Co-Processing in Refineries of Thermal Liquefaction Products from Biomass and Waste

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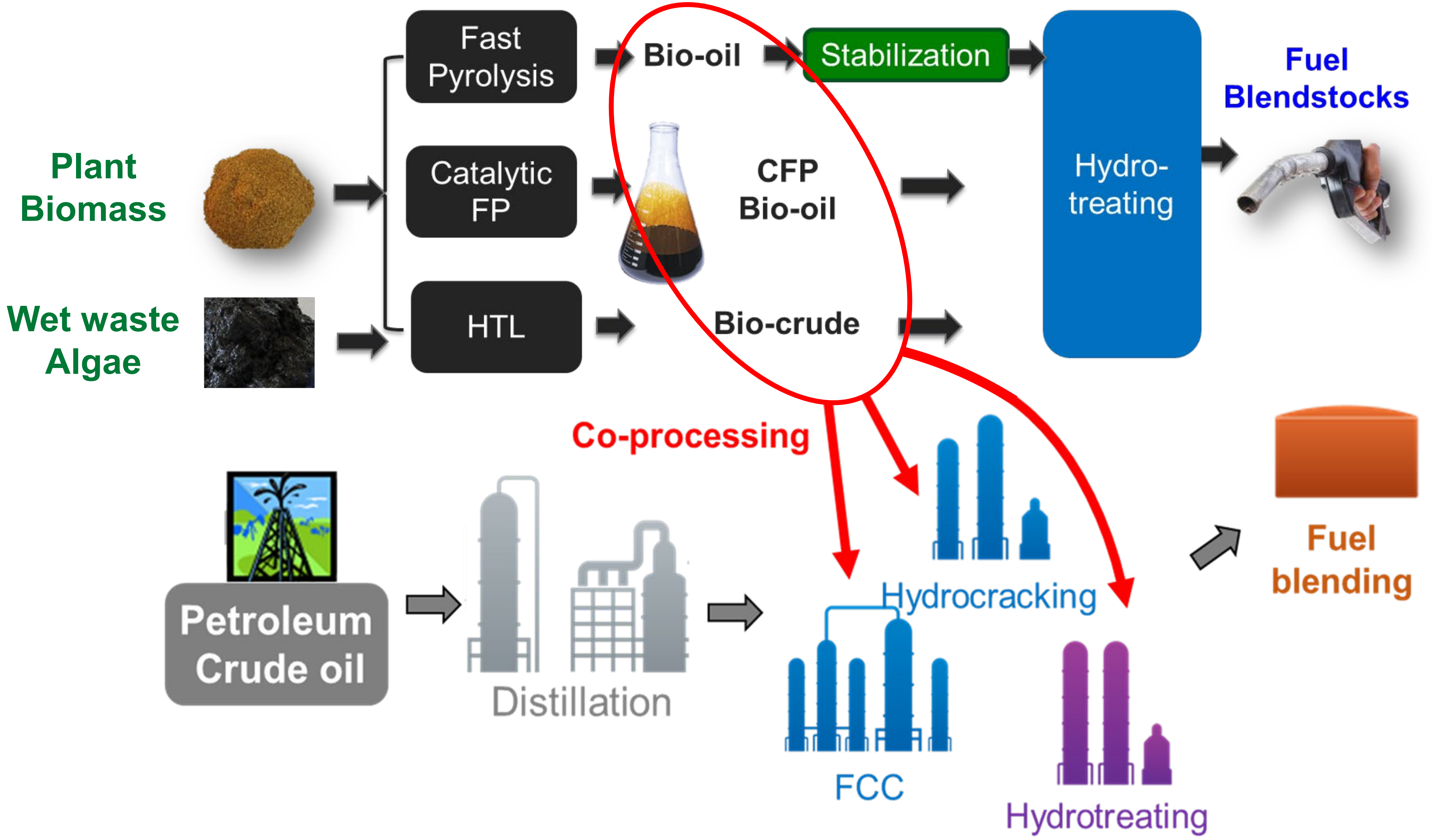
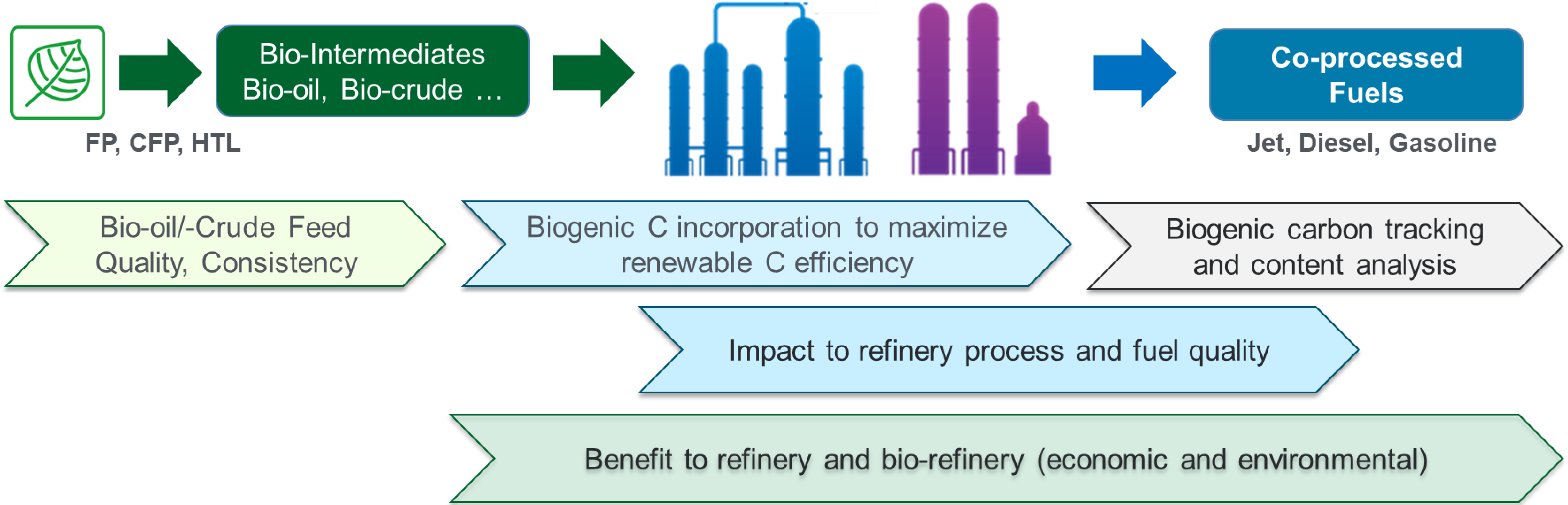
PNNL is operated by Battelle for the U.S. Department of Energy

We can leverage existing refining infrastructures to leverage billions of US$



De-risking co-processing requires extensive R&D



- Bio-oil/bio-crude co-processing not currently practiced by refiners
- Pilot scale work shows 1-10 wt% bio-oil feed is possible in FCC units
- Bench scale work shows potential of co-processing in HT/HC units with limited research on woody bio-oils and wastewater sludge HTL bio-oils

An interdisciplinary and collaborative effort to de-risk co-processing in refinery

Wood, Herbac.
WWTP Sludge, Algae

FP, CFP (NREL)
HTL (PNNL)

VGO Blends
Bio-oil/Crude

FCC
(NREL)

HT/HC
(PNNL)

Fuel Analysis
NREL, PNNL, LANL

Biogenic Tracking
LANL, PNNL, NREL

Process TEA, LCA
(PNNL, NREL)

IAB, Refinery
Assessment
Integration

BP
CARB
Chevron
DOE-BETO
ENSYN
Exxon Mobil
Honeywell/UOP
Kern Oil
Suncor
U. Brit. Columbia
U. Of Calgary
WR Grace

Bio-oil/Bio-crude

- PNNL HTL projects
- NREL CFP project
- NREL Co-HT project
- Ensyn

Catalyst Development

- Johnson Matthey
- WR Grace
- Haldor Topsoe

C Analysis

- LLNL (^{14}C)
- UC Irvine
- CEC, CARB
- Aerodyne

* California Air Resources Board, California Energy Commission

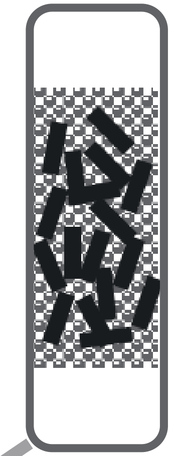
April 19: Stable Carbon Isotope Approach for Tracking Biogenic Carbon Distribution in Bio-oil/crude Co-processing with VGO, *by Zhenghua Li, LANL*

A comprehensive study of co-processing in hydrotreating and hydrocracking

H_2

VGO / SR Diesel / Kerosene / Fuel oil

Woody FP bio-oil, Woody CFP bio-oil
Sewage sludge/food waste HTL bio-crude
2-20% blending

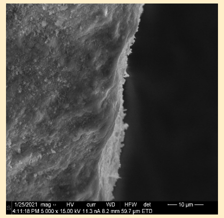


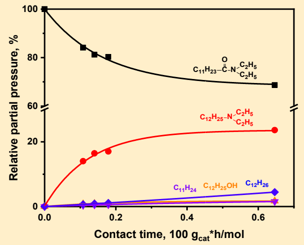
Commercial catalyst extrudates

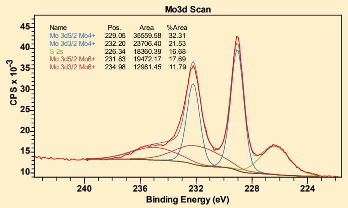
Feed analysis

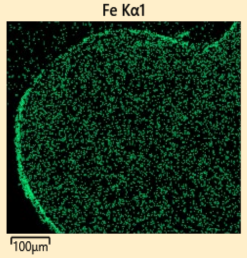
- Chemical composition
- Heteroatoms and contaminants

Catalyst Characterization









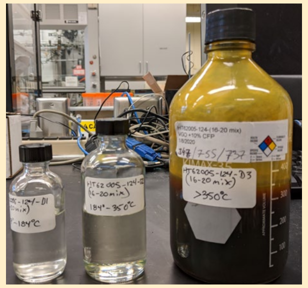
Hydrotreating performance

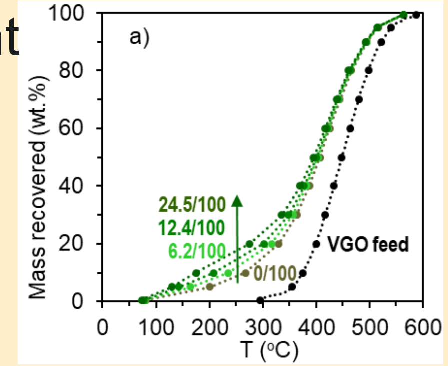
- >300 h TOS with steady state operation
- HT/HC performance
  - Fuel/gas/water yield
  - Heteroatom removal (N, S, O)
  - Hydrocracking (diesel yield)
- H_2 consumption

Fuel
Gas
Water

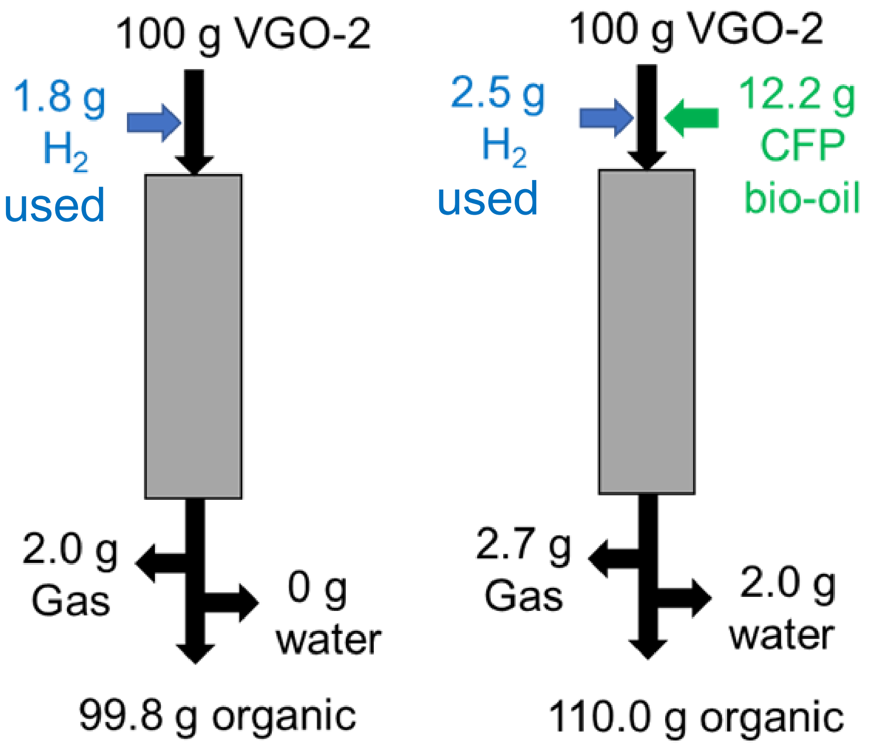
Fuel analysis

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





High biogenic carbon incorporation demonstrated for the CFP bio-oil co-processing



Organic yield, g/g dry bio-oil	**84%**
Organic carbon yield	**93%**

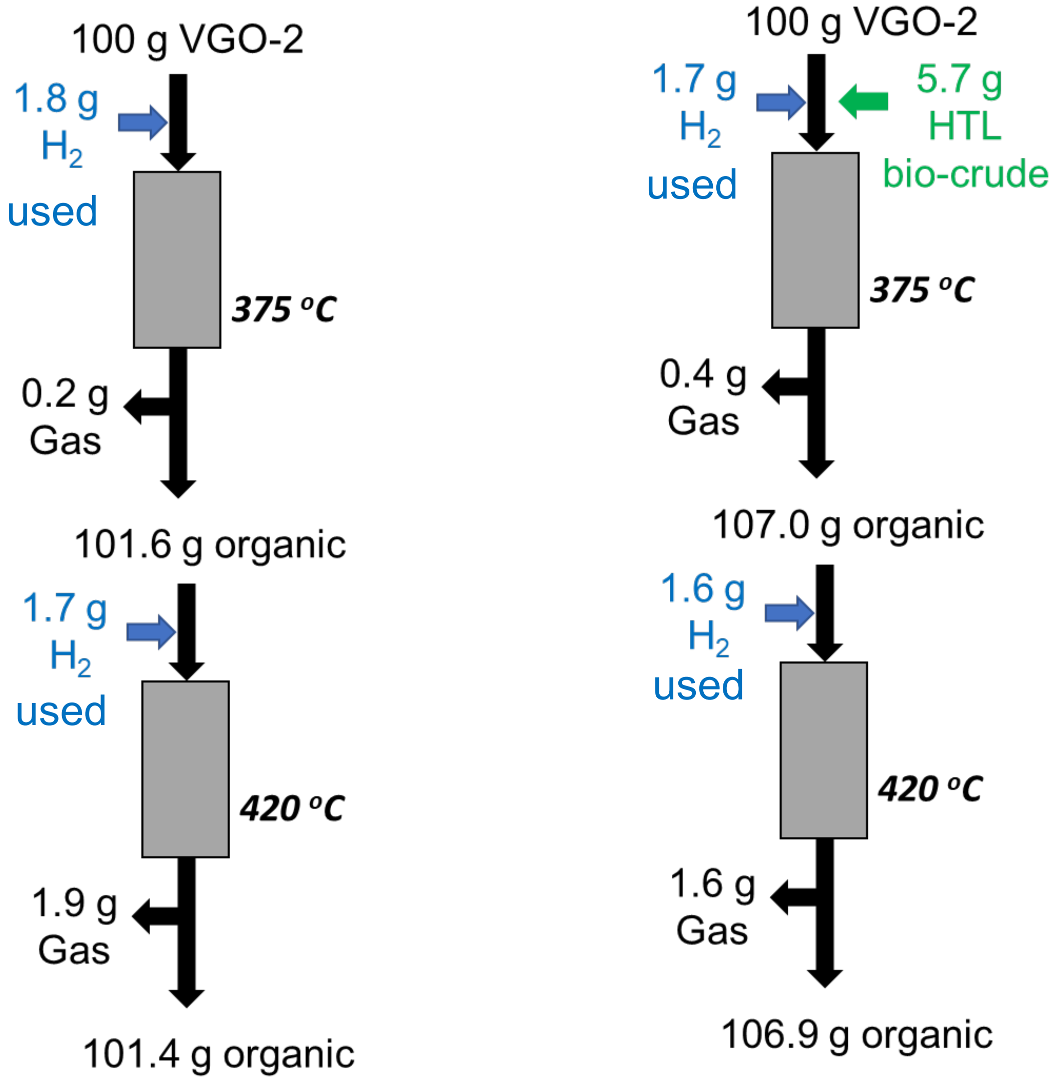
Diesel fraction

	VGO only	12.2/100 CFP/VGO
Cetane Number	45	39
S, ppm	<15	<15
N, ppm	33	49
S. g. at 20°C	0.889	0.886
T90, °C	355	358

- High incorporation of biogenic carbon in fuel products, consistent with standalone HT results, with minor impact to HT/HC chemistry
- Similar performance observed when co-processing CFP bio-oil with SR diesel
- Potential coke formation from CFP bio-oil is a big challenge

A. Dutta, et al. Ex Situ CFP 2020 State of Technology, https://doi.org/10.2172/1805204

High biogenic carbon incorporation demonstrated for the HTL bio-crude co-processing



Organic yield, g/g dry bio-crude	96%
Organic carbon yield	97%

Diesel fraction

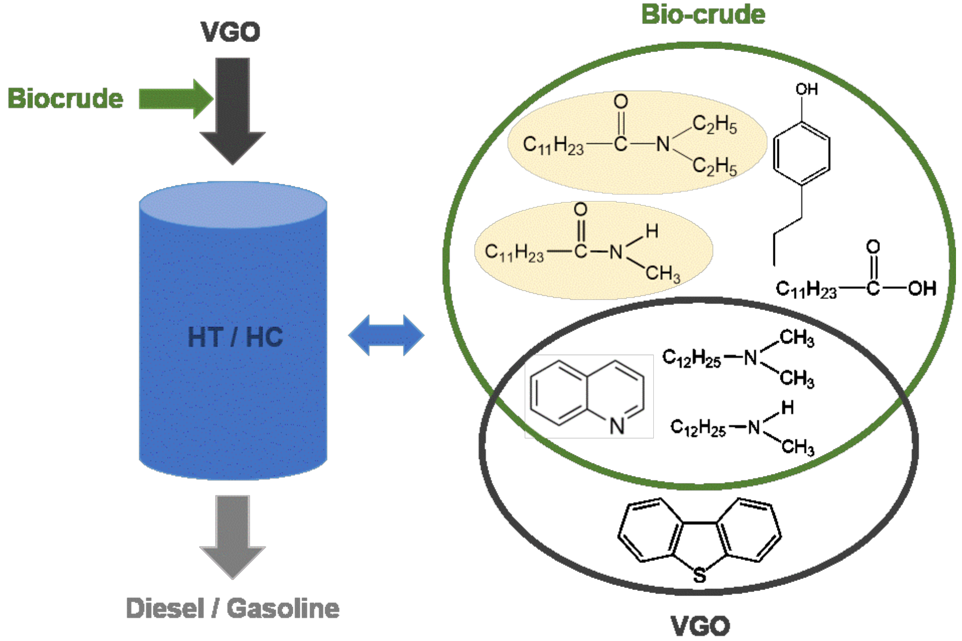
	VGO only	5.7/100 HTL/VGO
Cetane Number	42	47
S, ppm	<15	<15
N, ppm	30	93
S. g. at 20°C	0.883	0.881
T90, °C	353	358
pMC, %, by AMS	0.2±0	7.3±0.1

- Competition between heteroatom (S, N, O) removal is critical during co-processing in hydrotreating
- Demonstrated HT pretreatment to mitigate N issues of bio-crude and enable co-processing in mild HC

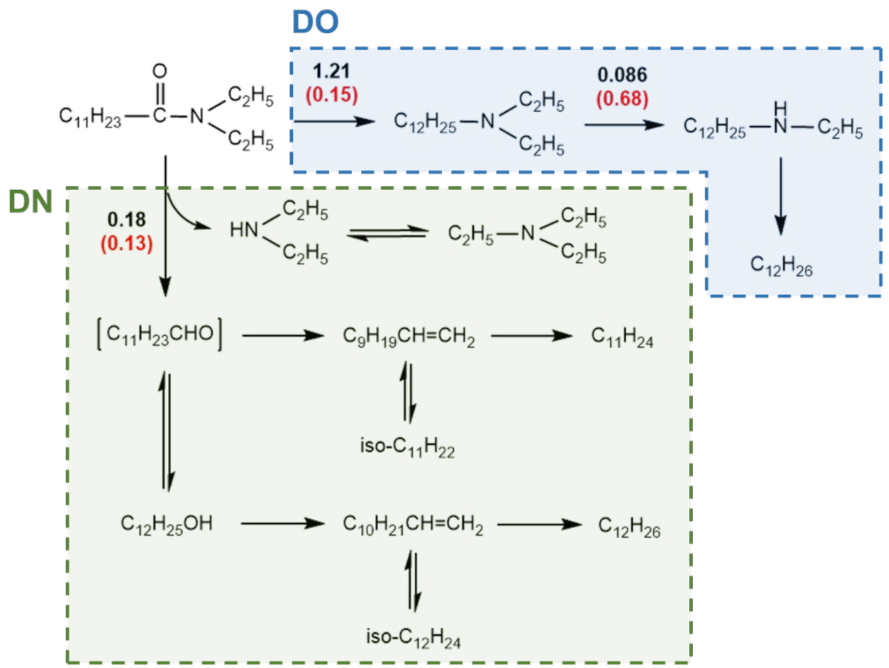
C. Zhu,… H. Wang, Energy and Fuels, 2022, to be published

Kinetic measurement of HDN/HDO/HDS of bio-crude/VGO guides catalyst selection and supports reactor model development

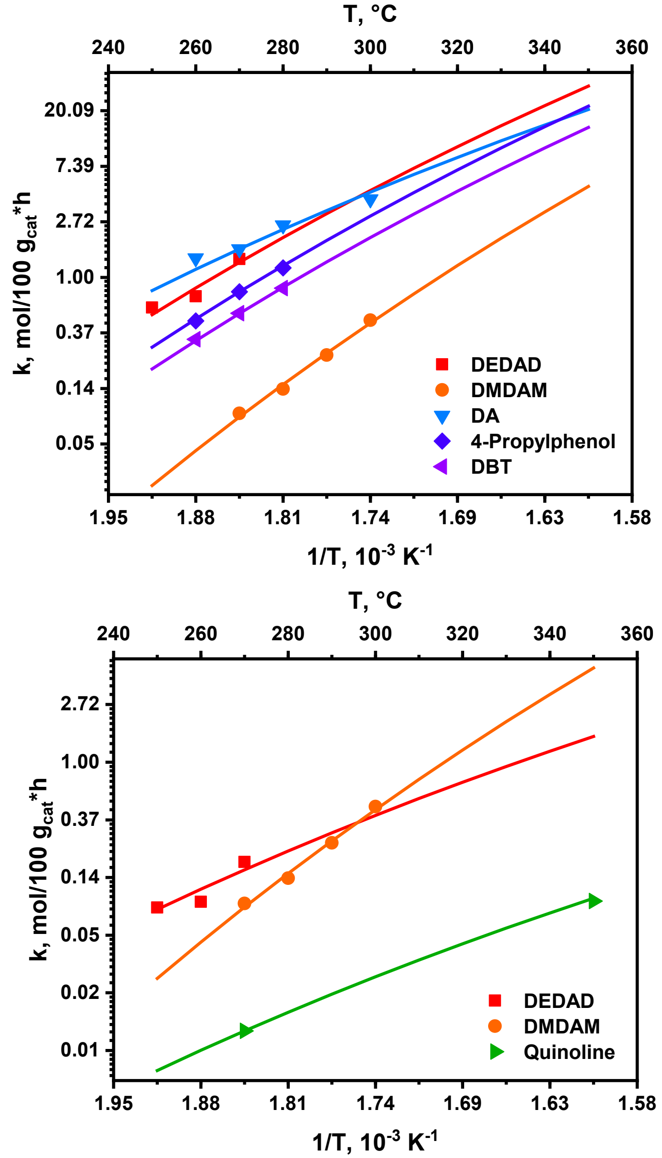
Representative molecules



Reaction network of fatty acid amide



Reaction kinetics and energy measurement

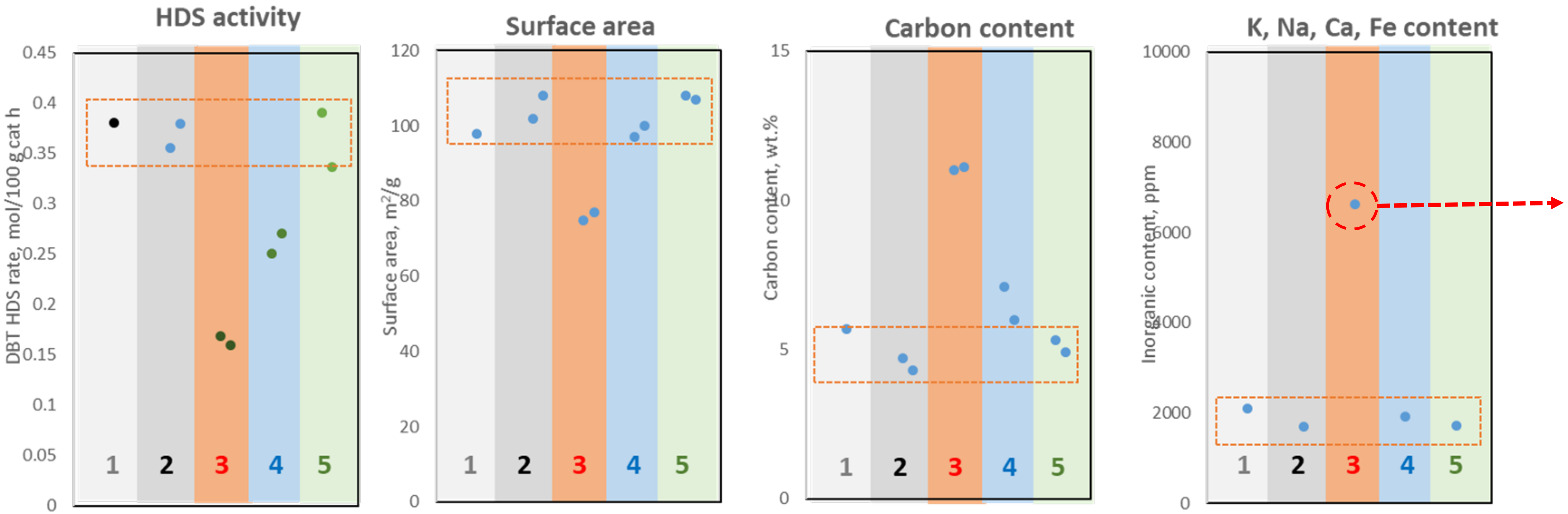


- Hydrodenitrogenation is critical for bio-crude co-processing
- Development of kinetic-based reactor model for co-processing is ongoing
  - Aspen HYSYS Refinery Models

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

Mitigation of catalyst deactivation by co-processing suggested

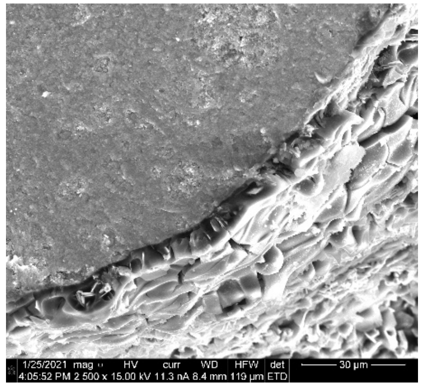
After ~300 h test

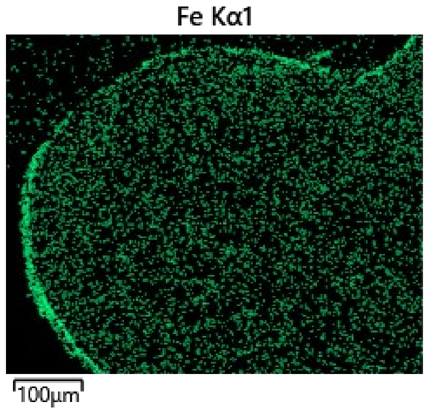


1. Fresh 2. Diesel only 3. Diesel with raw bio-crude

4. Diesel with pretreated bio-crude 5. Diesel with pretreated bio-crude and catalyst guard bed

Fouled catalyst after co-processing raw bio-crude





- Bio-crude pretreatment and guard bed use mitigate catalyst deactivation

April 21, 3:50: Coprocessing Biocrudes with Petroleum Gas Oil in Hydrotreating, *by Huamin Wang, PNNL*

C. Zhu,… H. Wang, Energy and Fuels, 2022, to be published

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

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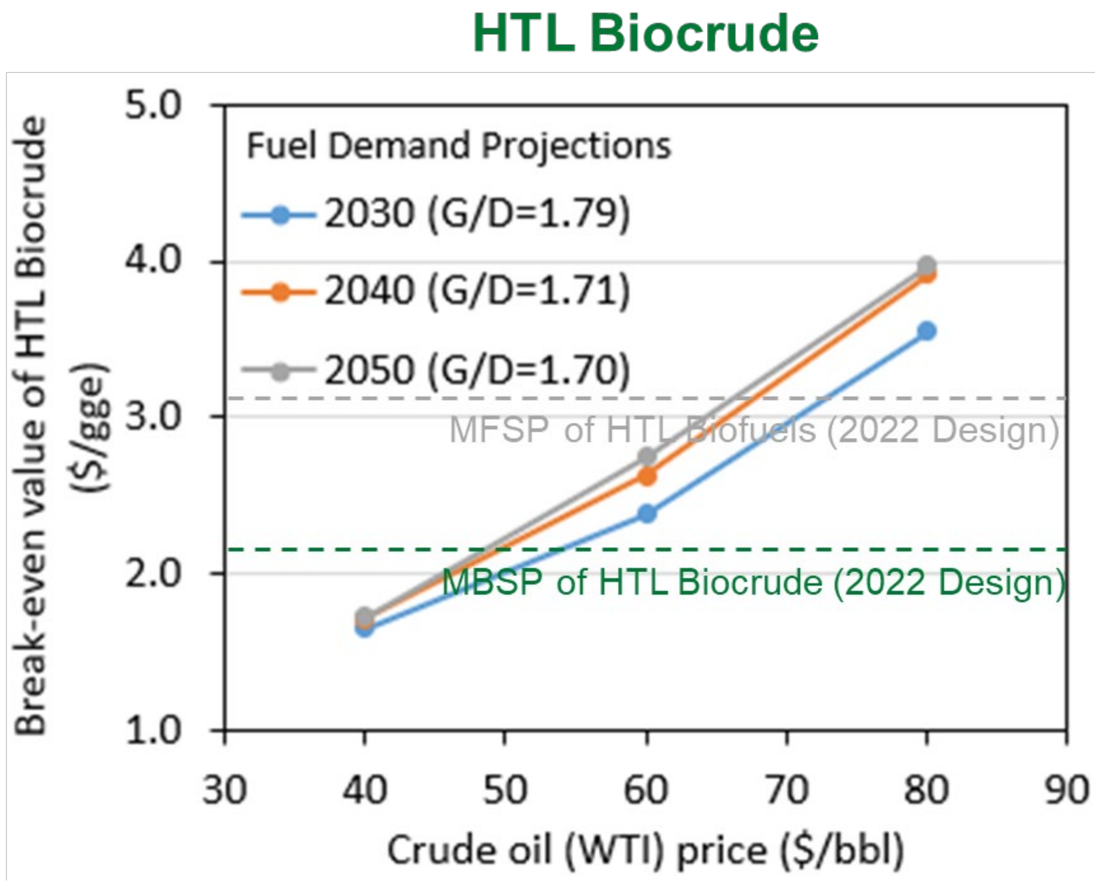
Effect of various factors on the upgrading cost of wet waste HTL biocrude with co-processing

ID	Scenarios	Catalyst and Operating Assumptions				Upgrading Capital Cost Assumptions			Upgrading Cost
		Catalyst Life (yr)	Catalyst Price ($/lb)	WHSV (Hr^{-1})	Change in P_{H2} (%)	Feeding system	H_2 Compressor and PSA	Wastewater Treatment	($/gge)*
1	Without Impacts	2	16.5	0.8	0	No	No	No	0.26
2	Lower Catalyst Life	1.5	16.5	1	0	No	No	No	0.26
3	Higher Catalyst Price	2	32.9	1	0	No	No	No	0.27
4	New Feed System	2	16.5	0.8	0	Yes	No	No	0.27
5	Additional Waste Treatment	2	16.5	0.8	0	No	No	Yes	0.28
6	2, 4 & 5 Combined	1.5	16.5	1	0	Yes	No	Yes	0.28
7	3, 4 & 5 Combined	2	32.9	1	0	Yes	No	Yes	0.29
8	Higher Partial H2 Pressure	2	16.5	0.8	10	No	Yes	No	0.32
9	4, 5, 8 Combined with Higher WHSV	2	16.5	1	10	Yes	Yes	Yes	0.33
10	Conservative (2, 3, 9 Combined)	1.5	32.9	1	10	Yes	Yes	Yes	0.34

$0.26 - 0.34 /gge

Upgrading cost at a standalone bio-refinery = $0.91/gge.

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



- Increase in operating severities and new capital investment will lead to higher biocrude upgrading cost to some extent
- 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

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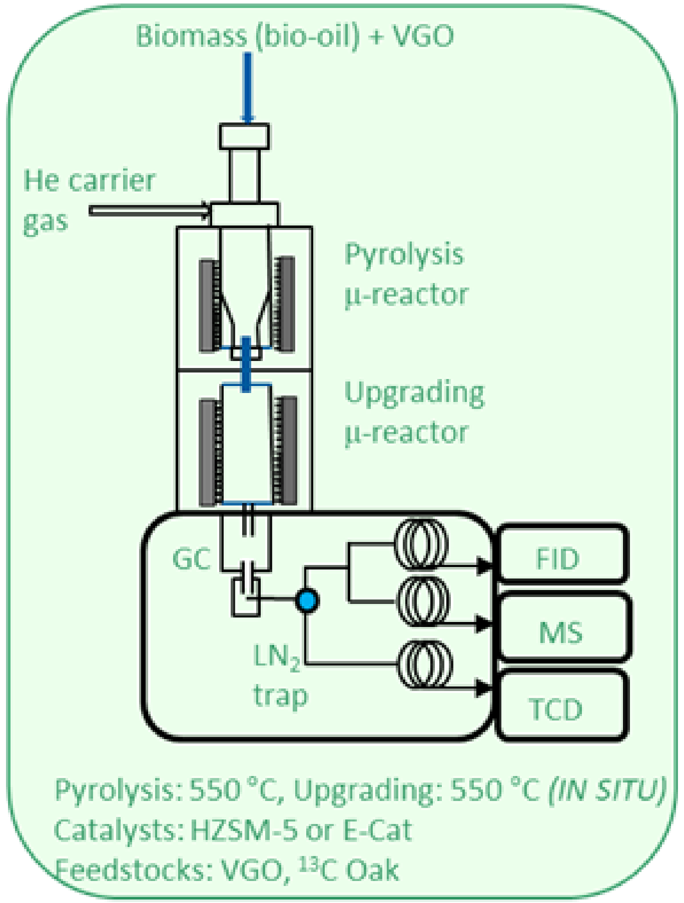
FCC: Modified Catalysts Improve Co-Processing

Micro scale screening reactor

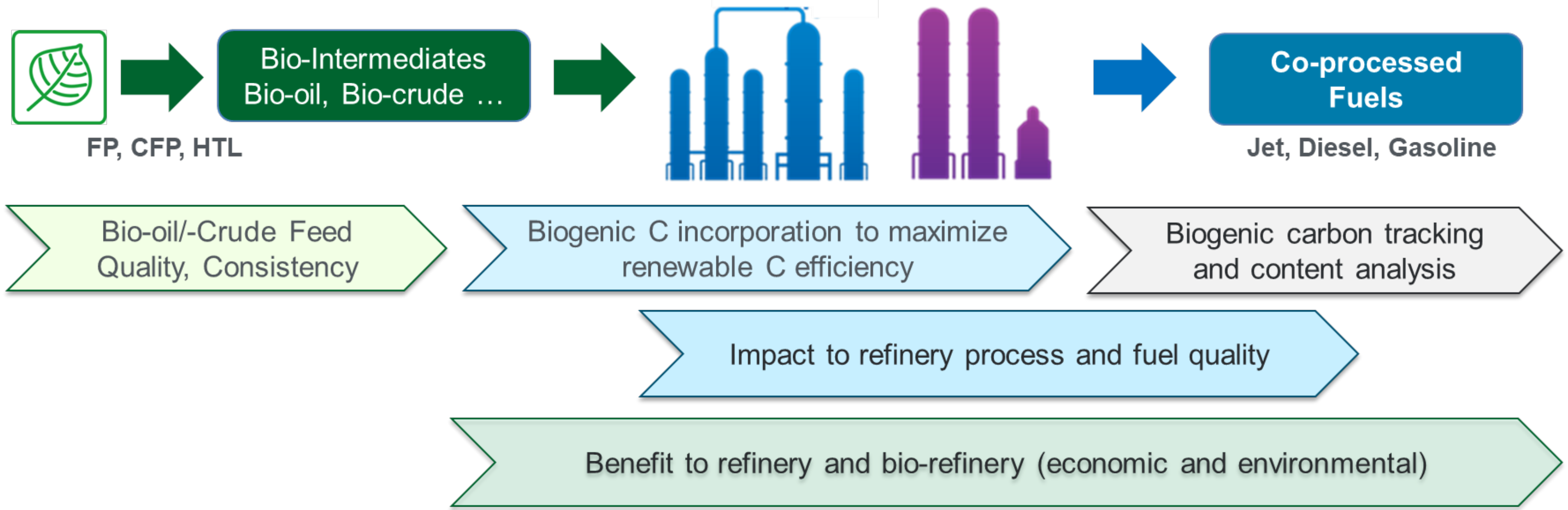


Feed	Catalyst	%Bio-based Carbon ($\%C_{bb}$)*	$\%C_{bb}$ product/ $\%C_{bb}$ feed	Wt% Coke	Oxygenate Breakthrough (Mass% in liquid)
VGO	E-Cat	0.0	NA	2.75	NA
VGO/CFPO	E-Cat	9.7	1.01	1.09	6.03
VGO/CFPO	E-Cat/MFI 5w% Mn	7.3	0.76	0.83	5.19
VGO/CFPO	E-Cat/MFI 5w% La	9.2	0.96	0.62	4.90
VGO/CFPO	E-Cat/MFI 5w% 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/HZSM5	5.4	0.66	0.23	1.80
VGO/CFPO	E-Cat/HZSM	5.9	0.72	ND	2.33

La- and no mesoporosity-MFI catalysts:
- maximized biogenic C in product
- reduced coke
- reasonable oxygenate breakthrough
- to be tested at DCR scale

April 20, 3:20: Feedstock and Catalyst Impact on Bio-Oil Production and FCC Co-Processing to Fuels Feedstock and Catalyst Impact on Bio-Oil Production and FCC Co-Processing to Fuels, *by Kim Magrini, NREL*

We can leverage existing refining infrastructures to leverage billions of US$



- High biogenic carbon incorporation by co-processing CFP bio-oils and bio-crudes in HT/HC and by co-processing CFP bio-oil in FCC
- For co-hydrotreating, competition of heteroatom removal is critical. Specifically, for HTL bio-crude with high N content, HDN is the key to enable co-processing in hydrocracking
- Catalyst deactivation by co-processing can be mitigated
- Co-processing can be beneficial to both biorefinery and refinery

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SDI Program: Josh Messner, Jim Spaeth

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April 21, 3:50: Coprocessing Biocrudes with Petroleum Gas Oil in Hydrotreating, *by Huamin Wang, PNNL*

April 21, 4:10: Quantification of Biogenic Carbon in Fuel Blends through LS C14/C Measurement and Assessment, *by James Lee, LANL*