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DOE Bioenergy Technologies Office (BETO)
2023 Project Peer Review

Bio-oil Co-processing with Refinery Streams

April 4th, 2023

SDI Project Peer Review

Reinhard Seiser, Huamin Wang, Zhenghua Li

NREL, PNNL, LANL

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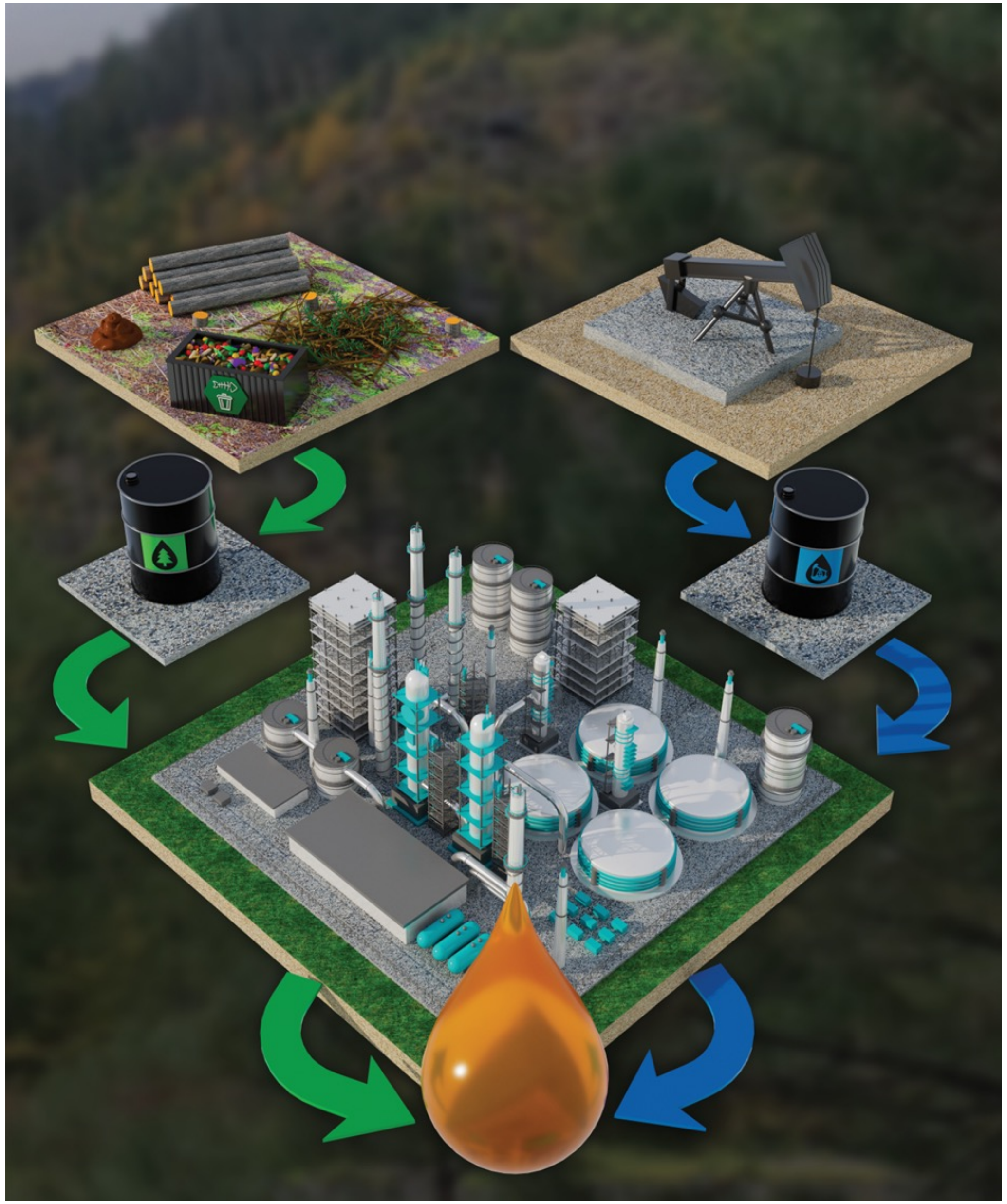


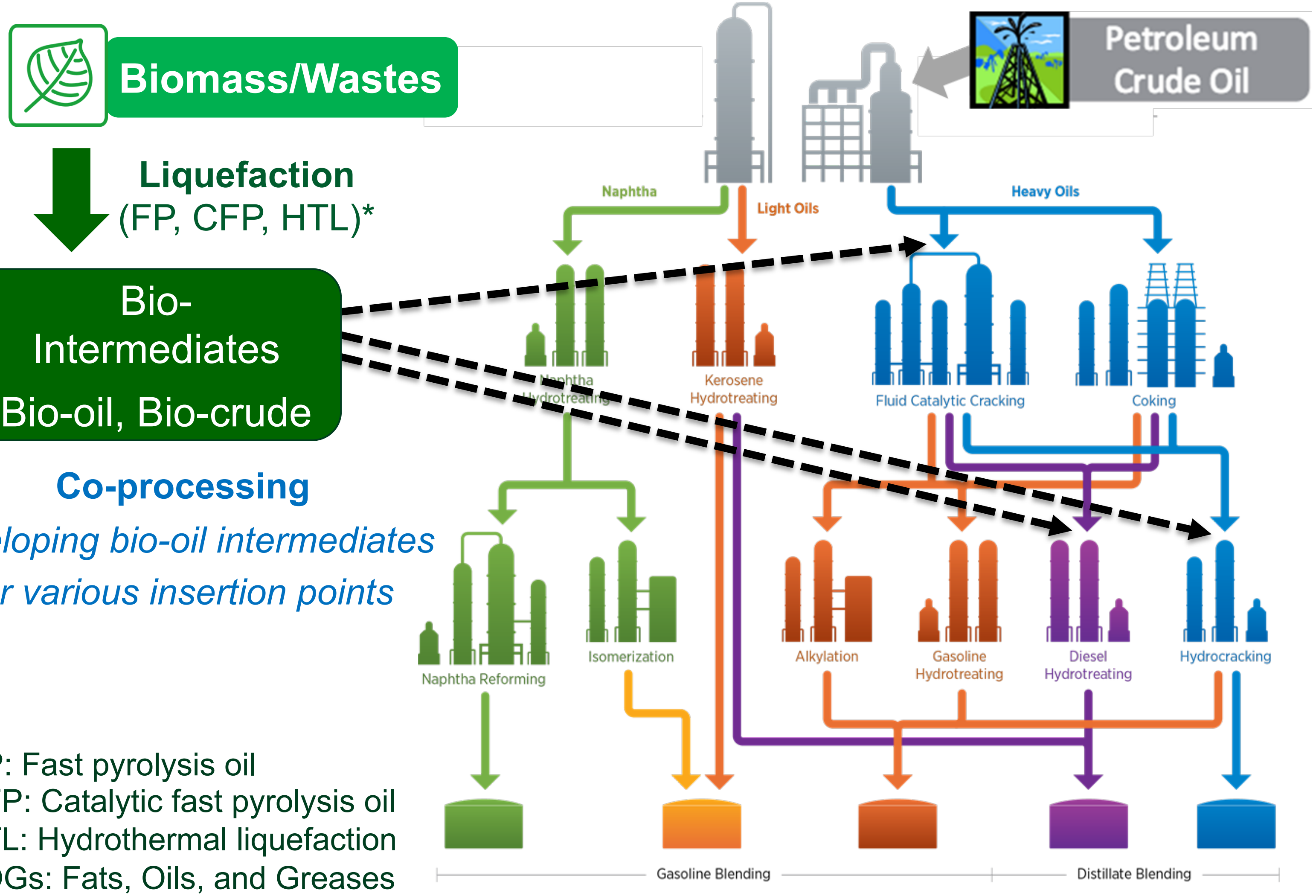
Project Overview

Leveraging Existing Refining Infrastructure for Biogenic Feedstocks

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

Expand from co-processing FOGs (resource < 43 M tons/yr[1])
to lignocellulosic and waste feedstocks (forestry, agriculture, algae, wastes) with a resource of > 1,100 M tons/yr.[2]

Risks: Bio-oils are difficult to co-process due to their molecular structure and non-hydrocarbon constituents.



*FP: Fast pyrolysis oil
CFP: Catalytic fast pyrolysis oil
HTL: Hydrothermal liquefaction
FOGs: Fats, Oils, and Greases

[1] IHS Chem. Econ. Handbook (2021). FOGs Industry Overview
[2] Billion Ton Update (2016)

BETO Goals / State of the Art

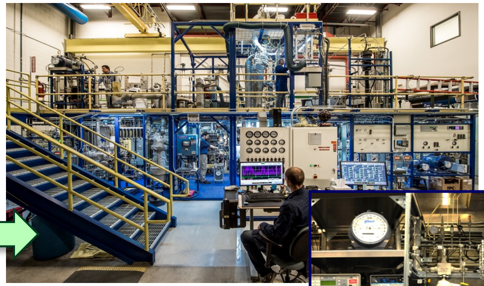
Developing Foundational Data and Providing Co-processing (CP) Strategies

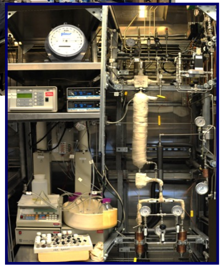
Multi-pronged approach to address BETO goals and innovation

- FCC and HT/HC process development using **refinery compatible reactor systems** of various scales.

- Refinery compatible, **state of the art catalysts** with industrial partners for FCC and HT/HC co-processing pathways.

- **Bio-oil/Bio-crude production** from various feeds with different techniques and composition.





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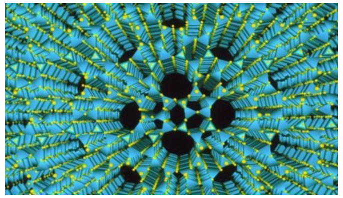

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- **Isotope tracking** to determine biogenic carbon in products and online biogenic carbon measurement (refiner ask).

- Detailed analysis of feeds, products, and catalysts to **determine the influence of biogenic feeds**.

- **Kinetic modeling** of processes such as hydrotreating.

- **Technoeconomic analysis and lifecycle analysis** to assess process cost and GHG impact.

Aspen PIMS

FCC: Fluid Catalytic Cracking; HT: hydrotreating; HC: hydrocracking

Risk Identification and Mitigation Strategies

Existing Challenges:

- A critical ***operability risk*** comprising long term process stability around catalyst deactivation and fouling of feed systems and 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

Mitigation Strategies:

- Quantify biomass contaminant impact to catalyst stability (i.e., K, S, N)
- 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

Management Plan – Communication and Collaboration

Wood, Herbaceous, WWTP Sludge, Algae

5 Tasks across 3 National Labs

1. FP, CFP (NREL) HTL (PNNL)

Bio-oil/Crude VGO Blends

2. FCC (NREL)
3. HT/HC (PNNL)
4. Fuel Analysis (NREL, PNNL) Biogenic Tracking LANL, PNNL, NREL
5. Process TEA, LCA (PNNL, NREL)

Industrial Advisory Board (IAB)

BASF	Kern Energy
BP	Parkland Refinery
BTG	Phillips 66
CARB	Preem
Chevron	Suncor
ENSYN	U. Brit. Columbia
Exxon Mobil	U. Of Calgary
Honeywell/UOP	WR Grace
Johnson Matthey	

DOE-BETO

External Partners
- Johnson Matthey
- Grace
- Topsoe
- Utah State U.

Diversity, Equity, and Inclusion
- Trainings on DEI, hiring, partnerships
- Internships for underrepresented students pursued
- Workshops on Partnerships with Minority Serving Inst.
- LDRD-funded Energy Justice analysis

^{14}C Analysis
- Beta Analytic
- LLNL (^{14}C), UC Irvine
- CEC, CARB*

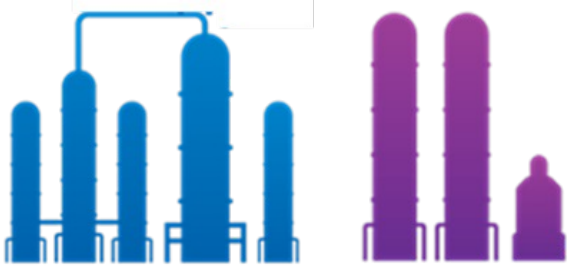
* California Energy Commission California Air Resources Board.

DEI efforts not part of 2021 AOP, but ramped up since 2022.

Progress for Addressing the Co-Processing Project Goals

Bio-Intermediates
Bio-oil, Bio-crude …

FP, CFP (NREL)
HTL (PNNL)



FCC Co-processing
NREL

HT/HC Co-processing
PNNL

Co-processed Fuels

Fuel Analysis:
Biogenic C
LANL/PNNL/NREL

2021 Peer Review

Current

Feed Quality/Consistency

- Measurements on bio-oil/crude properties and liquid products
- Quantified and tracked contaminants

Biogenic C incorporation

- Demonstrate significant incorporation of biogenic C by FCC and HT/HC
- Extended to other feeds, catalysts

Biogenic carbon tracking

- Further improved isotope methods (δ^{13}C and ^{14}C LSC) at reduced costs.
- Improved accuracy and relevance to difficult samples

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
- Determined impact to catalyst (lifetime), H_2 consumption, and reactor
- Modified reactor model based on kinetic measurements

Benefit to refinery and bio-refinery

- TEA and refinery impact analysis
- Provided updated yield data and composition for TEA models

Various CFP Oil Production for Further Co-Processing

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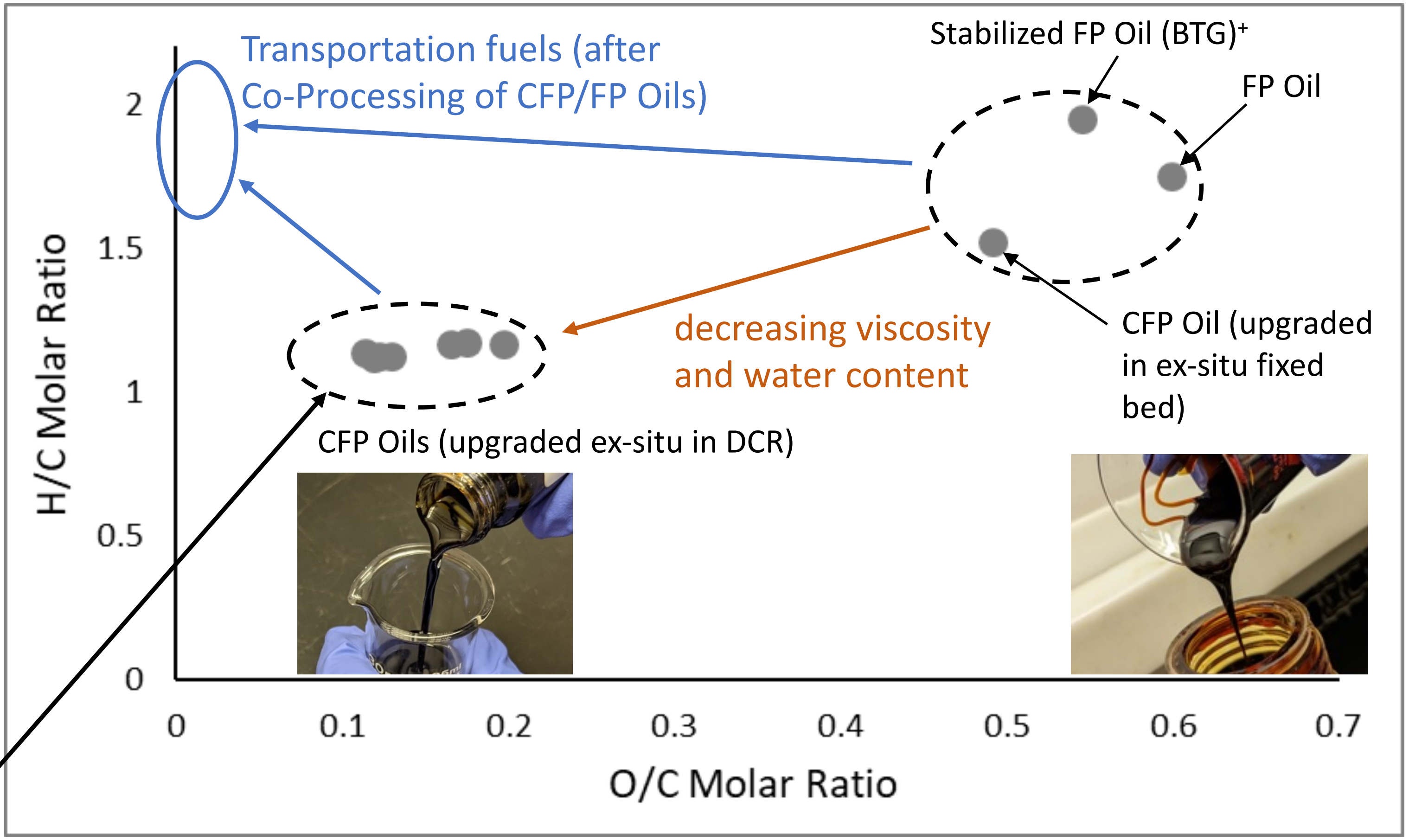
Goal: Produce/acquire a variety of bio-oils for optimizing the properties for co-processing. Properties include oxygen content, moisture, and viscosity.

DCR (Davison Circulating Riser) for upgrading FP vapors without hydrogen using zeolite-based catalysts produces bio-oils with significantly less oxygen.

Woody feedstock (pine) → liquid intermediate (for transport to refineries)



Bio-oils are shown on a wet-basis

Study the impact of different bio-oils on co-processing. Bio-oils with lower O improve storage/transport and compatibility with refinery infrastructure.

Co-Processing of CFP Oils with VGO in FCC

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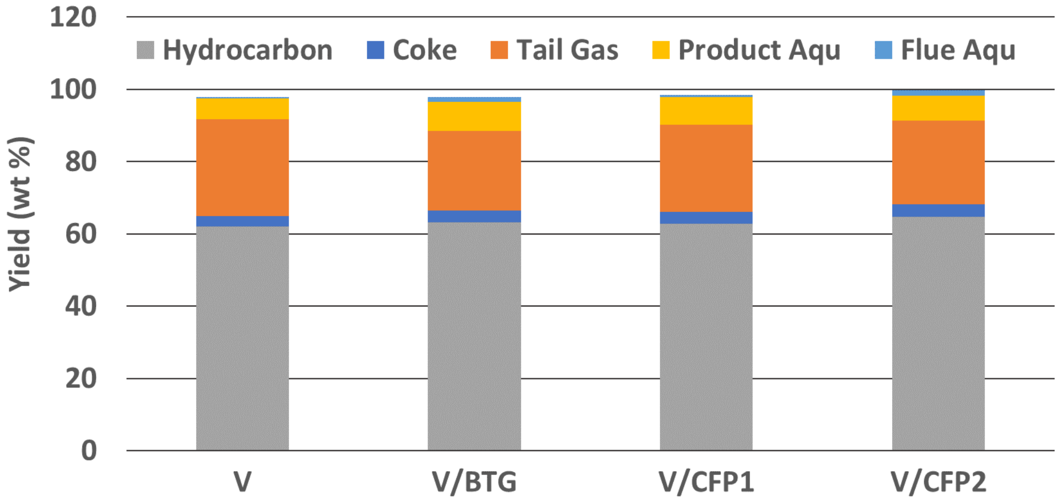
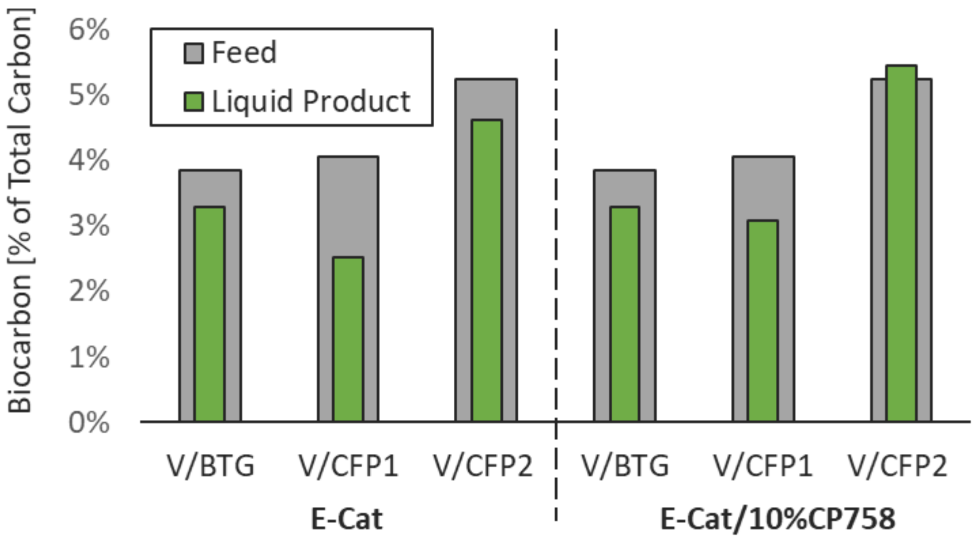
- Three different bio-oils (5 vol%) were recently co-processed with Vacuum Gas Oil (low-S VGO) in a Davison Circulating Riser.
- Oxygen contents of oils were between 20 and 39%.
- Two different catalysts were used.
- Yields were comparable with VGO-only.
- Oxygen in product was 1-2.5%.
- Relative biocarbon incorporation was improved by adding JM CP758 catalyst.



Yields are comparable when co-processing bio-oils.



Addition of JM CP758 catalyst increases biocarbon incorporation into liquid product.

The type of bio-oil can be chosen by refiners depending on their configuration and specifications.

High Incorporation of Biogenic C and Tailoring HT/HC for Product Distribution

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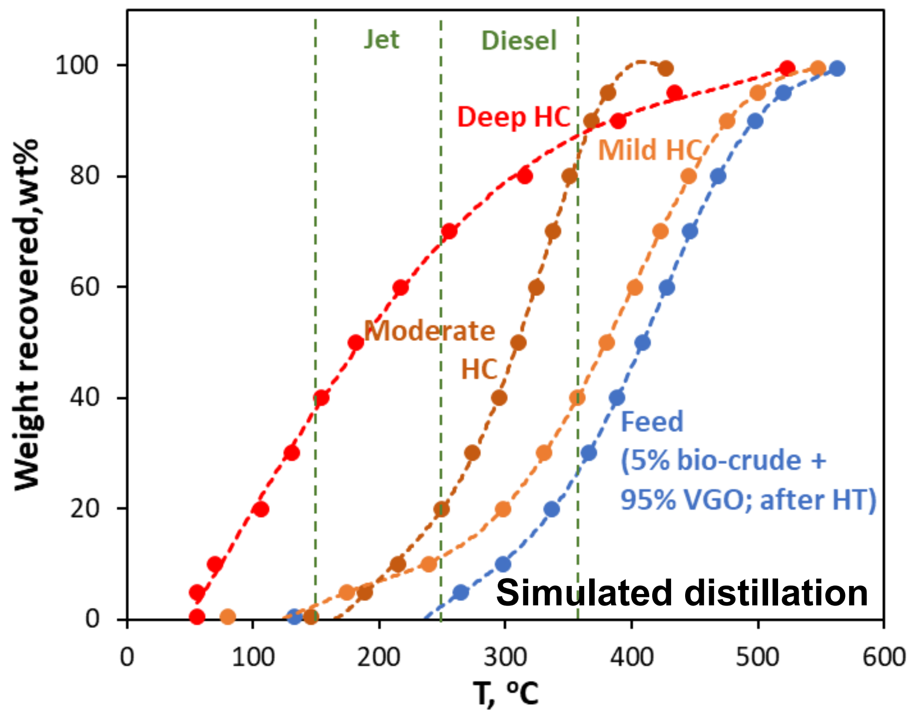
Evaluating various feedstocks and HT/HC insertion points

	Woody FP bio-oil	Woody CFP bio-oil	Sewage Sludge HTL biocrude
Co-processing Unit	SR Diesel HT / VGO mild HC	**SR Diesel HT* / VGO mild HC***	SR Diesel HT / **VGO HC***
Bio-C incorporation in fuel products#	60-80 %	80~90%	>95%
Challenges	• Instability • Fuel quality • Water and oxygen	• Fuel quality • Instability • Water and oxygen	• High N • Inorganics • Reactive oxygenates
Mitigation	• Bio-oil stabilization or fractionation	• CFP process modification	• Preconditioning • HT-pretreatment • Guard bed

** Preferred insertion point; SR: straight run; # Bio-carbon yield in 5-20 wt.% blending.*

- High biogenic carbon incorporation demonstrated for woody CFP bio-oil and HTL biocrude – including pretreatment to mitigate high nitrogen issues of bio-crude.

Sludge HTL biocrude (5%) and VGO co-processing at different conditions and catalysts

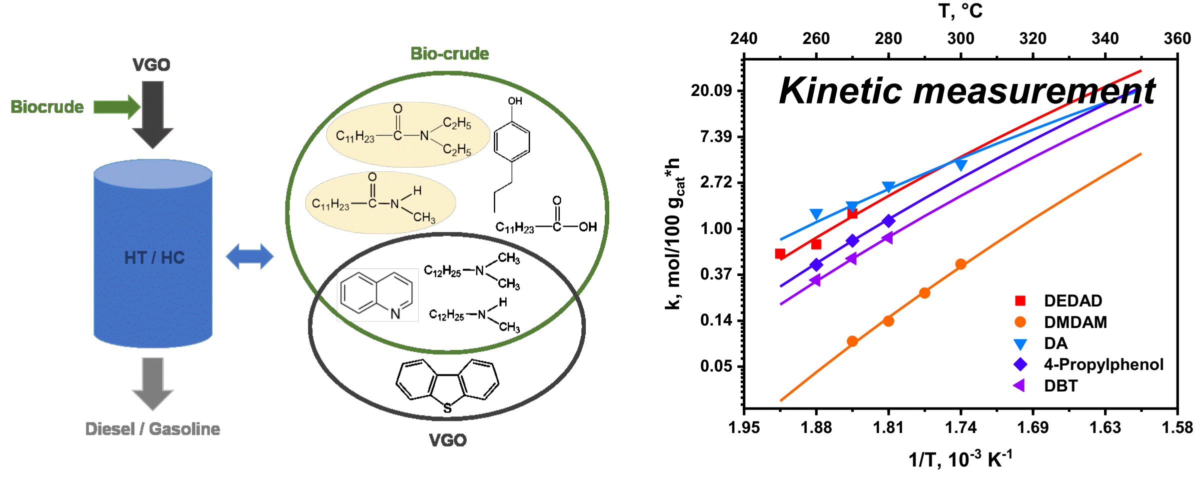


- Tuning HT/HC process (catalyst and reaction conditions) to tailor product distribution (Jet or Diesel)

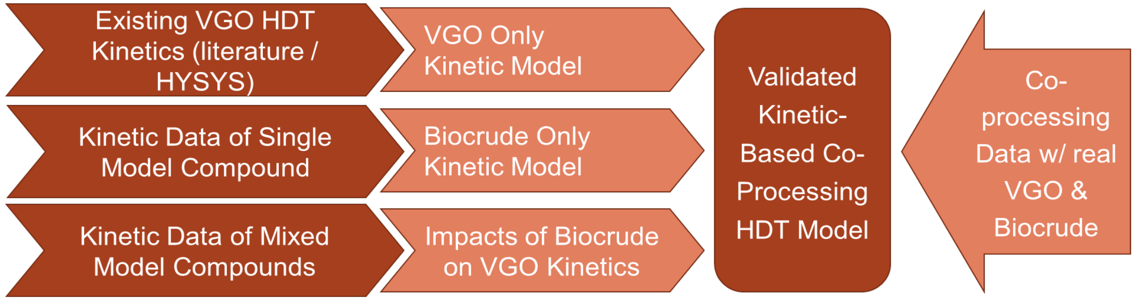
Tuning HT/HC process to enable co-processing various bio-oils/bio-crudes and producing desired fuel products

Mitigating the Impact on Chemistry and Catalyst

Impact on Hydrotreating Chemistry

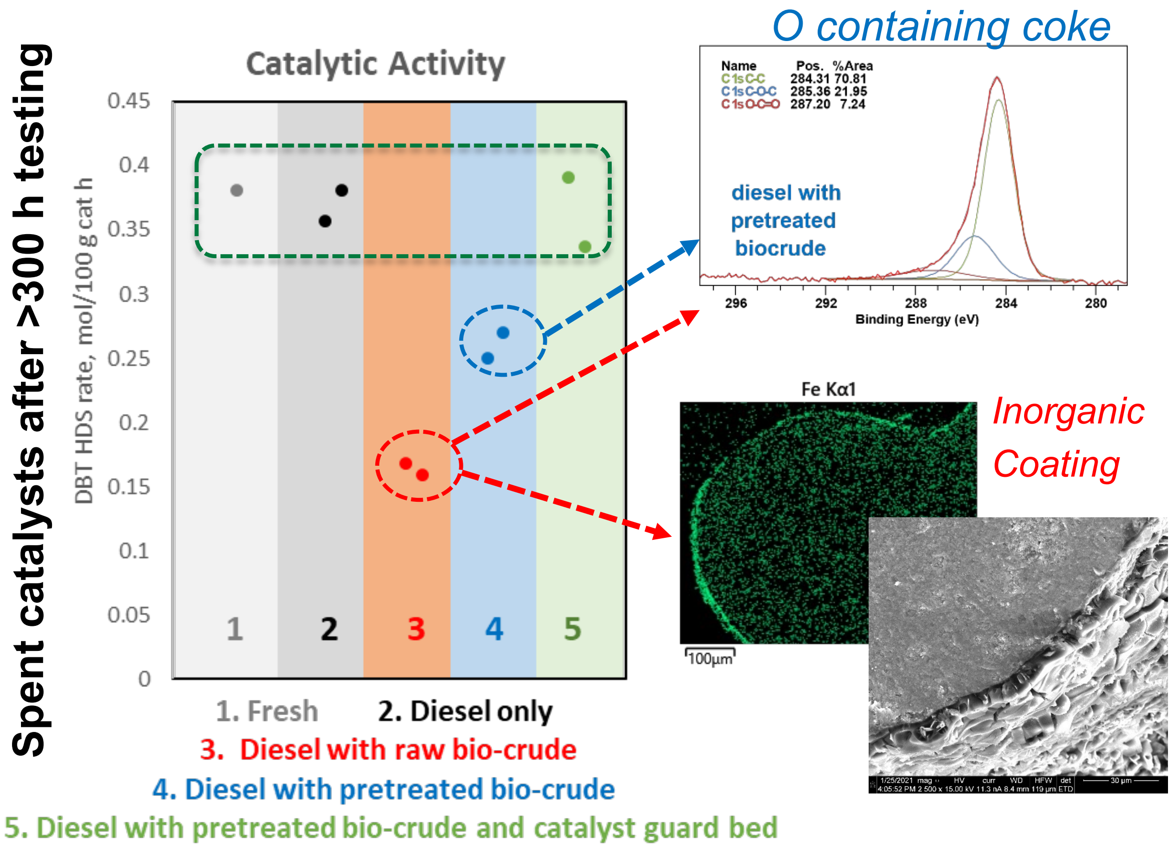


Reactor model



Kinetic-based reactor model for co-processing developed, enabling predictive capability

Impact on Catalyst Stability



Mitigation plan identified for catalyst deactivation from co-processing HTL biocrude

LSC ^{14}C for Tracking Biocarbon in Co-Processing

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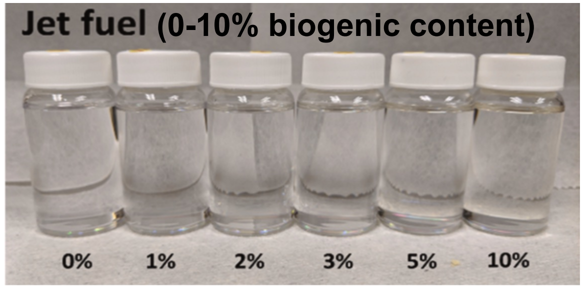
1. Clear fuels



Biodiesel

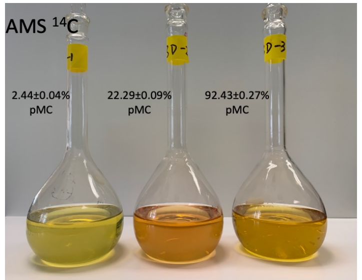
B100

Direct LSC Measurement

Optimized data range, counting time, and data interpretation. Achieved +/-0.4 % points relative to ASTM 6866 (^{14}C AMS) in the range of 1-10% biocarbon.

Liquid Scintillation Counter (LSC)

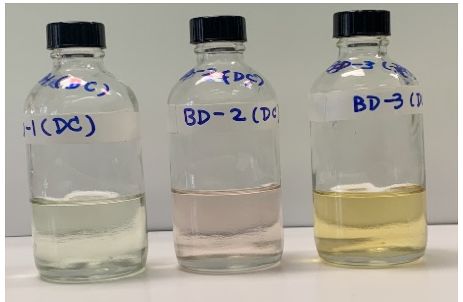
2. Lightly colored fuels (diesel)



B0 B20 B100

Decolorization

Adsorbents



LSC Measurement

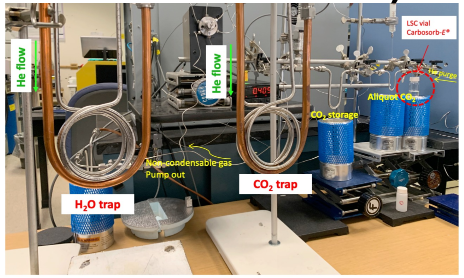
Decolorized fuels can be analyzed in LSC, but decolorization reduced biogenic carbon.

LSC Measurement

3. Dark fuels and solids (bio intermediates and feeds)

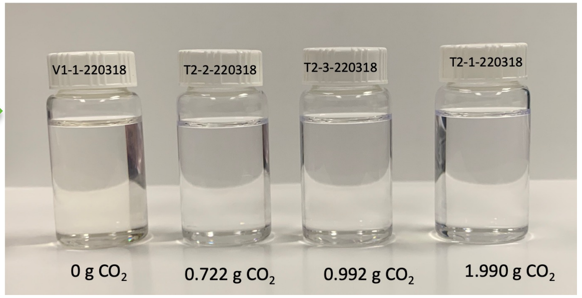
CO_2 Conversion

Oxy-combustion



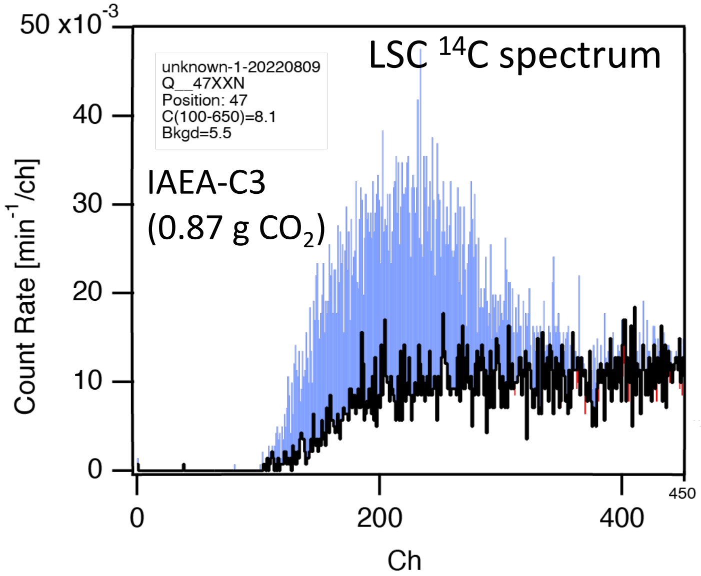
CO_2 capture

In absorbent/ scintillate



LSC ^{14}C method can be used for quantifying biogenic C in clear and dark fuels from co-processing.

Biocarbon Determination of Solid Biomass and CO_2 Gas Samples by LSC



IAEA-C3 standard cellulose

LSC method compared to ASTM 6866

Sample ID	Saturation rate	Carbon mass (g)	Bio C%, LSC	Bio C%, AMS
IAEA-1-0809	37.56 %	0.238	130.87	129.41

CO_2 standard gas samples

Sample ID	Tank CO_2	Tank1 CO_2 (g)	Tank 2 CO_2 (g)	Saturation	Bio C%, LSC	Bio C%, AMS
T1T2-1-0630	Tank 1 & 2 CO_2	0.483	1.739	89.22%	76.9	75.9
T1T2-2-0630	Tank 1 & 2 CO_2	1.136	1.035	89.29%	48.1	47.3

IAEA

IAEA-C3 cellulose

^{14}C = 129.41 pMC`

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CO_2 conversion method with LSC enables low-cost biocarbon tracking with good agreement with AMS.

Developing Online Biogenic Carbon Tracking Method Based on Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS)

Aerodyne Research

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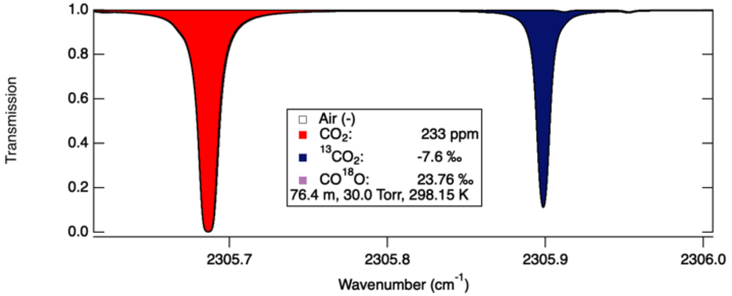

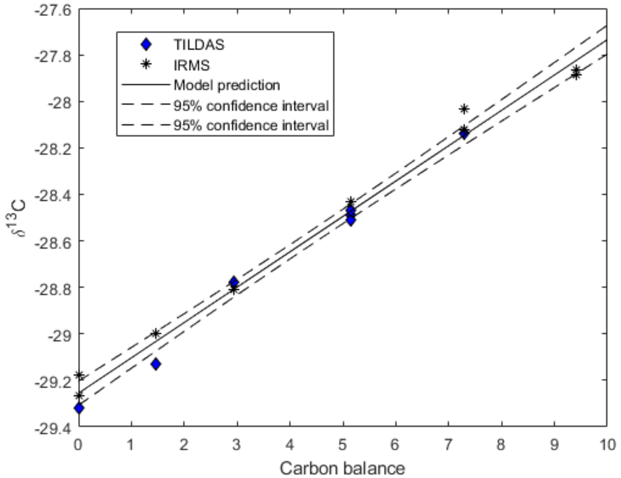

No statistically significant difference exists between results from TILDAS and IRMS

TILDAS can be a low-cost, fast, and precise method for biogenic carbon tracking, via $\delta^{13}C$ approach, including online measurement.

3 – Impact Commercialization Potential of Co-Processing on Biofuels Production

- Refinery Capacity
  - Diesel hydrotreaters (diesel mode) 70 BGal/yr
  - Distillate and/or gas oil hydrocrackers (jet mode) 37 BGal/yr
  - Fluid catalytic crackers (fuels and chemicals mode) 85 BGal/yr

Co-processing at 5% would allow > 7.5 BGal/yr bio-fuels from 140 Mt/yr of biomass.

- Specific to SAF 2030 Goals
  - HTL of wet waste (sludge, food waste, manure)
    - 77 million dry tons feed; 6.8 BGal fuel; **1.4 BGal SAF** (20% in jet range)
  - Lignocellulosic (forest waste, agricultural residues)

    → Gasification – Fischer-Tropsch synthesis
    - 27 million tons feed; SAF: 0.6 BGal (direct) + **0.3 BGal** (**wax upgrading**)

    → Pyrolysis (CFP/stabilized FP)
    - 53 million tons feed; **0.6 BGal SAF** (co-processing)

SAF of 2.3 BGal/yr, using currently available feedstocks, through FCC/HT/HC co-processing.

3 – Impact of Project on Co-Processing Industry

- Project directly supports BETO's mission of reducing GHGs by transforming biomass into refinery integrable biofuels (jet, diesel, gasoline).
- Addresses a critical need for conversion enabling technology development using the existing refinery infrastructure - limited CAPEX required. CP in existing refineries enables cost reductions.
- Project metrics/technical targets are defined/vetted by TEA and the IAB.
- We work directly with catalyst and instrument manufacturers, refiners.

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Connection of approach toward significant impact and outcomes

- 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 HT/HC performance

3 – Impact Dissemination of Results to Industry and Academic Community

- **Yearly IAB Meetings**
  - Recent meeting at Los Alamos National Laboratory with 60 participants (20 from industry)
- **Ongoing industry Collaborations**
  - CRADA with Johnson Matthey
  - Sharing of samples and results with BTG, Topsoe
- **Publications and presentations**
  - 14 publications since 2021 peer review (see additional slides)
- **Patents**
  - K. Magrini, Y. Parent, M. Jarvis, J. Olstad, "SYSTEMS AND METHODS FOR PRODUCING FUEL INTERMEDIATES", US Patent 11401474B2, Aug. 2, 2022.
  - K. Magrini, P. Peterson, C. Engtrakul, N. Wilson, "CATALYTIC HOT-GAS FILTRATION OF BIOMASS PYROLYSIS VAPORS", US Patent 11459509B2, Oct. 4, 2022.
  - K. Magrini, M. Sprague, Z. Abdullah, J. Olstad, R. Seiser, "NOZZLES FOR REDUCED COKING AND PLUGGING IN HIGH TEMPERATURE OPERATIONS" US Patent Application US20220355260A1, published Nov. 10, 2022.

Summary

Project Goal

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

Approach

- **Addressing major risks** and efficient **communication**
- **Interdisciplinary and collaborative effort** with three national labs and industrial partners
- 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 critical needs for **biomass conversion enabling technology** development
- Project deliverables are **transferrable to refiners.** Refiners are interested in co-processing with active participation in IAB meeting and several of them **moving beyond lipids.**

Progress and Outcomes

- **High biogenic C incorporation** demonstrated
- **Biogenic carbon tracking** method improved (incl. dark liquids)
- Different **bio-oils successfully co-processed** in FCC (up to 10%)
- **Hydrotreating of HTL biocrude completed** with catalyst deactivation mitigated.
- **Process kinetic models** to predict HT/HC performance

Future work

- Perform detailed analyses of feeds (assays) for refiners
- Continue tracking contaminants in bio-oils/bio-crudes
- Increase olefins and jet fuel as major product from FCC
- Increase biogenic feed percentages including a variety of feeds

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Kevin Stup (Vacuum Analytics)
Robbie Venderbosch (BTG)

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ZETON
PILOT PLANT TECHNOLOGY

Quad Chart Overview

Timeline

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

	FY22 Costed	Total Award
DOE Funding	*$664.8k (NREL)* *$794.7k (PNNL)* *$334.8k (LANL)*	*$2,250k (NREL)* *$2,250k (PNNL)* *$1,125k (LANL)*

TRL at Project Start: 4
TRL at Project End: 5

Project Goal

Accelerate adoption of co-processing (CP) biomass-derived feedstocks with petroleum streams in current petroleum refineries by developing and disseminating foundational data for processing renewable intermediates to SAF and marine fuel by providing CP strategies via FCC and Co-HT/HC.

End of Project Milestone

Demonstrate at least 100 h of FCC co-processing cleaned FP or CFP with VGO with up to 15 vol% blending level, 75 wt% relative biogenic carbon incorporation into SAF, MFSP approaching $2.50/GGE and 70% GHG reduction; 500 h stable operation of co-hydrotreating HTL bio-crudes with diesel or VGO with 2-10 vol% blending ratio, at least 80% biogenic carbon incorporation into fuel, maintained diesel fuel quality compared to diesel or VGO only, minimal impact on HT/HC catalyst, and less than 10% faster deactivation compared with baseline.

Funding Mechanism

Beto SDI Lab Call, 2019.

Project Partners

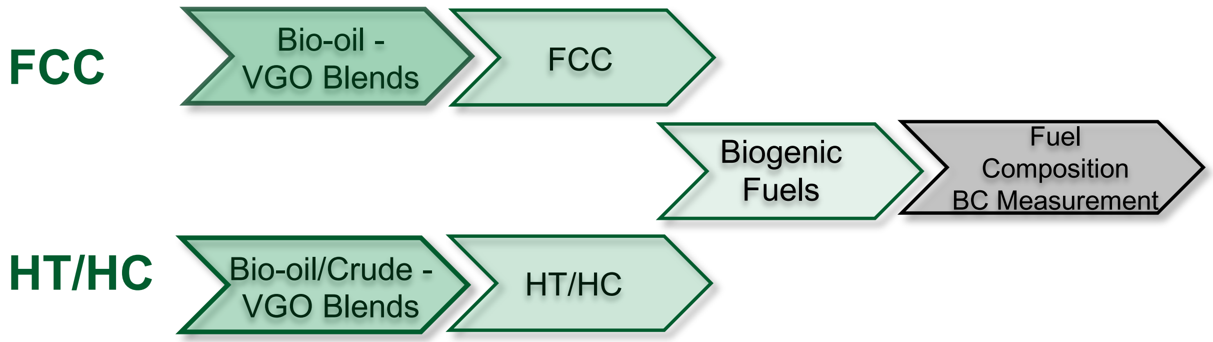
- Johnson Matthey, Chevron, Topsoe, Kern Oil, Ensyn, BTG, Aerodyne

Additional Slides

Project Acronyms and Pathways

AMS: accelerator mass spectrometer
BC: biogenic carbon
CFP: catalytic fast pyrolysis
CP: co-processing
E-Cat: equilibrium FCC refinery catalyst
FCC: fluid catalytic cracking
FP: fast pyrolysis
HC: hydrotreating
HT: hydrocracking
HTL: hydrothermal liquefaction
JM: Johnson Matthey
LSC: liquid scintillation counter
SPO: stabilized pyrolysis oil

Considered Pathways



F2021 Reviewer Comments/Responses

Comment: "This is a great project that is directly addressing knowledge gaps limiting the commercial processing of bio-oils; it has excellent industry participation, has clearly identified challenges and a research approach to address them, and has plans for a published database to disseminate information post-project."

Response

We thank the reviewers for their positive comments about this co-processing project including their support of the knowledge gaps the project is addressing, database development and industry participation through the project's industrial advisory board

F2021 Reviewer Comments/Responses

Comment: "Good, but need more refinery insight and ops experience. Is HT/HC and FCC possible in one refinery? Need to clearly understand value (advanced opt needed) Why is biogenic C tracking needed? Shouldn't a simple C accounting balance be enough? Value of added bio-oils, value created. How was TEA performed? LP should be calculating cost of external (bio) stream to achieve fuel costs. A different way to look at it."

Response

We agree that increased refinery insight and operations experience is needed, and we are expanding refiner participation in the next 3 years of this project. We did not mention in the review that we are currently performing FCC co-processing tests for two major refiners using NREL's DCR system with their specific feedstocks and catalysts to define process parameters. Additionally, biogenic carbon tracking is an ask of our industrial advisory board: to understand where biogenic carbon is reporting both during co-processing and in the final product. Note that California is requiring 14C analysis of biogenic C containing fuels for RINs. Finally, TEA was performed using an Aspen refinery model and project generated co-processing data.

F2021 Reviewer Comments/Responses

Comment: "The tasks of the refineries was not clear. It would appear that they were involved at an advisor role only. It would be of benefit if NREL could entice these entities into a greater participatory role. It would be beneficial to know what refineries have told BETO regarding the willingness to adopt a new catalyst recipe. Refinery buy-in is absolutely critical for this path and it isn't clear if refiners are being brought in to monitor the progress of this technology. The project is aware of the further challenges in refinery adoption but there arent any further plans to do this work at a pilot scale. 8% displacement is massive in industry even if it is a small number. The corn ethanol industry displaces 10% of petroleum and supports thousands of jobs and billions of dollars in GDP. Would be good to understand the non-RIN value of the blend vs. the standard FCC output (Slide 12). The project has done a good job of providing tasks to each of the known risks of this technology blend and is clearly working towards eliminating roadblocks to the development of bio-oil and FCC blending. Project discusses the long term catalyst stability risk but the presentation is not clear on how this is being measured experimentally. Reviewers would like to know how the project has assessed performance, how frequently it has regenerated its catalyst and how it projects performance. Potassium and Sulfur are mentioned as elements under study for catalyst deactivation - however the impact of other more minor elements, or those that are known to easily be resolved through regeneration do not appear to be under study. If the catalyst needs to be regenerated more frequently, that too would have a serious impact on the refinery. The metrics of the demonstration of FCC/HTC fuel production were not provided. Without these metrics it is hard to evaluate whether this project has successfully impacted the state of biofuel production. "Linked to FCIC database" is unclear. The interface should be a singular consistent UI, not a conglomeration of different programs merged together. Not clear whether the development of the instrument is on-going or is considered complete. The fidelity of the carbon monitoring device is critical on equipment that is pumping millions of gallons a day. The presentation noted it could measure down to a percent, but this does not provide sufficient information to determine its benefit."

F2021 Reviewer Comments/Responses

Response

The Johnson Matthey catalysts used in the FCC co-processing work are HZSM-5 catalysts modified to enhance bio-oil conversion while retaining their original ability to convert vacuum gas oil. Catalyst characteristics have to be maintained for FCC operation and the modifications adhere to this requirement - thus refiners should not have issues using these catalysts in their FCC systems. Project plans in years 2-3 will address catalyst lifetime and potential deactivation from fugitive contaminants as will regeneration requirements for both FCC and HTC co-processing. The bio-oil database can be linked to the FCIC feedstock database as both are using LabKey as the platform; this approach leverages the information in both databases for researchers and refiners. The biogenic C measurement systems under development are slated for ease of use and ruggedness in a refining environment.

F2021 Reviewer Comments/Responses

Comment: "This is a solid project overall. Good Management and Risk Mitigation Plan, excellent outreach to catalyst vendors and refiners, effective plan to target the right feedstocks for the right processes and to acquire data, both primary (conversion to products) and secondary (catalyst life, operational issues, etc.). Progress so far has been good, and success vs. the stated Objectives seems likely. The one major concern is that by targeting low-level blending, the project may be a tactical success but a strategic dead end. We don't need 5-10% bio content in a couple of process units, we need refineries that are processing 75%-plus renewable feedstocks. If this is clearly a step along that path, fine, but it wasn't clear from the material presented that was so. The BETO Vision for existing petroleum refineries should be that they will process mostly renewable feedstocks or they will go out of business."

Response

We agree that the more bio content in fuels the better! However, refiners have told us that for FCC co-processing, 10wt% bio-oil blend is the upper limit to that can be current co-processing in FCC units. Greater than 10wt% upsets downstream processes. Also consider that biomass resources may limit how much bio-oil is available for co-processing.

F2021 Reviewer Comments/Responses

Comment: "This is an excellent project that is achieving good results. I am amazed at the complexity of the project and how the objectives are being met in spite of this complexity. The team may want to review its objectives to ensure that they are not over stretched and are able to continue to function at a high level. It is well managed with excellent industrial involvement. As with other projects I really like that they are looking at co-processing, and co-processing in numerous unit operations. This reviewer also likes that they are tracking and documenting the feed quality and consistency, a deficiency of other projects. Great project and great team"

Response

We thank the last reviewer for their positive comments - very much appreciated. We believe tracking feed quality and consistency is a critical process parameter that must be understood if co-processing is to be successfully adopted by refiners.

Publications, Patents, Presentations, Awards, and Commercialization

Publications (2021-2023)

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- Reinhard Seiser, Jessica L. Olstad, Kimberly A. Magrini, Rebecca D. Jackson, Braden H. Peterson, Earl D. Christensen, and Michael S. Talmadge. Co-Processing Catalytic Fast Pyrolysis Oil in an Fcc Reactor. Biomass and Bioenergy 163 (2022): 106484. https://doi.org/https://doi.org/10.1016/j.biombioe.2022.106484.
- Kimberly A. Magrini, Jessica L. Olstad, Braden H. Peterson, Rebecca D. Jackson, Yves Parent, Calvin Mukarakate, Kristiina Iisa, Earl D. Christensen, and Reinhard Seiser. "Feedstock and Catalyst Impact on Bio-Oil Production and Fcc Co-Processing to Fuels." Biomass and Bioenergy 163 (2022): 106502. https://doi.org/https://doi.org/10.1016/j.biombioe.2022.106502.
- Abhijit Dutta*, Hao Cai, Michael Talmadge, Calvin Mukarakate, Kristiina Iisa, Huamin Wang, Daniel Santosa, Longwen Ou, Damon Hartley, Nolan Wilson, Joshua Schaidle, Michael Griffin, Model quantification of the effect of coproducts and refinery co-hydrotreating on the economics and greenhouse gas emissions of a conceptual biomass catalytic fast pyrolysis process, Chemical Engineering Journal, 2022, 451, 138485.
- Cheng Zhu, Oliver Y. Gutiérrez, Daniel M. Santosa, Igor Kutnyakov, Roland Weindl, Hui Shi, Huamin Wang*, Impact of Co-processing Biocrude with Petroleum Stream on Hydrotreating Catalyst Stability, Energy & Fuels, 2022, 36, 9133.
- Cheng Zhu, Oliver Y. Gutiérrez, Daniel M. Santosa, Matthew Flake, Roland Weindl, Igor Kutnyakov, Hui Shi, Huamin Wang*, Kinetics of nitrogen-, oxygen- and sulfur-containing compounds hydrotreating during co-processing of bio-crude with petroleum stream, Applied Catalysis B, 2022, 307, 121197.
- Stefano Dell'Orco, Steven M. Rowland, Anne E. Harman-Ware, Daniel Carpenter, Thomas Foust, Earl D. Christensen, and Calvin Mukarakate. "Advanced Spectrometric Methods for Characterizing Bio-Oils to Enable Refineries to Reduce Fuel Carbon Intensity During Co-Processing." Applied Spectroscopy Reviews 57, no. 1 (2022): 77-87. https://doi.org/10.1080/05704928.2021.1920030.
- Abhijit Dutta, Calvin Mukarakate, Kristiina Iisa, Huamin Wang, Michael Talmadge, Daniel Santosa, Kylee Harris, Frederick Baddour, Damon Hartley, Hao Cai, Longwen Ou, Joshua Schaidle, and Michael Griffin, Ex Situ Catalytic Fast Pyrolysis of Lignocellulosic Biomass to Hydrocarbon Fuels: 2020 State of Technology, National Renewable Energy Lab, 2021, doi:10.2172/1805204
- Edwin Yik, Huamin Wang, Enrique Iglesia,* Hydrogenation and C-S bond activation pathways in thiophene and tetrahydrothiophene reactions on sulfur-passivated surfaces of Ru, Pt, and Re nanoparticles, Applied Catalysis B, 2021, 291, 119797
- Huamin Wang*, Pimphan A. Meyer, Daniel M. Santosa, Cheng Zhu, Mariefel V. Olarte, Susanne B. Jones, Alan H. Zacher, Performance evaluation and techno-economic analysis of co-processing stabilized bio-oil and recycled residual fraction of hydrotreated bio-oil in hydrotreating reactor, Catalysis Today, 2021, 365, 357.
- 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 14C content, Fuel, 2021, 291, 120084.
- James E. Lee, Zheng-Hua Li, Earl D. Christensen, Teresa L. Alleman. 2022. Decolorization of Biofuels and Biofuel Blends for Biogenic Carbon Quantification with Liquid Scintillation Radiocarbon Direct Measurement. Energy & Fuels. 36, 14, 7592–7598. https://doi.org/10.1021/acs.energyfuels.2c01166
- James Lee, Zheng-Hua Li, Huamin Wang, Andrew E. Plymale and Charles G. Doll, 2022. Quantification of biogenic carbon in fuel blends through LSC 14C direct measurement and assessment of uncertainty. Fuel, JFIE-S-21-09082. https://doi.org/10.1016/j.fuel.2021.122859.

Publications, Patents, Presentations, Awards, and Commercialization

Presentations (2021-2023)

- Reinhard Seiser, Jessica Olstad, Rebecca Jackson, Clark Yarbrough and Kim Magrini, "Co-processing of Bio-Oils in FCC Reactor", oral presentation, 2023 AIChE Spring meeting, Houston.
- Reinhard Seiser, Jessica Olstad, Braden Peterson, Rebecca, Jackson, Earl Christensen, Kim Magrini; Robert Baldwin, "Biocarbon Tracking in FCC Co-processing of Biogenic Feedstocks", oral presentation, TCBiomass 2022, Denver.
- 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", 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.
- 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.
- Huamin Wang, "Challenges and Progress in Catalytic Upgrading of Liquefaction Intermediates from Biomass and Waste", 2021 AIChE Annual Meeting, invited oral presentation, November 11, 2021
- Huamin Wang, Daniel M. Santosa, Igor V. Kutnyakov, and Cheng Zhu. "Co-processing bio-crudes with petroleum gas oil in hydrotreating: simultaneous heteroatom removal and incorporation of biogenic carbon in produced fuels", 2021 ACS Spring Virtual Meeting, 2021, oral presentation.
- Cheng Zhu, Miki Santosa, Igor Kutnyakov, Oliver Gutierrez, Huamin Wang , "Co-processing Bio-crudes with Petroleum Stream in Hydrotreating", the North American Catalysis Society meeting (NAM27), 2022, oral presentation.
- Huamin Wang, Kim Magrini, Zhenghua Li, "Co-Processing in Refineries of Thermal Liquefaction Products from Biomass and Waste", tcBiomass 2022, 2022, invited oral presentation.
- Huamin Wang, Cheng Zhu, Miki Santosa, Oliver Gutierrez Tinoco, Igor Kutnyakov, "Co-processing Bio-crudes with Petroleum Stream in Hydrotreating: Impact on Chemistry and Catalyst Stability", tcBiomass 2022, 2022, oral presentation.
- Huamin Wang, "Hydrothermal Liquefaction R&D at PNNL: Biocrude Coprocessing", NGRF workshop, 2022, invited oral presentation.

Publications, Patents, Presentations, Awards, and Commercialization

Patents

K. Magrini, Y. Parent, M. Jarvis, J. Olstad, “SYSTEMS AND METHODS FOR PRODUCING FUEL INTERMEDIATES”, US Patent 11401474B2, Aug. 2, 2022.

K. Magrini, P. Peterson, C. Engtrakul, N. Wilson, “CATALYTIC HOT-GAS FILTRATION OF BIOMASS PYROLYSIS VAPORS”, US Patent 11459509B2, Oct. 4, 2022.

K. Magrini, M. Sprague, Z. Abdullah, J. Olstad, R. Seiser, “NOZZLES FOR REDUCED COKING AND PLUGGING IN HIGH TEMPERATURE OPERATIONS” US Patent Application US20220355260A1, published Nov. 10, 2022.

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.

DEI Plan

The three national labs have increased their participation in diversity, equity and inclusion programs:

- Support a diverse workforce and promote the interviewing of candidates with a wide variety of backgrounds.
- Applied to hiring interns from MSIs through Research Participant Program (RPP) internship – demand was larger than supply.
- Participated in workshops on different internship programs and fellowships such as GEM (Graduate Education for Minorities).
- Participated in LDRD-sponsored Energy Justice analysis:
    - Evaluate impact of research on disadvantaged communities – positively by renewable industry programs and negatively by emissions and waste generation.
    - Broaden publication research to other regional areas
    - Dissemination of research results in global, open access journals
- Participated in workshops on partnering with MSI institutions. Administration compiled a list of MSIs with contacts.
- Participated in Justice Equity Diversity and Inclusion (JEDI) group's programs and seminars inviting speakers and visitors from MSIs.

Abstract

The objective of this three-laboratory project is to accelerate adoption of co-processing biomass-derived feedstocks with petroleum streams in current refineries by developing and broadly disseminating foundational data for processing renewable intermediates and offering co-processing strategies. It will enable utilizing U.S. refineries which in 2020 have 8.8 million barrels/day capacity for hydrotreating and 5.6 million barrels/day capacity for FCC. Three critical challenges were identified by the project's industrial advisory board (IAB): 1) A critical operability risk comprising process stability around catalyst deactivation. 2) A regulatory risk comprising the need to rapidly measure biogenic carbon and oxygenates in processed streams. 3) A significant knowledge risk centered on the lack of co-processing data including feedstock compositions and contaminants, product compositions, the reaction kinetics of unique bio-compounds, and associated TEA/LCA. Outcomes of addressing the three challenges are: 1) Preventing catalyst deactivation by reducing alkali species through hot-gas filtering (FCC) and reducing nitrogen compounds by pre-treatment (HT/HC). 2) Developed methods for inexpensive/rapid biocarbon analysis through 14C and delta 13C analysis methods. 3) Provided detailed compositions on bio-oil feeds and co-processing products, including contaminants, operational data including biocarbon yields, an improved kinetic reactor model for HT, and associated TEA/LCA.