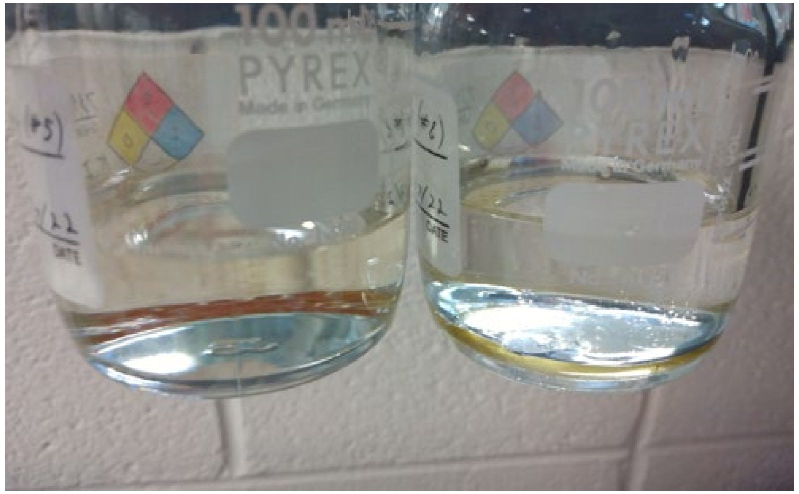
Biocarbon Tracking in FCC Co-processing of Biogenic Feedstocks



Reinhard Seiser, Jessica Olstad, Braden Peterson, Rebecca Jackson, Earl Christensen, Kim Magrini, and Robert Baldwin

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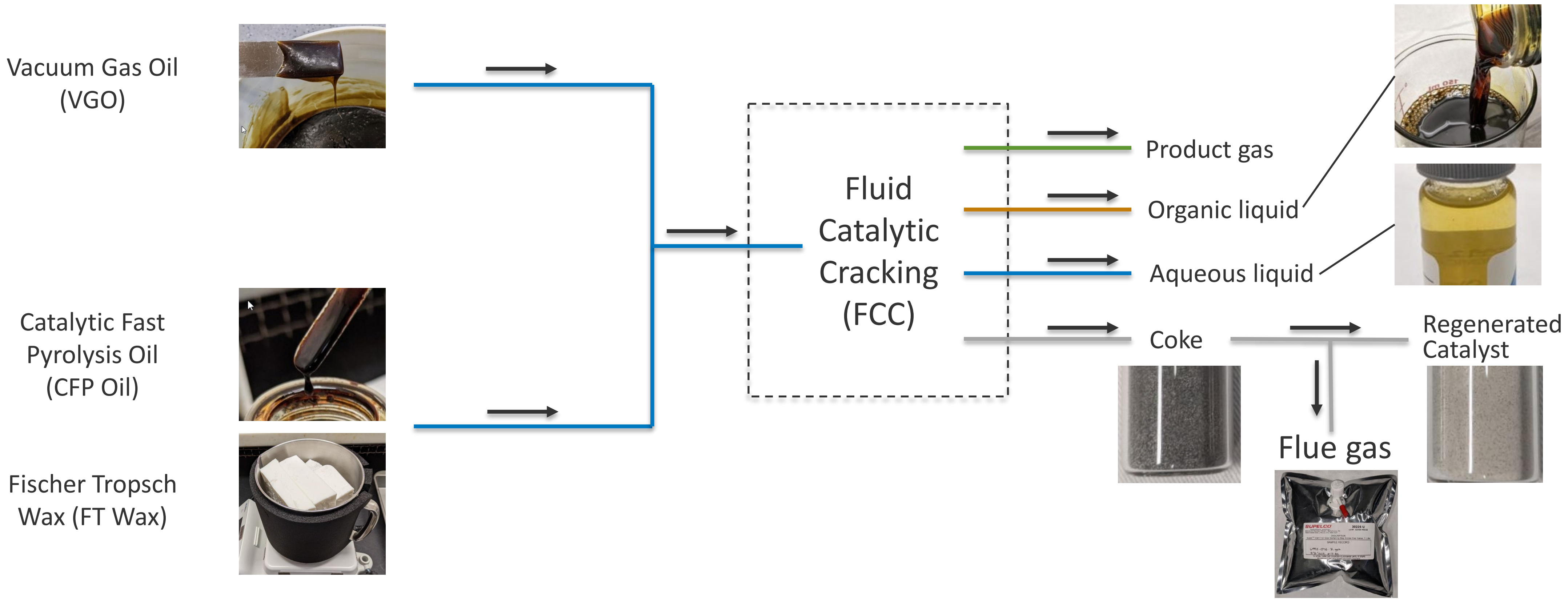
Co-processing of Biogenic Fuels with VGO



- Measure biocarbon in liquid product to determine biocarbon incorporation.
- Track biocarbon across other output fractions.

Similar study: G. Fogassy et al., The fate of bio-carbon in FCC co-processing products, Green Chemistry 14(5) (2012).

Definitions

^{14}C – isotope
Half life of 5730 years.
Appears as a small fraction (1e-12) in biogenic feedstocks.

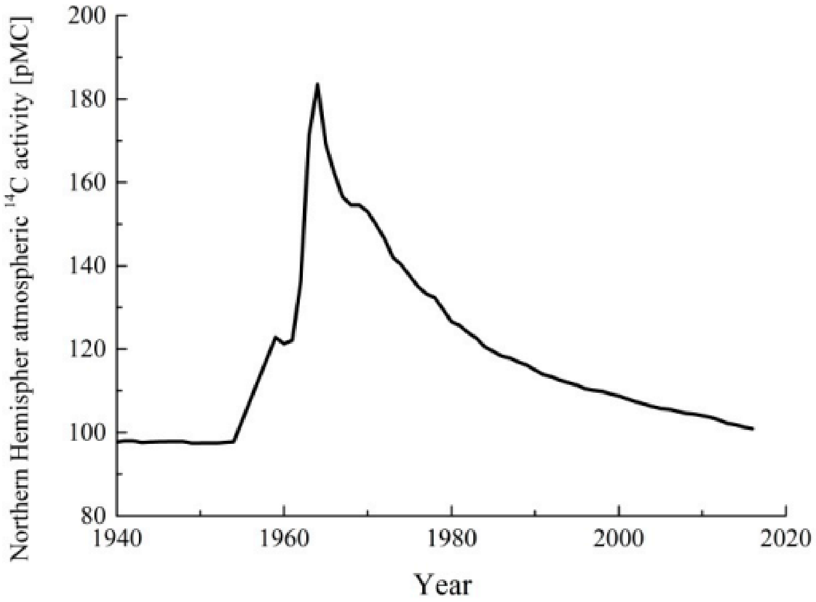
AMS – Accelerated Mass Spectrometer
Measures $^{14}C/^{12}C$ ratio.

pMC – percent Modern Carbon
Referenced to biogenic material in 1950.
Can be above 100% depending on time of growth of biomass.

Percent biogenic carbon (percent biocarbon)
Normalized between fossil feed sample (0% biocarbon) and biogenic feed sample (100% biocarbon).

Example:

	pMC	% biocarbon
CFP Oil	102.90	100.00%
Liquid Product	5.66	5.33%
VGO	0.18	0.00%



S. Hammer, I. Levin, Monthly mean atmospheric D14CO2 at Jungfraujoch and Schauinsland from 1986 to 2016, 2017

AMS Laboratories

Beta Analytic
Commercial Testing Laboratory in Florida

University of California Irvine
Keck – CCAMS Group
Earth System Science Department

pMC	UC Irvine	Beta Analytic	Theoretical Value
FT wax	83.30	83.70	
FT wax diluted with VGO	16.50		16.43
CFP Oil	102.90	102.40	
Co-processed FT wax	11.20	11.82	
Co-processed CFP oil	6.00	5.74	

$$pMC_{feed} = \frac{Y_{CFPO} \cdot Ccontent_{CFPO} \cdot pMC_{CFPO} + Y_{VGO} \cdot Ccontent_{VGO} \cdot pMC_{VGO}}{Y_{CFPO} \cdot Ccontent_{CFPO} + Y_{VGO} \cdot Ccontent_{VGO}}$$

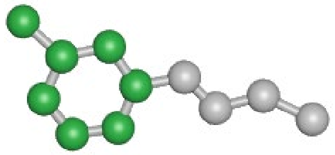
pMC … percent Modern Carbon (from ^{14}C analysis) …alternatively also works for percent biocarbon

Y …component mass fraction

$Ccontent$ …from ultimate analysis

Carbon Scrambling

Fragments from biogenic molecules can attach to fossil molecules and vice versa. E.g., a molecule originating from biomass pyrolysis may pick up a short fossil carbon chain and produce a molecule in the jet fuel range that is now partially biogenic and partially fossil.



^{13}C 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, i.e., no biogenic carbon atoms combine with fossil molecules. Typical in decomposition reactions.
  → E.g., biogenic content in jet fuel shows that biogenic feed produced jet-fuel range molecules.

- Perfect carbon scrambling, i.e., all biogenic and fossil carbon atoms randomly exchange/combine. Typical in synthesis reactions.
  → All product fractions show the same biocarbon percentage as in the feed.

- Analysis of biogenic carbon incorporation into fuels is valid for any carbon scrambling.
- Following reactions paths via biocarbon analysis becomes less useful if carbon scrambling occurs.

Co-Processing of CFP Oil in Davison Circulating Riser

Key System Specifications

Feed Type: Liquids

Feed Rate: 1.2 L/hr (1.14 L/hr VGO, 60 mL/hr CFP Oil)

Catalyst Type: E-Cat.

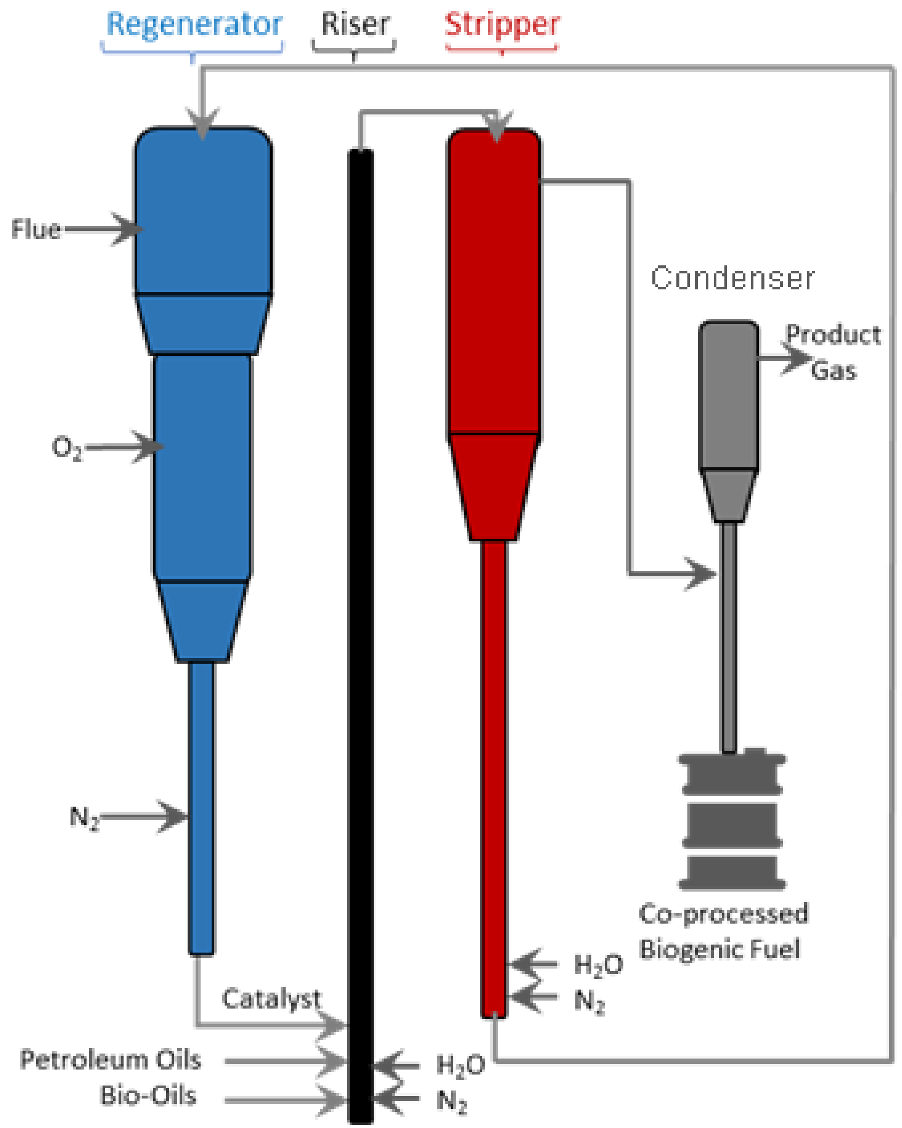
Catalyst Charge/Feed Rate: 1.8 kg, circulation rate 7-10 kg/hr

Operating Temperature Range: 521°C

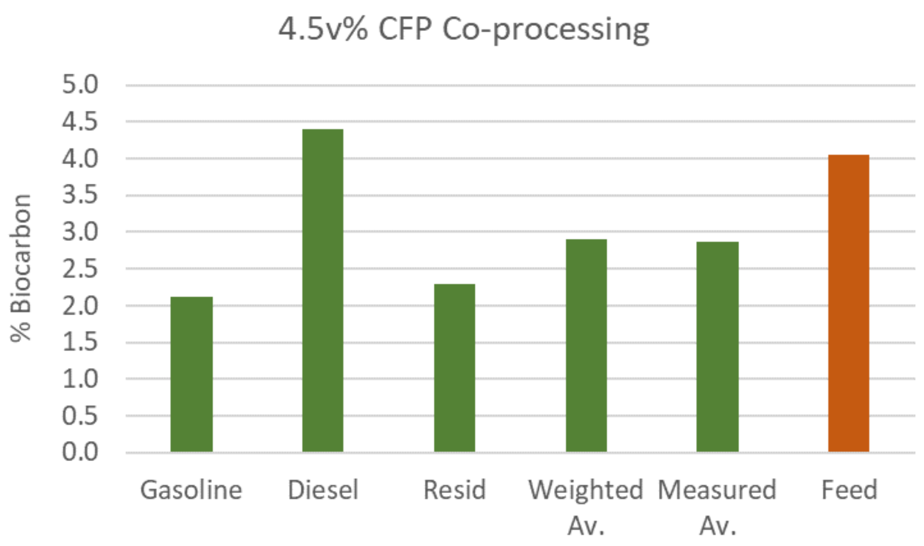
Operating Pressure Range: 2.6 bar

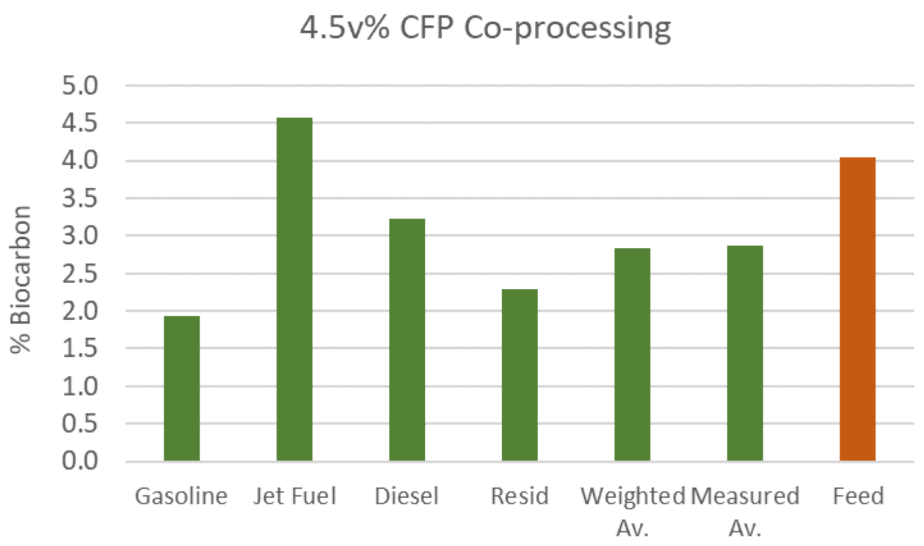
Biocarbon Analysis

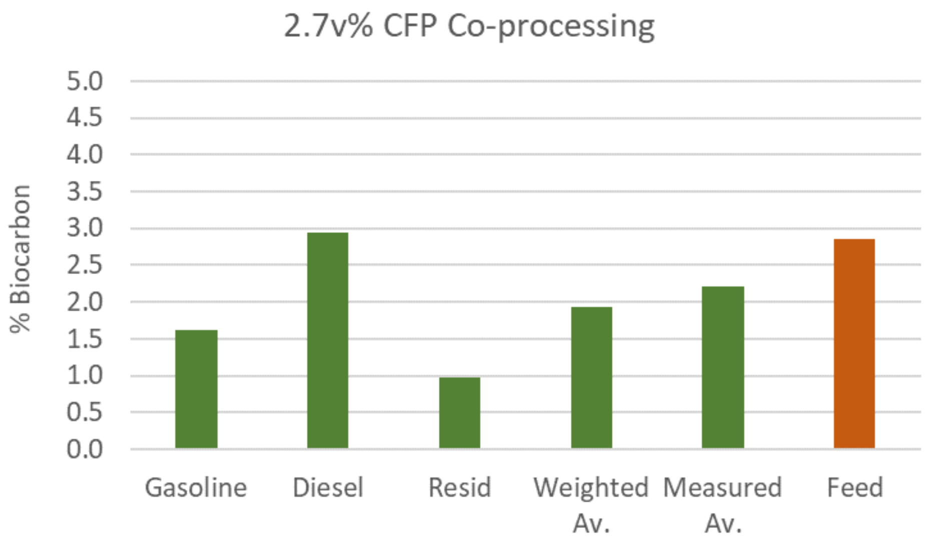
- Liquid product and distilled fractions

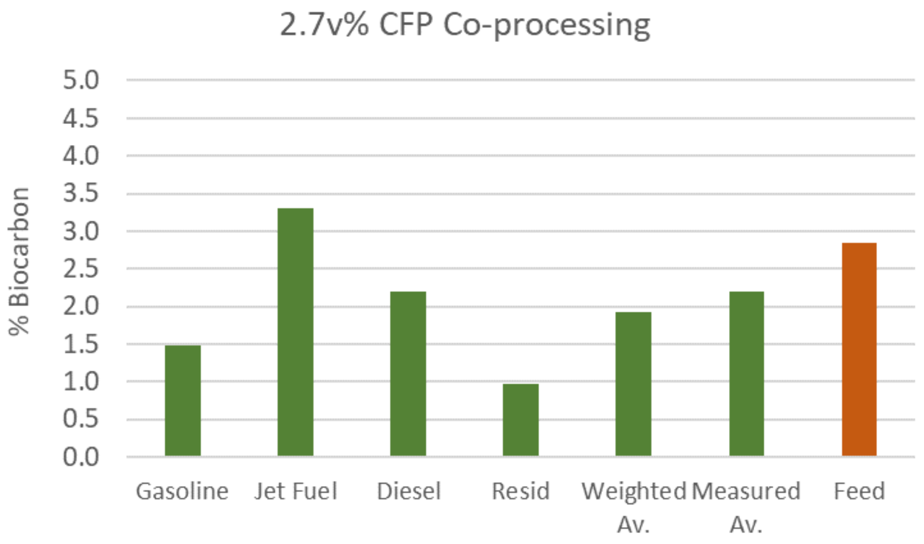


Biocarbon Measurements in Co-Processing Products

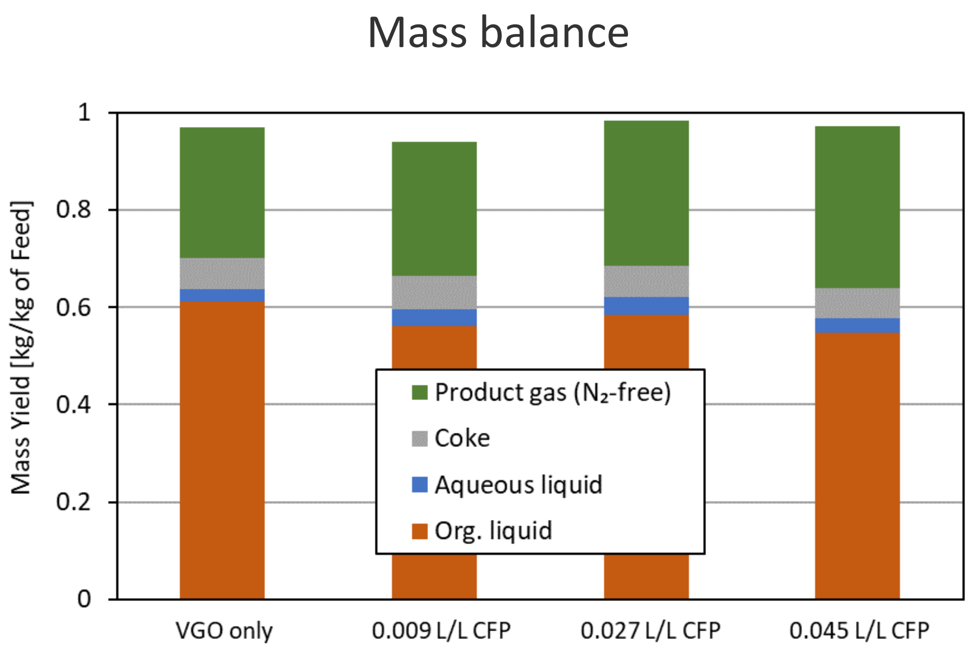


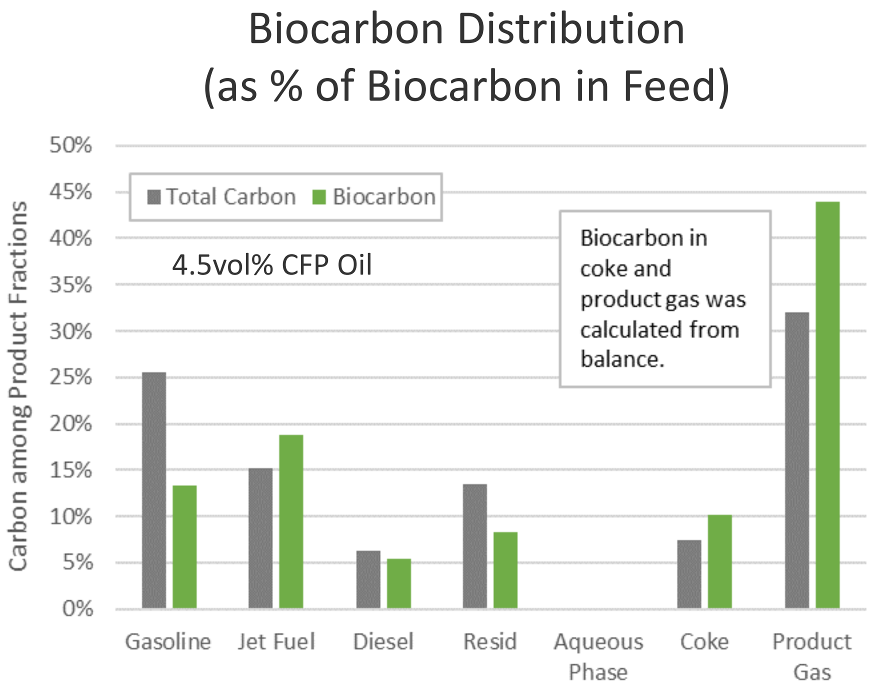






Biocarbon Incorporation into Liquid Fuels





- A simple biocarbon incorporation into the liquid products can be calculated with the following equation:

$$bioC\ incorporation\ into\ liquid = \frac{\frac{bioC_{product}}{bioC_{feed}}}{\frac{totalC_{product}}{totalC_{feed}}} = \frac{\frac{bioC_{product}}{totalC_{product}}}{\frac{bioC_{feed}}{totalC_{feed}}} = e.g.\ \frac{44\%}{62\%} = \frac{2.8\%}{4.0\%} = 70\%$$

Co-processing of Fischer-Tropsch Wax in DCR

Key Specifications

Feed Type: 20w% FT wax with VGO

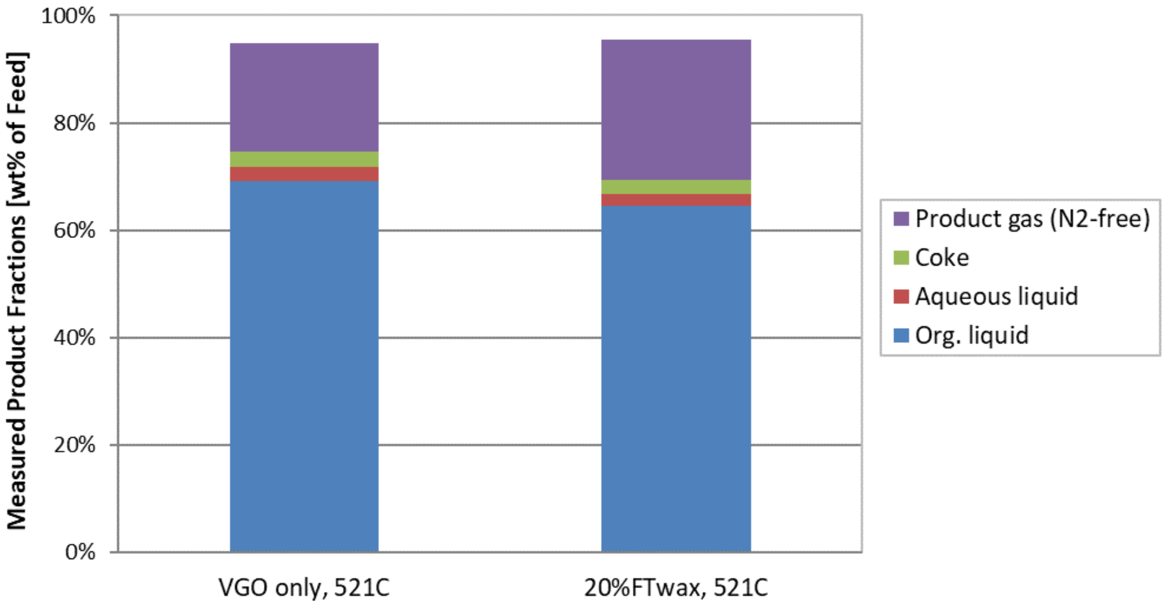
Catalyst Type: E-Cat.

Operating Temperature Range: 521°C

Operating Pressure Range: 2.6 bar

Biocarbon Analysis:

- Liquid product
- Gas bag from oxidized coke
- Catalyst after stripper

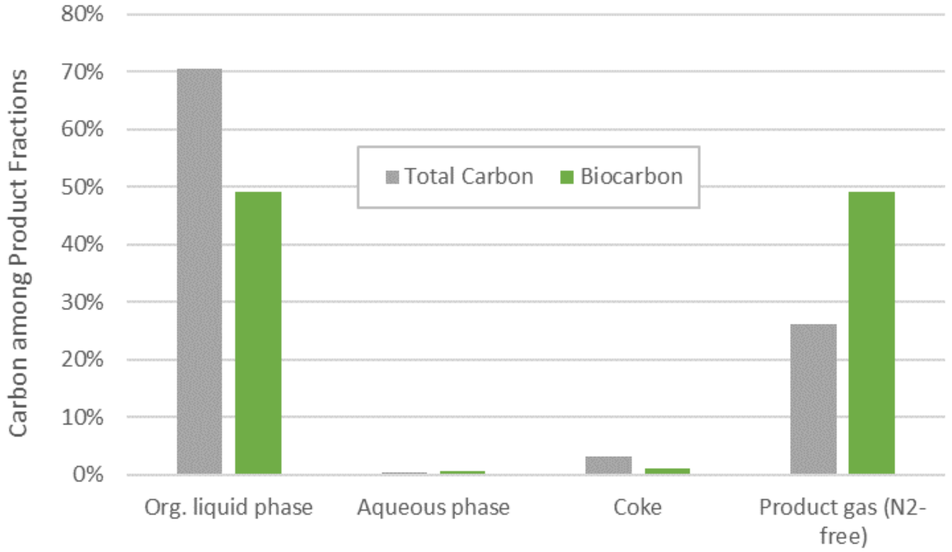


Results

Lower liquid production with co-processing of FT wax

Lower coke formation

- Gas bags showed 5.2% biogenic carbon (versus 16.3% in feed)
- Catalyst sample was too small to detect bio carbon



Co-process FT Wax in ACE Reactor

Advanced Cracking Evaluation Reactor – Kayser Technology

Co-processing of 40 wt% FT wax with 60% VGO

Temperature: 530°C

Submitted for Biocarbon Analysis:

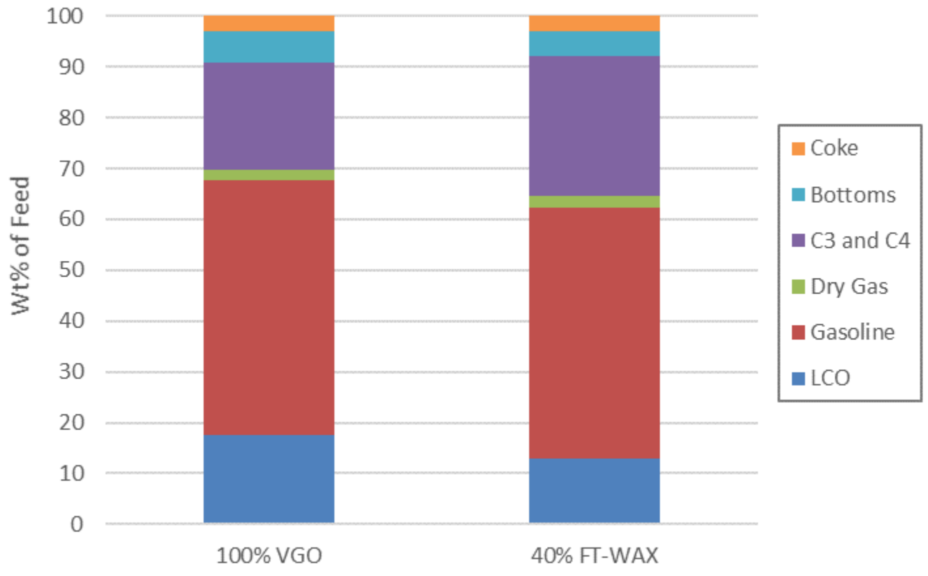
- Liquids
- Gas bags from coke oxidation
- Gas bags from product gas oxidation
  - Mix air with product gas (Lambda 4)
  - Flow mixture over CuO (600°C)
  - Methane remaining at below 0.01 mole%

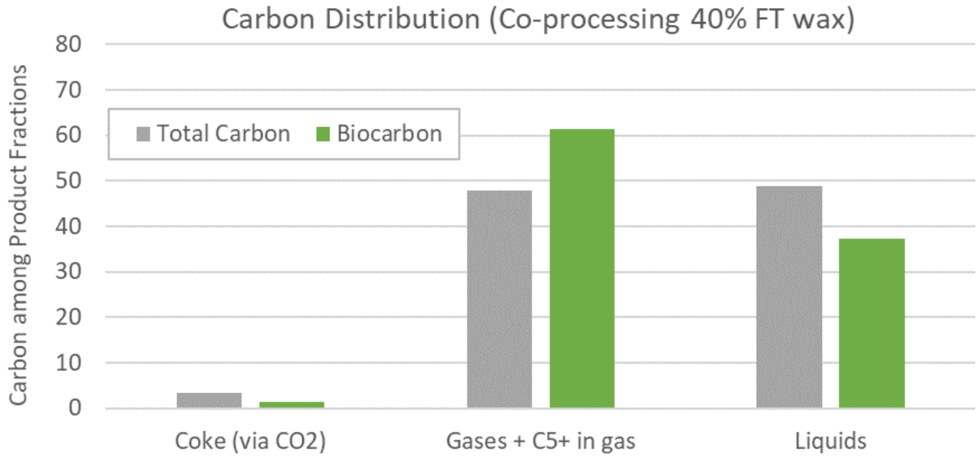
Results

Lower diesel yields

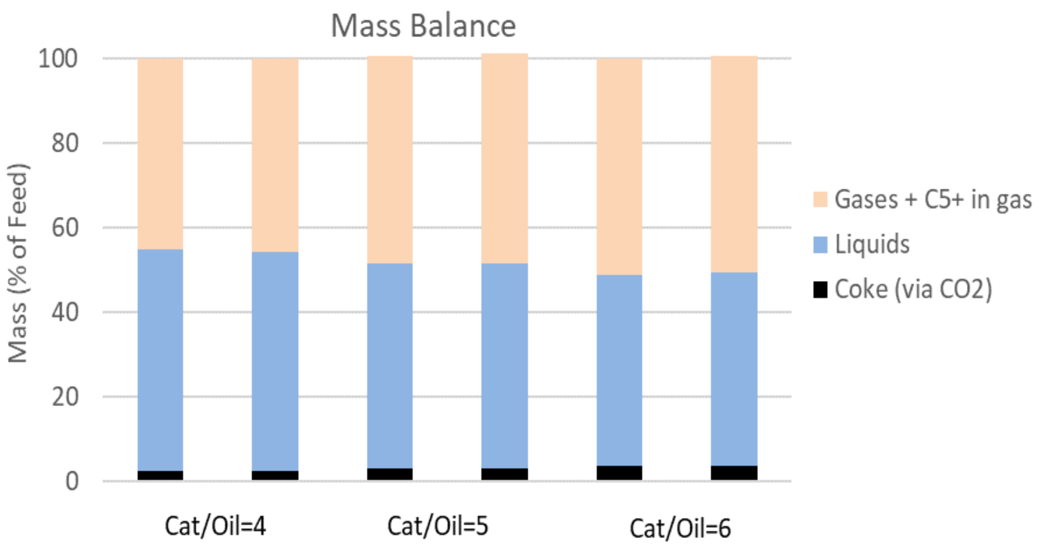
Higher LPG yields (especially C_3 and C_4 olefins)

All product fractions confirmed by biocarbon analysis

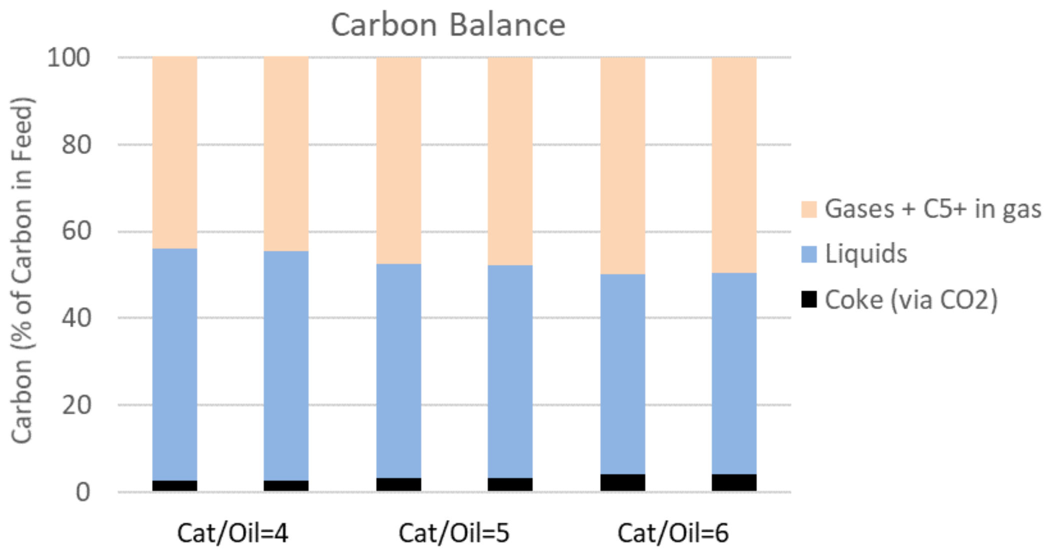


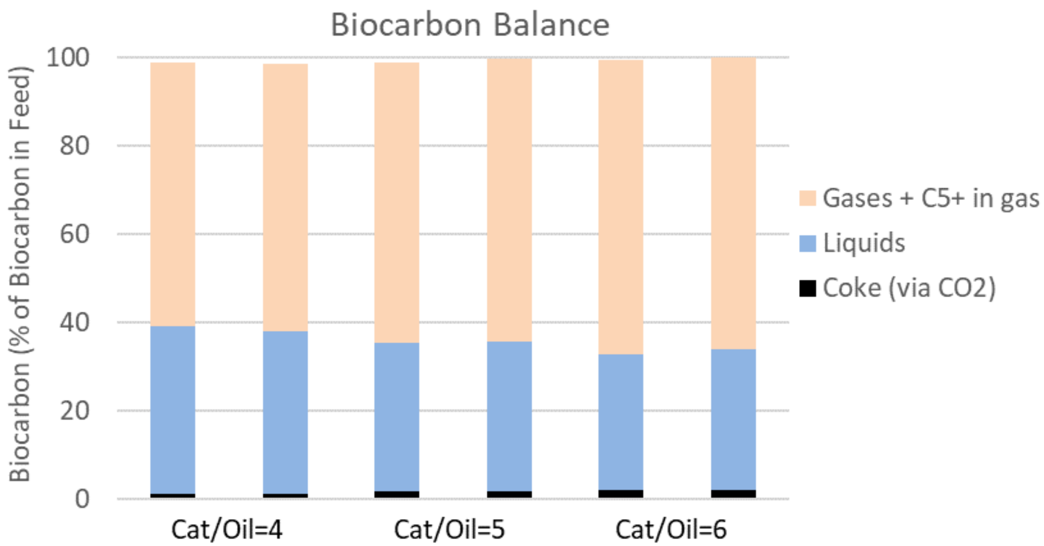


ACE Reactor Results



- Experiments performed for three cat/oil ratios
- Experiments performed in duplicates
- Good mass, carbon, and biocarbon balances
- Biocarbon preferentially flows to gases





Summary

- AMS ^{14}C measurement generally provides good information for biocarbon balance.
- Some difficulties are observed for small biocarbon (<3%) or small carbon percentages (coke).
- ^{14}C measurement can confirm differences in liquid yields.
- On E-Cat, both CFP Oil and FT waxes cracked more easily than VGO and led to reduced liquid yields.
- Some fractions from distillation of products from co-processing CFP Oil received more biocarbon than others.

Thank You

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