DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Integrated Separations to Improve Biocrude Recovery for Biofuels and Bioproducts

WBS 3.4.3.305

April 4, 2023

System Development and Integration

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RTI International

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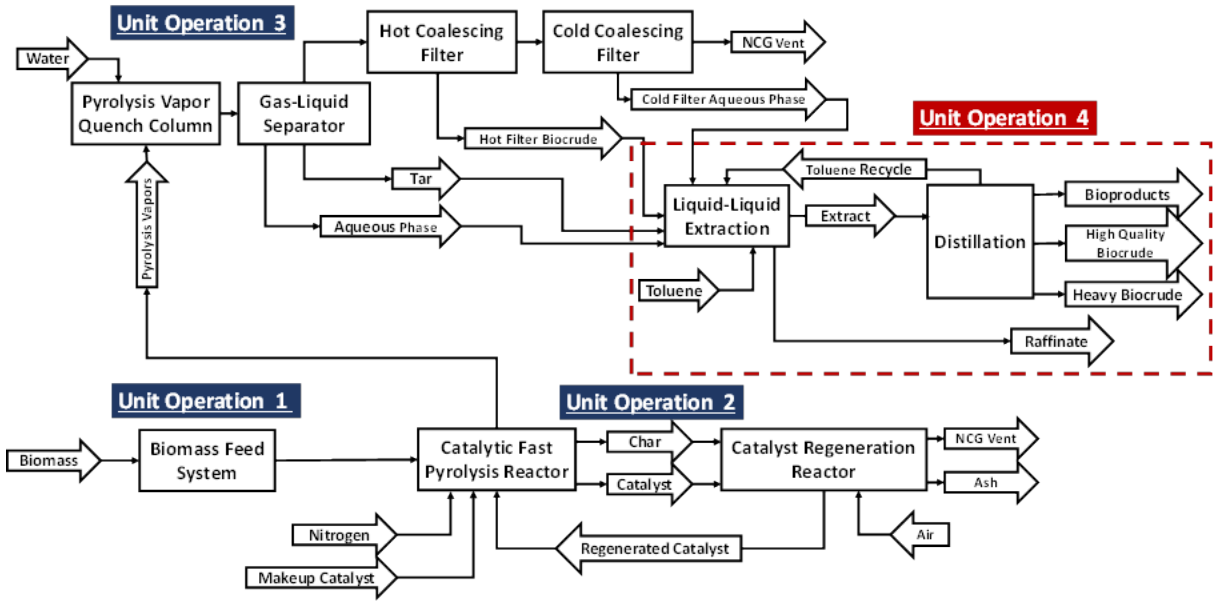
Project Overview

Project Goal

Integrate pilot-scale separations with catalytic fast pyrolysis to enhance biocrude recovery and process efficiency by:

- Improving solids separation from the vapor stream
- Enhancing rapid quenching and collection of pyrolysis vapors
- Separating highly oxygenated bio-products from the liquid intermediates before upgrading the remainder into advanced biofuel.



Summary

1) 500 hours (100 hours continuous) integrated separations in RTI's 1TPD unit
2) Isolate methoxyphenols and other potential bio-products from process streams.
3) Co-process biocrude fractions with petroleum refining intermediates
4) Update TEA and identify optimum location and scale for integrated biorefineries

Targets

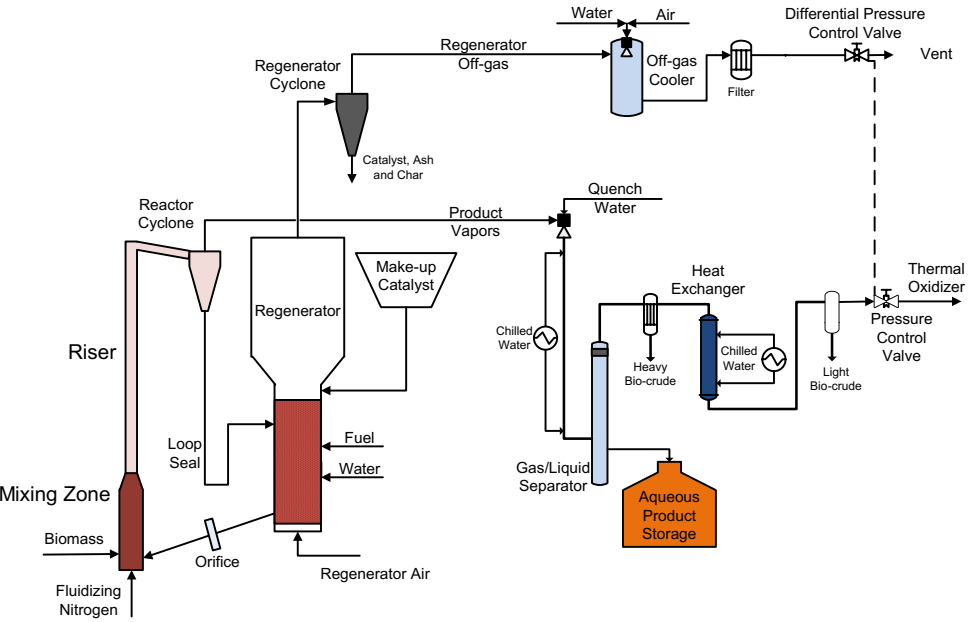
- Scale-up separations unit operations in RTI's 1TPD catalytic biomass pyrolysis unit to achieve 25% biocrude collection efficiency
- 10 wt% of the biocrude intermediate is recovered as chemical building blocks for bio-products and the remainder upgraded into biofuels.

Background – Previous Projects

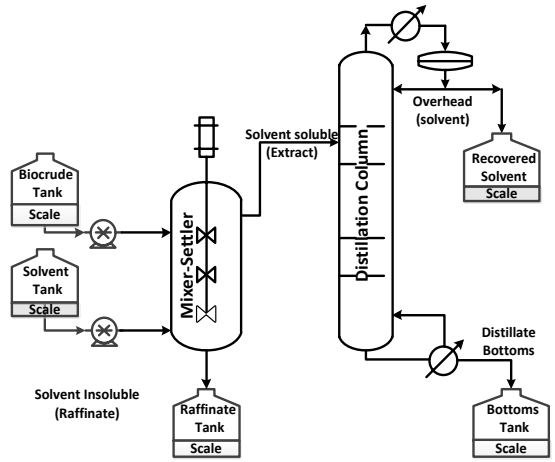
RTI International has been developing an advanced biofuels technology that integrates catalytic biomass pyrolysis and hydrotreating to produce advanced hydrocarbon biofuels and high-value chemicals

A summary of recent RTI projects supported by DOE

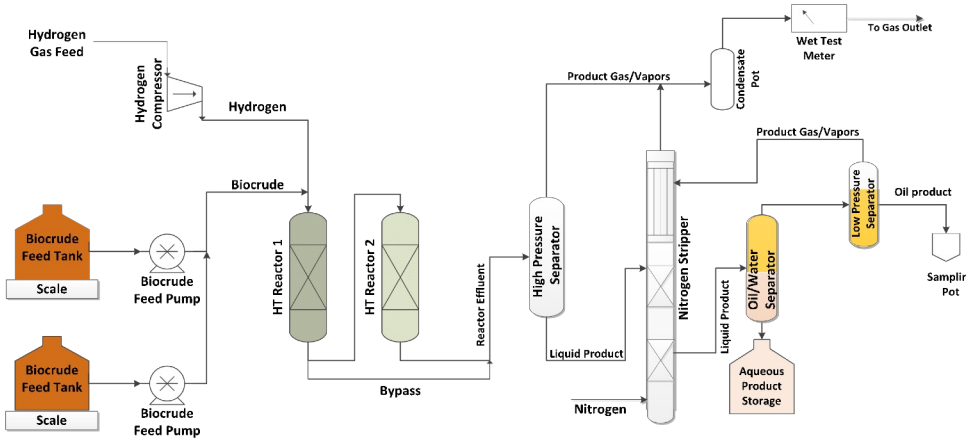
Award No.	Project Title	Activities
DE-AR0000021	Catalytic Biocrude Production in a Novel, Short-Contact Time Reactor	CFP catalyst development; 1TPD biomass unit
DE-EE-0005358	Catalytic Upgrading of Thermochemical Intermediates to Hydrocarbons	1TPD CFP operation; Pilot-scale hydroprocessing unit
DE-EE-0007730	Building Blocks from Biocrude: High Value Methoxyphenols	Bioproducts separation; Lab-scale separations unit
DE-EE0008509	Biocrude Production and Upgrading to Renewable Diesel	Biocrude fractionation to produce renewable diesel



1TPD Catalytic Biomass Pyrolysis



Lab-scale Biocrude Separations



Pilot-scale Hydroprocessing

Approach

BP1 - Initial Verification (award date October 2020 completed June 2022)

- Review claims in the proposal and review separations results collected and verified in a previous DOE/BETO project.
  - Go/No-Go Decision: Process information and data support the technology readiness level of the overall process, the unit operations within the process, and the original application. Technical metrics are based on preliminary data and represent a meaningful baseline and set of targets.

BP2 – Integrated Design, Coprocessing and Co-products Development (started October 2022)

- Regional feedstock resource assessment
- Biocrude production and bench-scale separations to inform pilot-scale separation unit operation design
- Design, preliminary cost estimate, and process hazard analysis for 1TPD Biomass Unit modifications
- Co-processing strategy development and co-product assessment
  - Go/No-Go Decision: Complete Integrated Separations Design Review to obtain the approval for construction; Identify refinery co-processing opportunities; Evaluate co-product applications for methoxyphenols and other potential bioproducts to show a pathway for improving economic viability of integrated CFP process. .

BP3 – 1TPD pilot plant modifications, commissioning, and operation. Biocrude production, separation, and upgrading. (Not started)

- Complete modifications to the 1TPD Biomass Unit
- 500 h of integrated operations (at least 100 continuous hours) with 25wt% biocrude recovery and fractionation.
- Recovery of methoxyphenols for bioproducts application testing and market assessment
- Identify and optimize a suitable biocrude co-processing option
  - Final Project Goal: TEA based on experimental results and the results of a comprehensive biomass feedstock resource assessment and supply chain models to optimize intake capacity and substantiate the economic viability of a fully integrated process design to produce bioproducts and finished bio-blendstocks with at least a 60% reduction in greenhouse gas (GHG) emissions over the petroleum derived equivalents.

Ecostrat is a North American leader in assessing, developing, optimizing, and managing biomass supply chains.

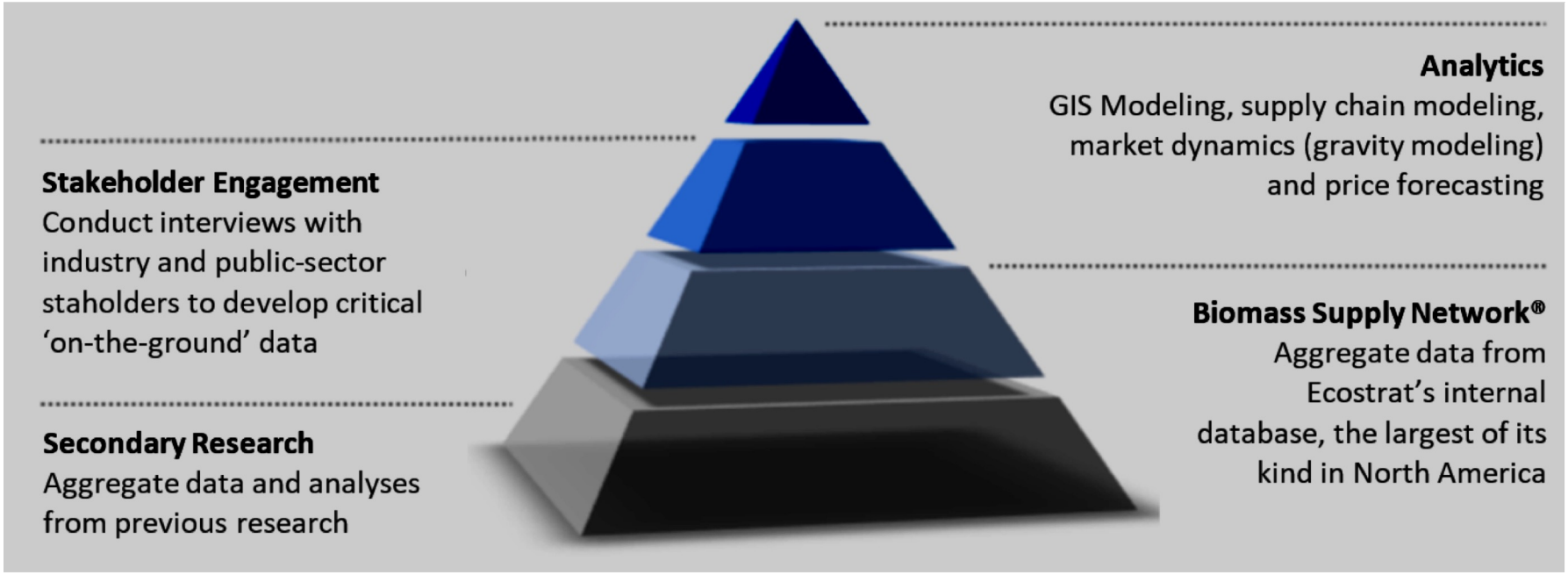
Biomass Advisory Group - focused exclusively on assessing, validating and optimizing bio-based supply chains for projects across the following sectors: Biofuels & Biochemicals; Biomass Heat & Power; Pellets/Biomaterials; and Biogas & Compost

The Biomass Supply Chain Risk (BSCR) Standards and Risk Ratings

Direct Point-Source Supply Information

Biomass Supply Group - North American leader in sourcing, aggregating and supplying biomass

ECOSTRAT METHODOLOGY



Scope of Work

Budget Period 2: Renewable Biomass Resource Assessment

Provide a landscape-level assessment of the competitive availability of Renewable Biomass (as defined by EPA in the Renewable Fuel Standard) resources in each Region, including qualifying pulpwood, logging residues (precommercial thinnings and slash), and mill residuals.

Case Studies

Conduct detailed analyses of the competitive availability and price of Renewable Biomass to: 1) generate marginal cost curves for each location expressing volumes of each type of Renewable Biomass available as a function of price - a means by which we can evaluate each location's capacity to support biorefineries of varying intake capacities; and 2) estimate Renewable Biomass availability at selected locations as a function of price.

Feedstock Availability

Budget Period 3: Optimizing Biorefinery Intake Capacities and Supply Chains

Biorefinery size based on Renewable Biomass availability and feedstock price tolerances

Model Optimization Model Development

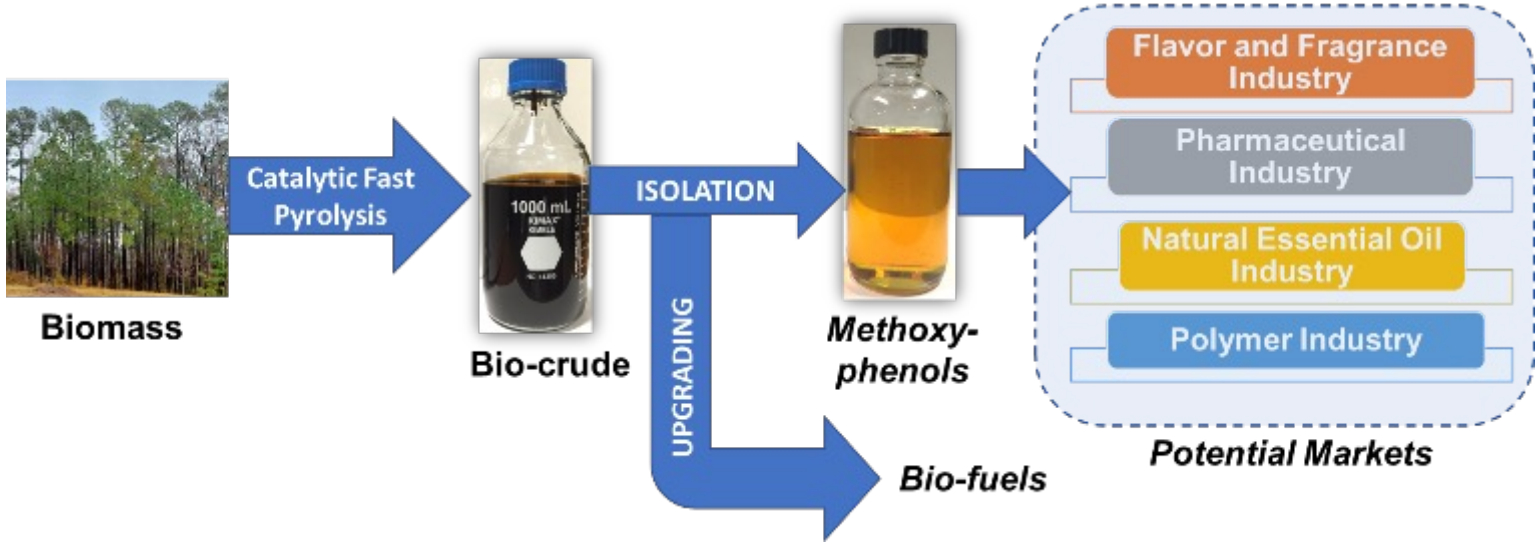
Develop a GIS-based optimization model to estimate Renewable Biomass availability as a function of price at any location

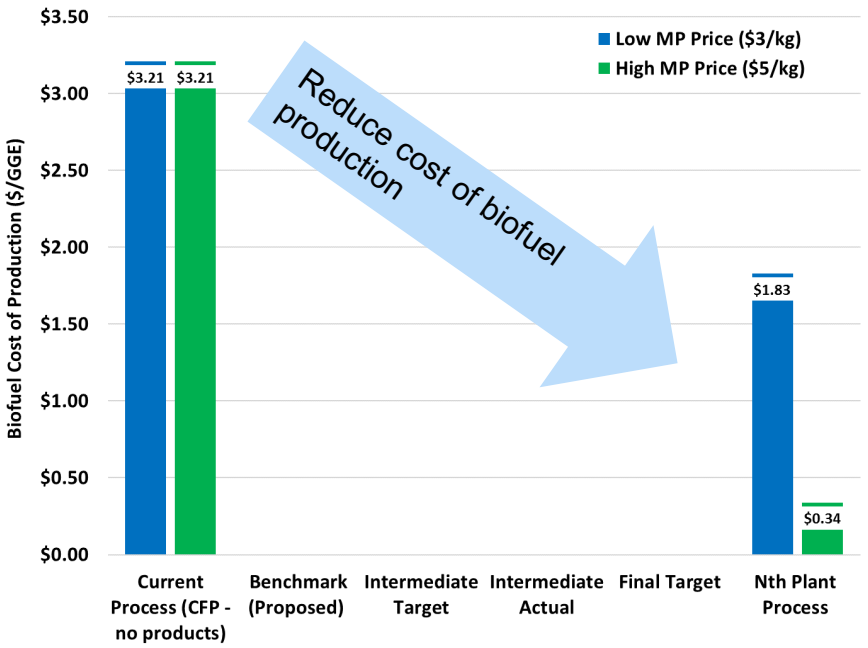
Supply Chain Design and Risk Mitigation

Design Renewable Biomass supply chains for each location, informed by *US Standards for Biomass Supply Chain Risk,* that minimizes supply chain risk.

Building on Previous Bioproducts Development

- A market assessment of the methoxyphenols (MPs) with demand and prices determined based on import-export flows for the US.
- Identified four potential applications of MPs and chemistries for synthesis of vanillin, a flame-retardant additive, and caprolactone.

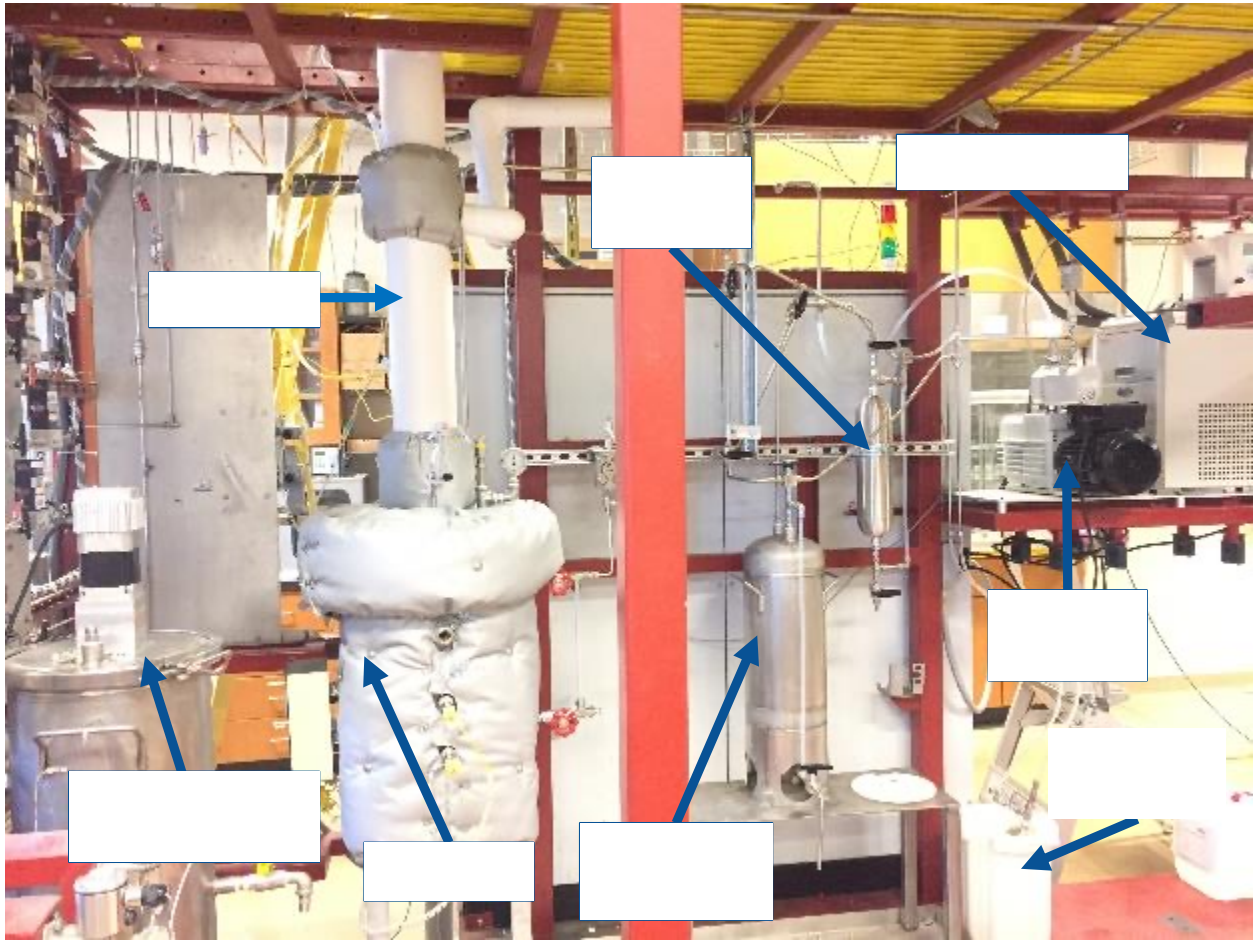


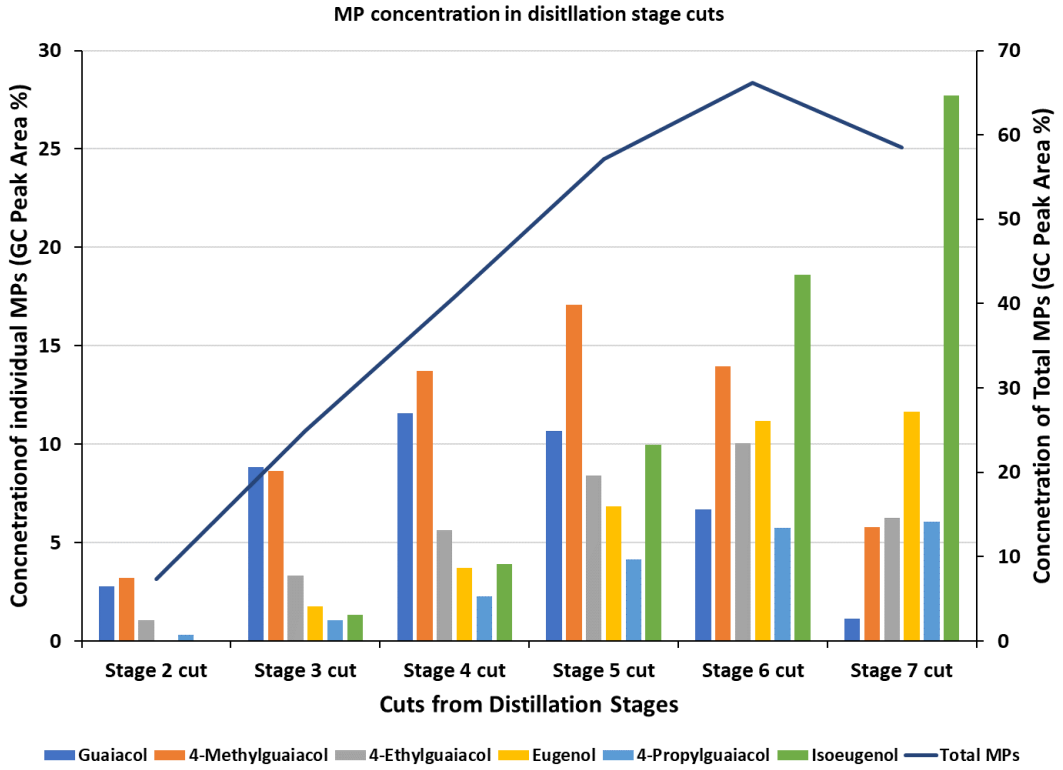


Scaleup strategies to capitalize on revenue from bioproducts as part of cost-competitive biofuel production

Separations Scale-up

- Successfully developed three scalable strategies for recovery of MPs from biocrude by modification and integration of solvent extraction, distillation and chromatography techniques.
- Addressed challenges such as residue formation, non-selectivity, and low recovery typically associated with the selected techniques for biocrude separation.





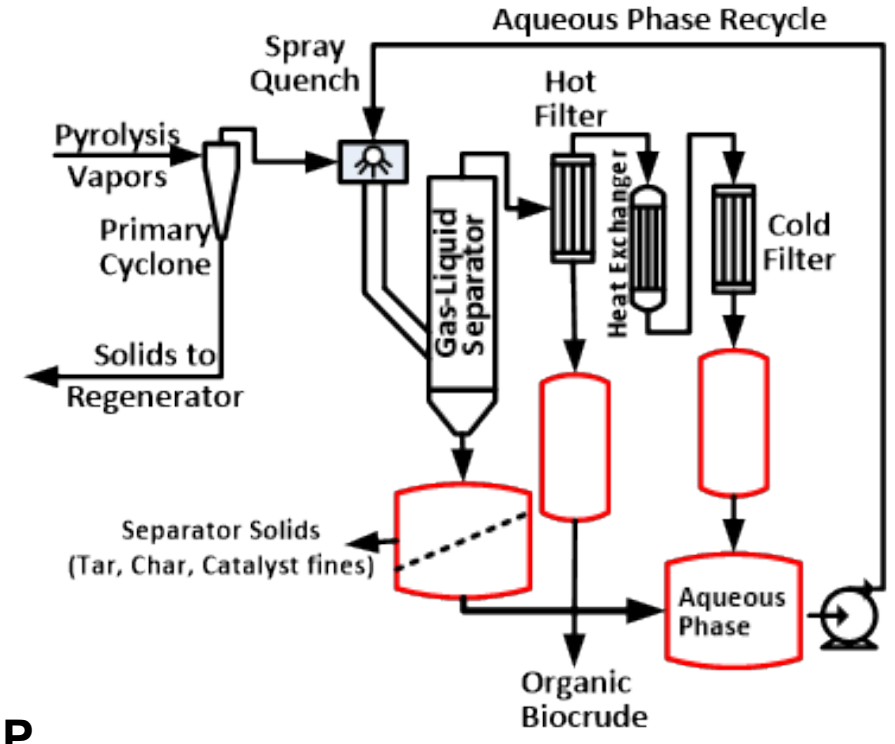
Key Milestones

- ***Developed approach achieves 75% recovery efficiency, over 90wt% purity, and no residual losses.***
- ***Designed, fabricated, and installed a 7-gallon per day lab-scale separation unit***

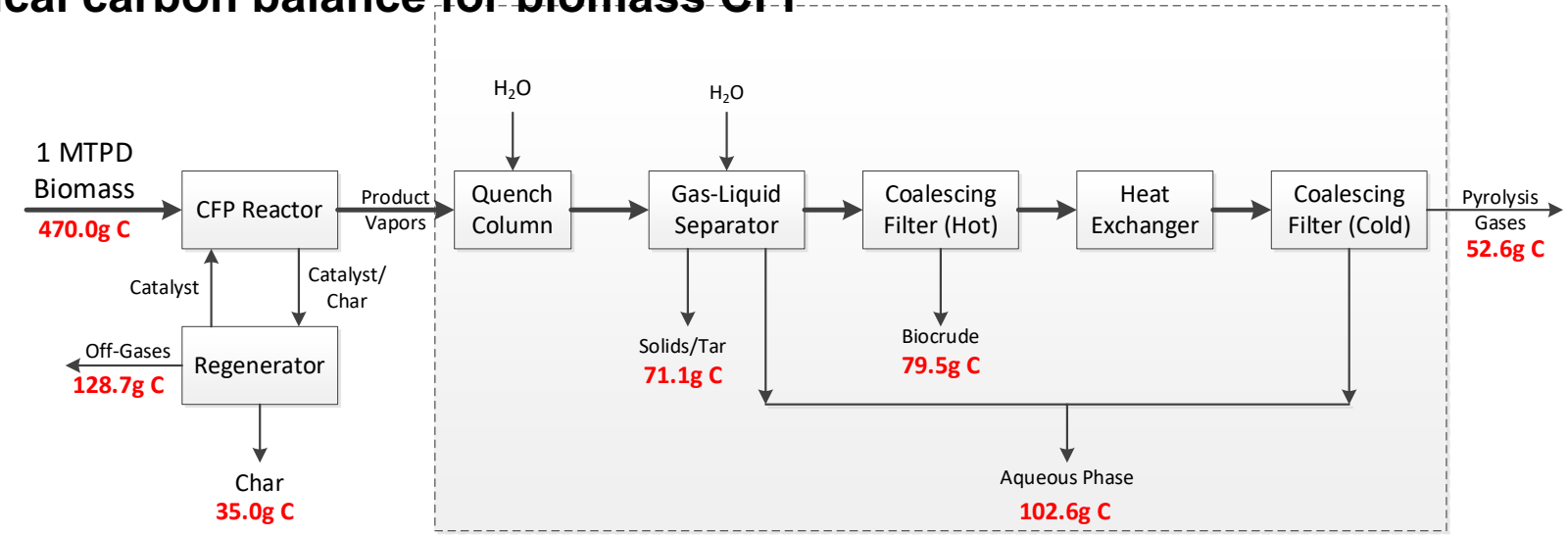
RTI 1TPD Biomass Unit - Current Product Recovery

Saturate carbon in the aqueous phase to improve biocrude recovery and minimize waste

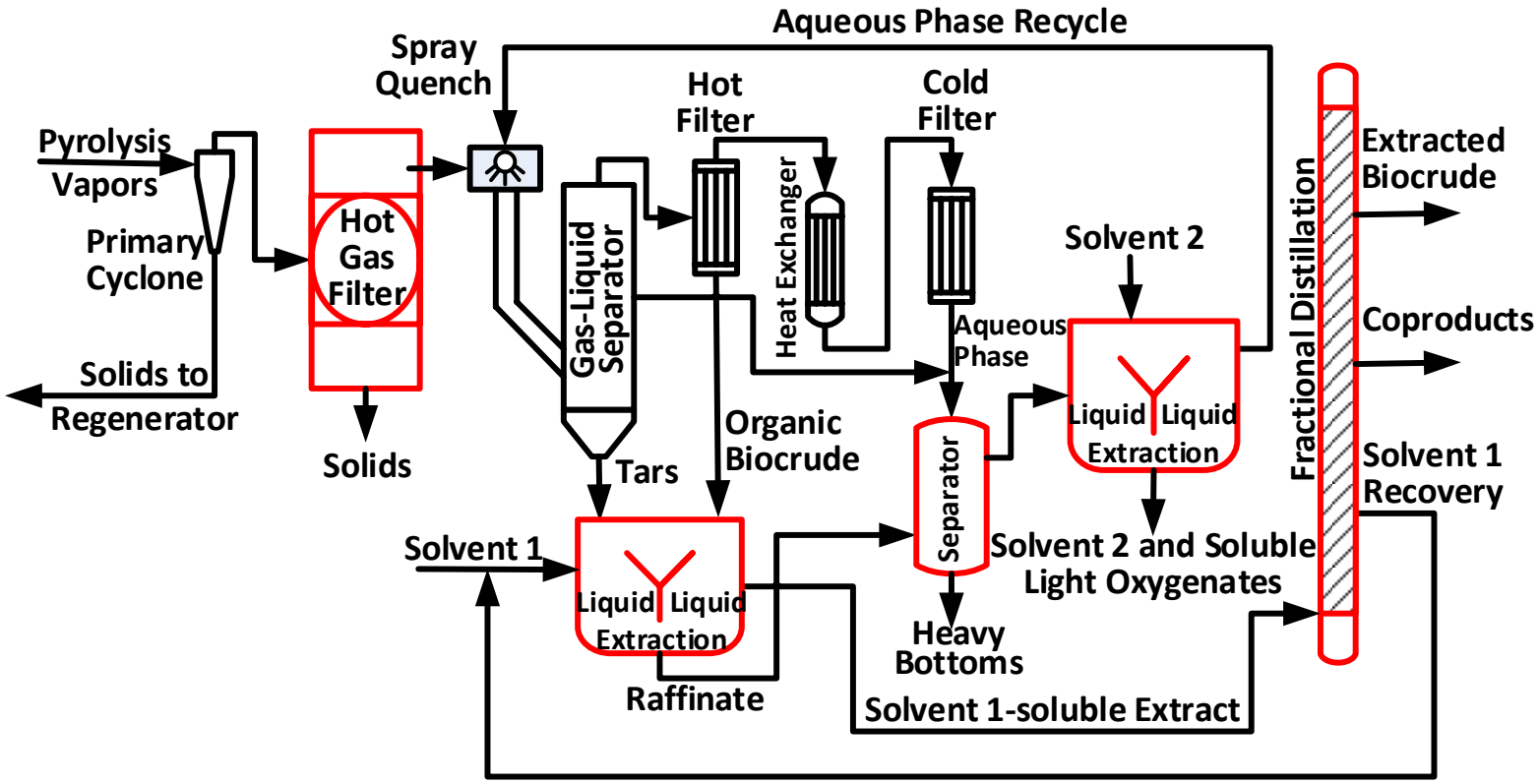
Water inlet	Flow rate (L/min)
Primary spray quench	1-2.7
Separator quench	0.27-0.73



Typical carbon balance for biomass CFP

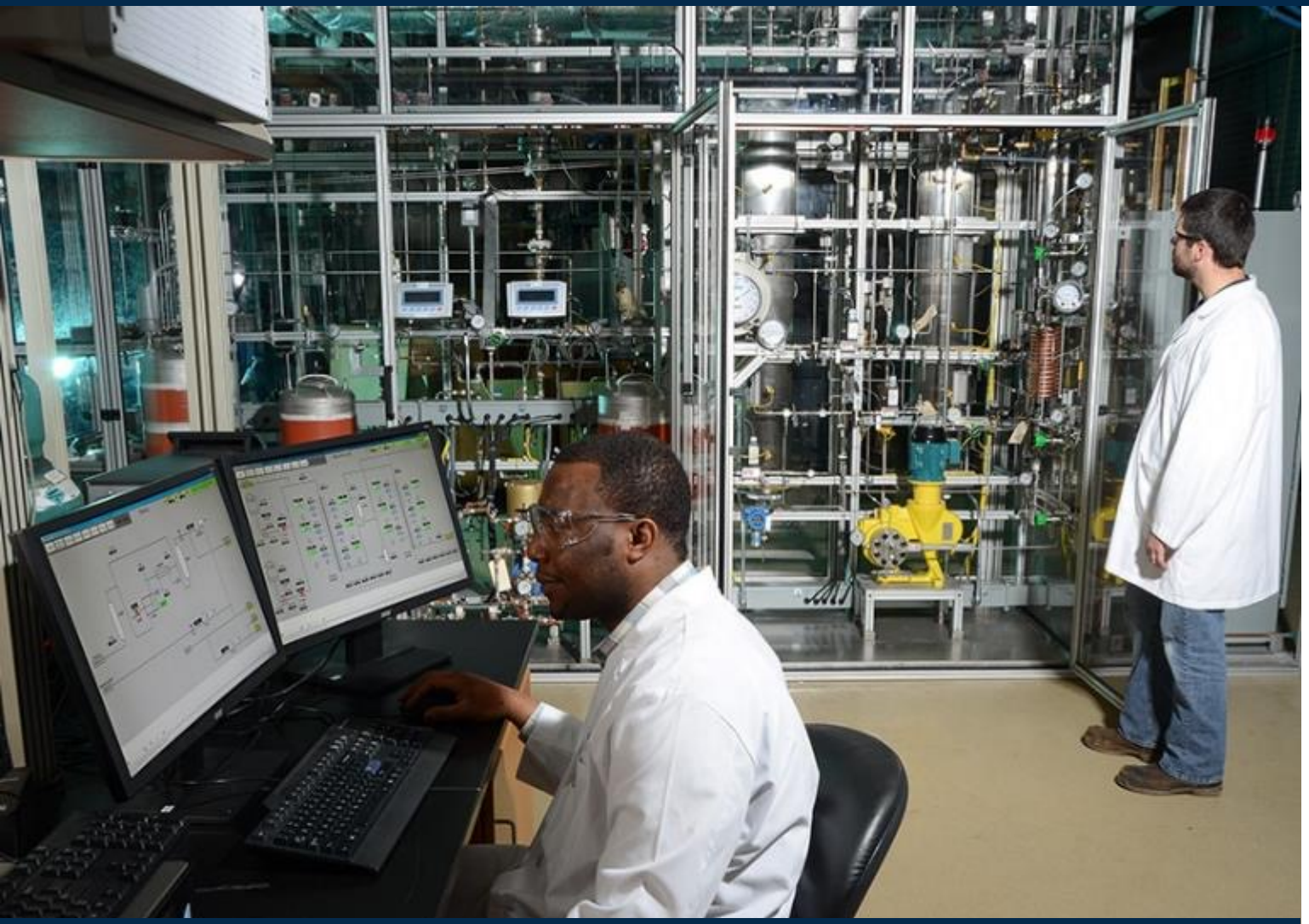


RTI 1TPD Biomass Unit – Separations Modifications



Separation system to enhance product recovery to bioproducts and biofuels. New unit operations in red

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

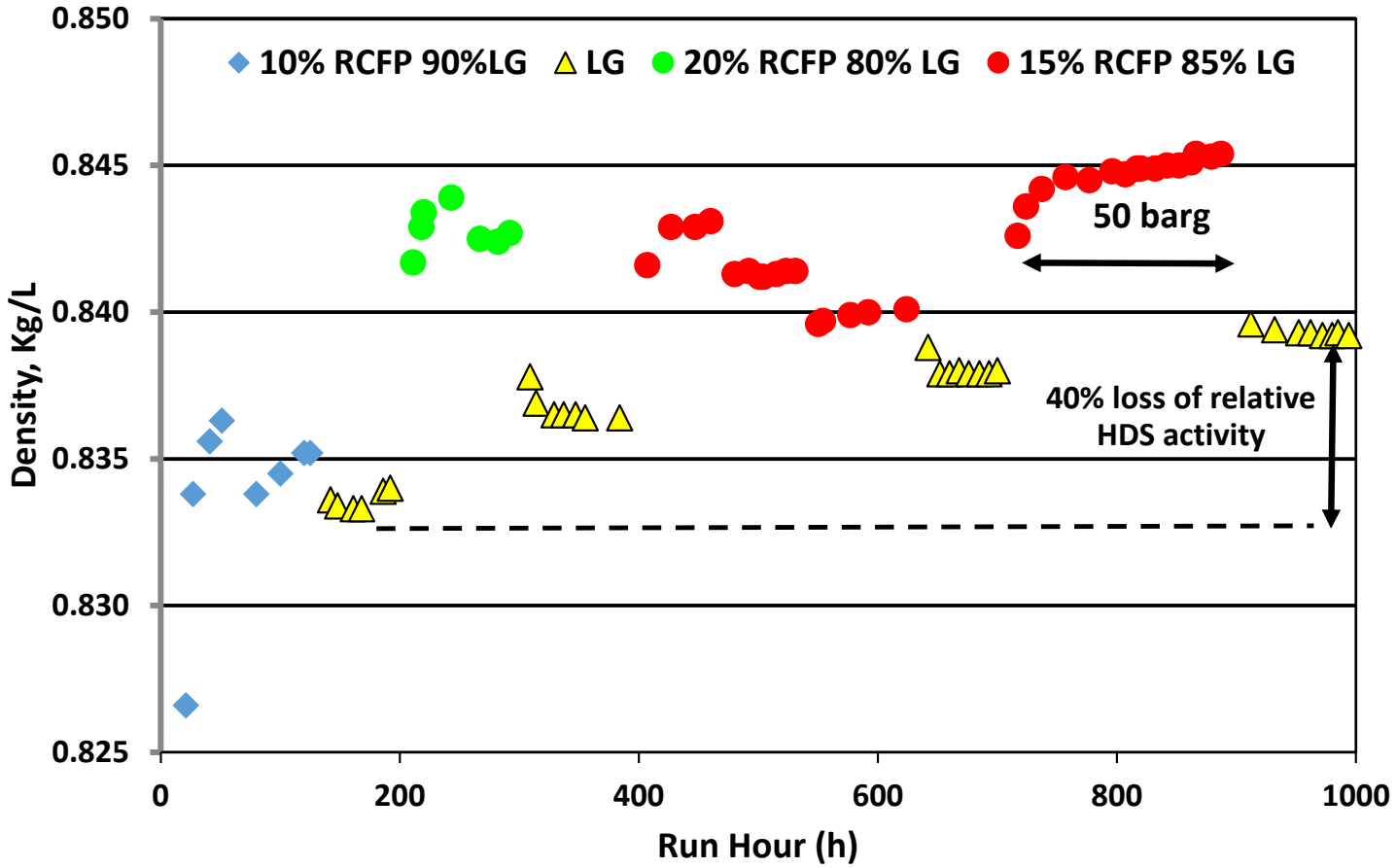
Reactor volume - 350 mL
Catalyst volume - 20 to 250 mL
Design temperature: 450C
Max. operating temperature: 430C
Max. operating pressure: 170 bar (2500 psig)

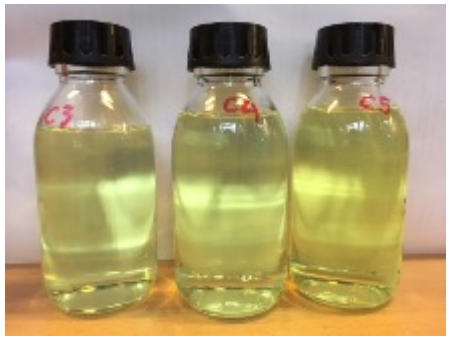
Biocrude Upgrading Goals:
- Steady-state deoxygenation activity, hydrogen demand, and process severity as a function of biocrude quality (wt%O)
- Long-term operation to determine catalyst stability and lifetime (500-1000 hrs)

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

Prior Work - Biocrude Co-processing with Light Gas Oil





Pressure (Inlet pH_2)	50 – 70 barg
Reactor temperature	340 – 360°C
LSHV	2 h^{-1}
H_2/oil ratio	500 Nl/l

Integrated Biofuels and Bioproducts Development at RTI

Catalytic Biomass Pyrolysis Development

- Over a decade operating a 1 ton/day catalytic biomass pyrolysis unit for biocrude production
- Recently produced ~100 gallons of biocrude from Douglas Fir Crumbles®

Biocrude Separations Development

- Developed a 3-step lab-scale (500-g) separations approach (isolation, concentration, and purification) to achieve 74% separations efficiency, 93% product purity and 0% residual loses
- Bench-scale (~30-kg) batch biocrude separations unit with LLE and distillation achieved 66% separation efficiency, 90% methoxyphenol product purity, and 0% residual loss
- Separated biocrude into solvent-soluble, aqueous, and raffinate fractions with 99+% mass closure and less than less than 1% loss

Hydroprocessing Development - Upgrading Biocrude Fractions

- Pilot-scale hydroprocessing unit development – 8 years of operation with numerous feeds
- Solvent-soluble biocrude fraction hydrotreated for 145 hrs in RTI's pilot-scale hydroprocessing unit at 2000 psig hydrogen pressure, and liquid hourly space velocity of 0.35/hr
- Biocrude fractions hydrotreated with 89.5% average carbon yield: toluene soluble – 99 wt%C; water-soluble – 74 wt%C; raffinate – 87 wt%C
- 30% average overall carbon yield from biomass to upgraded products

Impact

Feedstock | Conversion | Separations | Bioproducts | Upgrading | Biofuel






Continued development of advanced biofuels pathway that integrates catalytic biomass pyrolysis and biocrude upgrading

Address technical issues across the entire value chain from feedstock, through conversion, to biofuels and bioproducts.

Pilot-scale testing of separations unit operations to enable efficient bioproducts recovery

Maximize utilization of the inherent oxygenated nature of biomass by separating process streams into valuable products to develop cost-competitive biofuels and bioproducts

Enable biocrude co-processing in existing refineries.

Summary

- Biomass supply chain models to optimize biorefinery intake capacity (scale) and location
- Maximize utilization of the inherent oxygenated nature of biomass by separating process streams into cost-competitive biofuels and bioproducts.
  - Improve biocrude recovery efficiency in 1TPD pilot scale catalytic biomass pyrolysis unit
  - Scale-up separation unit operations for integration into 1TPD biomass unit for biocrude fractionation to facilitate bioproducts recovery and upgrading
- Investigate strategies for co-processing biocrude fractions and refinery intermediates
  - Pilot-scale hydroprocessing performance: catalyst activity, process parameters. long-term stability
  - De-risk biocrude co-processing in existing refineries.
- Updated TEA for CFP/hydrotreating pathway to substantiate the economic viability of a fully integrated process design to produce bioproducts and finished bio-blendstocks that includes with at least a 60% reduction in greenhouse gas (GHG) emissions over the petroleum derived equivalents.

Integrated Separations to Improve Biocrude Recovery for Biofuels and Bioproducts (DE-EE0009262)

Timeline

- Award Date: 10/1/2020
- Award Negotiations Concluded: 9/28/2021
- Proposed Budget Period 1 end date: 12/31/2021
- Initial Verification – June 2022
- Authorization to move into BP2: 8/11/2022
- Budget Period 2: 7/1/2022 – 9/30/2023
- Budget Period 3: 10/1/2023 – 9/30/2025

Start: TRL 4 **End: TRL 5**

Project Goal

Scale-up separations unit operations in RTI's 1TPD catalytic biomass pyrolysis unit to achieve 25% biocrude collection efficiency. 10 wt% of the biocrude intermediate is recovered as chemical building blocks for bio-products and the remainder upgraded into biofuels.

End of Project Milestone

Complete 1TPD pilot plant modifications to achieve 500 h of integrated operations with at least 100 continuous hours with 25wt% biocrude recovery. Isolate 10 wt% MP bioproducts for application testing and identify biocrude co-processing options for refinery integration.

Partners

RTI International: Project lead, integrated process development; biocrude production and upgrading, project management
Ecostrat: Biomass supply chain analysis to define optimum biorefinery scale and identify appropriate site locations
Proficio Consultancy, Inc.: Engineering and fabrication of separation unit operations and 1TPD pilot plant modifications
Mott Corporation: Hot gas filter design and fabrication
Bioproduct and Refinery partners TBD

Budget	Federal	Cost Share	Total Costs	Actuals to date (FY23Q1)	
				Federal	Cost Share
BP1	$48,445	$16,152	$64,597	$48,445	$16,152
BP2	$1,200,945	$316,689	$1,517,634	$15,252	$3,996
BP3	$2,440,612	$589,660	$3,030,272		
	$3,690,002	$922,501	$4,612,503	$63,697	$20,148

FY20 Bioenergy Technologies Multi-Topic FOA (DE-FOA-0002203 issued 1/23/2020))
Topic Area 1: Scale Up of Bench Applications (SCUBA)

Reduce the scale-up technology uncertainty and risk of integrating biorefinery technology pathways by focusing on engineering solutions for key process steps

Additional Slides

Responses to Previous Reviewers' Comments

Not applicable

Initial Verification

Verification Criteria :

Validate technical data, performance metrics, and targets for the proposed research.

- Catalytic biomass pyrolysis process that produces a liquid biocrude intermediate with 25 wt%C efficiency
- Biocrude separation to recover MP-rich fraction that is 50% MPs with 75% recovery efficiency.

Pre-read Documents:

1. Revised Block Flow Data
2. Revised Statement of Project Objectives
3. Verification Reports from previous projects
    - Initial Verification: Integrated Separations to Improve Biocrude Recovery for Biofuel and Bioproducts (EE-0009262) (“Verification Report”)
    - MEGA-BIO: Bioproducts to Enable Biofuels – Final Verification Report (“MEGA-BIO Report") authored by National Renewable Energy Laboratory (“NREL”)
    - Building Blocks from Biocrude: High-Value Methoxyphenols Final Scientific/Technical Report (“MP Report”) authored by RTI International
    - Integrated Reactive Catalytic Fast Pyrolysis System for Advanced Biofuels – IER2 Intermediate Verification Report authored by ICF.

Initial Verification - Summary of Verifications from Previous Projects

Award No.	Metrics	Summary	Outcome
DE-EE0007730: Building Blocks from Biocrude: High Value Methoxyphenols			
Intermediate Verification (10/2017)	• 85 wt% separation efficiency • 90% product purity • 15% residual loss	Developed a 3-step lab-scale (500-g) separations approach (isolation, concentration, and purification) to achieve 74% separations efficiency, 93% product purity and 0% residual loses.	Go/NoGo MET
Final Verification (1/28/2021)	90% performance in scaled-up equipment: • 76.5 wt% separation efficiency • 90% product purity • 10% residual loss	Achieved 66% separation efficiency, 90% product purity, and 0% residual loss in bench-scale (~30-kg) separations unit with LLE, distillation, and chromatographic separation. Completed TEA and market opportunity assessment for MP bioproduct	End of project
DE-EE0008509: Biocrude Production and Upgrading to Renewable Diesel			
Initial Verification (August 2019)	• Produce 10 gallons of biocrude with less than 30 wt% oxygen at 20 wt% yield • Separate biocrude into 3 fractions • Upgrade biocrude into diesel at 350C, 2000 psig hydrogen, and 0.25 WHSV for 100 hours	• 10.7 gallons of biocrude with 27 wt%O produced in 1TPD biomass unit with 18% yield • Separated biocrude into solvent-soluble, aqueous, and raffinate fractions with 99+% mass closure in bench-scale unit • Solvent-soluble biocrude fraction hydrotreated for 145 hrs in RTI's pilot-scale hydroprocessing unit at 2000 psig hydrogen pressure, and liquid hourly space velocity of 0.35/hr.	Go/NoGo met with plan to increase biocrude yield
Intermediate Verification (October 2021)	• Produce 10 gallons of biocrude from 3 feedstocks • Fractionate each biocrude into 3 fractions with less than 1% material loss • Hydrotreated biocrude fractions achieve > 90% carbon yield in upgraded products • 25% overall carbon of biomass to biofuel • Go/NoGo: 30% reduced modelled cost of biofuel based on TEA	• 9.45 gallons from 1mm Douglas fir; 52 gallons from 2mm Douglas fir 3.46 gallons from 4mm Douglas fir • 3 fractions from each biocrude produced with less than 1% loss • Each fraction was hydrotreated with 89.5% average carbon yield: toluene soluble – 99 wt%C; water-soluble – 74 wt%C; raffinate – 87 wt%C • 30% average overall carbon yield from biomass to upgraded products • 27% reduction in modelled MFSP from TEA	Go/NoGo NOT MET. Assumptions for calculating carbon yields not sufficiently verified. Revised BP2 scope approved to continue experiments to achieve targets.

Initial Verification – Independent Engineers Review*

Overview of Initial Verification Test Data (January 2021)				
Key Performance Parameter	**Red Flags**	**Anything Lacking?**	**Readiness to Proceed**	**Path Forward**
Methoxyphenol Separation: two-stage extraction and seven-stage distillation (DE-EE007730)	None	Distillation of Methoxyphenol at pilot scale will need refinement with fewer cuts	Yes	Proceed to BP2
Renewable Biocrude Production and Upgrading to Renewable Diesel	None	Assumptions made in final report need verification	Yes	Proceed to BP2 with plan to verify assumptions made in Project 8509

Conclusions

- RTI has reasonably demonstrated the ability to separate methoxyphenols from biocrude in a two-stage laboratory-scale extraction process with toluene at 93% efficiency. In a seven-stage laboratory-scale distillation process, RTI was able to recover the toluene from the extract and methoxyphenol at 77% distillation efficiency and at 38.7% concentration from the combined distillation cuts as referenced in the NREL MEGA-BIO Report.
- RTI has reasonably demonstrated its ability to separate biocrude into toluene soluble extract and toluene insoluble raffinate components in a two-stage extraction and single stage distillation approach while recovering toluene from the extract. RTI subsequently successfully demonstrated that it can upgrade the distilled extraction portion of the recovered intermediate biocrude.

Reproduced from Independent Engineers Report to DOE dated July 12, 2022

Publications, Patents, Presentations, Awards, and Commercialization

- Publications: None
- Patents: None
- Presentations: None