Scaling Up Reactive Catalytic Biomass Pyrolysis

RTI INTERNATIONAL

tcbiomass2024

David C. Dayton, Ph. D.
RTI Senior Fellow and Director of Biofuels

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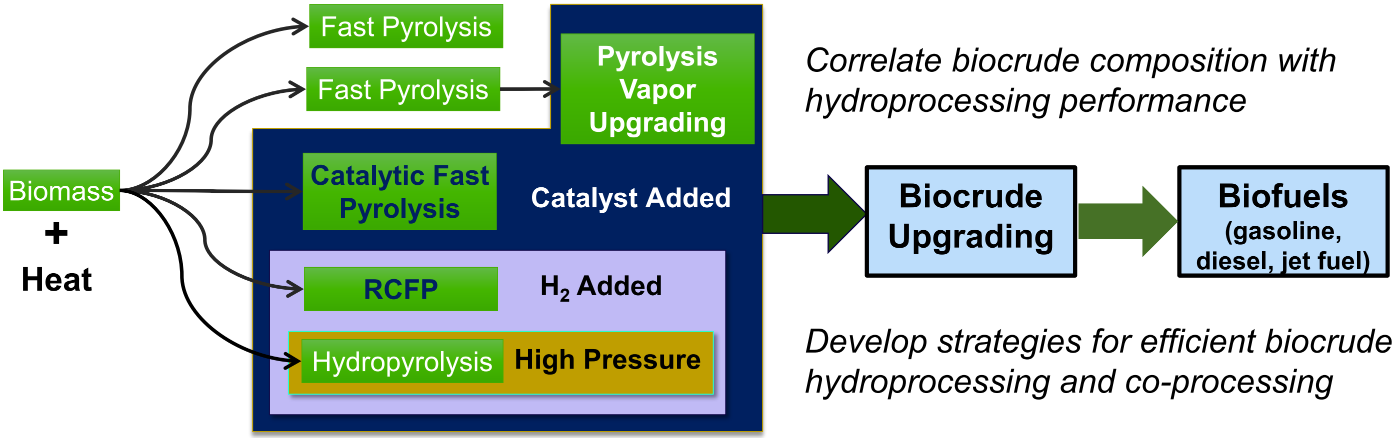
Biomass Pyrolysis Pathways for Advanced Biofuels

Apply catalysts and reagents to maximize yields and improve biocrude ***quality*** (oxygen content, chemical composition, thermal stability)



Correlate biocrude composition with hydroprocessing performance

Develop strategies for efficient biocrude hydroprocessing and co-processing

RCFP = Reactive Catalytic Fast Pyrolysis

- Mante, O. D., Dayton, D. C., Carpenter, J. R., Wang, K., & Peters, J. E. (2018), Pilot-scale catalytic fast pyrolysis of loblolly pine over γ-Al_2O_3 catalyst. *Fuel*, *214*, 569–579.
- 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.

Overview

Motivation

- RCFP process demonstrates improved biocrude yields and lower char yields compared to CFP
- RCFP biocrude upgrading demonstrates better performance (no reactor pressure drop increase) compared to CFP biocrudes

Objectives

- Design, fabricate, and install an engineering-scale (1-5 kg/hr) RCFP reactor system based on operation of a 300 g/hr laboratory fluidized be reactor system
- Scale up a fluidizable RCFP catalyst based on the formulation of commercially available extrudates
- Optimize the process and maintain steady-state hydrodeoxygenation (HDO) catalyst activity to maximize biocrude yield and quality

Design Features

- Tail gas recycling to minimize hydrogen use
- Catalyst addition while drawing down the bed to maintain HDO activity

RCFP Process Development

Parameter	Target Range
Pyrolysis (°C)	445-475
Char/coke oxidation (°C)	500-600
Catalyst reduction (°C)	530
System pressure (psia)	16-25
Biomass feed rate (g/h)	240-420
H_2 concentration (vol%)	80
Catalyst Loading (g)	300-500
Total gas flow rate (slm)	20-30

Laboratory Fluidized Bed Reactor System

Biomass Feedstock

- Loblolly pine (Piedmont Pellets, NC)
- 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

- Mo-based (HT-105343) extrudate
- Crushed and sieved to recover 105-300 µm particle size range.
- Spray dried Mo-based catalyst development

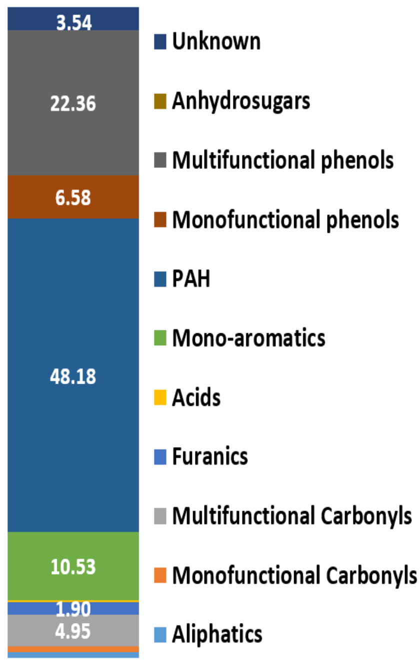
RCFP Biocrude Production

12-L RCFP bio-crude 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%)

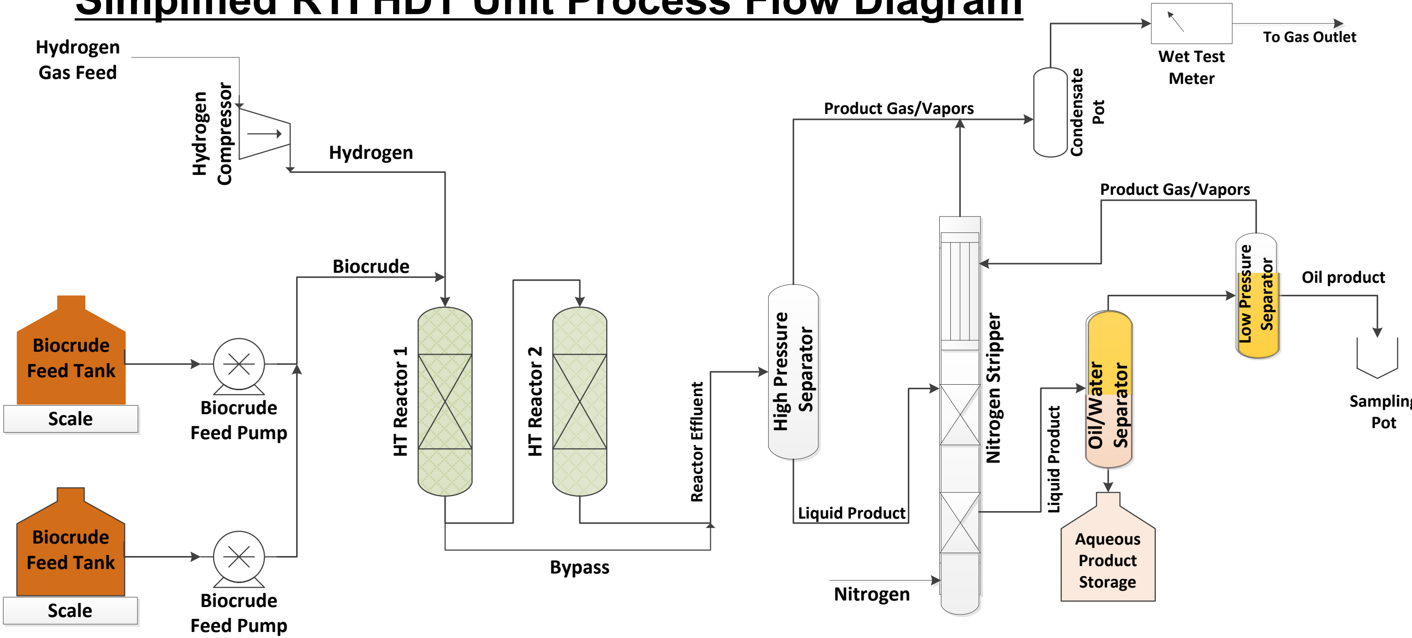


Elemental

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

Biocrude Upgrading Overview

Simplified RTI HDT Unit Process Flow Diagram



Reactor volume: 350 mL
Catalyst volume: 20 - 250 mL

LHSV - 0.1 to 1.0
Flow rates - 50 to 250 mL/h

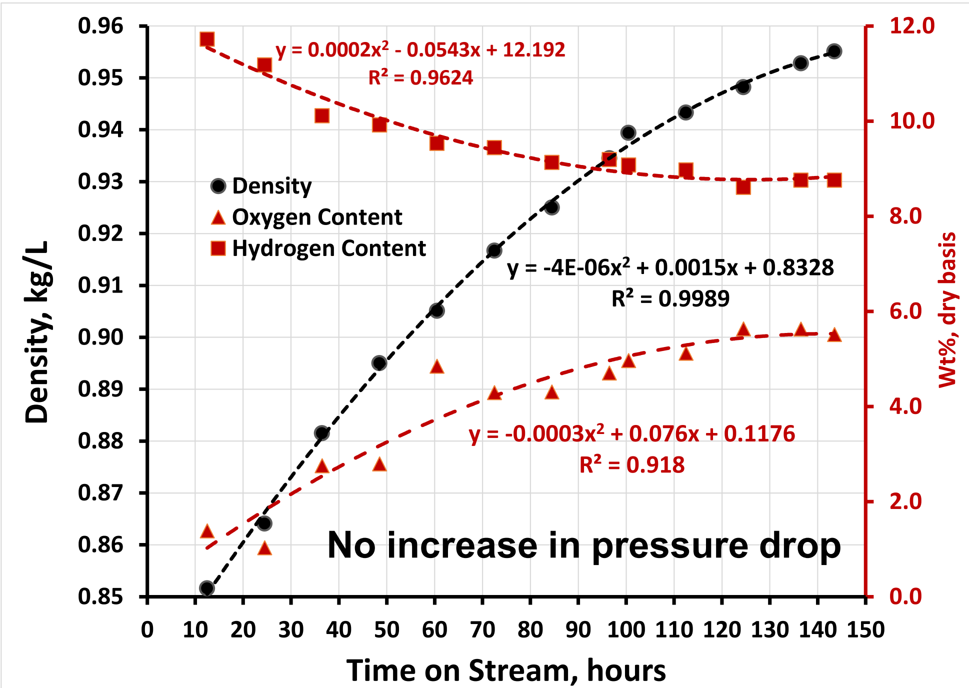
Max. design pressure - 3000 psig
Max. design temperature - 450 C

Analysis of Biocrude and HDT products include:

Elemental Analysis(CHNSO), GC-MS, FTIR, NMR, Carbon Number Distribution, Distillation by ASTM D1160, SG 60/60 by ASTM D4052, Kinematic Viscosity by D445, and Karl Fischer Titration.

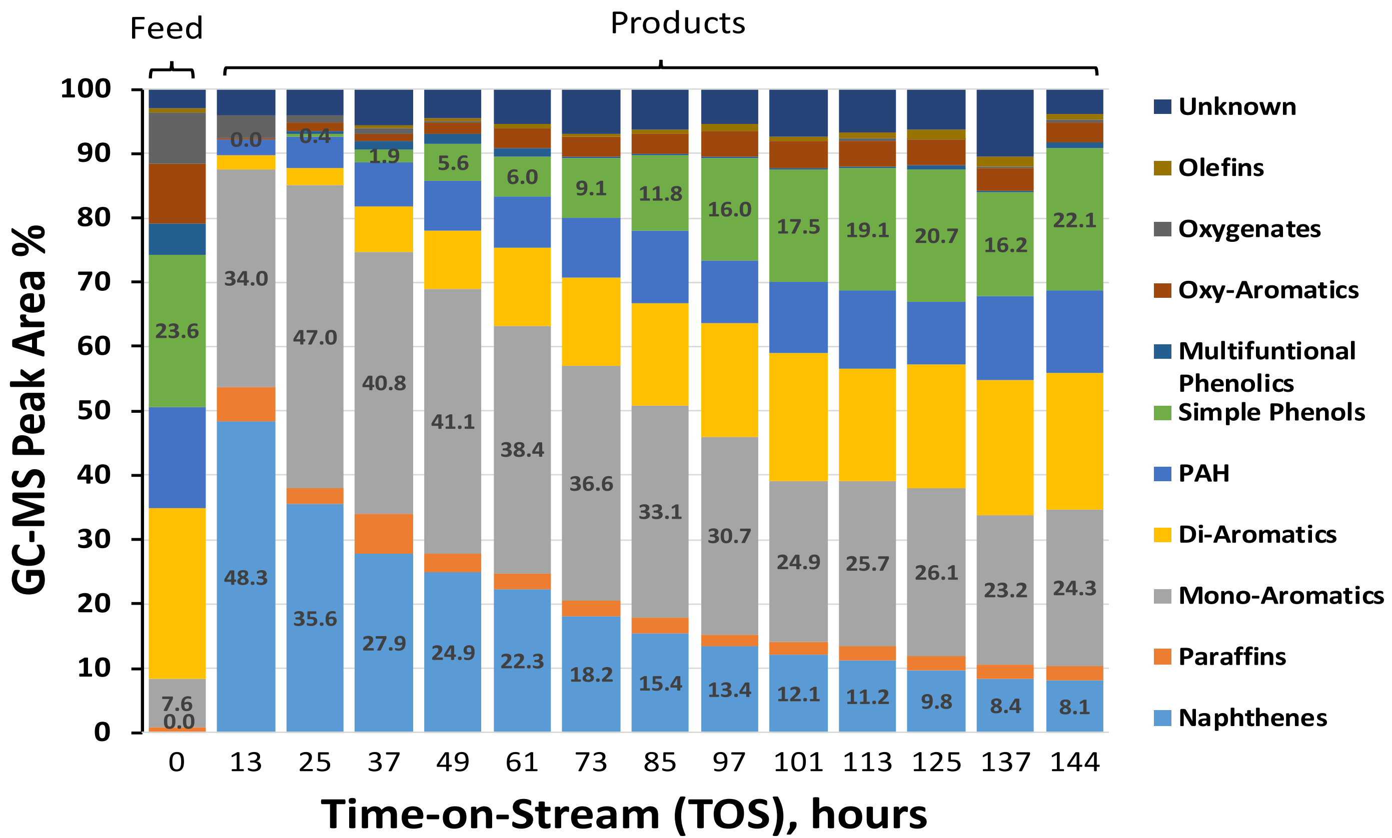
RCFP Biocrude Upgrading: Physicochemical Properties

Catalyst	TK-341	Pressure (barg)	137.9
LHSV (h^{-1})	0.31	H_2/oil ratio (Nl/l)	3300
Average Temperature (°C)		300	

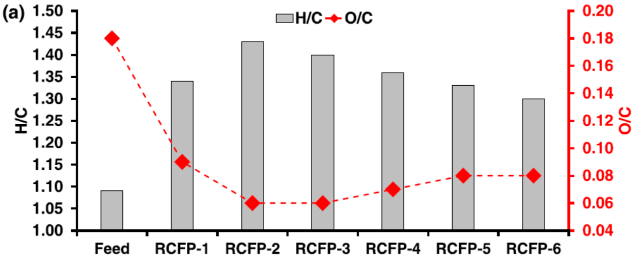


Dayton, D. C.; Mante, O. D.; Weiner, J.; Komnaris, C.; Verdier, S.; Gabrielsen, J., Integrated Reactive Catalytic Fast Pyrolysis: Biocrude Production, Upgrading, and Coprocessing. *Energy&Fuels* **2022,** *36* (16), 9147-9157

RCFP Biocrude Upgrading: Hydrotreated Product Compositions



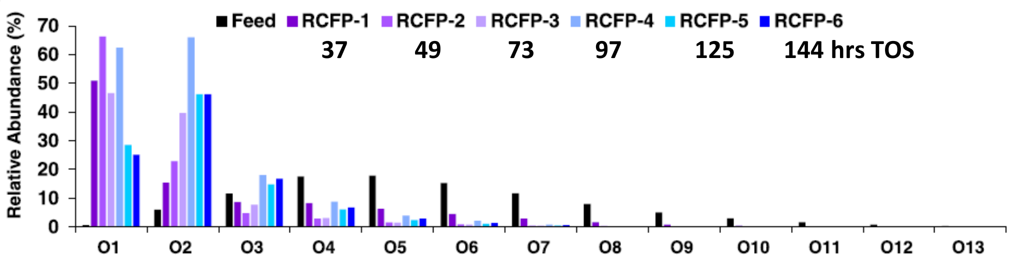
Advanced Analytical (FT-ICR-MS) Sample Analysis

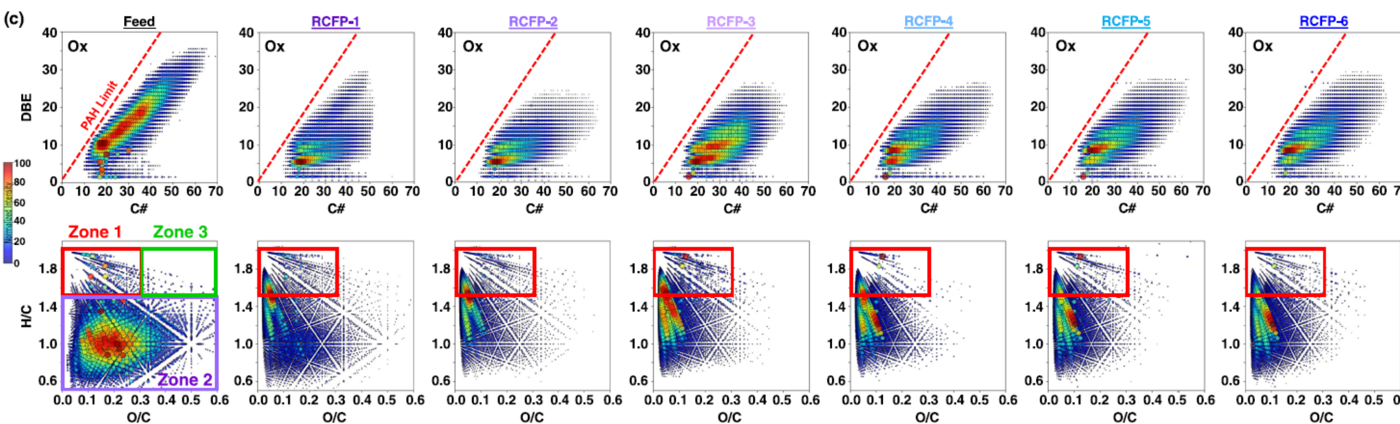


NATIONAL HIGH MAGNETIC FIELD LABORATORY

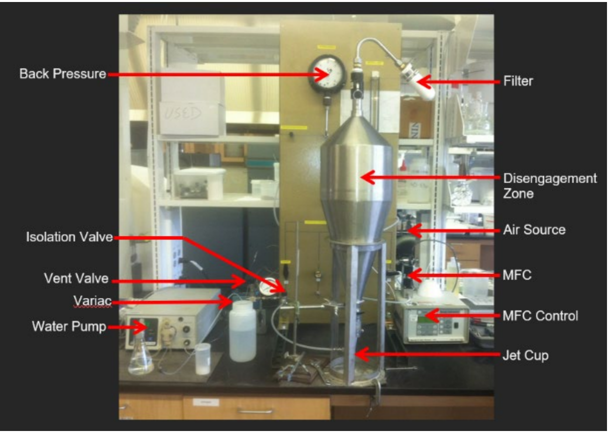
iC2MC INTERNATIONAL – COMPLEX MATRICES MOLECULAR CHARACTERIZATION

Chacón-Patiño, M. L.; Mase, C.; Maillard, J. F.; Barrère-Mangote, C.; Dayton, D. C.; Afonso, C.; Giusti, P.; Rodgers, R. P., Petroleomics Approach to Investigate the Composition of Upgrading Products from Pyrolysis Bio-Oils as Determined by High-Field FT-ICR MS. *Energy & Fuels* **2023**.





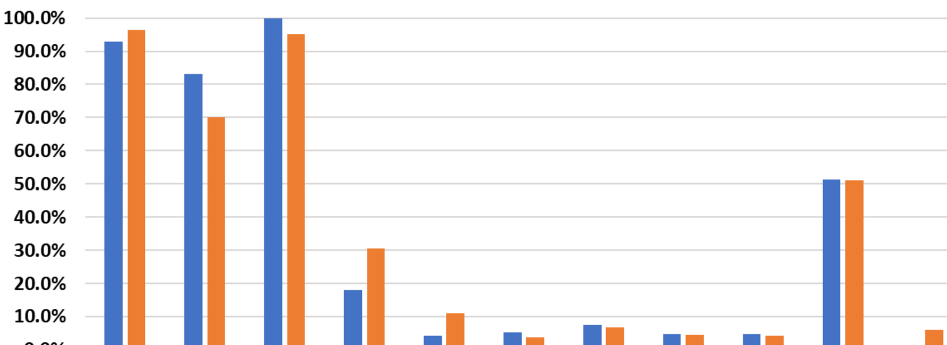
RCFP Catalyst Scaleup – Attrition Testing



Jet Cup Attrition (ASTM D8414)

- Mimics particle-wall impacts in cyclones, fluidized beds and risers
- Attrition index = % of original sample turned into fines (21µm and 42µm)
- Compared to Ecat

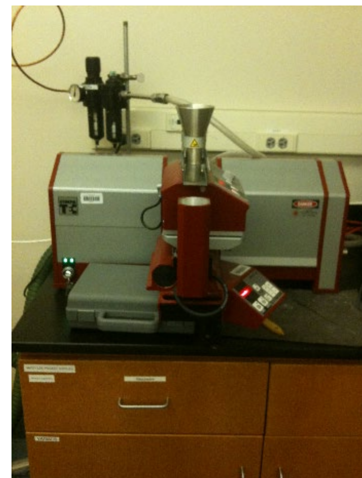
Attrition Index of Spray-Dried RCFP Catalyst



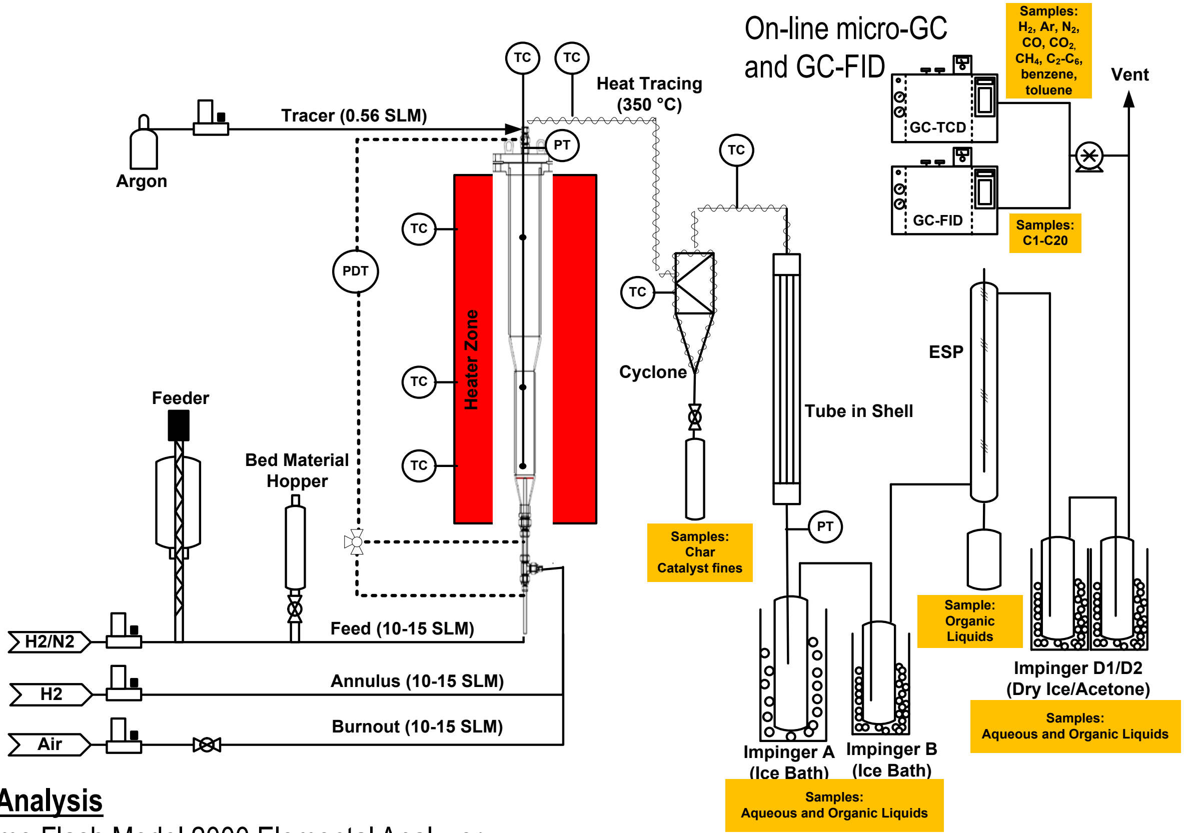
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Ecat
21 µm	92.9%	83.2%	99.8%	18.0%	4.2%	5.2%	7.6%	4.7%	4.9%	51.3%	1.4%
42 µm	96.5%	70.1%	95.2%	30.5%	11.0%	3.7%	6.8%	4.6%	4.2%	51.1%	6.1%

■ 21 µm ■ 42 µm

Helios Particle Size Analyzer



RCFP Catalyst Screening and Biocrude Production



Sample Analysis

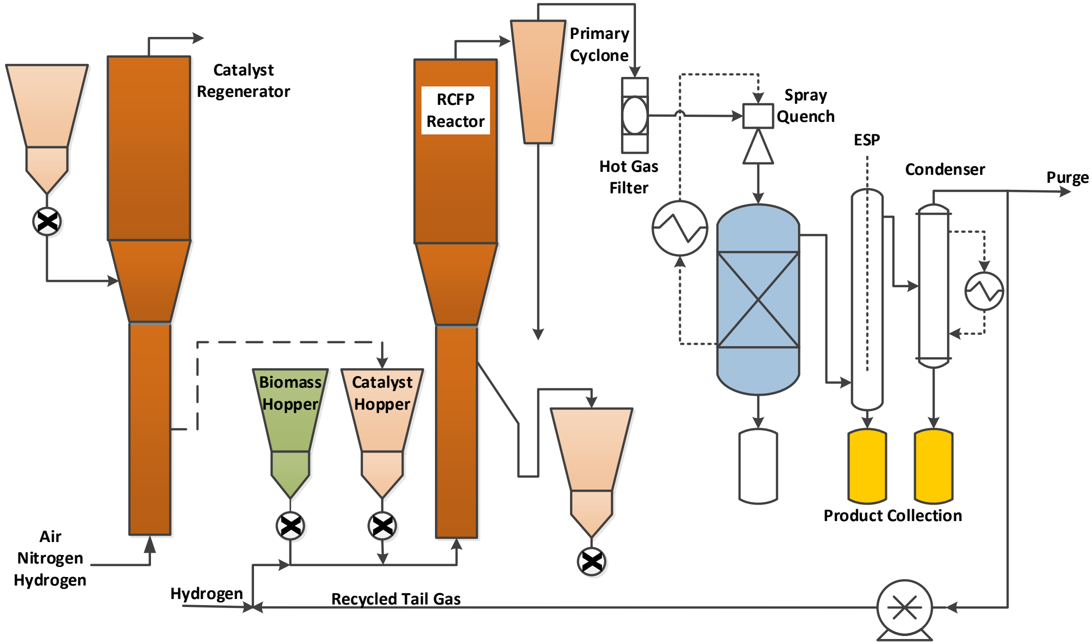
- Thermo Flash Model 2000 Elemental Analyzer
- Mettler Toledo V20 Titrator for Karl-Fischer Moisture measurements
- Agilent 7890A gas chromatograph and 5975C mass spectrometer detector for semi-volatile compound identification and semi-quantification

Catalyst Scaleup - Summary of Performance Testing

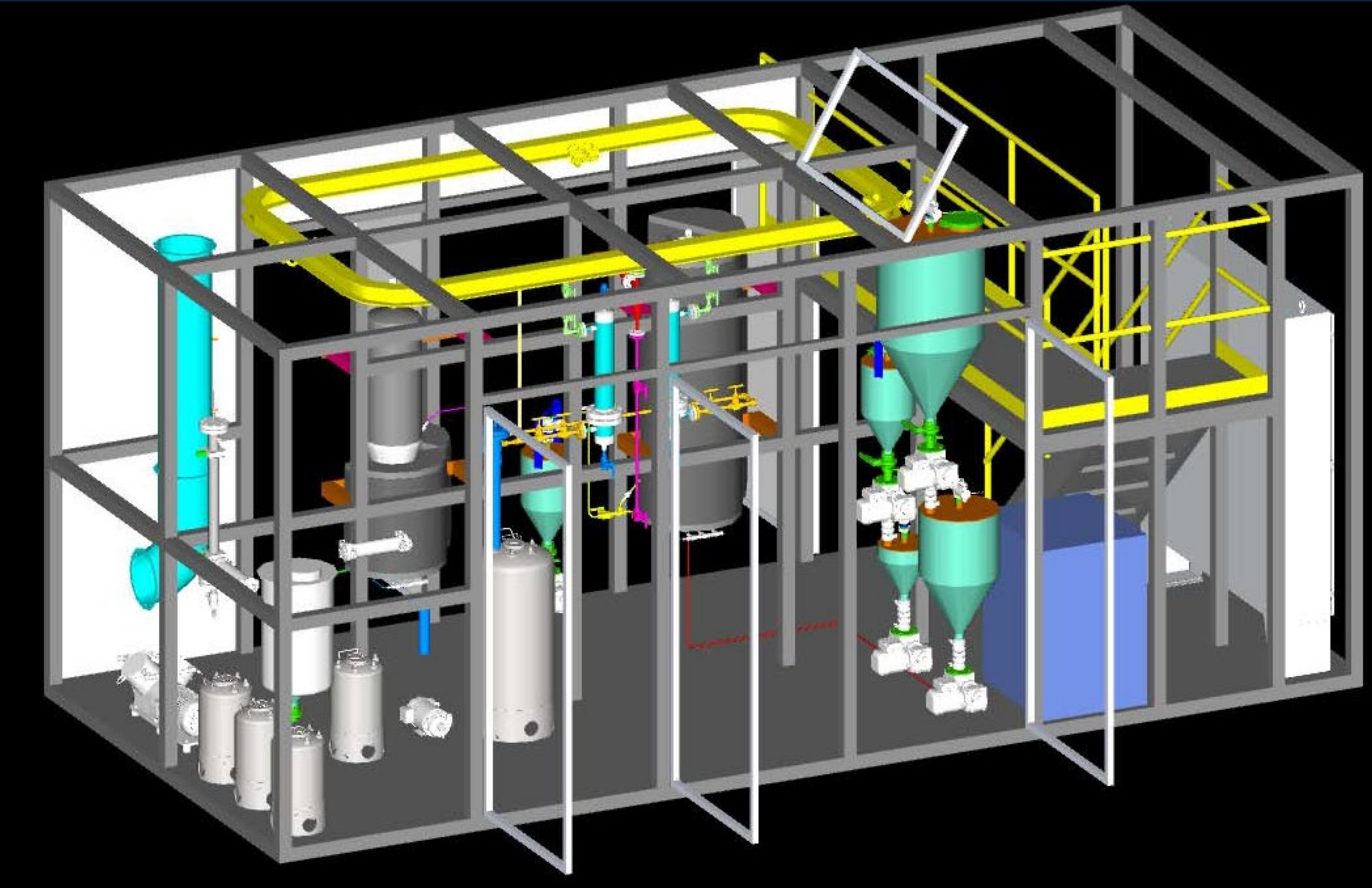
wt%C	Sample 4 Average	Sample 8 Average	Sample 9 Average
Biocrude	27.13%	19.3%	27.6%
Imp A	*11.25%*	*3.9%*	*10.9%*
Imp B	*0.76%*	*0.9%*	*0.8%*
ESP	*13.13%*	*12.6%*	*13.7%*
Imp D	*1.98%*	*2.0%*	*2.3%*
Aqueous	4.14%	2.2%	2.5%
Imp A	*3.42%*	*1.8%*	*1.8%*
Imp B	*0.23%*	*0.2%*	*0.2%*
ESP	*0.00%*	*0.0%*	*0.0%*
Imp D	*0.49%*	*0.4%*	*0.5%*
Solids	30.81%	38.5%	32.8%
Total Gas	34.77%	34.5%	33.1%
C1-C3 gas	*10.63%*	*9.9%*	*9.5%*
C4+ Gas	*12.03%*	*8.2%*	*7.8%*
CO	*7.16%*	*11.3%*	*11.0%*
CO2	*4.94%*	*5.2%*	*4.9%*
"Uncondensed"	4.12%	3.4%	3.1%
Ceff	43.27%	30.8%	38.4%
Carbon Balance	100.9%	97.9%	99.1%
Mass Balance	100.8%	96.4%	97.2%
Biocrude wt%O-dry	16%	14.9%	10.4%

RCFP Process Scaleup

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



Engineering Scale RCFP Unit – Layout

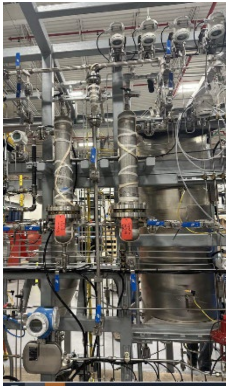


Fabrication

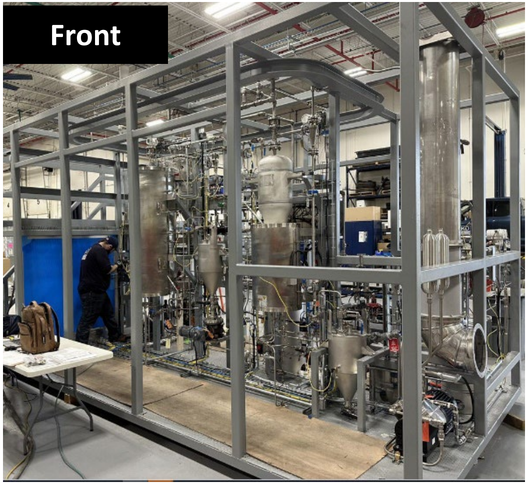
Biomass and Catalyst Hoppers and Weigh Bins

Primary RCFP Reactor

Regenerator and Catalyst Receiver



Hot Gas Filters



Installation and Commissioning

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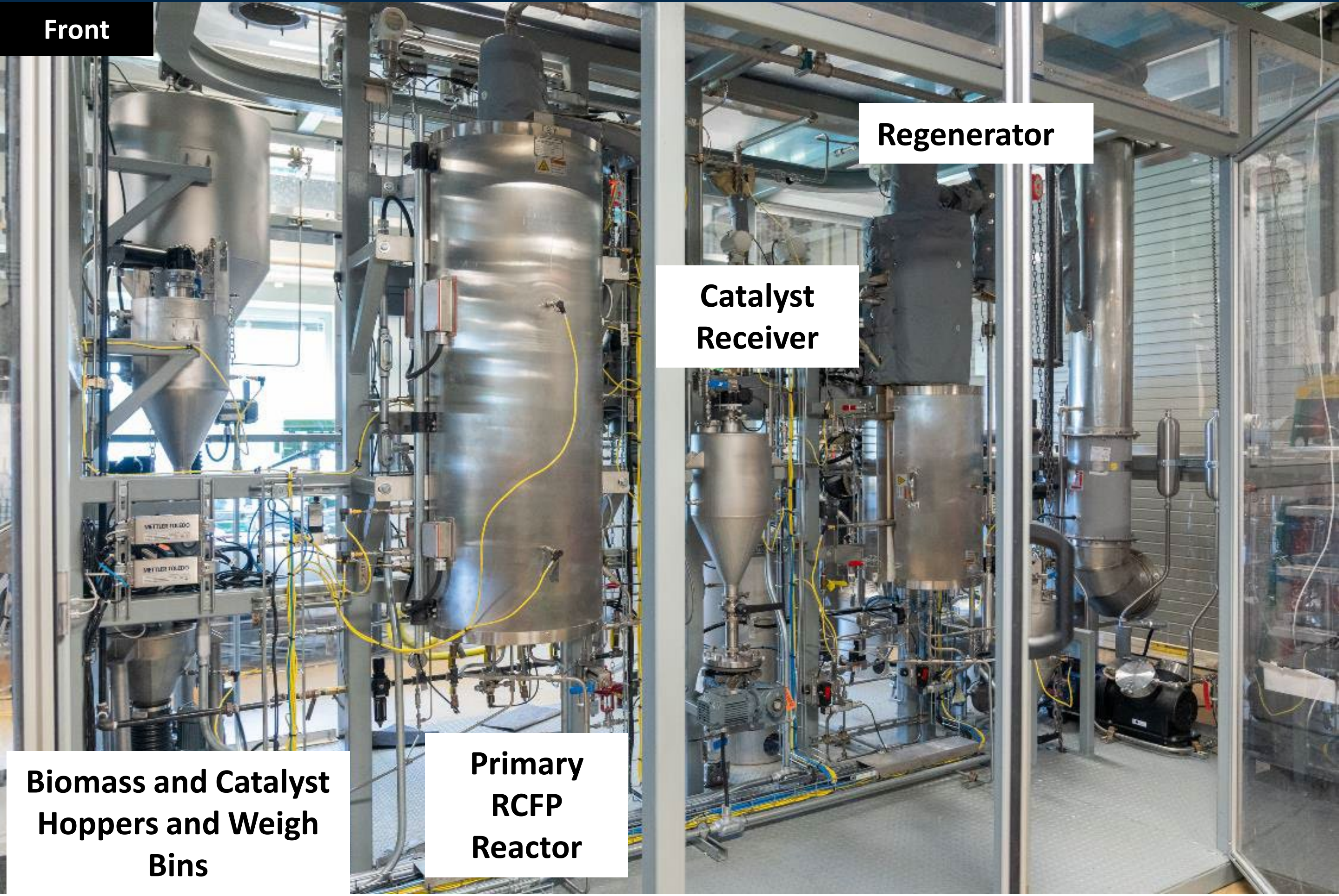
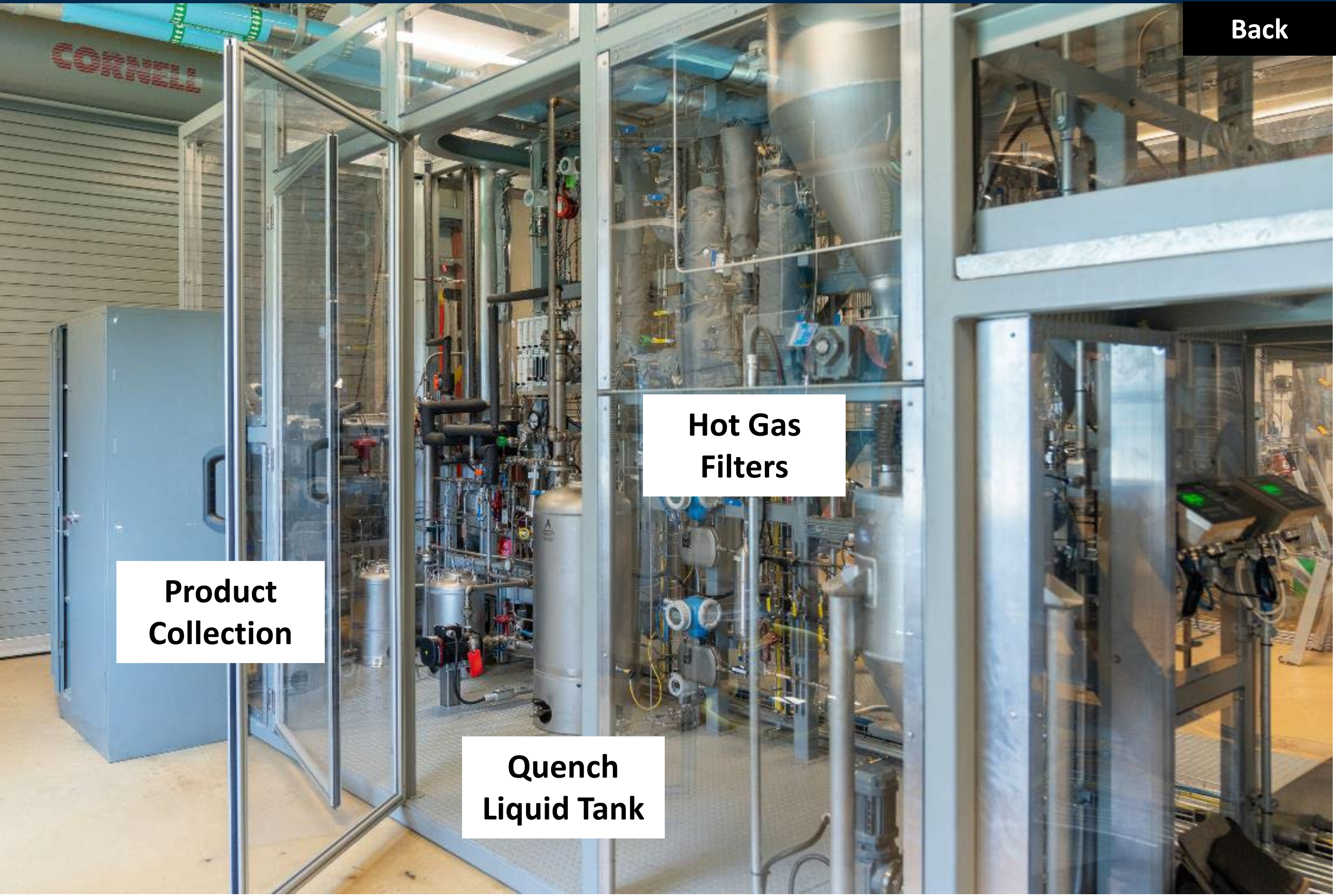


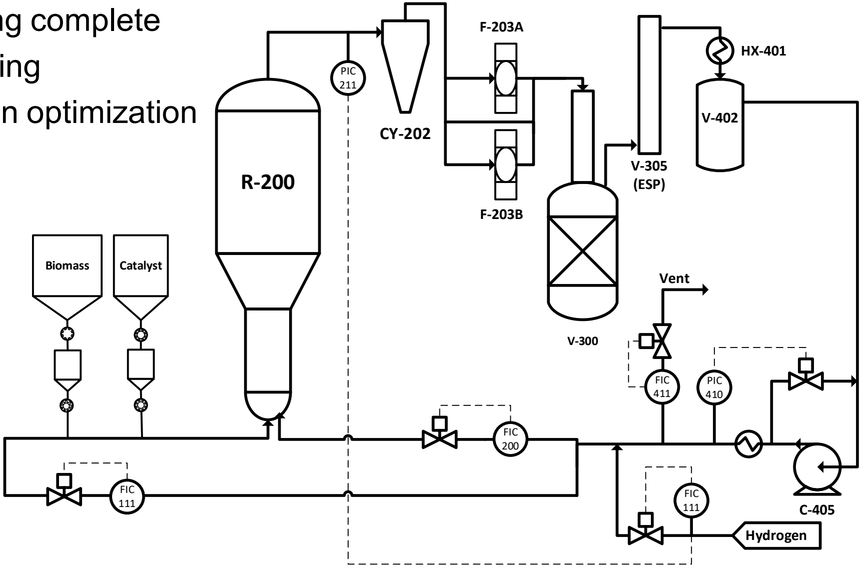
Installation and Commissioning

Back



Staged Commissioning Plan Timeline

- Factory Acceptance Test April 15-18, 2024
- Delivery – May 29, 2024
- Utility Connections (power, gases, chilled water, vents, ventilation) – Completed June 15, 2024
- Cold Flow Testing, nitrogen only (leak check, control system shakedown, etc.) – Completed July 15, 2025
- Hot Flow Testing, nitrogen only July 15, 2024 – September 30, 2024
  - Heater testing complete
  - Inert solids and CFP catalyst loading complete
  - Biomass feeding optimization ongoing
  - Biomass CFP for biocrude collection optimization
- RCFP Process Operations
  - Scheduled to begin Oct 1, 2024
  - Catalyst delivery in Sept 2024



Summary and Conclusions

The integrated biomass pyrolysis biocrude hydrotreating process is a pathway to infrastructure compatible, hydrocarbon biofuels

- 10x RCFP process scale up and demonstrate extruded commercial catalyst performance in a fluidizable form

Maximize biofuel yields for attractive process economics

- RCFP liquid organic biocrude yields are generally higher than CFP
- Decrease char yields
- Investigate improved yields with tail gas recycling

Biocrude thermal stability, oxygen content, and type of oxygenates are quality metrics

- Maximize carbon efficiency of the hydrotreating step
  - RCFP biocrudes contain lower oxygen content than CFP biocrudes with less anhydrosugars and acids
  - Mitigate HDT catalyst deactivation and reactor plugging by removing or eliminating reactive biocrude components

Increase long-term catalyst activity to achieve commercial performance (1000 hrs TOS)

- Preliminary upgrading shows no reactor fouling after 144 hours time on stream
- Validate RCFP biocrude quality for long term upgrading

Acknowledgements

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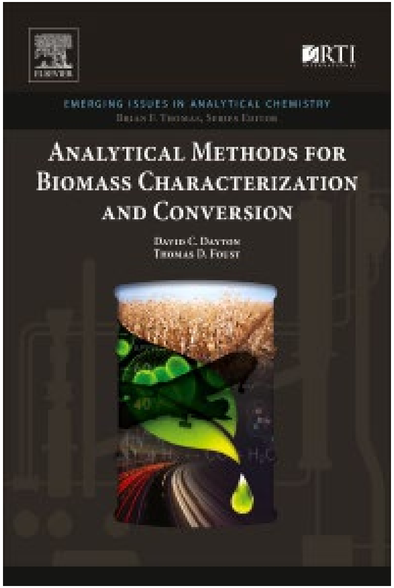

https://www.elsevier.com/books/analytical-methods-for-biomass-characterization-and-conversion/dayton/978-0-12-815605-6