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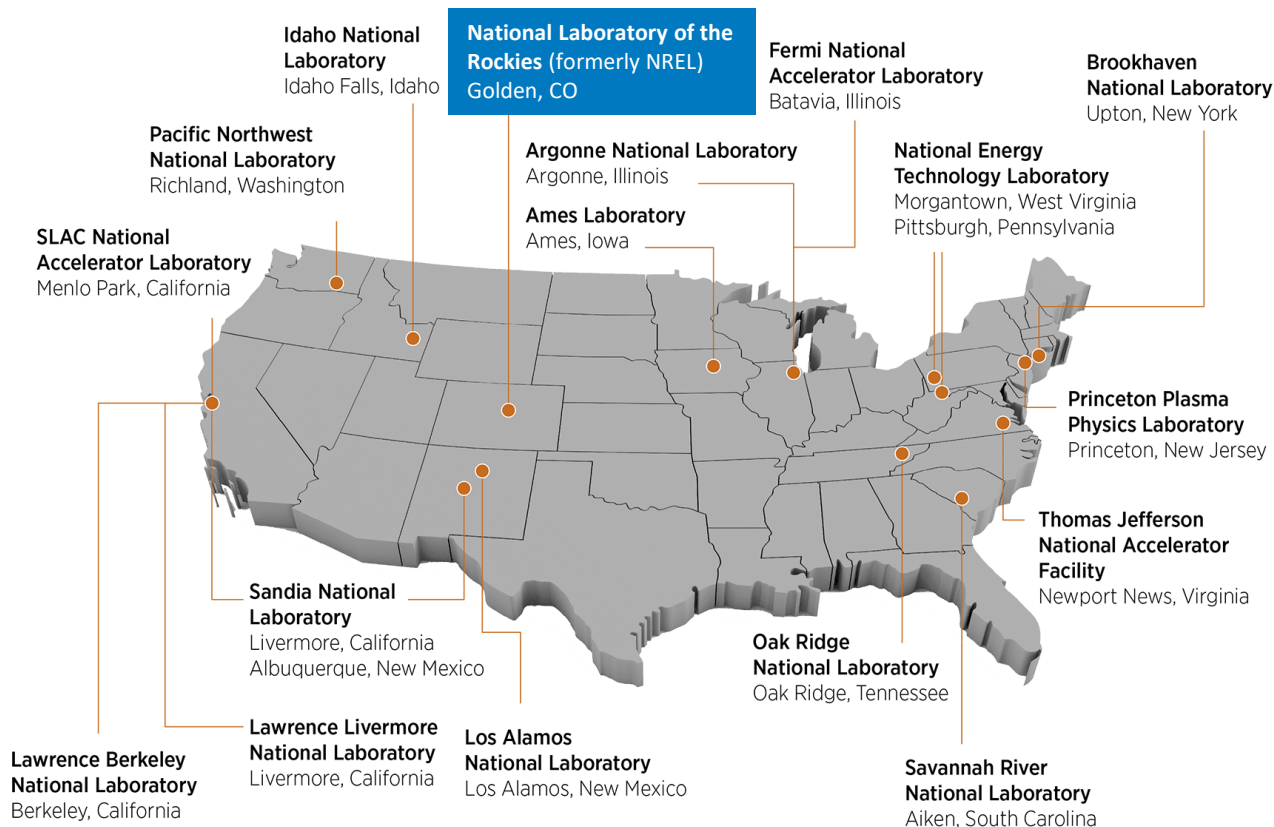
Advances in FCC Co-processing: Tracking Biogenic Carbon

tcbiomass2026

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DOE's National Laboratory System

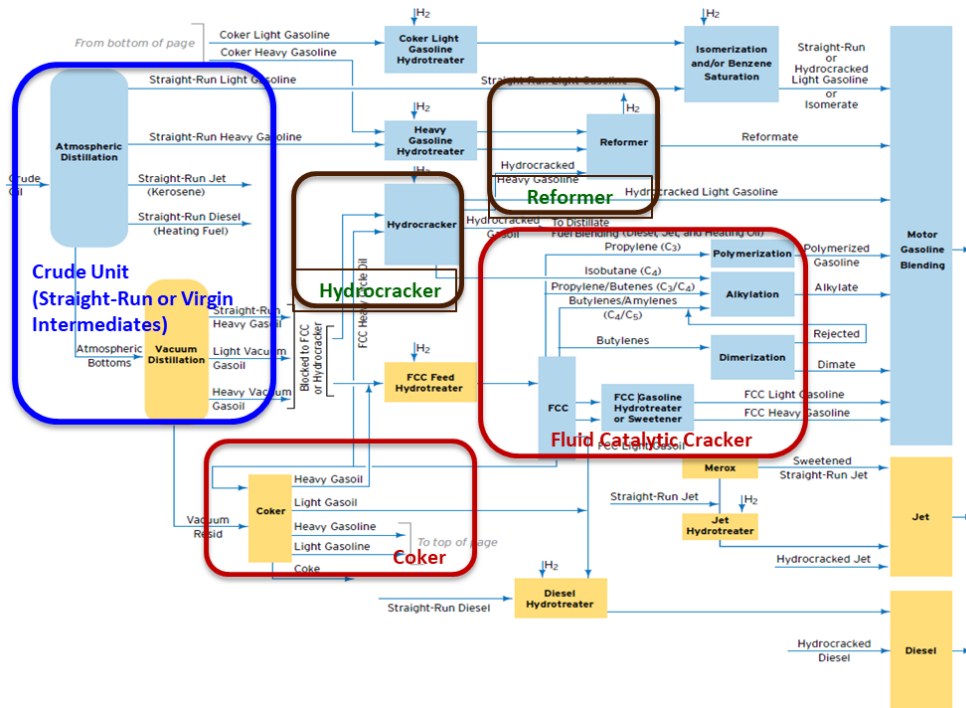


What is Co-Processing?

Use of existing petroleum refinery unit operations, hardware, and infrastructure to process a mixture of conventional fossil feedstocks with bio-feedstocks

Refinery Insertion Points

- Crude unit (X)
- Coker
- Hydrocracker
- Fluid Catalytic Cracker
- Reformer
- Hydrotreater(s)



Why Co-processing?

- 1) Pathway for quickly introducing bio-carbon into transportation fuels industry
 - a) Produce fuels with bio-carbon **at scale**
 - b) Lower cost; Increase consumer choice; utilize secure and resilient domestic resources and supply chains
- 2) Utilize multi-trillion-dollar infrastructure already in place worldwide
 - a) Petroleum refineries
 - b) Transportation and distribution systems
 - c) Fits with industry strategies¹
- 3) High impact outcomes
 - a) Carbon credits for refiners => \$\$
- 4) Path to a clean energy future

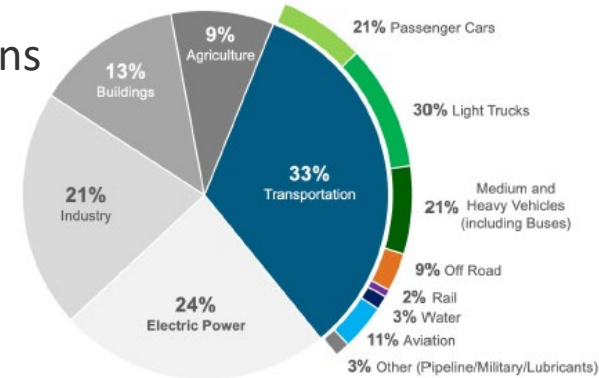
Major question => where does the bio-carbon go?

1. ExxonMobil *Advancing Climate Solutions* (2025): “With constructive policy, co-processing would enable faster, lower-cost delivery of these fuels to customers versus constructing new facilities.”

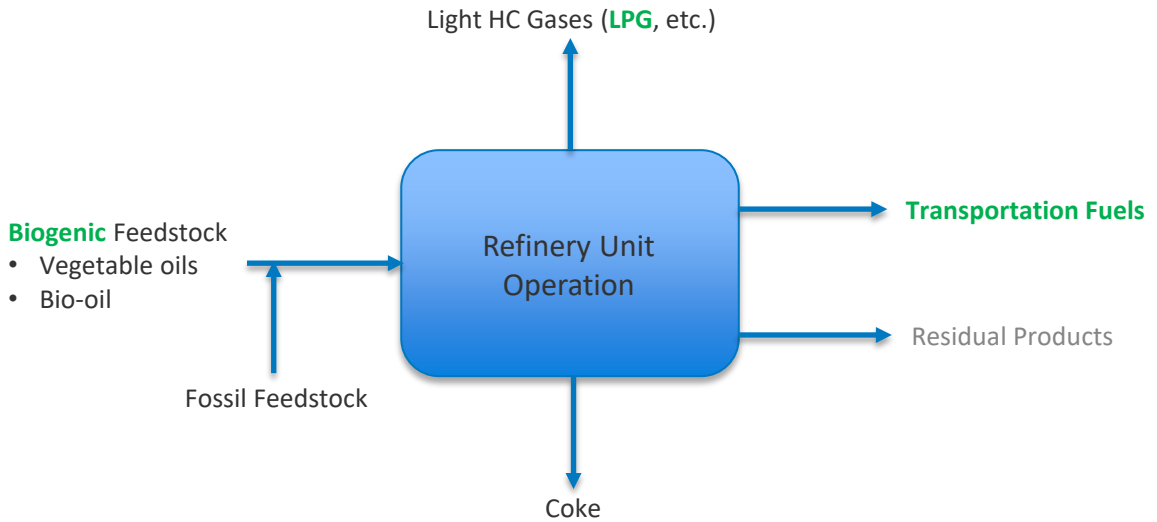
Why FCC?

- Almost every refinery has one
 - Feedstock flexible (garbage can of the refinery)
- Traditional role => make gasoline
 - Gasoline represents a near-term opportunity & addresses a huge market
 - Excess capacity due to EVs

- Why biomass?
 - Use domestic, secure & resilient feedstock supply chains
 - Increase consumer choice (low-carbon product)
 - Energy abundance: petroleum for higher-value uses
 - Job creation



How can we track Biogenic Carbon?



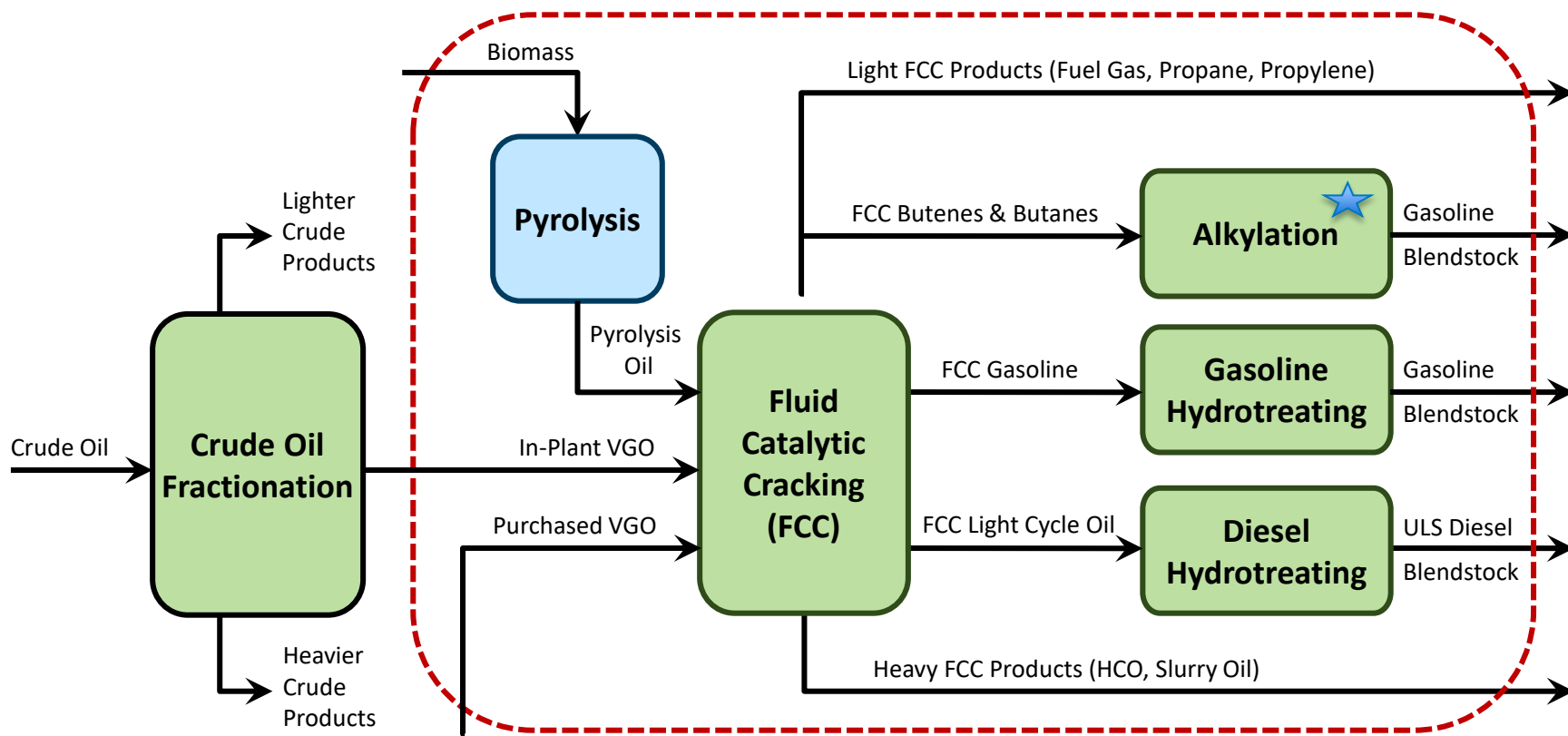
Tracking bio-carbon => 2 approaches

- 1) Mass balance => "what goes in must come out"
- 2) Biogenic carbon speciation (^{14}C) => how does the bio-carbon **actually** apportion in the products?

From the refiner's perspective

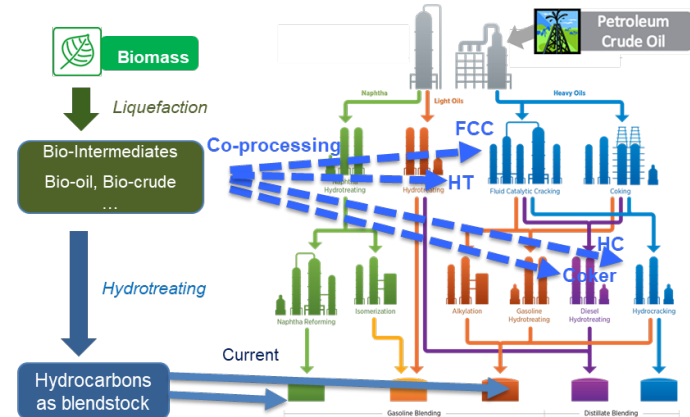
- Max biogenic carbon in fuels and LPG
- Min biogenic carbon in resid and coke

Integration for Bio-oil in the FCC



The Problem of Scale

- Petroleum Refinery
 - ~300,000 BPD (typical “medium-sized” refinery)
- Lignocellulosic Biorefinery @ 2,000 tonnes/day
 - ~ 4,000 BPD pyrolysis liquids (bio-oil)
- Finding sufficient supplies of biogenic feedstocks will be challenging at refinery scale
- Blend levels will initially be low (<5 vol%)
- May require blending of several different types of bio-feeds to reach scale



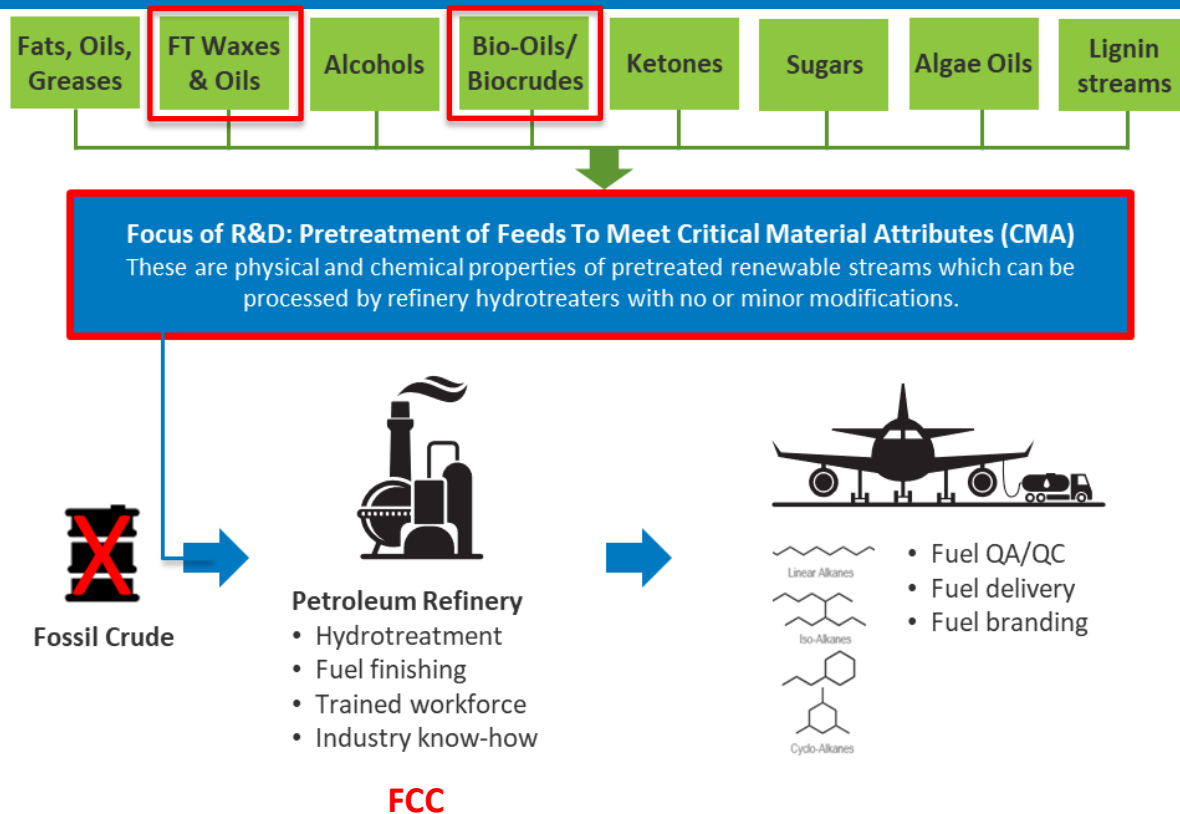
Bio-feedstock Options for the Petroleum Refinery

Near term

- No single feedstock likely to satisfy demand
- Blending of bio-feedstocks will be required

Motivation for this study

- Impact of feedstock differences on biocarbon distribution in products
- Two extreme cases
 - Bio-oil
 - FT wax

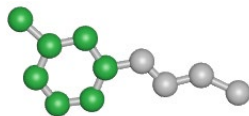


Some Science: Micro-Scale Experiments

^{13}C -labeled biomass => carbon atom scrambling

Carbon Scrambling

Via the hydrocarbon pool mechanism, fossil and biogenic carbon atoms can be 'scrambled' in products. A molecule originating from biomass pyrolysis may produce a molecule in the products that is partially biogenic and partially fossil.



¹³C Study: C. Mukarakate et al., Isotopic Studies for Tracking Biogenic Carbon during Co-processing of Biomass and Vacuum Gas Oil, ACS Sustainable Chemistry & Engineering (2020).

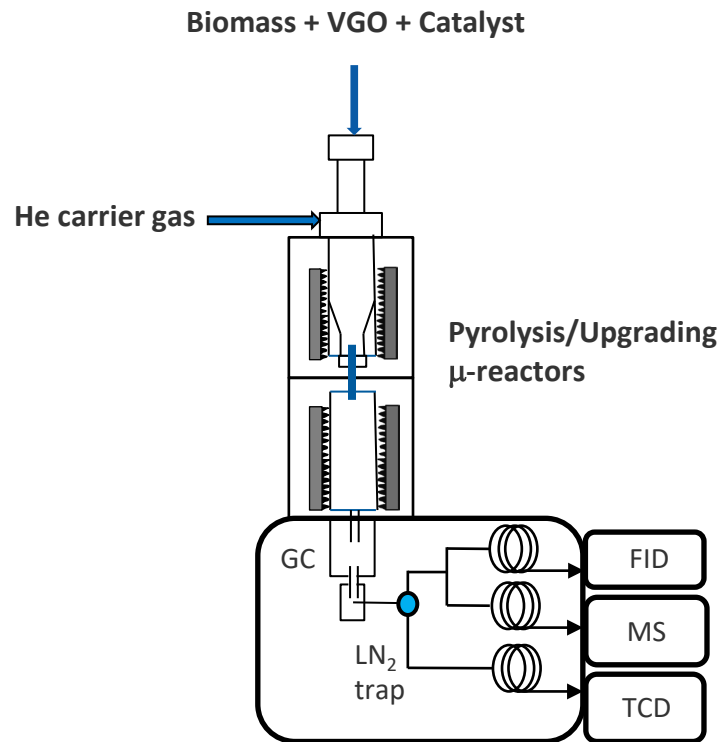
Consider the extremes:

- No carbon scrambling (no biogenic carbon atoms combine with fossil molecules)
 - Biogenic content in fuel fractions shows that biogenic feed produced only biogenic product molecules
- Perfect carbon scrambling (all biogenic and fossil carbon atoms randomly exchange/combine)
 - All product fractions show the same biocarbon percentage as in the feed.

Why does this matter?

- Maybe it doesn't! Fraction of biogenic carbon in products is all that matters; mixtures of fossil- and bio-carbon in molecules is not important
- Do we care if the product molecules have 1 or 2 or 20 'green' carbon atoms?

Catalytic Pyrolysis of VGO with ^{13}C -Labeled Biomass



Pyrolysis/Upgrading = 550 °C

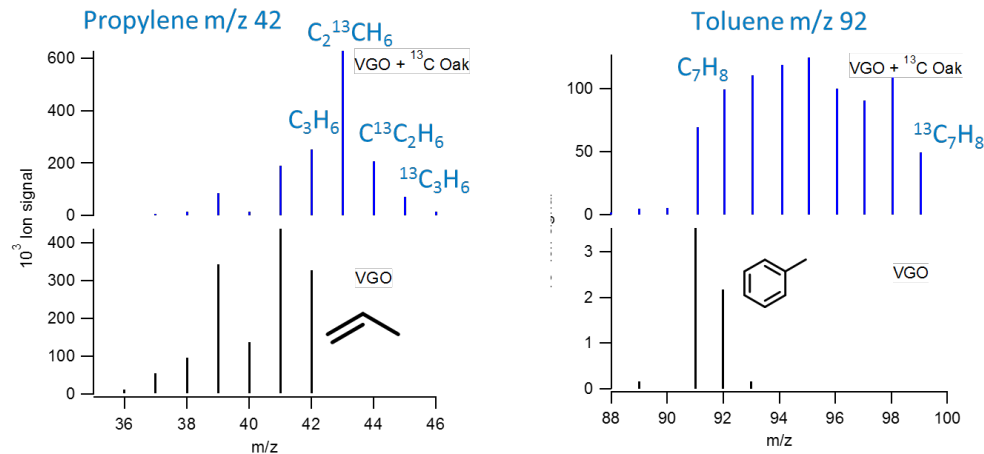
Frontier MicroPyrolyzer system

Catalyst: CP758 (JohnsonMatthey)

Feedstocks: VGO, Oak, & ^{13}C Oak (IsoLife)

^{13}C incorporation in Products

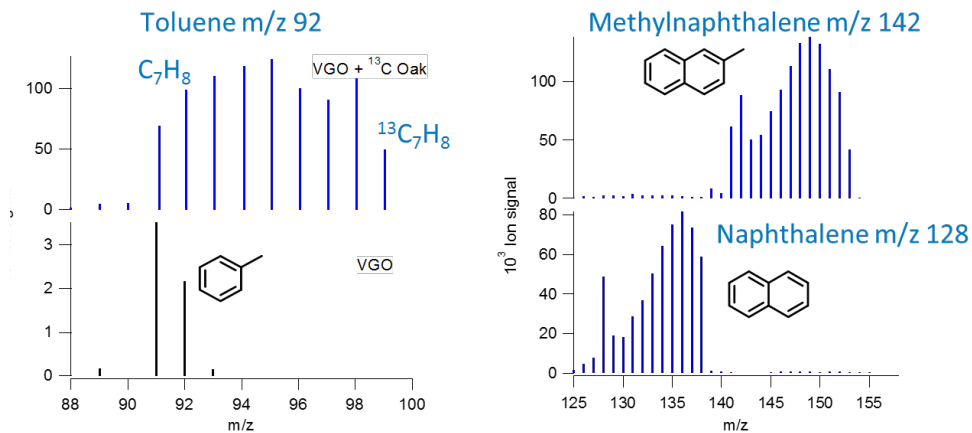
There is evidence for incorporation of **biogenic carbon** into **olefins and aromatic hydrocarbons** (from “hydrocarbon pool” chemistry). This indicates that **biogenic carbon** can be found in **LPG** and **gasoline range fractions** from FCC co-processing



- Propylene: We observe peaks for C_3H_6 , $\text{C}_2^{13}\text{CH}_6$, $\text{C}^{13}\text{C}_2\text{H}_6$, $^{13}\text{C}_3\text{H}_6$ (LPG & alkylate)
- Toluene: We observe peaks for C_7H_8 , $\text{C}^{13}\text{C}_6\text{H}_8$, $^{13}\text{C}_7\text{H}_8$ (Gasoline)

Aromatics, Alkanes, Coke

Biogenic carbon is extensively incorporated into single and multi-ring aromatic hydrocarbons (LCO fraction); hydrocarbon pool chemistry



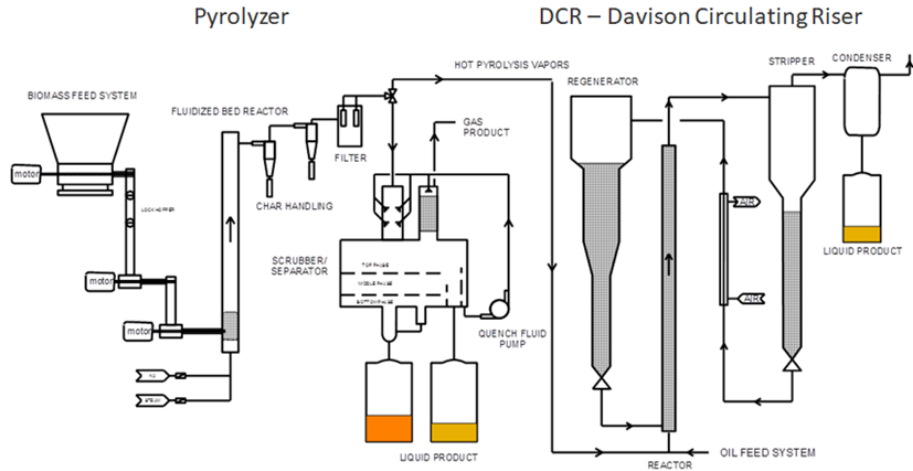
Very limited incorporation of ¹³C in alkanes => they are not formed through the “hydrocarbon pool” chemistry (cracking on catalyst surface?)

Coke-on-catalyst was mostly biogenic carbon

Co-processing in DCR at NLR

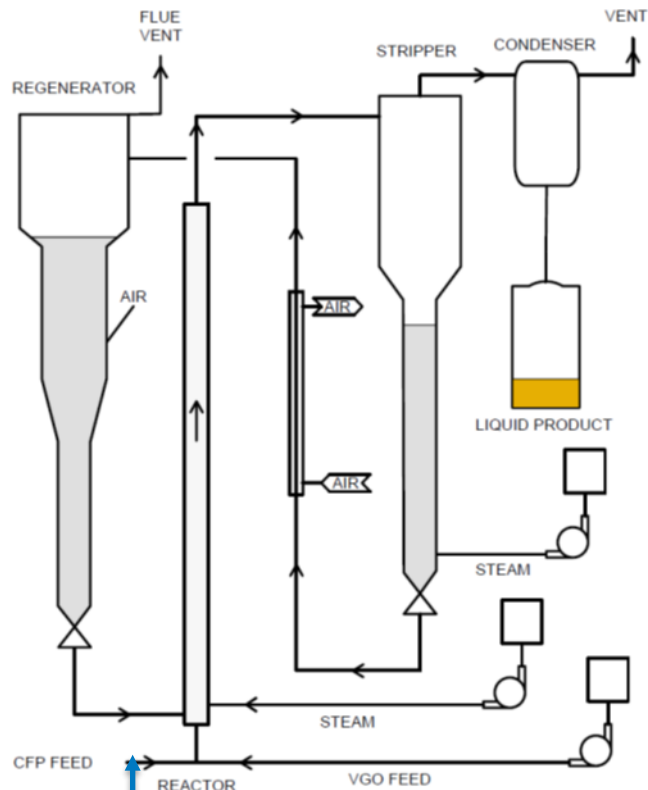
- 1) Model biogenic feedstock: Fischer-Tropsch wax (BEST, Vienna)
- 2) Real lignocellulosic feedstocks
 - a. BTG Bio-oil
 - b. NLR catalytic fast pyrolysis (CFP) bio-oil produced by DCR
 - c. Alder Renewable Crude

NLR Tandem Pyrolysis/Davison Circulating Riser (DCR)



- Semi-batch fluidized bed pyrolysis system coupled to Davison Circulating Riser
- Co-processing of fossil and biogenic feedstocks with dual liquid feed injection points
- Enables direct feeding of pyrolysis vapors to riser
- On-line analysis and speciation with MBMS

DCR Experimental



Pressure	1 – 4	bar
Riser Temperature	500 - 575	°C
Regenerator Temperature	650 - 750	°C
Stripper Temperature	500 - 600	°C
Total Catalyst Volume	1.5 - 3.5	l
Catalyst Circulation Rate	2.5 - 15	kg/h
Liquid Feed Rate	0.3 - 1.5	kg/h
Riser Vapor Residence Time	1 – 5	s

Product analysis

¹⁴C – Beta Analytic (USA)

- All liquids by AMS
- Gases by combustion/AMS from gas bag samples

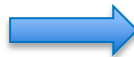
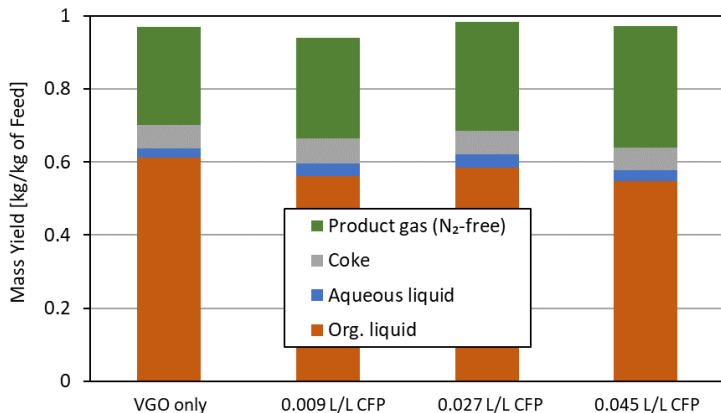
Elemental, PIANO, 2-D GCxGC/TOFMS, micro-distillation, sim-dist, VUV

Carbon on coke (where possible)

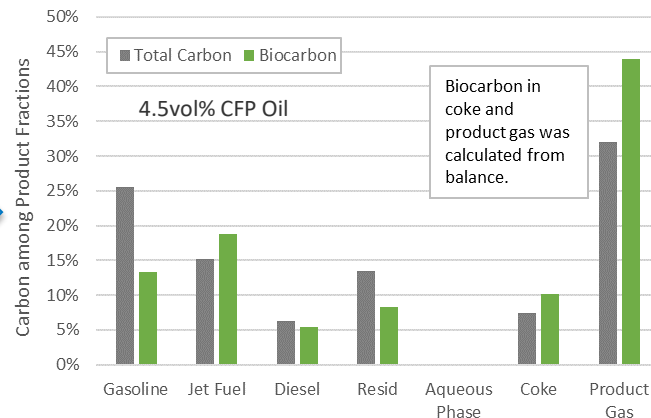
**Pyrolysis
System**

Following the Biocarbon: Incorporation into Products

1) Have to have good mass balances!!



Biocarbon Distribution
(as % of Biocarbon in Feed)



2) Simple way to calculate biocarbon incorporation in a given product; all bio-carbon by ¹⁴C-AMS (Beta Analytic, USA)

$$\text{relative bioC incorporation into liquid} = \frac{\frac{\text{bioC}_{\text{product}}}{\text{bioC}_{\text{feed}}}}{\frac{\text{totalC}_{\text{product}}}{\text{totalC}_{\text{feed}}}} = \frac{\frac{\text{bioC}_{\text{product}}}{\text{totalC}_{\text{product}}}}{\frac{\text{bioC}_{\text{feed}}}{\text{totalC}_{\text{feed}}}} = \text{e.g. } \frac{44\%}{62\%} = \frac{2.8\%}{4.0\%} = 70\%$$

Co-processing of Fischer-Tropsch Wax in DCR

Key Specifications

Feed: 20w% FT wax with VGO (miscible)

Catalyst Type: E-Cat.

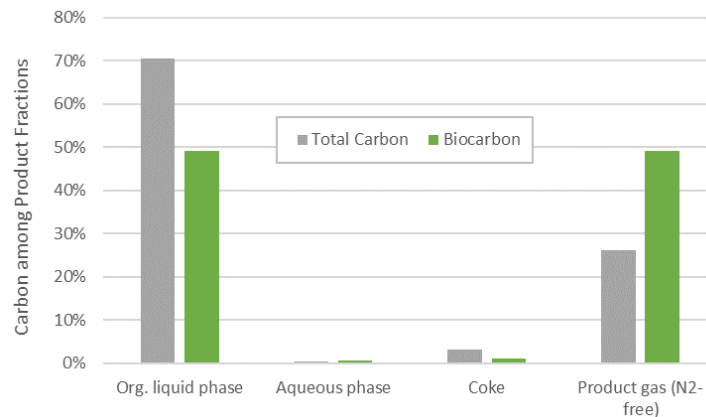
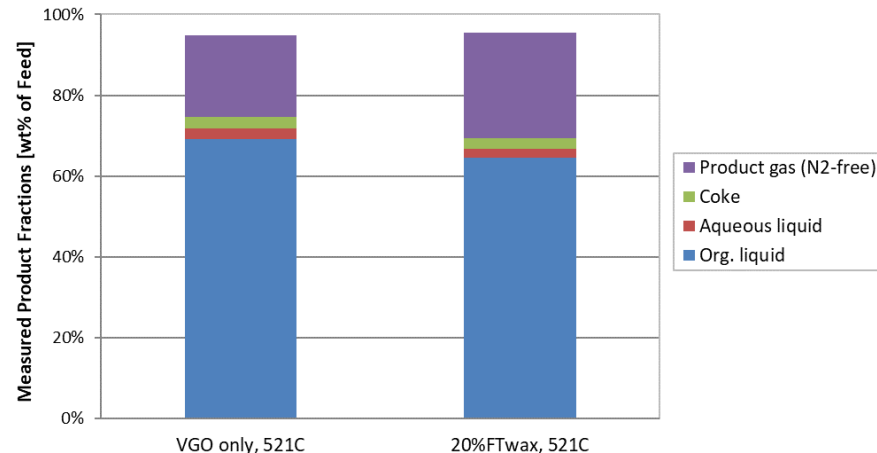
Operating Temperature: 521°C

Operating Pressure: 2.6 bar

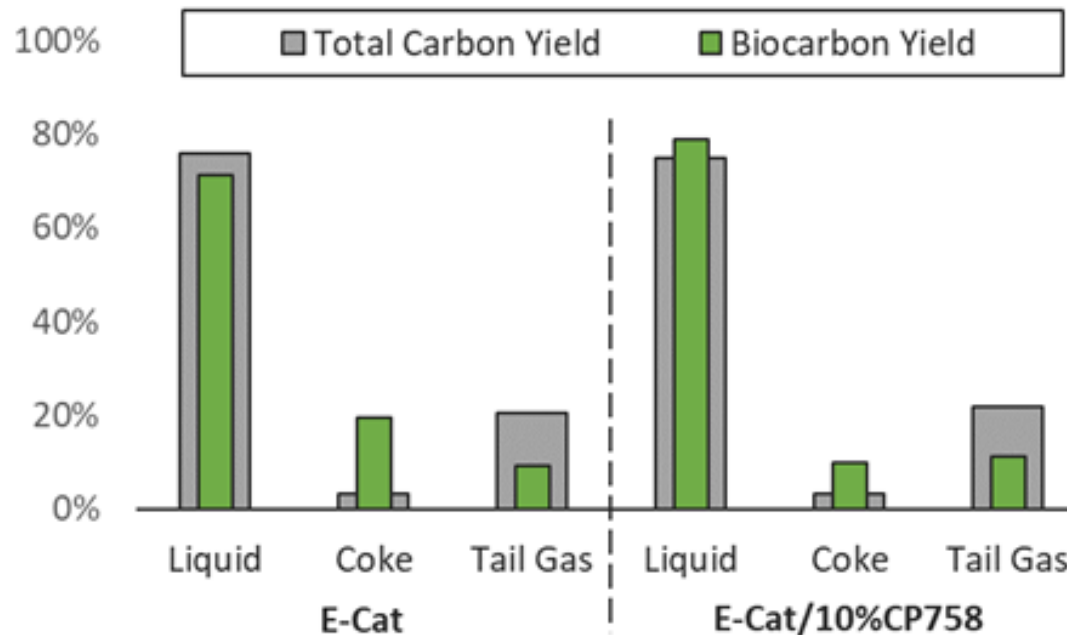
Wax: BEST (Vienna)

Results

- Co-processing FT wax results in **higher gas yields** with **about equal bio-carbon distribution to gases and liquids**
 - confirms ACE testing results
- Gases (C5s, C4s, C3s, C2s, C1, CO, CO₂) are rich in C3/C4 olefins
- Very little bio-carbon on catalyst or in aqueous phase



Co-Processing Bio-oil in DCR

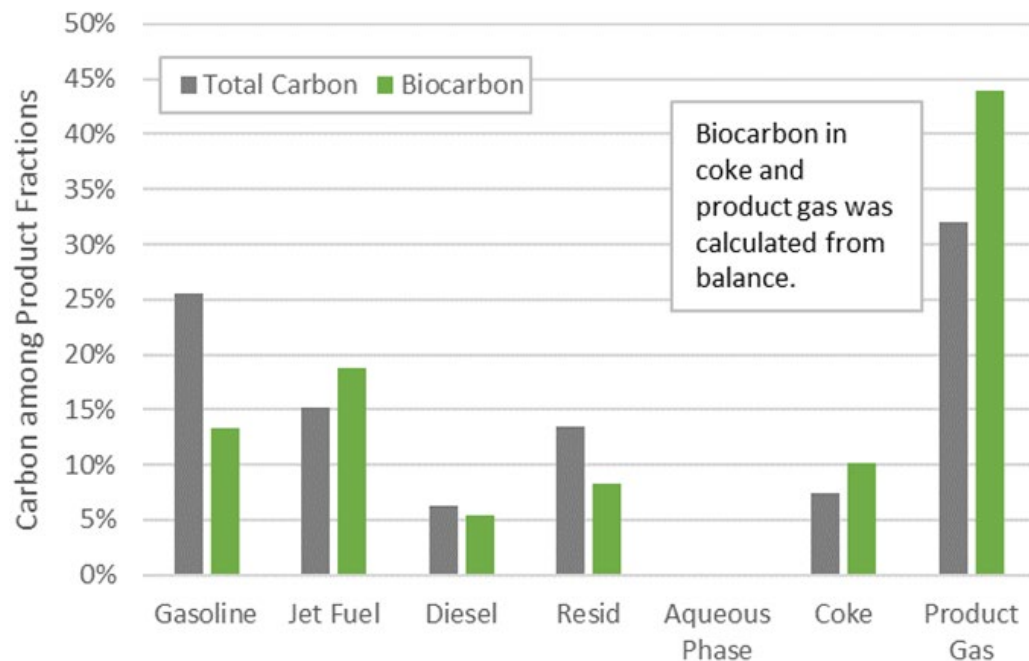


- 5% bio-oil in low-sulfur VGO (from bp)
- CP758 => high ZSM-5 FCC catalyst from Johnson Matthey
- Bio-oil => Stabilized (mild hydrotreating) bio-oil from BTG
 - Oxygen content 19.36% (wet)
 - Water about 5%
- Tail gas = C1, C2s, C3s, C4s, C5s, CO, CO2

Results

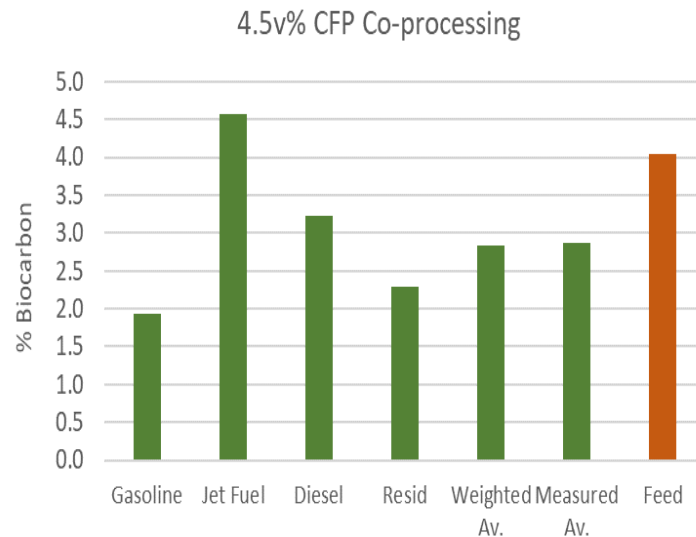
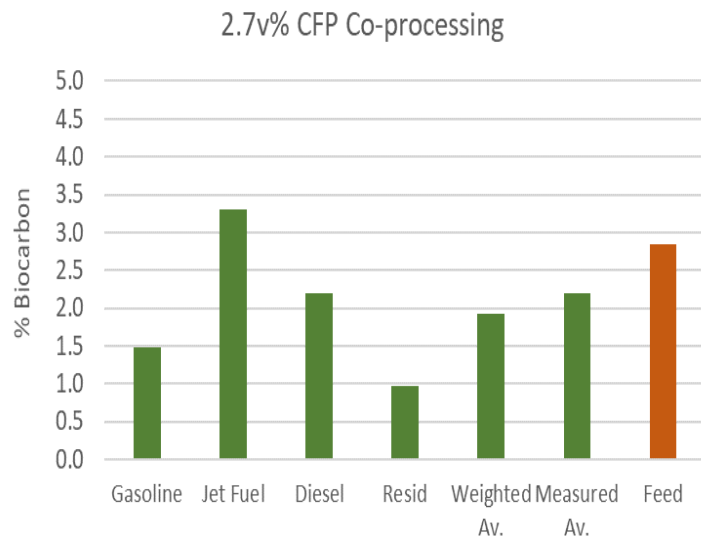
- **Most of the bio-carbon goes to the liquids**
- More bio-carbon as coke-on-catalyst
- Catalyst does make a difference!

Bio-oil Co-processing: Fuel Products



- CPC758 DCR product liquids fractionated into transportation fuels by boiling range (BTG bio-oil)
- **Bio-carbon does not distribute uniformly across products**
- **Bio-carbon distribution does not follow same pattern as fossil carbon**

Biocarbon Distribution: Co-Processing Products



- NLR *ex situ* CFP bio-oil
- Results consistent with BTG bio-oil
- Impact of blend level consistent in terms of bio-carbon distribution
- Some preference shown for partitioning of bio-carbon to jet fraction

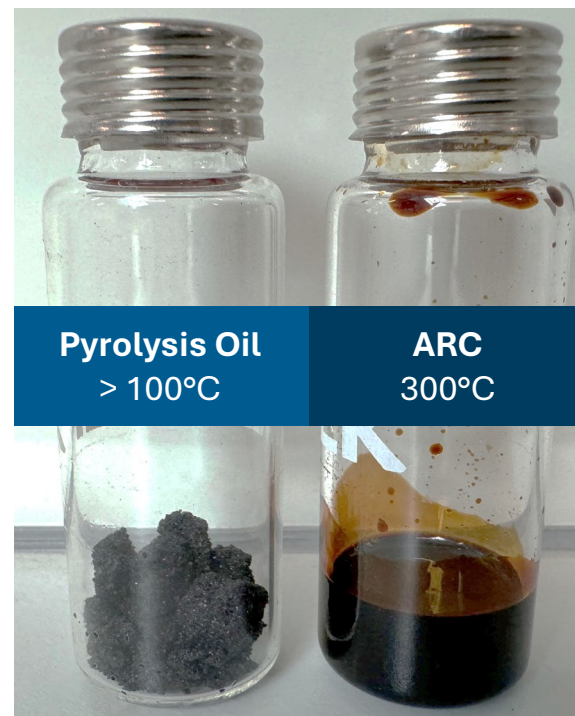
Alder Renewable Crude (ARC)

Removal of sugar-rich fraction reduces coke precursors and oxygenate carryover in downstream processing

Advantages of ARC for Refinery Integration

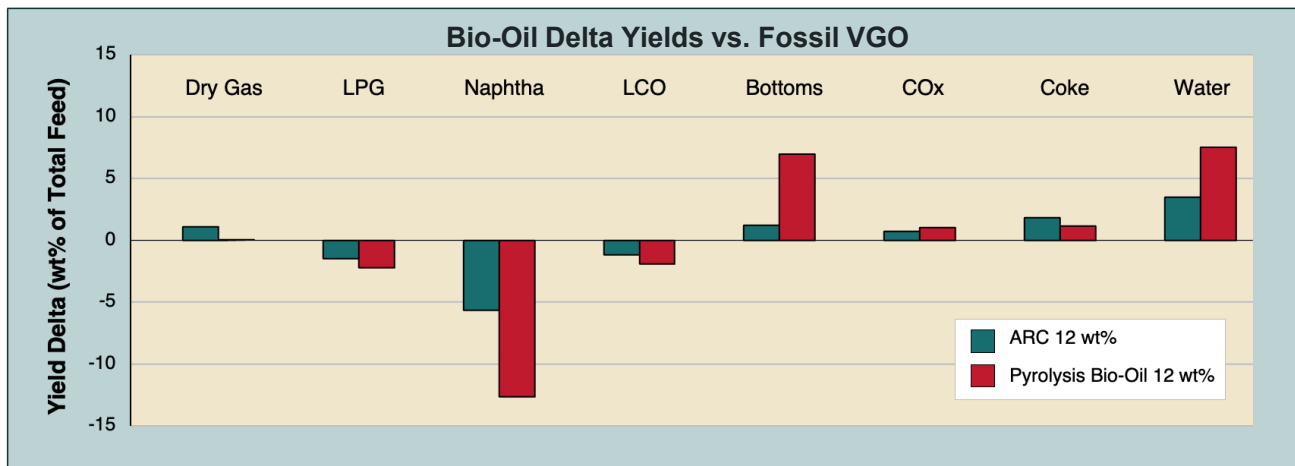
- **Less coking & plugging** – ARC stable when heating $> 250^{\circ}\text{C}$
- **Storage stability > 8 months** – Prevents phase separation
- **Lower metals & water** – Reduces metals by 10x & removes water
- **More carbon** – ARC increases feed carbon by 50%

Property	Wood Fast Py-Oil	Wood ARC
Heat $> 250^{\circ}\text{C}$	Solid	Liquid
Total metals	50 to 100 ppm	< 10 ppm
Water	23-25 wt%	< 1 wt%
Carbon	40 wt%	60 wt%
Oxygen	50 wt%	30 wt%



Yields: Co-Processing VGO and ARC

At 12 wt% co-processing, ARC provides a product distribution closer to VGO baseline, while pyrolysis bio-oil shifts yields toward bottoms and aqueous products. **Catalyst from BASF: formulated for co-processing to maximize conversion of bio-carbon to liquid products. Catalyst equilibrated by steaming without metals addition prior to the testing at NLR.**



Delta total yields include both fossil-derived and biogenic contributions at fixed cat-to-oil-ratio relative to neat VGO.



ARC preserves total LPG, naphtha, and LCO yields relative to fast pyrolysis oil at same wt% blend rate.



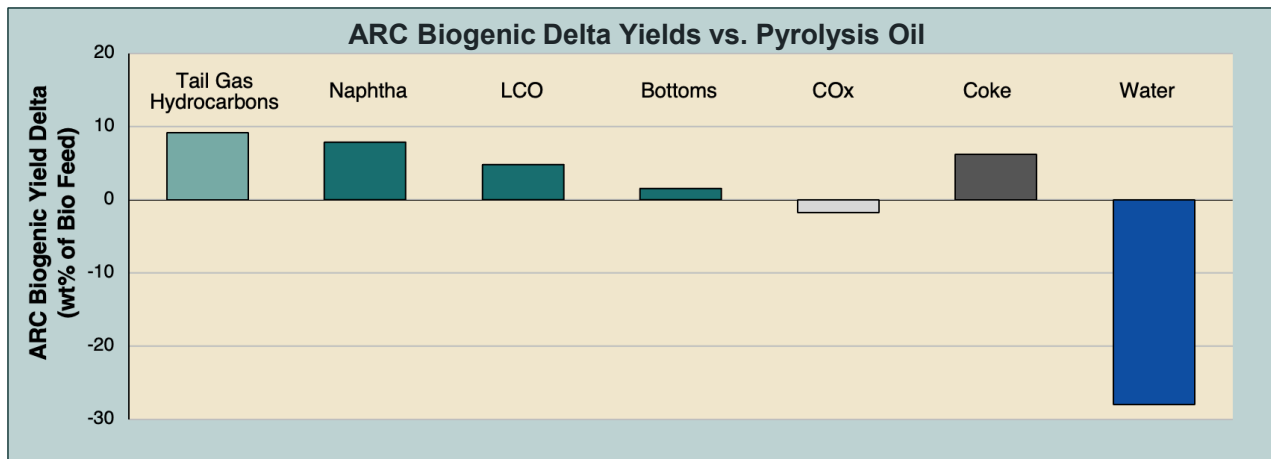
ARC produces modestly higher coke due to increased conversion and reduced bottoms formation.



Fast pyrolysis oil shifts conversion toward heavy bottoms and water, indicating lower cracking severity.

Biogenic Carbon Distribution

At 12 wt% co-processing, ARC increases the yield of biogenic gas and liquid hydrocarbons, with a modest increase in coke, while fast pyrolysis bio-oil diverts a greater fraction to COx and aqueous products.



Delta biogenic product yields from ARC relative to fast pyrolysis bio-oil. Biogenic yields determined by ^{14}C analysis.



^{14}C analysis determined ARC produced 50% higher yields of total biogenic hydrocarbons than fast pyrolysis oil.



Greater fraction of the fast pyrolysis bio-oil feed was diverted to the aqueous phase, coke, and COx.



Improvement reflects ARC's higher effective feed carbon and negligible feed water content.

Petrobras/NREL Project: Pilot FCC (Brazil)

Petrobras “SIX” demo unit has same hardware as a commercial FCC

- Feed nozzles
- Heat balanced
- Riser cyclone
- Mass flowrate: 200 kg/h
- Packed stripper
- Riser: L=18 m, d= 2”



Co-Processing Experiments

- Two pine-derived pyrolysis oils with consistent physical properties
- Mass balance range of 96 – 100%
- 3-hour test runs
- Cumulative time w/ py-oil > 400 hours
- Up to 20 wt% pyrolysis oil in FCC feed
- 54 experimental data points

Fuel Processing Technology 131 (2015) 159-166

Co-processing raw bio-oil and gasoil in an FCC Unit

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Fuel 188 (2017) 462-473

Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production

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Observations and Conclusions

- 1) Feedstock matters! Easily cracked feedstocks make a lot of light HC gases and preferentially sends bio-carbon to light gases (mixed blessing)
- 2) Heavier feedstocks like bio-oil have more bio-carbon in liquids (desirable) but also send a significant amount to coke-on-catalyst (highly undesirable)
- 3) Catalyst does make a difference in bio-carbon distribution
- 4) Blending strategies to optimize bio-carbon distribution will be complex but necessary to maximize credits
- 5) Small differences can have massive economic impact due to scale

We Have the Solution!



Thank You! Questions?

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