

BETO 2021 Peer Review:

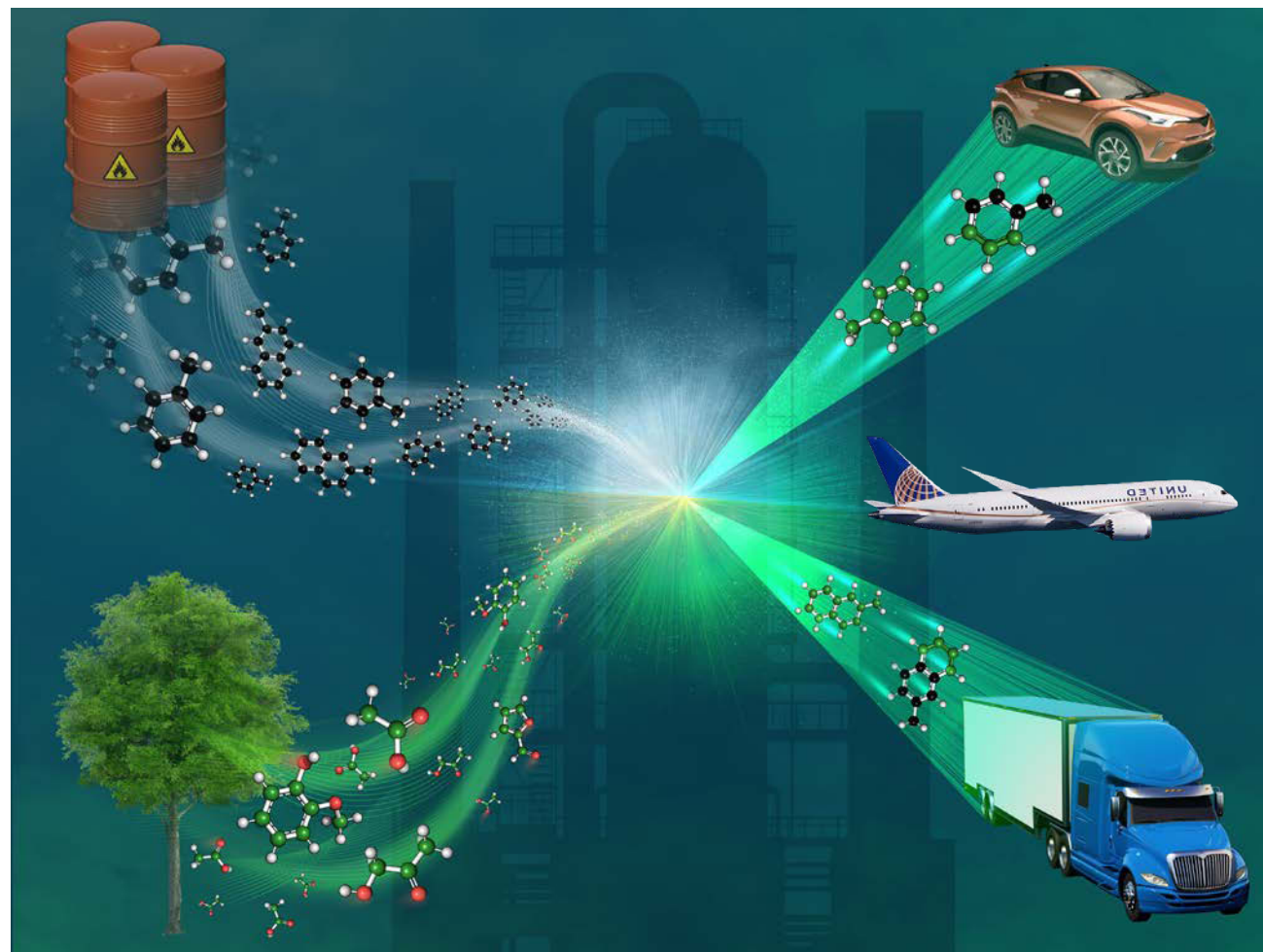
Co-Processing Bio-Oils in Refineries

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NREL, PNNL, LANL

SDI Project Peer Review
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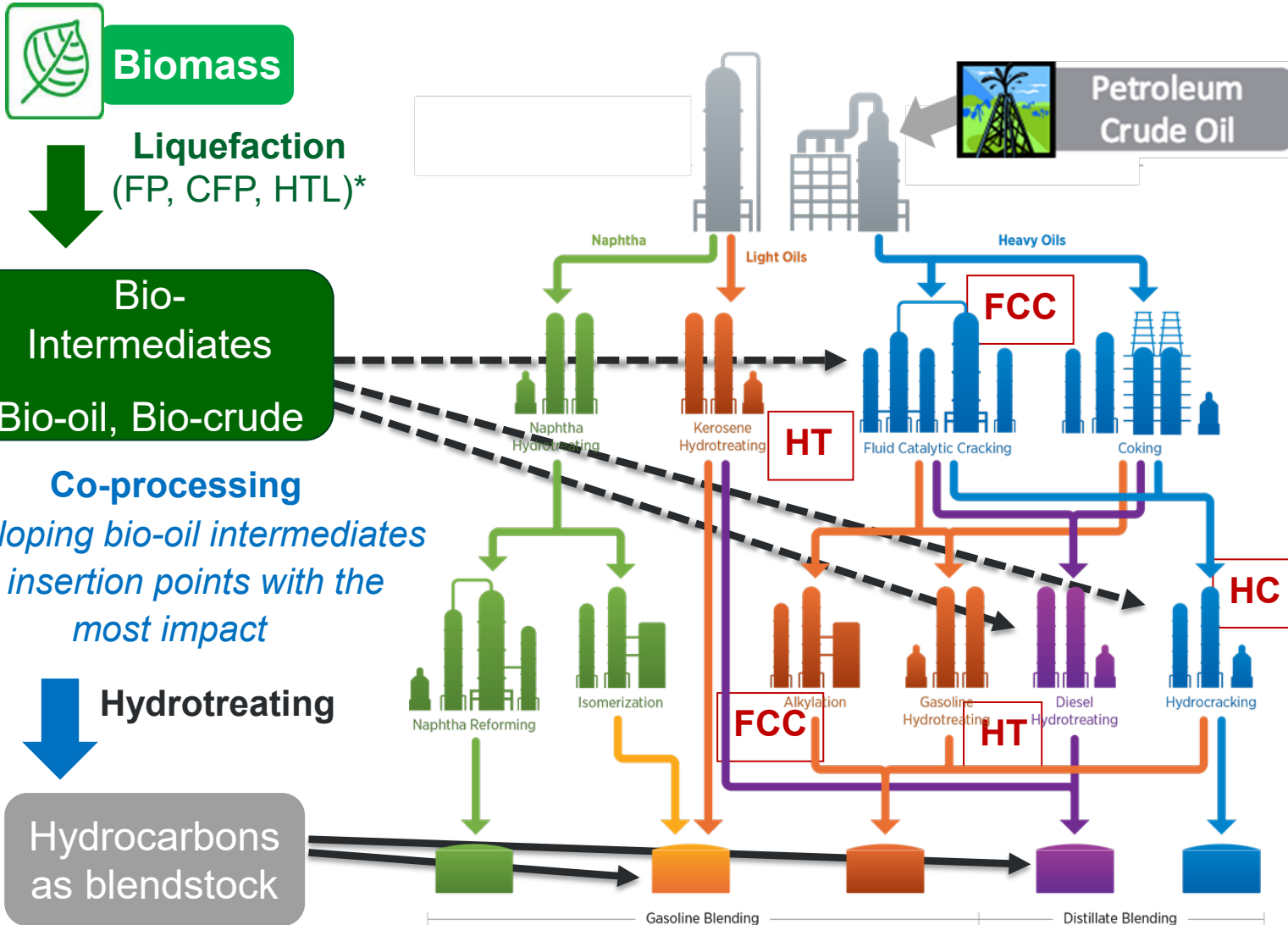
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Cover art by NREL in *ACS Sustainable Chem. Eng.* 2020, 8, 2652–2664.

Project Overview

Leveraging existing refining infrastructure leverages billions US\$ in CAPEX and 5 million bpd of crude refining



* FP: Fast pyrolysis oil
CFP: Catalytic fast pyrolysis oil
HTL: Hydrothermally liquefied bio crude

Objective: Accelerate adoption of co-processing (CP) biomass-derived feedstocks with petroleum streams in operating petroleum refineries to produce biogenic carbon (BC) containing fuels

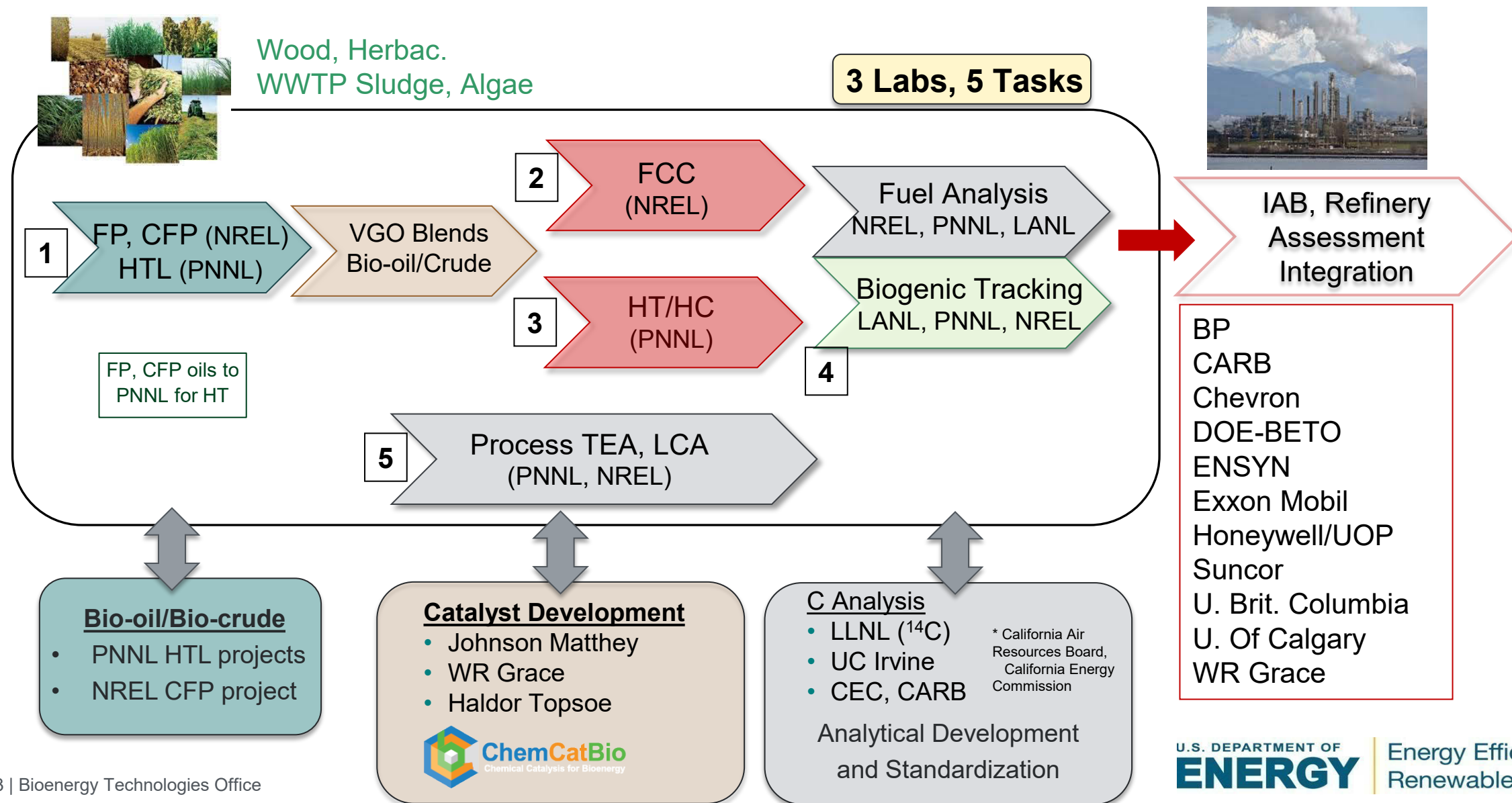
Outcome:

- Foundational data for de-risking co-processing
- Co-processing strategies to refiners
- Tools for biogenic carbon tracking

Impact: Faster introduction of renewable fuels into the transportation sector to reduce GHG by 2025

1 – Management

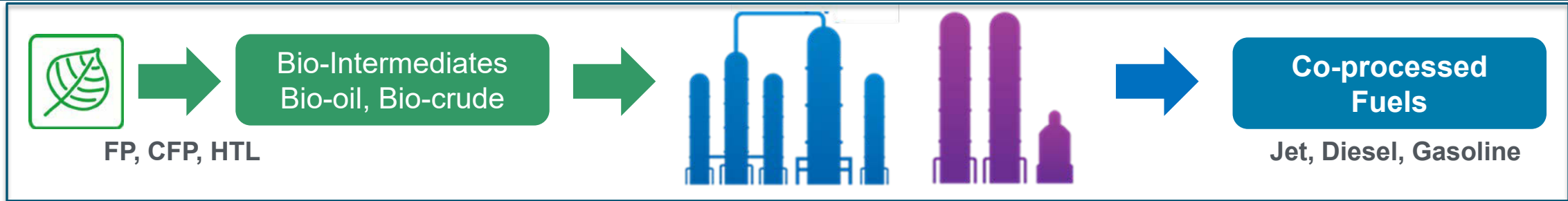
An interdisciplinary and collaborative effort



FP, CFP oils to PNNL for HT

1 - Management

Significant knowledge gaps for co-processing requires extensive R&D



Knowledge Gaps

Can bio-oil/crude feed quality, consistency be controlled?

How can biogenic C incorporation into fuels be maximized?

Is biogenic C tracking and fuel content analysis deployable?

If Successful

Co-processing impact to refinery processes and fuel quality is minimized

Economic and environmental benefits to both refineries and bio-refineries are realized (GHG, RINs)

- Co-processing not currently practiced by refiners (pilot work ENSYN, Petrobras)
- Pilot scale work shows 1-10 wt% bio-oil feed is possible in FCC units
- Bench scale work shows woody and wastewater sludge HTL bio-oil feeds are possible in HT/HC units
- These knowledge gaps identified in collaboration with project's Industrial Advisory Board

1 – Management

Risk management and efficient communication



Project Management

- Monthly virtual meetings (LANL, PNNL, NREL, BETO); team meetings bi-weekly
- Process data, sample analysis, bio-oils and catalysts shared with team. Relevant data added to shared database
- Quarterly milestones with explicit technical targets (i.e. ≥ 5 wt% biogenic C in FCC fuels)
- Go/No Go decision 2/2022 identifying and mitigating contaminant risks to process and catalysts
- Bi-annual IAB progress review

Risk Management (Process Driven)

- Catalyst deactivation by inorganics in bio-oil/bio-crudes is a major CP issue: contaminant risk will be evaluated, and mitigation processes developed (hot gas filtration, guard beds) to remove contaminants pre-CP
- Plugging during FCC CP an issue: new nozzle designs and materials are reducing plugging
- Targeted catalyst development to improve BC incorporation and accurate/rapid biogenic carbon measurement underway



2 – Approach

Existing challenges and future work vetted by IAB



Additional research needs vetted by IAB boarding meeting (2.12.2020) incorporated in the FY2021-2023 project plan

Existing challenges:

- A critical **operability risk** comprising long term process stability around catalyst deactivation and plugging during operation



- A **regulatory risk** comprising the need to rapidly measure biogenic carbon and oxygenates in process streams and products

- A **knowledge risk** centered on the lack of co-processing data including feedstock compositions and contaminants, product compositions, reaction kinetics of unique bio-compounds, and associated TEA/LCA

Key Research Areas:

- Quantify biomass contaminant impact to catalyst stability (i.e. K, S)
- Track contaminants in bio-oils/bio-crudes
- Develop deployable biogenic carbon tracking
- Reactor model modification to improve prediction
- Process improvements assessed via TEA/LCA and refinery impact analysis



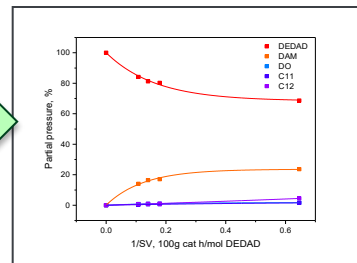
2 – Approach

Developing foundational data and providing co-processing (CP) strategies

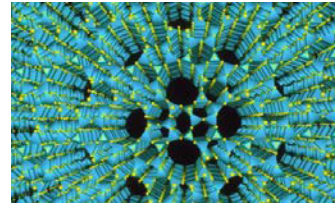


Technical Approach: accelerate adoption of CP biomass-derived feedstocks with petroleum streams in operating petroleum refineries by **developing and publicizing foundational data for processing renewable intermediates and providing co-processing strategies** through:

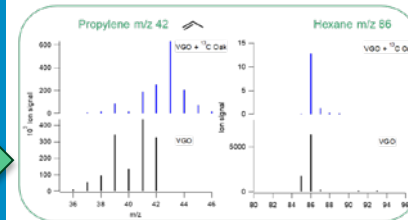
- FCC and HT/HC process development using refinery compatible reactor systems, innovative catalysts, composition tailored bio-oil feeds
- Use model or isotope labeled feeds to determine CP kinetics and mechanisms
- Refinery compatible, novel catalyst development with industrial partners for FCC and HT/HC CP pathways



Johnson Matthey



- Isotope tracking to determine biogenic carbon in products and online biogenic carbon measurement (refiner ask)
- Novel ^{13}C -labelled biomass CP to track biogenic species through CP and in fuels
- Searchable database of feedstock, process conditions and product compositions for refiner use
- Technoeconomic analysis and lifecycle analysis to assess process cost and GHG impact



3 – Impact

Leveraging billions of US\$ (CAPEX) in 136 US refineries processing 5 million gallons of crude/day

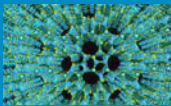


Facilitating refiner adoption of co-processed biogenic hydrocarbon fuels via catalyst and co-processing pilot scale development for FCC and HT/HC can produce biogenic transportation fuels in the near term by *using existing refineries*

- Project directly supports BETO's mission to transform biomass into refinery integrable biofuels (jet, diesel, gasoline):
CP TEA for FCC estimates fuel cost of \$3.16/GGE
- Addresses a critical need for conversion enabling technology development using the existing refinery infrastructure - no CAPEX required
- Project metrics/technical targets are defined/vetted by TEA and the IAB
- We work directly with catalyst and instrument manufacturers, refiners:



Project deliverables are transferrable to refiners:

- Refinery compatible FCC, HT/HC bio-oil conversion catalysts developed with industry leaders 
- Refinery co-processing conditions for FCC and Co-HT/HC
- CP nozzles that reduce / eliminate plugging
- Accurate biogenic carbon measurement for RINs and GHG reduction
- On-line biogenic carbon and oxygenate measurement for process feedback and control
- Process kinetic models to predict CP performance

3 – Impact

Leveraging billions of US\$ (CAPEX) in 136 US refineries processing 5 million gallons of crude/day



Key Finding

Tailoring catalyst and process to enable co-processing demonstrated

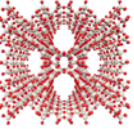
Biogenic C incorporation into fuels via FCC and HT/HC demonstrated

Co-processing database generated for refiner and researcher use

New nozzle materials and design improve bio-oil feeding in FCC CP

Outcome and Impact

- Refinery compatible catalysts being developed with industrial partners and co-processing strategy being established
- *The global refinery catalysts market size expected to grow from USD 4.0 billion in 2020 to USD 4.7 billion by 2025*



- >80% biogenic carbon incorporation into FCC and HT/HC co-processed fuels achieved at bench and small pilot scales with up to 10vol% bio-oil co-feeds
- *At 5M bpd crude refining in the US, 1 refinery can CP 3700 bpd of bio-oil*



- LabKey-based database of bio-oil compositions developed that will be searchable and published, similar to www.crudemonitor.US
- *Potential users are refiners, catalyst manufacturers, researchers*

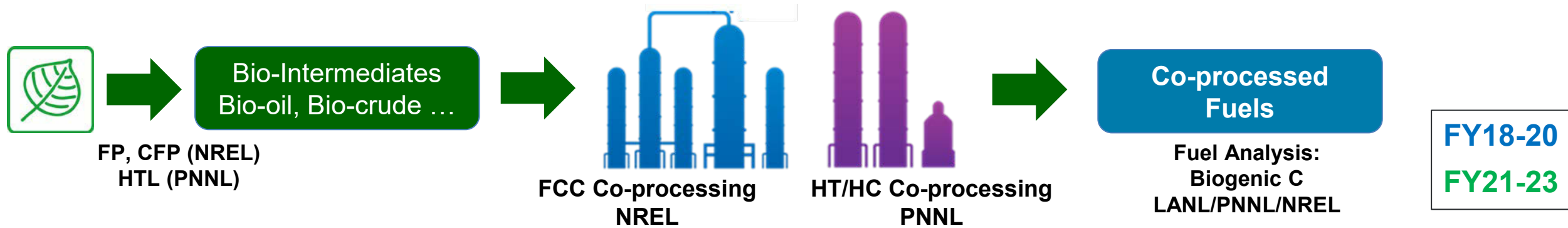


- New nozzle designs and materials reduce plugging during FCC co-processing
- *USPTO Application submitted February 2021 on anti-plugging nozzles*



4 – Progress and Outcome

We are addressing significant challenges for co-processing (5 tasks)



Feed Quality/Consistency

- Bio-oil/crude properties and CP database
- Quantify and track contaminants

Biogenic C incorporation

- Demonstrate significant incorporation of biogenic C by FCC and HT/HC
- Extend to other feed and unit ops

Biogenic carbon tracking

- Further improved isotope methods ($\delta^{13}\text{C}$ and ^{14}C LSC)
- Quick and inexpensive method for precise on-line detection and accurate fuel analysis

Impact to refinery process

- Impact of co-processing to FCC and HT/HC chemistry and kinetics (S, N removal and distillate yield; actual feed and model systems)
- Impact to fuel quality
- Impact to catalyst (lifetime), H_2 consumption, and reactor
- Modified reactor model

Benefit to refinery and bio-refinery

- TEA and refinery impact analysis
- Continuous update and improvement

4 – Progress and Outcome

Joint Database of Process Conditions, Catalysts, Feedstocks, Materials



- Data comprises process, operating, feed and product compositions, BC content per refinery pathway (FCC, HT/HC)
- Similar to petroleum database <http://www.crudemonitor.us/>
- Database is searchable, to be linked with FCIC feedstock database (LabKey), and to be published for refiner use
- Potential users: 136 US refineries, multiple catalyst and instrument manufacturers, research community

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Process

- Fast Pyrolysis
- Catalytic Fast Pyrolysis
- Co-processing (bio-oil and petroleum)
- Hydrotreating
- Hydrothermal liquifaction

Feedstock Type

- Agriculture Residues
- Herbaceous
- Novel Feeds
- Petroleum Feeds
- Waste Streams

Feedstock

- Clean Pine
- Loblolly Pine
- Lodgepole Pine
- Juniper
- Maple

Catalyst

- E-Cat
- ZSM-5
- Metal Oxide
- Unspecified
- Red Mud

Analysis

- OIL: GC x GC / GC-MS
- OIL: Proximate
- OIL: Ultimate
- FEEDSTOCK: Metals
- AQUEOUS: Physical Properties

Organization

- Los Alamos National Laboratory (USA)
- National Hi-Tech Research Program (Chi)
- National Renewable Energy Laboratory
- Pacific Northwest National Laboratory (U)
- RTI International (USA)

Search

Mockup of the final LabKey User Interface for the website of the published database. Potentially link with the FCIC feedstock database.



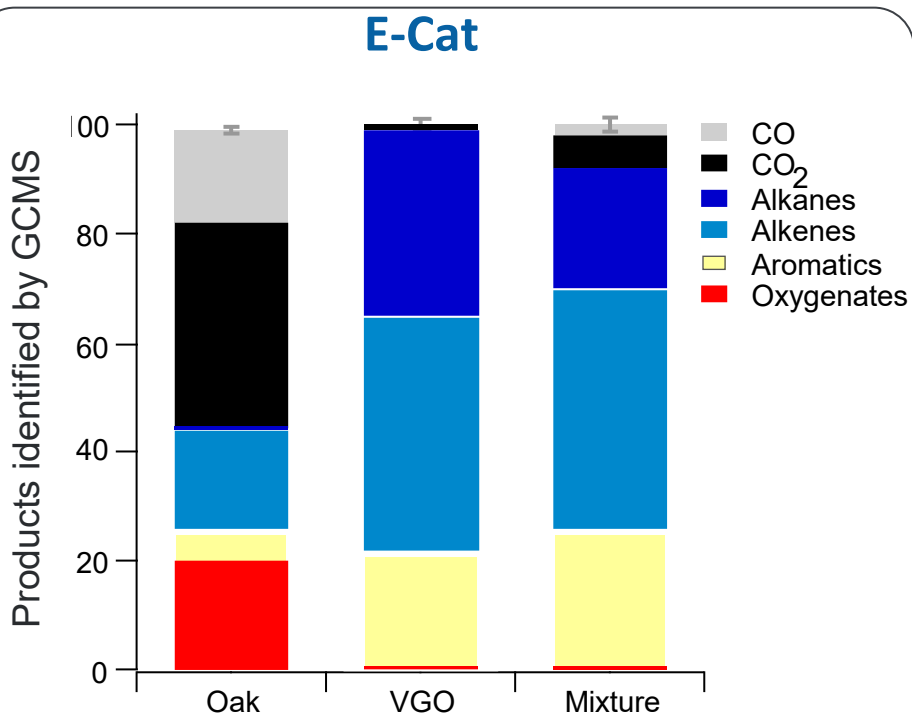
4 – Progress and Outcome

Catalyst impact to fuel chemistry – co-processing in FCC



FCC of VGO, oak or CFPO, and 10% oak—90% VGO mixture over E-Cat and Johnson Matthey CP758 at 550 °C, product analysis with

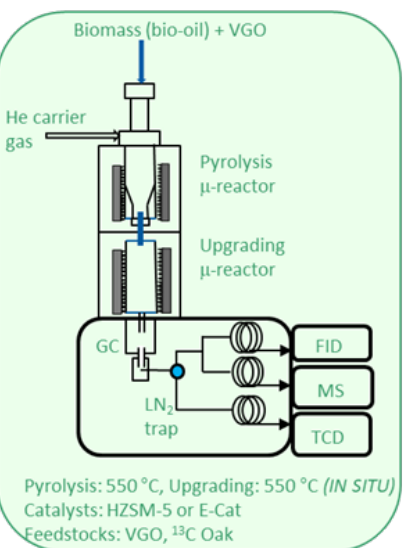
Targeted FCC catalyst development produces bio-oils for varied refinery insertion points



- E-Cat** co-processed product has:
- **Enhanced aromatics**, CO, CO₂
 - Reduced alkanes

Feed	Catalyst	% Bio-based Carbon (%C _{bb})*	(%C _{bb})product/ (%C _{bb})feed	Wt.% coke	Breakthrough h (mass % liq.)
VGO	E-Cat	0.0	NA	2.75	NA
VGO/CFPO	E-Cat	9.7	1.01	1.09	6.03
VGO/CFPO	E-Cat/MFI 5 wt% Mn	7.3	0.76	0.83	5.19
VGO/CFPO	E-Cat/MFI 5 wt% La	9.2	0.96	0.62	0.49
VGO/CFPO	E-Cat/MFI 5 wt% Ca	5.5	0.57	0.68	5.39
VGO/CFPO	E-Cat/MFI no meso	10.4	1.08	2.8	4.25
VGO/CFPO	E-Cat/MFI meso	8.8	0.91	1.1	1.88
VGO/CFPO	E-Cat/HZSM-5	5.4	0.66	0.23	1.80
VGO/CFPO	E-Cat/HZSM-5	5.9	0.72	Nd	2.33

La/MFI and MFI zeolites optimized product %BC, wt% coke, oxygenate breakthrough – to be tested for FCC CP



4 – Progress and Outcome

Impact to chemistry and fuel quality – co-processing in HT/HC



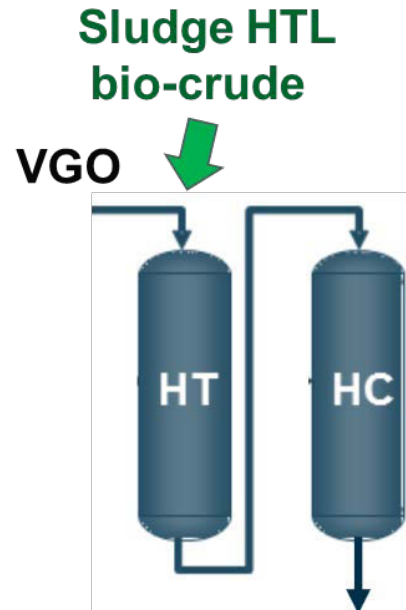
Critical factors in bio-oil/bio-crude properties impacting co-processing chemistry and fuel quality determined, guiding catalyst/process/fuel blending modification in refinery

Competition between heteroatom (S, N, O) removal is critical during co-processing in hydrotreating

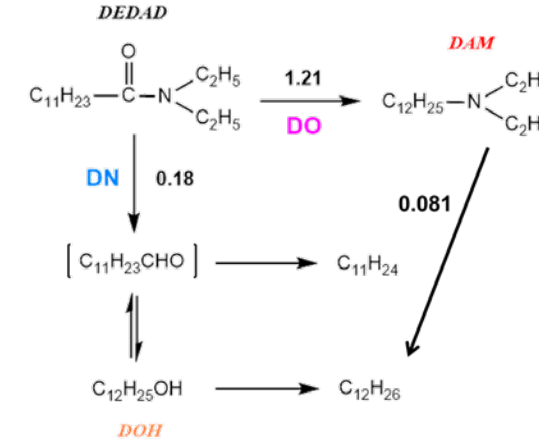
Without co-processing	With co-processing
Diesel (11310 ppm S) + 5% woody CFP bio-oil	
70 ppm S	155 ppm S
VGO (2.5 wt.% S) + 5% sludge HTL bio-crude	
0.05 wt.% S	0.22 wt.%

Stronger inhibition by sludge HTL bio-crude than woody CFP bio-oil because of the high N content of the former

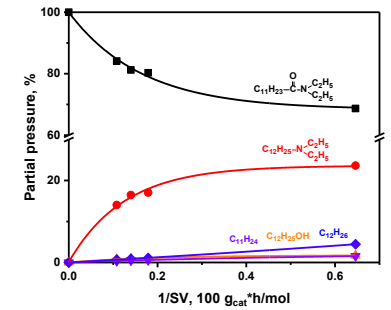
Demonstrated HT pretreatment to mitigate N issues of bio-crude and enable co-processing in HC



Detailed kinetic study of HDN of bio-crude provide guidance on catalyst/parameter selection



Fatty acid amide HDN



Impact on fuel quality determined

- VGO + 6.2% woody CFP bio-oil: diesel cetane 45 to 39.3 ↓
- VGO + 5.7% WW sludge HTL bio-crude: diesel cetane 42 to 47 ↑

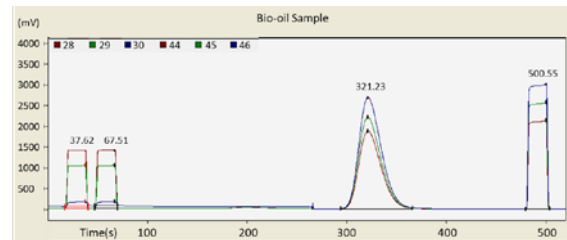
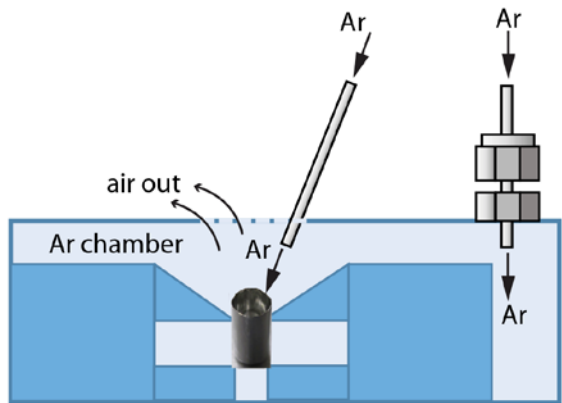
4 – Progress and Outcome

Biogenic carbon tracking method improved

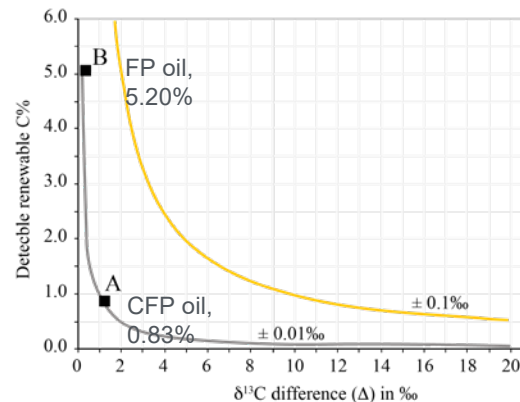
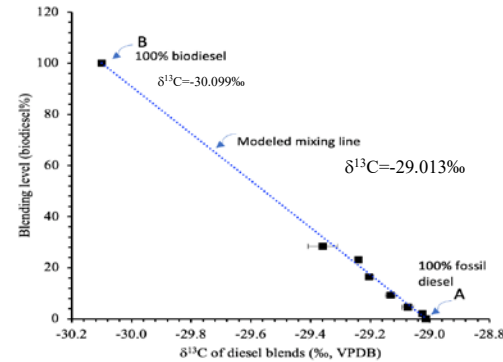


Combing two inexpensive and deployable isotope methods could potentially meet refinery's biogenic carbon analysis requirements

$^{13}\text{C}/^{12}\text{C}$ Ratio Analysis

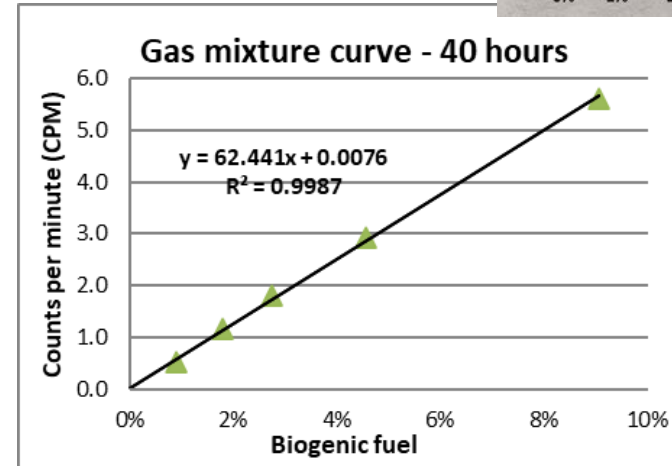
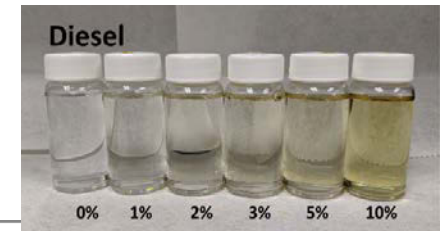


- Developed analytical protocol and algorithm for high-precision analysis of $\delta^{13}\text{C}$ and biogenic carbon content
- Demonstrated $\delta^{13}\text{C}$ analysis can be used for **online tracking biogenic C** in the co-processing



^{14}C LSC (Liquid Scintillation counting)

- Direct LSC method
- Compared over three instruments



- Feasible to accurately determine 1% biogenic carbon in fuel
- Direct LSC could be an option for **quality assurance at co-processing facilities**

4 – Progress and Outcome

High biogenic C incorporation demonstrated



Go/No Go: Both FCC and HT/HC are viable co-processing pathways which meet/exceed the performance target: >50% biogenic carbon incorporation at a blend level 5-20%



Co-processing in FCC

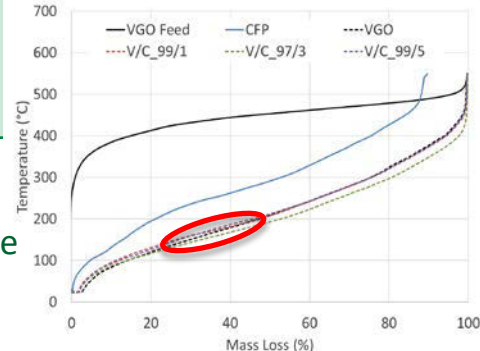
Product ID	VGO (vol %)	CFP Oil (vol %)*	% BC* in CFP Oil	% BC in HC Product
VGO	100	0	0	
V/C_99/1	99	1	0.8	na
V/C_97/3	97	3	3.0	na
V/C_95/5	95	5	3.8	3.1

Rcn. T, P = 520°C, 25 psig; Feed rate = 1.2 liter/h

CP758 Johnson Matthey zeolite catalyst

Pine CFP oil in VGO

* Biogenic carbon measured by ¹⁴C analysis



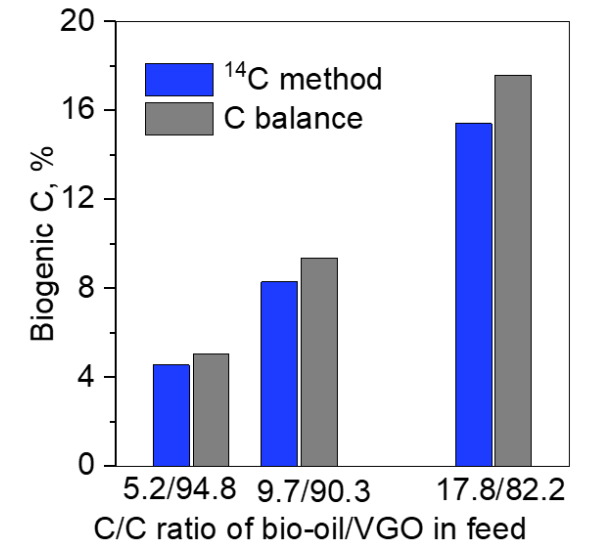
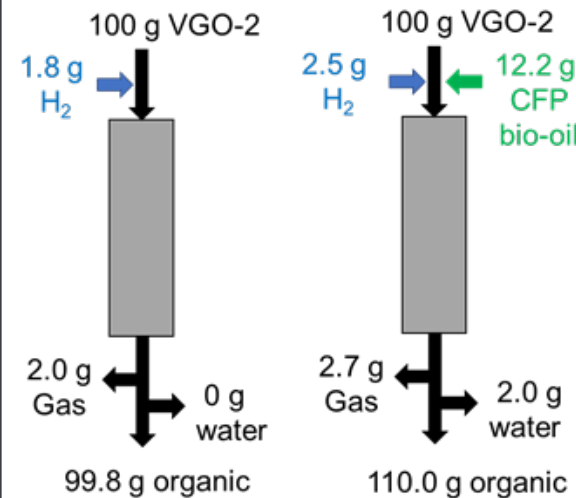
Simulated distillation shows similar BP range (expected at the low CFP concentrations)

>80% biogenic carbon incorporation in fuel products for:

- Woody CFP bio-oils with VGO
- Potential for MSW-derived biomass feedstocks

Co-processing in HT/HC

Woody CFP bio-oil with VGO



>90% biogenic carbon incorporation in fuel products for:

- Woody CFP bio-oils with VGO
- Woody CFP bio-oils with straight run diesel
- Sludge HTL bio-crude with VGO

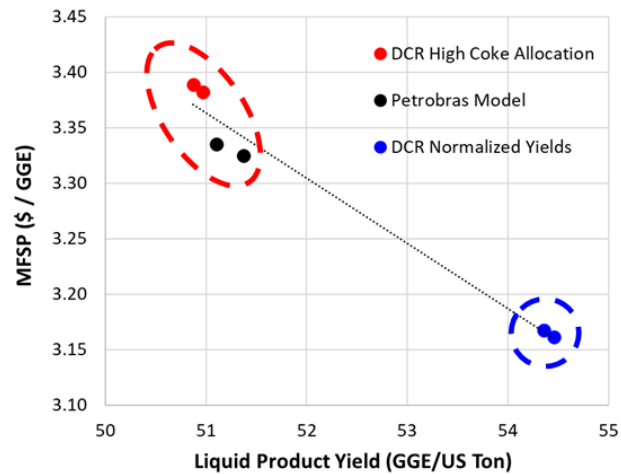
4 – Progress and Outcome

TEA and refinery impact analysis



Preliminary analysis showed co-processing has potential to reduce biomass conversion cost for biorefinery and benefit refinery by profitable feedstock and renewable carbon in fuel product

TEA of FCC Co-Processing Bio-Oils

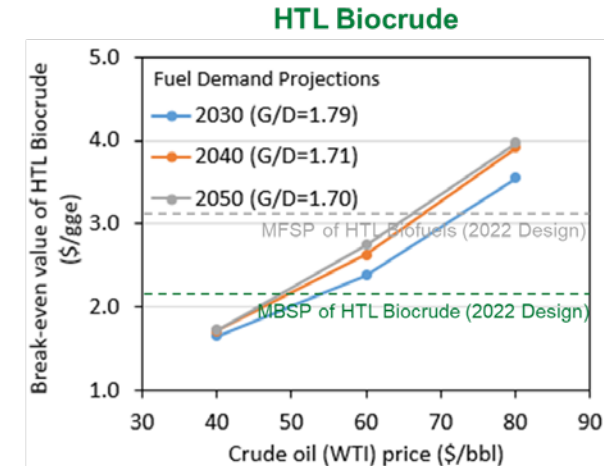


- Co-processing CFP oil with VGO in FCC produces fuel range molecules and co-products with a modeled MFSP as low as \$3.16/GGE (2019 SOT = \$3.33/GGE).

Note: MSFP considers capital and operating costs for co-processing CFP oil to finished blendstocks and recovered co-products. This includes catalyst make-up, plant utilities and hydrogen demands.

Refinery Impact Analysis of Co-Processing Bio-Oil/Bio-crude and VGO at Mild Hydrocracking Unit

- With on-going R&Ds, the modeled **break-even values** of CFP bio-oil and HTL biocrude will be **greater than their modeled MBSPs** at 2022 design cases



- Bio-oil co-processing in FCC experiments show high relative olefins yields (propylene, butylene to alkylate), which help economics and interest from refining industry.
- The break-even values of biomass intermediates depends highly on their potential impacts on petroleum refineries as well as crude oil price and fuel demands
- Current evaluation of break-even values may subject to uncertainties from data gaps in long-term testing, potential impacts of co-processing on catalyst life, operating condition (temperature, H₂ partial pressure, etc.)

Summary



Project Goal

- **Accelerate adoption of co-processing** biomass-derived feedstocks with petroleum streams in operating petroleum refineries to produce biogenic carbon containing fuels

Management

- Addressing **major risks** and efficient **communication**
- **Interdisciplinary and collaborative effort** with three national labs and partners

Approach

- Developing **foundational data** and offering **co-processing strategies**
- Combining **multiple technologies and unique capabilities**
- Progress reviewed and future work vetted by **Industrial Advisory Board**

Impact

- Address a critical need for **biomass conversion enabling technology** development
- Project deliverables are **transferrable to refiners**

Progress and Outcomes

- **High biogenic C incorporation** demonstrated (Go/No Go Passed)
- **Impact to chemistry and fuel quality** determined
- **Biogenic carbon tracking** method improved
- **TEA and refinery impact analysis** shows Benefit to refinery and bio-refinery
- **Joint Database** of Process conditions, catalysts, product compositions

Future Work

- Impact to catalyst stability
- Track Contaminants in bio-oils/bio-crudes
- Biogenic carbon tracking
- Reactor model modification
- TEA/LCA and refinery impact analysis

Quad Chart Overview



Timeline

- Project start date: 10/1/2020
- Project end date: 9/30/2023

	FY20	Active Project (FY21-23)
DOE Funding	1,100 K (NREL) 1,100 K (PNNL) 510 K (LANL)	2,000 K (NREL) 2,050 K (PNNL) 900 K (LANL)

Project Partners*

- Johnson Matthey (catalyst development)
- WR Grace (FCC operations)
- BETO: ChemCatBio, CCPC, ACSC

Barriers addressed

ADO-G: Co-Processing with Petroleum Refineries

ADO-H: Materials Compatibility, and Equipment Design and Optimization

Funding Mechanism

BETO Lab Call 2019

Project Goal

To accelerate adoption of co-processing biomass-derived feedstocks with petroleum streams in current petroleum refineries by developing and broadly disseminating foundational data for processing renewable intermediates, offering co-processing strategies, and accurately measuring biogenic carbon in finished fuels.

End of Project Milestone

The end of project milestone will provide relevant co-processing data for both pathways (FCC, HT/HC) that addresses refiner risk on:

- Catalyst performance and potential deactivation from contaminants carried down in bio-oil/bio-crude feedstocks
- Robust biogenic carbon and oxygenate measurement for RFS determination
- LCA and TEA analyses per pathway
- A comprehensive database of co-processing parameters (catalyst, process conditions, feedstock and product compositions, associated analytical methods) for refiner use.

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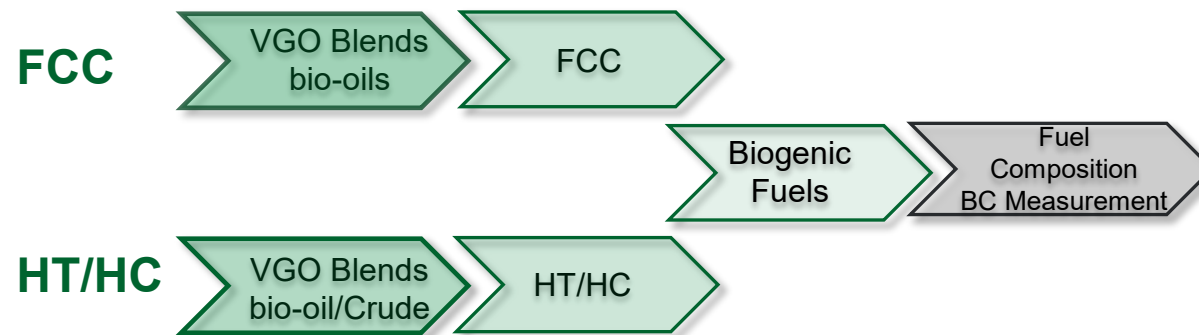


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Project Acronyms and Pathways



- 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
- HT: hydrotreating
- HTL: hydrothermal liquefaction



F2019 Reviewer Comments/Responses

Strength: Good approach - collaboration between fossil and bio-refiners promises to take advantage of the scale of economics achievable in the fossil industry while providing the benefits of bio-sourced carbon to a finished product. Success factors well defined for incorporation of biogenic carbon in transportation fuels.

Challenges of incorporating oxygenates in existing refinery operations well described. Determination of how biogenic carbon reports throughout the refinery is useful for commodization of biogenic carbon. Good industry participation helps ensure efficiency of approach; helping to avoid "dead-ends" of investigation.

Response

We thank the reviewers for their support

F2019 Reviewer Comments/Responses

Weakness: Significant differences in process scale will likely impose higher costs on an established means of transportation fuel production. Goal is NOT production of 'biogenic fuels', but fuels with biogenic' content.

Response

One approach is to ship bio-oils from their production facility to the refiners much as VGO is shipped. This approach may reduce any higher costs associated with bio-oil scale of production. The ENSYN/Tesoro project should generate information on costs associated with bio-oil co-processing. We agree that the terminology should be fuels with biogenic content

F2019 Reviewer Comments/Responses

Weakness: The catalyst development work needs to be carefully thought through. The refineries will not likely change the existing FCC catalyst to blend 5% bio-oil. This FCC and ZSM-5 catalysts have been optimized for the last 50 years and because of huge risk, there will not be any appetite for change. However, bio-oil stabilization for HP/HC routes may benefit from advanced catalysts.

Response:

For FCC catalysts, the changes are minor and include "tweaking" existing HZSM-5 properties to increase bio-oil conversion to be mixed with a refinery equilibrium catalyst. Limited details on the tweaking are discussed because the catalyst development work is being conducted with Johnson Matthey, a major refinery FCC catalyst supplier. Note that baselining FCC co-processing with bio-oils and E-Cat is being done to address the possibility that refiners will not use a modified additive to their preferred catalyst

F2019 Reviewer Comments/Responses

Weakness: Disruption of mature processes and existing operations is bound to increase final cost of production.

Response: A true statement but by using existing infrastructure and de-risking the addition of small amount of bio-oil co-feed, cost impact should be kept to a minimum and offset by RINs.

Additional Slides

Publications, Patents, Presentations, Awards, and Commercialization

Publications

- Stefano Dell'Orco, Earl Christensen, Kristiina Iisa, Anne Starace, Abhijit Dutta, Michael Talmadge, Kim Magrini and Calvin Mukarakate, "On-line Biogenic Carbon Analysis Enables Refineries to Reduce Carbon Footprint during Co-processing Biomass- and Petroleum-derived Liquids", *ACS Analytical Chemistry*, accepted February 15, 2021, ID: ac-2020-041085.R3
- Charles G. Doll, Andrew E. Plymale, Alan Cooper, Igor Kutnyakov, Marie Swita, Teresa Lemmon, Mariefel V. Olarte, Huamin Wang. "Determination of low-level biogenic gasoline, jet fuel, and diesel in blends using the direct liquid scintillation counting method for ^{14}C content". *Fuel*, **2021**, 291, 120084.
- Huamin Wang, Pimphan A. Meyer, Daniel M. Santosa, Cheng Zhu, Mariefel V. Olarte, Susanne Jones, Alan H. Zacher. "Performance and techno-economic evaluations of co-processing residual heavy fraction in bio-oil hydrotreating", *Catalysis Today*, **2020**, Doi: 10.1016/j.cattod.2020.08.035
- Geeza, T.; Li, Z.; Maltsev, O.; Lee, J.; "Carbon Isotope Analysis of Co-Processed Biofuels Using a Continuous-Flow Isotope Ratio Mass Spectrometer," *Energy & Fuels*, **2020**, <https://doi.org/10.1021/acs.energyfuels.0c02114>.
- Zhenghua Li, Huamin Wang, Kimberly Magrini-Bair, James E. Lee, Thomas Geeza, Oleg Maltsev, Jacob Helper. "Quantitative Determination of Biomass-derived Renewable Carbon in Fuels from Co-processing of Bio-oils in Refinery Using a Stable Carbon Isotopic Approach". *ACS Sustainable Chemistry and Engineering*, **2020**, 8, 47, 17565.
- Calvin Mukarakate, Kellene Orton, Yeonjoon Kim, Stefano Dell'Orco, Carrie A. Farberow, Seonah Kim, Michael J. Watson, Robert M. Baldwin, and Kimberly A. Magrini, "Isotopic Studies for Tracking Biogenic Carbon during Co-processing of Biomass and Vacuum Gas Oil", *ACS Sustainable Chem. Eng.* **2020**, 8, 2652–2664.
- Zhenghua Li, Kimberly Magrini-Bair, Huamin Wang, Oleg V. Maltsev, Thomas J. Geeza, Claudia I. Mora, James E. Lee, "Tracking renewable carbon in bio-oil/crude co-processing with VGO through $^{13}\text{C}/^{12}\text{C}$ ratio analysis", *Fuel* 275 (**2020**) 117770.
- Dutta, Abhijit, Iisa, Maarit K, Talmadge, Michael, Mukarakate, Calvin, Griffin, Michael B, Tan, Eric C, Wilson, Nolan, Yung, Matthew M, Nimlos, Mark R, Schaidle, Joshua A, Wang, Huamin, Thorson, Michael, Hartley, Damon, Klinger, Jordan, and Cai, Hao. Ex Situ Catalytic Fast Pyrolysis of Lignocellulosic Biomass to Hydrocarbon Fuels: 2019 State of Technology and Future Research. United States: N. p., **2020**. Web. doi:10.2172/1605092.
- Huamin Wang, Kim Magrini, Zhenghua Li, Co-processing biomass thermal liquefaction bio-oil/bio-crude in refineries, IEA Bioenergy Task 34 PyNe 44 newsletter, July **2019**, http://task34.ieabioenergy.com/wp-content/uploads/2019/07/PyNe44_final.pdf.

Publications, Patents, Presentations, Awards, and Commercialization

Milestone Reports

Q1FY21: Finalize the documents required for a direct funding opportunity (DFO). This project will use a DFO to call for participation of biogenic carbon instrument developers to identify and advance biogenic carbon tracking technology for co-processing application. In Q1, the call for proposal and the language for CRADA will be in place for announcing the DFO in Q2 or Q3. (Task 3, NREL, PNNL, and LANL).

Q4FY20: Document Optimized Co-processing Results for FCC (NREL) and HT/HC Pathways (PNNL)

Q4FY20: Publish free and searchable online database w/physiochemical characterization of relevant oils, fractions and products, and document process relevant data for potential FCC and HC/HT refinery insertion and integration. Steering Committee to serve as reviewers before submission. Final TEA/LCA analysis to be included in the publication.

Q3FY20: HT/HC: Complete determination of the fuel quality for co-processing CFP bio-oil and/or sludge HTL bio-crude with VGO

Q2FY20: Isotopic Biogenic Carbon Determination of Co-processed FCC and HT/HC Fuels

Q2FY20: FCC: Catalyst Evaluation, Down Select and Scale Up for FCC CP Verification (with Johnson Matthey); HT: Catalyst and process parameters for co-processing in two-step HT-HC for sludge bio-crude.

Q1SFY20: Conduct Bi-Annual ISC Face to Face Meeting to Review Progress

Q4FY19: Technoeconomic Analysis of FCC and HT/HC Co-processing Assessed for MFSP (minimum fuel selling price)

Q4Y19: FCC: Develop a catalyst or catalyst combination for co-processing FP or CFP/VGO mixtures that targets $\geq 5\text{wt}\%$ biogenic carbon incorporation efficiency (target olefins). These results will be used to measure improvements in FY2020 catalyst performance for biogenic carbon incorporation and lifetime and documented in a draft for journal article.

Q4FY19: Identify opportunities for reduced coke formation in zeolite catalysts for Catalytic Fast Pyrolysis. (joint with WBS 2.3.1.314)

Q3FY19: Demonstrate improved carbon efficiency for zeolite CFP by recycling tail gas in the DCR using metal-modified zeolite catalysts.

Q3FY19: Biogenic Carbon Determination of Co-processed FCC and HT/HC Fuels

Q3FY19: FCC: Complete Initial Micro Scale Catalyst Screening Tests to Identify Best Co-Processing Performers

Q2FY19: FCC: Establish Catalyst Composition and Morphology to Baseline Co-Processing (post-use) Induced Changes; HT/HC: Establish baseline for kinetic study using model compounds for co-processing with a commercial catalyst.

Publications, Patents, Presentations, Awards, and Commercialization

Milestone Reports

2/28/2019 Go/No-Go: Identify the viable co-processing pathway(s) (i.e., bio-oil type and refinery processing unit) compared with baseline FCC processing of raw bio-oil: Proposed decision metrics (to be finalized with industrial steering committee) include for FCC and HT: maximize biogenic carbon content in distillate products to achieve a 50% biogenic carbon incorporation at a given blend level in the 5 to 20% range. Minimize yield loss. Maintain yields for distillate fuels at no less than 90% of baseline values (maximum 10% yield loss). Data to be generated at the micro- and/or DCR scale for FCC and lab-scale for HT/HC.

Patents

"K. Magrini, P. Peterson, C. Engtrakul, N. Wilson, "CATALYTIC HOT-GAS FILTRATION OF BIOMASS PYROLYSIS VAPORS", US Patent Application No.16/940,190, July 27, 2020.

K. Magrini, J. Olstad, Y. Parent, "SYSTEMS AND METHODS FOR PRODUCING FUEL INTERMEDIATES", US Patent Application No.16/869,101, May 7, 2020.

K. Magrini, M. Sprague, R. Seiser, Z. Abdullah, NREL ROI-20-76 "Feed nozzle designs and materials that reduce/eliminate coking/plugging during co-processing bio-oils with petroleum feedstocks to biogenic hydrocarbon fuels" filed March 23, 2020. USPTO patent application filed February 2021.

Commercialization

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

3-Phase project with Chevron to assess co-processing with their feedstocks and catalysts (200K)

MOU-19-523: K. Magrini and D. Chiaramonte, Memorandum of Understanding finalized with the University of Florence, Florence, IT for developing products from biomass pyrolysis streams. Hosted Stefano Dell'Orco from February-July 2020 for doctoral work in thermochemical biomass conversion.

Publications, Patents, Presentations, Awards, and Commercialization

Presentations

R. Seiser, J. Olstad, K. Magrini, R. Jackson, B. Peterson, E. Christensen, M. Talmadge, A. Dutta, “Co-Processing Catalytic Fast Pyrolysis Oil in an FCC Reactor”, accepted for oral presentation at the European Biomass Conference and Exhibition, April 26-29, 2021, Marseille, FR.

Kim Magrini, Jess Olstad, Brady Peterson, Rebecca Jackson, Yves Parent, “Feedstock and Catalyst Impact on Bio-Oil Production and FCC Co-Processing to Fuels”, accepted for oral presentation at the European Biomass Conference and Exhibition, April 26-29, 2021, Marseille, FR.

Zhu, C.; Santosa, M.; Wang, H.; “Co-processing bio-crudes with petroleum gas oil in hydrotreating: Kinetics of heteroatom removal,” oral presentation, 2020, TCS 2020 virtual meeting.

Yeonjoon Kim, Seonah Kim, Anne Starace, Earl Christensen, Kellene Orton, Calvin Mukarakate, Kim Magrini, Carrie Farberow, “Hydrogen transfer to mitigate phenolic coke formation during co-processing of bio-oil with vacuum gas oil over Y zeolite”, 2020 Thermal & Catalytic Sciences Virtual Symposium (2020 TCS), October 5–7, 2020.

Braden Peterson, Chaiwat Engtrakul, Matthew Coats, Michael Griffin, Jessica Olstad, Yves Parent, Kim Magrini, “ Pyrolysis Vapor and Bio-oil Preconditioning via Ex Situ Hydrodeoxygenation and Alkylation Using a Heteropolyacid Catalyst”, 2020 Thermal & Catalytic Sciences Virtual Symposium (2020 TCS), October 5–7, 2020.

K. Magrini-presenter, J. Olstad, B. Peterson, Y. Parent, M. Sprague, R. Jackson, “SCR Industrial Advisory Board and F2F Meeting: FCC Co-Processing”, February 12, 2019, Richland, WA.

K. Magrini-presenter, J. Olstad, B. Peterson, Y. Parent, S. Deutch, A. Starace, K. Iisa, K. Orton, M. Sprague, M. Watson, L. Tuxworth, “Reactor, Catalyst and Feedstock Considerations for Upgrading Biomass Pyrolysis Vapors and Liquids to Fungible Hydrocarbon Intermediates”, tcbiomassplus 2019, October 8, 2019, Chicago, IL.

Stefano Dell’Orco, Edoardo Miliotti, Nolan Wilson, Andrea Maria Rizzo, Kimberly A. Magrini and David Chiaramonti, “Overcoming scale-up industrial barriers of hydrothermal liquefaction of lignin-rich streams: Carbon recovery from residual aqueous phase”, tcbiomassplus 2019, October 7, 2019, Chicago, IL.

K. Magrini - presenter, Calvin Mukarakate, Kellene Orton, Yeonjoon Kim, Stefano Dell’Orco, Carrie A Farberow, Seonah Kim, Michael J Watson, Robert Baldwin, “Isotopic Studies for Tracking Biogenic Carbon during Co-processing of Biomass and VGO”, tcbiomassplus 2019, October 8, 2019, Chicago, IL.

Braden Peterson, Chaiwat Engtrakul, Nolan Wilson, Stefano Dell’Orco, Jessica Olstad, Mike Sprague, Yves Parent, Kim Magrini, “Preconditioning Pyrolysis Vapors for Downstream Upgrading Processes via Coupled Catalytic Hot-Gas Filtration and Fractional Condensation”, tcbiomassplus 2019, October 6- 8, 2019, Chicago, IL.

Publications, Patents, Presentations, Awards, and Commercialization

Presentations

J. Olstad, B. Peterson, Y. Parent, M. Sprague, K. Magrini, "Co-Processing Catalytic Fast Pyrolysis Oil with Vacuum Gas Oil in a Davison Circulating Riser", tcbiomassplus 2019, October 6- 8, 2019, Chicago, IL.

J. Olstad, "Co-Processing Vacuum Gas Oil and Bio-Oils in a Davison Circulating Riser," ACS 2020 (San Francisco, CA, 8/16-8/20/2020) and TCS2020 (Kennewick, WA, 10/5-10/7/2020).

R. Jackson "Variations in bio-oil characteristics produced from three catalytic fast-pyrolysis systems", TCS 2020 (Kennewick, WA, 10/5-10/7/2020) and ACS 2020 (San Francisco, CA, 8/16-8/20/2020).

Huamin Wang, "Challenges and progress in catalytic hydrotreating of liquefaction intermediates from biomass and waste", ACS Spring 2020 National Meeting.

Huamin Wang, Daniel M. Santosa, Cheng Zhu, Igor Kutnyakov, Matt Flake, "Co-processing bio-crudes with petroleum gas oil in hydrotreating: kinetics of heteroatom removal and incorporation of biogenic carbon in produced fuels". Abstract accepted for oral presentation at International Congress of Catalysis, San Diego, 2020

Huamin Wang, Daniel M. Santosa, Cheng Zhu, Igor Kutnyakov, Matt Flake, "Co-processing bio-oil/bio-crudes with petroleum gas oil in hydrotreating/hydrocracking." ACS 2020 Fall meeting.

Cheng Zhu, Huamin Wang, "Hydrotreating Kinetics of Nitrogen-, Oxygen- and Sulfur-Containing Model Compounds for Co-Processing Biocrude Oils with Vacuum Gas Oil". AIChE 2020 annual meeting.

MOU-19-523: K. Magrini and D. Chiamonte, Memorandum of Understanding finalized with the University of Florence, Florence, IT for developing products from biomass pyrolysis streams.

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.

Huamin Wang, Miki Santosa, Igor Kutnyakov, Matt Flake, Cheng Zhu, Co-processing bio-oil/bio-crude with gas oil in hydrotreating /hydrocracking, TcBiomass plus 2019, Chicago, IL, October 8, 2019.

Huamin Wang, Co-processing bio-oil/bio-crudes in hydrotreating /hydrocracking, 2019 ACS National Meeting, San Diego, CA, August 18, 2019.