DOE Bioenergy Technologies Office (BETO)
2023 Project Peer Review

Integrated Reactive Catalytic Fast Pyrolysis System for Advanced Hydrocarbon Biofuels
WBS 3.5.1.204

April 4, 2023
System Development and Integration
Principal Investigator: David C. Dayton
RTI International

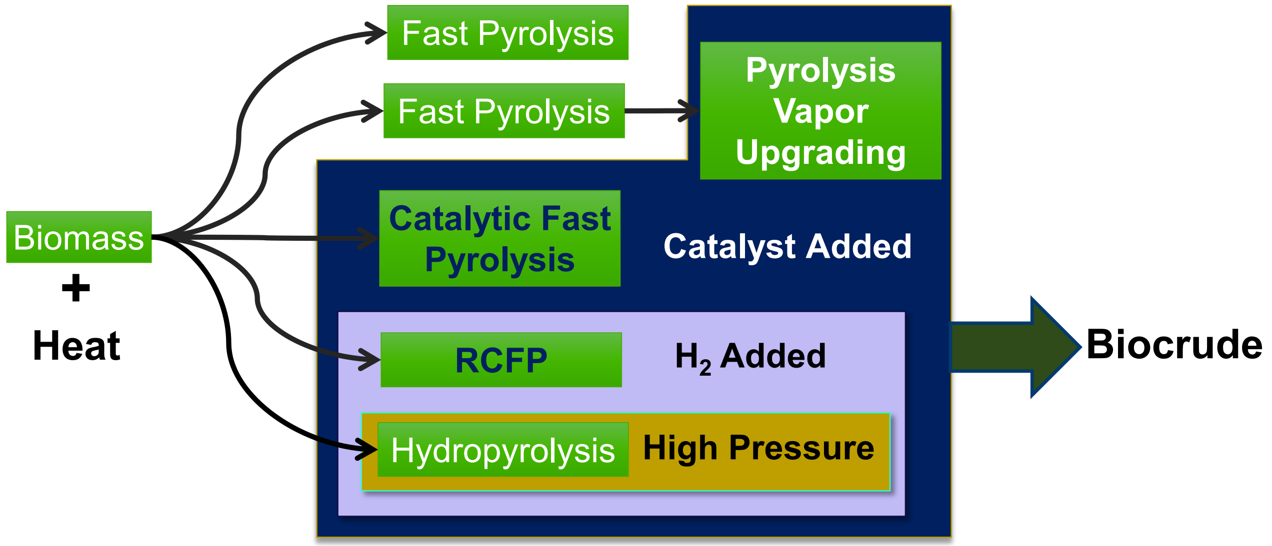
This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project Overview

Project Goal

Design, fabricate, and operate an engineering-scale reactor system that can continuously maintain steady-state HDO activity to produce enough low oxygen content RCFP biocrude to support extensive upgrading studies and produce <u>100 gallons of drop-in renewable diesel</u>

Catalyst applied to maximize yields and improve biocrude quality (oxygen content, chemical composition, thermal stability)



Summary:

1) Design, fabricate, and install an engineering-scale (1-5 kg/hr) reactive catalytic fast pyrolysis (RCFP) reactor system
2) Scale up a fluidizable RCFP catalyst based on the formulation of commercially available extrudates
3) Optimize the process and maintain steady-state hydrodeoxygenation (HDO) catalyst activity to maximize biocrude yield and quality
4) Extensive upgrading studies to enhance the technical understanding of biocrude hydrotreating

Targets

- Verify 50 mole %C yield in RCFP biocrude at engineering scale.
- Demonstrate that the renewable diesel pathway has 50% less GHG emissions compared to fossil-derived diesel.

Approach

BP1 - Initial Verification (Award date October 2019, completed April 2021)

- Review claims in the proposal and verify proof-of-principle experimental results collected in a previous DOE/BETO project.
  - Go/No-Go Decision: Block Flow Data have been reviewed and verified, experiments to replicate baseline data witnessed and verified, goals and performance metrics established to track technical progress for the remainder of the proposed project, and project goals and objectives are in alignment with BETO’s programmatic goals.

BP2 - Design a continuous RCFP reactor system and develop a fluidizable RCFP catalyst based on commercial formulation (completed July 2022)

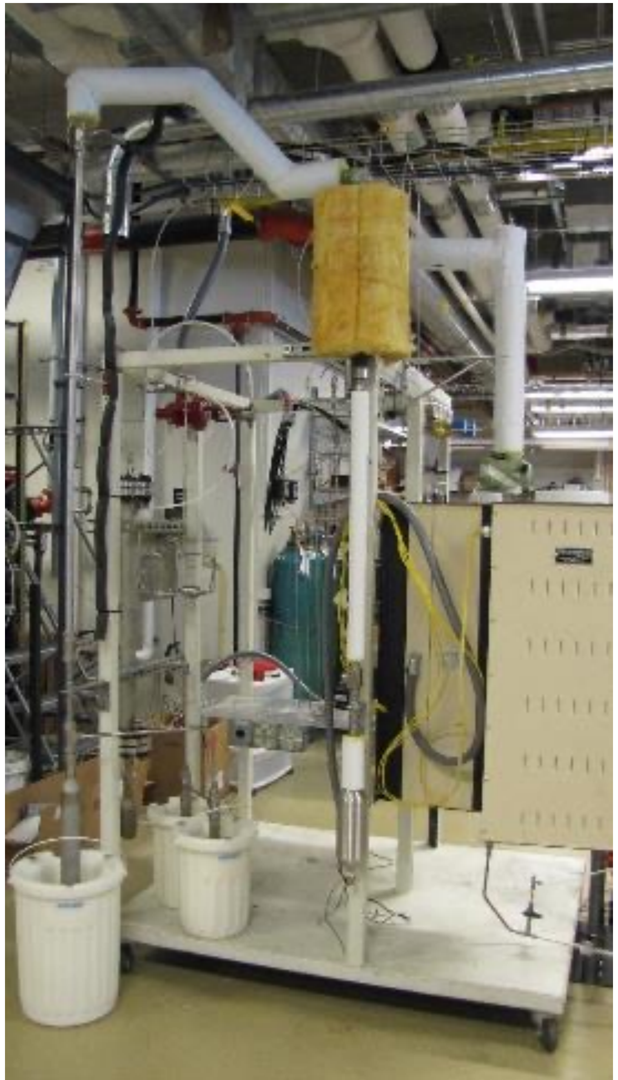
- Scale-up RCFP process to 1-5 kg/hr. Process design based on mass and carbon balances measured a laboratory-scale 2” fluidized bed reactor system (2FBR)
- Translate commercial catalyst formulation for extrudates into a fluidizable form for scaleup. Validate catalyst performance in 2FBR
  - Go/No-Go Decision:
    - Approved Engineering-scale Design for Fabrication
    - Fluidizable Catalyst: Demonstrated > 45 mole% C efficiency in C_4^+ products with less than 15 wt% oxygen in RCFP biocrude.

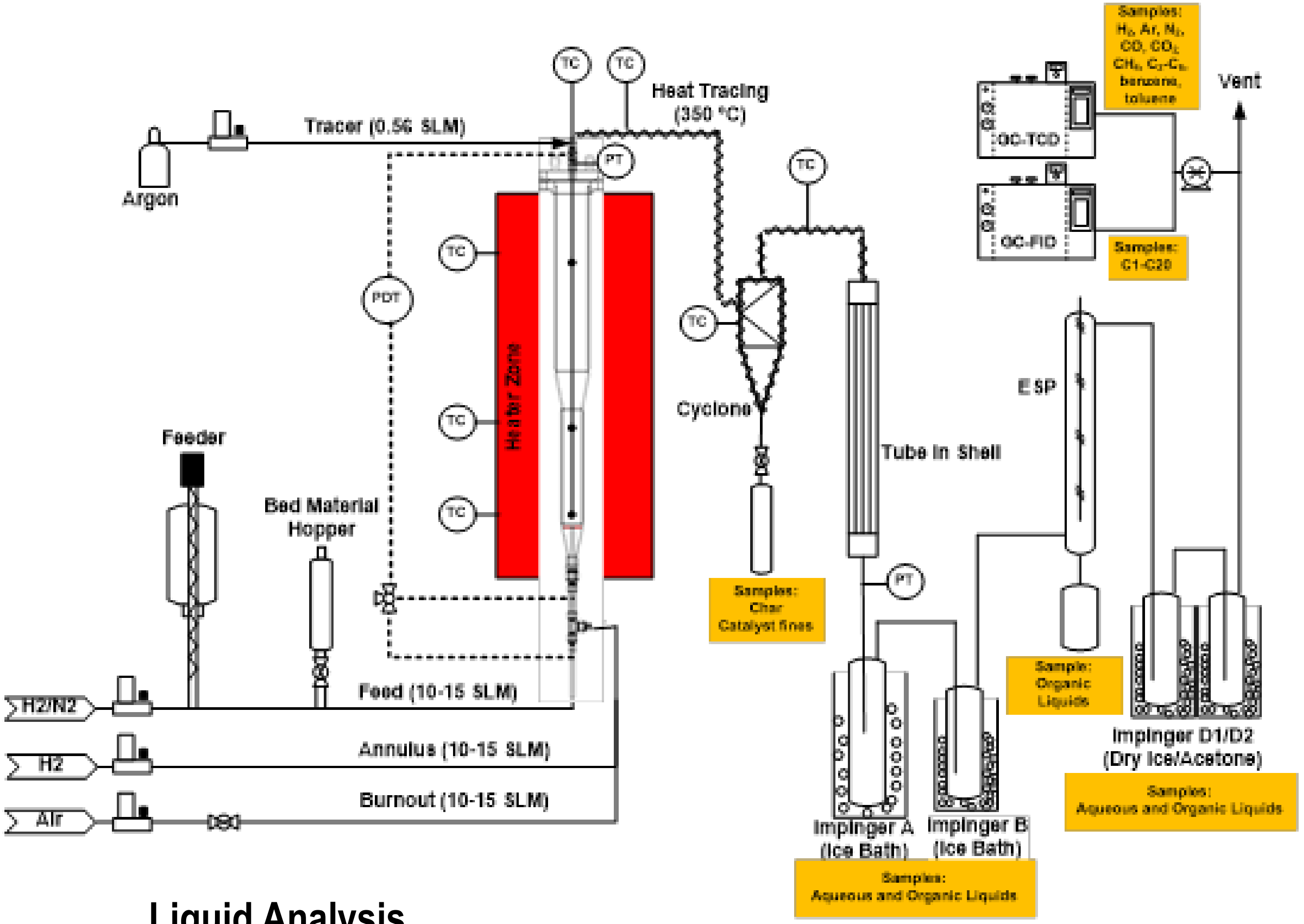
BP3 - Fabricate the engineering-scale (1-5 kg/hr) RCFP reactor system for RCFP biocrude production and upgrading (ongoing)

- Complete fabrication, installation and commissioning of RCFP unit.
- Biocrude production and upgrading
- Final TEA and LCA
  - Final Project Goal: Biocrude upgrading to produce 100 gallons of a diesel blendstock to produce a 50/50 blend that meets ASTM D975 specifications. $3.00 MFSP from TEA and 50% GHG reduction from LCA

Experimental Approach - RTI 2FBR System

2.5’’ fluidized bed reactor with 4’’ disengagement zone
Biomass feeding rate: 2-5 g/min
Liquid collection: 3 condensers and 1 ESP
On-line Inficon Micro-GC 3000 for process gas analysis





Liquid Analysis

- Thermo Flash Model 2000 Elemental Analyzer
- Mettler Toledo V20 Titrator for Karl-Fischer Moisture measurements
- Agilent 7890A gas chromatograph and 5975C mass spectrometer detector for semi-volatile compound identification

Materials and Process Conditions

Biomass Feedstock

- Locally sourced loblolly pine (Piedmont Pellets, NC) sawdust (2mm top size; 8-10 wt% moisture)
- 47.8wt%-dry C; 6.4 wt%-dry H; 0.08 wt%-dry N; 45.8 wt%-dry O by difference
- Milled and sieved to a particle size distribution between 90-300 µm

RCFP Catalysts

- Commercial extrudates crushed and sieved to recover 105-300 µm particle size range.
- Spray dried catalysts – Sample 4 and Sample 5

Parameter	Target Range	Design Basis
Pyrolysis temperature (°C)	445-475	400–650
Char/coke oxidation temperature (°C)	500-600	500–700
Catalyst reduction temperature (°C)	530	500–600
System pressure (psia)	16-25	15–90
Biomass feed rate (g/h)	240-420	0-1000
Hydrogen concentration (vol%)	80	0-80
Catalyst Loading (g)	300-500	200-1000
Total gas flow rate (slm)	20-30	0-45

Summary of RCFP Catalyst Performance Testing

run ID	-172	-174	-178	-182	-184	-186	-188	-190
Temperature [°C]	460	460	475	460	475	475	460	475
feedrate [g/min]	6.38	6.62	6.65	6.63	4.5	6.01	5.41	6.12
Feed [g Pine]	804.3	847.5	850.9	850.3	684.6	853.9	852.4	850.7
Total Flow [SLM]	30	20	20	20	20	20	20	20
Organic	**33%**	**34%**	**42%**	**37%**	**28%**	**33%**	**31%**	**33%**
Aqueous	**10%**	**4%**	**3%**	**5%**	**2%**	**4%**	**4%**	**4%**
Solids	**45%**	**48%**	**37%**	**23%**	**28%**	**27%**	**37%**	**33%**
Gas	**10%**	**8%**	**10%**	**11%**	**16%**	**13%**	**12%**	**14%**
C_1-C_3	10%	9%	10%	10%	14%	12%	10%	12%
CO	7%	7%	8%	7%	7%	8%	7%	7%
CO_2	5%	4%	5%	5%	5%	5%	5%	5%
Carbon Closure	**119%**	**116%**	**115%**	**97%**	**101%**	**101%**	**106%**	**108%**
C_4^+ Efficiency	*43%*	*42%*	*52%*	*47%*	*45%*	*46%*	*44%*	*46%*
wt% O - dry	*13%*	*11%*	*22%*	*16%*	*15%*	*20%*	*17%*	*18%*

Engineering Design

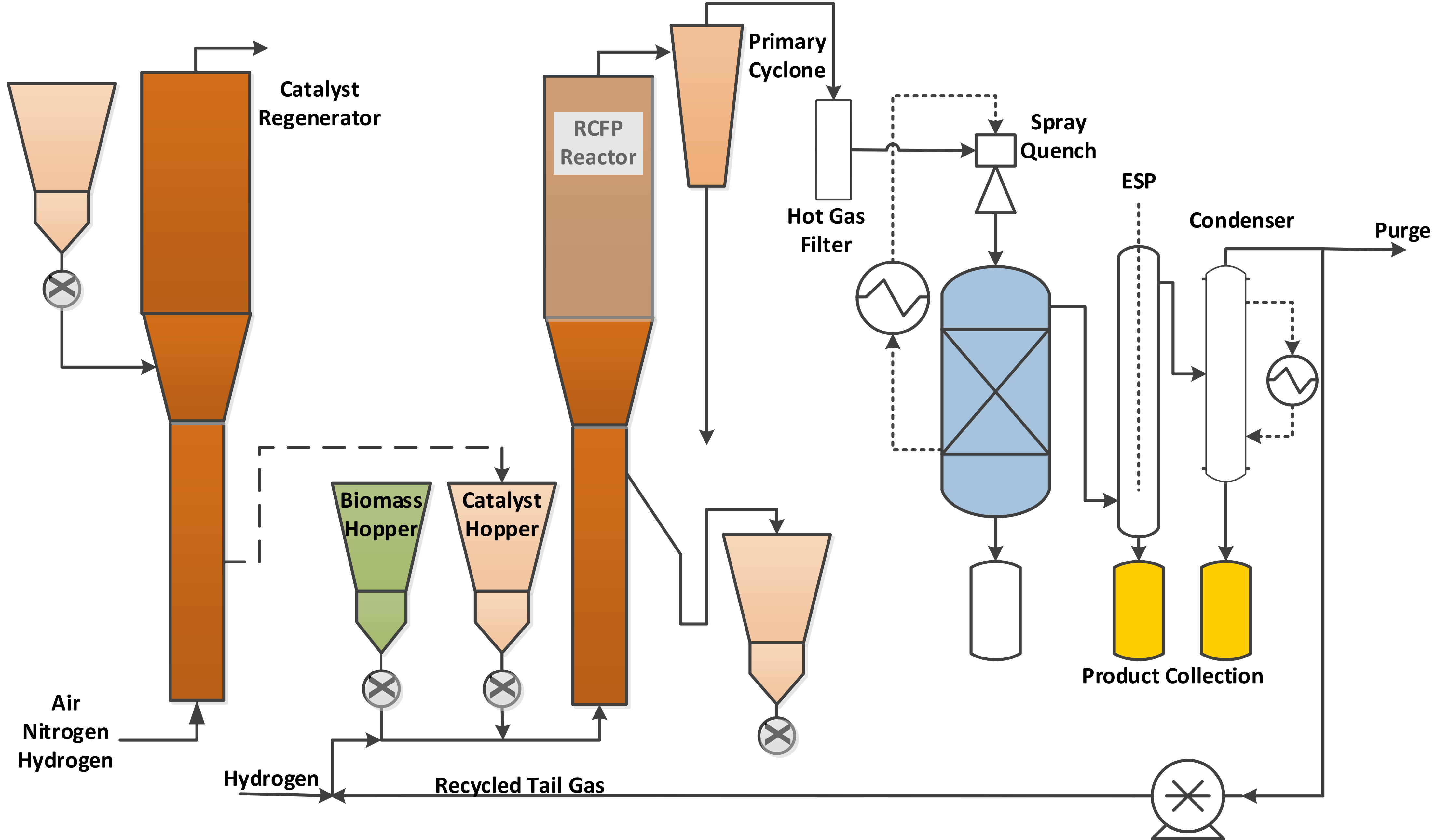
Engineering Design

- Proficio Consultancy, Inc. completed the detailed engineering design package on April 30, 2022 (P&IDs, Bill of Materials, Utility Requirements, Line List, I/O list, and Process Layout).
- Recommendations from PHA were incorporated into a revised design that has been issued for fabrication
- Subcontracts and Purchase Orders in place for fabrication
- Expected delivery September 2023

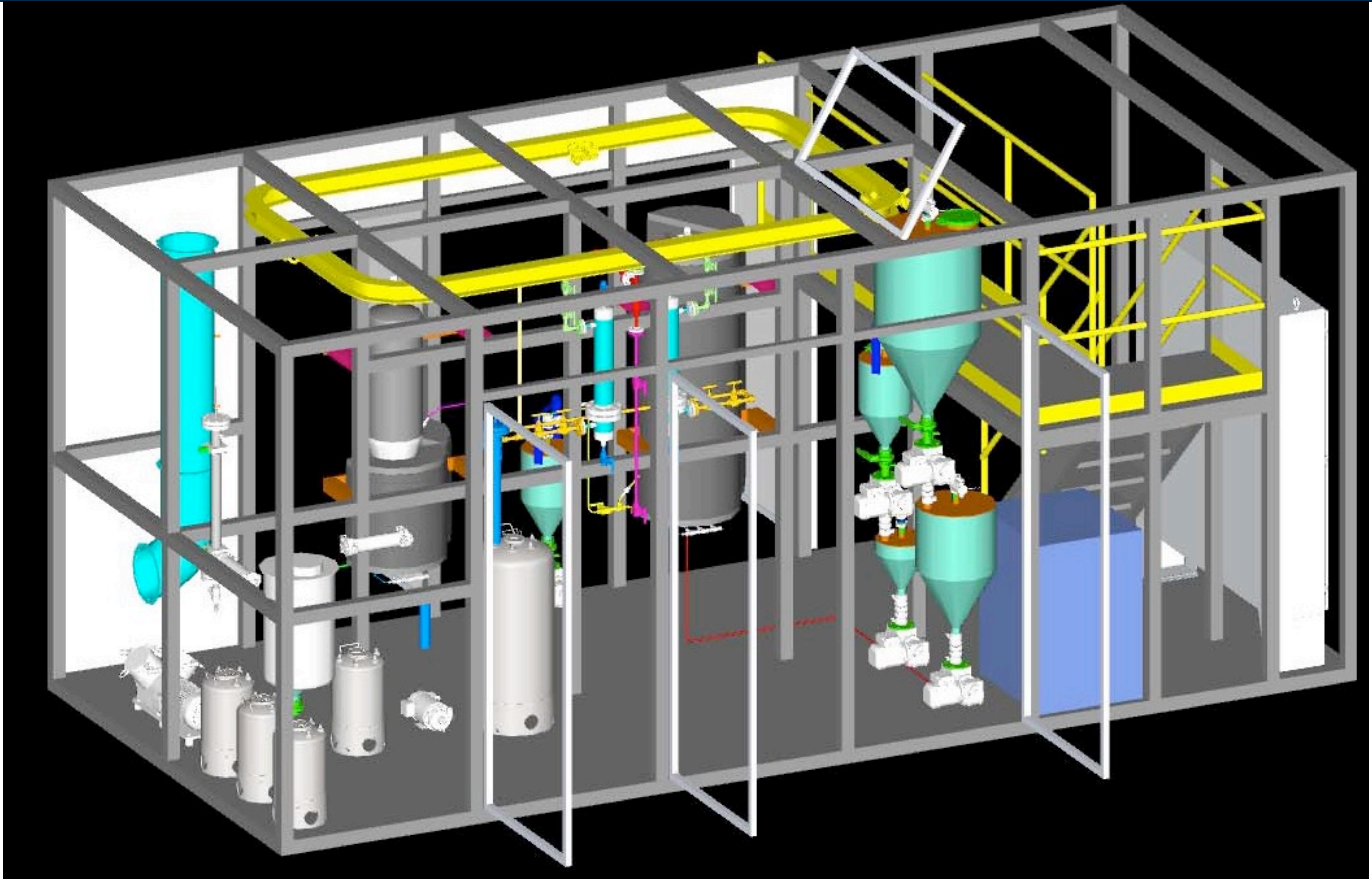
Process Hazard Analysis

- Saltegra Consulting led a Hazard and Operability (HAZOP) Study, an accepted Process Hazard Analysis (PHA) technique using a detailed and systematic approach for well-defined processes or operations.
- The methodology divides the process into nodes and applies select deviations, generates credible causes for each deviation and develops the consequences, safeguards, and risk within each node.
- The objectives of the HAZOP study were:
  1) To identify potential safety and operability hazards associated with the subject processes
  2) To determine whether existing safeguards are enough, to keep risk at a tolerable level for each scenario.
- HAZOPS Meeting at RTI on September 27-29, 2022
- Final HAZOPS report completed October 21, 2022

Engineering Scale RCFP Unit – PFD (~3 kg/hr Biomass Feedrate)



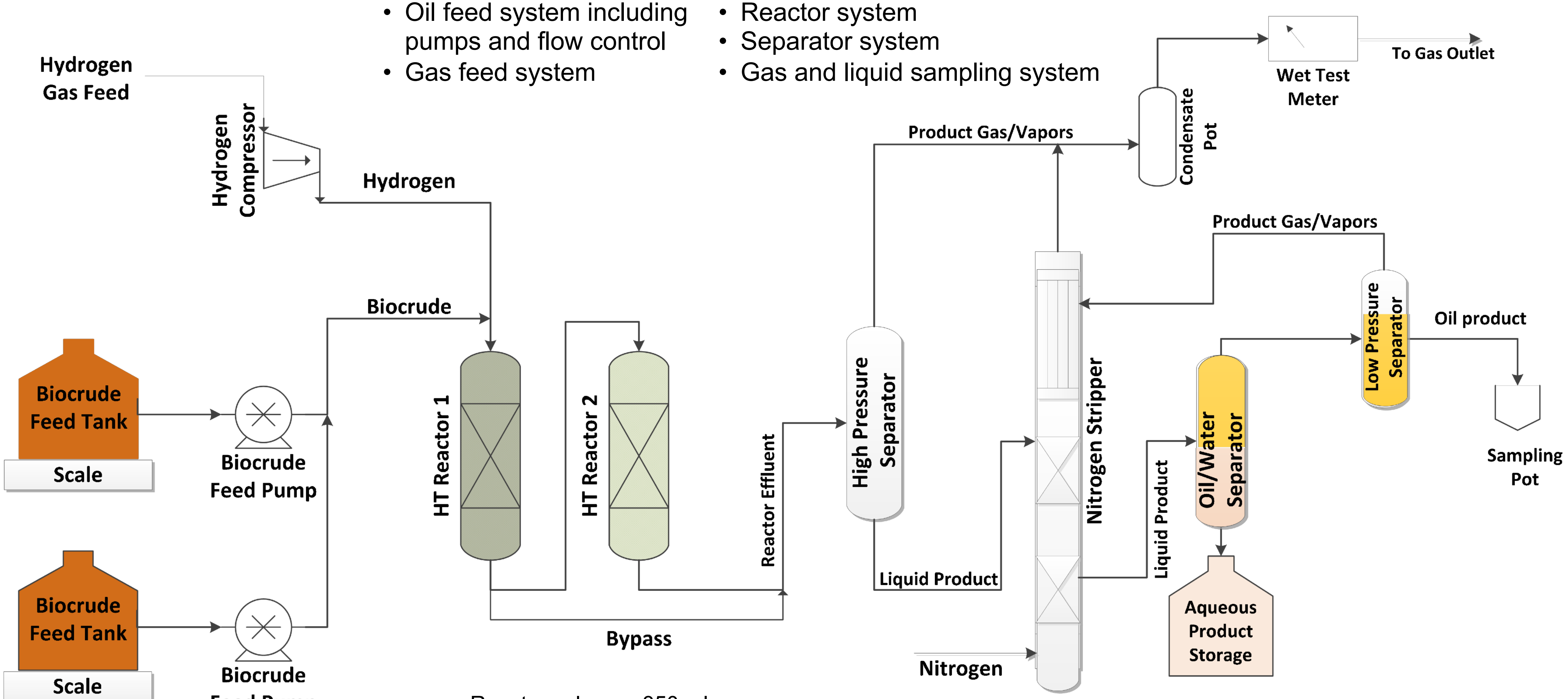
Engineering Scale RCFP Unit – Layout



Biocrude Upgrading – Pilot-scale 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)

Preliminary RCFP Biocrude Production and Upgrading (Previous Work)

12-L RCFP biocrude produced in 2”FBR over 10 months

Average Hydrogen Consumption: 2.3 wt% Biomass

Reaction Conditions

Catalyst: Mo/Al_2O_3

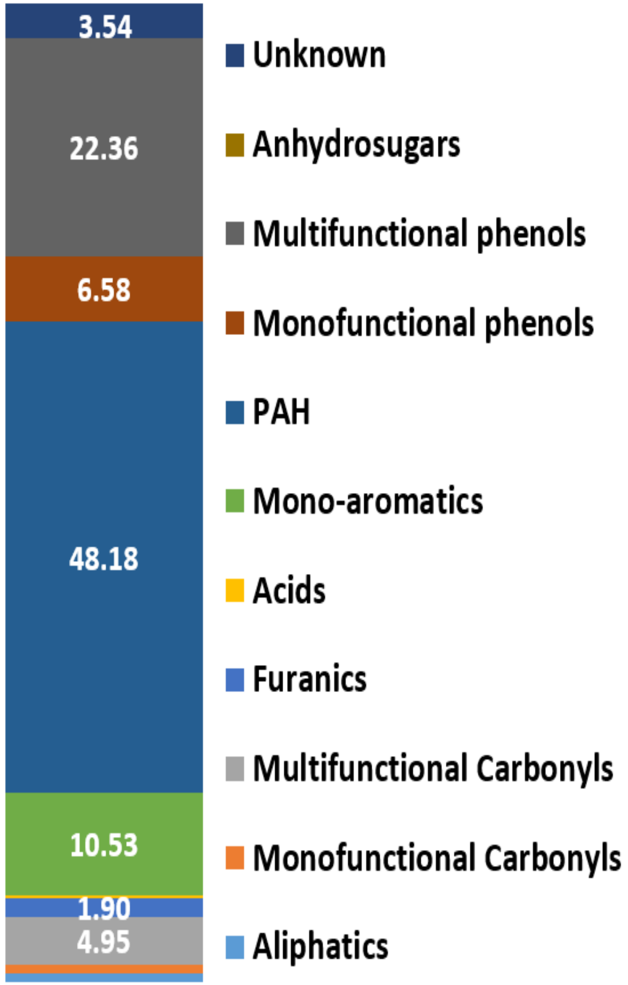
Hydrogen: 80 vol%

Temperature: 460°C

	Carbon Balance*	Mass Balance
Aqueous	2.5	27.4
Organic (C_4^+)	43.0	19.6
Liquid Bio-crude	*26.4*	*15.9*
C4-C6	*16.6*	*3.7*
Gas	26.8	13.1
Char+Coke	30.1	35.9
Total	102.4	96.0

RCFP Biocrude Composition

(GC-MS Area%)

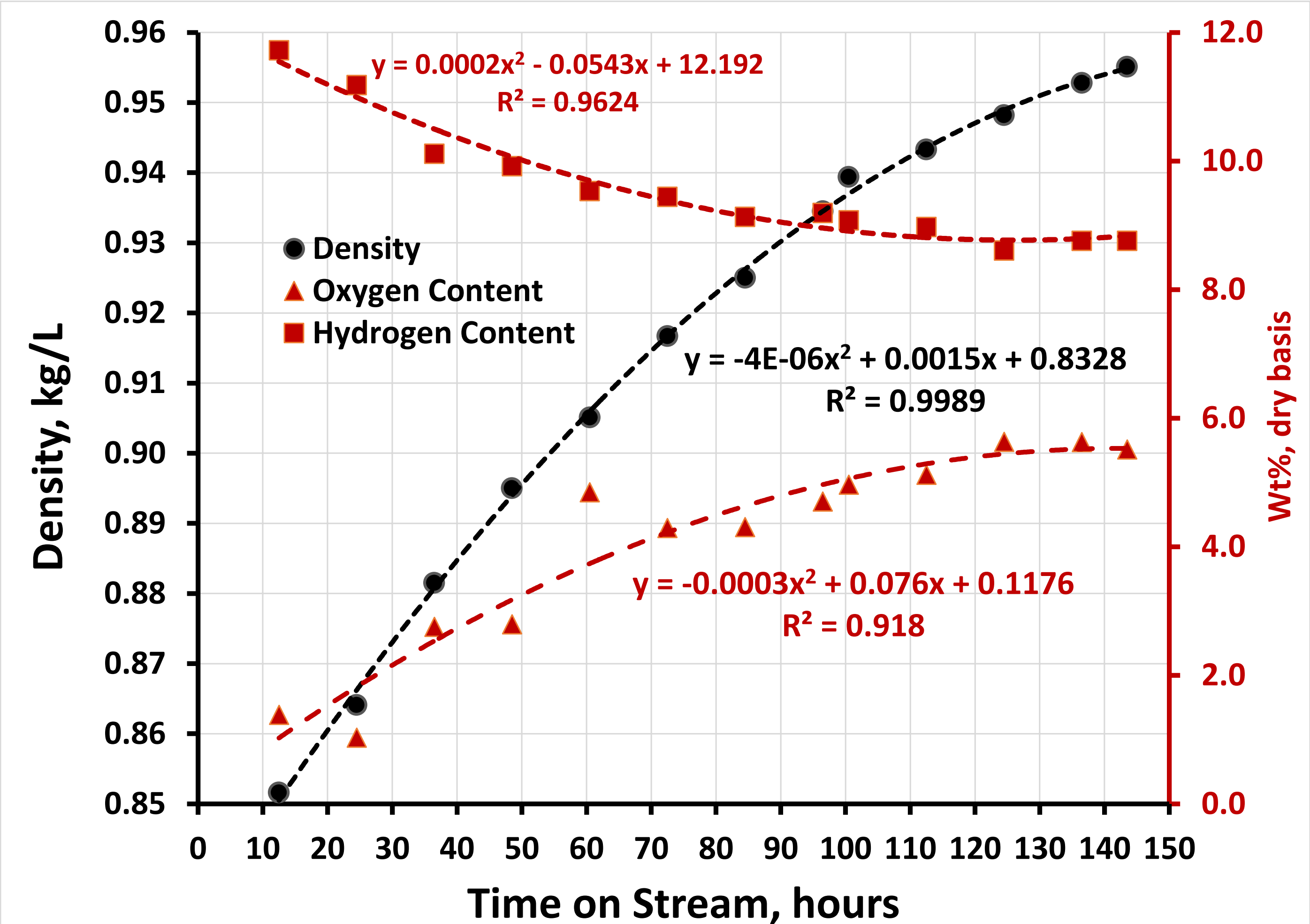


Elemental

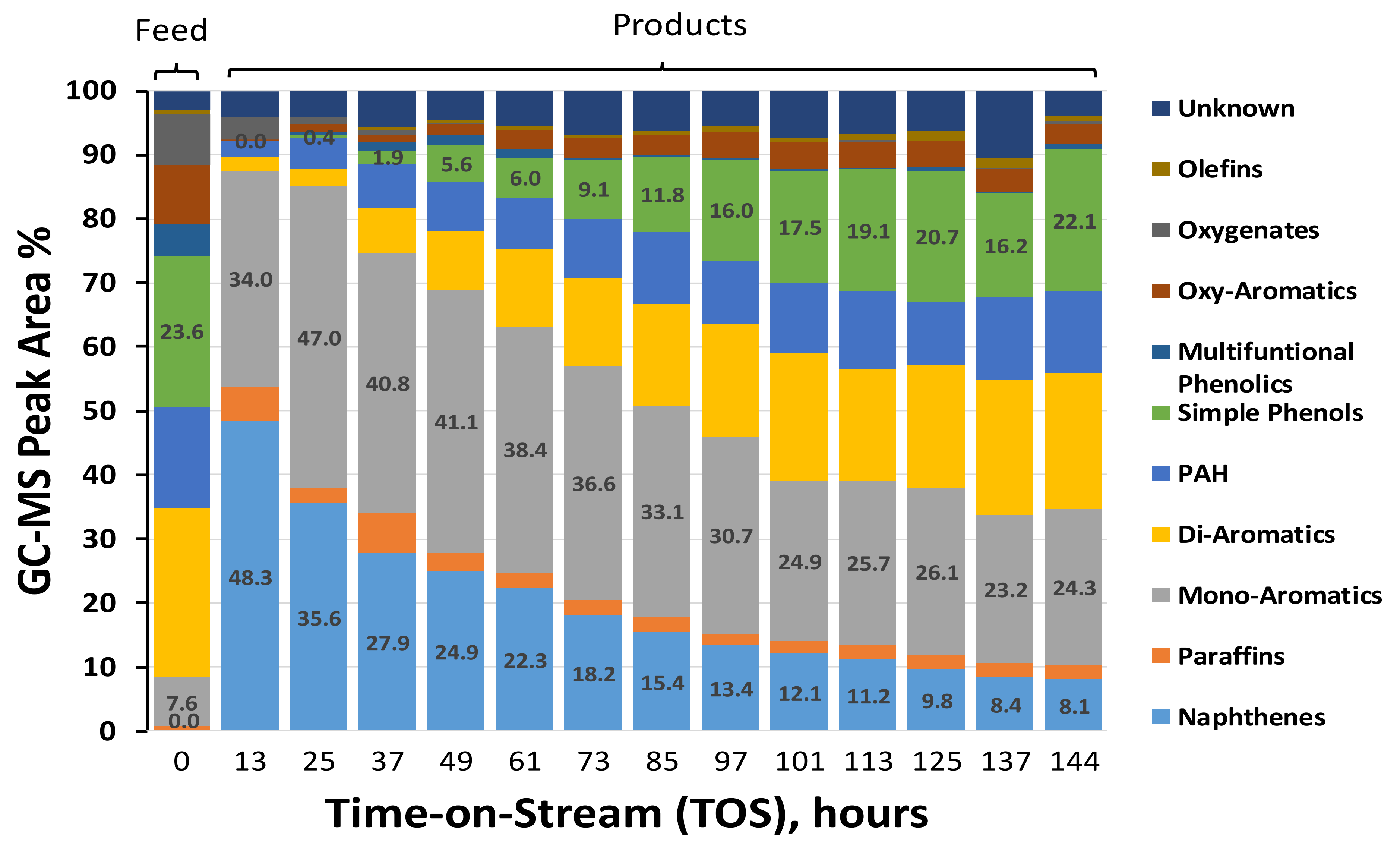
Properties	
Moisture, wt%	8.5
C wt%, dry	73.2
H wt%, dry	7.3
N wt%, dry	0.2
O (by diff)	19.3

RCFP Biocrude Upgrading: Physicochemical Properties

Catalyst	TK-341	Pressure (psig)	2000
LHSV (h^{-1})	0.31	H_2 Flow Rate (sccm)	400
Feed Rate (g/h)	62	H_2/oil ratio (Nl/l)	3300
Average Temperature (^oC)		300	



RCFP Biocrude Upgrading: Hydrotreated Product Compositions



Remaining Scope – BP3

Intermediate Verification resulted in a Go decision to continue with scale-up unit fabrication, installation, commissioning, and operation in BP3.

Fabrication, Installation, and Commissioning

- Proficio Consultancy – complete fabrication. Tentative delivery date: September 2023
- RTI - commission unit. Install water electrolysis equipment for hydrogen supply (outside project scope)

RCFP Catalyst Scale-up – Topsoe

- Verify fluidizable catalyst performance in laboratory 2FBR
- Produce up to 100-kg for pilot testing

RCFP Biocrude Production – RTI

- Process optimization to demonstrate that tail gas recycling meets or exceed C_4^+ carbon efficiency measured in laboratory reactor system
- Target 100 gallons of RCFP biocrude production with at least 100 continuous hours of operation.

RCFP Biocrude Upgrading – RTI, Topsoe

- Demonstrate RCFP biocrude upgrading for at least 500 continuous hours
- ASTM characterization of bio-blendstock

Final TEA and LCA – RTI

- Process design and economics for a 2000 TPD integrated reactive catalytic biomass pyrolysis/ hydroprocessing process demonstrating $3/GGE with a minimum of 50% greenhouse gas emissions reduction compared to petroleum gasoline and diesel to qualify as an advanced biofuel.

Impact

Demonstrate a direct biomass liquefaction advanced biofuels pathway that produces a low-oxygen content, thermally stable biocrude intermediate that can be upgraded to hydrocarbon biofuels in a standalone biorefinery or co-processed in an existing petroleum refinery.

Technology Highlights:

- Hydrogen in the pyrolysis reactor improves biocrude yield and quality while reducing char and coke formation
- Low pressure process avoids potential operational issues feeding biomass across a pressure boundary
- RCFP biocrude intermediate does not foul or plug the hydrotreating reactor during upgrading.

The integrated RCFP/Upgrading process has the potential to reduce biofuels production cost with a novel, low-severity in situ CFP process to convert lignocellulosic biomass to hydrocarbon fuels. This directly supports the DOE/BETO 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.

Summary

- Design, fabricate, and operate an engineering-scale reactor system (1-5 kg/hr) that can continuously maintain steady-state HDO activity during reactive catalytic biomass pyrolysis (RCFP). Scale up a fluidizable RCFP catalyst based on the formulation of commercially available extrudates
- Optimize the RCFP process and maintain steady-state hydrodeoxygenation (HDO) catalyst activity to maximize biocrude yield and quality.
- Will tail gas recycling improve C_4^+ yields?
- Produce enough low oxygen content RCFP biocrude to support extensive upgrading studies.
- Produce 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.

Integrated Reactive Catalytic Fast Pyrolysis System for Advanced Hydrocarbon Biofuels (DE-EE0008918)

Timeline

- Award Date: 10/1/2019
- Award Negotiations Concluded: 10/6/2020
- Initial Verification Meeting – January 11-15, 2021
- Proposed Budget Period 1 end date: 3/31/2021
- Authorization to move into BP2: 4/1/2021
- Budget Period 2: 4/1/2021 – 7/31/2022
- Intermediate Verification: May 4-5, 2022
- Authorization to move into BP3: July 7, 2022
- Budget Period 3: 8/1/2022 – 3/31/2024

Start: TRL 4 **End: TRL 6**

Project Goal

Design, fabricate, and operate an engineering-scale (1-5 kg/hr) reactor system that can continuously maintain steady-state HDO activity to produce enough low oxygen content RCFP biocrude to support extensive upgrading

End of Project Milestone

Advanced biofuels technology that integrates reactive catalytic biomass pyrolysis and hydrotreating to produce100 gallons of renewable diesel blendstock that meets ASTM D975 specifications

Partners

RTI International: Project lead, RCFP process development and biocrude upgrading, project management
Haldor Topsoe, A/S: RCFP catalyst scaleup, biocrude upgrading support, and hydrotreating catalyst provider
Proficio Consultancy, Inc.: Engineering and fabrication of RCFP unit

Budget	Federal	Cost Share	Total Costs	Actuals to date (FY23Q1)	
				Federal	Cost Share
BP1	$54,126	$13,532	$57,658	$14,405	$25,000
BP2	$428,863	$107,216	$536,079	$375,120	$123,717
BP3	$1,873,675	$468,419	$2,342,094	$69,413	$5,742
Total	$2,356,665	$589,166	$2,945,831	$525,422	$154,459

FY19 Bioenergy Technologies Office Multi-Topic Funding Opportunity Announcement (DE-FOA-0002029 issued 5/3/2019)
Area of Interest 4: Systems Research of Hydrocarbon Biofuel Technologies

Verify innovative technologies at engineering-scale to enable cost-competitive integrated biofuels technology pathways.

Additional Slides

Responses to Previous Reviewers' Comments

- This is a very interesting take on reactive catalytic fast pyrolysis (RCFP) under moderate H_2 pressure to control the creation of oxygenated compounds, etc. It is always complex to get the right H_2 balance among generation, use, and circulating amount. Some of the initial results are a bit underwhelming, but it is in the early days yet. The team should concentrate on arriving to steady state and then improving performance. Catalyst lifetime is key. It is good to consider different upgrading options and arrangements.
- This is an excellent management plan. The Research Triangle Institute and the PI's experience in developing and executing technology experimental and development plans is evident in the comprehensive and detailed management plan. The project is making good progress, but it has not been able to hit steady state or process longer than 150 hours due to plugging and other issues. The project is still fairly new, so there is still time to meet the goals, but it would have been great if the proposed approach to meet those goals, given the difficulties, had been outlined. Although the management plan and approach are excellent, they should be revised to address the technical issues. Due to the technical issues, at this time, it is unclear if the impact will be significant or if the goals will be reached
- The project noted that they were attempting to test the catalyst for 500–1,000 hours to determine the lifetime, as is best practice, but it is not sufficient for a refinery application (8,000-hour testing). Depending on a number of factors, producing a batch of catalyst within only a 3-month period—if not requiring equipment or an outside manufacturer—would seem highly unlikely. This is an excellent representation of the efforts made in collecting and analyzing data. It appears that the data are being well managed on this project. .
- This is a very interesting project with a very good management plan; the WBS and milestones are clear, there is an industry partner/advisor, and the go/no-go criteria for budget period 3 are specific, measurable, attainable, and time-related. Having just recently started, it is hard to assess the progress to date, especially given the continually decreasing catalyst performance. Additional detail around the TEA and the \$3/GGE claim would have been appreciated.

The addition of H_2 in the pyrolysis reactor enhances the hydrodeoxygenation of the biomass pyrolysis vapors and tends to inhibit char formation, thus increasing the yield of the liquid hydrocarbon intermediate compared to other biomass pyrolysis technology options. The RCFP process targets similar performance to hydropyrolysis at low pressure to avoid the technical challenges associated with feeding biomass across a pressure boundary. This project supports further process development to increase biocrude yields in a continuous RCFP process design that will include tail gas recycling to conserve H_2 and return the C2–C6 hydrocarbon gases and light oxygenates back to the pyrolysis reactor. The condensation unit operations in the engineering-scale RCFP system will also be designed to improve the biocrude collection efficiency compared to the smaller laboratory reactor system.

There are two integrated catalytic processes in this advanced biofuel pathway. Both processes utilize commercially available catalysts provided by our partners at Haldor Topsoe. The RCFP is available as an extrudate that was crushed and sieved to the appropriate PSD for RCFP process development. Fluidizable catalyst development and scale-up is focused on converting that formulation into a spray-dried fluidizable catalyst. These catalysts will be screened for RCFP performance in the laboratory 2-inch fluidized bed reactor to meet or exceed the performance of the extruded catalyst. The best-performing material will be used in the engineering-scale reactor system to further optimize the RCFP process to maximize the biocrude yield and to produce hundreds of liters of biocrude for upgrading.

A commercially available hydrotreating catalyst is used in our pilot-scale hydroprocessing unit for biocrude upgrading. Only 13 L of RCFP biocrude were produced in our previous project so we only had enough RCFP biocrude feedstock for 144 hours of operation but the pressure drop across the reactor did not increase, suggesting no reactor fouling. With the much larger quantities of RCFP biocrude, we will be able to operate the hydrotreater for much longer periods to focus on the steady-state hydrotreating catalyst performance and reducing process severity (temperature, pressure H_2/oil ratio, and liquid hourly space velocity).

The end-of-project goal is to produce 100 gallons of a renewable diesel blendstock from this integrated process and to verify that the blends meet the ASTM D975 specifications. The TEA will be updated based on the results obtained in this project to validate an nth plant modeled MFSP of \$3/GGE (2014\$) for a pathway to hydrocarbon biofuel with a GHG emissions reduction of 50% or more compared to petroleum-derived fuel.

Initial Verification

Verification Criteria :

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

- RCFP C_4^+ yields > 45 mole%C with less than 15 wt% O in biocrude
- Review RCFP biocrude upgrading results

Pre-read Documents:

1. Revised Block Flow Data
2. Revised Statement of Project Objectives
3. RTI Publications:

Cross, P.; Wang, K. G.; Weiner, J.; Reid, E.; Peters, J.; Mante, O.; Dayton, D. C., Reactive Catalytic Fast Pyrolysis of Biomass Over Molybdenum Oxide Catalysts: A Parametric Study. Energy & Fuels 2020, 34 (4), 4678-4684.

Dayton, D.C., et al., CHAPTER 5 Catalytic Biomass Pyrolysis with Reactive Gases, in Fast Pyrolysis of Biomass: Advances in Science and Technology. 2017, The Royal Society of Chemistry. p. 78-95.

Wang, K., Dayton, D., Peters, J. E. & Mante, O. D. Reactive catalytic fast pyrolysis of biomass to produce high-quality bio-crude. Green Chemistry, (2017) 19(14): p. 3243-3251.

Mante, O. D.; Dayton, D. C.; Gabrielsen, J.; Ammitzboll, N. L.; Barbee, D.; Verdier, S.; Wang, K. G., Integration of catalytic fast pyrolysis and hydroprocessing: a pathway to refinery intermediates and "drop-in" fuels from biomass. Green Chemistry 2016, 18 (22), 6123-6135

Current Progress and Status:

- Project started 10/6/2020
- Verification Plan completed Dec 2020
- Initial Verification Virtual meeting January 11-15, 2021
- DRAFT Verification Report submitted February 8, 2021
- Finla recommendations to proceed 4/1/2021

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**
45 Percent Carbon Efficiency	None	Below Target	Yes	Develop engineering design and plan to increase C4+ efficiency
Less than 15 Weight Percent Oxygen in biocrude	None	No	Yes	Develop operating parameters or alternative carbon capture to enhance biocrude production

Conclusions

- The verification demonstrated that the technology worked consistently.
- The verification carbon efficiency target appeared to be optimistic, and the Owner has never accomplished 45% C4+ carbon efficiency.
- Distillation of aqueous solutions can increase the carbon capture.
- We recommend that RTI develop a plan to improve bio-crude yield with their RCFP process within the design parameters of the pilot facility

Reproduced from Independent Engineers Report to DOE dated March 18, 2021

Intermediate Verification

Verification Criteria :

- Proposed: RCFP C_4^+ yields 45% carbon efficiency with 15 wt% O or less in biocrude
    - Actual: Average C_4^+ efficiency = 44.5%; Average biocrude oxygen content = 16 wt% O

- Proposed: Approved Engineering-scale Design for Fabrication
    - Actual: The detailed engineering design (P&IDs) and layout were reviewed during the Intermediate Verification meeting.

Initial Verificaiton Summary

- Spray-dried catalysts produced by Topsoe were tested for RCFP activity in 18 experiments
- Ten of these experiments yielded, on average, 45% C_4^+ carbon efficiency (41-53 wt% C) with 15 wt% O (11-20 wt% O) in the biocrude product.
- Two of the experiments were conducted prior to the on-site Intermediate Verification meeting held at RTI May 4-5, 2022 were presented while a third was performed during this meeting.
    - Average mass closure: 100.8%
    - Average carbon closure: 100.9
    - Average C_4^+ efficiency: 43%
    - Average biocrude wt% oxygen (dry): 16%

Intermediate Verification – Independent Engineers Review*

Overview of Intermediate Verification Test Data (May 2022)				
Key Performance Parameter	**Red Flags**	**Anything Lacking?**	**Readiness to Proceed**	**Path Forward**
45 Percent Carbon Efficiency	None	1 of 3 tests met target	Yes	Develop engineering design and a plan to increase C4+ efficiency
Less than 15 Weight Percent Oxygen in biocrude	None	1 of 3 tests met target	Yes	Develop operating parameters to enhance biocrude production

Conclusions

- The verification demonstrated that the technology worked consistently
- The verification carbon efficiency target of 45% or near 45% C4+ carbon efficiency was achieved in the data presented for review
- An online Gas Chromatograph with flame ionization detection ("GC-FID") analysis of the vapor stream detected C7+ compounds that could reasonably be expected to be recovered at a larger scale
- We recommend that RTI be allowed to proceed to BP3 as stated in the Recipient's SOPO after completing the engineering scale up requirements.

Reproduced from Independent Engineers Report to DOE dated May 31, 2022

Publications, Patents, Presentations, Awards, and Commercialization

- Publications:
  - Cross, P.; Wang, K. G.; Weiner, J.; Reid, E.; Peters, J.; Mante, O.; Dayton, D. C., Reactive Catalytic Fast Pyrolysis of Biomass Over Molybdenum Oxide Catalysts: A Parametric Study. Energy & Fuels 2020, 34 (4), 4678-4684.
  - Dayton, D. C.; Mante, O. D.; Weiner, J.; Komnaris, C.; Verdier, S.; Gabrielsen, J., Integrated Reactive Catalytic Fast Pyrolysis: Biocrude Production, Upgrading, and Coprocessing. Energy&Fuels 2022, 36 (16), 9147-9157
- Patents: none
- Presentations:
  - Virtual Verification Meeting, Integrated Reactive Catalytic Fast Pyrolysis System for Advanced Hydrocarbon Biofuels (DE-EE0008918), RTI International, RTP, NC. January 11, 2021
  - Project presentation was made at the FY21 BETO Peer Review during the Systems Development and Integration session on March 21, 2021.
  - D.C. Dayton. Oral Presentation entitled “Recent Progress in Catalytic Biomass Pyrolysis and Biocrude Upgrading” at TCBiomass2022 in Denver, CO April 19-21, 2022.
  - D.C. Dayton, Intermediate Verification presentation - Intermediate Verification Meeting Integrated Reactive Catalytic Fast Pyrolysis System for Advanced Hydrocarbon Biofuels. RTI International, RTP, NC May 4-5, 2022.