DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Integrated Reactive Catalytic Fast Pyrolysis System for Advanced Hydrocarbon Biofuels

WBS 3.5.1.204

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System Development and Integration

Principal Investigator: David C. Dayton
RTI International

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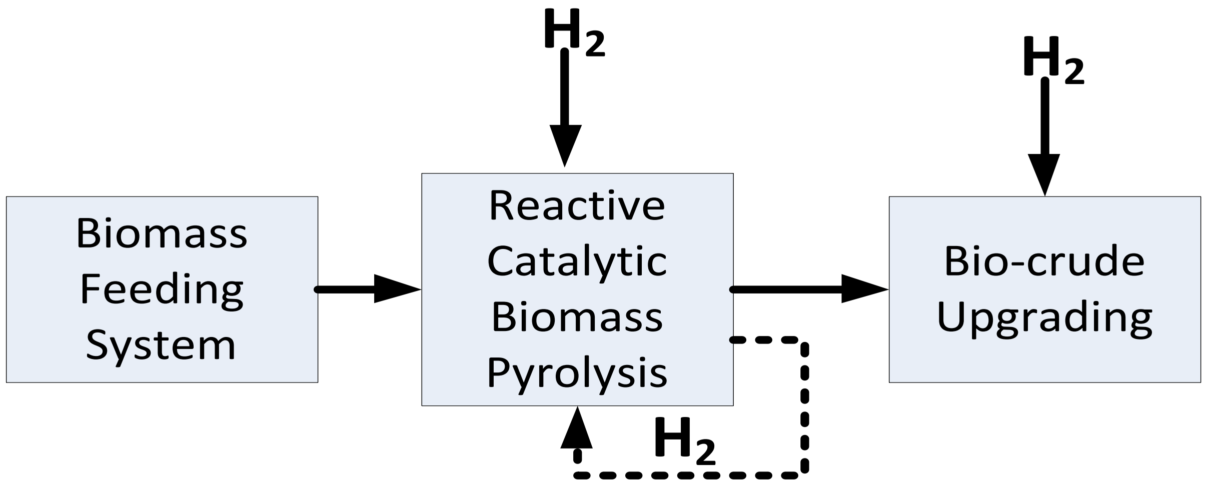
Project Overview

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 100 gallons of drop-in renewable diesel



Summary:

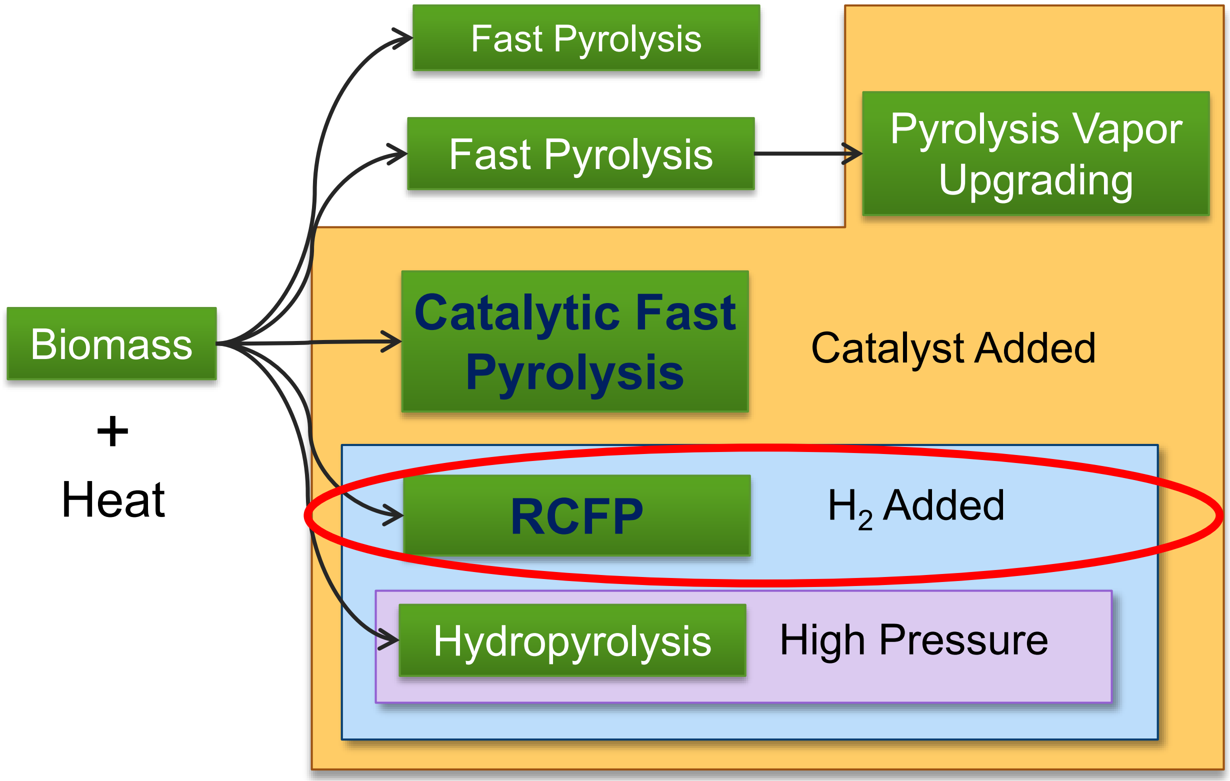
1) Design, fabricate, and install an engineering-scale (1-5 kg/hr) reactive catalytic fast pyrolysis (RCFP) reactor system
2) Scale up a fluidizable RCFP catalyst based on the formulation of commercially available extrudates
3) Optimize the process and maintain steady-state hydrodeoxygenation (HDO) catalyst 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.

Overview - Pyrolysis Pathways for Advanced Biofuels

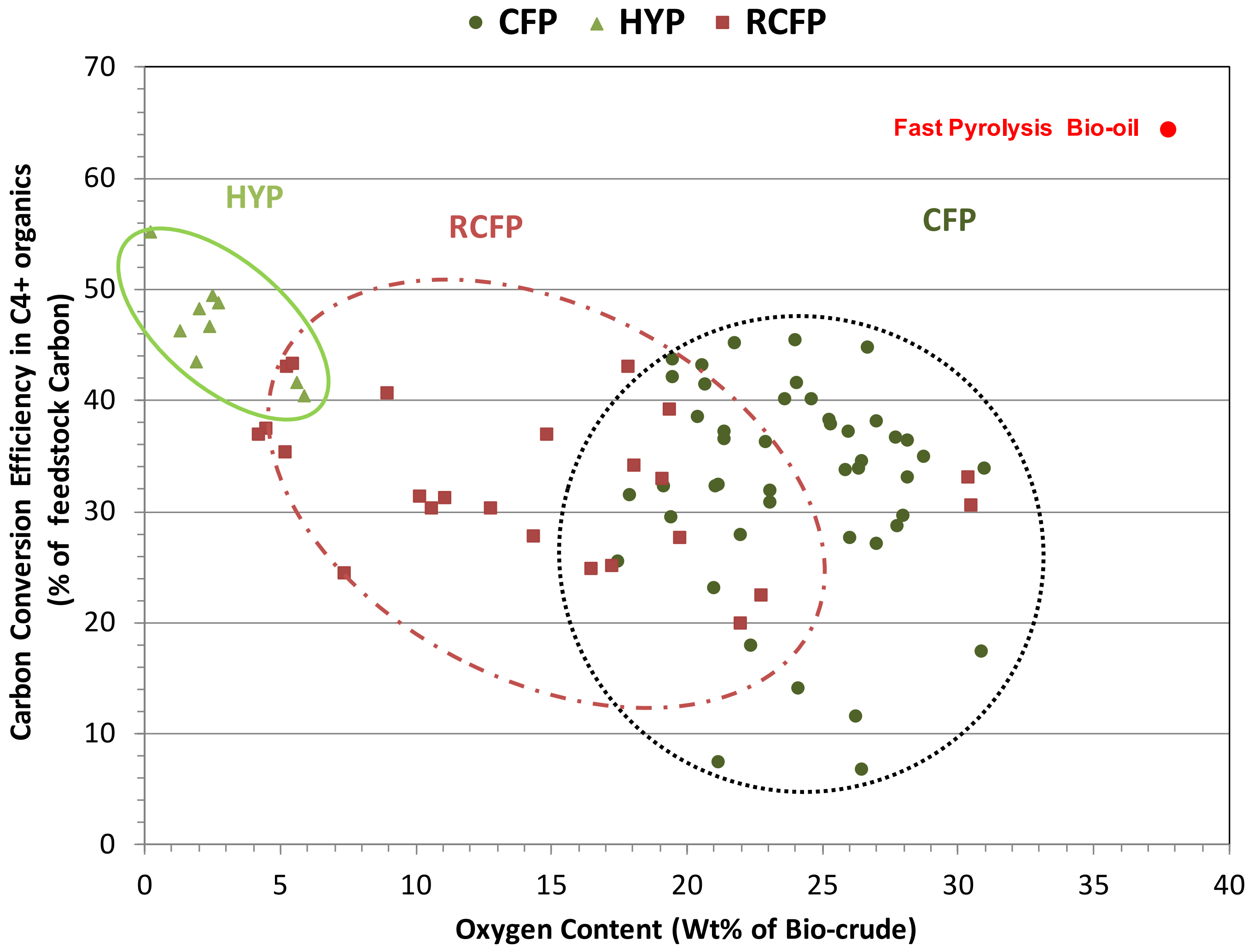
Application of catalysts to maximize yields and improve biocrude ***quality*** (oxygen content, chemical composition, thermal stability)



1. 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.
2. 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 - Biocrude Yield vs. Quality

Product Quality (wt% O) vs. Yield



Dayton, D.C., Wang, K., Peters, J.E. and Mante, O.D. 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.

Management Approach - Overview

Project will be executed in three budget periods (BPs) with 12 tasks that will span the 39-month period of performance.

- BP1 - Initial Verification (3 months)
- BP2 - Design a continuous RCFP reactor system (9 months)
- BP3 - Fabricate the engineering-scale (1-5 kg/hr) RCFP reactor system for RCFP biocrude production and upgrading (27 months)

<u>Go/NoGo Decision Criteria</u>

- GN1: Go/No-Go Decision Point (Month 3): 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.
- GN2: Go/No-Go Decision Point (Month 12):
  - 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.

<u>Final Project Goal:</u> 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

Management Approach– Task Structure

BP1 (Months 1–3)

- **Task 1—Initial Verification (Months 1–3)**

<u>GN1</u>

BP2 (Months 4–12)

- **Task 2—Preliminary Design of Engineering Scale RCFP Unit (M4–M6)**
  - **Subtask 2.1—Process Flow Diagram**
  - **Subtask 2.2—Process Design Basis**
  - **Subtask 2.3 – Preliminary Technoeconomic Analysis**
- **Task 3—Detailed Engineering Design (M6–M12)**
  - **Subtask 3.1—Design Review and Process Hazard Analysis**
- **Task 4—RCFP Catalyst Scaleup (M4–M12)**
  - **Subtask 4.1—Fluidizable RCFP Catalyst Development**
  - **Subtask 4.2—Lab-scale Catalyst Evaluations**
- **Task 5—BP2 Project Management (M4–M12)**
  - **Subtask 5.1—Interim Verification**

<u>GN2</u>

BP3 (Months 13–39)

- **Task 6—RCFP Unit Fabrication (M13–M18)**
  - **Subtask 6.1—Factory Acceptance Test**
- **Task 7—RCFP Unit Installation and Commissioning (M19–M21)**
- **Task 8—RCFP Catalyst Production (M13–M21)**
  - **Subtask 8.1—Fluidizable RCFP Catalyst Production**
  - **Subtask 8.2—Fluidizable RCFP Catalyst Performance Testing**
- **Task 9—RCFP Bio-crude Production (M22–M33)**
  - **Subtask 9.1—RCFP Unit Optimization**
- **Task 10—RCFP Bio-crude Upgrading to Biofuel Blendstock (M22-M37)**
  - **Subtask 10.1—Biofuel Characterization**
  - **Subtask 10.2 – Catalyst Characterization**
- **Task 11—Process Modeling (M32–M38)**
  - **Subtask 11.1—TEA**
  - **Subtask 11.2—LCA**
- **Task 12—BP3 Project Management**

Management Approach – Milestones

	Milestone	Month
M2.1	Preliminary design package will form the basis of a request for proposals to find a vendor for detailed engineering in Task 3 and unit fabrication in Task 6.	6
M3.1	Complete RCFP unit design package.	12
M3.1.1	Complete process hazard analysis and document recommended design changes.	11
M4.1	Develop method to scale up fluidizable RCFP catalyst.	12
M4.1.1	Finalize methods for catalyst scale-up.	9
M6.1	Complete fabrication of RCFP unit for delivery and installation at RTI.	16
M6.1.1	Verify that all major component specifications are met and basic functions of the system work.	17
M7.1	Install engineering-scale RCFP unit.	21
D8.1	Deliver fluidizable RCFP catalyst	15
M9.1	Complete continuous RCFP biocrude production.	30
M9.1.1	Determine operating conditions for maximum biocrude yields	25
M10.1	Complete at least 100 uninterrupted hours of RCFP biocrude upgrading.	33
M10.2	Complete at least 500 cumulative hours of RCFP biocrude upgrading.	36
M10.1.1	Develop characterization protocols for biocrude and upgraded products.	22
M11.1	Techno-economic analysis (TEA) and life-cycle assessment (LCA) of a 2,000 TPD nth RCFP plant	36

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.

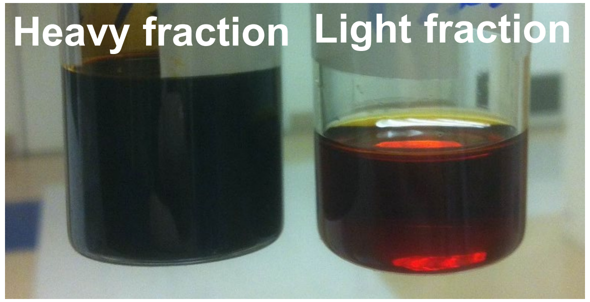
Dayton, D.C., et al., CHAPTER 5 Catalytic Biomass Pyrolysis with Reactive Gases, in Fast Pyrolysis of Biomass: Advances in Science and Technology. 2017, The Royal Society of Chemistry. p. 78-95.

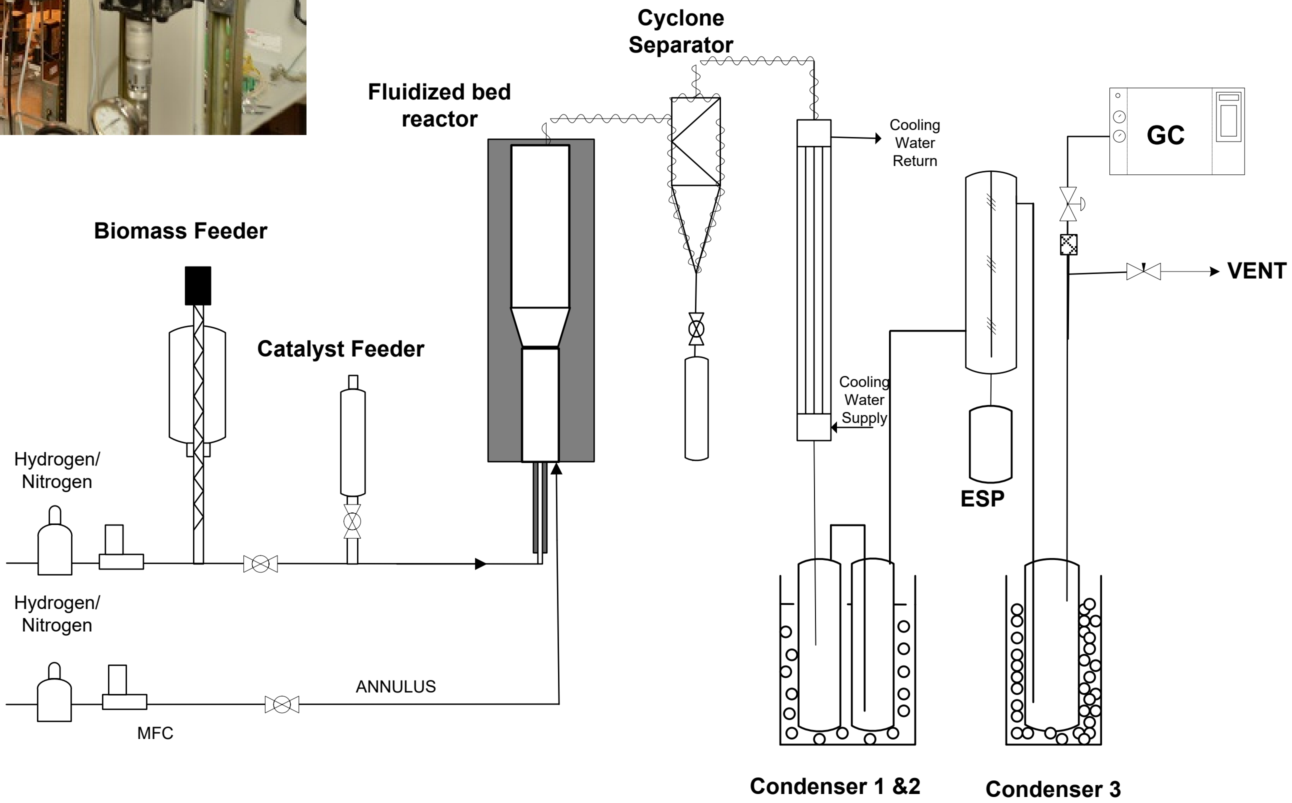
Wang, K., Dayton, D., Peters, J. E. & Mante, O. D. Reactive catalytic fast pyrolysis of biomass to produce high-quality bio-crude. Green Chemistry, (2017) 19(14): p. 3243-3251.

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

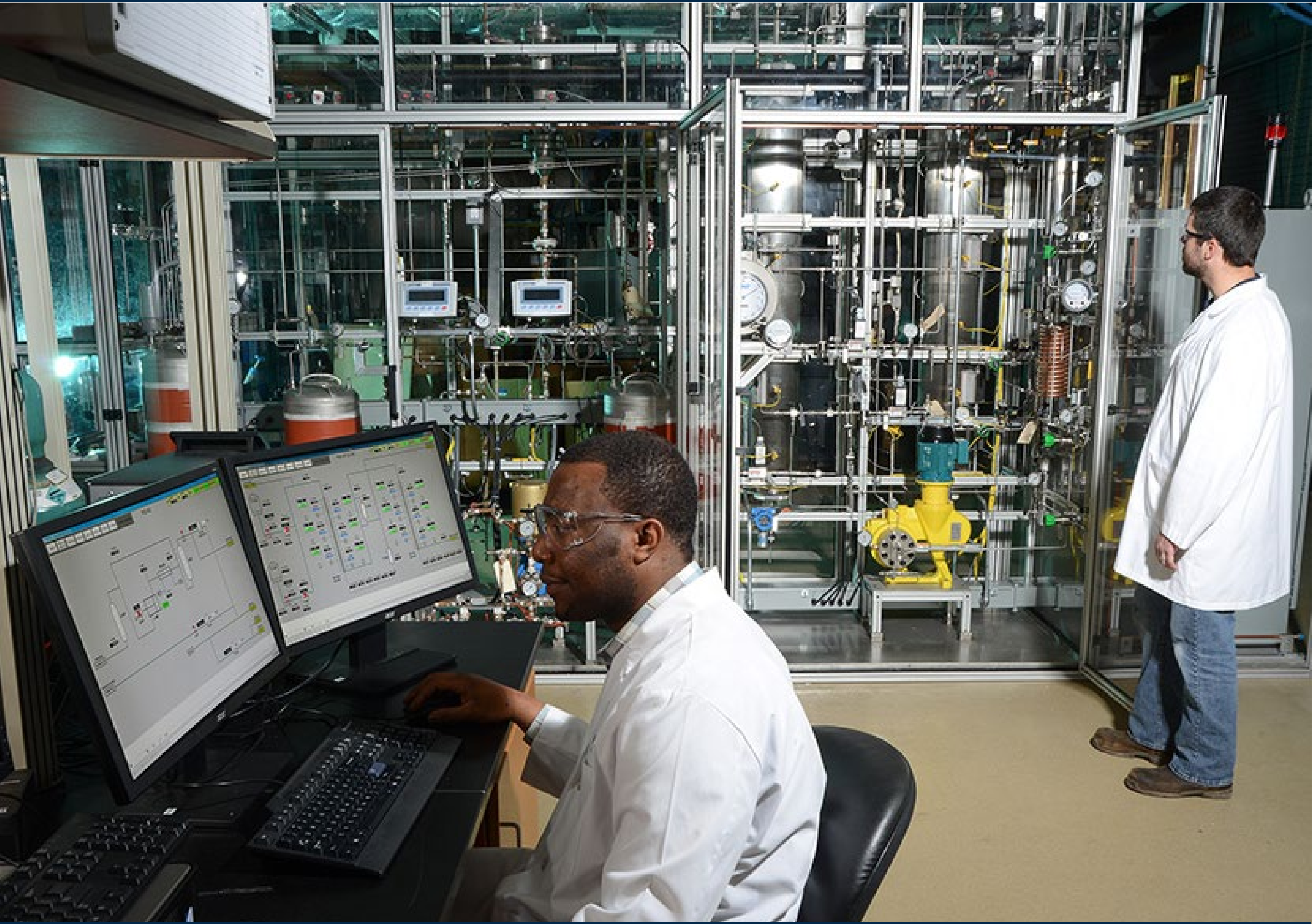
Process Development and Biocrude Production

- 2.5'' fluidized bed reactor with 4'' disengagement zone
- Biomass feeding rate: 2-5 g/min
- Liquid collection: 3 condensers and 1 ESP
- Non-condensable gases analyzed by on-line microGC
- Liquid product analyzed by Karl Fischer titration, elemental analysis, GC/MS, etc.





Biocrude Upgrading - Hydrotreating



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

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)

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 bio-crude 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.

RCFP Biocrude Production and Upgrading

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

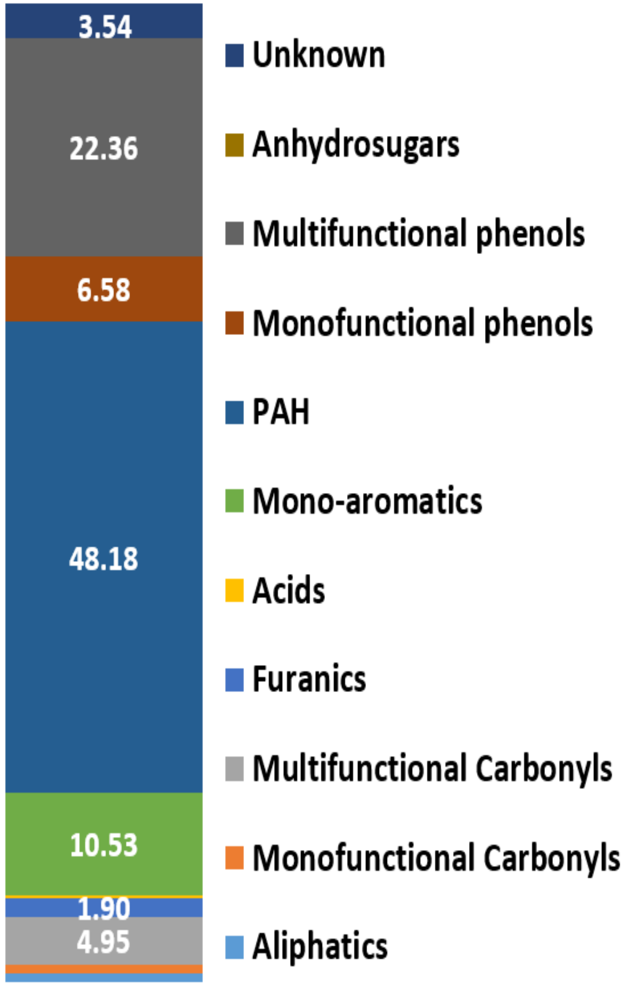
Hydrogen: 80 vol%

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%)

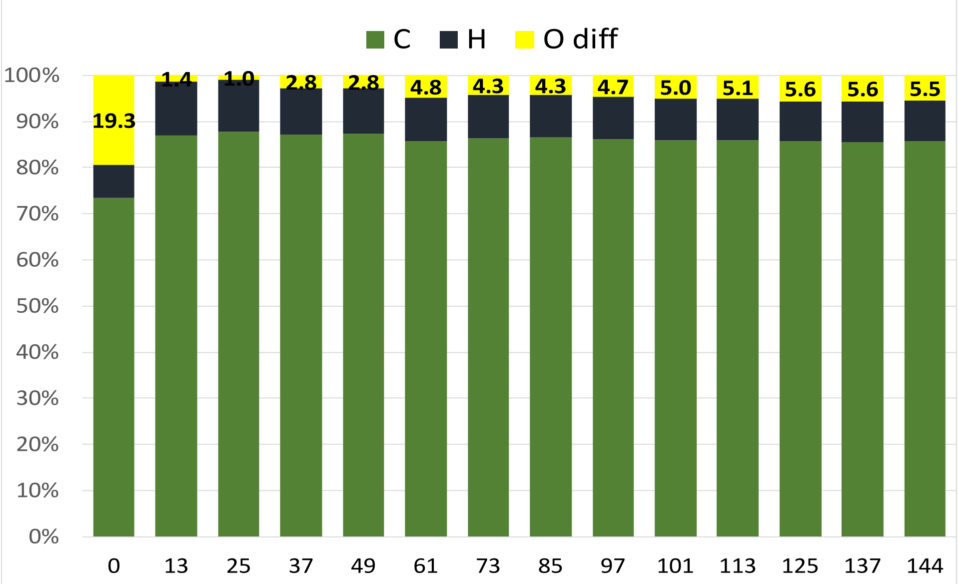


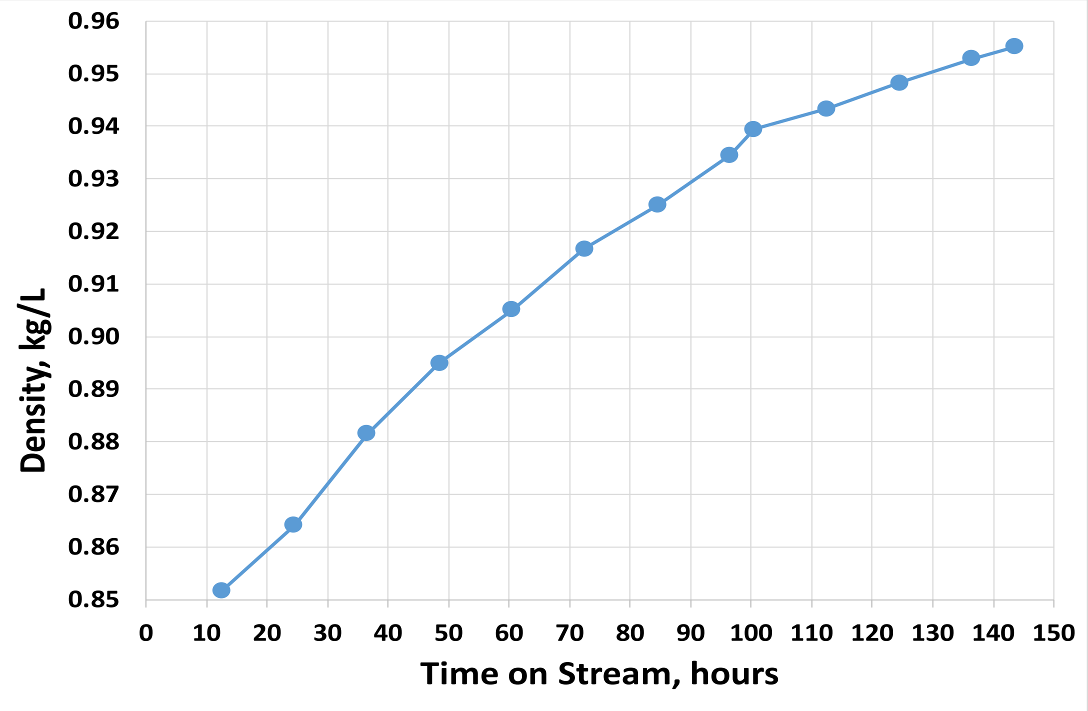
Elemental

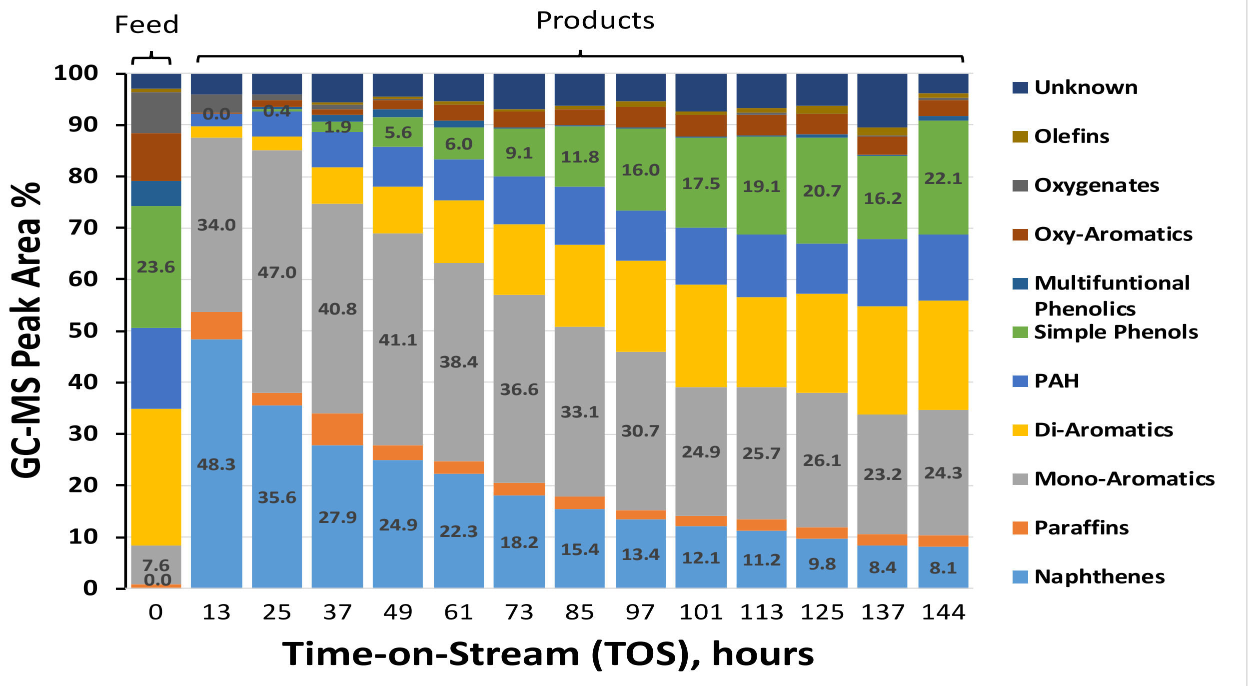
Properties	
Moisture, wt%	8.5
C wt%, dry	73.2
H wt%, dry	7.3
N wt%, dry	0.2
O (by diff)	19.3

RCFP Biocrude Upgrading: Physico-chemical Properties

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

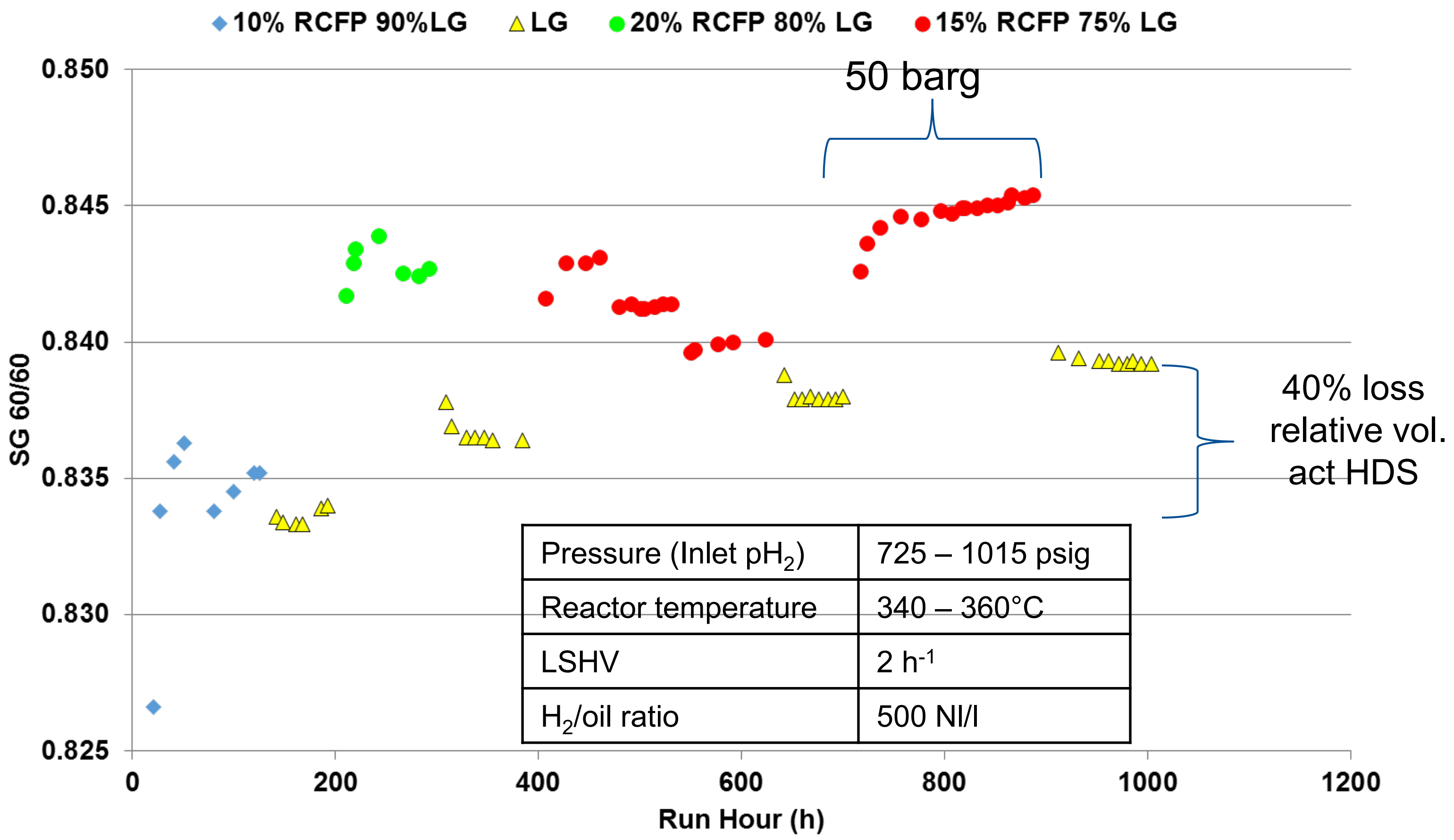






RCFP Biocrude Co-processing with Light GasOil

Analysis	Unit	LG	RCFP	10/90 RCFP/LG	15/85 RCFP/LG	20/80 RCFP/LG
SG at 60/60°F		0.8541	1.005	*0.8667*	0.8726	*0.8782*
O	wt %	-	9.65	-	-	*2.17*
S	wt %	1.30	0.001	*1.14*	1.04	*1.01*
N	wt ppm	148	425	*165*	180	*201*
H	wt %	13.09	8.28	*12.59*	12.43	*12.18*



Summary

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

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: TBD
- Budget Period 2: 4/1/2021 – 3/31/2022
- Budget Period 3: 4/1/2022 – 9/30/2023

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 bio-crude 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

Budget	Federal	Cost Share	Total Costs	FY20Q1 Actuals	
				Federal	Cost Share
BP1	$54,126	$13,532	$57,658	$14,405	$3,601
BP2	$428,863	$107,216	$536,079	---	---
BP3	$1,873,675	$468,419	$2,342,094	---	---
Total	$2,356,665	$589,166	$2,945,831	$14,405	$3,601

FY19 Bioenergy Technologies Office Multi-Topic Funding Opportunity Announcement
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

- Not applicable

Publications, Patents, Presentations, Awards, and Commercialization

- Publications: none
- 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