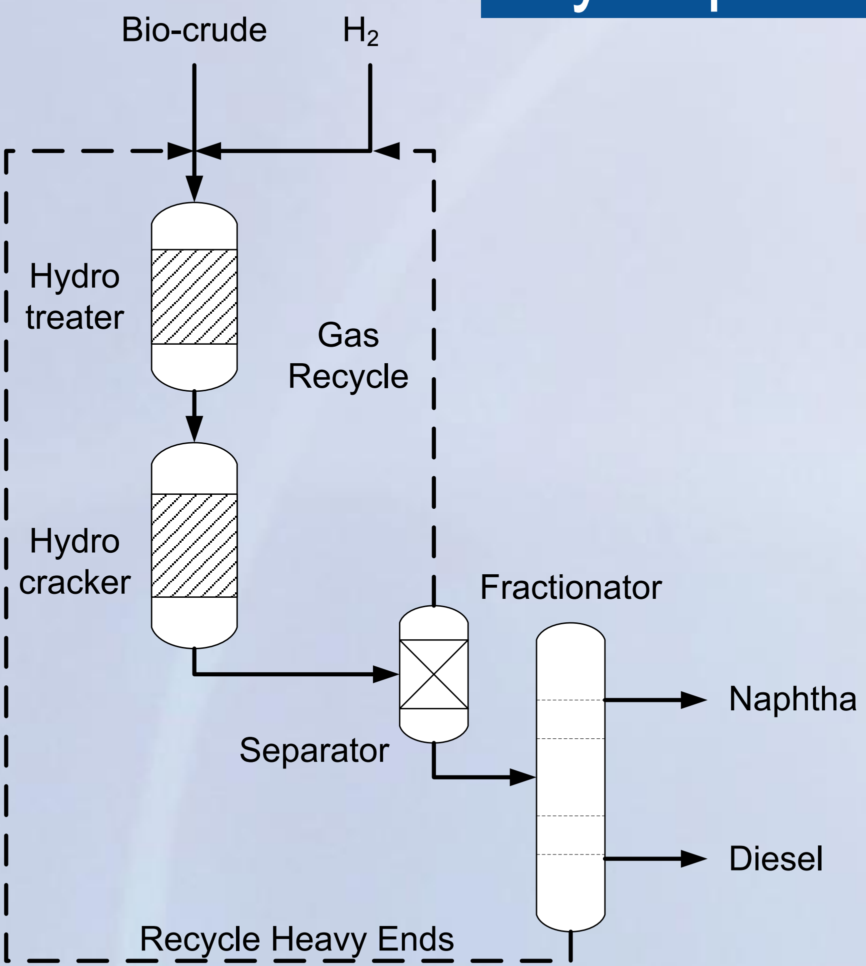
Competing reactions:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

Key process variables to determine

- H_2 consumption
- product yields
- catalyst inhibition
- reactant gas composition
- CO, CO_2, and CH_4 content in the hydroprocessing reactor
- heat balance

Hydroprocessing Unit Design Basis

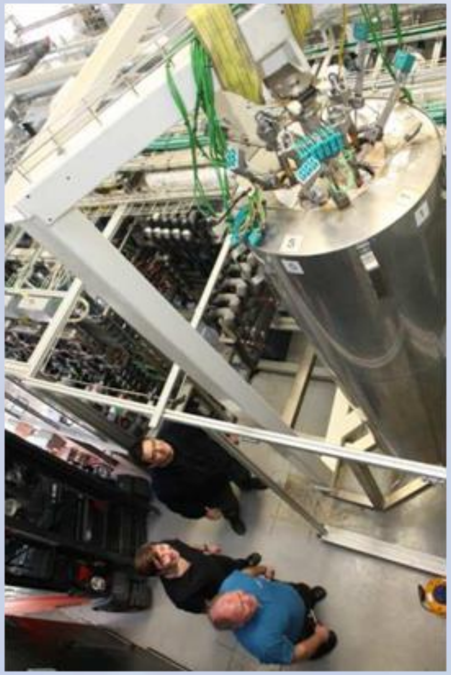


Conceptual Process Flow Diagram for Bio-crude Hydroprocessing (Recycle streams to be validated)

Hydroprocessing reactor with a high-pressure separator (HPS) followed by a low-pressure stabilizer (LPS) for removal of gases and other non-condensed light hydrocarbons

- Reactor volume - 250 ml
- Catalyst volume - 20 to 60 ml of catalyst
- Liquid hourly space velocity - 0.5 to 1.0
- Flow rates - 10 to 60 ml/h
- N_2 is used as the stripping agent
- H_2/bio-crude ratio will depend on the H_2 consumption that will be adjusted as needed.

Integrated Hydroprocessing Unit



- Hydroprocessing unit based on engineering design from Haldor Topsøe A/S
- Haldor Topsøe A/S is leading expert in hydroprocessing
  - 50 test units with over 90 reactors available for R&D
  - Expertise in pilot testing and scale-up
  - Three different configurations available to simulate commercial units
  - Known deviations between pilot and commercial units (fractionation, S in naphtha, etc.)
  - Reliable tests:
    - High reproducibility between two pilot units
    - Results close to performance in commercial units

Relevance

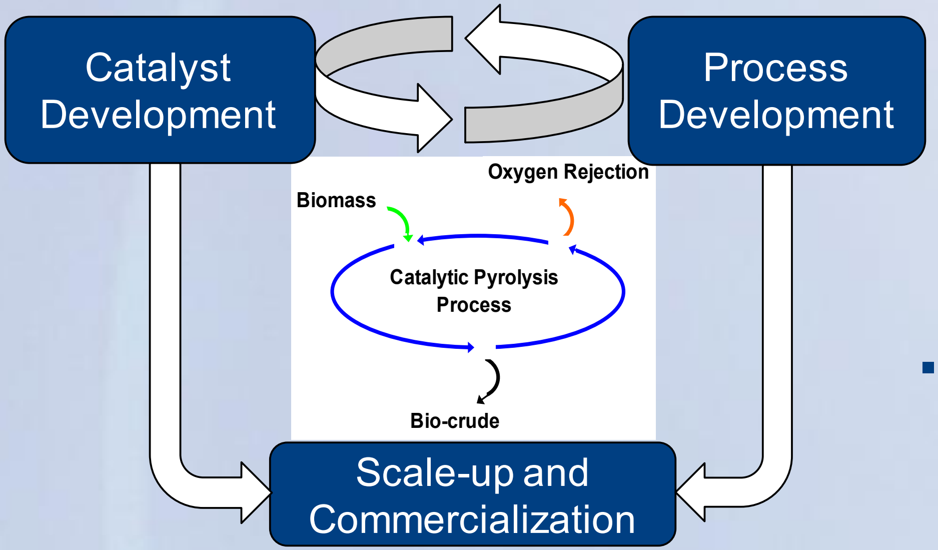
The Bio-Oil Pathways R&D strategic goal is to develop commercially viable technologies for converting biomass feedstocks into energy dense, fungible liquid fuels, such as renewable gasoline, jet fuel, and diesel, bioproducts and chemical intermediates, and bioenergy.

Bio-oil Pathway Milestones:

- By 2017, achieve a conversion cost of $1.83 per gallon of total blendstock ($1.73 /GGE, $2011) via a bio-oil pathway.

- By 2017, (Q4), validate fully integrated, pilot scale conversion processes for a "high impact" biomass feedstock to renewable gasoline or diesel via a direct liquefaction conversion process with bio-oil processing to a finished fuel.

Critical Success Factors



- Catalytic fast pyrolysis
  - Demonstrate 1-TPD operation over 1000h
  - Validate catalyst durability and properties
  - Demonstrate bio-crude yield and quality
  - Bio-crude production at scale relevant for integrated hydroprocessing demonstration
  - 3 high impact feedstocks (wood, corn stover, switchgrass)
- Bio-crude upgrading
  - Impact of bio-crude properties
  - Establish process conditions (T, P, pH_2)
  - Optimize hydroprocessing catalyst performance; product yield and quality
  - Over 1000 h integrated operation
  - Catalyst lifetime (regeneration)
  - Develop hydroprocessing model
- Techno-economic evaluation
  - Cost per gallon of upgraded bio-crude
  - Cost per gallon of finished fuel
  - Hydrogen demand

Future Work

Complete sub-award negotiations

Parametric Catalytic Biomass Pyrolysis Operation

- Determine impact of process variables on bio-crude yield and quality
- Produce >10L of bio-crude from 3 feedstocks for hydroprocessing
- Generate engineering data for scale-up and TEA

Hydroprocessing Evaluation and Optimization

- Process conditions for upgrading (T, P, pH_2)
- Determine catalyst properties critical to hydroprocessing
- Evaluate impact of bio-crude properties on hydroprocessing
- Hydroprocessing modeling

Integrated Process Development and Operation

- Fabrication of hydroprocessing unit based on Haldor Topsøe A/S design
- Commissioning and shakedown
- 2000h of operation with 3 high impact feedstocks

Process Modeling and Refinery Integration

- Product evaluation for determining refinery insertion point
- Techno-economic analysis demonstrate fuel cost for integrated process
- Life-cycle assessment of integrated process

Summary

- Directly supports BETO goals for in-situ catalytic fast pyrolysis to convert biomass to fuels
  - Direct liquefaction
  - Bio-crude upgrading
  - Fuel processing
- Building on successful completion of ARPA-E project
  - Proof-of-principle biomass catalytic fast pyrolysis and bio-crude upgrading
  - Catalyst development and scale-up
  - Design, installation, and commissioning of 1 TPD catalytic biomass pyrolysis unit
- Sub-award with Haldor Topsøe A/S pending
  - Project kickoff Nov 2012
  - Integrated work plan to begin as soon a agreements are fully executed
- Project success: Long term thermochemical intermediate production and upgrading bringing the technology to a process development unit (PDU) status at the end of the project.

Acknowldegments

BETO Project Officer: Melissa Klembara

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- Mark Hartney
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Biofuels Center of North Carolina

- W. Steven Burke
- Mark Conlon

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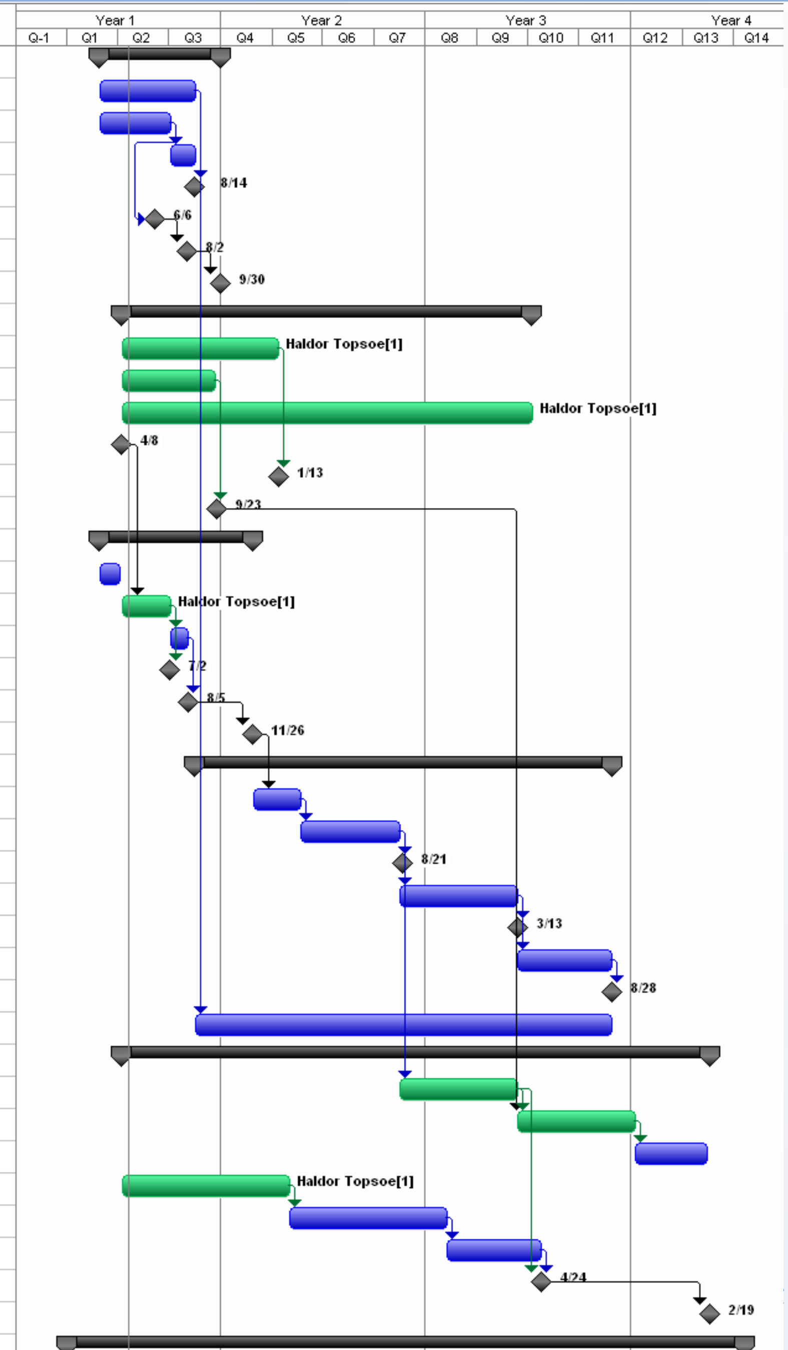
- Devaughn Body
- Jonathan Peters
- Gary Howe
- Atish Kataria
- Steve Mazzarelli

Additional Information

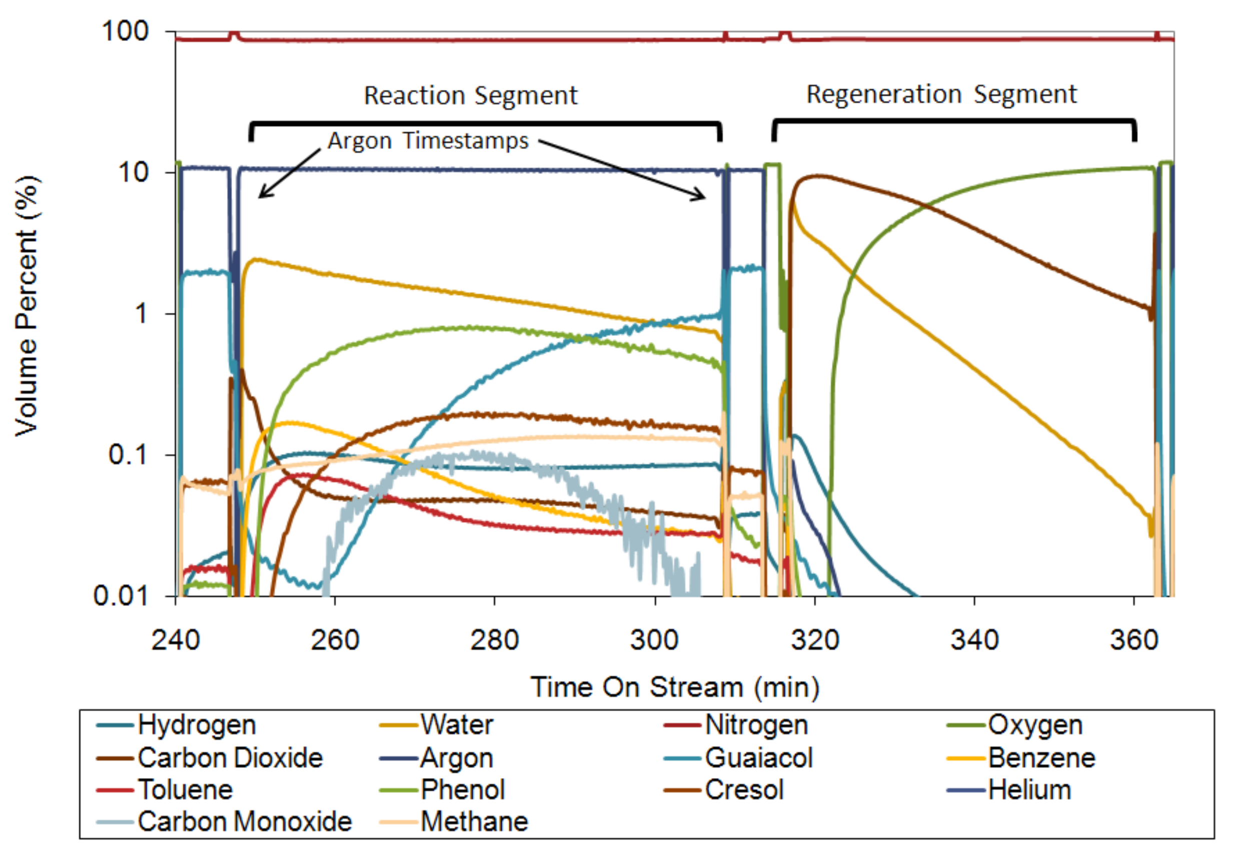
- No publications or presentations
- Project awarded in August 2012 so no previous reviewer comments

ID	Task Name
1	**Task 1: Parametric Catalytic Biomass Pyrolysis Optimization**
2	Determine balance between oxygen removal and energy recovery (yield)
3	Stability and quality/composition of intermediate bio-crude
4	Miscibility with refinery blendstock
5	***Process operating conditions optimized for stable bio-crude production***
6	*Deliverable: 10-L of wood bio-crude*
7	*Deliverable: 10-L of switchgrass bio-crude*
8	*Deliverable: 10-L of corn stover bio-crude*
9	**Task 2: Hydroprocessing Evaluation and Optimization**
10	Biocrude hydrotreating (catalyst/process - T, P, SV, etc.)
11	Bio-crude/refinery intermediate blends
12	Hydroprocessing modeling
13	***Hydroprocessing unit design basis***
14	***Hydroprocessing conditions for 3 bio-crude samples***
15	***Technical evaluation of bio-crude/refinery intermediate blends***
16	**Task 3: Integrated Process Development**
17	Catalytic pyrolysis reactor design and fabrication
18	Hydrotreating reactor design and fabrication
19	Integrated process development – design and fabrication
20	*Deliverable: Updated heat and material Balance for integrated process*
21	***Integrated Process Design Package***
22	***Integrated System Delivery***
23	**Task 4: Integrated Process Operation**
24	Commissioning and shakedown
25	Wood catalytic pyrolysis (1000 hours total) on blends
26	***Complete 1000 hours integrated operation with woody feedstock***
27	Switchgrass catalytic pyrolysis (500 hours) on blends
28	***Complete 500 hours integrated operation with switchgrass***
29	Corn stover catalytic pyrolysis (500 hours) on blends
30	***Complete 500 hours integrated operation with corn stover***
31	Catalyst Characterization
32	**Task 5:Process Modeling and Refinery Integration**
33	Insertion point determination
34	Blending ratios and other considerations
35	Finished product quality and specifications
36	Integrated hydroprocessing modeling
37	Techno-economic analysis
38	Life cycle assessment (GHG reductions, etc.)
39	***Refinery integration options for catalytic biomass pyrolysis technology***
40	***Design package for a 2000 tpd integrated process for TEA and LCA***
41	**Task 6: Project Management**



Model Compound Reactor Results

Guaiacol flow rate adjusted for 90% or less conversion to evaluate time-dependent deoxygenation activity

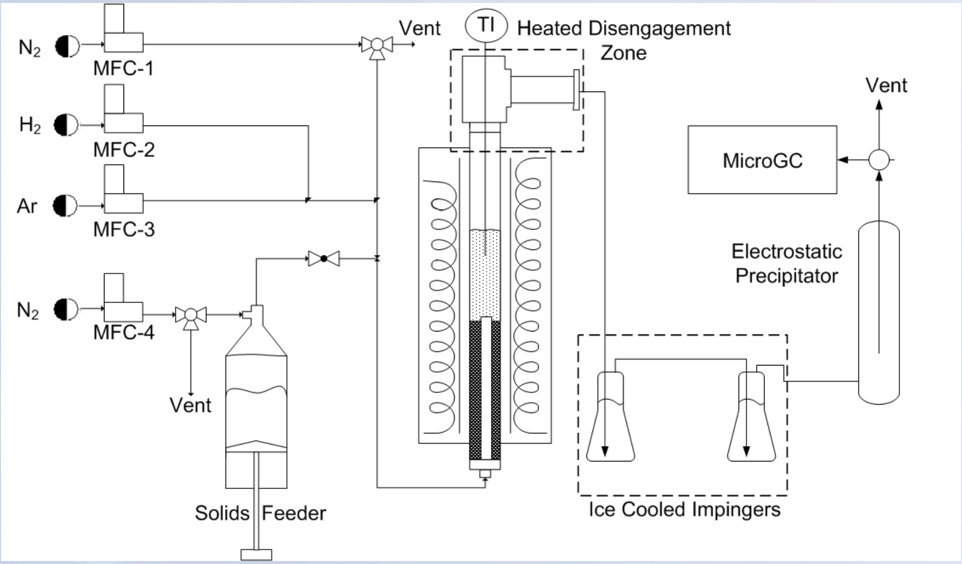


Real-time, online MS analysis

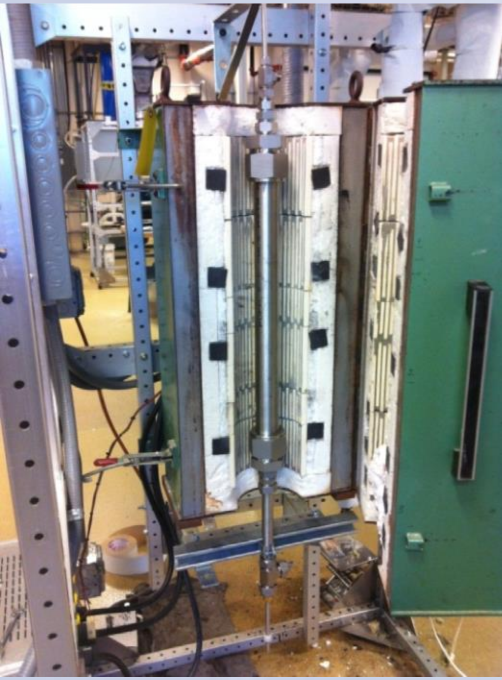
- Products correlated with specific ions (m/z)
- Products quantified by calibration and integration under curve
- Provides time resolved product composition
- Measure both reaction and regeneration

Catalytic Biomass Pyrolysis Proof-of-Concept

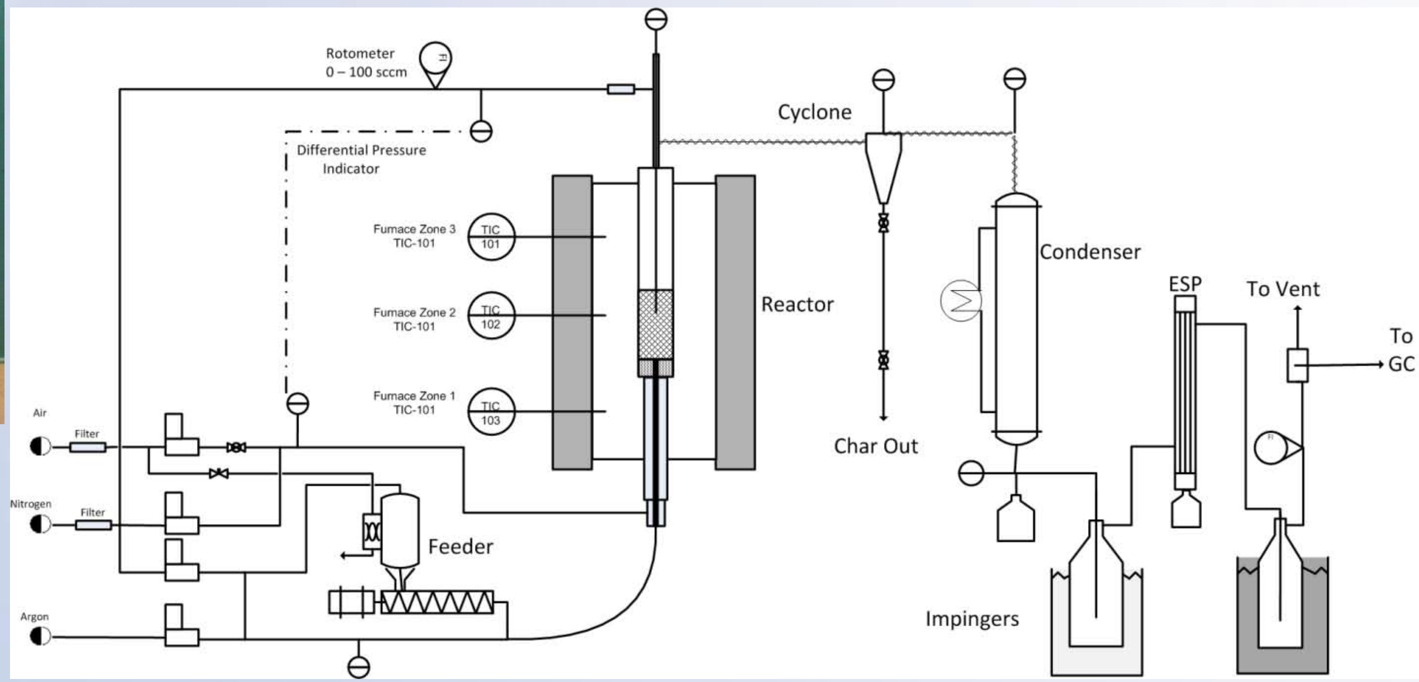
1”-diameter Fluid Bed Reactor System



- Catalytic pyrolysis studies in a bench-top fluidized bed reactor
- Rapid catalyst screening
- Biomass injected directly into fluidized catalyst bed
- Mass closures > 90%
- On-line gas analysis
- Liquid and solid product collection and analysis

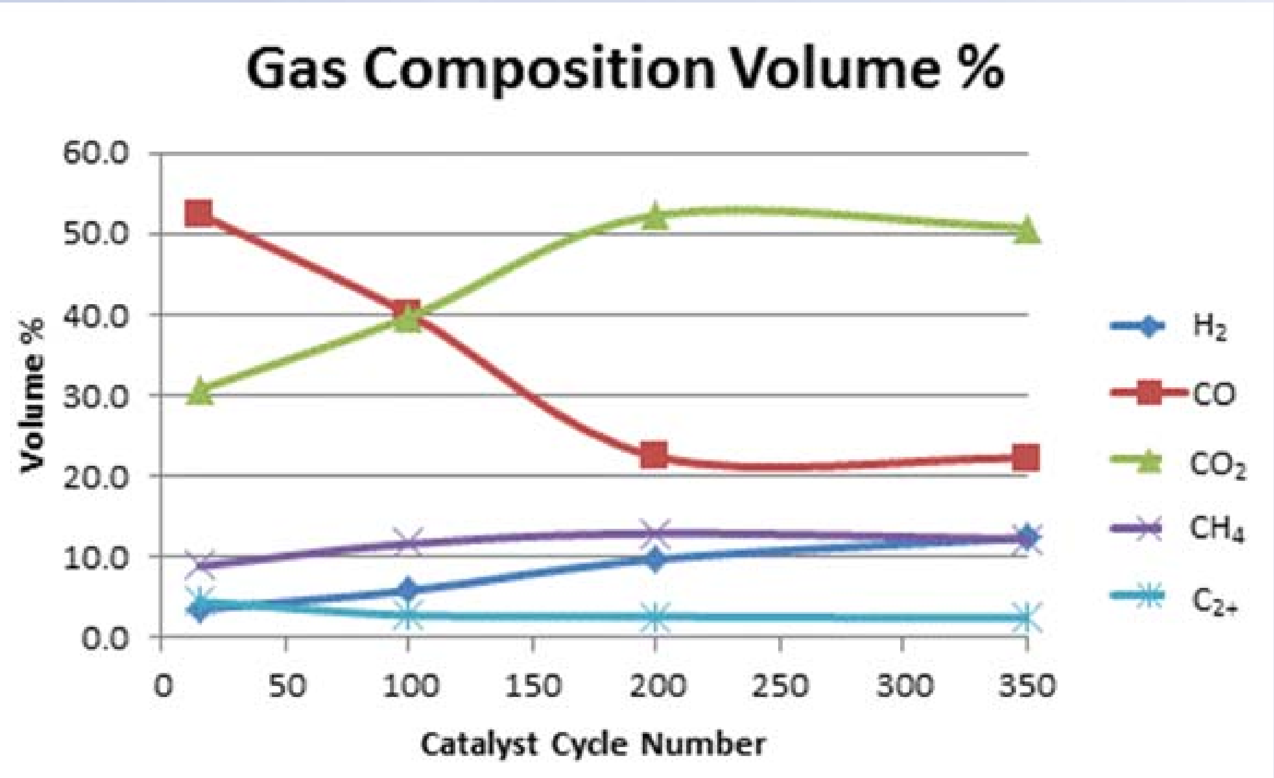


Bio-crude Production in 2” FBR



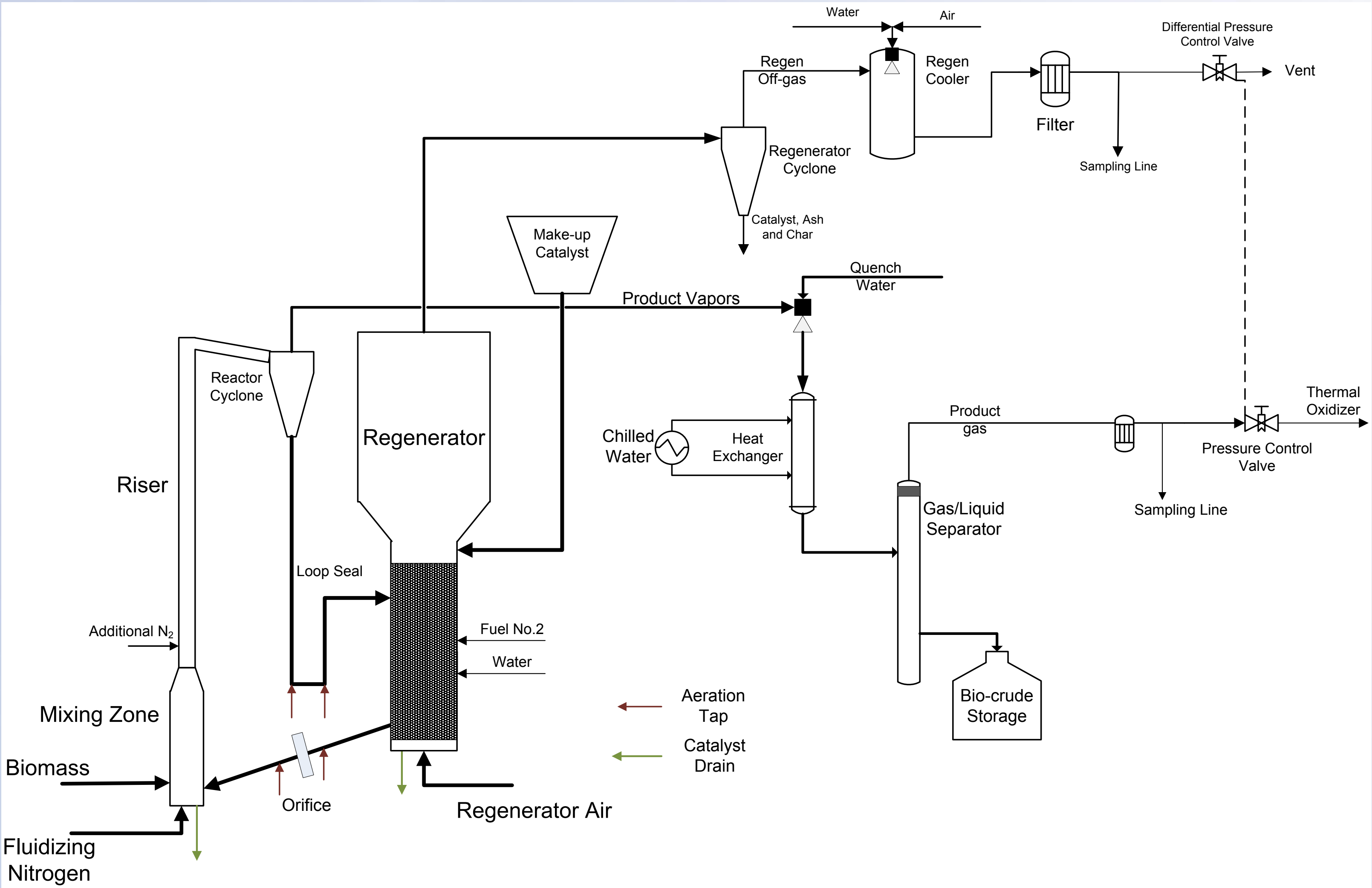
- Produce 1-L of bio-crude intermediate for 100 hour hydrotreating test
- Evaluate long-term catalysts stability by monitoring product composition as a function of time-on-stream (material balance and bio-crude oxygen content)
- Catalytic biomass pyrolysis and catalyst regeneration

Bio-crude Production Summary



- 14-kg of white oak converted
- 1.5-L bio-crude produced
- 345 reaction/regeneration cycles
- Total biomass/catalyst contact time of 87 hours time on stream
- Average mass balance: 90%
- Average bio-crude oxygen content: 19.5 wt%

1 TPD Catalytic Biomass Pyrolysis System PFD



Biomass Feed System Design – T.R. Miles

Feedstock Preparation

- Biomass received in super sacks (0.5" top size, 10% moisture, 15-30 lb/ft^3 bulk density)
- Bulk bag discharger for loading the feeder hopper

- Biomass Feeder
  - Double lock hopper design to purge and pressurize feed
  - Design feed rate: 100 lb/hr based on volumetric flow rate
  - Bottom bin capacity above level switch: 1.8 ft^3
  - Cycle time every 15-30 minutes
- Cooling water jacket surrounding the feeder screw
- Delivered - August 2012

Vessels – Riser Reactor and Regenerator