DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Bio-crude Production and Upgrading to Renewable Diesel

WBS 3.5.1.301

March 25, 2021

System Development and Integration

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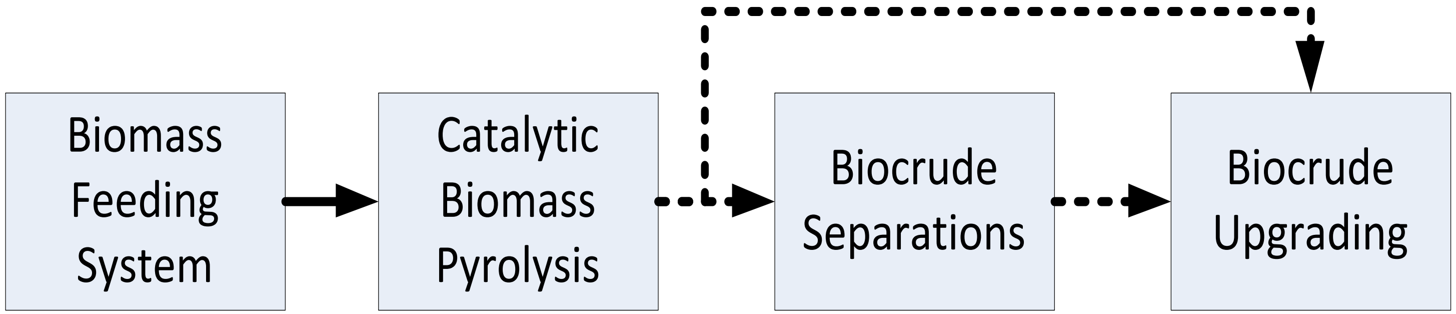
RTI International

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project Overview

Project Goal

Explore synergies between innovative technology solutions for biomass feedstock preparation, pilot-scale catalytic pyrolysis, biocrude separations, and biocrude hydroprocessing to improve the carbon efficiency and process economics for making <u>100 gallons of drop-in renewable diesel</u>



Summary: Project will be executed in three budget periods separated by Go/NoGo decision points. Ten tasks will be completed over a proposed 36-month period of performance.

The focus of the project is to:

1) Optimize the physical and chemical characteristics of biomass feedstock, in a commercially-viable manner, to maximize partially deoxygenated biocrude yields (independent of oxygen content) in catalytic biomass pyrolysis
2) Improve biocrude upgrading efficiency (reduce reactor fouling and increase time-on-stream) by fractionating the liquid intermediate and independently hydroprocessing each fraction to maximize biofuel production.

Targets

- Achieve 40% improvement of the current overall carbon efficiency of biofuel production in catalytic pyrolysis pathway
- Reduce the cost of biofuel production by at least 30%
- Demonstrate that the renewable diesel pathway has 50% less GHG emissions compared to fossil-derived diesel

Management Approach - Budget Period 1 (M1-M3)

Task 1: Initial Verification: Review and experimentally verify baseline data and project targets provided in the Block Flow Data - Complete

Go/NoGo Decision:

- Validate technical data, performance metrics, and targets for the proposed research.
- Forest Concepts, LLC will verify the ability to produce 1-2 mm top size crumbles from a hardwood feedstock and measure and control the particle size distribution.
- RTI will verify 1) the production of at least 10 gallons of partially deoxygenated (< 30%) bio-crude in the 1TPD CFP unit with 20 wt% yield; 2) the ability to separate this bio-crude into 3 fractions (solvent-soluble, water soluble, and pyrolytic lignin) with less than 5% residual losses; and 3) the ability to upgrade bio-crude to ASTM D975 diesel in a pilot-scale hydroprocessing unit at 350C, 2000 psig hydrogen pressure, and space velocity of 0.25 or greater for at least 100 continuous hours.

Management Approach - Budget Period 2 (M4-M18)

Task 2: Feedstock Preparation and Characterization (Forest Concepts and INL)

- Subtask 2.1—Particle Size and Distribution Effects on Biocrude Yield and Quality
- Subtask 2.2—Feedstock Characterization and Modeling

Task 3: Biocrude Production (RTI and NREL)

- Subtask 3.1—Catalyst Preparation and Evaluation
- Subtask 3.2: Biocrude Optimization

Task 4: Hydroprocessing Strategy Development (RTI and HTAS)

- Subtask 4.1—Biocrude Fractionation
- Subtask 4.2—Hydrocracking and Hydrotreating
- Subtask 4.3—Co-processing Refinery and Upgraded Streams

Task 5: Preliminary Techno-economic analysis and Life-Cycle Assessment (RTI, NREL, and Forest Concepts)

- Subtask 5.1—Update the Catalytic Fast Pyrolysis (CFP) TEA with Experimental Results
- Subtask 5.2—Preliminary LCA of Updated Process

Task 6: BP2 Project Management (RTI)

- Subtask 6.1—Interim Verification

Management Approach – Budget Period 2 (M4-M18)

Milestone		Month
M2.1.1	Research quantities of up to 250 kg each of softwood and hardwood feedstock to RTI and subsamples to INL (Forest Concepts)	6
M2.2.1	Feedstock properties versus performance model (INL)	12
M3.1.1	Performance of zeolite catalysts as a function of catalyst property, temperature, and biomass-to-catalyst ratio compared with baseline alumina catalyst (NREL)	9
M3.2.1	Influence of feedstock characteristics on the selected catalysts (RTI)	15
D3.2.1	10 gallons of biocrude from each prepared feedstock (RTI)	15
M4.1.1	Complete fractionation of at least 5 gallons of each biocrude	15
M4.2.1	Determine hydroprocessing conditions for pre-treating the pyrolytic lignin and the water-soluble biocrude fraction with carbon yield >90% (RTI and HTAS)	6
M4.3.1	Establish HDT conditions for upgrading all streams to achieve >90% carbon yield (RTI and HTAS)	17
M5.1	Updated TEA and LCA for proposed process (NREL and RTI)	18

Completed	In Progress	Not started

<u>Go/No Go Decision Point 2 (M18):</u> TEA shows that the improved biomass pyrolysis pathway reduces the cost of biofuel production by 30%. LCA shows that renewable diesel produced have 50% less GHG emission compared to fossil-derived diesel.

Management Approach - Budget Period 3 (M19-M36)

Task 7. Integrated Biocrude Production (RTI and Forest Concepts)

Subtask 7.1—Feedstock Selection

Subtask 7.2—Resource Procurement and Feedstocks Production

Subtask 7.3—Catalyst Procurement

Task 8: Biocrude Upgrading to Diesel Blendstock (RTI and HTAS)

Subtask 8.1—Biocrude Fractionation

Subtask 8.2—Biofuel Characterization

Task 9: Process Modelling (RTI and NREL)

Subtask 9.1—Process Design and Process Modeling

Subtask 9.2: TEA

Subtask 9.3—LCA

Task 10: BP3 Project Management (RTI)

Management Approach – Budget Period 3 (M19-M36)

	Milestone	Month
M7.2.1	Identify feedstock and provide at least 7 tons of selected biomass feedstock for bio-crude production (Forest Concepts and INL)	21
M7.2.1	Provide between 500 kg and 1,000 kg of selected catalysts	21
D7.1	Produce 200 gallons of biocrude with <30 wt.% oxygen at >20 wt.% yield for separation and upgrading to diesel blendstock (RTI)	24
M8.1	Complete production of 100 gallons of diesel fuel that meets ASTM D975 standards (RTI)	33
M8.1.1	Complete fractionation of biocrude and stream pretreatment	27
M9.1	TEA of an integrated process that includes innovative feedstock preparation, CFP conversion, biocrude separations, and upgrading unit operations tested at the pilot scale (All)	30
M10.1	Final verification	36

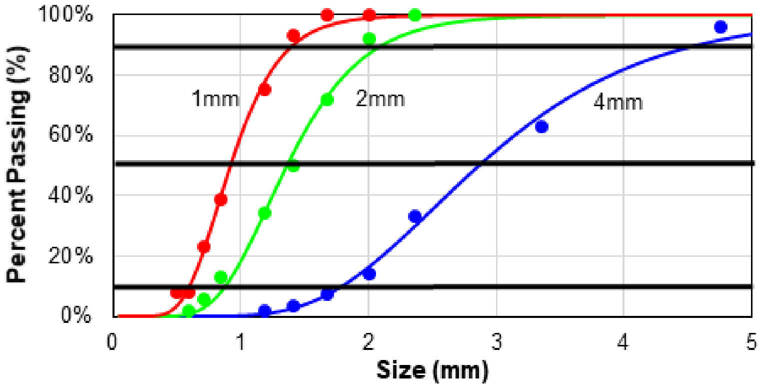
End of Project Goals:

1) Correlation between biocrude yields and feedstock PSD and other physical properties.
2) Innovative biocrude fractionation strategy for upgrading
3) Collective optimization of biocrude production and upgrading to produce 100 gallons of diesel fuel that meets ASTM D975 specifications.

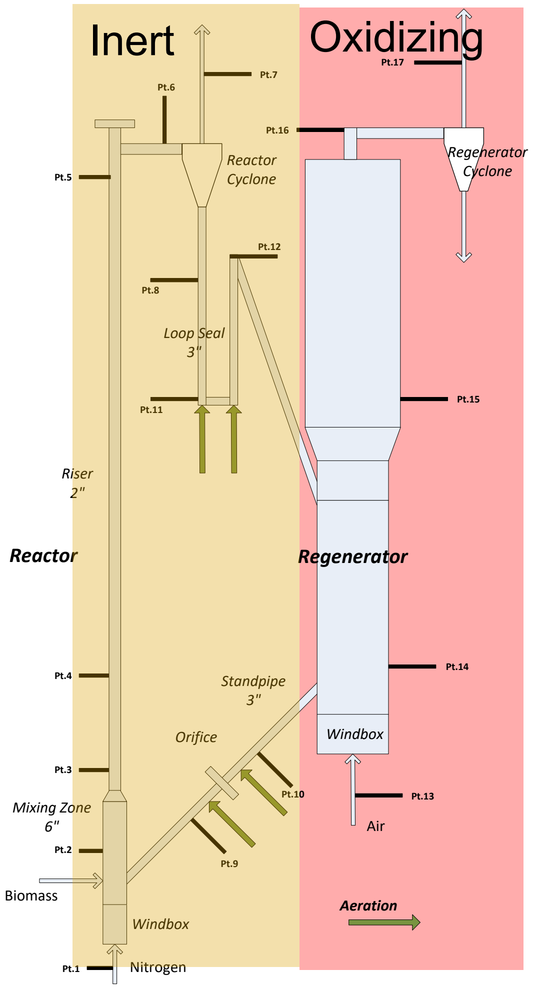
Catalytic Fast Pyrolysis Process Development

Improve biocrude yield and quality to reduce biofuel production cost

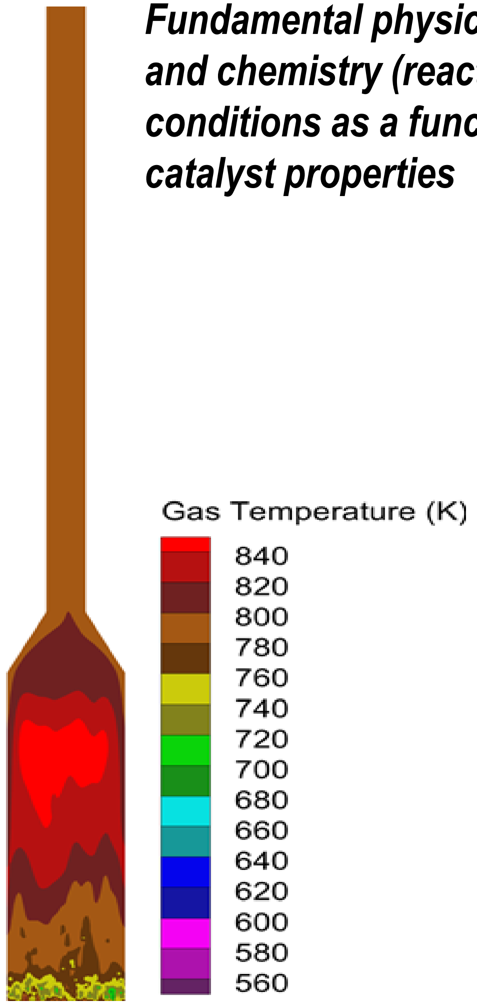
- Investigate feedstock particle size and shape to maximize heat transfer efficiency
- Reactor modeling, including catalyst performance, to provide insights for process optimization

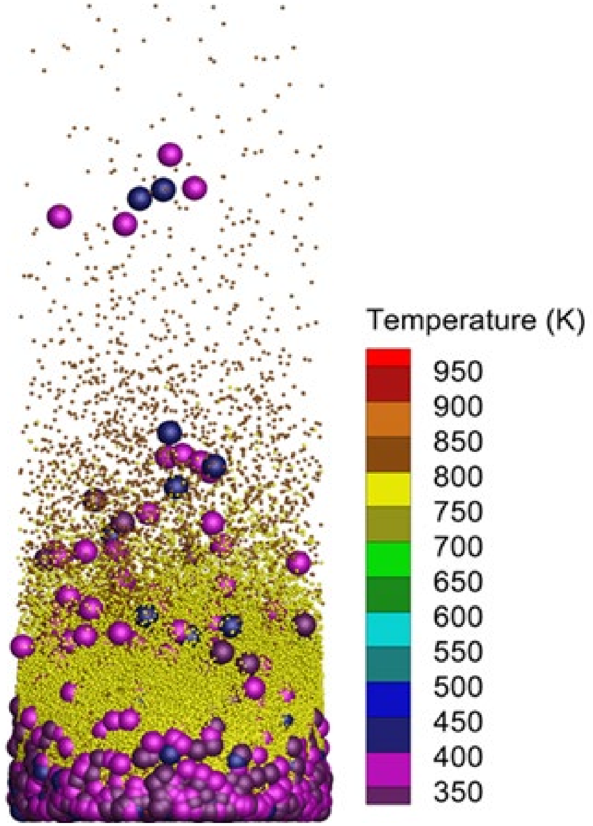


Processing costs and feeder performance as a function of feedstock physical properties



Fundamental physics (multiphase flow CFD modeling) and chemistry (reaction kinetics) to optimize process conditions as a function of feedstock particle size and catalyst properties





Technical Approach – Feedstock Preparation

- Forest Concepts' feedstock processing unit will be used to process raw biomass in baled, chipped, ground, and/or chopped form.
- Crumbles rotary-shear system to mill the biomass to a desired size
- Screen process biomass for size and length
- Deliver reactor-ready feedstock to project specifications

Crumbler® Rotary Shear & Crumbles® Feedstocks

Modeling material properties: density, moisture content, compressibility, elasticity, particle size and shape distributions, cohesion, internal friction angle, angle of repose, and Poisson's ratio

1TPD CFP Biocrude Production

Parameter	Design Basis	Operational Values (Avg.)
Pyrolysis temperature (°C)	500	464
Regenerator temperature (°C)	700	604
System pressure (psia)	20	19.7
Biomass feed rate (lbs/hr, as received)	100	107
Catalyst circulation rate (catalyst-to-biomass ratio)	10	10:1
Pyrolysis reaction residence time (s)	0.75	0.85

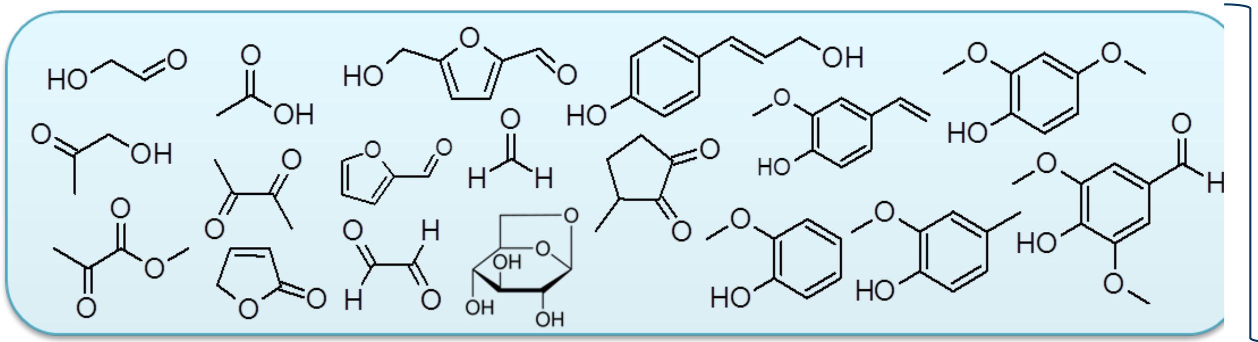
Summary of Douglas Fir Crumbles CFP

	1mm Douglas fir	2mm Douglas fir	4mm Douglas fir
Pyrolysis Temperature	***480***	***480***	***520***
Total Fed (kg)	527	603	403
Collection Point		Carbon Balance	
Total	96%	98%	96%
Ash pot	11%	12%	11%
Separator Solids	10%	13%	13%
Cold Filter Organic		1%	
Cold Filter Aqueous	5%	3%	8%
Hot Filter Organic	12%	10%	7%
Pyrolysis Gas	9%	9%	14%
Regen Gas	39%	43%	31%
Aqueous Recycle	10%	6%	12%
Liquid	27%	20%	27%
Solid	60%	68%	55%
Gas	9%	9%	14%

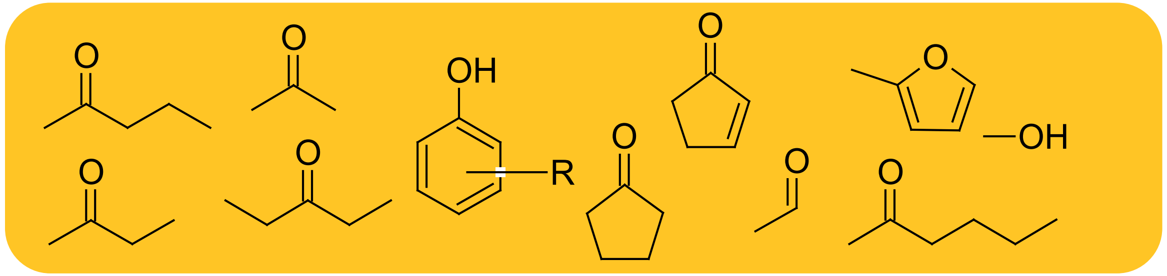
The Challenge of Biocrude Hydroprocessing

Liquid yield decreases as oxygen is removed

Multifunctional oxygenates

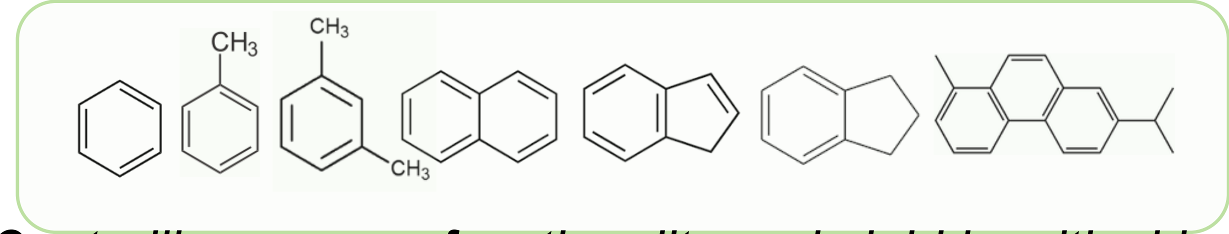


Monofunctional oxygenates



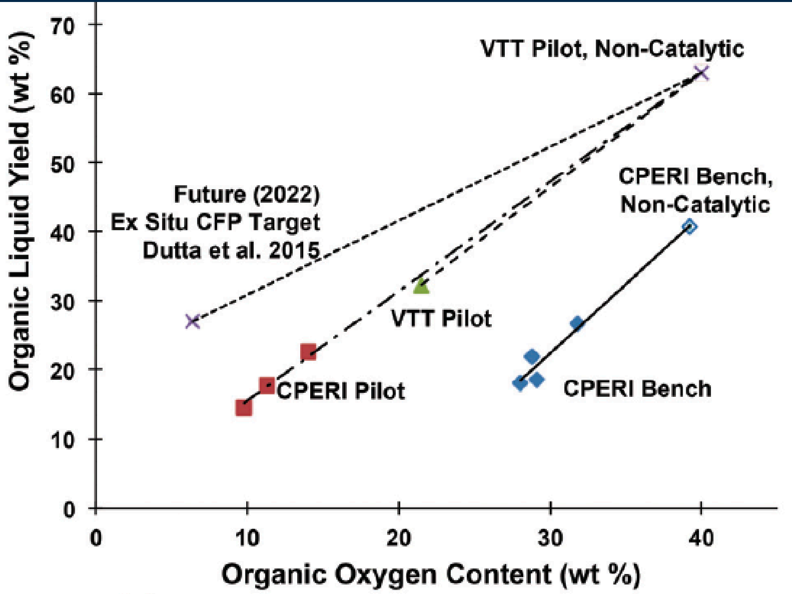
Oxygenated bioproducts

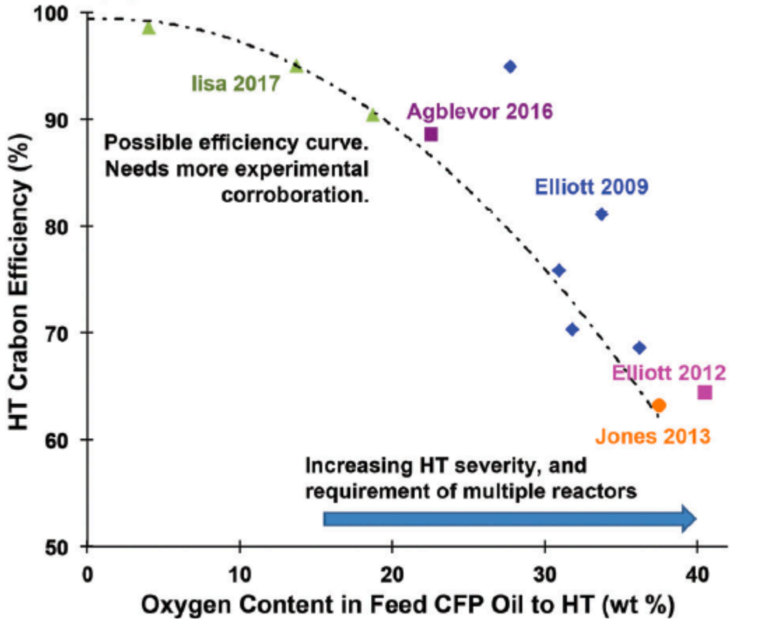
Aromatic Hydrocarbons



Controlling oxygen functionality and yield is critical in the pyrolysis step for production of biofuels

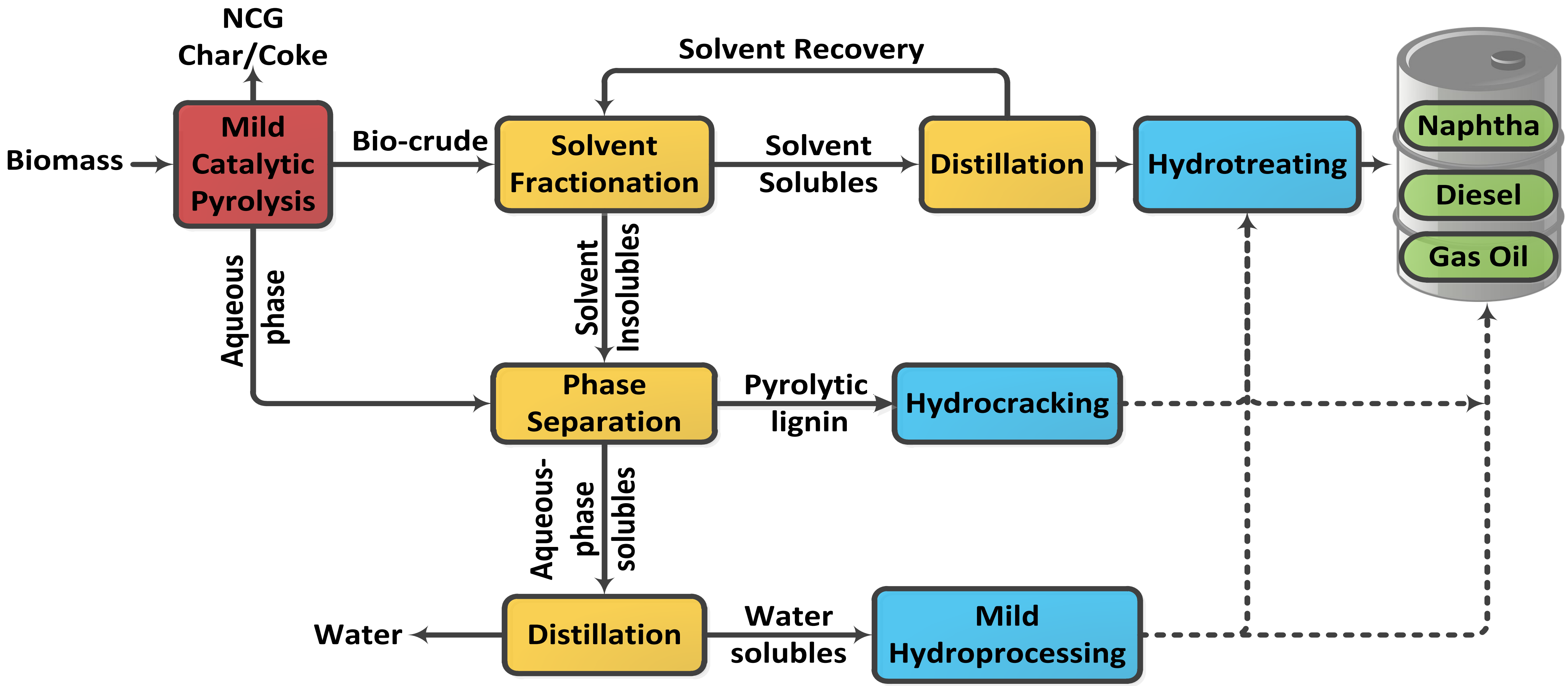
Instability and chemical complexity increases as oxygen is retained





Iisa, K.; Robichaud, D. J.; Watson, M. J.; ten Dam, J.; Dutta, A.; Mukarakate, C.; Kim, S.; Nimlos, M. R.; Baldwin, R. M., *Green Chemistry* **2018,** *20* (3), 567-582.

Technical Approach – Separations and Upgrading



- Fractionate CFP liquid into different major functionality streams
- Utilize distinct suitable catalysts and process conditions to promote targeted hydroprocessing chemistries for efficient processing into biofuels.

Biocrude Upgrading - Hydrotreating

UNIT OPERATIONS
- Oil feed system including pumps and flow control
- Gas feed system
- Reactor system
- Separator system
- Gas and liquid sampling system

Reactor volume - 350 mL
Catalyst volume - 20 to 250 mL
Design temperature: 450C
Max. operating temperature: 430C
Max. operating pressure: 170 bar (2500 psig)

Biocrude Upgrading Goals:
- Steady-state deoxygenation activity, hydrogen demand, and process severity as a function of biocrude quality (wt%O)
- Long-term operation to determine catalyst stability and lifetime (500-1000 hrs)

Biocrude upgrading Options:
- Process whole biocrude in one or multiple steps
- Refinery integration and co-processing strategies
- Fractionate biocrude and process each fraction separately

Challenges:
- Reactor plugging
- Process severity correlated to biocrude composition

Impact

Demonstrate a direct biomass liquefaction advanced biofuels pathway - Integrated, commercially-relevant pilot-scale unit operations for feedstock preparation, catalytic biomass pyrolysis (conversion), and biocrude separations and hydroprocessing (upgrading)

Technology Advancements:

- Reactor-ready feedstock that meets critical performance specifications
- Correlation between feedstock properties and conversion process performance
- Develop a strategy to improve biocrude upgrading efficiency (reduce reactor fouling and increase time-on-stream) by fractionating the liquid intermediate to separate chemical constituents best suited for bioproducts and biofuels, respectively, and processing different fractions independently, as warranted

This project directly supports the DOE/BETO Program FY22 Verification to validate an nth plant modeled MFSP of $3/GGE (2014$) for a pathway to hydrocarbon biofuel with GHG emissions reduction of 50% or more compared to petroleum-derived fuel.

Initial Verification Summary

Validate technical data, performance metrics, and targets for the proposed research	Summary of Results
Forest Concepts, LLC will verify the ability to produce 1-2 mm top size crumbles from a hardwood feedstock and measure and control the particle size distribution. RTI will : 1. Produce of at least 10 gallons of partially deoxygenated (< 30%) bio-crude in the 1TPD CFP unit with 20 wt% yield 2. Separate biocrude into 3 fractions (solvent-soluble, water soluble, and pyrolytic lignin) with less than 5% residual losses 3. Upgrade biocrude in a pilot-scale hydroprocessing unit at 350°C, 2000 psig hydrogen pressure, and space velocity of 0.25 or greater for at least 100 continuous hours.	• Forest Concepts LLC held an Open House on August 1, 2019 to demonstrate how they produce Crumbles. • RTI procured 3 tons of 2mm top size Douglas Fir Crumbles from Forest Concepts. • RTI produced 64.4 kg (51.5-L or 13.6 gallons) of biocrude from 562-kg of the Douglas Fir Crumbles (dry basis). Oxygen content: 27 wt% (dry basis); 18% carbon efficiency. • Two biocrude samples (27-kg total) produced from softwood feedstocks (Loblolly pine and Douglas Fir) were used for two separation experiments. 98+% mass closure with no residual losses. • 9.2-kg of the solvent-extracted biocrude was hydrotreated for 145 continuous hours in RTI's pilot-scale hydroprocessing unit at 2000 psig hydrogen pressure, and liquid hourly space velocity of 0.35/hr.

Progress and Outcomes - Recent BP2 Accomplishments

Feedstock Preparation

Forest Concepts LLC

- 1mm, 2mm, and 4mm Douglas Fir Crumbles. ~1600 lbs of each
- 3000 lbs hardwood (Alder) 1mm and 2mm Crumbles

Idaho National Lab

- Define quality metrics/variables for mechanical feedstock processing

CFD and Kinetic modeling – National Renewable Energy Lab

- Mixing zone/riser reactor model
- Solid acid (alumina) CFP kinetics based on previous zeolite mechanism

Biocrude Production - RTI

- 64.6 gallons of biocrude from CFP of 1mm, 2mm, and 4mm Douglas Fir Crumbles (1533-kg)
- ~14 gallons of solvent extracted biocrude total
- Aqueous phase recycle eliminates freshwater consumption and reduces aqueous stream volume by 84%

Biocrude Separations and Upgrading

RTI

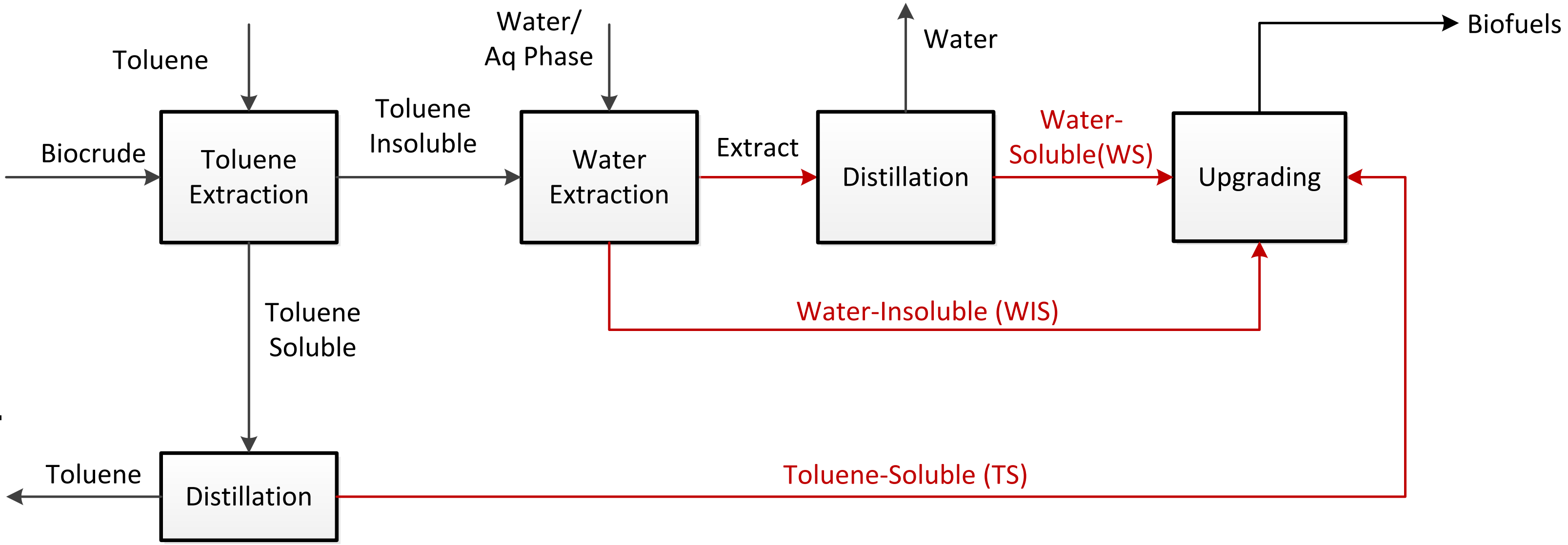
- Hydrotreated solvent extracted biocrude, distillate bottoms, raffinate, and water-washed raffinate

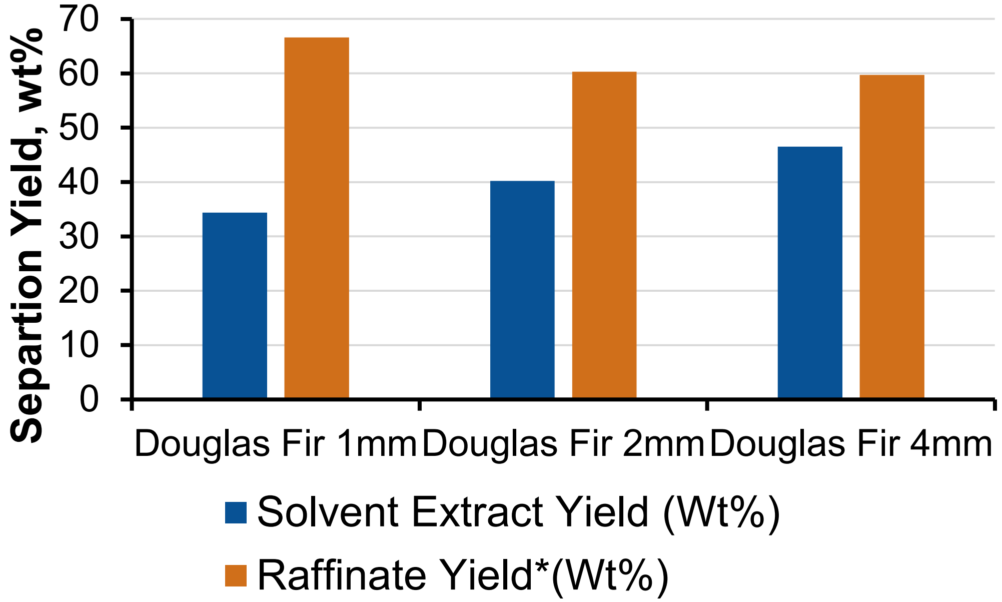
Haldor Topsoe

- Evaluate catalyst activity and process conditions to develop new upgrading strategy for solvent extracted biocrude

Biocrude Fractionation Approach

- 1:1 volume ratio of solvent to biocrude.
- Two-stage extractions per batch of biocrude so raffinate from the first extraction was re-extracted.
- 2-hour extraction time
- Extracts distilled at 55-75°C under vacuum (74-201 torr) for solvent recovery.
- Water washing raffinate produced water-soluble (WS) and water-insoluble (WIS) fractions.

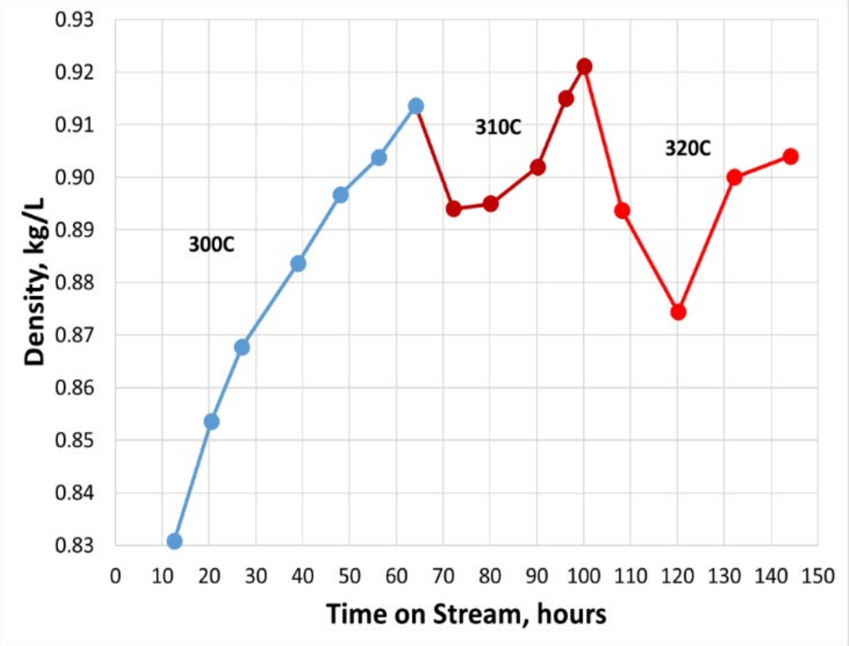


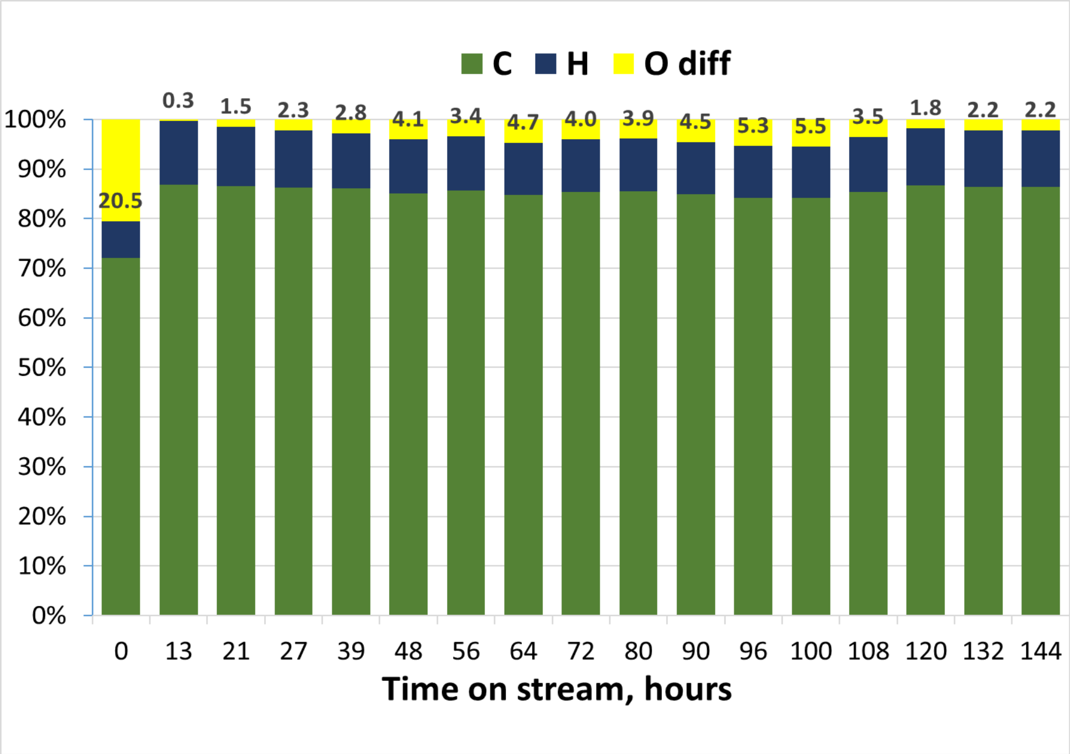


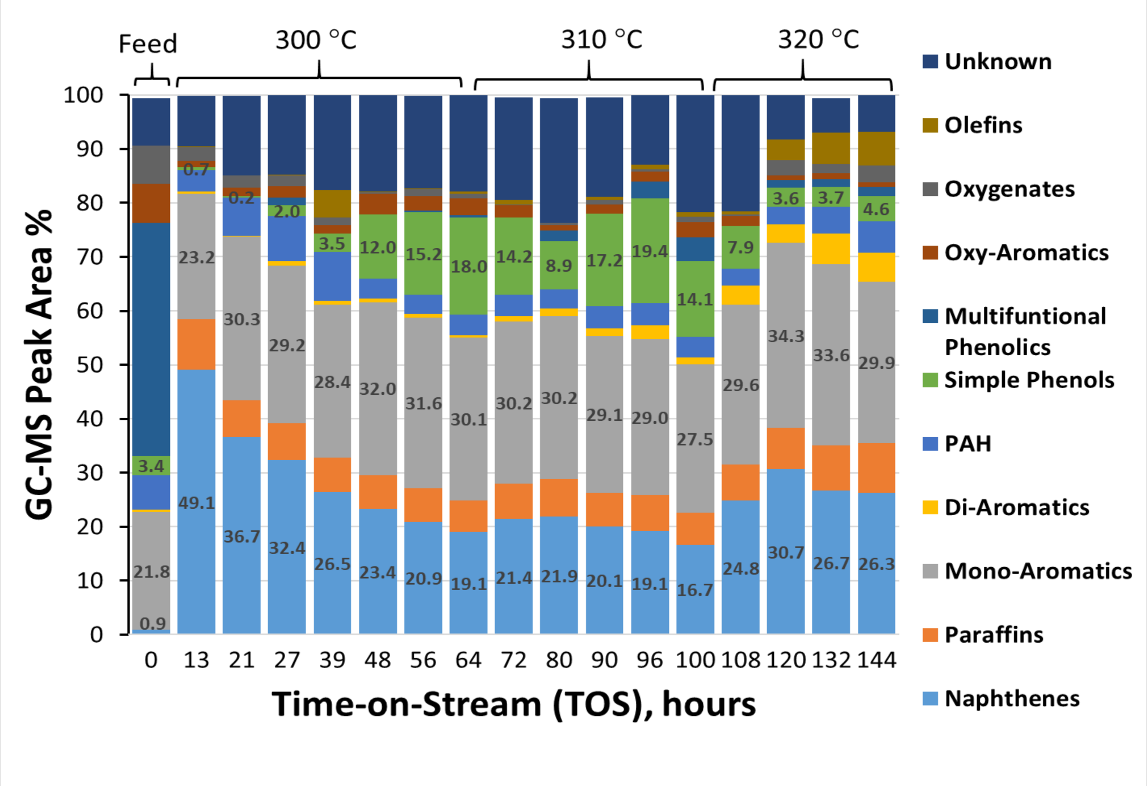
	1mm Douglas Fir	2mm Douglas Fir	4mm Douglas Fir
INPUT	Extraction Step Mass (kg)		
Biocrude	29.44	30.97	15.75
Toluene	43.49	50.83	36.94
OUTPUT			
Raffinate	19.62	18.67	9.39
Extract	51.01	60.40	42.62
Mass Closure	96.84%	96.65%	98.72%
INPUT	Distillation Step Mass (kg)		
Extract	50.72	59.75	42.59
OUTPUT			
Toluene	36.44	42.03	32.85
Product	10.18	12.46	7.32
Mass Closure	91.91%	91.20%	94.07%

Solvent-extracted Biocrude Upgrading Summary

Parameters	MB1 (6.5 hrs)	MB2 (8 hrs)	MB3 (10 hrs)	Average
Mass yield of product oil, wt.%	76.6	77.4	77.3	77.10
Carbon yield product oil, %	98.7	99.02	99.9	99.21
Mass yield aqueous fraction, wt.%	19.1	17.39	17.8	18.10
Carbon yield aqueous fraction, %	0.3	0.27	0.28	0.28
Product Gas yield, wt.%	2.0	1.97	1.66	1.88
Carbon yield product gas, %	1.8	1.93	1.57	1.77
H_2 consumed, g H_2/g dry bio-oil	0.071	0.088	0.087	0.082
Mass Balance, %	97.1	96.15	96.13	96.46
Carbon Balance, %	100.8	101.22	101.72	101.25

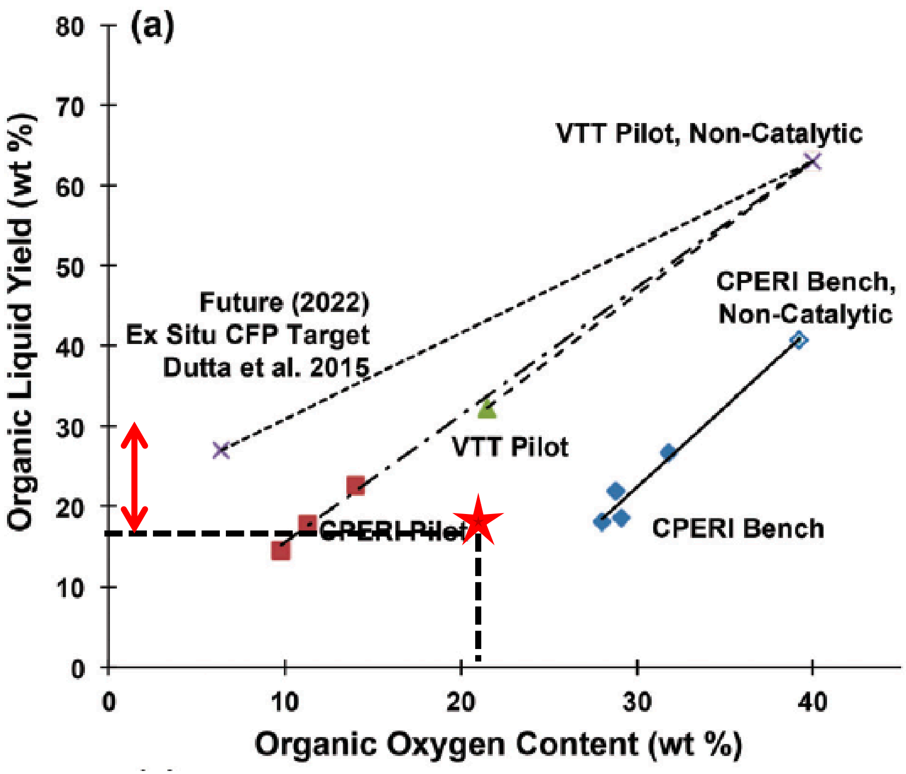






Summary

- Validate a commercially-relevant technology to produce reactor-ready feedstocks with specified critical performance factors
- Correlate feedstock properties with pilot-scale catalytic biomass pyrolysis process performance and achieve 40% higher biocrude yields
- Develop a novel separation strategy and a modified hydroprocessing process to improve biocrude upgrading performance
- Produce 100 gallons of diesel blendstock that meets ASTM D975 specifications
- Support DOE/BETO Program goal to validate an nth plant modeled MFSP of $3/GGE (2014$) for a pathway to hydrocarbon biofuel with GHG emissions reduction of 50% or more compared to petroleum-derived fuel.



Iisa, K.; Robichaud, D. J.; Watson, M. J.; ten Dam, J.; Dutta, A.; Mukarakate, C.; Kim, S.; Nimlos, M. R.; Baldwin, R. M., Improving biomass pyrolysis economics by integrating vapor and liquid phase upgrading. *Green Chemistry* **2018,** *20* (3), 567-582.

Bio-crude Production and Upgrading to Renewable Diesel (DE-EE0008509)

Timeline

- Award Date: 10/1/2018 (Original End Date: 9/30/2021)
- Award Negotiations Concluded: 04/18/2019
- Initial Verification Meeting – July 19, 2019
- Proposed Budget Period 1 end date: 9/30/2019
- Actual Budget Period 1 end date: 3/30/2020
- Authorization to move into BP2: 4/29/2020
- Budget Period 2: 4/1/2020 – 6/30/2021
- Budget Period 3: 7/1/2021 – 12/31/2022

Project Goal

Improve the technical feasibility of renewable diesel production from cellulosic biomass by demonstrating the production of 100 gallons of a renewable diesel blend stock that meets ASTM specifications

End of Project Milestone

Pilot demonstration of an advanced biofuels technology that integrates catalytic biomass pyrolysis and hydrotreating to produce 100 gallons of renewable diesel blend stock that meets ASTM D975 Specifications

Partners

RTI International: Project lead, CFP, separations, and upgrading technology development, project management
INL: Feedstock modeling
NREL: CFD reactor modeling, process modeling and TEA, LCA
Forest Concepts, LLC: Innovative feedstock preparation, primary feedstock provider, modeling
Haldor Topsoe, A/S: Develop a new strategy (catalyst and process conditions) to upgrade bio-crude.

Budget	Federal	Cost Share	Total Costs	FY19-FY20Q1 Actuals	
				Federal	Cost Share
BP1	$253,996	$63,499	$317,496	$206,183	$55,606
BP2	$1,020,679	$255,170	$1,275,849	$313,184	$74,235
BP3	$1,279,248	$319,812	$1,599,060	---	---
Total	$2,553,924	$638,481	$3,192,405	$519,368	$129,841

DE-FOA-0001926: Process Development for Advanced Biofuels and Biopower (Issued May 3, 2018)
Topic Area 2: Drop-in Renewable Diesel Fuel Blendstocks

Bridge technologies from research to engineering, to integrate unit operations, and to engage in the R&D of integrated processes designed to produce drop-in renewable jet fuel or diesel blendstocks, or biopower.

Additional Slides

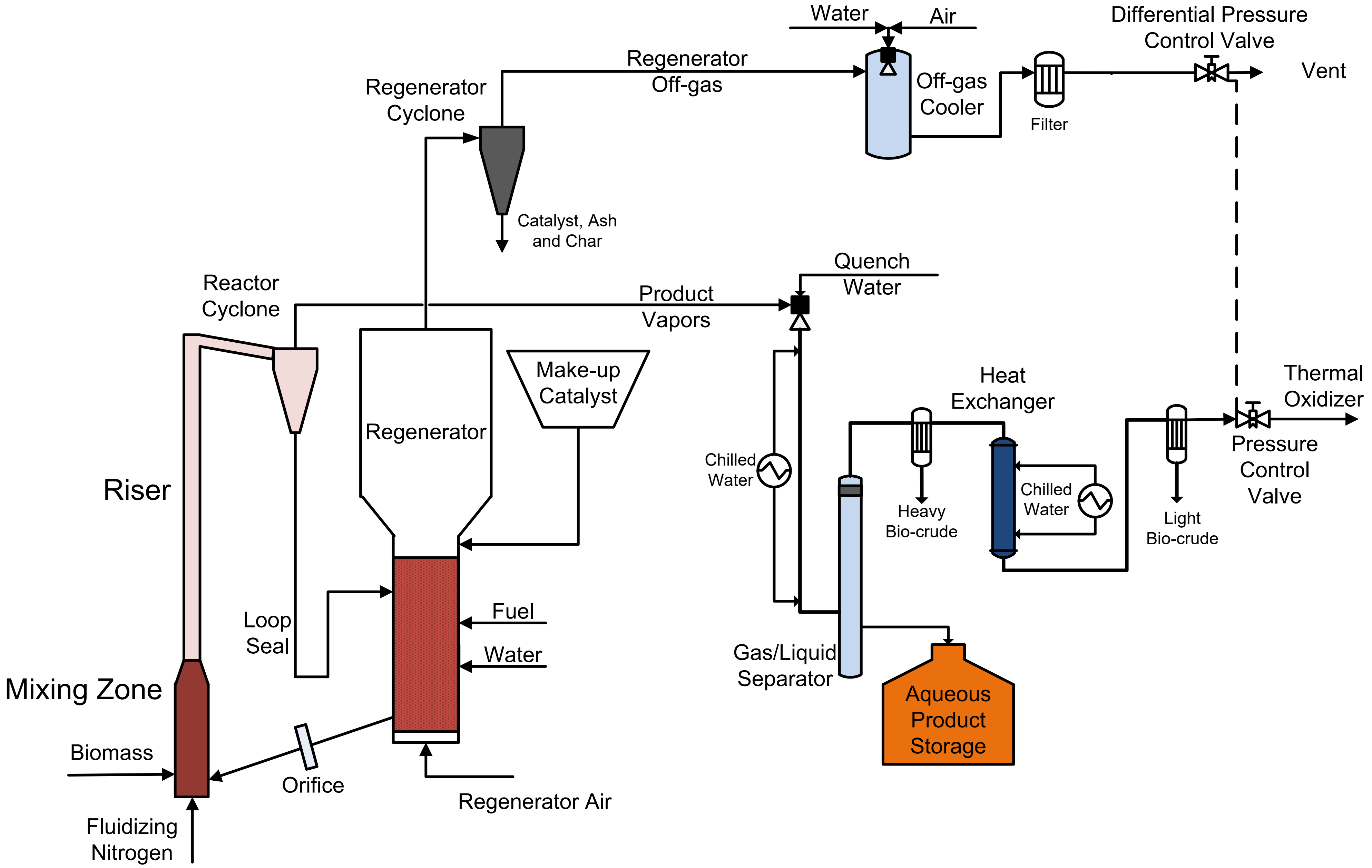
Responses to Previous Reviewers' Comments

- Not applicable

Publications, Patents, Presentations, Awards, and Commercialization

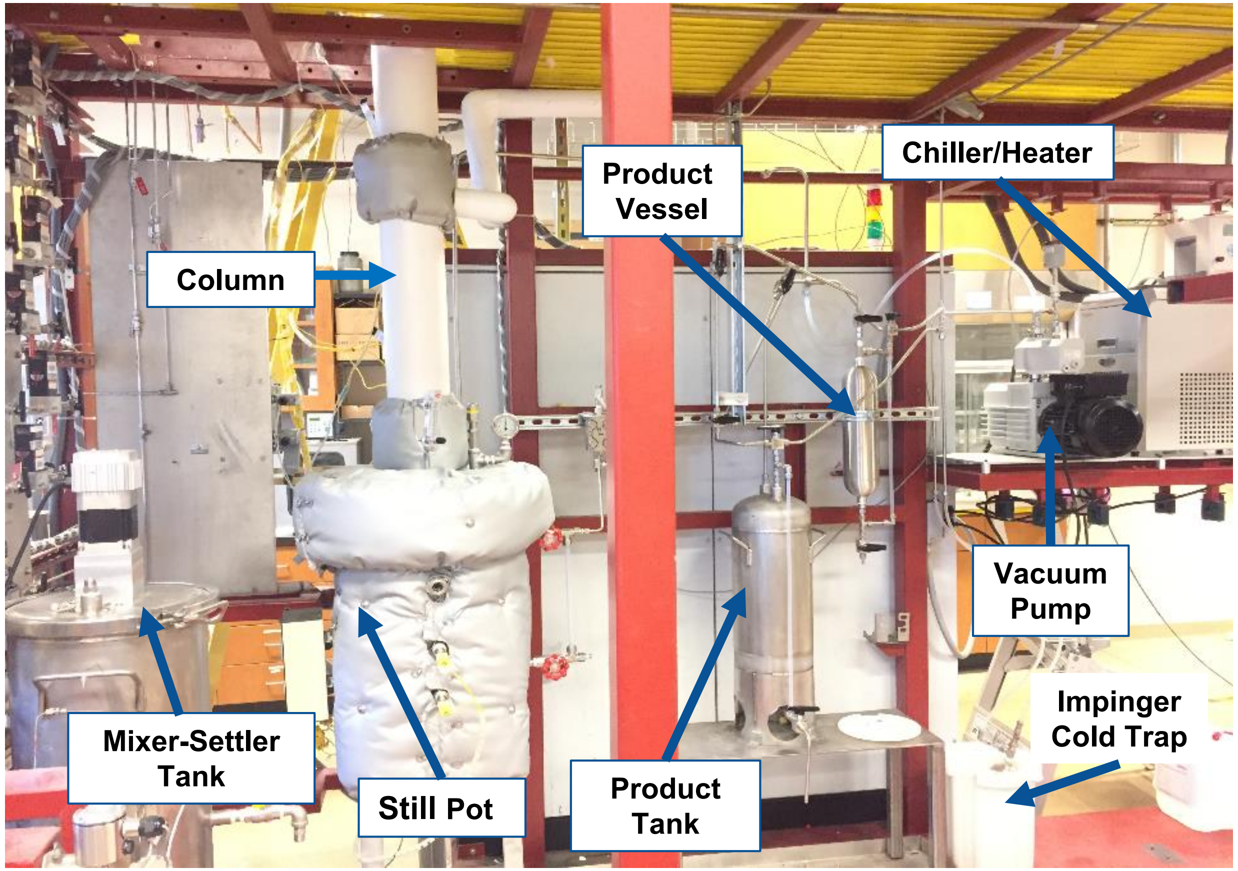
- Publications: none
- Patents: none
- Presentations:
  - On-site Verification Meeting - Bio-crude Production and Upgrading to Renewable Diesel (DE-EE0008509), RTI International, RTP, NC. July 10, 2019.
  - TCS2020 Virtual Conference, October 5-7, 2020. Oral Presentation – "Pilot-scale Catalytic Fast Pyrolysis of Douglas Fir Crumbles." P. Cross.
  - TCS2020 Virtual Conference, October 5-7, 2020. Oral Presentation – "Upgrading Strategies for Fractionated Biocrude." D.C. Dayton
  - TCS2020 Virtual Conference, October 5-7, 2020. Oral Presentation – "Impact of Naphthenic Bio-blendstocks on Diesel Fuel Properties." O. Mante.

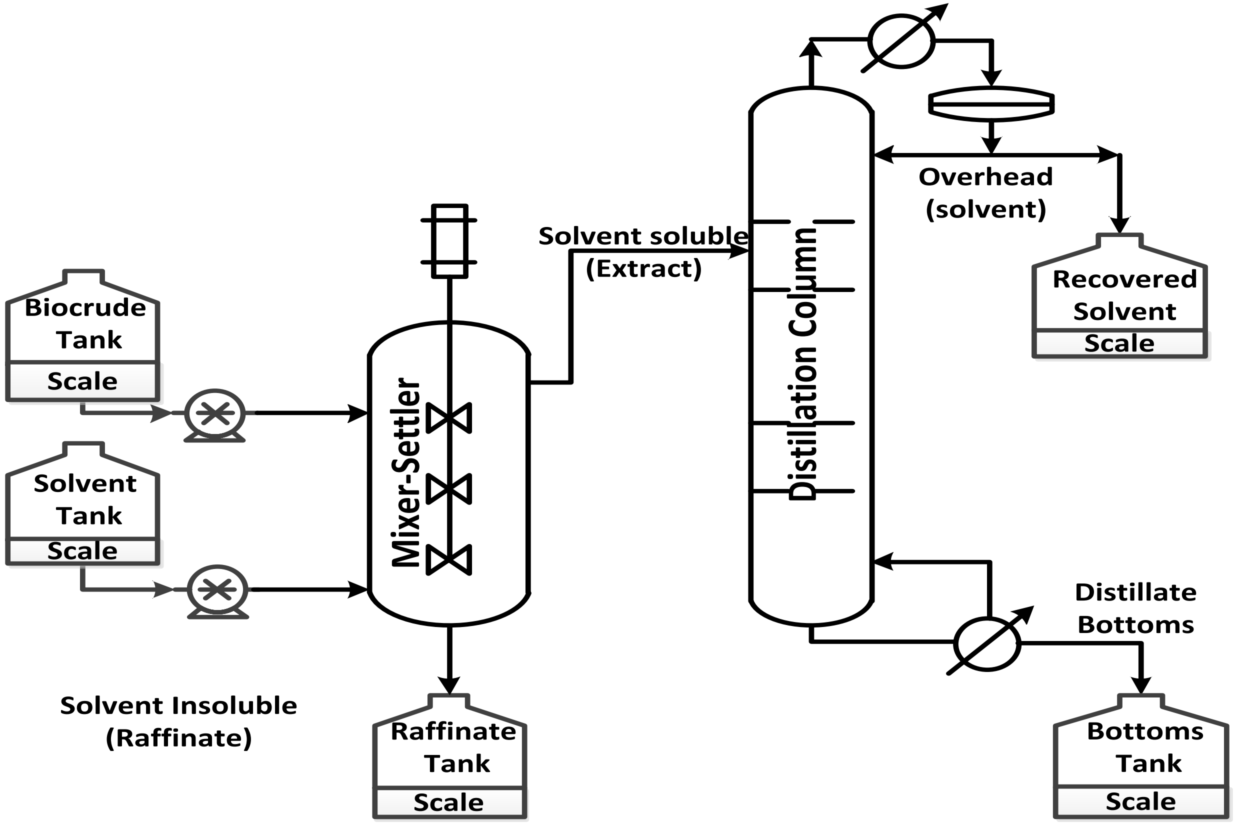
1TPD CFP Biocrude Production



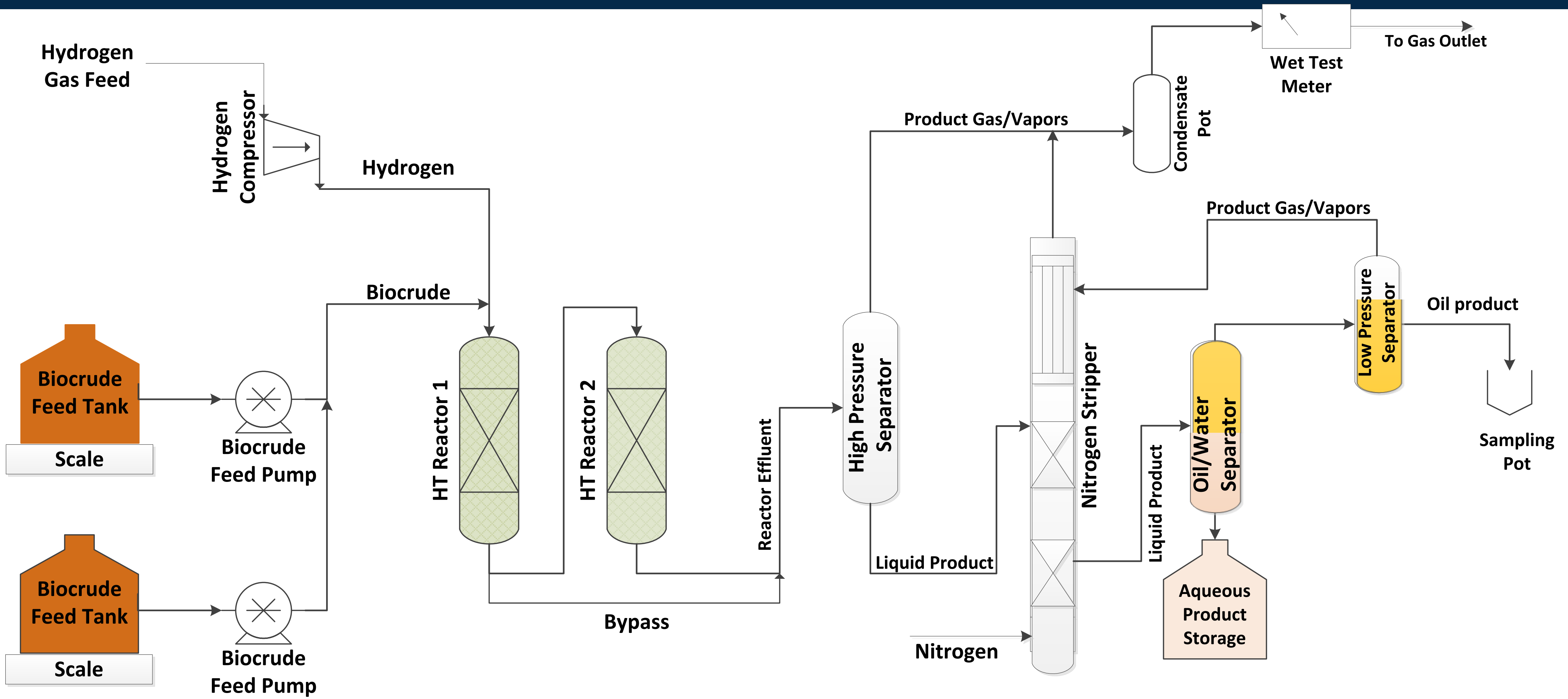
Biocrude Separations

Process up to 7 gallons of biocrude per day





Biocrude Upgrading - Hydrotreating



UNIT OPERATIONS

- Oil feed system including pumps and flow control
- Gas feed system
- Reactor system
- Separator system
- Gas and liquid sampling system

Reactor volume - 350 mL
Catalyst volume - 20 to 250 mL
Design temperature: 450C
Max. operating temperature: 430C
Max. operating pressure: 170 bar (2500 psig)