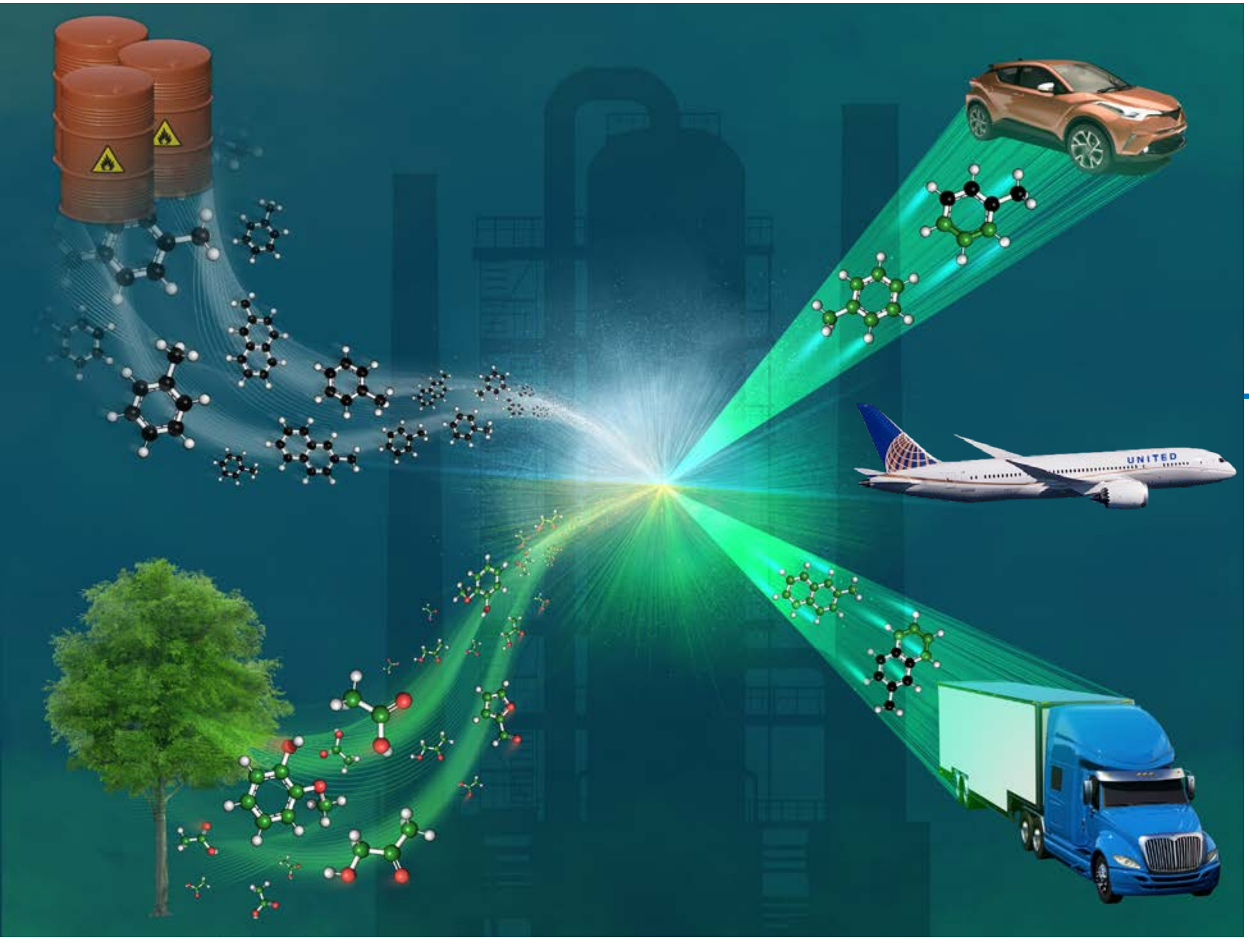

Feedstock and Catalyst Impact on Bio-Oil Production and FCC Co-Processing to Fuels

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Outline

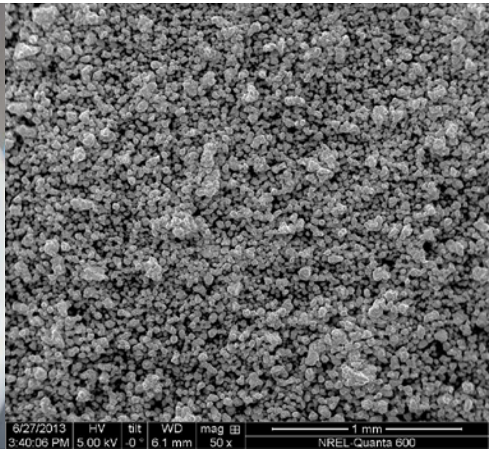
- Catalytic Fast Pyrolysis (CFP) Oil Production
  - Catalysts and Feedstocks
  - Pyrolyzer/DCR System
  - CFP Oil Composition

- Co-Processing (CP) to Fuels

Catalysts and Feedstocks

Feedstocks

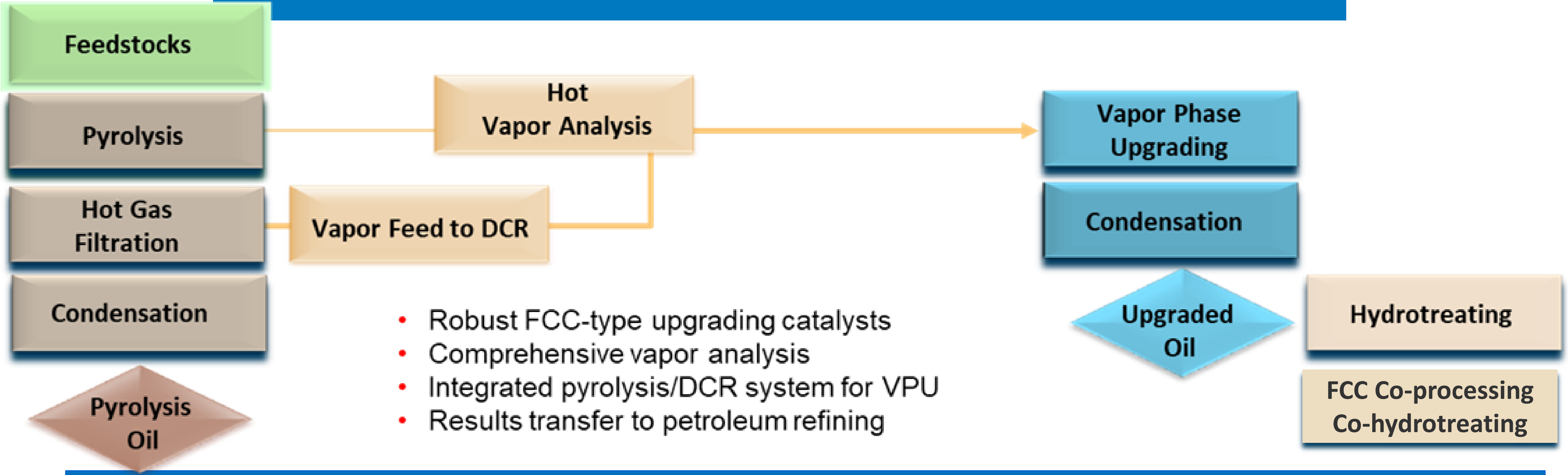
- Miscanthus
- Pine residues
- Debarked clean pine



Johnson Matthey Catalysts

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

CFP Oil Production and Qualities

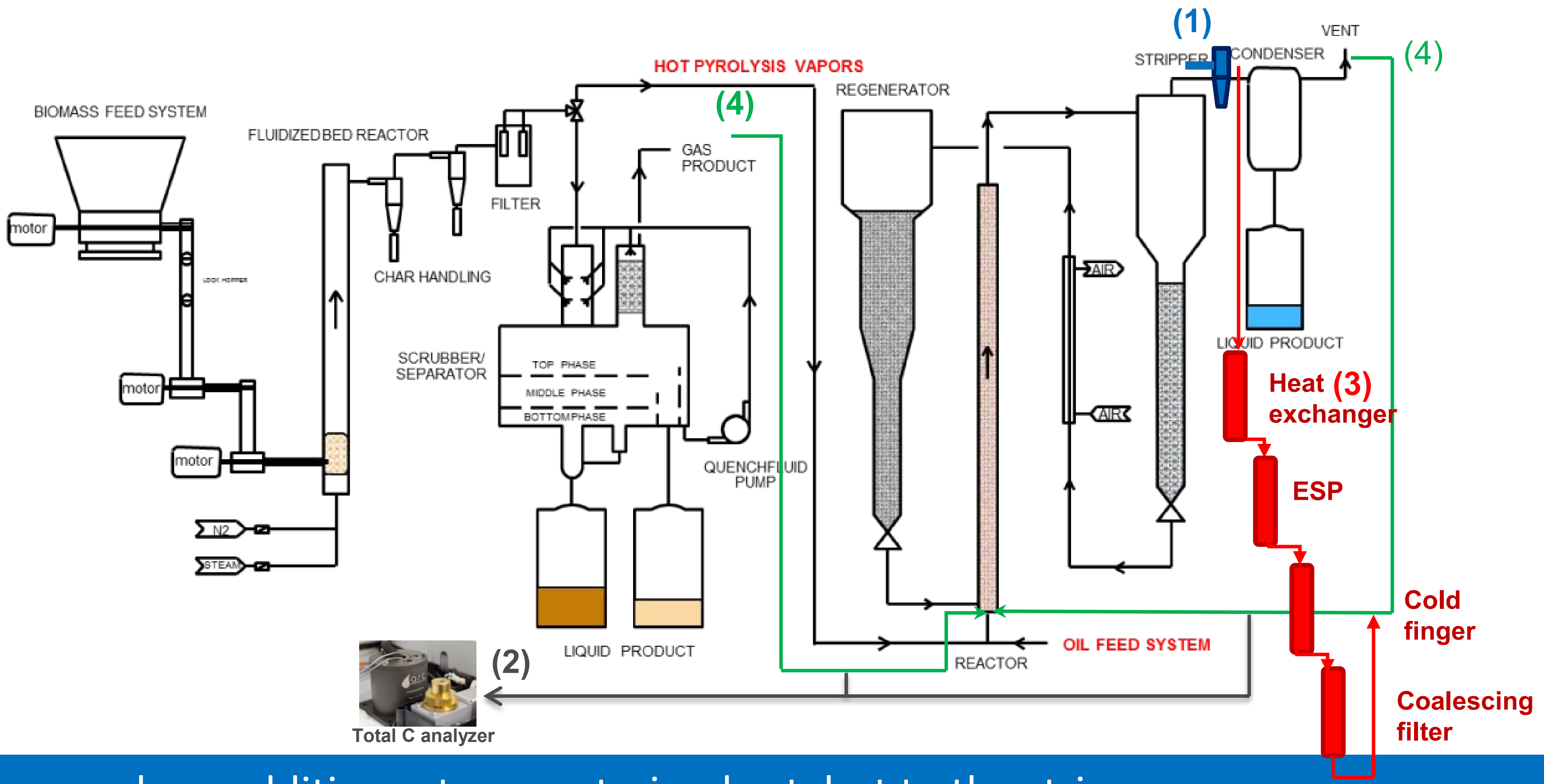


- Robust FCC-type upgrading catalysts
- Comprehensive vapor analysis
- Integrated pyrolysis/DCR system for VPU
- Results transfer to petroleum refining

Produce high quality CFP oils with modified FCC catalysts and biomass pyrolysis vapors at the small pilot scale to produce refinery compatible intermediates of:

- 10-20 % oxygen content
- High carbon efficiency in the 20-25% range, but tied to oxygen content for economic optimum
- Goal to lower (modeled) costs, consistent with BETO’s goal of a $2.50/GGE range fuel production cost

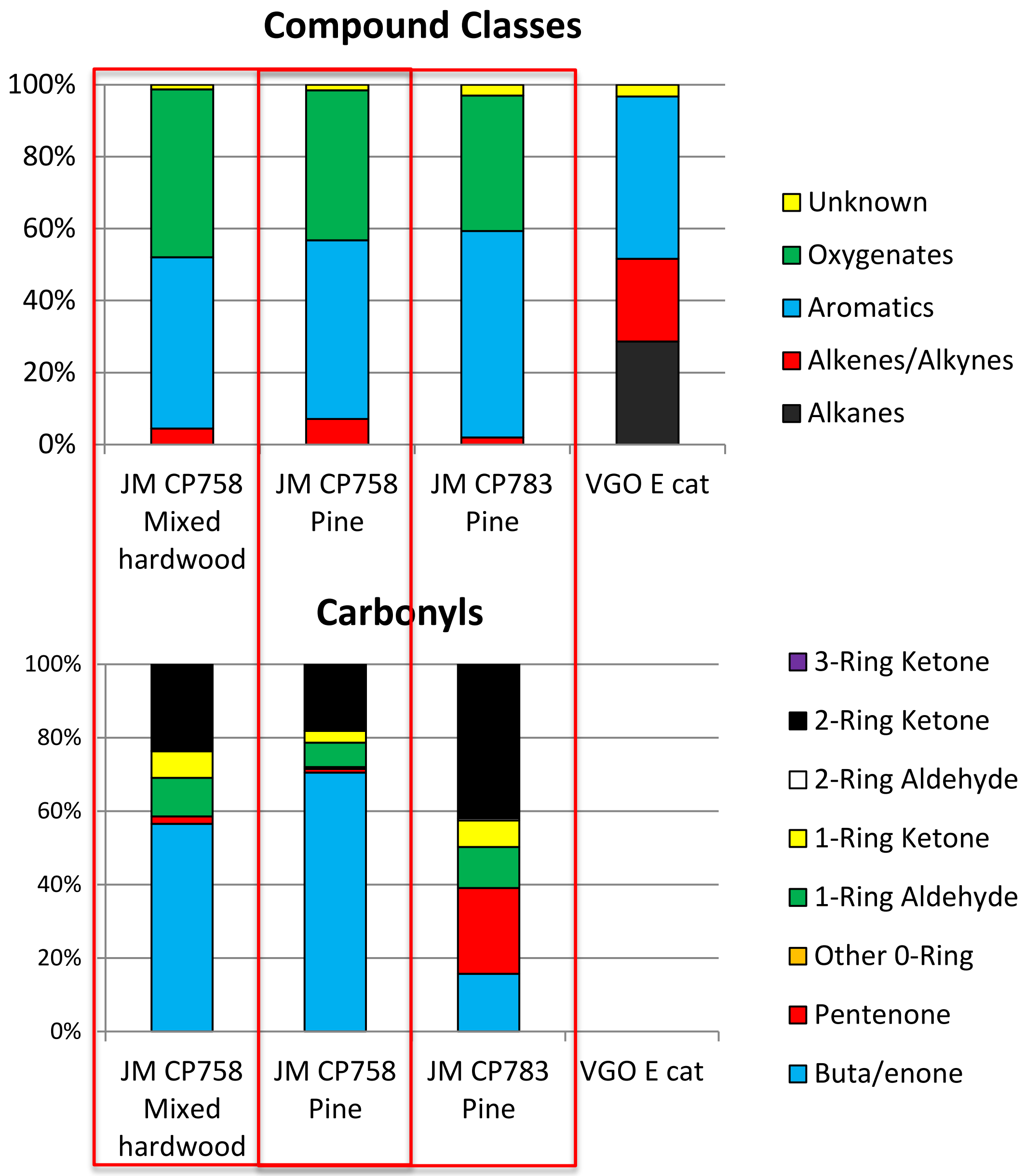
Pyrolyzer/DCR Modifications for CFP and CP



(1) Stripper cyclone addition returns entrained catalyst to the stripper
(2) PolyArc total carbon detector: total C content of feed/product gases simplify C mass balance
(3) Fractional condensation train: improve product recovery
(4) Developed multi feed, independently heated nozzles for co-processing

Improvements provide a feedstock flexible (vapors, liquids, co-feeds) DCR FCC system

Catalyst and Feedstock Impacts
2D GC^2 TOFMS Oil Analysis



Feedstock Impact: Pine vs. Oak

+ Alkenes, aromatics
+ Buta/enone

Possibly due to differences in lignin/hemicellulose/cellulose contents

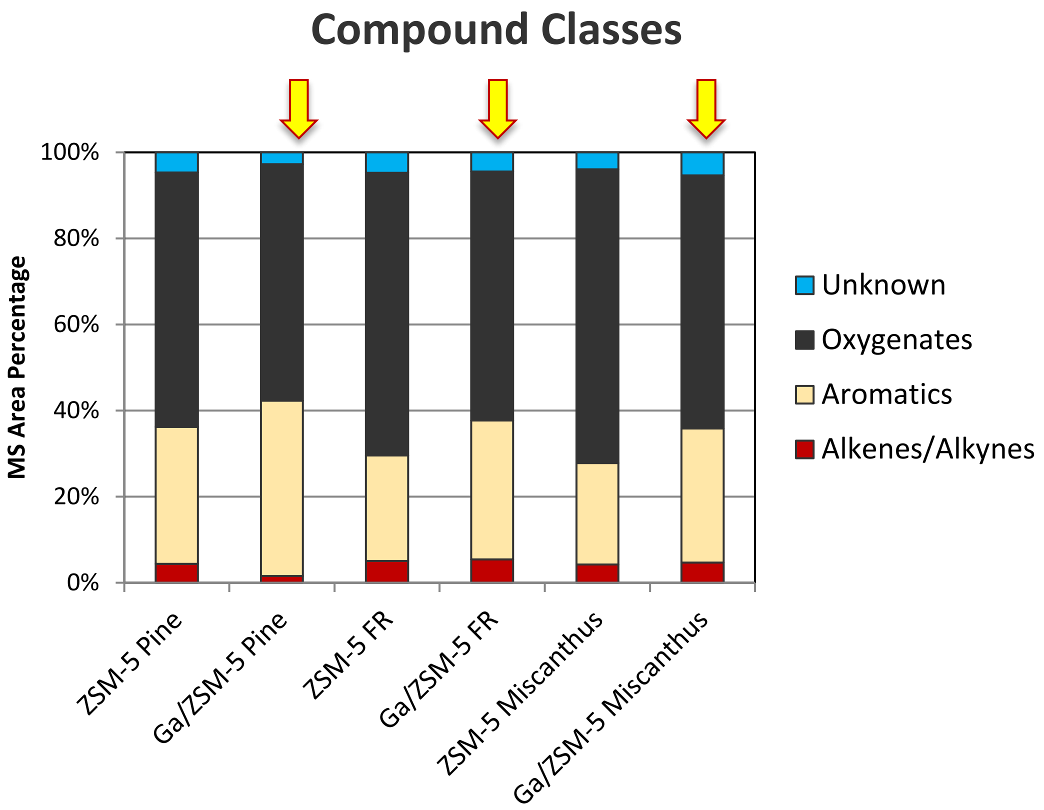
Catalyst Impact: CP783 vs. CP758

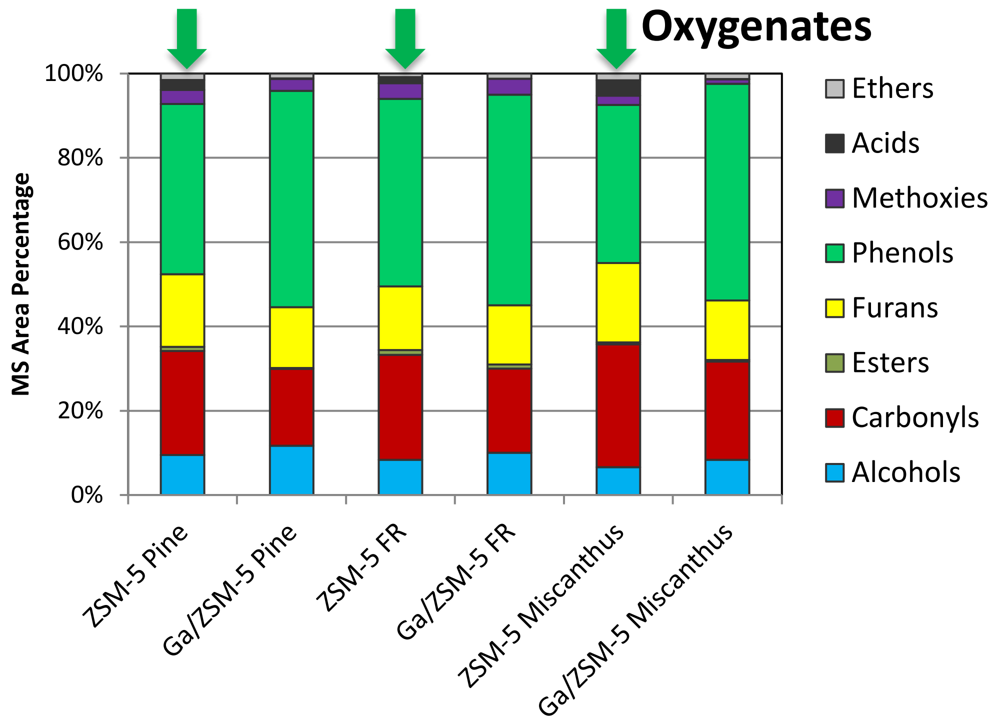
(25, 40 % zeolite/same binder – possibly ketonize)

+ aromatics, – alkenes/alkynes
+ 1-, 2-ring ketones, pentenone
– buta/enone

Catalyst and Feedstock Impacts

2D GC^2 TOFMS Oil Analysis





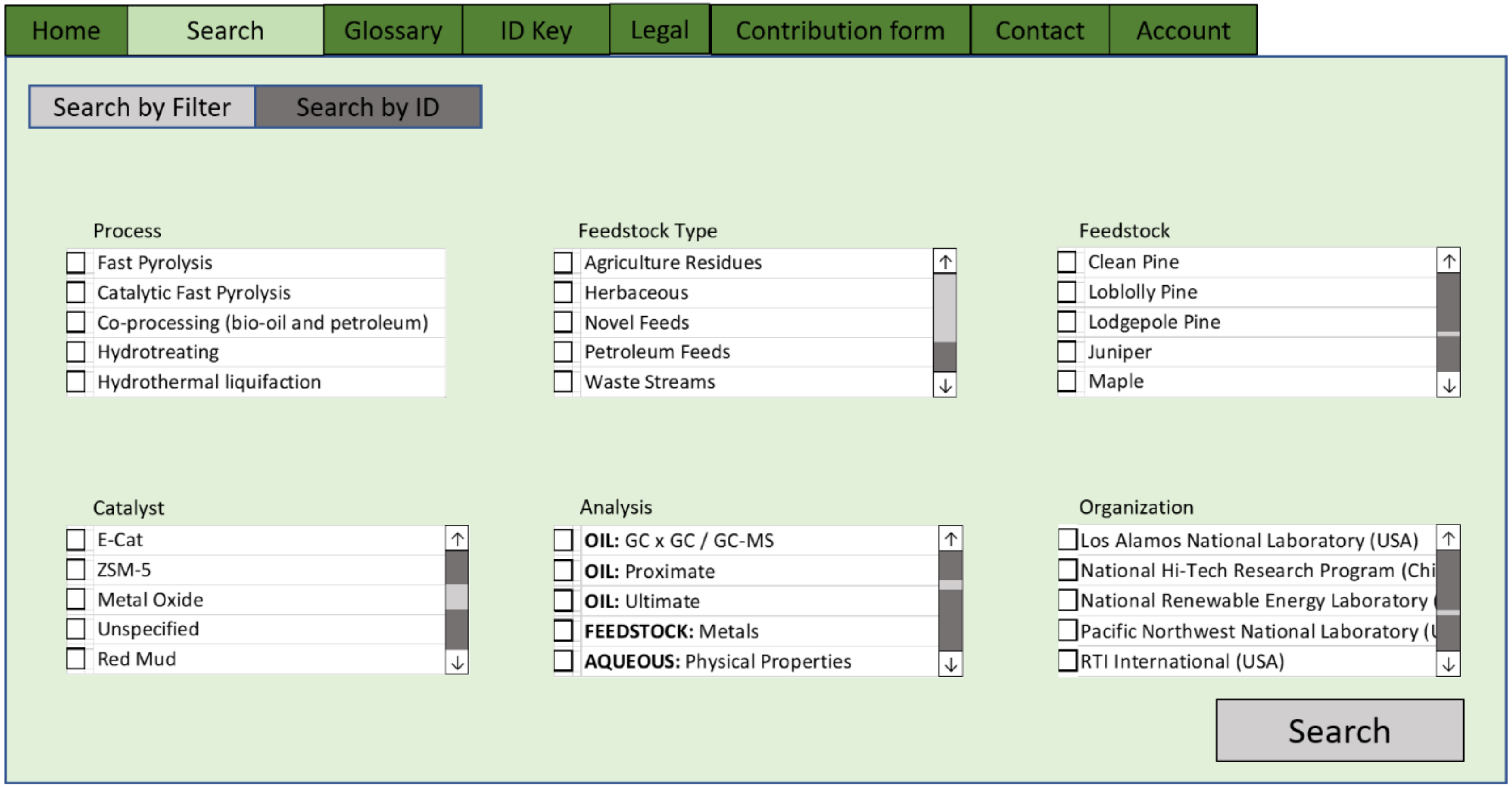
Catalysts
- ZSM-5
- Ga/ZSM-5
  - increased aromatics, phenols
  - reduced oxygenates (furans, carbonyls: cellulose deoxygenation)

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

Searchable Database of Process Conditions, Catalysts, Feedstocks, Oil Compositions

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



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

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*

Biomass

Liquefaction (FP, CFP)*

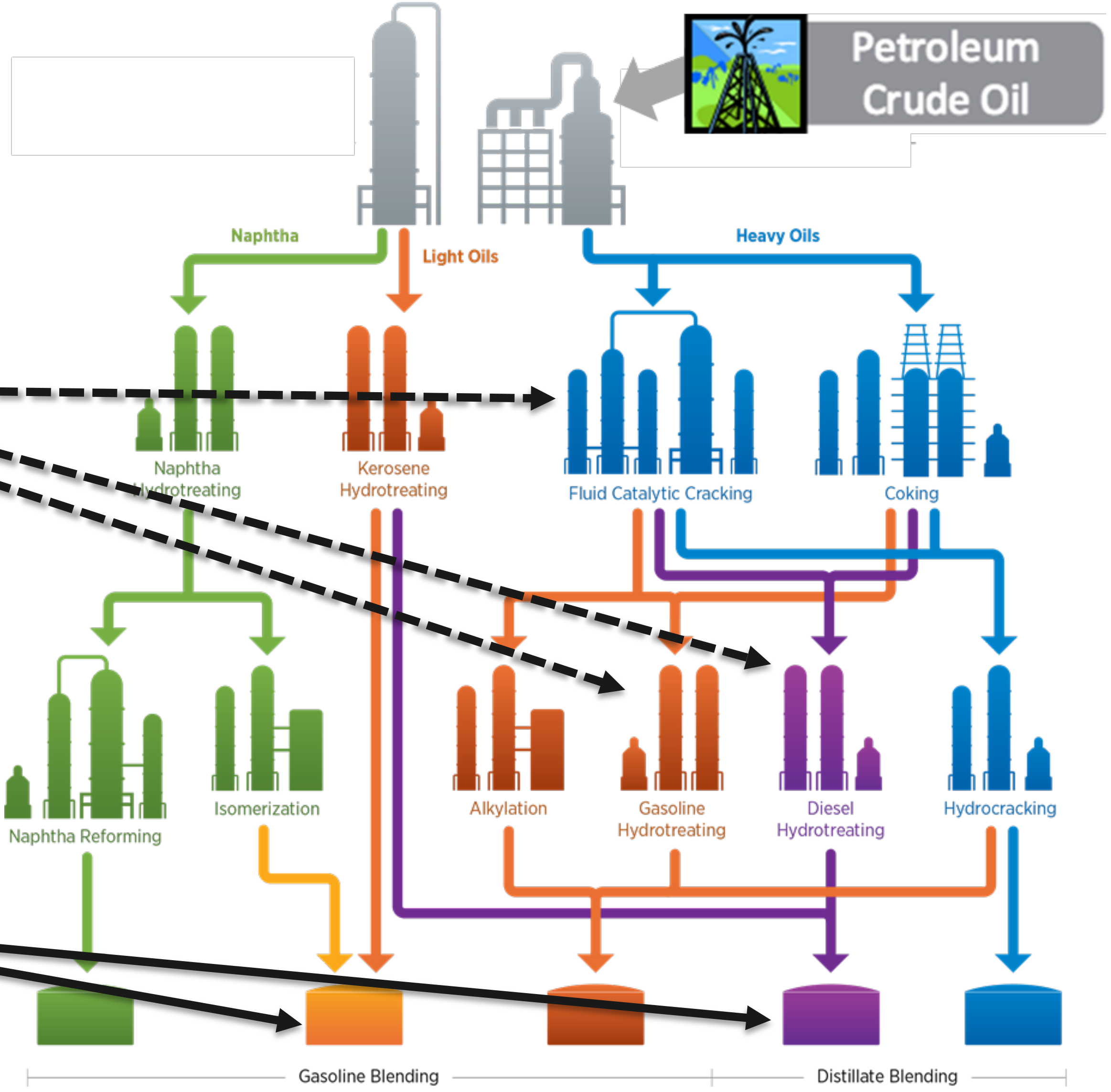
Bio-Oil Intermediates

Co-processing

Developing bio-oil intermediates for insertion points with the most impact

Hydrotreating

Hydrocarbons as blendstock



* FP: Fast pyrolysis oil
CFP: Catalytic fast pyrolysis oil

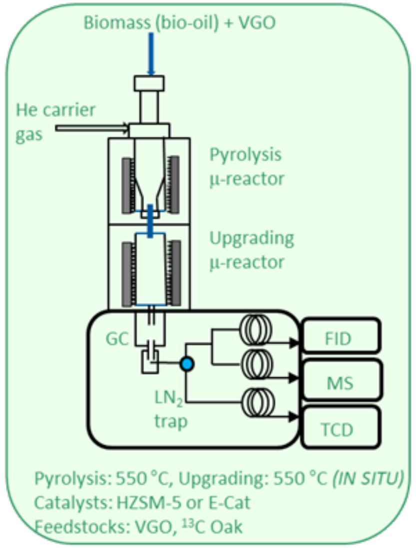
Objective: Produce fungible bio- oils that can be co-processed in petroleum refineries to produce biogenic carbon containing fuels

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

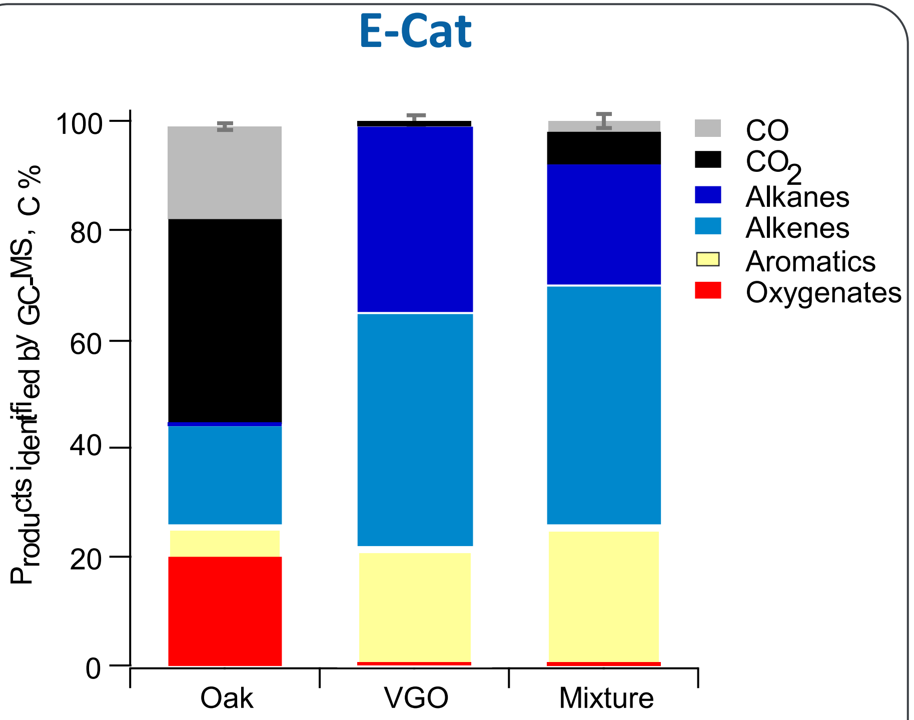
Impact: Faster introduction of renewable fuels into the transportation sector to reduce GHG by 2030

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

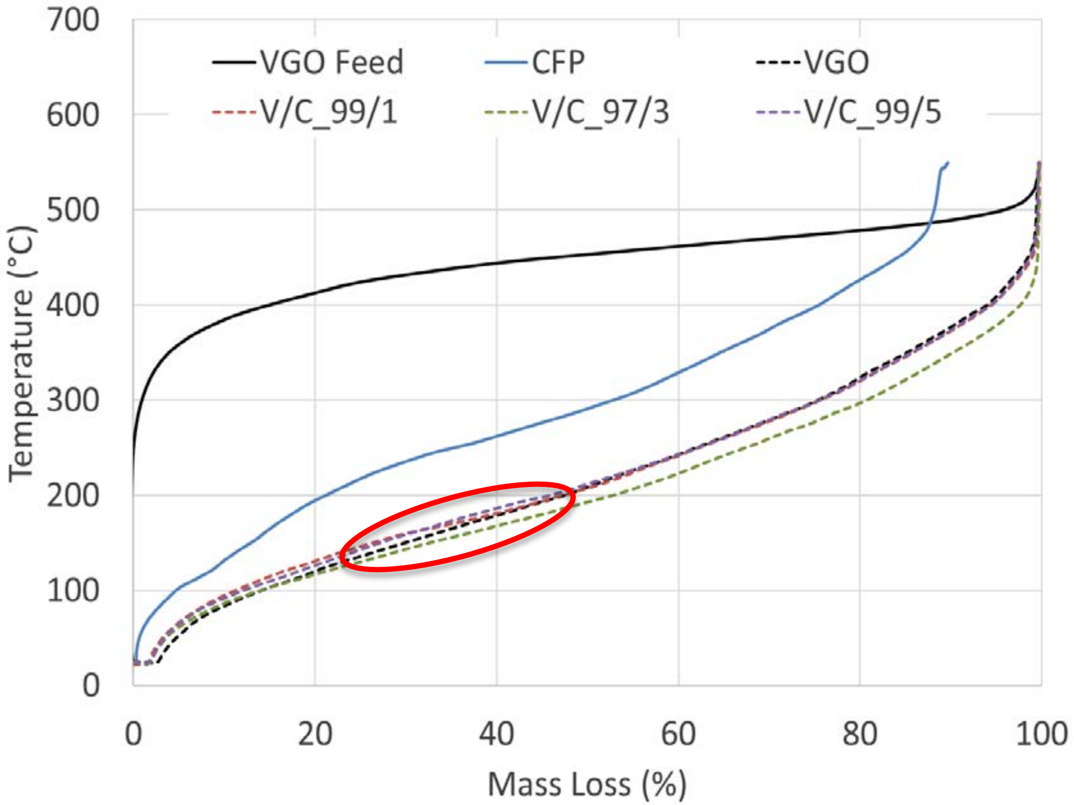
FCC Co-Processing

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)

Hydrotreated CFP Oil: 100% Biogenic Fuels

DCR conditions:
- CP758 zeolite, 550ºC
- Residence time ~1s,
- 20% 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

DCR CFP oil

Hydrotreated DCR CFP oil

46% gasoline
39% diesel

	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		

- 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

Summary

- Consistent quality CFP oils produced with a coupled pyrolyzer/FCC system

- Feedstock impact on oil composition:
  - Pine enhances aromatics, alkenes and buta/enone compared to oak, possibly due to lignin/hemicellulose/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

- Biogenic carbon in hydrocarbon fuels from CFP oil co-processing with VGO approaches 80%

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

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