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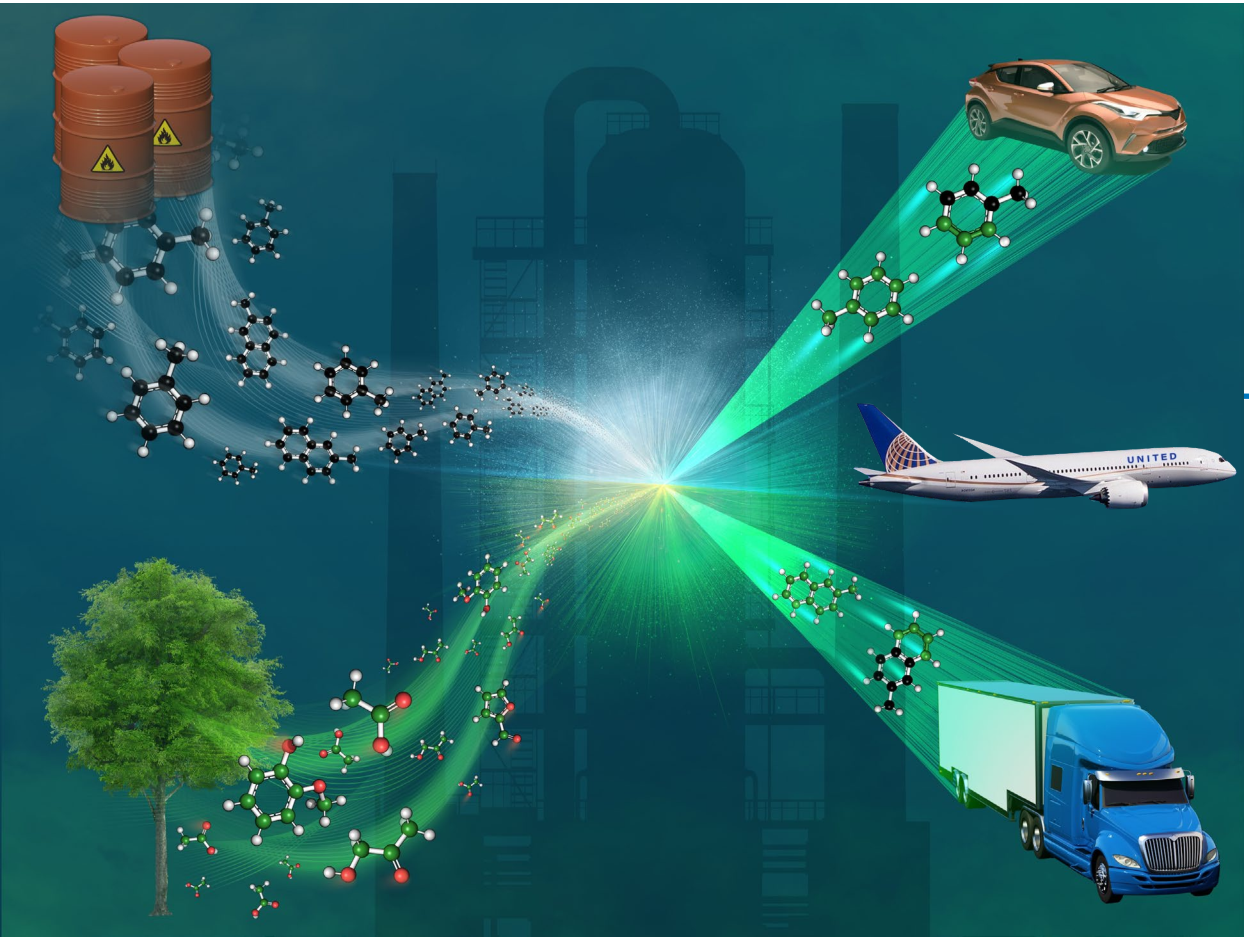

Feedstock and Catalyst Impact on Bio-Oil Production and FCC Co-Processing to Fuels

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tcbiomass 2022

April 20, 2022

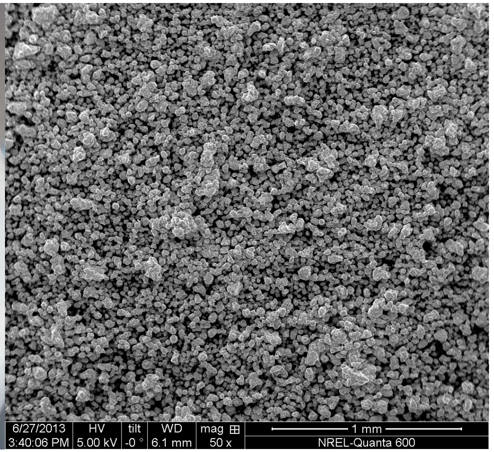
Outline

- Catalytic Fast Pyrolysis (CFP) Oil Production
  - Catalysts and Feedstocks
  - Pyrolyzer/DCR System
  - CFP Oil Composition and Fractionation
- Co-Processing (CP) Bio-Oils to Fuels

Catalysts and Feedstocks

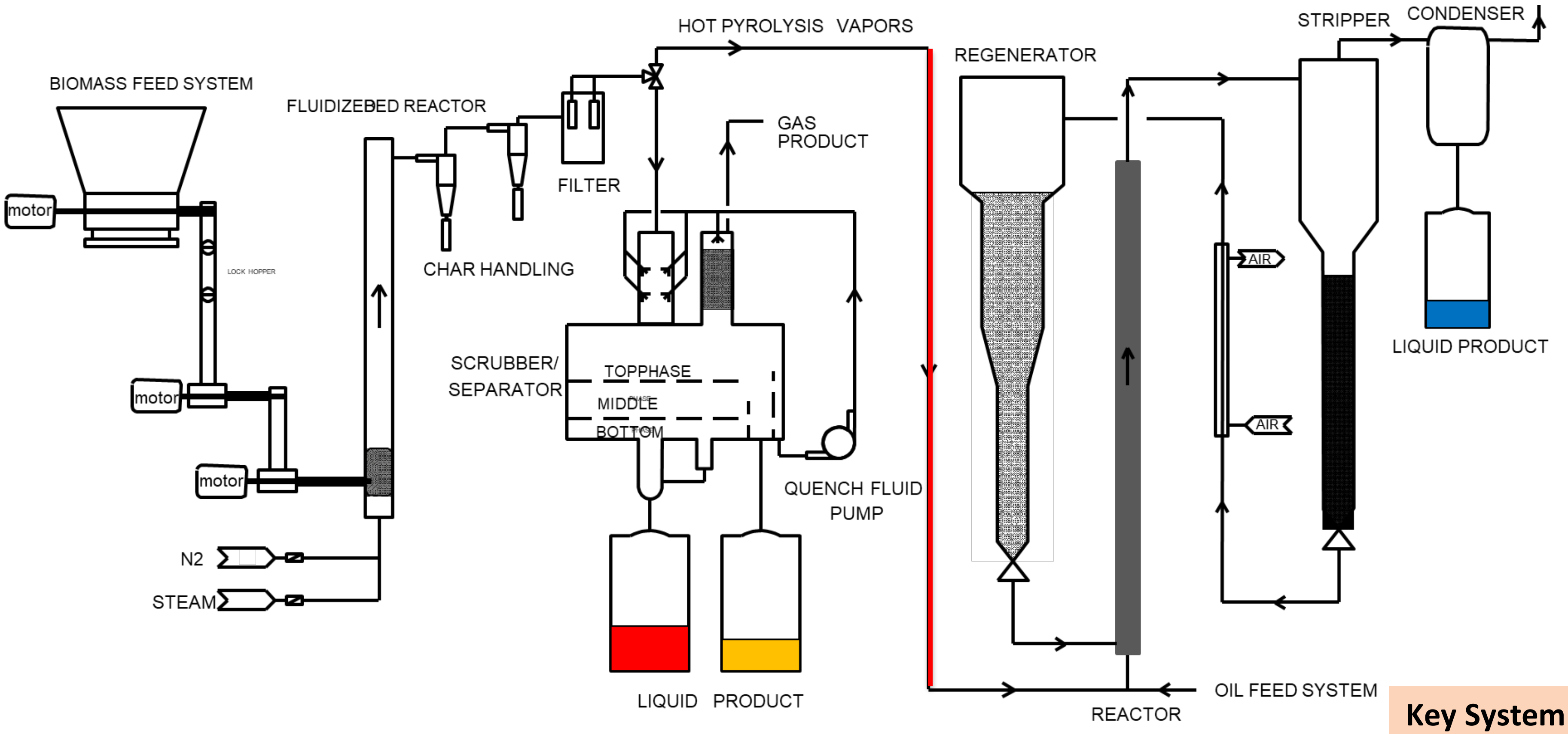


Feedstocks
- Miscanthus
- Pine residues
- Debarked clean pine

Johnson Matthey Catalysts
- HZSM-5 (SAR = 30),
- 25 and 40% [HZSM-5]
- Ga-HZSM-5

Davison Circulating Riser (DCR): CFP Overview



The Davison Circulating Riser System when coupled with a biomass pyrolyzer is used to generate bio-oils from a riser reactor leveraging zeolite-based catalysts

Key System Specifications - Pyrolyzer

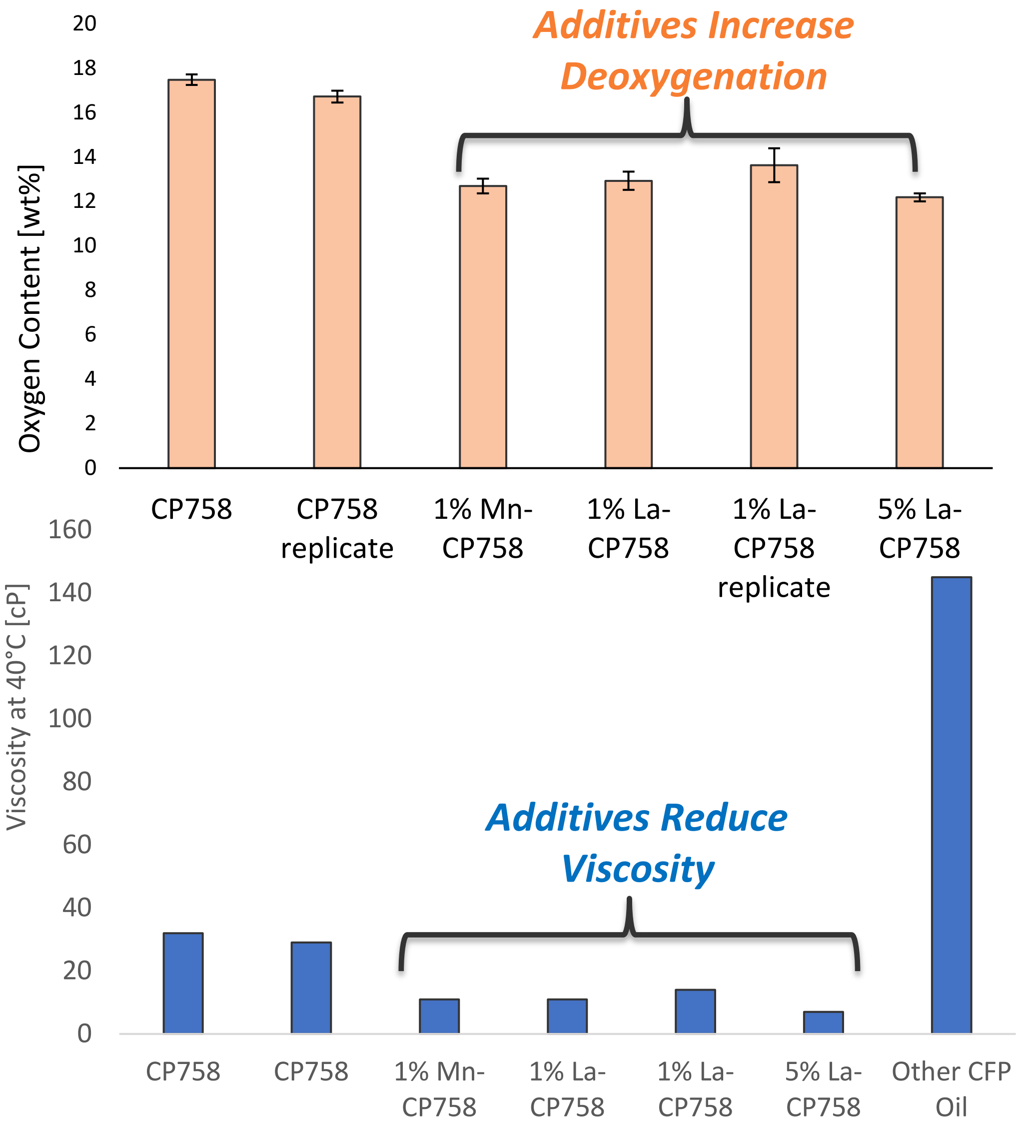
- Feedstock Type and Form Factor/Size: Wood and grasses, milled to 2 mm. Feed rate: 1-2 kg/hr
- Bed material: Olivine, 0.5 kg, 200-300 µm
- Operating Temperature/Pressure: 450-550°C, 2 bar
- Reactor Configuration: Bubbling fluidized bed

Key System Specifications – DCR for CFP

- Feed Rate: 1 kg/hr (pyrolysis vapors + product gases + inert gases)
- Catalyst Type and Form Factor/Size: Refinery-type, zeolite-based, fluidizable (FCC), 80 µm
- Catalyst Charge/Feed Rate: 1.8 kg, circulation rate 7-10 kg/hr
- Operating Temperature/Pressure: 500-600°C, 1.8 bar
- Reactor Configuration: Riser reactor + stripper + regenerator
- Additional Specifications: Catalyst recirculated for regeneration (coke removal).

Properties of CFP Bio-Oil: Tailored by Basic Catalyst Modification

- High oxygen content impacts hydrotreating and co-processing
  - Decreased miscibility
  - Increased reactivity
  - Increased corrosivity
- High viscosity can impede biocrude introduction into conversion reactors



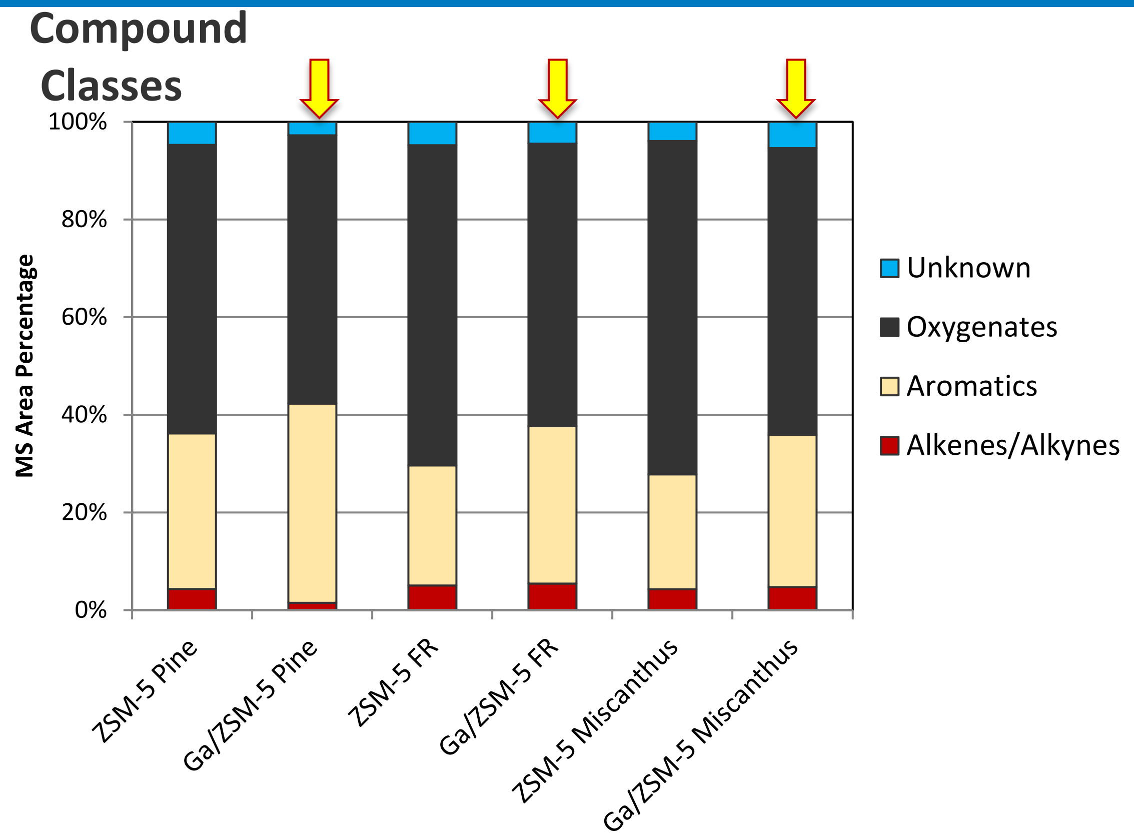
- JM impregnated commercial (CP758) zeolite catalyst with metals known to be Lewis acids
- DCR CFP experiments with pine FP vapor and analyzed liquid crude

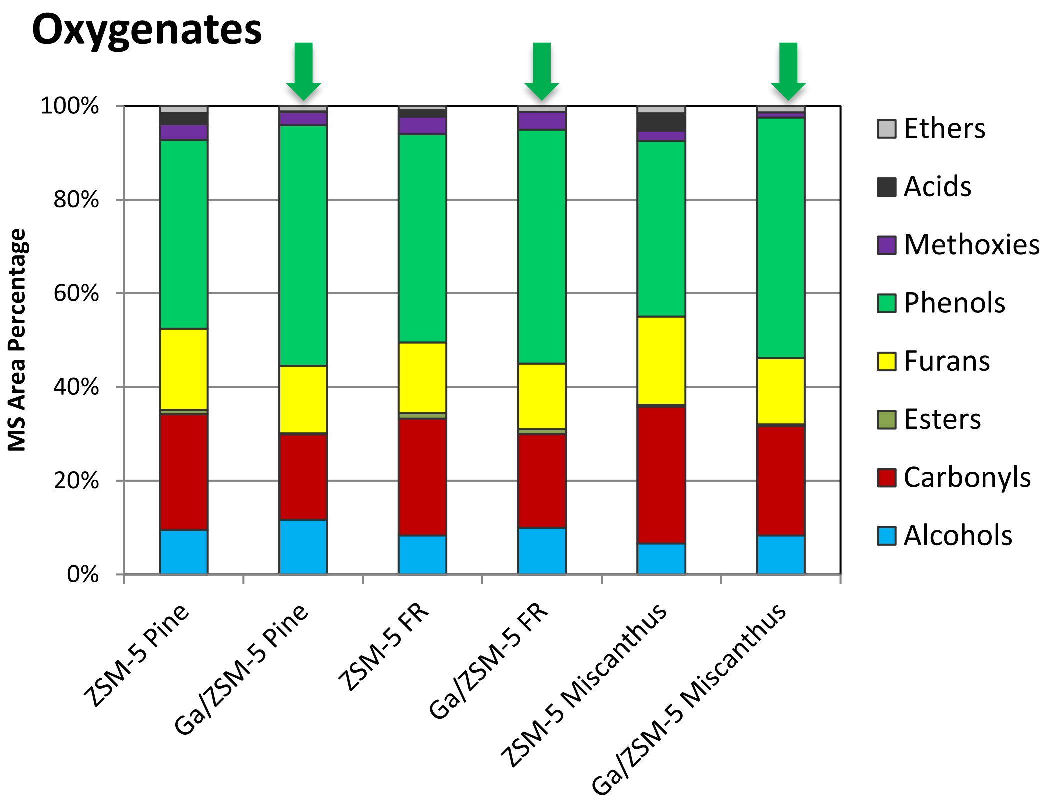
Outcome: Metal loading reduced oxygen content by 30% and viscosity by 75%

Pyrolyzer: 500°C, transfer lines at 400°C , pine feedrate of 1.2 kg/h in ~1.8 kg/h nitrogen fluidization gas
Riser: 550°C

Catalyst and Feedstock Impacts on Bio Oil

2D GC^2 TOFMS Oil Analysis





Catalysts
- ZSM-5
- Ga/ZSM-5
  - increased aromatics, phenols
  - reduced oxygenates (furans, carbonyls: cellulose deoxygenation)

Feedstocks
- Pine and pine forest residues (FR)
- Miscanthus

- Pine, FR and Miscanthus
  - Pine and FR similar oxygenates
  - Miscanthus: reduced phenolics (less lignin), enhanced carbonyls and furans

Hydrotreated CFP Oil: 100% Biogenic Fuels

DCR conditions:
- CP758 zeolite, 550ºC
- Residence time ~1s,
- 30% carbon efficiency with 500ºC pine pyrolysis vapor at a 1:1 biomass:N_2 ratio.

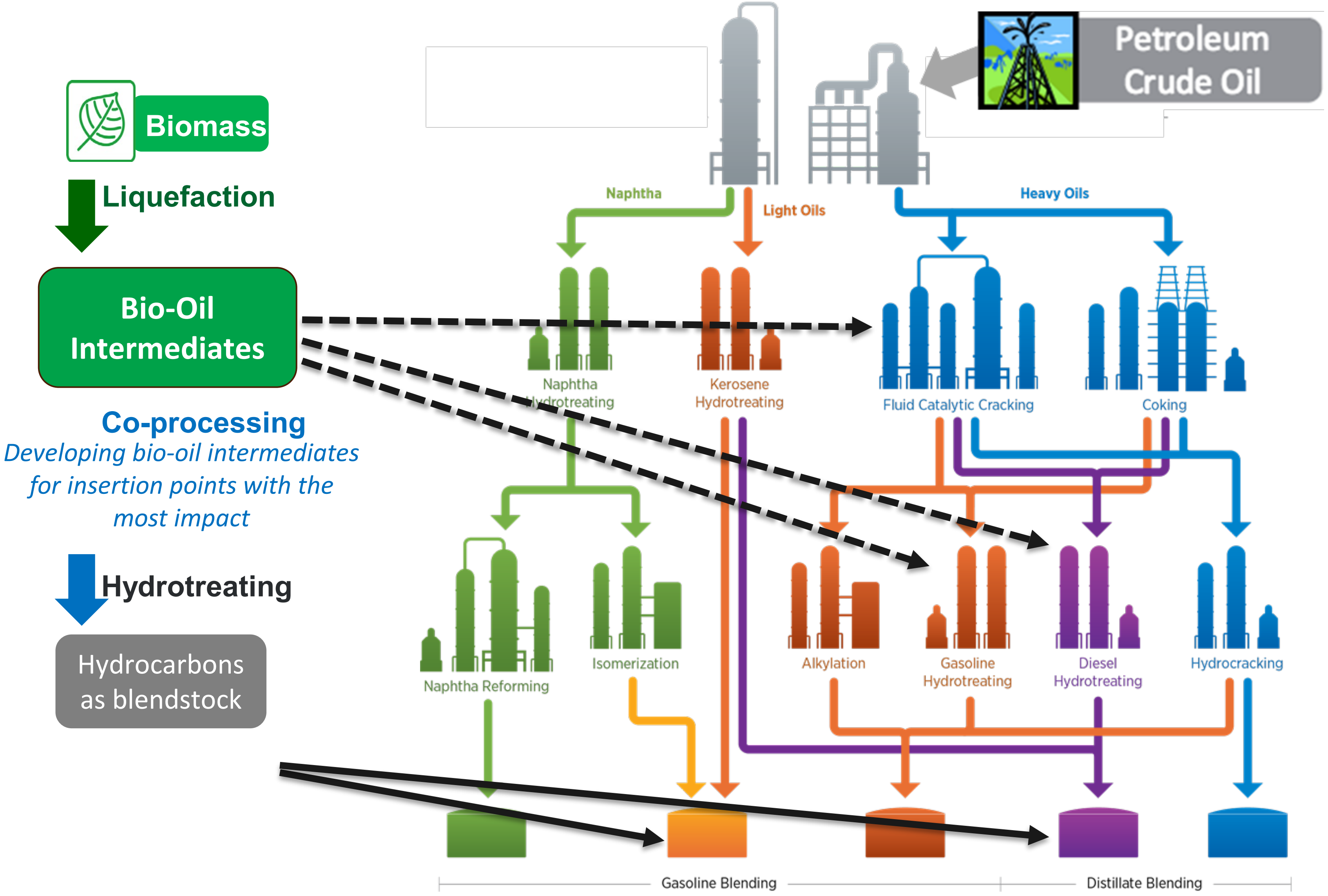
Hydrotreating:
- 400 ºC
- LHSV 0.20h^{-1} for ~90 h

	Net Weight (g)	Percent	Volume
Boiler Initial	51.53	100%	60
Lights	1.68	3	
Gasoline (71-182)	23.91	46	
Diesel (182-320)	20.20	39	
	Fraction Recovery	45.79	89%
	Total Recovery	49.97	97%
	Losses	1.57	3%
Gasoline: RON	74		
MON	69		
AKI	71		
P_{vapor}, psi	1.8		
Diesel: CN	22		

DCR CFP oil   Hydrotreated DCR CFP oil   46% gasoline 39% diesel

- Challenges: fuel composition
- Low octane numbers due to naphthenes (cycloparaffins)
- Low cetane numbers due to multi-ring compounds
- Ring opening and/or C-C coupling required, less hydrogenation for gasoline

Co-Processing: FCC co-processing of bio-oils leverages existing refining infrastructure leverages with billions US$ in CAPEX and 5 million bpd of crude refining



Objective: Produce fungible bio- oils that can be co-processed in petroleum refineries to produce biogenic carbon containing fuels

Outcome:
- Tailoring CFP oil composition for refinery insertion
- Modified refinery compatible FCC catalysts
- Co-processing strategies to refiners

Impact: Faster introduction of renewable fuels into the transportation sector to reduce GHG by 2030

DCR: Co-Processing Overview

Evaluate refinery FCC, co-processing strategies by feeding CFP oils or other biogenic materials (FOGs, waxes) with VGO into the riser to produce BC-containing fuels

Key System Specifications – DCR for Co-processing

Feed Type: Liquids

Feed Rate: 1.2 kg/hr

Catalyst Type and Form Factor/Size: Refinery-type, zeolite-based, fluidizable (FCC), 80-100 micron.

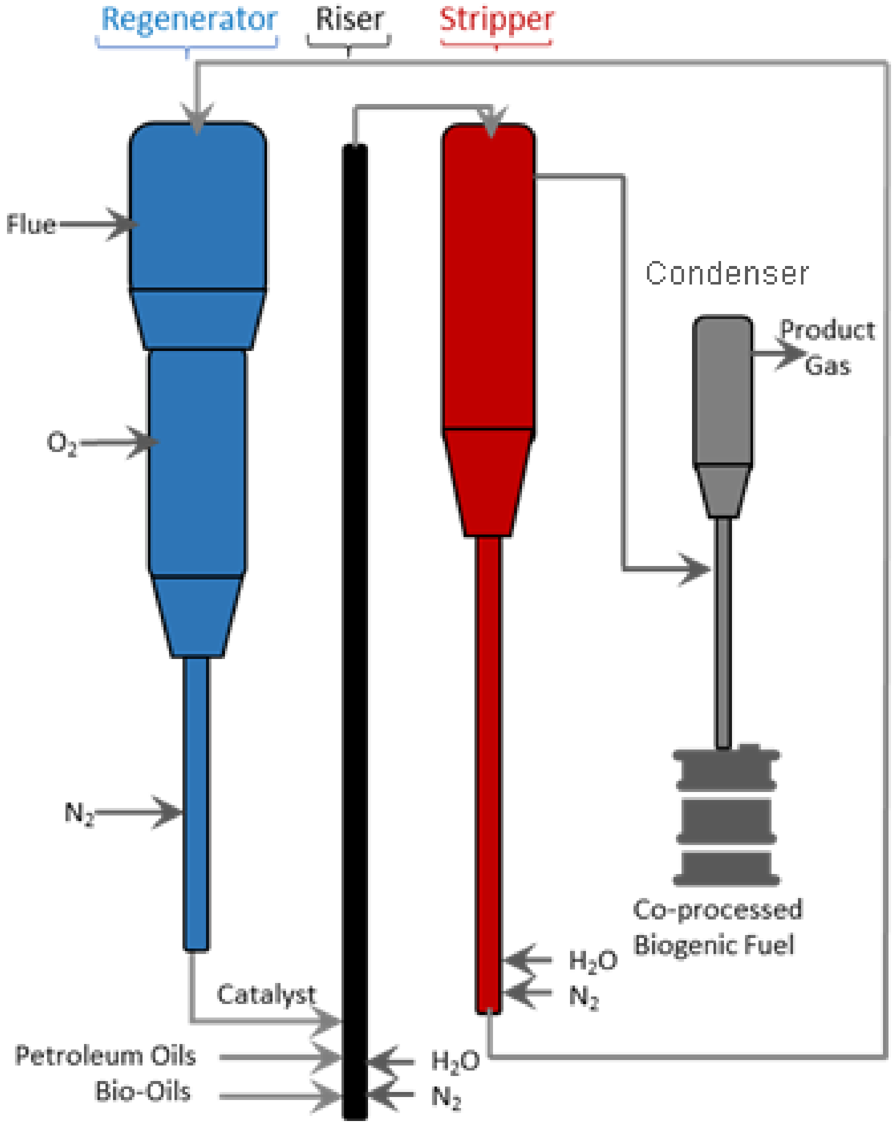
Catalyst Charge/Feed Rate: 1.8 kg, circulation rate 7-10 kg/hr

Operating Temperature Range: 475-550°C

Operating Pressure Range: 2-2.6 bar

Reactor Configuration(s): Riser reactor + stripper + regenerator

Additional Specifications: Catalyst recirculated for stripping (HC removal) and regeneration (coke removal). DCR mimics FCC refinery operations by cracking large molecules to fuel-range molecules.



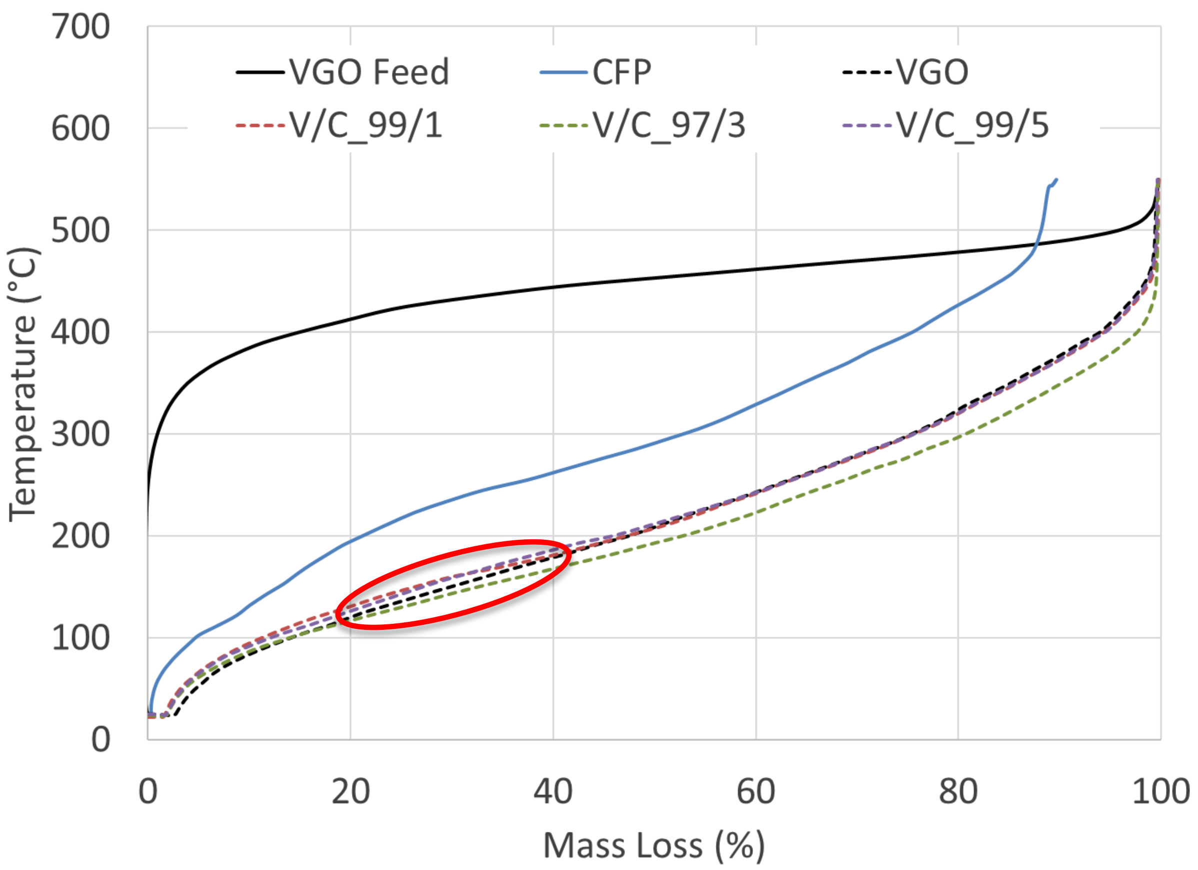
FCC Co-Processing

High biogenic C incorporation demonstrated

Co-Processing in FCC

Product ID	VGO (vol %)	CFP Oil (vol %)*	% BC* in CFP/VGO	% 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 ^{14}C analysis



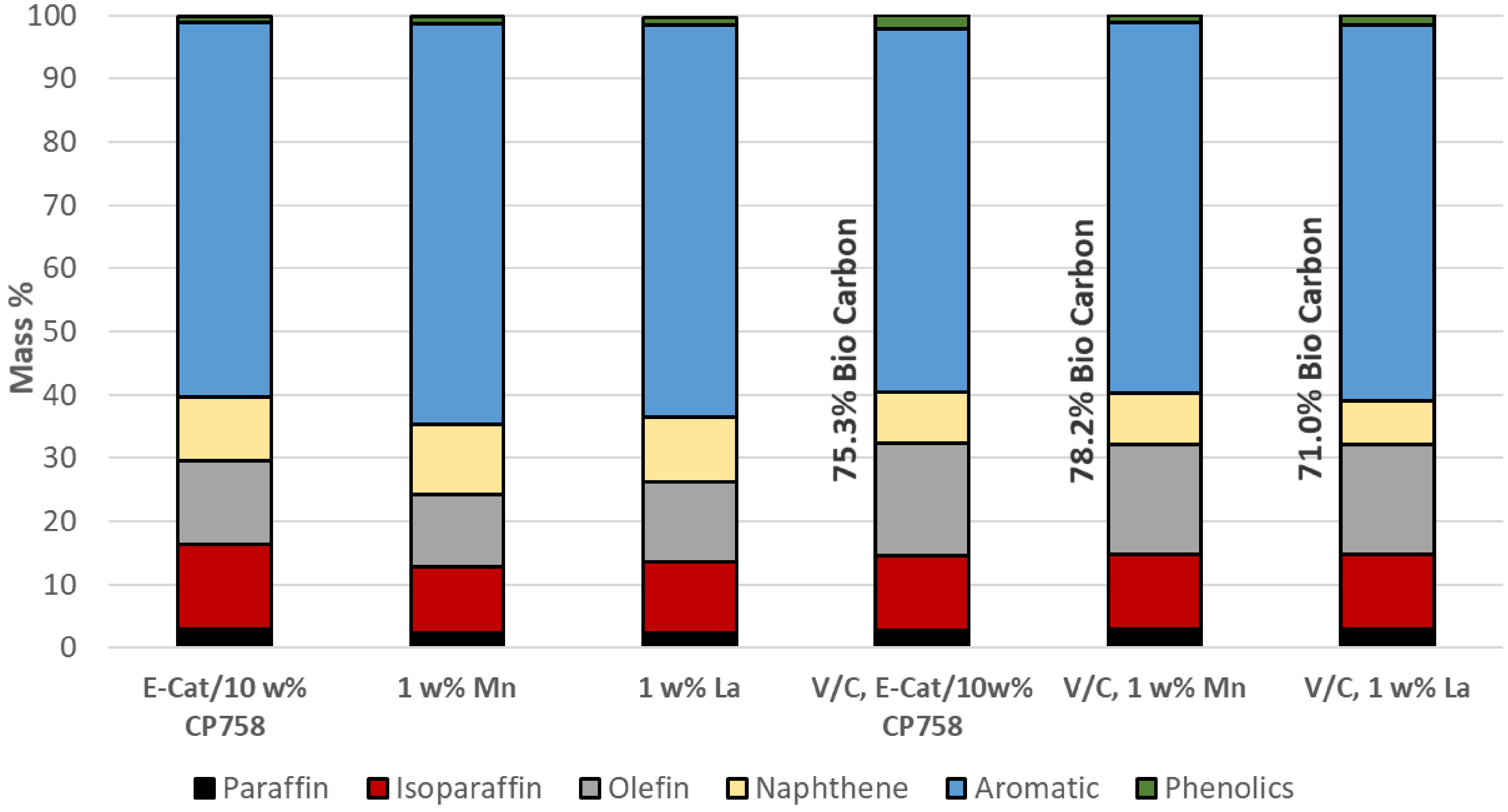
>80% biogenic carbon incorporation in fuel products for:

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

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

Pine CFPO: 77.7% C, 14.8% O, 7.7% H, < 31 ppm S

FCC (DCR) Co-Processing Bio Oil with VGO using Metallized Catalysts



- Product compositions (GC-VUV PIONA) from co-processing VGO with 5wt% CFPO (32% oxygenates) and JM modified zeolite catalysts (10wt% mixtures in E-Cat)
- Increased olefins, reduced naphthenes with metallized catalysts
- > 70% biogenic carbon content determined by ^{14}C analysis

VGO: 60.3% paraffins and isoparaffins, 14.7% olefins and cycloparaffins, 5.5% aromatics, non-detectable thiophenes

CFPO: 53.4% carbon, 32.7% oxygen, 11.9% water, and < 15 ppm sulfur

Summary

- Consistent quality, low oxygenate (< 18%) CFP oils produced with a coupled pyrolyzer/FCC system and varied feedstocks and catalysts

- Feedstock impact on oil composition:
  - Pine enhances aromatics, alkenes and buta/enone compared to oak, possibly due to lignin, hemicellulose, and cellulose content
  - Pine and pine FR CFP oils are similar
  - Miscanthus produces less phenolics (less lignin)

- Catalyst impact on oil composition:
  - Ga addition to HZSM-5 increases aromatics as does increased [HZSM-5]
  - Ga increases phenolics, reduces carbonyls
  - La and Mn increase olefins

- Biogenic carbon in hydrocarbon fuels from CFP oil co-processing with VGO > 70% dependent on catalyst and feed type

- Hydrotreating pine CFP oil produces biogenic gasoline, jet and diesel hydrocarbons

Co-Processing Presentations

- **Stable Carbon Isotope Approach for Tracking Biogenic Carbon Distribution in Bio-oil/crude Co-processing with VGO,** Zhenghua Li, LANL
- **Co-Processing in Refineries of Thermal Liquefaction Products from Biomass and Waste**, Huamin Wang, PNNL
- **Biocarbon Tracking in FCC Coprocessing of Biogenic Feedstocks,** Reinhard Seiser, NREL
- **Coprocessing Biocrudes with Petroleum Gas Oil in Hydrotreating,** Huamin Wang, PNNL
- **Quantification of Biogenic Carbon in Fuel Blends through LS C14/C Measurement and Assessment,** James Lee, LANL

Acknowledgements

SDI Program: Josh Messner, Jim Spaeth

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Bob Baldwin
Earl Christensen
Kristiina Iisa
Rebecca Jackson
Calvin Mukarakate
Jessica Olstad
Yves Parent
Brady Peterson
Glenn Powell
Reinhard Seiser
Mike Sprague
Anne Starace

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Jacob Helper

Industrial Collaborators
Casey Hetrick (BP America)
Jeff Lewis (Equilibrium Catalysts)
Gordon Weatherbee (WR Grace)
Mike Watson, Andrew Heavers, Luke Tuxworth (Johnson Matthey)
Larry Doyle, Chris Brown, Sean Murray (Zeton)
Kevin Stup (Vacuum Analytics)

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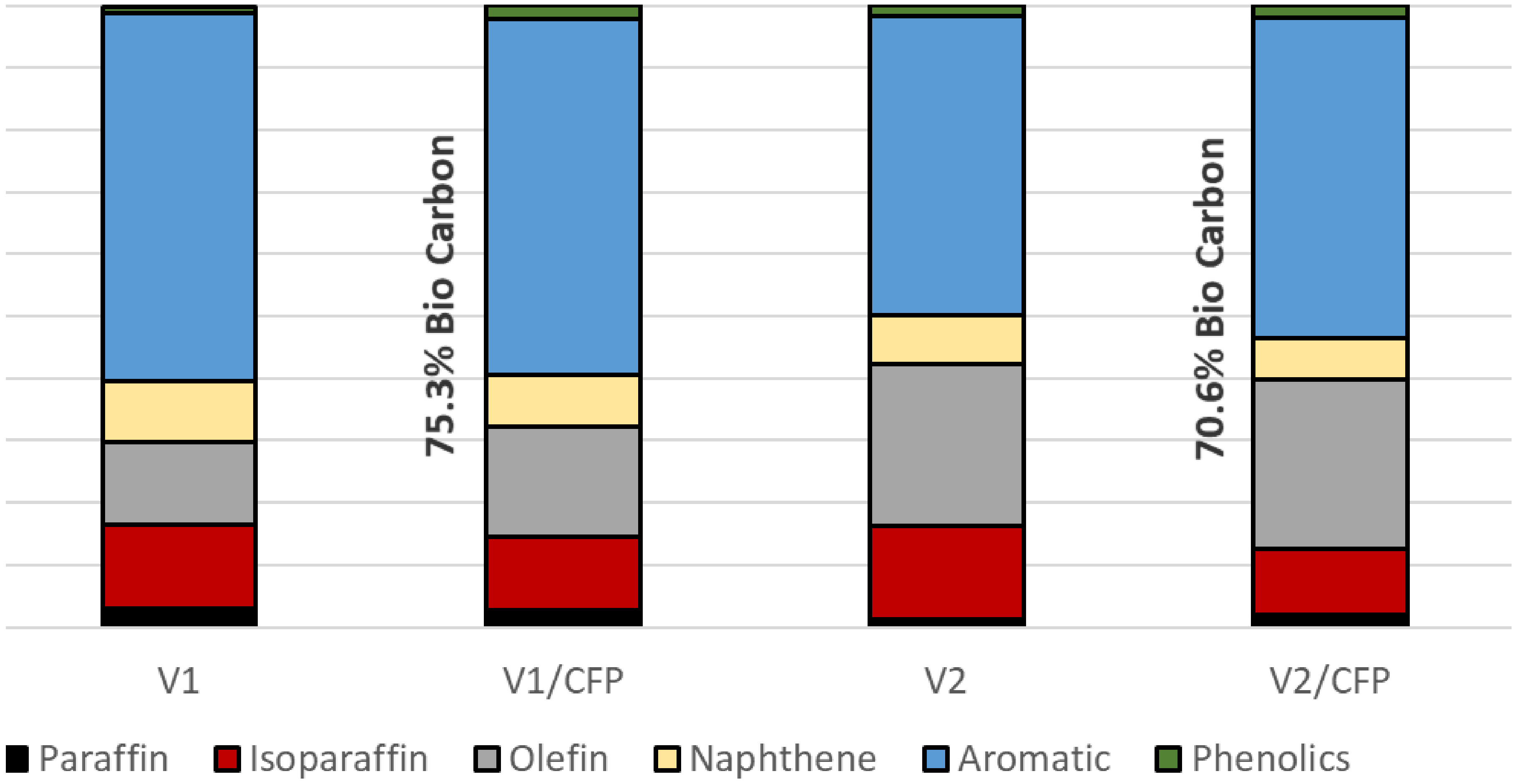
Additional Slides

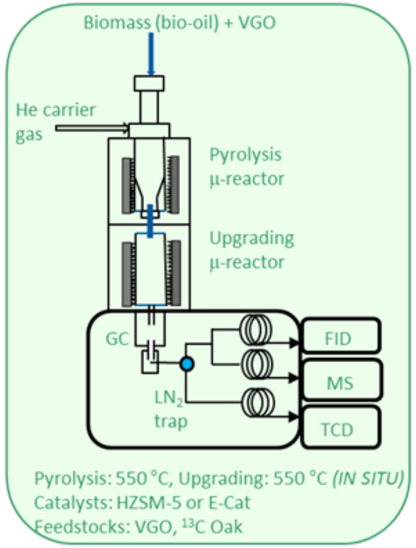
FCC (DCR) Co-Processing Bio Oil with Low and High-S VGO



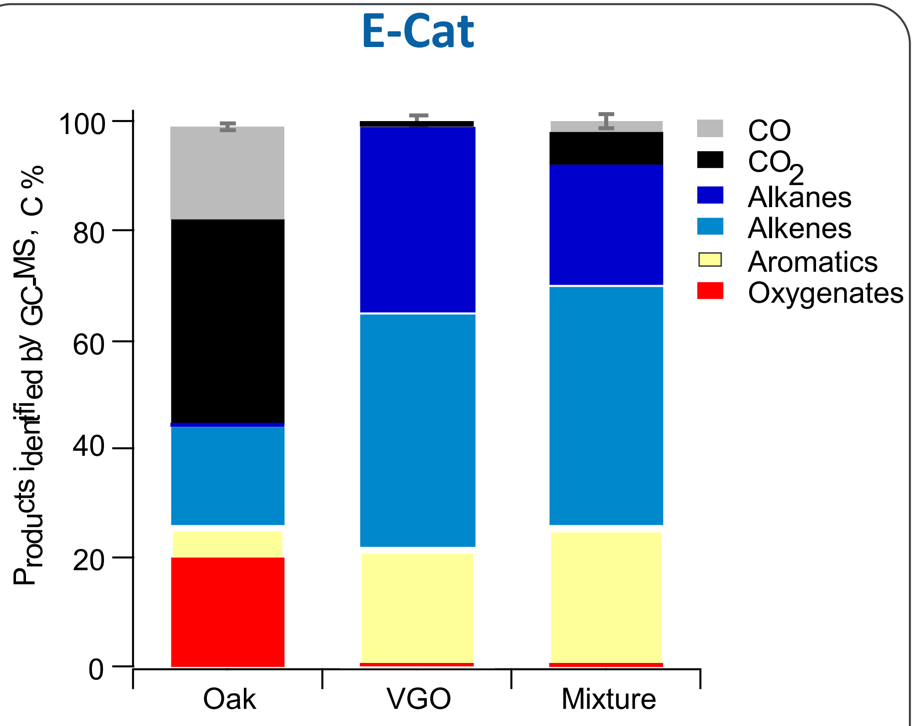
Liquid product compositions from GC-VUV from co-processing low-S (V1) and high-S VGO (V2) experiments with 5wt% pine CFPO (32% oxygenates) and 10/90 wt% CP758/E-Cat catalyst mixture.

Catalyst Impact to Fuel Chemistry: FCC Co-Processing

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, CO_2
- Reduced alkanes

Feed	Catalyst	% Bio-based Carbon ($\%C_{bb}$)*	$(\%C_{bb})$product/ $(\%C_{bb})$feed	Wt.% coke	Breakthrough 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