U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

Webinar

Co-processing Fast Pyrolysis Bio-Oils and Hydrothermal Liquefaction Biocrudes in Fluid Catalytic Cracking and Hydroprocessing in Refineries

September 20th, 2023

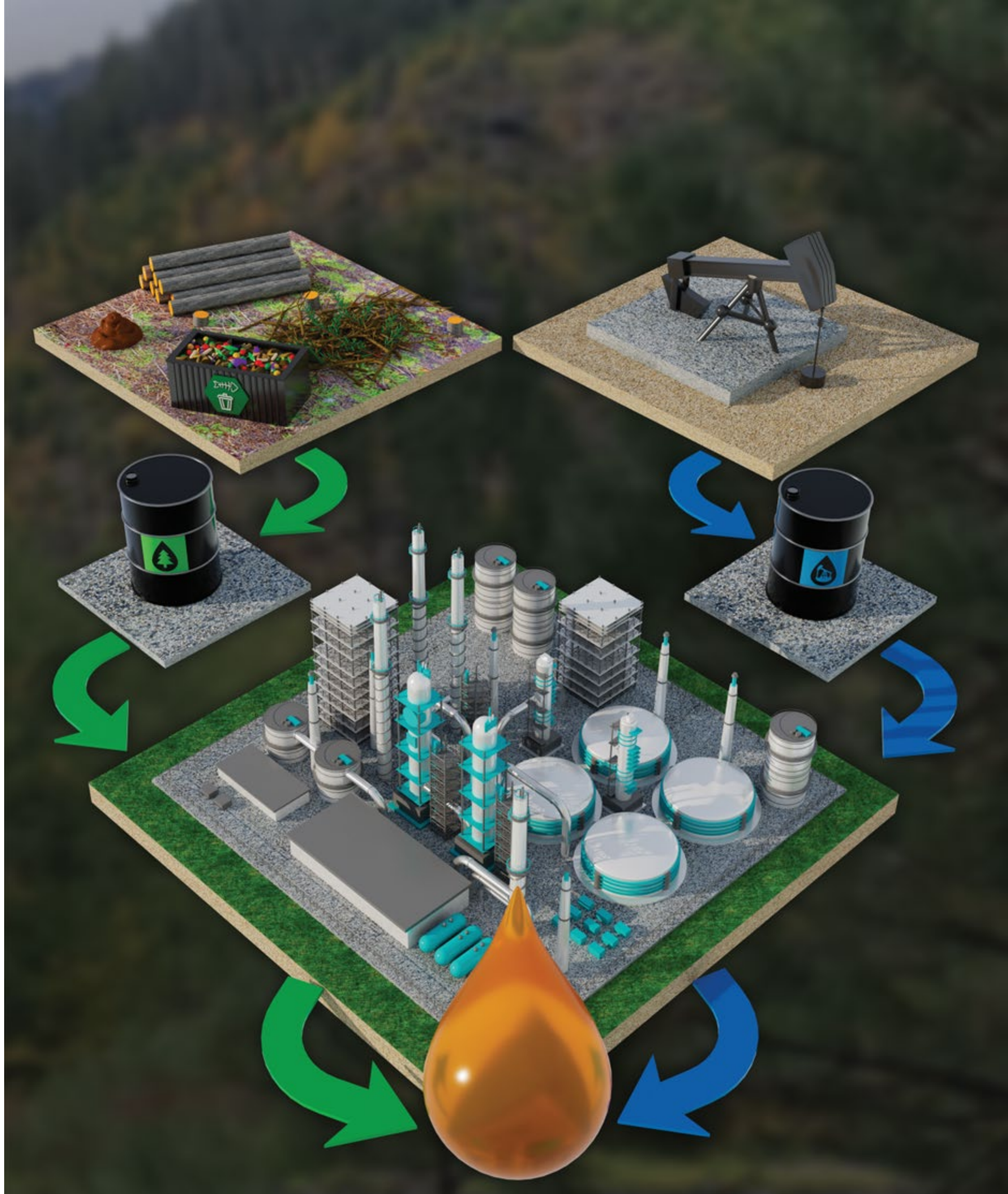
Presenters:

Dr. Reinhard Seiser, National Renewable Energy Laboratory

Dr. Huamin Wang, Pacific Northwest National Laboratory

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Pacific Northwest
NATIONAL LABORATORY



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- Audience does not have the ability to unmute and/or turn on camera during this presentation
- Please submit all questions using the Q&A function at the bottom of your screen (chat is disabled)
- Submit questions at any point during the presentation
- Every effort will be made to address all relevant questions

Agenda

This Webinar (9/20/2023)

- Housekeeping
- Overview of BETO
- Overview of the Co-Processing Project
- Co-Processing of Bio-Oils in Fluid Catalytic Cracking
- Co-Processing of HTL Biocrudes and Bio-Oils in Hydroprocessing
- Q&A

Next Week's Webinar (9/27/2023)

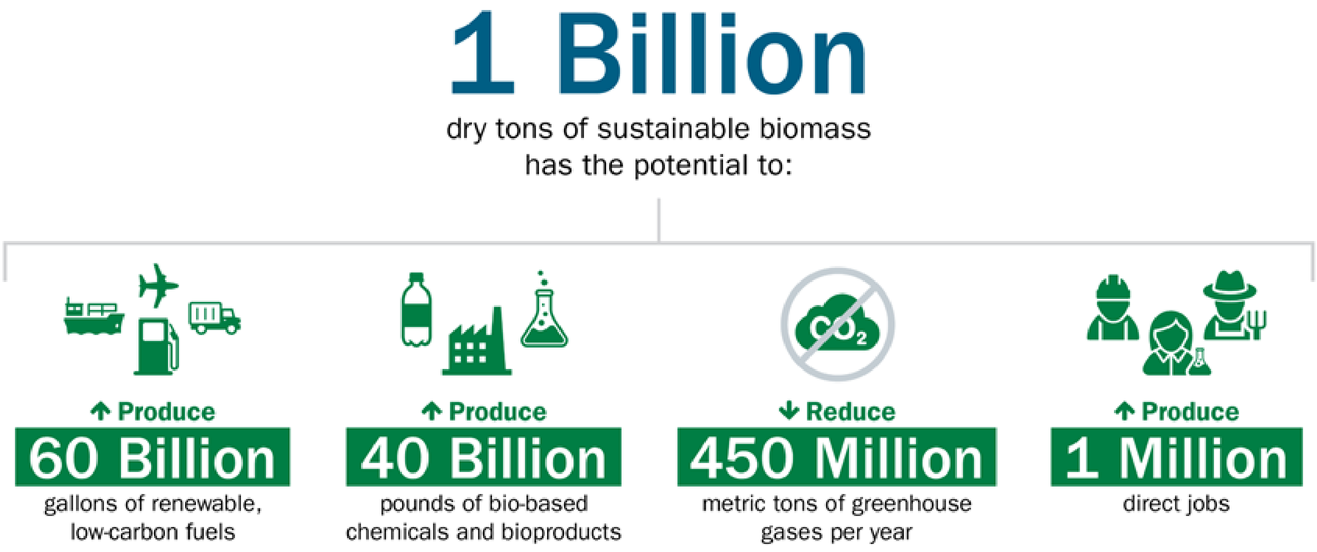
- Biogenic Carbon Tracking and Measurement

→ More GHG reductions, faster!

→ Focusing on Sustainable Aviation Fuel (SAF) and other strategic transportation fuels

- BETO 2023 Multi-Year Program Plan
- Sustainable Aviation Fuel Grand Challenge Roadmap
- U.S. National Blueprint for Transportation Decarbonization

→ Unlocking the potential of the full range of renewable carbon resources



Bioenergy Technologies Office Program Areas

Renewable Carbon Resources

Conversion Technologies

Systems Development and Integration

Data, Modeling, and Analysis

- Support 3 billion gallons SAF by 2030
- Support 35 billion gallons SAF by 2050
- Cost-effective SAF and other strategic fuels with at least 70% greenhouse gas reductions
- Decarbonization of chemicals

Today's Presenters

Dr. Reinhard Seiser

Senior Research Engineer

National Renewable Energy Laboratory

Dr. Huamin Wang

Chief Research Engineer

Pacific Northwest National Laboratory

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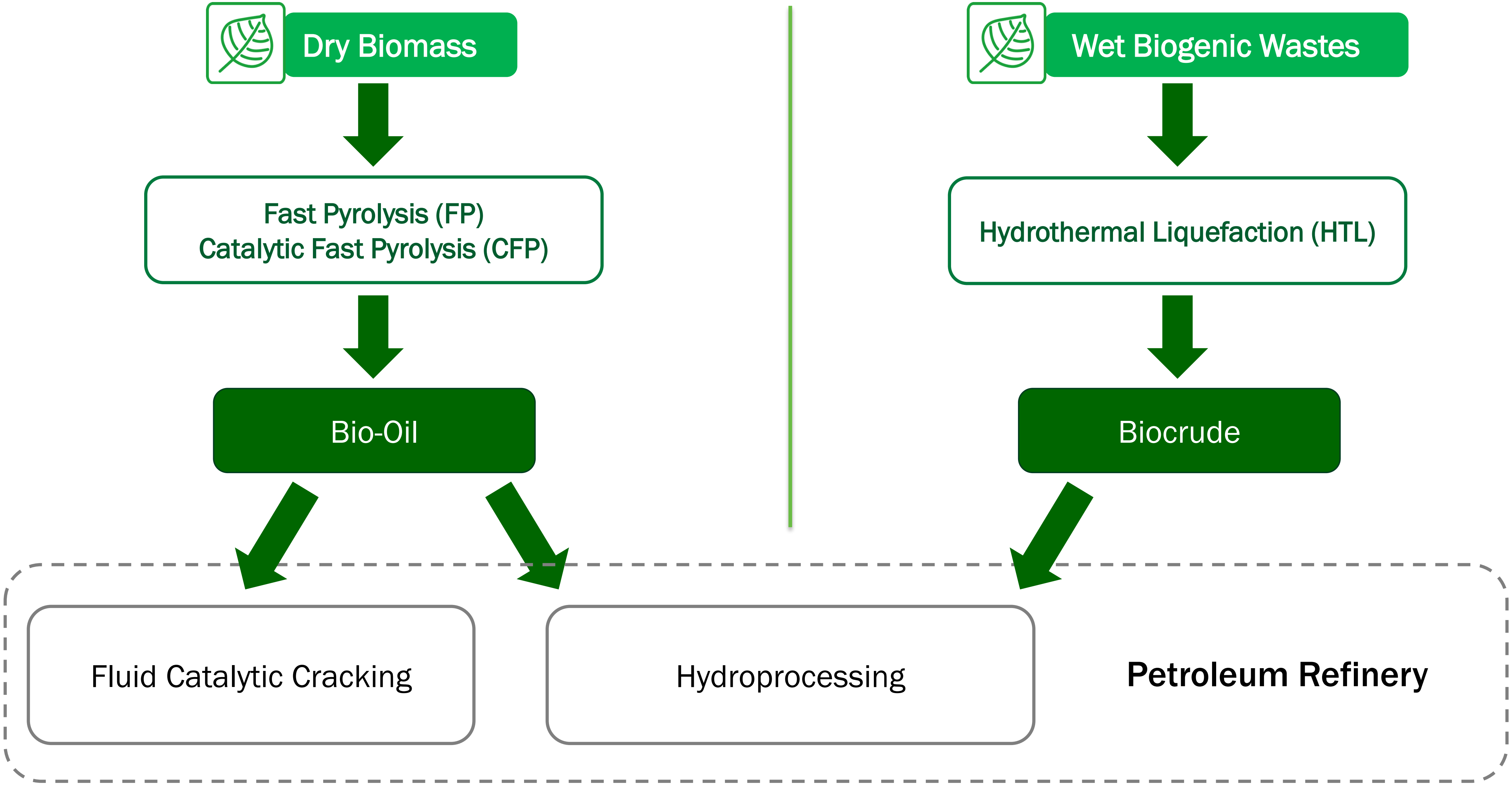
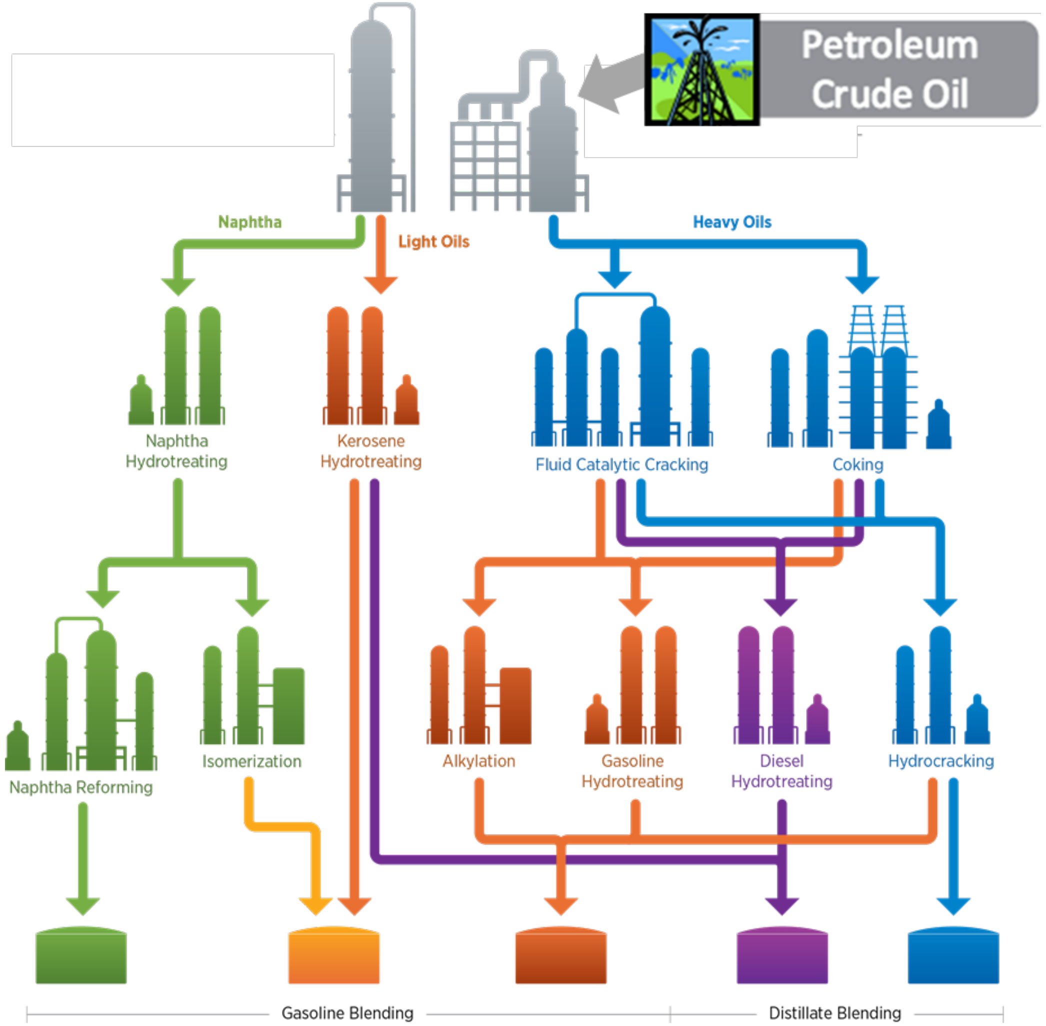
Project Overview – Two Sources of Biogenic Feeds and Two Co-processing Methods



Project Overview – Co-Processing Leverages Existing Refining Infrastructure

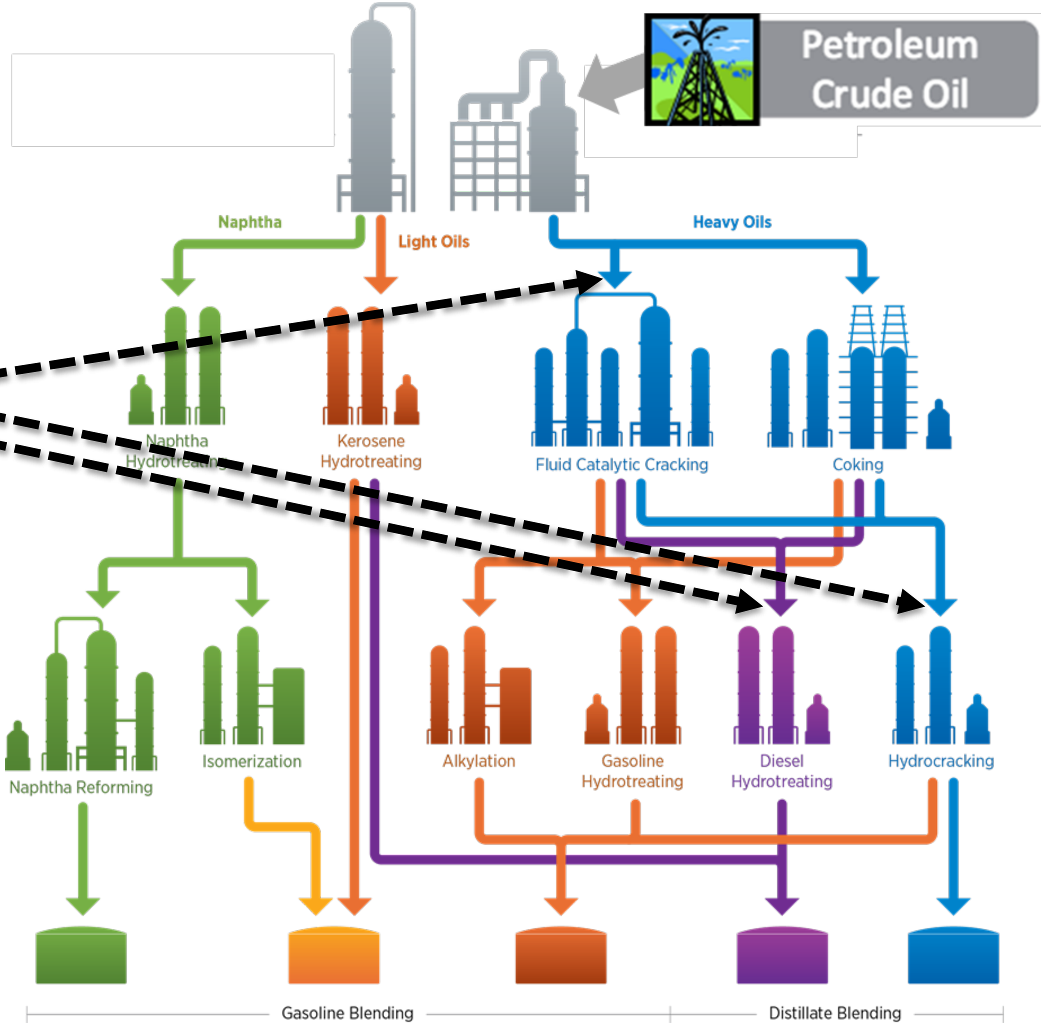


Current US Refinery Capacities

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

Project Overview – Investigate Co-Processing Options at Various Insertion Points

FP and CFP Bio-Oils
HTL Biocrude



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Expand from co-processing fats, oils, and greases (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]

FP: Fast pyrolysis oil
CFP: Catalytic fast pyrolysis oil
HTL: Hydrothermal liquefaction

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

Project Overview – De-Risking Co-Processing Requires Extensive R&D

Properties of typical
Bio-oil and biocrude feedstocks

	Woody FP Bio-Oil	Woody CFP Bio-Oil	Sewage Sludge HTL Biocrude	Petroleum
H/C	1.4-1.6	1.0-1.1	~1.5	1.5-1.8
O	36-52	15-36	~2-8	0.1-1.0
S	~0	~0	~0.5	0.1-6
N	<0.2	<0.2	~5	0.1-2
H_2O	17-30	~5-10	~2-12	0.02-0.1

FP and CFP Bio-Oils

- High oxygen content
- Sulfur content is low
- High water content

HTL Biocrudes

- High nitrogen content
- High water content

FP: Fast pyrolysis oil
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Challenges

- 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
- 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

Project Overview – Project Objectives and Goals

- Extensively evaluating the co-processing of various FP and CFP bio-oils and HTL biocrudes in FCC and hydroprocessing
- Understanding the impact of co-processing on chemistry, catalyst
- Identifying mitigation approaches to operational problems and risks
- Developing reactor models for predictive capability
- Conducting TEA and refinery impact analysis
- Evaluating and improving methods for biogenic carbon detection in products

Project Overview – BETO Funded Project – An Interdisciplinary and Collaborative Effort

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Pacific Northwest NATIONAL LABORATORY

Los Alamos NATIONAL LABORATORY

Wood, Herbaceous, WWTP Sludge, Algae

Petroleum stream (Diesel, VGO…)

FP, CFP (NREL)
HTL (PNNL)

FCC (NREL)

HT/HC (PNNL)

Fuel Analysis (NREL, PNNL)

Biocarbon Tracking (LANL, PNNL, NREL)

Process TEA, LCA (PNNL, NREL)

Industrial Advisory Board (IAB)

- 8 refining companies
- 4 catalyst developers
- 2 bio-oil providers
- 3 academic and government institutions

External Partners

- Catalyst
- Feedstock
- Biogenic Carbon Analysis

WWTP:	Wastewater treatment plant
VGO:	Vacuum gas oil
FP:	Fast pyrolysis oil
CFP:	Catalytic fast pyrolysis oil
HTL:	Hydrothermal liquefaction
FCC:	Fluid-catalytic cracking
HT/HC:	Hydrotreating/hydrocracking
TEA:	Techno-economic analysis
LCA:	Life-cycle Analysis

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Overview of Bio-Oils – Fast Pyrolysis Oils Have High Oxygen Content

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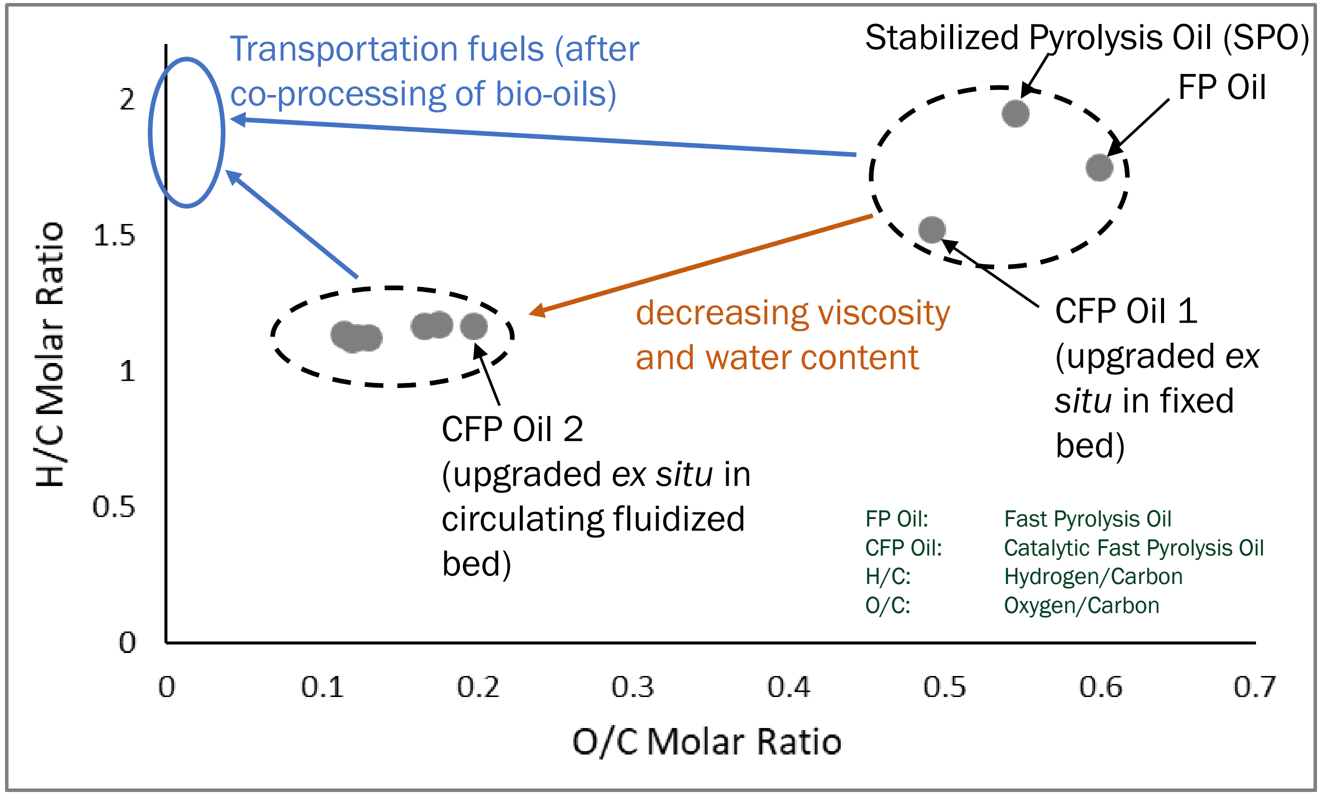
- FP Oil – for reference (no catalyst used during production).
- CFP oils were produced in-house with oxygen contents between 12 and 36%.

- Stabilized pyrolysis oil (SPO) was provided by BTG.

btg



Bio-oils are shown on a wet-basis

- Catalytic Fast Pyrolysis Oil – Ex-situ Upgrading of Pyrolysis Vapors
  Ruddy et al., Green Chemistry, 2014; Magrini et al., Biomass and Bioenergy, 2022
  → High quality oil, low-oxygen, low viscosity.
- Stabilized Pyrolysis Oil (BTG) – Fast Pyrolysis Oil Stabilized by Mild Hydrotreating
  Yin et al., Fuel Processing Technology, 2021
  → High production yield, more stable than FP oil.

Production of Catalytic Fast Pyrolysis Oil from Biomass

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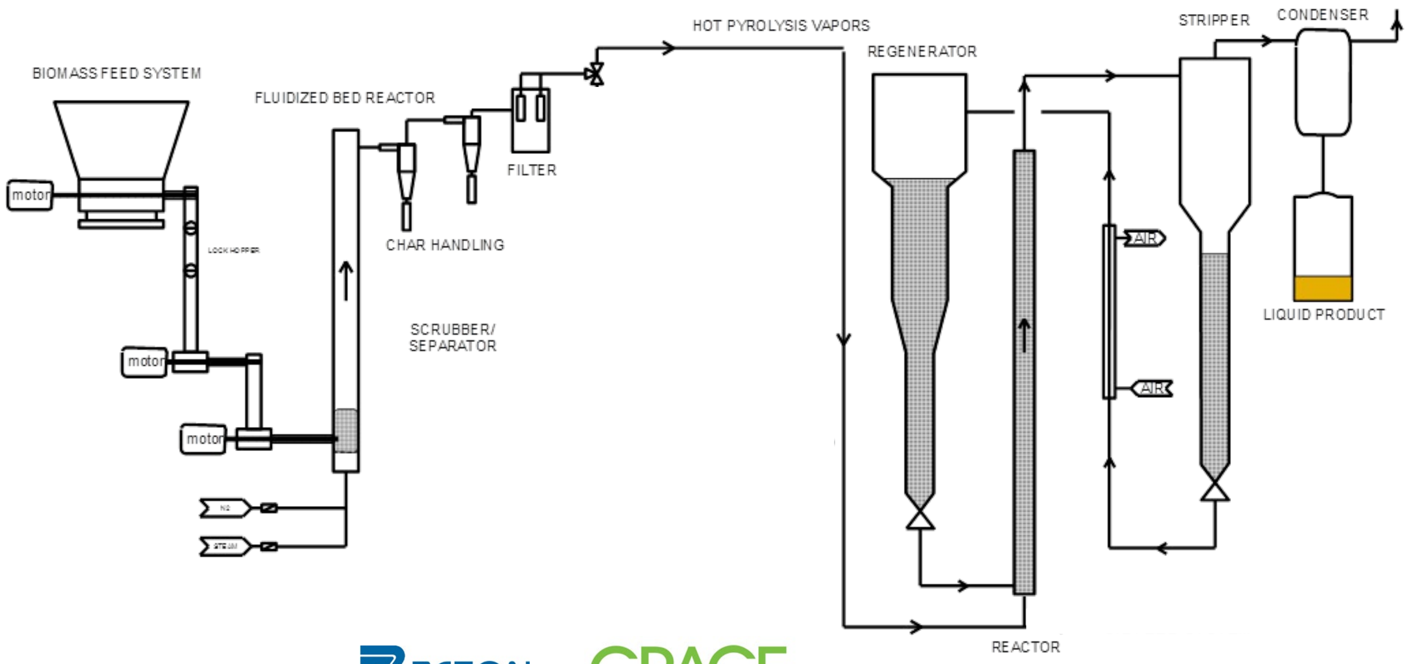
- Bubbling fluidized bed for production of fast pyrolysis oil.
- Vapors can be upgraded in fixed bed, fluidized bed, or circulating fluidized bed to produce catalytic fast pyrolysis oils.
- In a circulating fluidized-bed reactor (below), zeolite-based catalysts are able to produce low-oxygen-containing bio-oils.

Pyrolyzer

Circulating Bed Reactor for Pyrolysis Vapor Upgrading



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Analysis of Bio Oils – Stabilization Methods Achieve Different Bio-Oil Compositions

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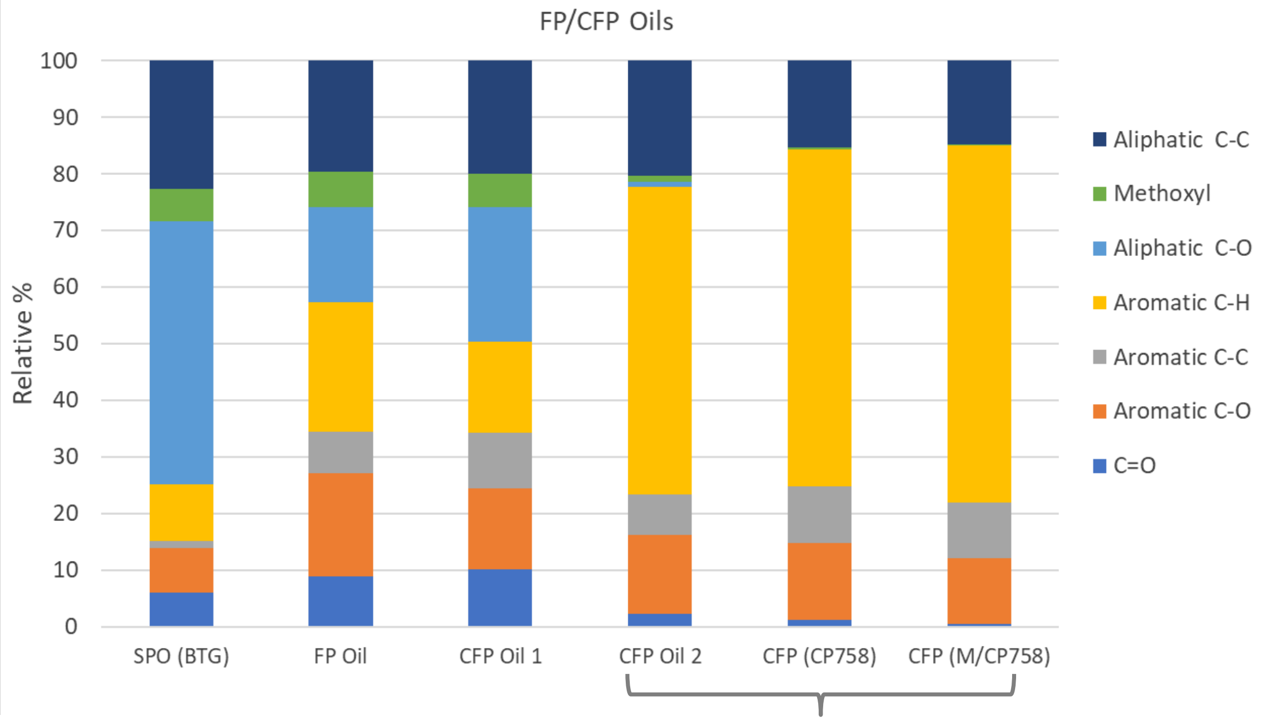
Characterization by ^{13}C NMR



- Stabilized Pyrolysis Oil (SPO) from BTG shows high oxygenates.
- With stabilization, aromatic content decreases and aliphatic content increases.

- CFP oils from upgrading of fast pyrolysis vapors using zeolite catalysts show lower oxygenates.
- With zeolite catalysts, aromatic increase.

NMR:	Nuclear magnetic resonance
FP Oil:	Fast Pyrolysis Oil
CFP Oil:	Catalytic fast pyrolysis oil
SPO:	Stabilized pyrolysis oil (BTG)
M:	Metal-modified

CP758: Johnson Matthey catalyst, containing less than 50% HZSM-5.

Hot-Gas Filtration of Pyrolysis Vapors Improves Quality of Bio-Oils

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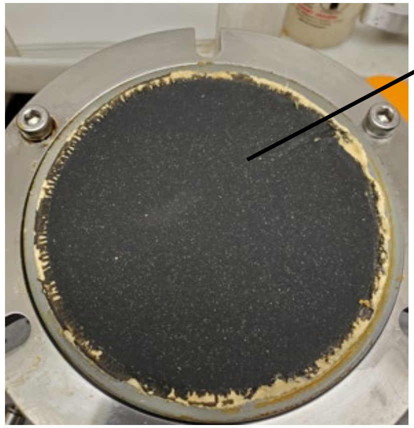
The Problem

- Bio-oils polymerize upon condensation of pyrolysis vapors
- Bio-oils polymerize upon re-heating
- Bio-oils can cause physical build up of deposits and plugging of orifices
- Contaminants such as alkali can reach downstream catalysts

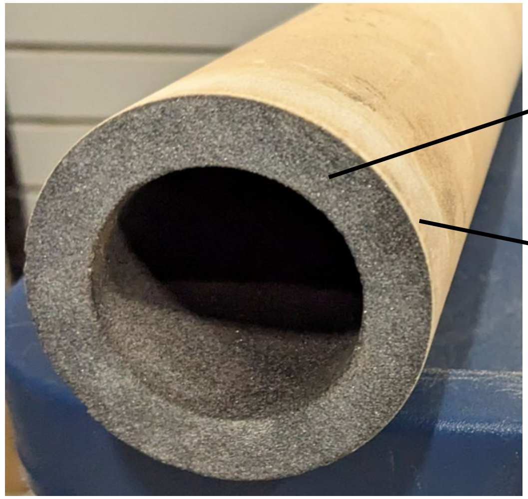
→ **Particulates in bio-oils amplify this problem**



Filtered residue from bio-oil

The Solution: Hot-Gas Filtering

- Improves quality and stability of bio-oil
- Reduces adverse effects in downstream processes



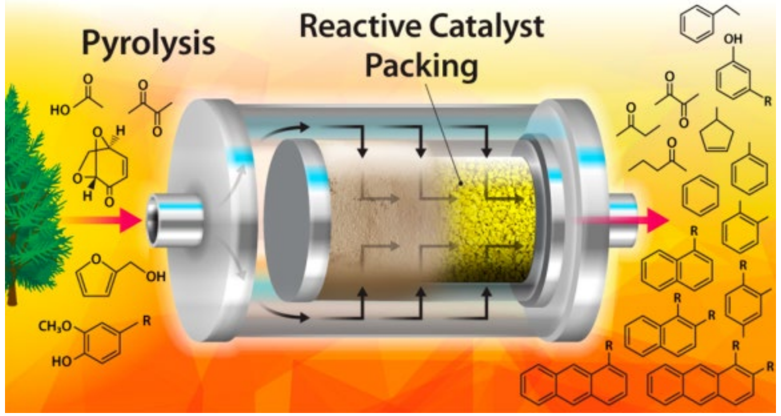
Coarse silicon carbide support

Fine alumina layer

Baldwin and Feik, Energy Fuels, 2013

Additional Opportunity: Combine Filtration with Catalytic Upgrading

- Mild upgrading of pyrolysis vapors
- Other chemistries



Peterson et al., ACS Sustainable Chem. Eng., 2019

Magrini et al., Patent US11459509B2

Davison Circulating Riser Adapted for Co-Processing Renewable Feeds

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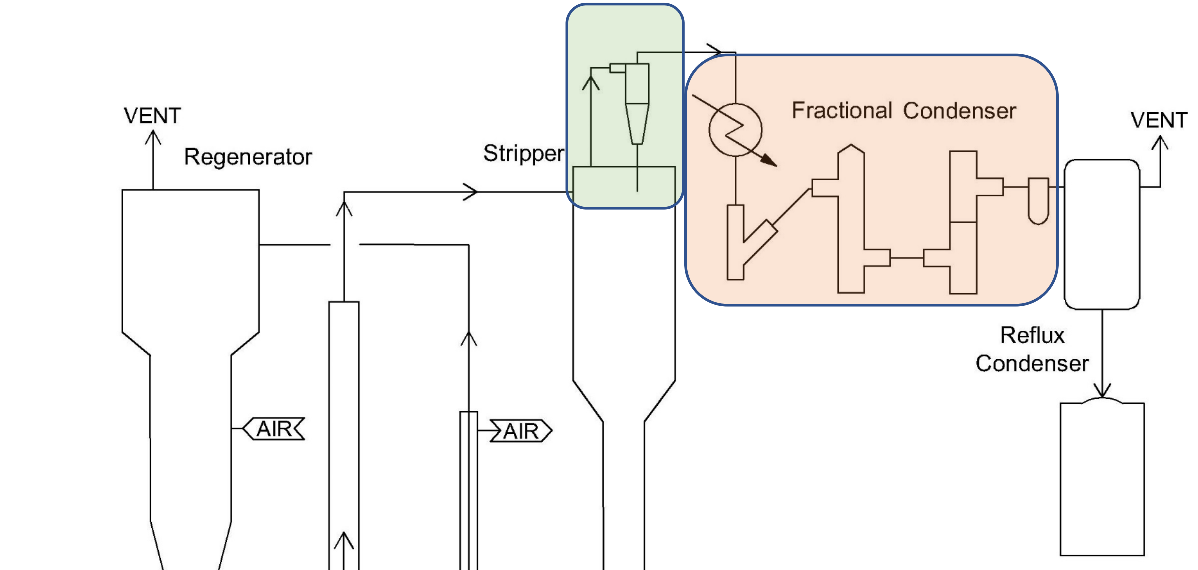
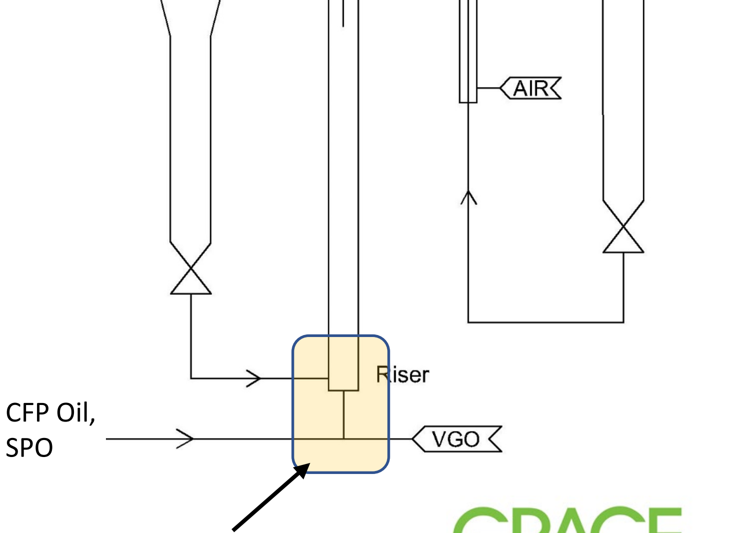
- NREL's DCR can be configured as a pilot-scale FCC reactor.
- FCC reactors in refineries are used to crack large molecules to smaller fuel-range molecules.
- Catalyst recirculated for stripping (hydrocarbon removal) and regeneration (coke removal).
- Added capabilities:
  - Stripper cyclone
  - Fractional condenser/aerosol filter
  - Modified nozzle (for biogenic feed)

  [Magrini et al., Patent US20220355260A1]





Feeding oxygenated streams into high-temperature reactor can cause operational challenges.

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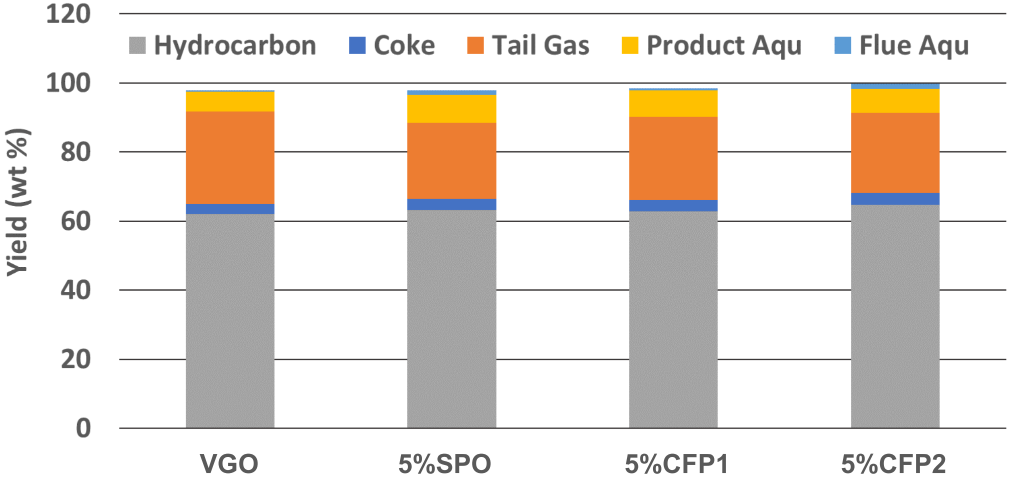
Co-Processing of Bio Oils with VGO in FCC – Results

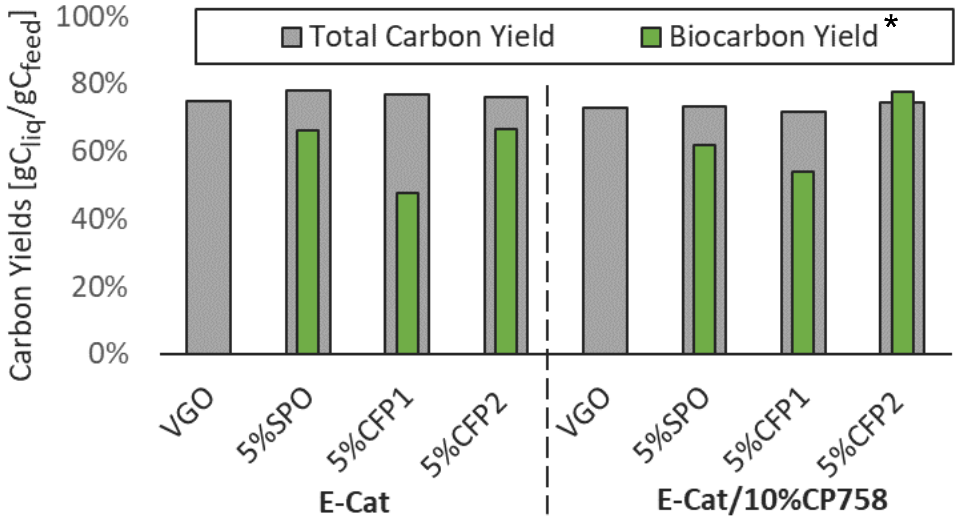
- Three different bio-oils were co-processed at 5 vol% with Vacuum Gas Oil (low-sulfur VGO) in a Davison Circulating Riser.
- Oxygen contents of oils were between 20 and 39%.
- Two different commercially available catalysts were used.
- Yields were comparable with VGO-only.
- Relative biocarbon incorporation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

*Biocarbon in product and feed measured by ^{14}C AMS (ASTM 6866).
E-Cat: Equilibrium Catalyst (standard for Fluid Catalytic Cracking).
CP758: Johnson Matthey catalyst, containing less than 50% HZSM-5.

Addition of 5% bio-oil to FCC streams does not significantly change the product fraction other than a slight increase in water



Bio-Carbon Yield to Liquid Product



- CFP1: High-oxygen (36%) bio-oil
- CFP2: Low-oxygen (20%) bio-oil

Co-Processing Mechanism Investigated with ^{13}C Analysis

Interaction between VGO and bio-oil creates fuel-type molecules and avoids biocarbon in tail gas and coke.

^{13}C-labeled Woody Stem (^{13}C>97%)

Approach

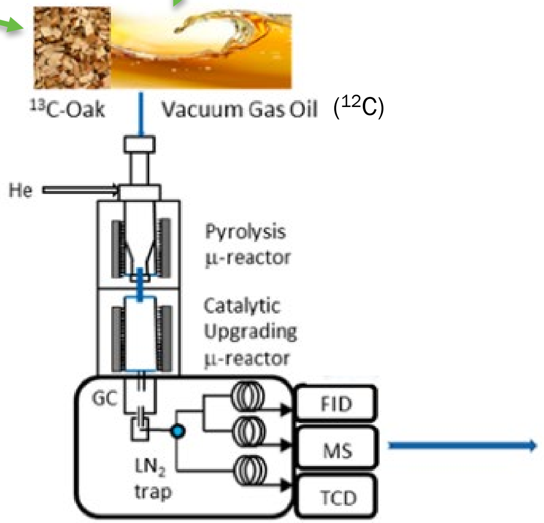
- Investigate interactions of bio-oil molecules with petroleum molecules during co-processing in micro-pyrolyzer.

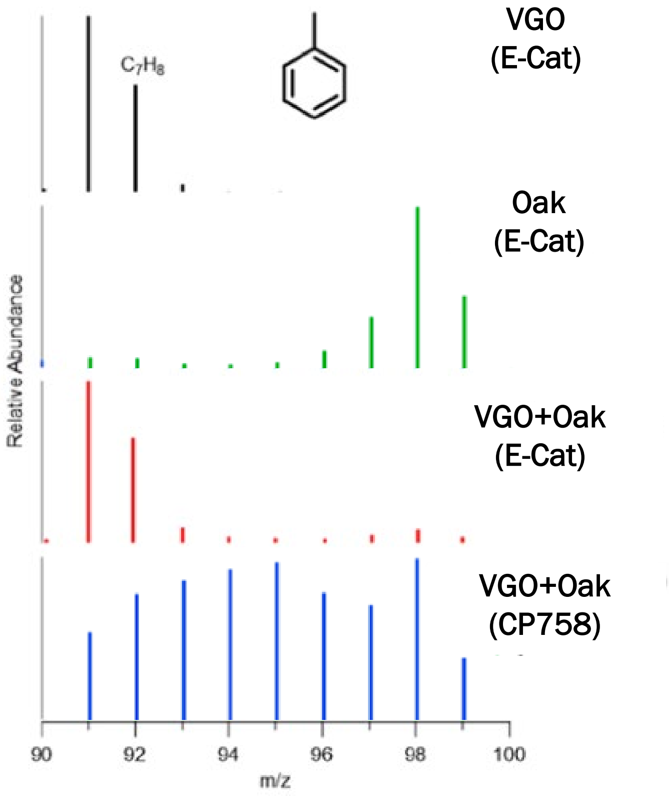
Result

- Compared to E-Cat, CP758 shows more interaction between petroleum and biogenic feeds. Molecules included aromatics, light olefins, and phenols.

Micro-Pyrolyzer Experiments to Track Biocarbon Incorporation

Petroleum (mainly ^{12}C)





Mukarakate et al., ACS Sustainable Chem. Eng., 2020

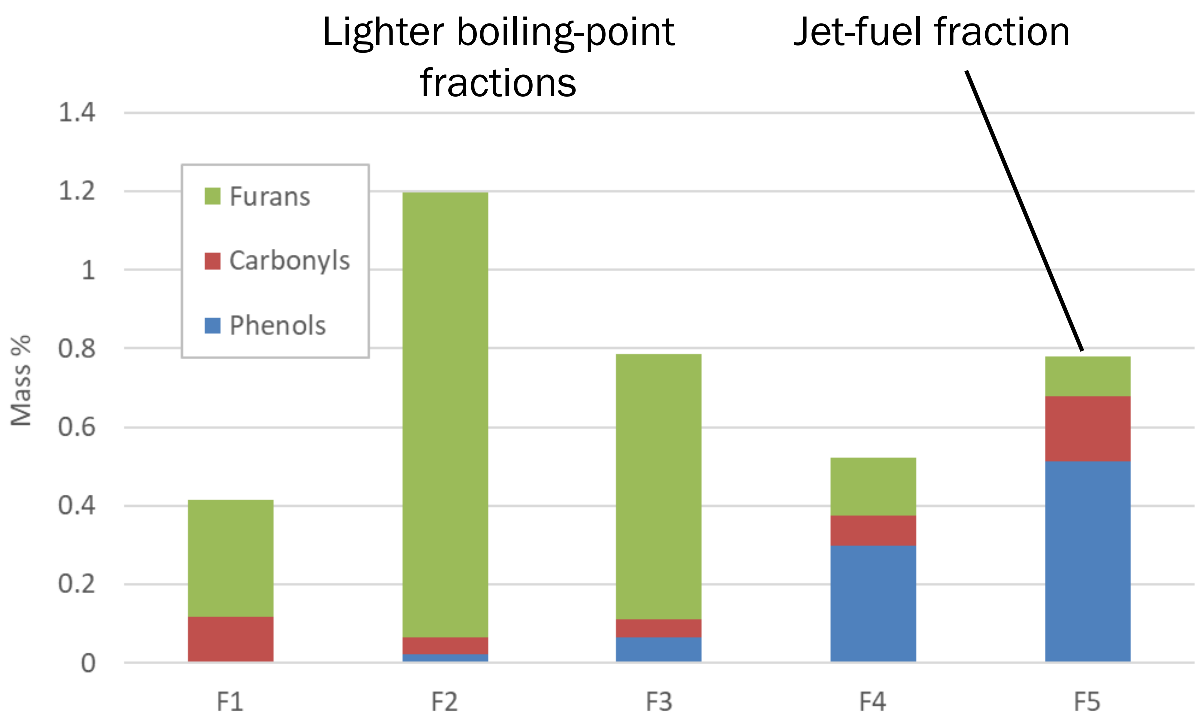
E-Cat: Equilibrium Catalyst (standard for Fluid Catalytic Cracking)
CP758: Johnson Matthey catalyst, containing less than 50% HZSM-5

NREL Has Facilities for Analysis of Oxygenated Streams

In-house Methods

- Direct oxygen analyzer
- ^{13}C nuclear magnetic resonance (NMR)
- Gas-chromatograph with mass spectrometer (GC-MS) and PolyArc/FID for identifying individual compounds
- GCxGC for analyzing polar compounds on second dimension
- Simulated distillation by thermogravimetric analyzer (TGA)
- Fractionation by spinning band distillation

Analysis of Different Boiling-Point Fractions by GC-MS

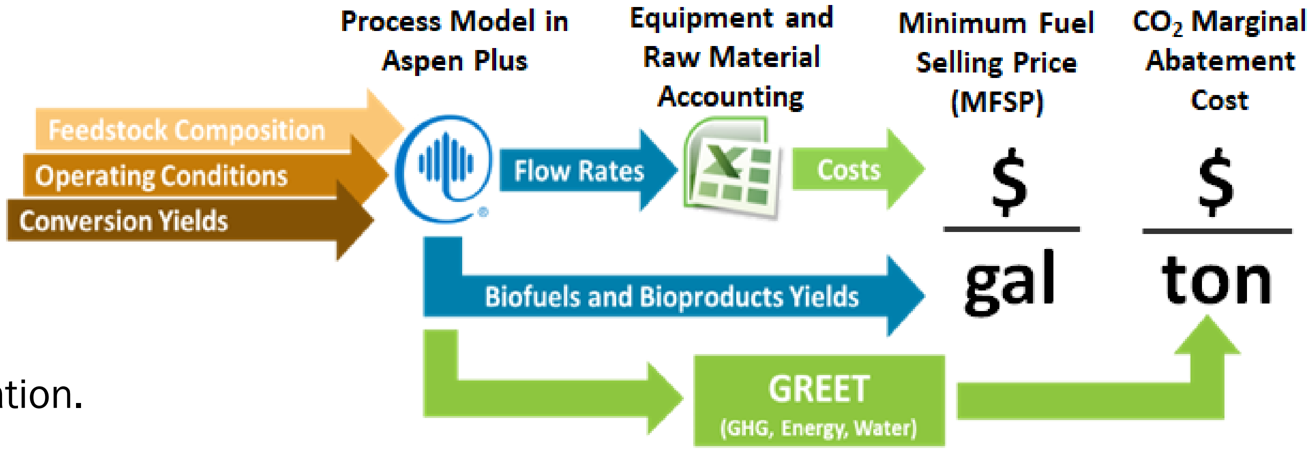


Oxygenates left over in jet fuel need to be removed in subsequent hydrotreating.

Techno-Economic Analysis (TEA) of Co-processing in FCC

Technical Approach

- Aspen Plus modeling for rigorous mass and energy balances.
- Cash flow calcs for Minimum Fuel Selling Price (MFSP).
- Credibility of analysis supported by expert consultants and external stakeholders vetting.
- TEA and sensitivity analysis guides R&D focus.



Analysis Focus Areas

- Integrating economic and sustainability analyses.
- Evaluating opportunities for refinery and infrastructure integration.
- Identifying refinery bottlenecks with bio-oil co-processing and unit repurposing.

Project Results

- TEA results show promising improvement by increasing bio-carbon incorporation. Seiser et al., Biomass and Bioenergy, 2021
- Opportunities for SAF production.

Summary – Co-Processing in Fluid Catalytic Cracking

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Progress and Outcomes

- Different bio-oils produced in ex-situ CFP with oxygen content ranging from 12-36%.
- Various bio-oils successfully co-processed in FCC (1 to 10%).
- High biogenic C incorporation demonstrated (at 5% co-processing). Mechanism of interaction between biocarbon and fossil carbon identified.
- Implemented tools for hot-gas filtration bio-oil feeding, liquid collection, and analysis.
- Choice between bio-oil quality, oxygen content can be made – depending on other process conditions (i.e., derating of equipment, tail-gas blowers/upgrading, wastewater production)

Summary – Co-Processing in Fluid Catalytic Cracking

Future work

- Use FCC to pre-process other biogenic streams
- Increase olefins and jet fuel as major product from FCC
- Increase variety of feeds and investigate synergies
- Increase biogenic feed percentages towards 100%
- Perform detailed analyses of feeds (assays) for refiners
- Continue tracking contaminants in bio-oils/biocrudes

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Chief Research Engineer

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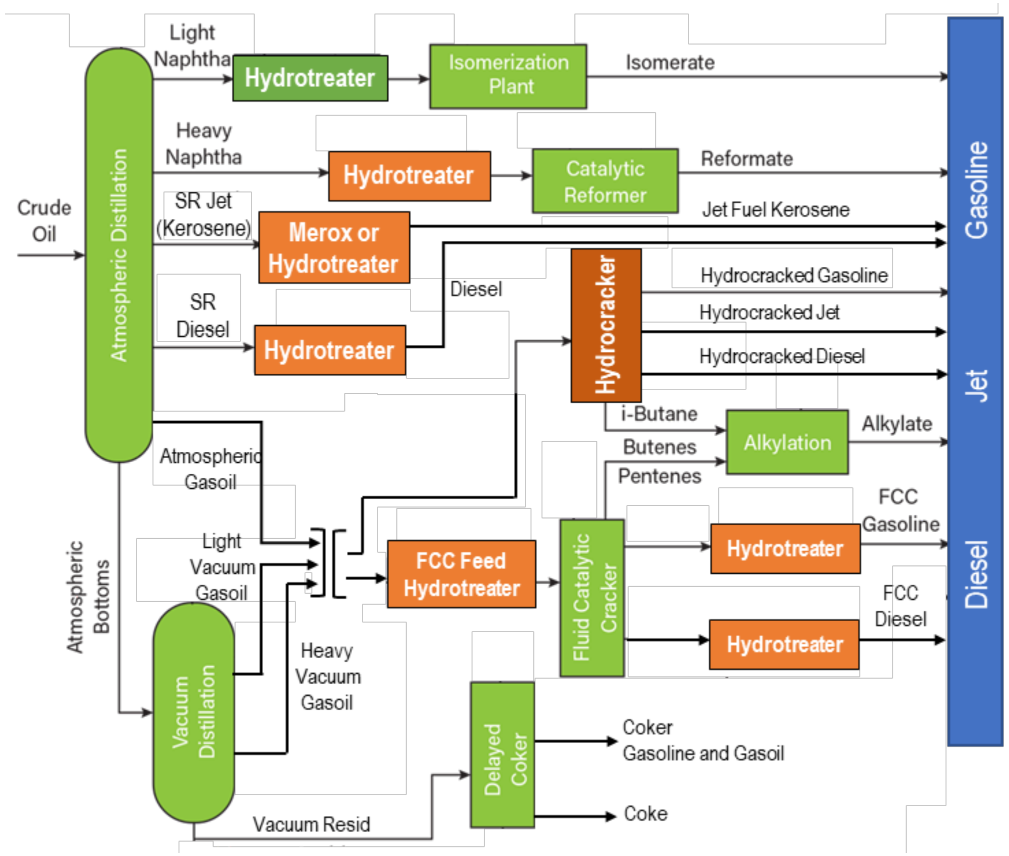
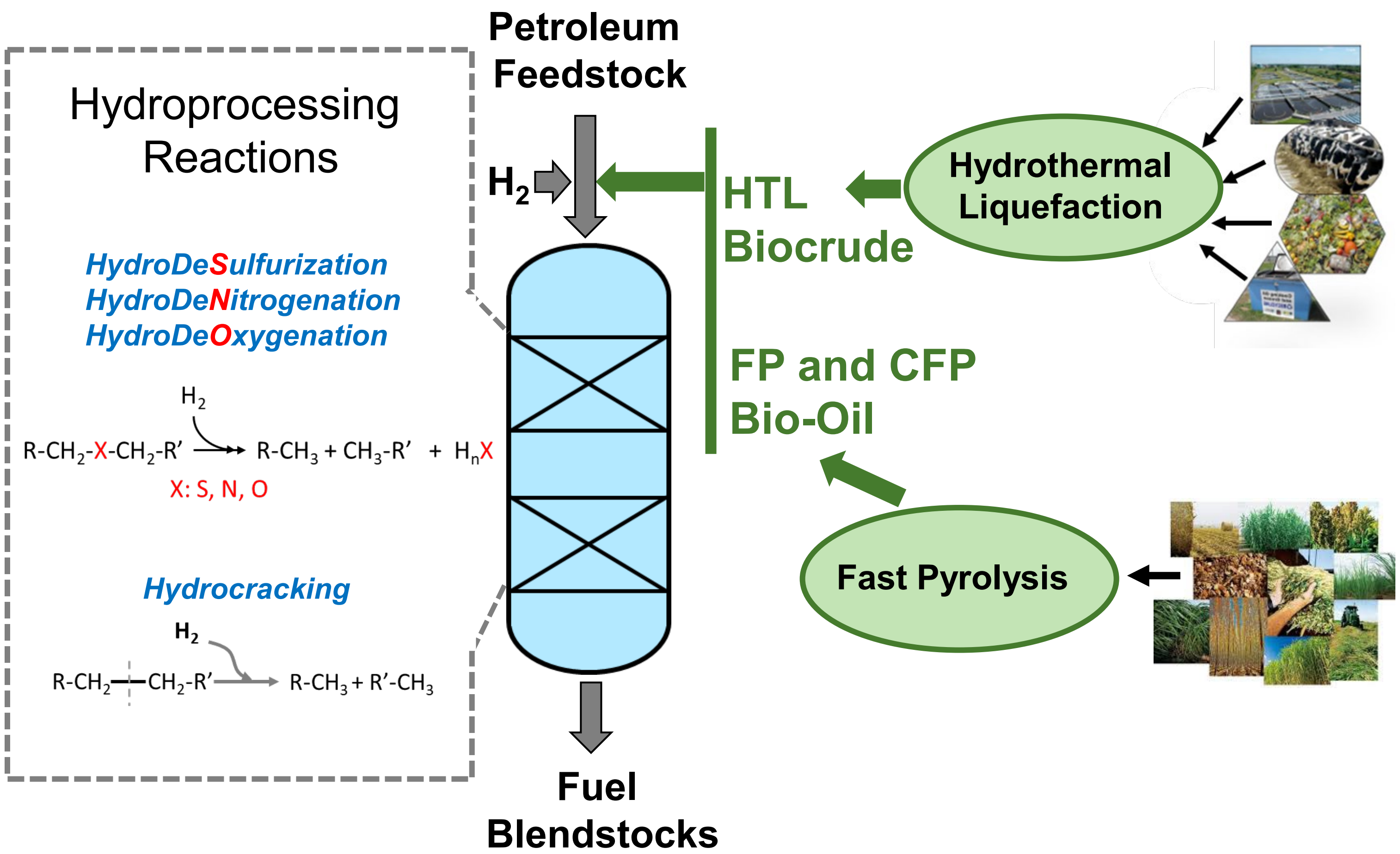
Hydroprocessing in Refinery can Co-Process Bio-oils and Biocrudes

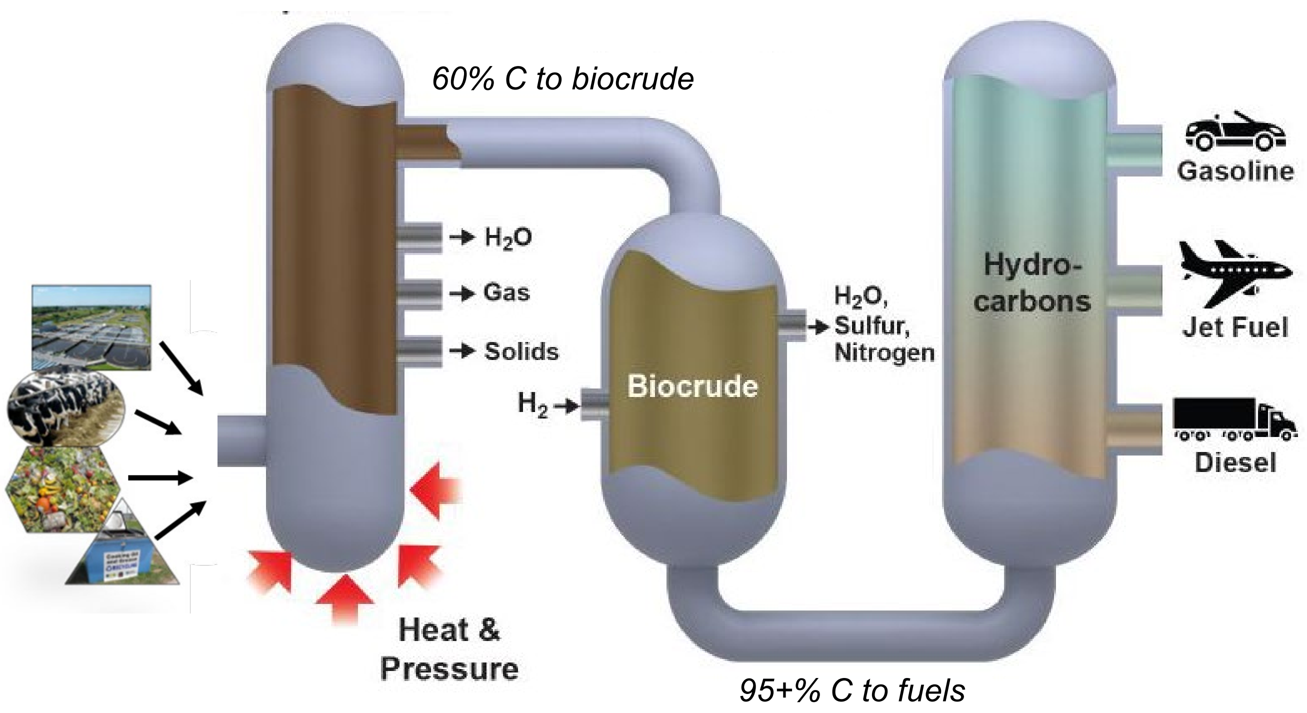
An example of a petroleum refinery





- Hydrotreating removes heteroatoms (S, N, O) and hydrocracking converts heavy gasoils into lighter fuel blends
- Hydrogen addition to prevent carbon rejection
- Fixed-bed operation, long catalyst lifetime, high pressure

Transforming Wet Wastes to Liquid Fuels by Hydrothermal Liquefaction (HTL)



HTL	Hydrotreating
330-350 ^{o}C 20 MPa 10-30 min	400 ^{o}C 10 MPa

- Conceptually simple (i.e., heated pipe), continuous process
- High carbon yields to liquid hydrocarbons
- Tolerates dirty, wet feedstocks

Benefit #1: **Potential for ~6 billion gallon/year of fuel in the U.S.**

Benefit #2: **Alternative disposal processes**

PNNL's HTL Process Development Unit (PDU)

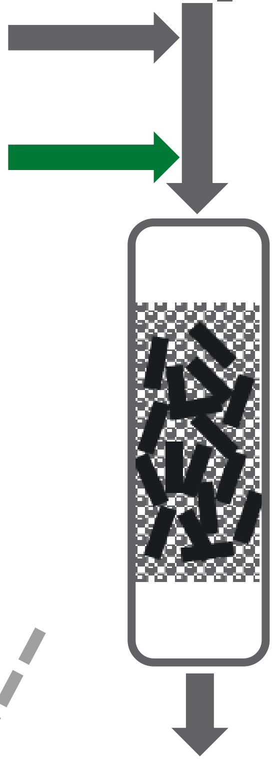
An Extensive Study on the Performance of Co-Processing in Hydroprocessing

Vacuum Gas Oil (VGO)
or Straight Run (SR) Diesel
or Kerosene or Fuel oil

Woody FP/CFP Bio-Oil
or Sewage Sludge HTL Biocrude

2-20 % blending

H_2



Commercial Catalyst Extrudates

Feed Analysis

- Chemical composition
- Heteroatoms and contaminants

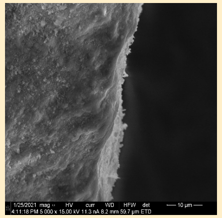
Hydroprocessing Performance

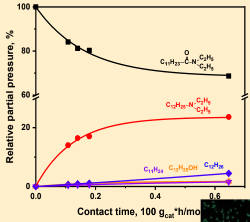
>300 h TOS with steady state operation

- Fuel/gas/water yield
- Heteroatom removal (N, S, O)
- Hydrocracking conversion
- H_2 consumption

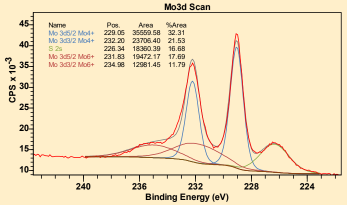
Fuel
Gas
Water

Catalyst Characterization

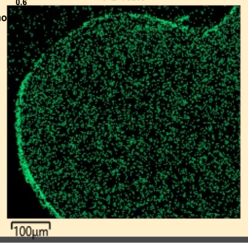




Kinetics using model compounds

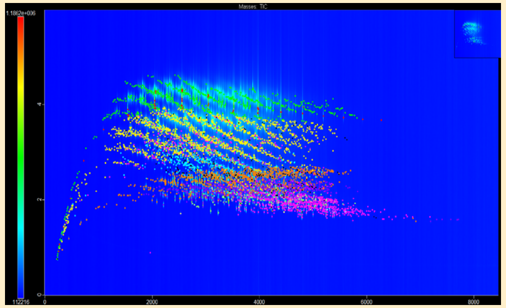


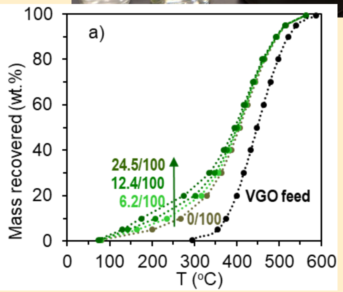
Fe Kα1



Fuel Analysis

- Gas and liquid product composition
- Diesel/Jet quality
- Biogenic carbon content





We Evaluate Co-Processing of Bio-Liquids in Various Hydroprocessing Units

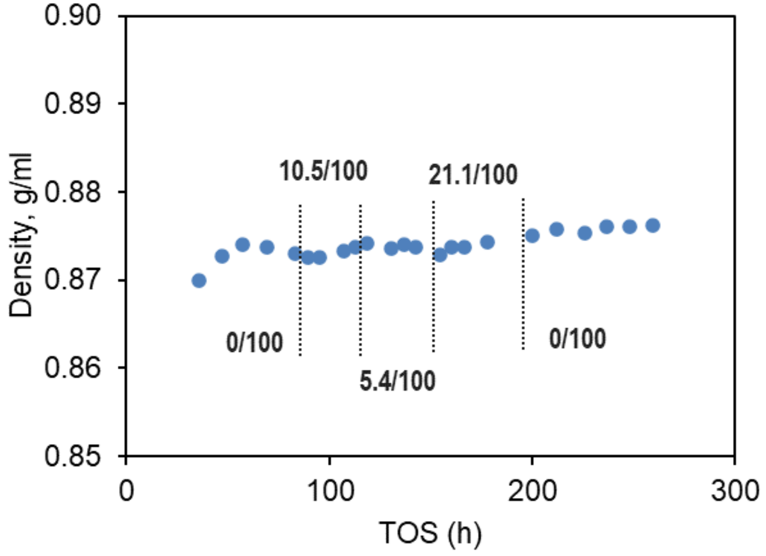
	Woody FP bio-oil	Woody CFP bio-oil	Sludge HTL biocrude	Hydrotreated HTL biocrude
Diesel HT	• Instability requires pre-stabilization • High water and O • Low (~70%) bio-carbon incorporation into fuel	• Mild impact on HT chemistry • High (80-95%) bio-carbon incorporation into fuel • Water, O, long-term "coke" formation	• Strong N inhibition of HT chemistry	
VGO HT	(same as Diesel HT)	(same as Diesel HT)	• HT pretreatment to mitigate N issue • High (>95%) bio-carbon incorporation into fuel • Increased fuel quality • Faster catalyst deactivation at long-term	
VGO HC			(same as VGO HT)	
Fuel oil HT			• Enable N and S reduction • Issues in homogeneity	
Kerosene HT				Synergy enables deep HDN (<1 ppm N for SAF)

- The feasibility of co-processing bio-oil and biocrude feedstocks with different petroleum streams in hydroprocessing greatly depends on their heteroatom content and speciation

More challenge (red) *Less challenge* (blue) *More data needed* (grey)

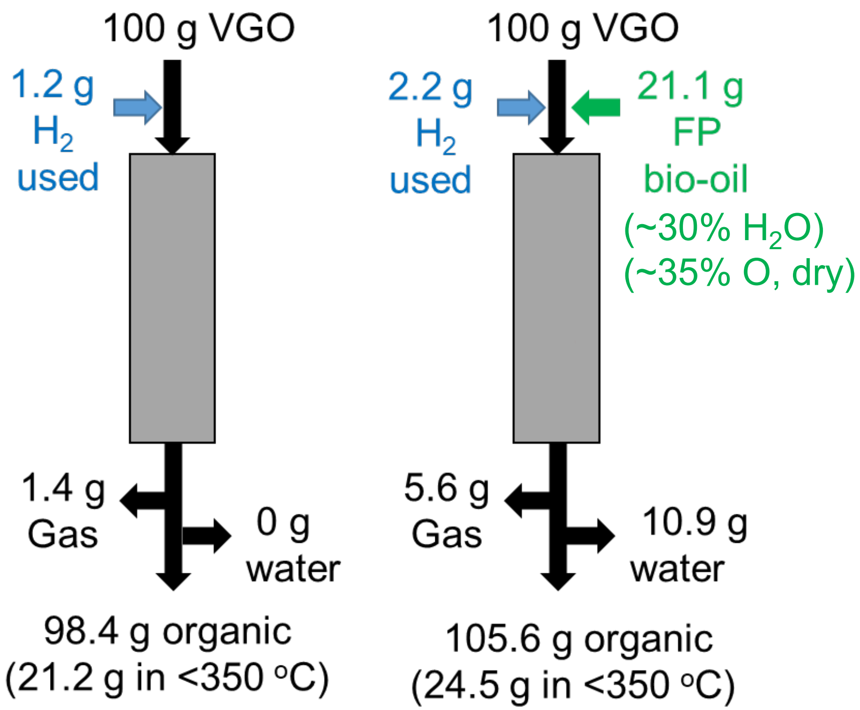
Fast Pyrolysis (FP) Bio-Oil Requires Stabilization for Co-Hydrotreating

Stable co-processing of stabilized FP bio-oil with VGO



- Raw fast pyrolysis bio-oil leads to co-processing reactor plugging because of its instability
- Bio-oil stabilization through hydrogenation enables its stable co-processing
- The minimal impact of bio-oils on the reaction of VGO and the simultaneous conversion of bio-oil and VGO reduce O and S

Bio-oil leads to water and more gas formation



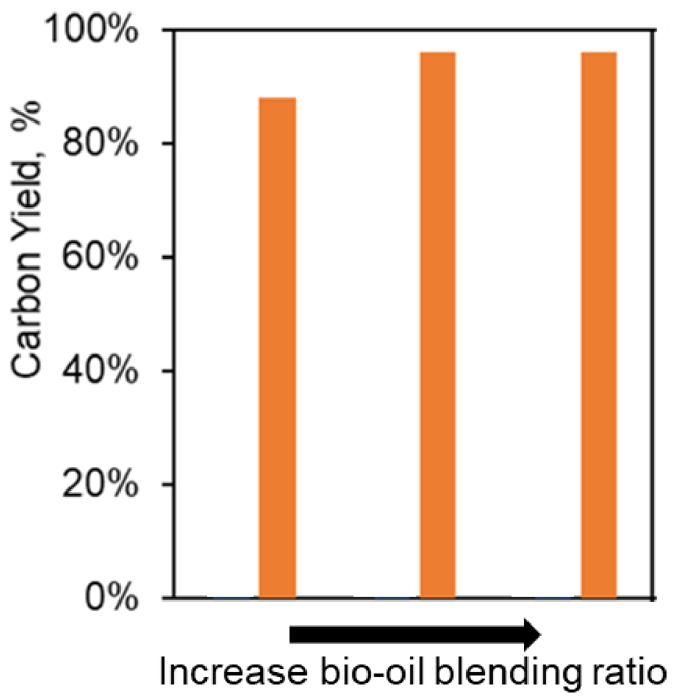
~70% biogenic carbon incorporated into fuels

Challenges:
- High water formation
- Low biogenic carbon incorporation in fuel
- Unclear long-term impact on catalyst stability

M. Santosa,… H. Wang, Energy & Fuels, 2022, 36, 12641

Catalytic Fast Pyrolysis (CFP) Enables Higher Biogenic Carbon Incorporation

~90% biogenic carbon incorporated into fuels



Bio-oil O dry wt.%: 12-15%, with VGO

M. Santosa,… H, Wang, Energy & Fuels, 2022, 36, 12641

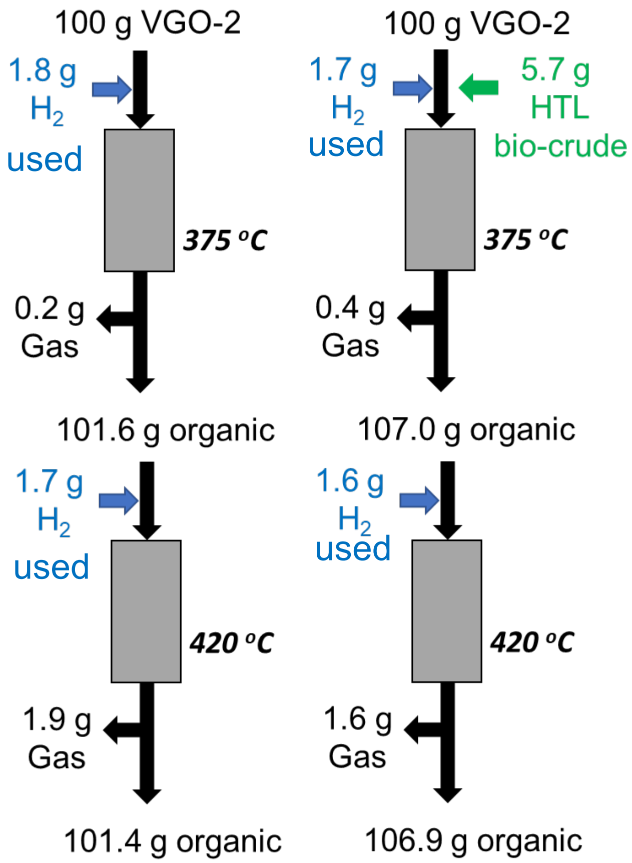
More biogenic carbon in diesel range

	VGO-Only	12/100 CFP/VGO
Diesel fraction (184-350 ^oC)		
Cetane number	**45**	**39**
Biogenic C,% (AMS)		**11.4 (~54% of total bio-C)**
Gasoil fraction (>350 ^oC)		
N, ppm	**80**	**100**
Aromatic, wt.%	**32**	**38**
Biogenic C,% (AMS)		**1.7 (~13% of total bio-C)**

- Stable co-processing of CFP bio-oil with high biogenic carbon incorporation into fuels
- Minimal impact of bio-oils on the reaction of VGO/straight-run diesel at deep HDS conditions
- *Challenges:* Water formation, reduced diesel fuel qualities, unclear long-term impact on catalyst stability

95+% Biogenic Carbon Incorporation Demonstrated for the HTL Biocrude

	Bio-crude	VGO
H/C	~1.5	1.6-1.7
O	~2-8	0.1-1.0
S	~0.5	0.1-2.5
N	~5	0.1-2
H_2O	~1-5	<0.05



95+%
biogenic carbon incorporated into fuels

Improved diesel (184-350 °C) quality

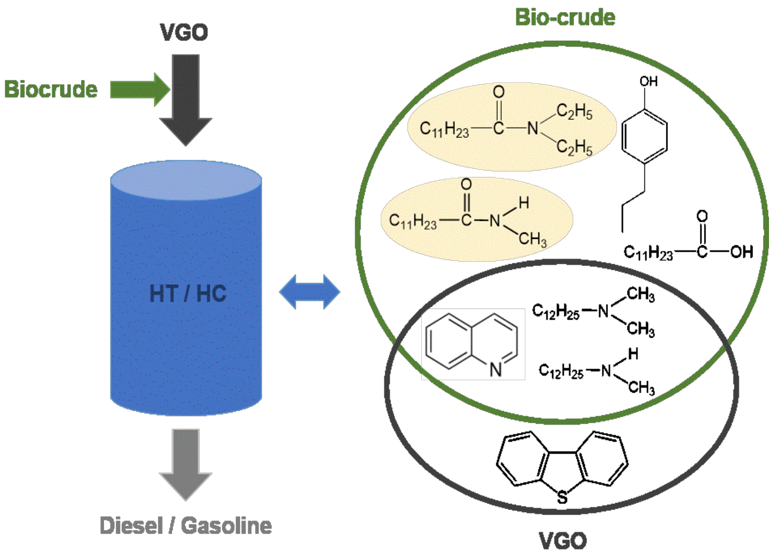
	VGO only	5.7/100 HTL/VGO
Cetane Number	**42**	**47**
S, ppm	**<15**	**<15**
N, ppm	**30**	**93**
Biogenic C, % (AMS)		**7.3 (~60% of total bio-C)**

M. Santosa, … H. Wang, Manuscript in preparation

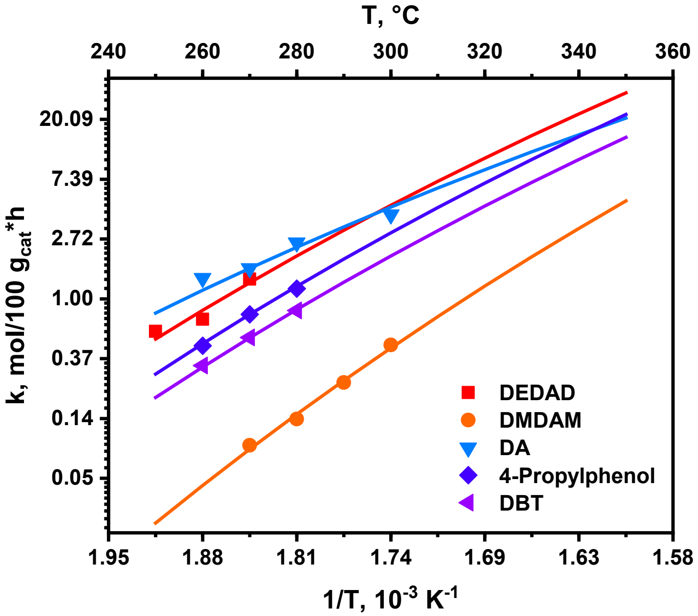
- High N in biocrude leads to competition among heteroatom (S, N, O) removal when co-processing
- A hydrotreating step is required to mitigate N issues of biocrude and enable co-processing in hydrocracking
- High biogenic carbon incorporation and improved diesel fuel quality through co-processing biocrude
- *Challenges:* N-containing species removal and maintaining catalyst stability

Hydrodenitrogenation (HDN) is Critical for Biocrude Co-Processing

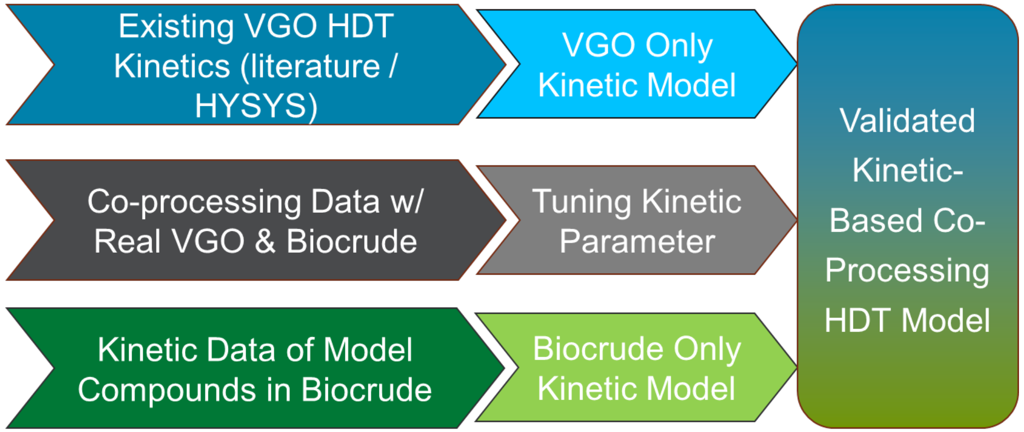
Biocrude introduce new N containing species



Hydrodenitrogenation is slow



Kinetic-based reactor model for co-processing



- Kinetic studies investigate the hydrotreating chemistry of unique heteroatom-containing species from biocrude
- HDN is critical for biocrude co-processing, especially concerning the aromatic heterocycles that inhibit HDS and hydrocracking reactions
- A kinetic-based reactor model for co-processing enables predictive capabilities and optimization for reactor configuration and operation conditions

C. Zhu,… H. Wang, Applied Catalysis B: Environmental, 2022, 307, 121197

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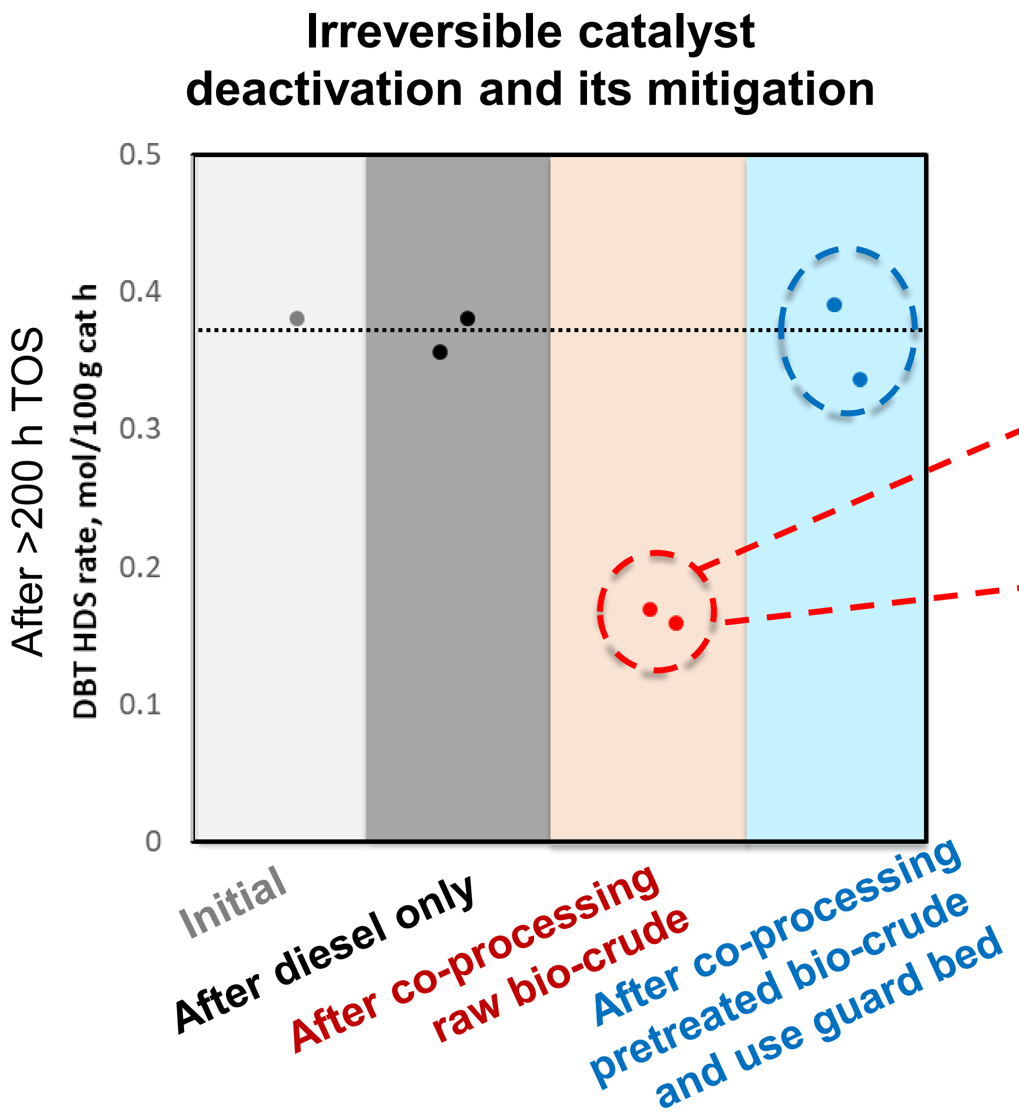
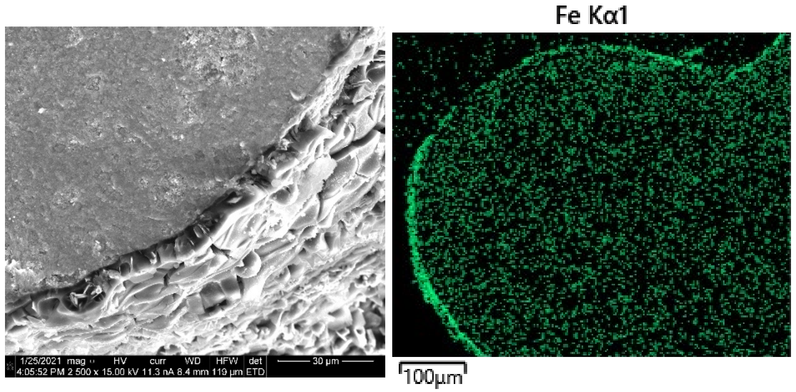
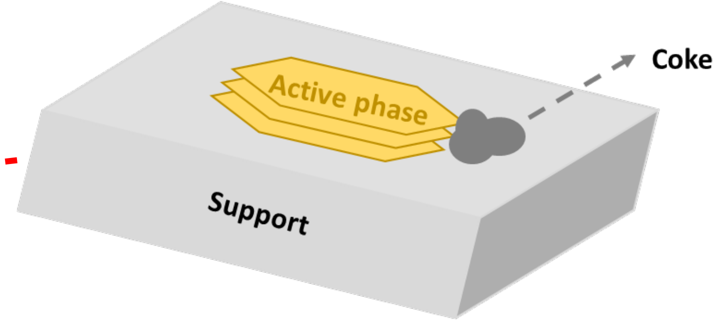
Mitigating Irreversible Catalyst Deactivation Induced by Co-Processing Biocrude



C. Zhu,… H. Wang, Energy & Fuels, 2022, 36, 9133



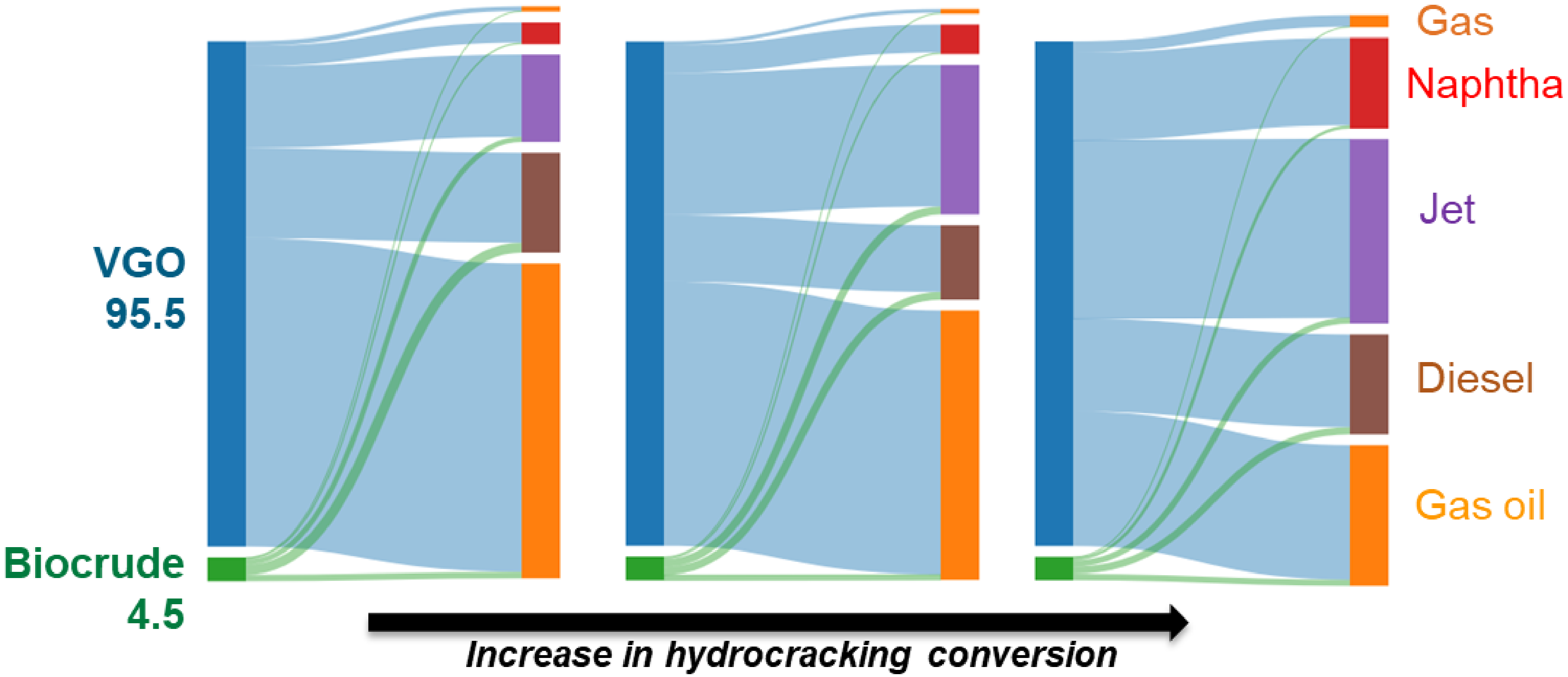
Inorganic contaminant deposition



Pore blocking and selective active sites fouling by coke

- Catalyst deactivation due to inorganic deposition and accelerated “coke” formation
- Deactivation mitigation through feedstock pretreatment and the use of a guard bed
- *Challenges:* Long-term impact on catalyst stability requires further investigation

Tuning Biogenic Carbon Distribution in Co-Hydrocracking



- Deep HDN in VGO + biocrude hydrotreating enables hydrocracking using the conventional zeolite-containing catalyst for a greater yield of jet and diesel range fuels
- Biogenic carbon is largely incorporated into the mid-distillate range fuel (jet and diesel)
- Biocrude is less sensitive than VGO on the hydrocracking severity

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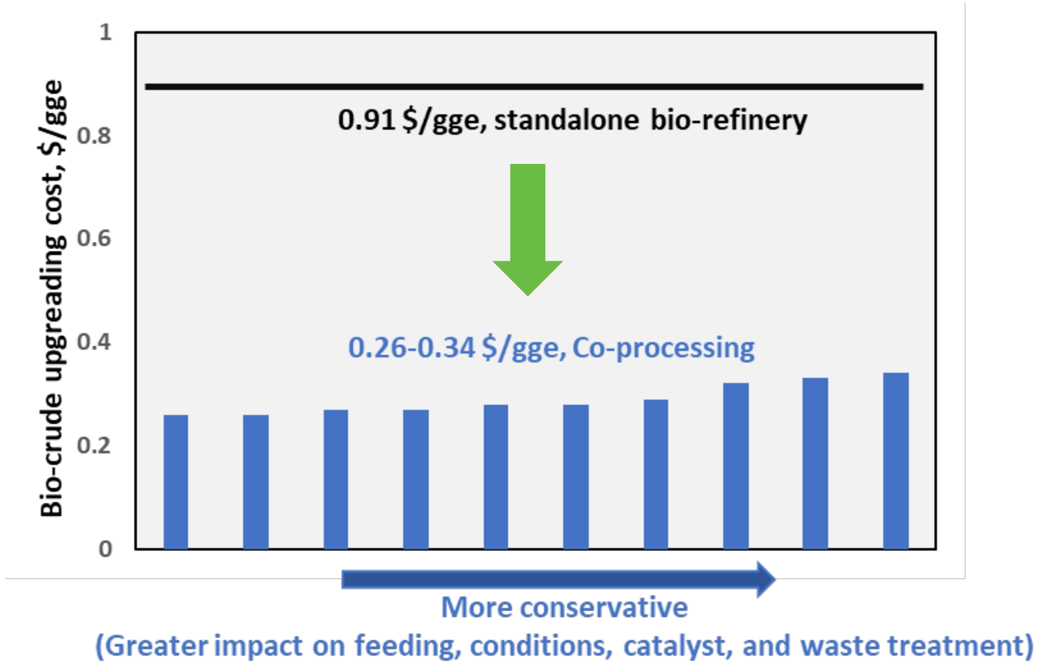
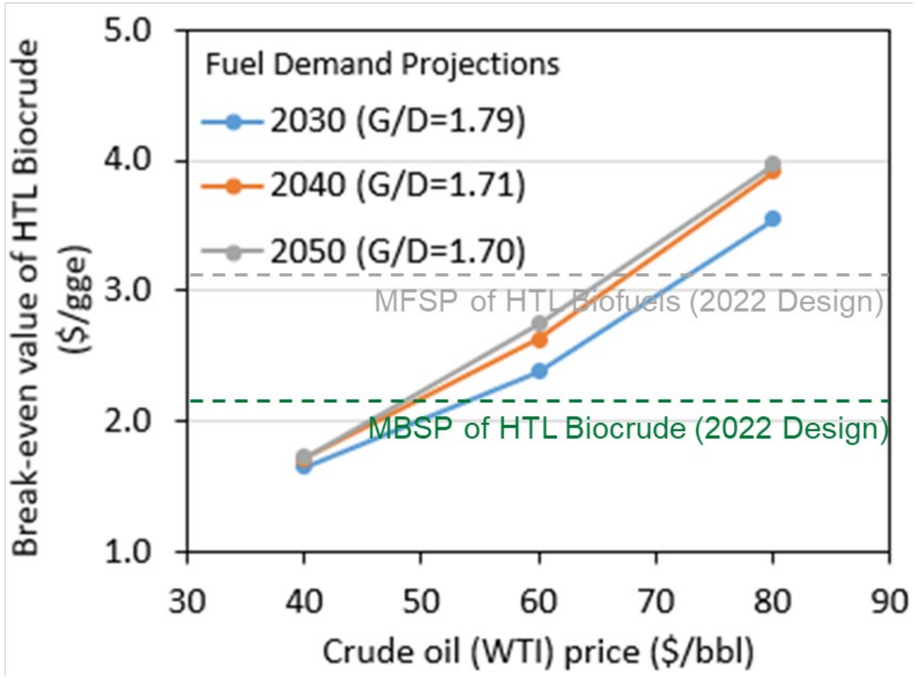
Co-Processing can be Beneficial to Both Biorefinery and Refinery

TEA for biocrude to diesel conversion cost for co-processing with VGO at hydrotreating



Refinery Impact Analysis of co-processing biocrude and VGO at hydrotreating



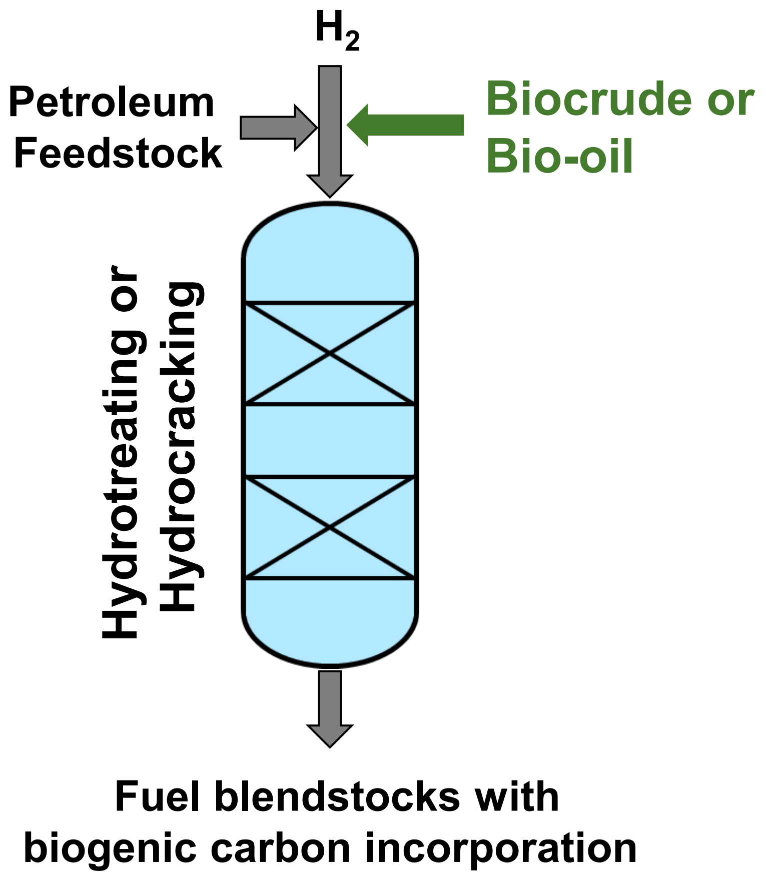
- Co-processing enables biocrude conversion cost reduction by reducing capital cost

- With ongoing R&Ds, the modeled break-even values of HTL biocrude will be greater than their modeled MBSPs at 2022 design cases

* Analysis was based on 2022 Wet Waste HTL Design Case study. All results are in 2016 pricing basis.

Y. Jiang, … H. Wang, Manuscript in preparation

Co-Processing Bio-oils and Biocrudes in Hydroprocessing Have Great Potential



- High biogenic carbon incorporation through co-processing CFP bio-oils or HTL biocrudes in hydroprocessing
- In co-hydrotreating, the competition for heteroatom removal is critical. Specifically, for HTL biocrude with high N content, HDN is the key to enable co-processing in hydrocracking
- Kinetics of hydrotreating biocrude-related components and co-processing reactor model enables predictive capabilities
- Co-processing biocrude could result in faster hydrotreating catalyst deactivation, which can be mitigated by feed pre-treatment and/or optimizing catalyst guard bed
- Co-processing can offer benefits to both the biorefinery and the refinery

Continuing efforts could focus on:

- Catalyst stability over longer durations and at larger scales
- Establishing feedstock specification, including contaminates and other factors
- Studying the impact of co-processing beyond catalytic reactor
- Increasing the blending level

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Collaborators

Johnson Matthey — Inspiring science, enhancing life
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BIOENERGY TECHNOLOGIES OFFICE

Agenda

This Webinar (9/20/2023)

- Housekeeping
- Overview of BETO
- Overview of the Co-Processing Project
- Co-Processing of Bio-Oils in Fluid Catalytic Cracking
  Reinhard Seiser (reinhard.seiser@nrel.gov)
- Co-Processing of HTL Biocrudes and Bio-Oils in Hydroprocessing
  Huamin Wang (huamin.wang@pnnl.gov)
- Q&A

Next Week's Webinar (9/27/2023)

- Biogenic Carbon Tracking and Measurement