DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Strategies for Co-Processing in Refineries (SCR)

March 4-8, 2019
ADO

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NREL, LANL, PNNL

Goal Statement

Accelerate co-processing biomass feedstocks with petroleum feedstocks in existing refineries to biogenic fuels by advancing co-processing technology through foundational science and early-stage applied engineering

106 of 137 US refineries have co-processing capacity

Outcomes:

Efficient pathway(s) to produce biogenic fuels using the existing US petroleum refining infrastructure

Relevance:

- Refinery compatible pathway(s) using biomass that meet/exceed BETO's 2020 goal of a < $3/GGE range fuel production cost
- Co-processing adoption enables refiners to generate their own RINs

Benefits to the US:

Cost competitive biogenic fuels for use in the US transportation sector

Key Project Milestones

	FY 2017				FY 2018				FY 2019			
KEY MILESTONE	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Establish industrial steering committee (ISC) and conduct biannual meetings to review task progress and update metrics. The ISC provides the program with an industry-relevant focus and knowledge of recent technology advances and challenges												
Produce 500 ml quantities of bio-oils and bio-crudes for FCC and HT/HC co-processing (CP) assessment												
Complete micro-scale biogenic carbon tracking in CP fuels using ^{13}C-biomass and VGO												
Establish baseline isotope analysis of feedstocks and CP products using the δ^{13}C method												
Establish baseline CP product yields, fuel compositions for FCC and HT/HC pathways												
Conduct preliminary TEA with FY2018 process data for FCC and HT/HC pathways to estimate cost												
Establish <u>FCC</u> (zeolite) catalyst compositions and morphology to baseline CP (post-use) induced changes; establish baseline HT/HC CP with a commercial catalyst												
Isotopic Biogenic Carbon Determination of Co-processed FCC and HT/HC Fuels using GC-C-IRMS												
<u>FCC</u>: Complete Initial Micro Scale Catalyst Screening Tests to Identify Best Co-Processing Performers; <u>HT</u>: Complete Preferred Catalyst Synthesis Method and Catalyst Composition Determination												
Technoeconomic analysis of FCC and HT/HC CP assessed for MFSP using optimized catalysts/conditions				START DATE					TODAY			

Project Budget Table

	Original Project Cost (Estimated)		Project Spending and Balance		Final Project Costs
Budget Periods	**DOE Funding**	**Contingency**	**Spending to Date**	**Remaining Balance**	**What funding is needed to complete the project.**
FY19	$2,000K		$395K	$1650K	
FCC, HT/HC Maintenance, Upgrades, Repair	$300K				
Generate bio-oil feedstocks, baseline CP, source, modify assess catalysts	$1,400K				
Installations (CP nozzle, VUV detector, catalysts, feedstocks)	$300K				
FY20	$2,500K				
FCC, HT/HC Maintenance, Upgrades, Repair	$375K				
Fuel production, characterization with new catalysts	$1,250K				
Installations (catalysts, feedstocks, H_2 addition)	$375K				
FY21	$3,000K				$3.0M in FY2020 for fuel production runs
FCC, HT/HC Maintenance, Upgrades, Repair	$600K				
Extended duration FCC, HT/HC CP fuel production	$2,400K				

Maintenance: 15%
Installation: 15%
Experiments: 70%

Quad Chart Overview

Timeline

- Project Start 10/1/2017
- Project End: 9/30/2020
- Percent Complete: 40%

	Total Costs Pre FY17	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded				
NREL		0K	600K	2,800K
PNNL		0K	461K	1,889K
LANL		K	300K	900K
Partners: NREL (50%), PNNL (34%), LANL (16%)				

Barriers Addressed

ADO-G. Co-Processing with Petroleum Refineries

Ct-F. Increasing the Yield from Catalytic Processes

Objective

Accelerate co-processing bio-oils with petroleum feedstocks in current refineries to produce biogenic transportation fuels

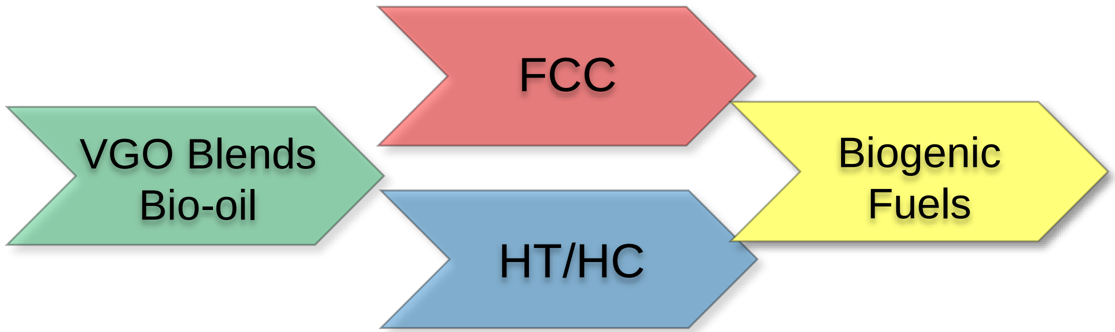
Partners

NREL (50%), PNNL (34%), LANL (16%)

Collaborators

- ChemCatBio (CFP, ACSC)
- Johnson Matthey
- WR Grace
- Thermochemical Analysis Team
- Integration/Scale Up team

Project Acronyms and Pathways



BC:	biogenic carbon
CFP:	catalytic fast pyrolysis
CP:	co-processing
E-Cat:	equilibrium FCC refinery catalyst
FCC:	fluid catalytic cracking
FP:	fast pyrolysis
HC:	hydrocracking
HDN:	hydrodenitrogenation
HDO:	hydrodeoxygenation
HDS:	hydrodesulfurization
HT:	hydrotreating
HTL:	hydrothermal liquefaction

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1 - Project Overview

Objective: Develop an efficient (5-20 wt.% bio-oil/bio-crude incorporation into fuel) co-processing technology using biomass (wood, agricultural residue, or WWTP sludge) derived liquids (bio-oil/bio-crude), petroleum feedstocks (VGO and others), and FCC and HC/HT processes

Existing Capabilities

	FCC	HT/HC
Bio-oil production (FP, CFP)	√	√
Bio-crude production (HTL)		√
Feed flexible FCC system	√	
Hydrotreating systems		√
Catalyst development	√	√
Biogenic carbon tracking	√	√
Comprehensive oil analysis	√	√

Market Opportunity: Significant co-processing opportunity as 106 of 137 U.S. refineries have conversion capabilities using FCC and/or HT

Baseline Work: Laboratory scale bio-oil/VGO co-processing verified for FCC and HT using commercial catalysts; developing biogenic C measurements

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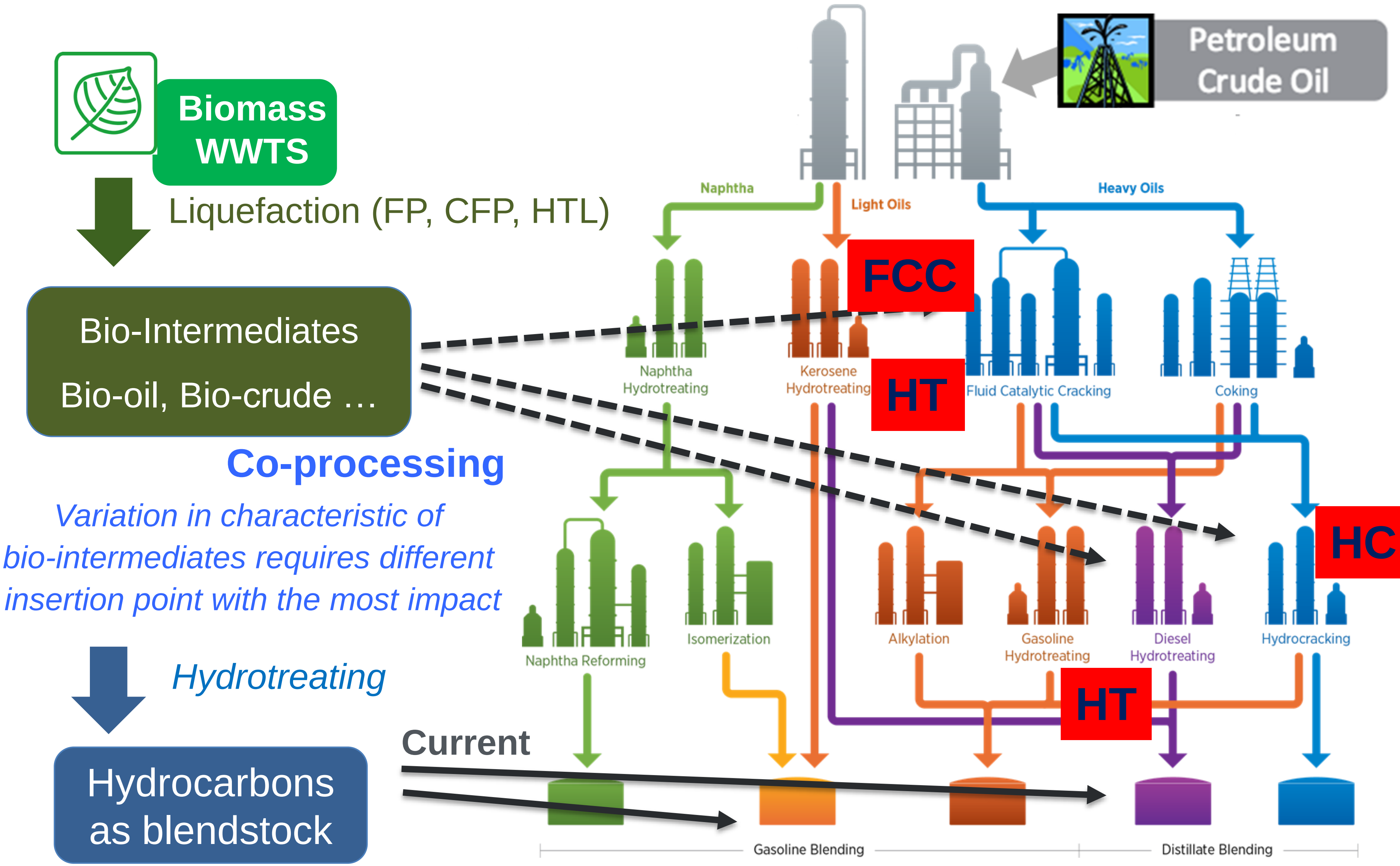
1 - Project Overview

Leveraging Existing Refining Infrastructure Leverages Billions US$



2 - Approach (Technical)

FCC and HT/HC co-processing of biomass feedstocks (FP, CFP, HTL) with petroleum feedstocks can be accelerated by modifying refinery compatible catalysts to incorporate biogenic C in produced fuels and by accurately measuring biogenic C in these fuels for RIN use by:

FCC: Produce fuels with ≥ 5wt% biogenic carbon using modified refinery compatible zeolite catalysts for bio-oil conversion and understanding CP chemistry

HT/HC: Produce fuels in diesel range with ≥ 5wt% biogenic carbon using improved refinery compatible sulfide catalysts and understanding CP chemistry

Carbon Measurement/Tracking: Using $\delta^{13}C$ biomass signatures to measure BC in co-processed fuels and correlating with ^{14}C analysis; track biogenic C through co-processing using ^{13}C-labelled biomass

End of Project: Assess CP pathway cost via TEA, LCA

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2- Approach (Technical)

Challenges

- FCC: continuous feeding without plugging; understanding 1) catalyst performance and lifetime, 2) bio-oil impacts on FCC chemistry, 3) fate of oxygenates
- HT/HC: mitigate bio-oil/bio-crude contaminant impacts; understand 1) catalyst performance and lifetime, 2) bio-oil/bio-crude impacts on HT/HC chemistry
- Carbon Tracking and Measurement: Track biogenic carbon, develop economical and accurate biogenic C measurement in finished fuels

Critical Success Factors

- Extended duration co-processing using refinery compatible catalysts that achieve ≥ 5wt% useable biogenic carbon in fuel
- Economical, efficient biogenic carbon measurement in fuels – usable by refiners

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2 – Approach (Technical)

1) *Identifying blend levels* for bio-oils/crudes that achieve ≥5wt% biogenic carbon incorporation into co-processed fuels via FCC and HT/HC:
   - Laboratory scale screening (5-20 wt% blends)
   - Pilot scale CP fuel production
   - Understanding feed impact on CP chemistry

2) *Advancing refinery compatible catalysts* to increase BC incorporation in fuels while maintaining refinery consistent catalyst performance
   - Modifying zeolites for bio-oil conversion (mesoporosity, metal addition, mixtures)
   - Providing foundational knowledge for modifying HT/HC catalysts for bio-oil/bio-crude co-processing (sulfide composition, secondary function)
   - Understanding feed impact on catalyst chemistry

3) *Developing accurate BC measurement* in co-processed fuels
   - Identifying pure biogenic C markers via ^{13}C-oak/VGO CP
   - Developing δ^{13}C measurement
   - Correlating with ^{14}C analysis

2 – Approach (Technical)

Co-processing baseline established by Petrobras

- 1-20wt% pine FP oil/FCC feed
- Dual feed nozzles
- Mass balance range of 96 – 100%
- 3-hour test runs
- > 400 hours run time

In 2015-17, Petrobras co-processed bio-oil/VGO using similar FCC units and found:

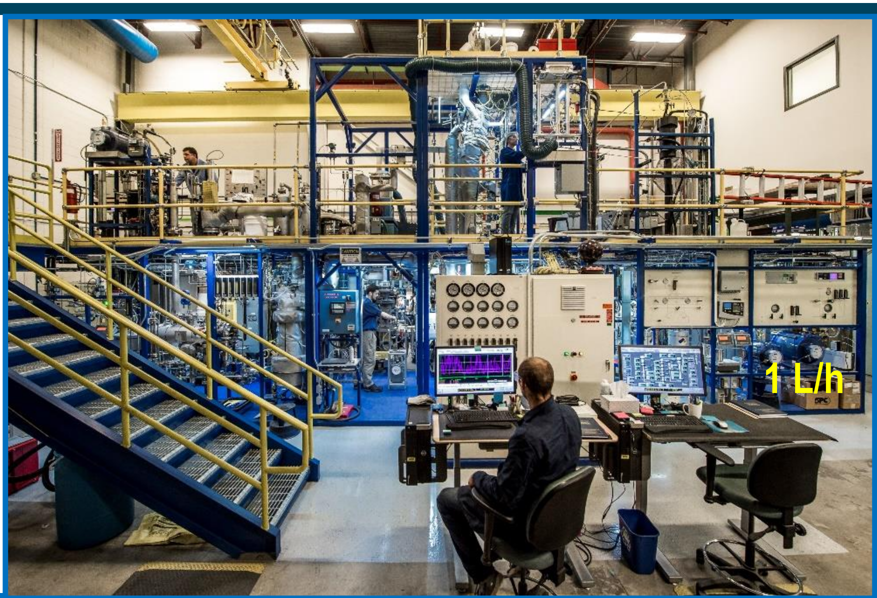
- Bio-oil feeding issues (plugging) requires 2 nozzles
- 2 wt% BC in product from 10 wt% bio-oil/ VGO feed – similar to VGO product
- 20 wt% bio-oil deteriorated product yields
- O_2 reports to H_2O, CO, CO_2, << alkyl phenols
- Coke yields less at larger scale
- CP feasibility demonstrated, promising route to renewable carbon in fuels
- Developing CP with ENSYSN

Pinho, et al., "Co-processing raw bio-oil and gasoil in an FCC Unit", *Fuel Processing Technology* 131 (2015) 159-166.

Pinho, et al., "Fast pyrolysis oil from pinewood chips Co-processing with vacuum gas oil in an FCC unit for second generation fuel production", *Fuel* 188 (2107), 462-473.

2 – Approach (Technical)

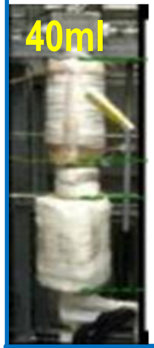
NREL and PNNL FCC and HT Systems



NREL's FCC DCR System

<u>Capabilities:</u>
- Produce bio-oils
- Dual feed nozzle system for co-processing liquids
- Fractional condensation for improved product collection
- Catalyst evaluation

<u>Industry partners:</u>
- Enerkem, Johnson Matthey, WR Grace, Zeton, VUV Analytics



PNNL's Hydrotreating Systems

<u>Capabilities:</u>
- Produce HTL bio-crudes
- Co-processing bio-oils/crudes
- Hydrotreating and hydrocracking
- Distillation/fractionation
- Catalyst performance evaluation
- Reaction kinetic evaluation

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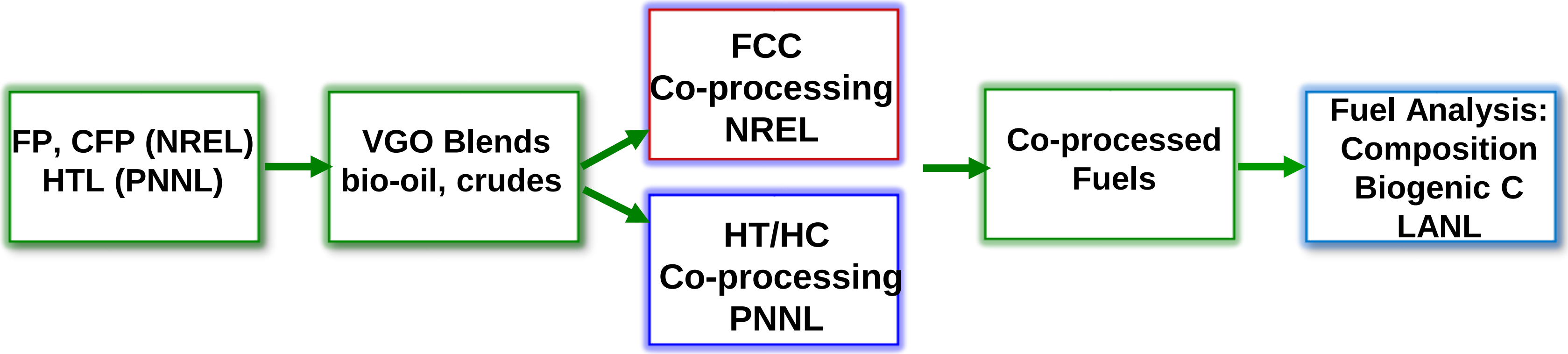
Process Operations Block Diagram



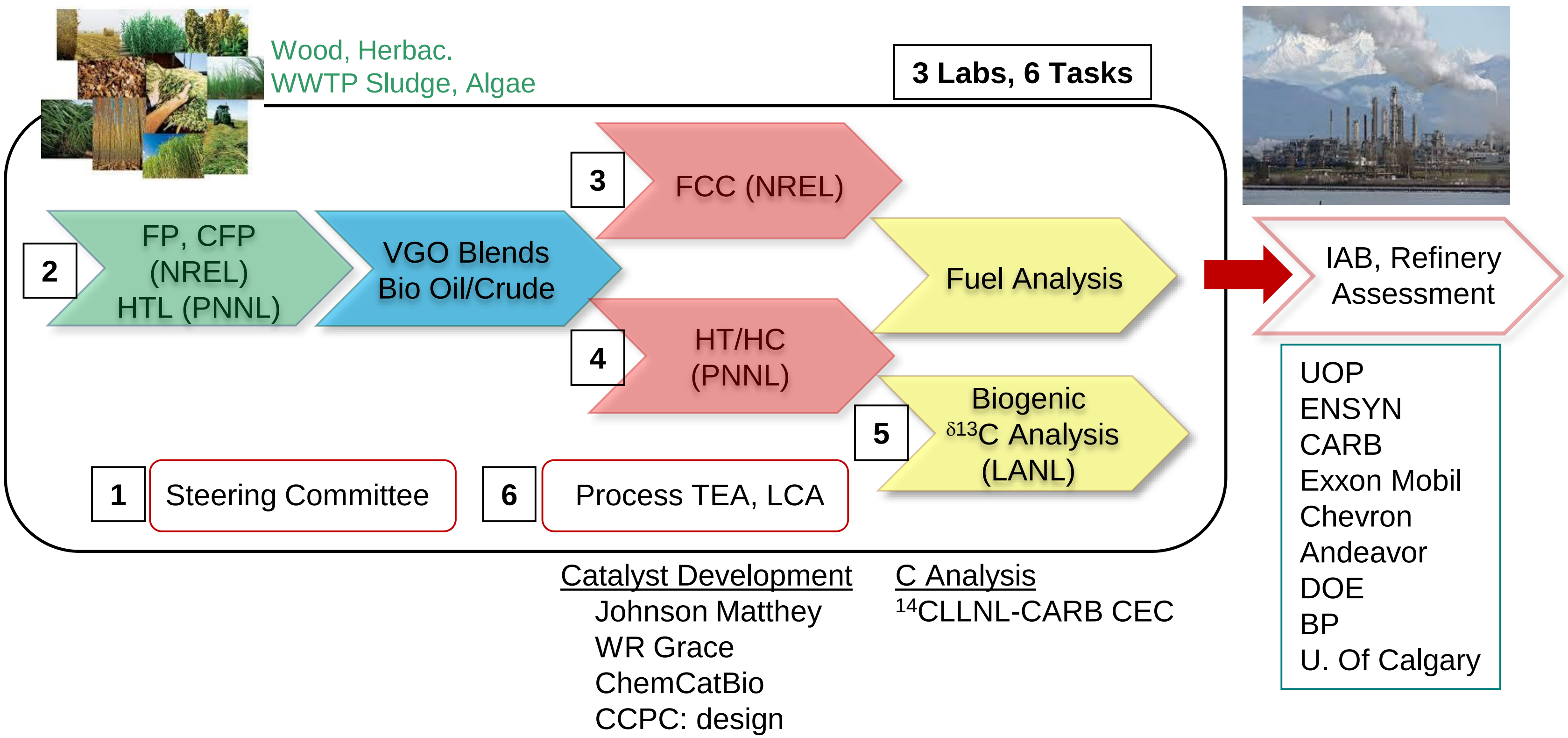
SKILL SETS Process Engineering Feed Handling Reactor Operations	Gas, Liquid Analysis	Process Engineering Reactor Operations		Fuel Analysis Isotope Analysis
CAPABILITIES Biomass Feeding FP, HTL Reactors On-line Analysis	Co-feed Production Blend Analysis	FCC Systems HT/HC Systems On-line Analysis	Biogenic Fuel Production BC Tracking	Accurate Biogenic Carbon Measurement

No Issues

Minor Issues

Moderate Issues

2 - Approach (Management)



Project Management

- Monthly webinars (LANL, PNNL, NREL)
- Bi annual IAB progress review
- Milestones with industry vetted technical targets to meet

* California Air Resources Board, California Energy Commission

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3-Technical Accomplishments/ Progress/Results

FCC

(1) Cyclone addition: returns entrained catalyst to the stripper

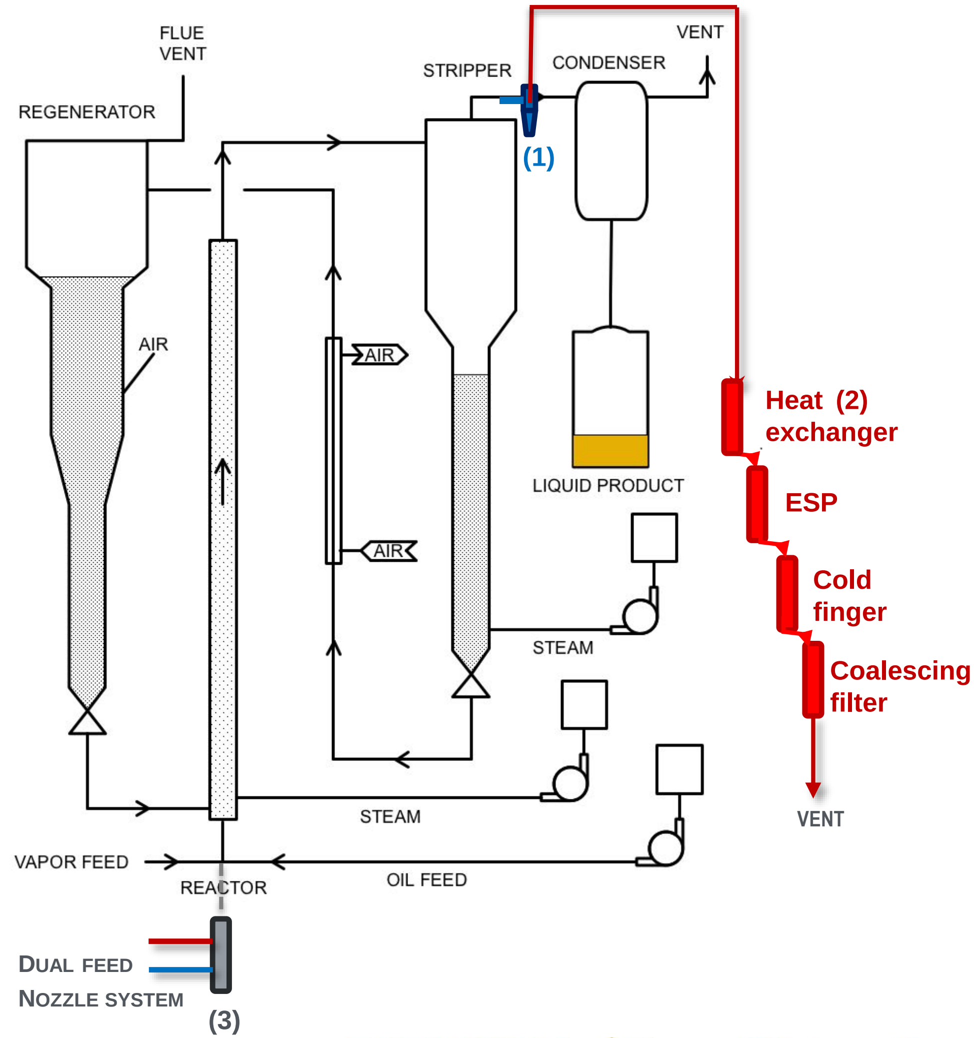
(2) Fractional condensation train: improves product recovery

(3) Multi feed, independently heated nozzles for co-processing dual liquids

(4) Total carbon detector (not shown) simplifies gas phase mass balance

Improvements provide a feedstock flexible DCR FCC system for co-processing expanded feedstocks: **CFP and HTL liquids with enhanced catalysts**

DCR Modifications for CFP/Co-Processing



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3-Technical Accomplishments/ Progress/Results FCC

FY18 Annual Milestone: Baseline performance established for co-processing bio-oils in a typical refinery FCC reactor to understand BC chemistry

Compound Category	Volume % CP Bio-Oil	Volume % FCC VGO
Paraffin	2.7	14.3
Isoparaffin	22.1	27.9
Olefin	17.0	13.2
Naphthene	12.1	9.2
Aromatic	34.5	25.4
Di-Aromatic	11.6	
Ethanol	0.0	9.9
iso-Octane	0.0	1.9
Benzene	0.5	0.4
Toluene	3.8	3.5
Ethylbenzene	1.1	
Xylenes	7.7	5.3
Naphthalene	0.6	0.3
Methylnaphthalenes	2.6	0.6
C2-Naphthalenes	3.2	
C3-Naphthalenes	3.3	
C4-Naphthalenes	1.3	
Biphenyl	0.0	

FCC Co-processing Bio-oil/VGO

Feed: 10wt% pine CFP oil (<20 wt% oxygenates) in VGO

Catalyst: 10 wt% HZSM-5/E-Cat*

Riser: 550°C

Residence time: 1 sec

Product Analysis:

- GC/VUV spectroscopy – gasoline enriched in olefins, aromatics
- Ring opening needed
- FCC CP concept validated

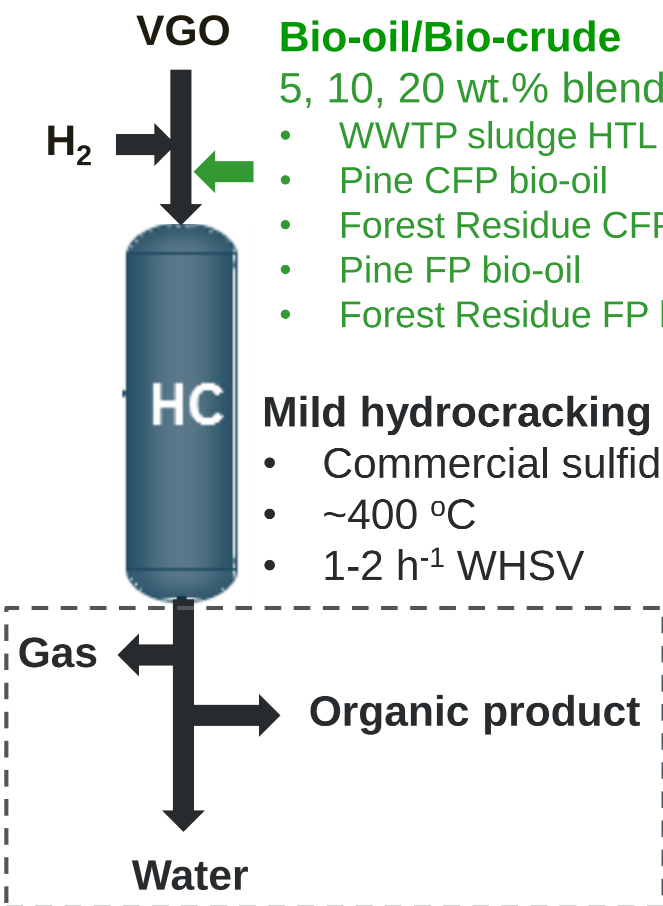
*E-Cat: refinery equilibrium catalyst, Y zeolite with HZSM-5 additive

3-Technical Accomplishments/ Progress/Results

HT/HC

FY18 Annual Milestone: Baseline performance established for co-processing biomass liquefaction intermediates in a typical refinery HC reactor

Co-processing Bio-oil/bio-crude with VGO in mild HC



Bio-oil/Bio-crude

5, 10, 20 wt.% blending

- WWTP sludge HTL bio-crude
- Pine CFP bio-oil
- Forest Residue CFP bio-oil
- Pine FP bio-oil
- Forest Residue FP bio-oil

Mild hydrocracking

- Commercial sulfide catalyst
- ~400 ^oC
- 1-2 h^{-1} WHSV

- Determined HC performance
  - Heteroatom removal (N, S, O)
  - Hydrocracking (diesel yield)
- Determined biogenic carbon incorporation
  - Mass and carbon balance
  - ^{13}C-labeled biomarkers

Product analysis

- Gas and liquid product composition
- Heteroatom content (N, S, and O)
- Simulated distillation
- Biogenic carbon tracking (LANL)

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3-Technical Accomplishments/ Progress/Results

HT/HC

Determined the impact of bio-oil/bio-crude co-processing in mild HC with VGO on HT/HC chemistry

Bio-oil/ Bio-crude	**WWTP Sludge HTL bio-crude**	**Pine / Forest residual CFP bio-oil**	**Pine / Forest residual FP bio-oil**
Major Properties	• High N, S, minerals • Low O, H_2O	• Medium O, H_2O • Low S, N	• High O, H_2O • Low S, N • Instability (thermal)
Co-processing with VGO in mild HC	• Simultaneous HDS, HDN, HDO • Organo-nitrogen inhibits hydrocracking	• Simultaneous HDS, HDO • Minor inhibition to hydrocracking	• Bio-oil stabilization required • Simultaneous HDS, HDO, hydrocracking

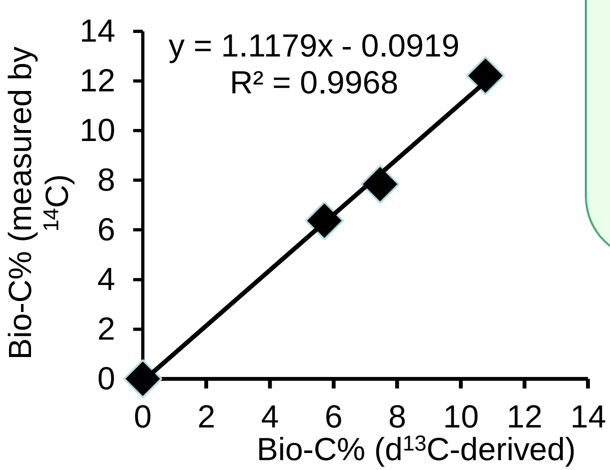
HDS: hydrodesulfurization; ***HDN***: hydrodenitrogenation; ***HDO***: hydrodeoxygenation

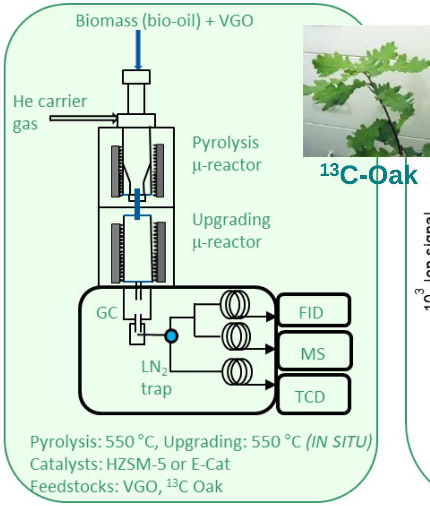
- Determined the impact of varied bio-oil/bio-crude properties on HT/HC co-processing chemistry
- Identified potential improvement for co-processing in HT/HC
  - Two step HT/HC for sludge HTL co-processing
  - Catalyst modification to address high heteroatom content (N and O)

3-Technical Accomplishments/ Progress/Results

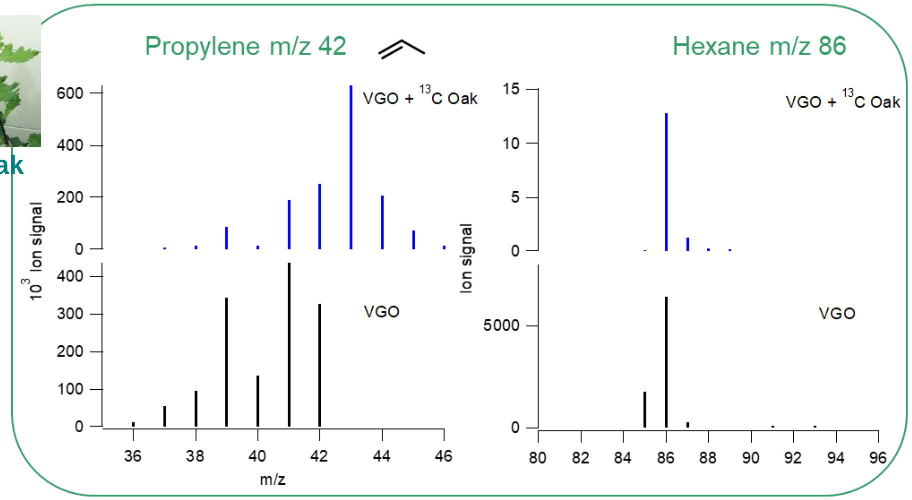
FCC: Understand Biogenic C Incorporation (FY2018 Milestone)

^{14}C, $\delta^{13}C$: measure total BC
^{13}C: measures BC chemistry





^{13}C-Oak

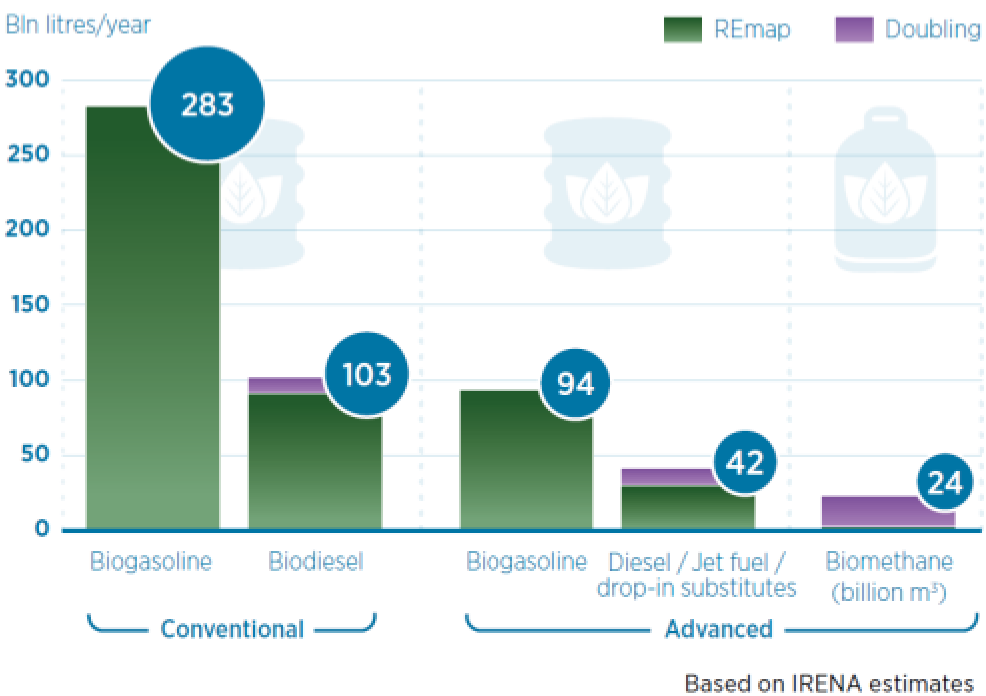


- BC is incorporated into olefins, aromatics (mix of ^{12}C and ^{13}C mass peaks) from FCC with zeolites; no BC incorporation into alkanes
- Pure ^{13}C-labeled BC biomarkers identified (possible refinery use)
- $\delta^{13}C$ BC measurement also measure BC - correlates with ^{14}C analysis
- *Green Chem*. article in review

4 - Relevance: Potential Impact of FCC Co-Processing

	United States	Global
FCC Processing Capacity (Bbl / Day)	6.0 Million	14.6 Million
Biofuels at 5 Wt% Pyrolysis Oil (B-GGE / Year)	1.0 – 2.8	2.4 – 6.8
Biofuels at 10 Wt% Pyrolysis Oil (B-GGE / Year)	2.0 – 4.4	4.9 – 10.7
Biofuels at 20 Wt% Pyrolysis Oil (B-GGE / Year)	5.0 – 6.3	12.1 – 15.2

IRENA Renewable Energy Roadmap 2016



Potential for **10+ Billion Gallons (GE) (40 B-Liters) biofuels per year** with 10% pyrolysis oil in FCCs.

4 - Relevance

Facilitating refiner adoption of co-processed biogenic hydrocarbon fuels via catalyst and co-processing development for FCC and HT/HC can produce biogenic transportation fuels in the near term by leveraging Billions of US$ (Capex)

- Project directly supports BETO's mission to transform biomass into refinery integrable biofuels

- Co-processing that may achieve BETO's 2022 goal of a $3/GGE range fuel production cost

- Project addresses a critical need for conversion enabling technology development using the existing refinery infrastructure - no CAPEX required

- Project outcomes are transferrable to refiners:
  - ➢ Refinery compatible FCC, HT/HC bio-oil conversion catalysts
  - ➢ Co-processing conditions
  - ➢ Accurate BC measurement for RINs, refinery on-line analysis

5 - Future Work

Plan (FCC and HT/HC)

- FCC: Understand bio-oil chemistry on co-processing (blend level, oxygenate content/type, feeding behavior, catalyst performance, yield, product composition and biogenic C content)
- HT/HC: Understand co-processing chemistry and catalyst (blend level, impact of heteroatoms, catalyst performance, product quality, biogenic C content, reaction kinetics, and catalyst composition-performance correlation)

Milestones

- Develop/evaluate catalysts for bio-oil/bio crude conversion; understand chemistry
- Validate accurate BC measurement in co-processed fuels
- Assess cost by TEA/LCA analyses for each pathway
- Leverage final IAB meeting to hold industry workshop at project completion

Go/No Go Decision (2.28.19)

Assess co-processing FCC and HT options that: maximize BC content in fuels to achieve a 50% BC incorporation at blend levels of 5 to 20%

Summary

Overview

The adoption of co-processing biomass derived feedstocks with petroleum feedstocks in current refineries is being advanced through FCC, HT/HC process development, refinery compatible catalyst development and accurate measurement of biogenic C in finished fuels

Approach

Develop co-processing bio-oils/biocrudes via FCC and HT/HC using modified commercial catalysts, tracking and measuring biogenic C incorporation in fuels, and assessing process data for cost via TEA

Technical Progress

- FCC and HT/HC co-processing baselines established:
  - 10wt% CFP oil/VGO FCC co-processed to fuel with 2-3wt% biogenic C; US patent filed
  - 5-20wt% CFP oil/VGO HC co-processed to fuel: 90% bio oil incorporation
- ^{13}C tracer studies show where biogenic C incorporates in fuels (olefins, aromatics, coke)
- $\delta^{13}C$ BC analysis correlates with radiocarbon ^{14}C analysis of fuels

Summary

Relevance

Project supports BETO/ADOs goals to facilitate refiner adoption of co-processed biogenic hydrocarbon fuels via catalyst and co-processing development for FCC and HT/HC that, if successful, will produce biogenic transportation fuels in the near term at or < $3.00/GGE in 2020

Future Work

- Develop FCC, HT/HC co-processing (blend level, yields, ≥ 5wt% BC incorporation); understand impacts on CP chemistry
- Develop/characterize co-processing catalysts (performance, deactivation, chemistry)
- Track biogenic carbon reporting during co-processing, measure BC in fuels
- Assess process cost via TEA, LCA

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Mike Watson, Andrew Heavers (Johnson Matthey)
Larry Doyle, Chris Brown, Sean Murray (Zeton)
Kevin Stup (Vacuum Analytics)

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Additional Slides

Publications, Patents, Presentations, Awards, and Commercialization

Publications

1.Calvin Mukarakate, Kellene Orton, Stefano Dell'Orco, Robert Baldwin, and Kim Magrini, "Isotopic Studies for Tracking Biogenic Carbon during Coprocessing of Biomass and VGO", in review *Green Chemistry* January 2019.

2.A. S. Stanton, K. Iisa, M. M. Yung, K. A. Magrini, "Catalytic fast pyrolysis with metal-modified ZSM-5 catalyst in inert and hydrogen atmospheres*", J. of Analytical and Applied Pyrolysis* 2018, https://doi.org/10.1016/j.jaap.2018.09.002.

3. J. Olstad, M. Jarvis, K. Magrini, Y. Parent, S. Deutch, M. Sprague, Catalytic Upgrading of Biomass Pyrolysis Oxygenates using a Davison Circulating Riser Reactor, in review at *Energy and Fuels*, Energy Fuels 2018, 32, 2, 1733-1743.

4.A. K. Starace, B. A. Black, D. D. Lee, E. C. Palmiotti, K. A. Orton, W. E. Michener, J. ten Dam, M. J. Watson, G.T. Beckham, K. A. Magrini and C. Mukarakate, "Characterization and Catalytic Upgrading of Aqueous Stream Carbon from Catalytic Fast Pyrolysis of Biomass", *ACS Sustainable Chem. Eng*. (October 23) 2017, 5, 11761.

Milestone Reports

Zhenghua Li, C. Mukarakate, K. Orton, K. Magrini, "Determine Biogenic Carbon Content in Co-Processed Fuels: Demonstrate that biogenic carbon in co-processed fuels can be determined by two methods: biomarker analysis from conventional analyses (2D GCxGC TOFS, 31P and 13C NMR, py-MBMS) and radiotracer analysis using ^{13}C and ^{14}C methods provided by LANL. The radiotracer analysis will be conducted jointly with the SCR task and biomarker analytical results will be shared for joint use", BETO ADO Milestone Completion Report, September 30, 2018.

C. Mukarakate, K. Orton, K. Magrini and Zhenghua Li , "Complete biogenic carbon tracking in co-processed products: LANL will evaluate the $^{13}C/^{12}1C$ carbon ratio method for tracking biogenic carbon in products from 1) FCC co-processing of VGO and at least one bio-oil or bio-crude from NREL; and 2) HT co-processing of VGO and at least one bio-oil or bio-crude from PNNL", BETO ADO Milestone Completion Report, June 30, 2018.

K. Magrini, C. Mukarakate, and H. Wang, "Baseline co-processing yields are established: Process data will be given to the analysis team for preliminary TEA/LCA analysis, and to the steering committee to measure progress towards initial targets (carbon efficiency, oxygenate content and type, biogenic carbon incorporation, conversion cost, and GHG reduction) and identify any additional critical data gaps to set process targets for FY19", BETO ADO Milestone Completion Report, September 30, 2018.

Publications, Patents, Presentations, Awards, and Commercialization

Intellectual Property

"SYSTEMS AND METHODS FOR PRODUCING FUEL INTERMEDIATES", USPTO No. 15/952,857, K. Magrini, Y. Parent, J. Olstad, M. Jarvis, April 17, 2018.

K. Magrini, C. Mukarakate, D. Robichaud, "Co-Processing Plastics with bio-oils to Produce Fuels and Chemicals", NREL Record of Invention (ROI-18-133), filed September 2018.

K. Magrini, B. Peterson, C. Engtrakul, "Catalytic Hot Gas Filtration System: Filters and Catalysts for Catalysts for Alkylating Biomass Vapors for Fuel Production", NREL Record of Invention (ROI-18-) filed October 4, 2018.

Commercialization

NREL/Johnson Matthey CRADA to develop refinery compatible biomass conversion catalysts

Business Development

K. Magrini and H. Wang (PNNL), "Catalyst Development for Co-Processing Biomass Derived Liquids in Refineries" BETO FY19 AOP MR Full Application funded in August 2018 for $1.1M in FY19.

B. Baldwin et al., CEC Proposal awarded, "NOTICE OF PROPOSED AWARD (NOPA) Renewable Intermediate Fuel Production for Jet Fuel in Heavy - Duty Transportation Sector", Grant Solicitation GFO-17-901, November 28, 2017. $1M to NREL for thermochemical conversion work to start in late FY19.

Presentations

D.M. Santosa, I. Kutnyakov, H. Wang, Catalytic Hydrotreating of Fast Pyrolysis and Catalytic Fast Pyrolysis Bio-oil from Woody Biomass, 2018 AIChE Annual Meeting, Pittsburgh, PA, October 28, 2018.

K. Magrini, B. Baldwin, C. Mukarakate, "Co-Processing CFP Oils with VGO using A Davison Circulating Riser System", presentation to the SCR Industrial advisory Board, October 18, 2018, Sacramento, CA.

K. Magrini, J. Olstad, M. Jarvis, B. Peterson, Y. Parent, K. Iisa, S. Deutch, "Upgrading Biomass Pyrolysis Vapors to Fungible Hydrocarbon Fuels"", TCS 2018, October 8-10, 2018, Auburn, AL.

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Jessica Olstad, Braden Peterson, Kim Magrini, and Yves Parent "Ex-situ catalytic upgrading of pyrolysis vapors over ZSM-5 and Ga-modified ZSM-5 catalysts", TCS 2018, October 8-10, 2018, Auburn, AL.

K. Magrini, J. Olstad, M. Jarvis, Y. Parent, S. Deutch, "Upgrading Biomass Pyrolysis Vapors to Hydrocarbon Fuels and Chemicals", invited talk and member of the organizing committee - the 9th World Congress on Green Chemistry and Technology, September 17-19, 2018 Amsterdam, Netherlands. (not presented due to reduced funding)

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K. Magrini, J. Olstad, M. Jarvis, Y. Parent, B. Peterson, S. Deutch, K. Iisa "Upgrading Biomass Pyrolysis Vapors to Fuels", oral presentation RESRB, June 18-20, 2018, Brussels, Belgium.

K. K. Magrini, M. Jarvis, J. Olstad, Y. Parent, M. Yung, K. Iisa, S. Deutch, M. Sprague, G. Powell, "Upgrading Biomass Pyrolysis Vapors to Fungible Hydrocarbon Intermediates" accepted for oral presentation at the 26th European Biomass Conference, May 14-18, Copenhagen, Denmark. (not presented due to reduced funding)

K. Magrini, B. Baldwin, H. Wang, C. Drennan, Z. Li, "Strategies for Co-processing in Refineries (SCR)", presentation to the SCR Industrial advisory Board, March 28, 2018, Denver, CO.

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K. Magrini, J. Olstad, M. Jarvis, Y. Parent, B. Peterson, S. Deutch, K. Iisa, M. Sprague, G. Powell, "Upgrading Biomass Pyrolysis Vapors to Fungible Hydrocarbon Intermediates", Exxon Mobil CRADA Meeting, November 9, 2017, Denver. CO.

Project Scope Change Table – Not Applicable

Risk Table

Name	Classification	Description	Mitigation Plan	Probability	Severity	Date
Products from co-processing contain high levels of problematic/refractory oxygenates	Scope, cost	High levels of oxygen in fuels blendstocks	Change co-processing conditions, blend level, catalysts	Med	High	9/30/2019
Biogenic carbon efficiency low (<2%) for preferred pathways	Scope, cost	Excessive carbon loss to CO/CO_2 and coke	Change catalysts; Change catalyst and/or blend ratio	Med	Med	9/30/2019
Hydrogen consumption high for preferred pathways (HT only)	Scope, cost	Excessive hydrogen going to light gases and saturating aromatics	Modify catalyst and/or change reactions conditions	Med	Med	9/30/2019
Severe catalyst poisoning by alkali and alkaline earth metals and/or char	Scope, cost	Catalyst deactivation by mineral and other contaminants	Addressed by changing the blend level and by employing bio-oils that have been improved by hot-gas filtration (FP and CFP) and by washing or acid treating HTL products to remove contaminants.	High	High	9/30/2019
Cost of unsupported catalyst too high (HT)	Scope, cost	Unsupported catalyst too expensive to demonstrate economic benefit (HT)	Rescope task focus to develop hydrocracking catalyst to maximize middle distillates production	Moderate	Moderate	12/31/2019

Petrobras Co-Processing Results

2014-2017

Petrobras/NREL FCC Co-Processing Data

Petrobras "SIX" demo unit has same hardware as a commercial FCC

- Feed nozzles
- Riser cyclone
- Packed stripper
- Heat balanced
- Mass flowrate: 200 kg/h
- Riser: L=18 m, d= 2"

Co-Processing Experiments

- Two pine-derived pyrolysis oils with consistent physical properties
- Mass balance range of 96 – 100%
- 3-hour test runs
- Cumulative time w/ py-oil > 400 hours
- Up to 20 wt% pyrolysis oil in FCC feed
- 54 experimental data points

Fuel Processing Technology 131 (2015) 159-166

Co-processing raw bio-oil and gasoil in an FCC Unit

Andrea de Rezende Pinho [a,*], Marlon B.B. de Almeida [a], Fabio Leal Mendes [a], Vitor Loureiro Ximenes [a], Luiz Carlos Casavechia [b]

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Fuel 188 (2017) 462-473

Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production

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Petrobras/NREL FCC Co-Processing Outcomes

- Up to 10 wt% of FP bio-oils can be co-fed with VGO with 2-3 wt% biogenic carbon captured in produced gasoline
- Feeding bio-oils at > 10 wt% negatively impacted both process and product
  - Due to the high oxygenate content of the bio-oil (50% oxygen), ***although the associated composition and relevant chemistry has not been determined***
- TEA of the Petrobras results showed that:
  - ***FCC co-processing can reduce the overall costs of biofuels production*** for both target and state of technology (SOT) scenarios relative to the full pathway minimum fuel selling price (MFSP)
  - ***Bio-oil producers and petroleum refiners have opportunities to realize shared profitability***, beyond the 10% IRR assumed for the MSP calculations, for co-processing when crude oil prices are as low as $65 per barrel co processing FP oils without policy credits

Co-Processing Biogenic Feedstocks: An Emerging Technology

- Significant data gaps still exist for FCC co-processing
  - Blends of VGO with raw, catalytic and hydrotreated pyrolysis oil reported
- Co-processing bio-oil/bio-crude in other processes, such as hydrocracking/hydrotreating (HC/HT), remain largely unexplored
  - Mostly related to co-processing with vegetable-derived oils

Currently Identified Bio-Oil Intermediates*

Bio-intermediates	# Properties Found	CHNOS	Density	Viscosity	TAN	Composition	Co-processing data		# Independent Sources	HDO Data
							FCCU	HCK		
Algae HTL	5	√	√	√	√	GC/MS			3	√
Algal LE	2	√				% acids, triglycerides			1	
Wood HTL	5	√	√	√	√	SimDis			3	√
Stover HTL	4	√	√	√	√				1	√
HYP	4	√	√		√	GC/MS, SimDis			3	√
CPO	5	√	√	√	√	GC/MS	√		14	√
HDO (partial)	5	√	√	√	√	GC/MS,SimDis	√		4	√
Biological Conv	4	√	√	√		SimDis			1	

HTL=hydrothermal liquefaction; LE= lipid extracted; HYP=hydropyrolysis; CPO=catalytic pyrolysis; HDO=hydrodeoxygenation

Ongoing Industrial Activities

- UOP/Andeavor (Tesoro)/Ensyn Commercial Demonstration
  - Co-processing Ensyn bio-oil in FCC at Andeavor's Martinez CA refinery
  - Preliminary run planned for2019 at low blend level (c.a. 1 vol%)
    - Test feeding system (UOP design)
    - Validate maintenance of catalyst activity
  - Demonstration run planned for 2019 at Martinez
    - Higher blend level (c.a. 5%)
    - Support from NREL (yield/mass balance calculations) and PNNL (LCA)
- CARB rolling out guidelines for LCFS credits for co-processing of bio-oil and other renewable oils in refinery unit operations
    - Co-processing in FCC and HT both initially included
    - NREL & PNNL have strong advisory role to CARB on co-processing
- CEC grant to NREL for co-processing route to bio-jet

Critical Research Needs for Co-processing (HT/FCC)

- Minimal studies to date on co-processing via either pathway
- Preliminary TEA shows co-processing via FCC and HC/HT is economically viable
- Significant gaps exist
  - Impact of organic oxygenates on:
    - FCC and HC/HT chemistry and reaction kinetics
    - Fuel product quality determined by comprehensive compositional analysis and fuel property testing
    - FCC or HC/HT catalysts and equipment
  - Impacts:
  - Of fossil feedstock composition variation on process yields and operations when blended with bio-derived intermediates
  - Of using fossil feedstocks beyond VGO
  - Of CO, CO_2, and H_2O on refinery operation
  - Biogenic carbon tracking