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# Bio-Carbon Accounting for Bio-Oil Co-Processing: $^{14}C$ and $^{13}C/^{12}C$

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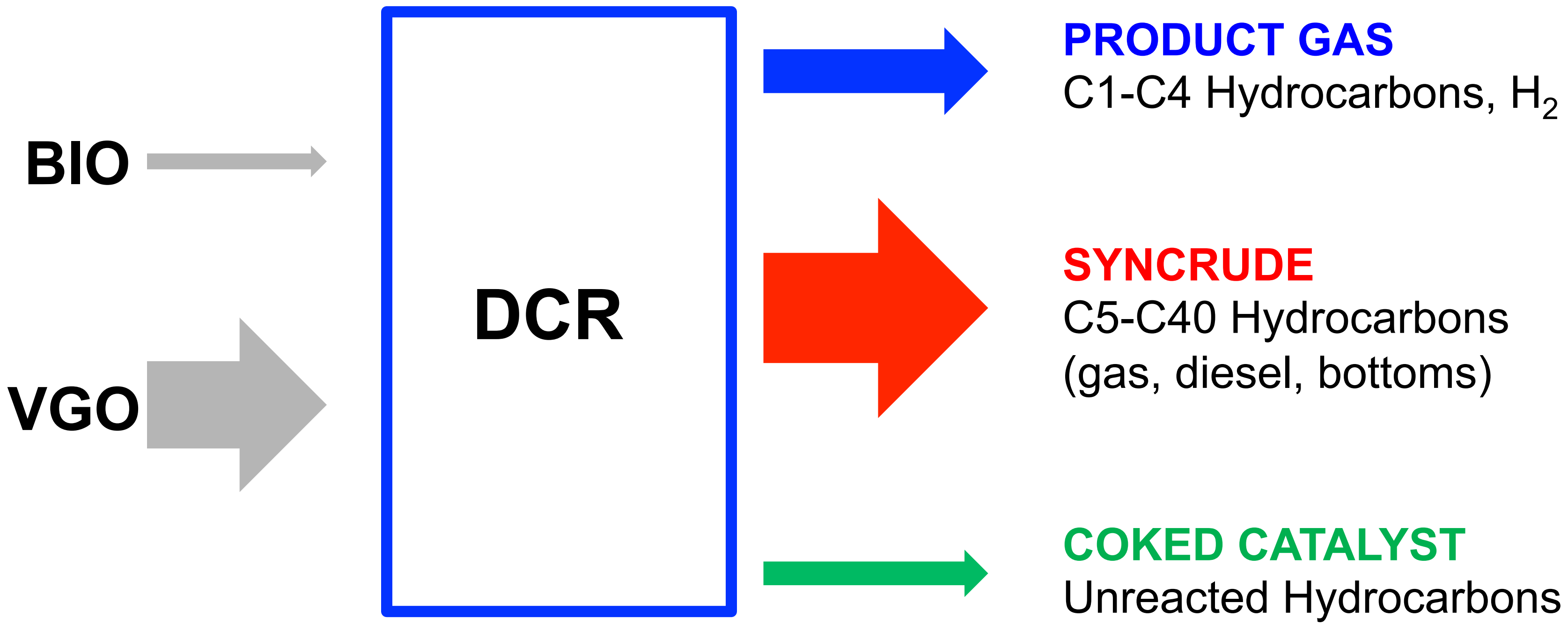
# Carbon Accounting




- TRACK BIOGENIC C THROUGH PROCESSING USING $^{14}C$
- TEST UTILITY OF STABLE C ISOTOPES TO TRACE RENEWABLE C

# Carbon Accounting by Radiocarbon, $^{14}C$

**$^{14}C$ (radioactive; $t_{1/2}$ = 5730 y)**

Standard test to identify modern biogenic C in mixed fuels (e.g., ASTM-D6866-12) using accelerator mass spectrometry.

Biofuel — Source of modern C, measured as percent Modern Carbon, pMC
Because of bomb-carbon in atmosphere, pMC bio-oil >100
(105 pMC in 2012, 102 pMC in 2016; more variable for tree-based feedstock)

Fossil fuel — Contains no modern C

Calculating mass balance to determine proportion of modern C in FCC products (PG=product gas, SYN=syncrude, COKE=uncombusted carbon)

$$\mathrm{pMC}feed = fPG * \mathrm{pMC}PG + fSYN * \mathrm{pMC}SYN + fCOKE * \mathrm{pMC}COKE$$

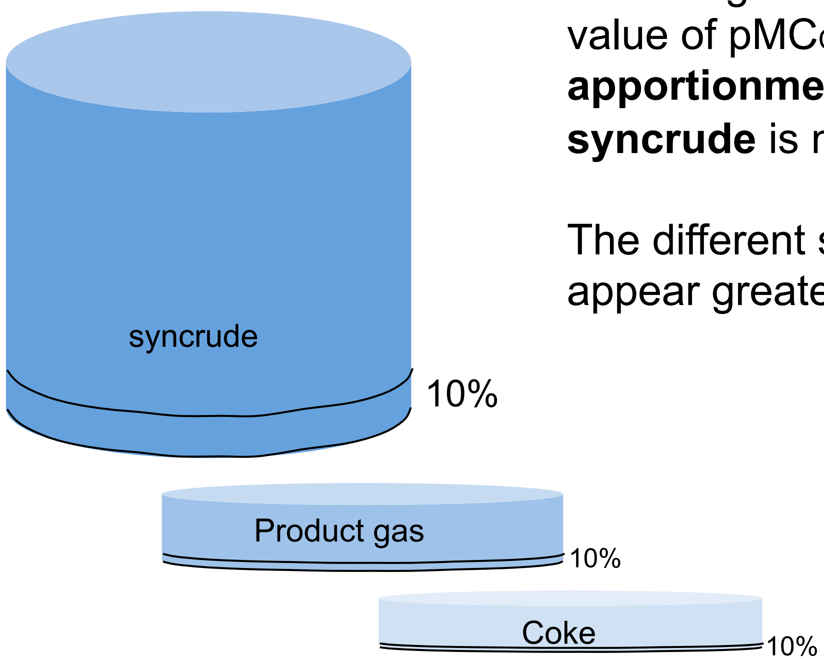
where $f_i$ is

$$\text{wt\% C in i} \big/ \text{wt\% C in feed}$$

and

$$fPG + fSYN + fCOKE = 1$$

# Mass Balance in C Accounting




Mass balance accounts for the different sizes of the C pools in syncrude v product gas v coke. Simply put, 10% of a large C pool is much greater than 10% of a small C pool. Thus, the measured value of $pMC_{COKE}$ may be greater than $pMC_{SYN}$ but the **total apportionment of modern carbon atoms from bio-oil to syncrude** is much greater.

The different sizes of the C pool also explain why pMC may appear greater in the products than in the feed.

## $^{14}C$ ANALYSIS OF FEEDSTOCKS AND FCC CO-PRODUCED PRODUCTS

| Expt | DCR ID | Bio-oil description | Product | pMC in pure bio-oil | Wt% bio-oil in FCC feed | pMC in FCC feed | pMC in product | % of feed bio-C in product* |
|---|---|---|---|---|---|---|---|---|
| DCR-1 | 2350 | Raw pine BX001 | SYN | 109.6 | 5 | 3.6 | 2.1 | 33.5 |
| | 2350 | | PG | 109.6 | 5 | 3.6 | 6.1 | 50.2 |
| | 2350 | | COKE | 109.6 | 5 | 3.6 | 6.4 | 16.3 |
| DCR-2 | 2508 | HT204/205 Severe pine | SYN | 115.1 | 10 | 10.9 | 14.9 | 75.0 |
| | 2508 | | PG | 115.1 | 10 | 10.9 | 11.4 | 17.5 |
| | 2508 | | COKE | 115.1 | 10 | 10.9 | 17.9 | 7.5 |
| DCR-3 | 2099 | HT207/208 Mild pine, upper | SYN | 112 | 5 | 4.3 | 7.6 | nd |
| | 2099 | | PG | 112 | 5 | 4.3 | 2.8 | nd |
| | 2099 | | COKE | 112 | 5 | 4.3 | nd | nd |

*Determined by mass balance. DCR-3 did not mass balance. Two-phase oil– many processing challenges during this run may have affected behavior of the feed.

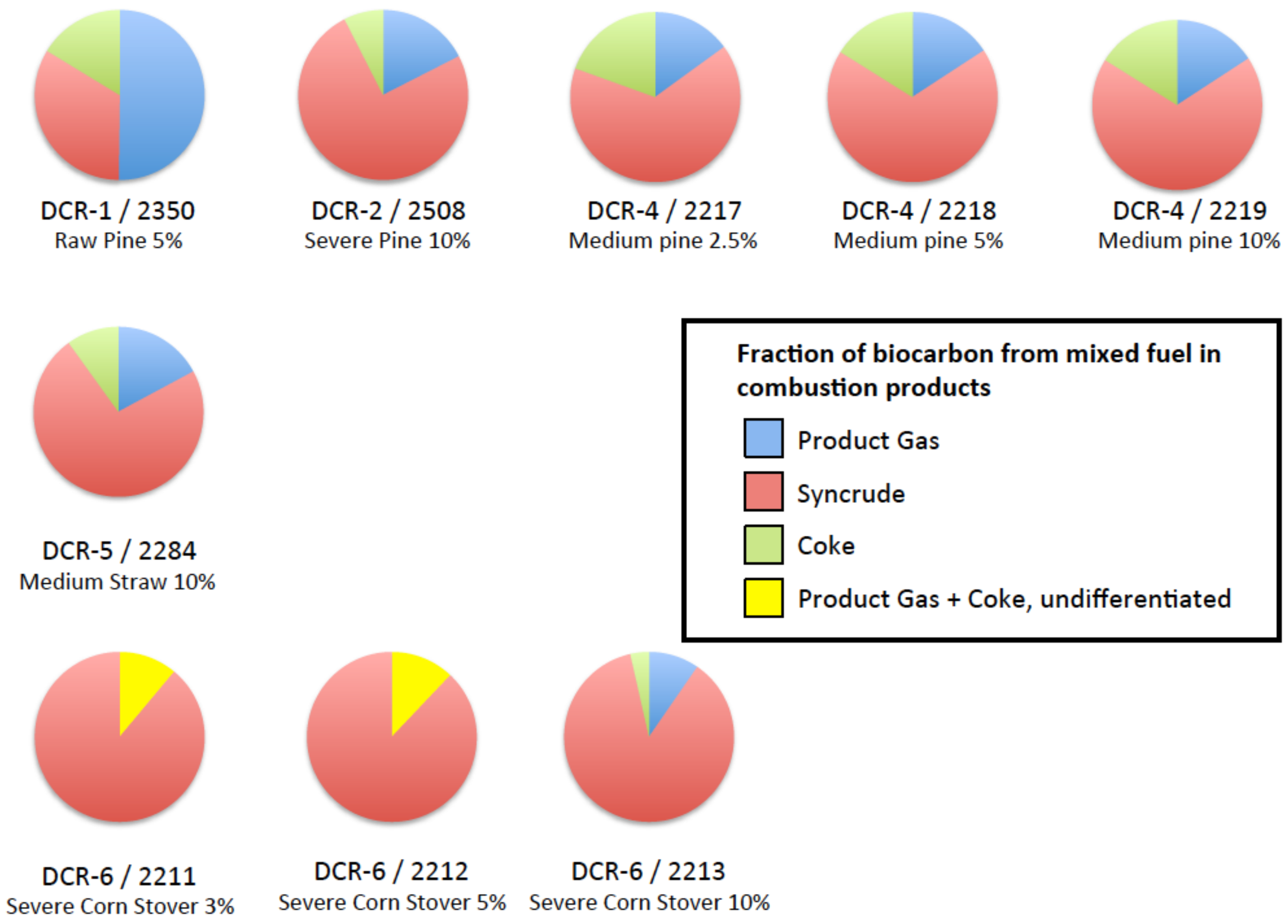
| $^{14}C$ ANALYSIS OF FEEDSTOCKS AND FCC CO-PRODUCED PRODUCTS | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Expt** | **DCR ID** | **Bio-oil description** | **Product** | **pMC in pure bio-oil** | **Wt% bio-oil in FCC feed** | **pMC in FCC feed** | **pMC in product** | **% of feed bio-C in product*** |
| DCR-4 | 2217 | HT215-216 Medium pine | SYN | 112 | 2.5 | 2.54 | 2.5 | 65.5 |
| | 2217 | | PG | 112 | 2.5 | 2.54 | 1.5 | 15.0 |
| | 2217 | | COKE | 112 | 2.5 | 2.54 | 7.5 | 19.5 |
| DCR-4 | 2218 | | SYN | 112 | 5 | 5.1 | 5.2 | 68.1 |
| | 2218 | | PG | 112 | 5 | 5.1 | 3.2 | 15.8 |
| | 2218 | | COKE | 112 | 5 | 5.1 | 12.2 | 16.1 |
| DCR-4 | 2219 | | SYN | 112 | 10 | 10.24 | 10.6 | 71.5 |
| | 2219 | | PG | 112 | 10 | 10.24 | 6.6 | 15.0 |
| | 2219 | | COKE | 112 | 10 | 10.24 | 20.2 | 13.5 |
| DCR-5 | 2284 | HT224-227 Medium straw | SYN | 104 | 10 | 9.66 | 9.8 | 72.9 |
| | 2284 | | PG | 104 | 10 | 9.66 | 7.4 | 17.2 |
| | 2284 | | COKE | 104 | 10 | 9.66 | 17.9 | 9.9 |

*Determined by mass balance. pMC pine-oil based on average of measured bio-oils. pMC straw based on atmospheric value in 2012.

| $^{14}C$ ANALYSIS OF FEEDSTOCKS AND FCC CO-PRODUCED PRODUCTS | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Expt | DCR ID | Bio-oil description | Product | pMC in pure bio-oil | Wt% bio-oil in FCC feed | pMC in FCC feed | pMC in product | % of feed bio-C in product* |
| DCR-6 | 2211 | HT233 Severe corn stover | SYN | 104 | 3 | 3.07 | 3.9 | 88.9 |
| | 2212 | | SYN | 104 | 5 | 5.22 | 6.4 | 87.9 |
| | 2213 | | SYN | 104 | 10 | 10.24 | 11.7 | 86.8 |
| | 2213 | | PG | 104 | 10 | 10.24 | 5.7 | 9.6 |
| | 2213 | | COKE | 104 | 10 | 10.24 | 10.9 | 3.5 |
| | | CountryMark VGO | | 0 | | | | |
| | | F09-0440 VGO | | 0 | | | | |
| | | BX001 raw pine oil | | 109.6 | | | | |
| | | HT205<.88 | | 115.1 | | | | |

*Determined by mass balance. pMC corn stover-oil based on atmospheric value in 2012.

# Apportionment of renewable C between FCC products



# Carbon Accounting Using Radiocarbon

- For all pretreated pine- and straw- biooils, 65-75% of renewable C in feed is apportioned to the syncrude. Gain in renewable C with medium pre-treatment versus severe pre-treatment is nominal, 5-10% increase.
- Renewable C is strongly apportioned to syncrude when using severely treated corn stover in feed, up to 89%.
- The amount of renewable C apportioned to the product gas is 15-20% for pre-treated pine- and straw-oil. For raw pine-oil, product gas yield is ~50%.
- Our results stand in contrast to Fogassy et al. (2012), who reported a strong preference for renewable C to remain unreacted (coke) or to be sorted to product gas. But, our raw pine results are similar to raw pine FCC co-processing reported by Pinho et al. (2015).
- Comparison with these other studies suggests that results are sensitive to

  Degree of bio-oil stabilization

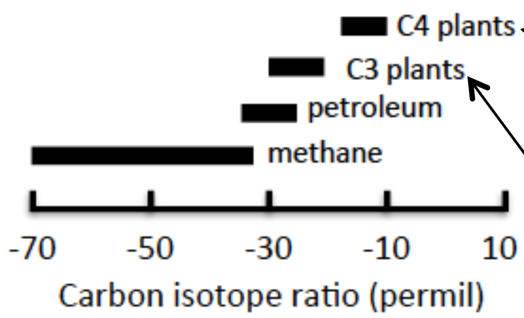
  Scale of FCC reactor unit (Fogassy used a micro-scale reactor– 12mm x 340mm, Pinho used a demonstration–scale unit (~150kg/hr)

# Stable Carbon Isotopes

Because of the overlapping range in the stable C isotope compositions of fossil oils and bio-oils from C3-type feedstocks, stable isotopes have not been widely used to characterize co-produced fuel products. In this study, we test the utility of stable C isotopes to track carbon during FCC co-processing using C3 and C4-based feedstocks.

Stable isotopes $^{13}C/^{12}C$, measured by isotope ratio mass spectrometry, as:

$$\delta^{13}C = \left( \frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1 \right) * 1000$$




bio-oil from corn stover, switchgrass, prairie cord grass, miscanthus, sugarcane

bio-oil from pine, rice, wheat

# Accelerator mass spectrometry versus IRMS

The much greater availability, operator ease, and relatively low cost of the instrument and cost per sample of isotope ratio mass spectrometers (IRMS) compared to accelerator mass spectrometers (AMS) are a principal motivation for this study.

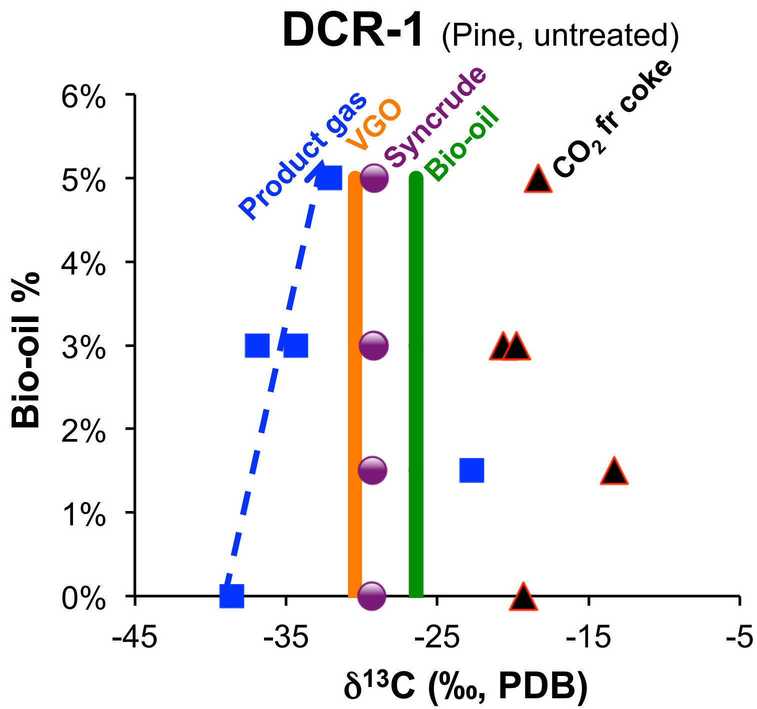
AMS at Queen's University, Belfast

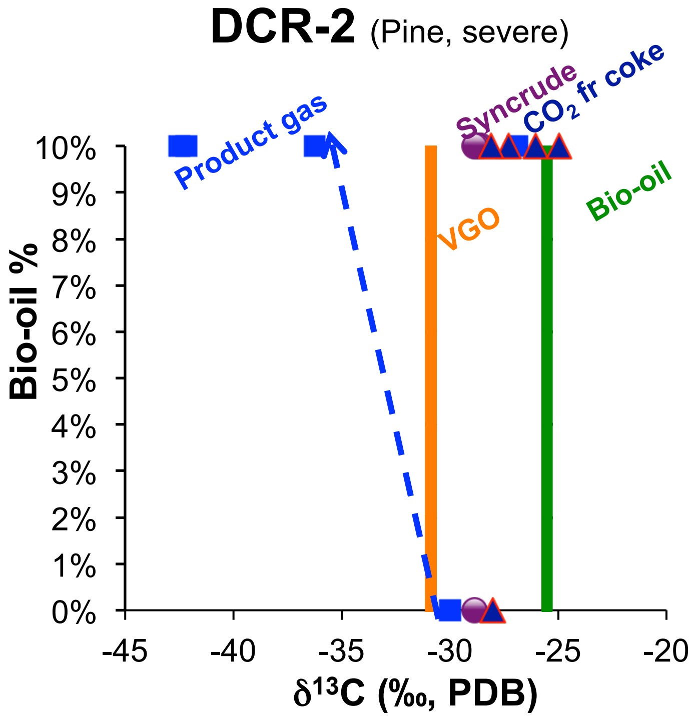
Typical IRMS with peripheral

$^{14}C$ is measured by AMS. This is a highly sensitive method for measuring isotopes present in very small abundances (natural abundance of $^{14}C$ is 0.00000000010% of all C), but establishing and maintaining an AMS costs millions of dollars.

Stable isotope ratios are measured with very high precision on an IRMS. Lab start-up costs are relatively low (~400k). Samples can be run in automated mode (~50 samples per day) and processing samples is much simpler than processing for AMS.

# Carbon Isotope ($\delta^{13}C$) Compositions of Products

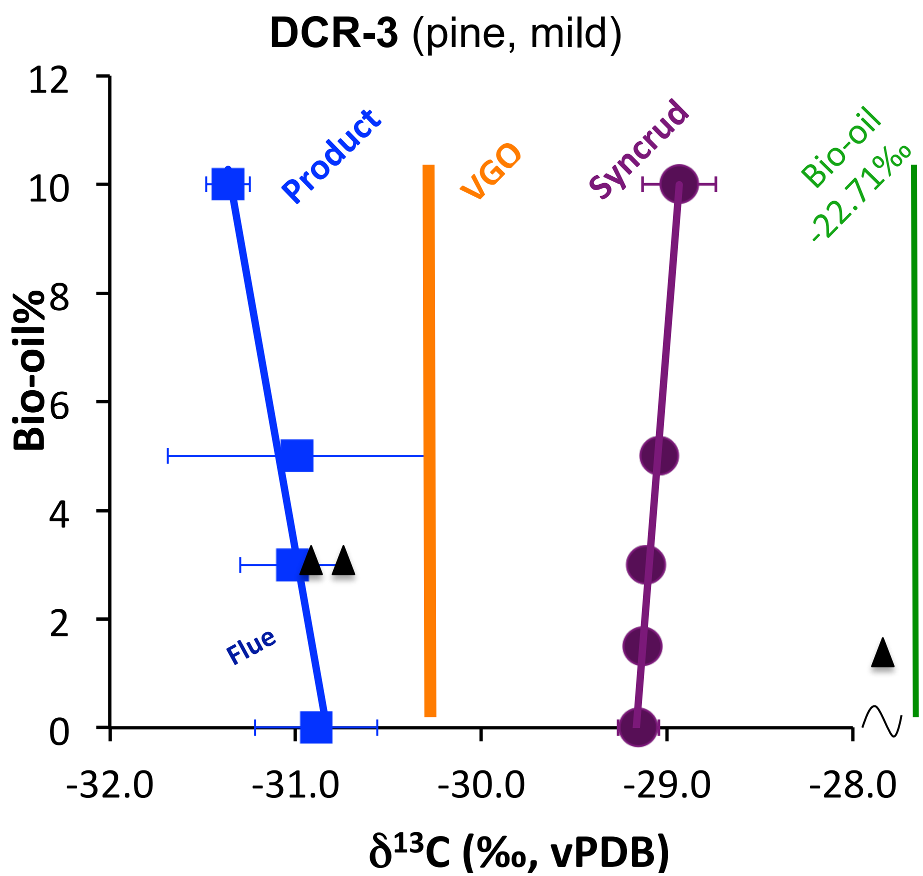



DCR-1: $\delta^{13}C_{PG}$ and bio-oil in feed (+) correlation. Suggests renewable C apportioned to PG. Consistent with radiocarbon, increased C1-C4 yields and decreased syncrude yield.

DCR-2: : $\delta^{13}C_{PG}$ indicates renewable C preferentially apportioned to syncrude. Consistent with radiocarbon data indicating 75% of bio-C enters liquid phase.

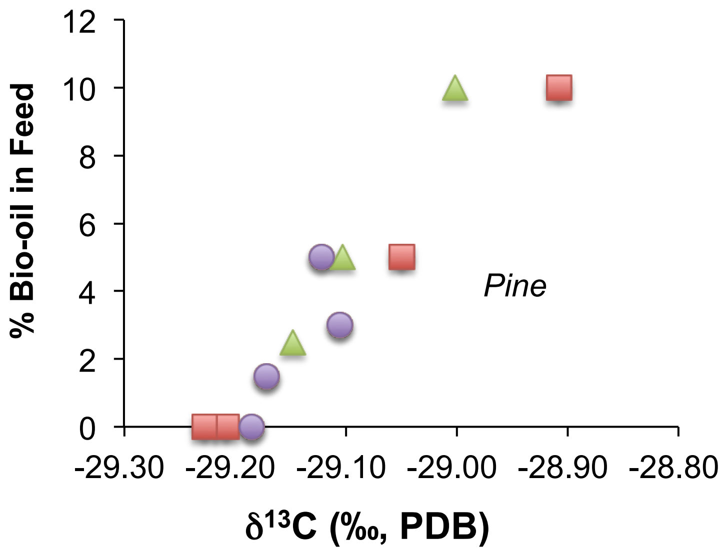
# Carbon Isotope ($\delta^{13}C$) Compositions of Products



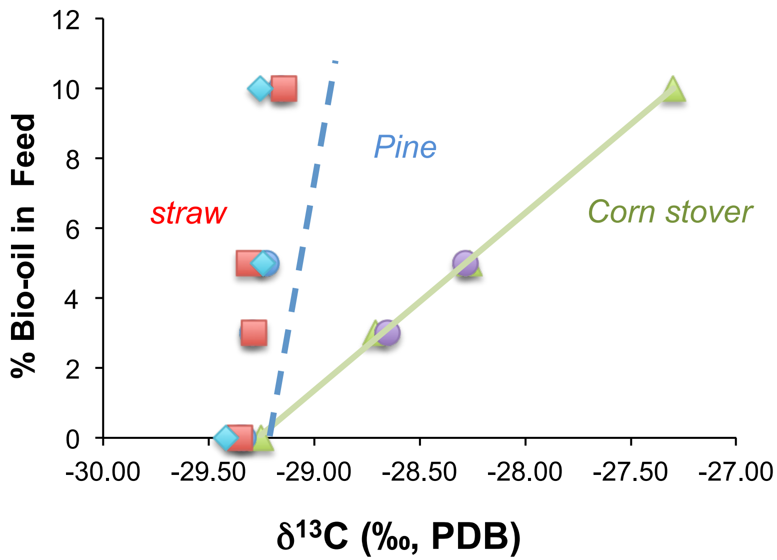

DCR-3 – : $\delta^{13}C_{BIO\text{-}OIL}$ was unusually "heavy" (i.e, relatively enriched in $^{13}C$ ) compared to the other bio-oil endmembers. This suggests isotopic fractionation occurred during phase separation of the oils or during co-processing. Modest, but statistically significant, trends in $\delta^{13}C_{PG}$ and $\delta^{13}C_{SYN}$ suggest that bio-oil carbon is incorporated preferentially into syncrude. This is confirmed by radiocarbon data.

# Carbon Isotope ($\delta^{13}C$) Compositions of Syncrude From Concentration Ladder Experiments

**DCR-4 (pine, medium) syncrude**




**DCR-5 (straw, medium) and**
**DCR-6 (corn stover, severe) syncrude**



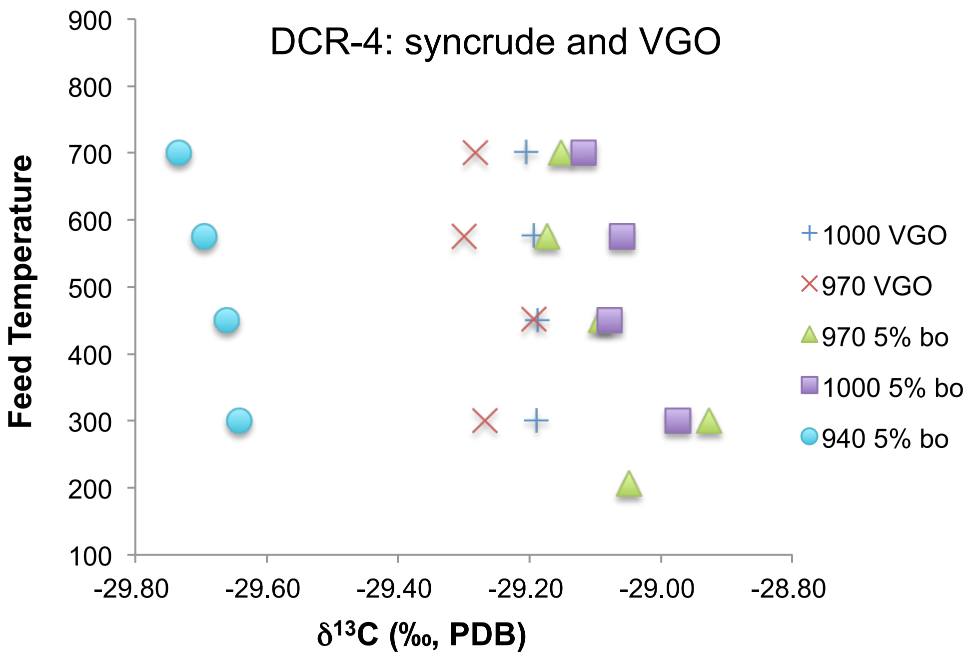

Syncrude trends in concentration ladder experiments for three different feedstock (pine, straw, corn stover); note change in scale of the two diagrams. As the amount of bio-oil in feed increases, the isotopic effect of mixing between endmembers is more apparent. The data are consistent with the observation that renewable C is apportioned to syncrude, confirmed by DCR run yields. The isotopic effect is much more apparent when using bio-oil produced by C4 biomass, but even the smaller changes in DCR4 and 5 are statistically significant.

# Evaluating Significance of Isotopic Differences When End-members are similar in composition

When VGO and bio-oil end-members are close in isotopic composition, it can be challenging to discern trends. Pairs (I-J) of syncrude with statistically significant $\delta^{13}C$ values are shown in blue.

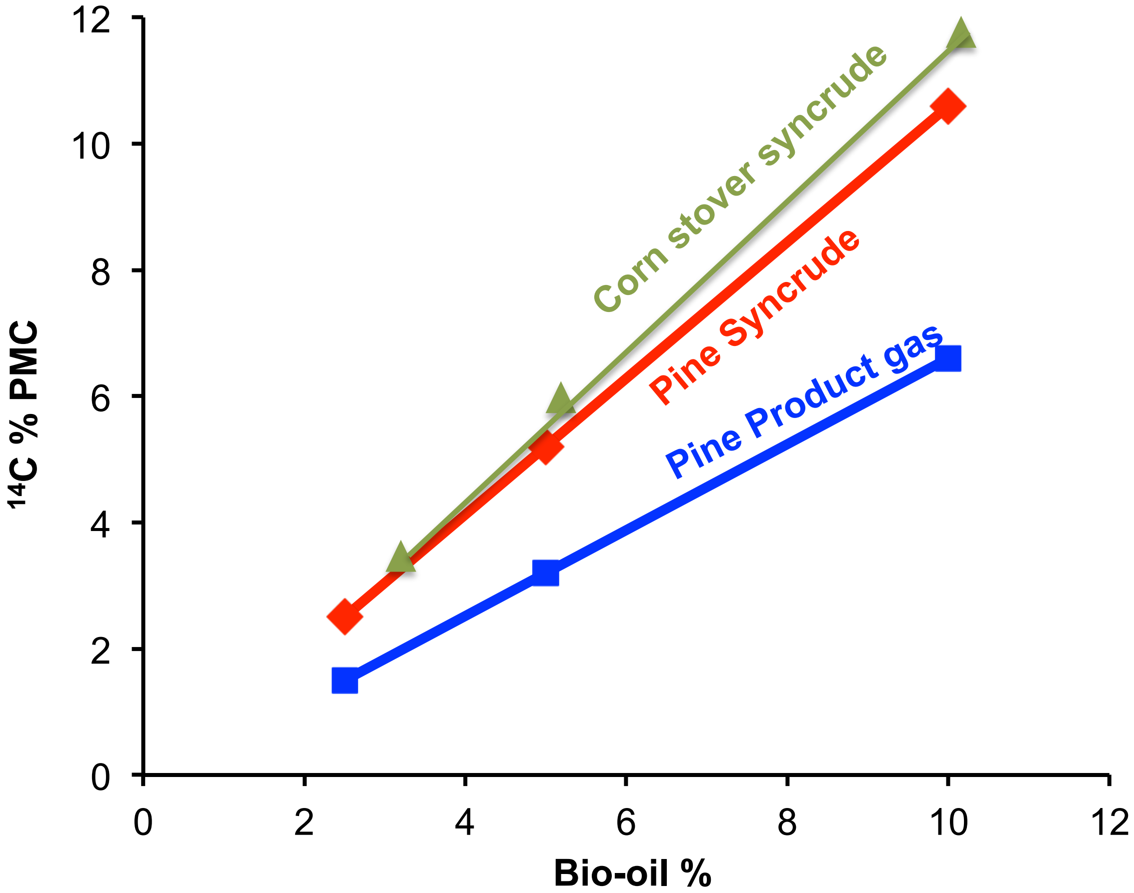
| ALL SAMPLES FROM DCR-4 SYNCRUDE PRODUCTS (I) RUN_ID | (J) RUN_ID | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval Lower Bound | 95% Confidence Interval Upper Bound |
|---|---|---|---|---|---|---|
| **5% bio normal** | base | .17475* | .044876 | .011 | .03618 | .31332 |
| | high temp 5% bio | -.02875 | .044876 | .966 | -.16732 | .10982 |
| | high temp base | .10800 | .044876 | .167 | -.03057 | .24657 |
| | low temp 5% bio | .14650* | .044876 | .036 | .00793 | .28507 |
| **base** | 5% bio normal | -.17475* | .044876 | .011 | -.31332 | -.03618 |
| | high temp 5% bio | -.20350* | .044876 | .003 | -.34207 | -.06493 |
| | high temp base | -.06675 | .044876 | .585 | -.20532 | .07182 |
| | low temp 5% bio | -.02825 | .044876 | .968 | -.16682 | .11032 |
| **high temp 5% bio** | 5% bio normal | .02875 | .044876 | .966 | -.10982 | .16732 |
| | base | .20350* | .044876 | .003 | .06493 | .34207 |
| | high temp base | .13675 | .044876 | .054 | -.00182 | .27532 |
| | low temp 5% bio | .17525* | .044876 | .010 | .03668 | .31382 |
| **high temp base** | 5% bio normal | -.10800 | .044876 | .167 | -.24657 | .03057 |
| | base | .06675 | .044876 | .585 | -.07182 | .20532 |
| | high temp 5% bio | -.13675 | .044876 | .054 | -.27532 | .00182 |
| | low temp 5% bio | .03850 | .044876 | .908 | -.10007 | .17707 |
| **low temp 5% bio** | 5% bio normal | -.14650* | .044876 | .036 | -.28507 | -.00793 |
| | base | .02825 | .044876 | .968 | -.11032 | .16682 |
| | high temp 5% bio | -.17525* | .044876 | .010 | -.31382 | -.03668 |
| | high temp base | -.03850 | .044876 | .908 | -.17707 | .10007 |

# Stable Isotope Variations with Changes in Reactor and Feed T



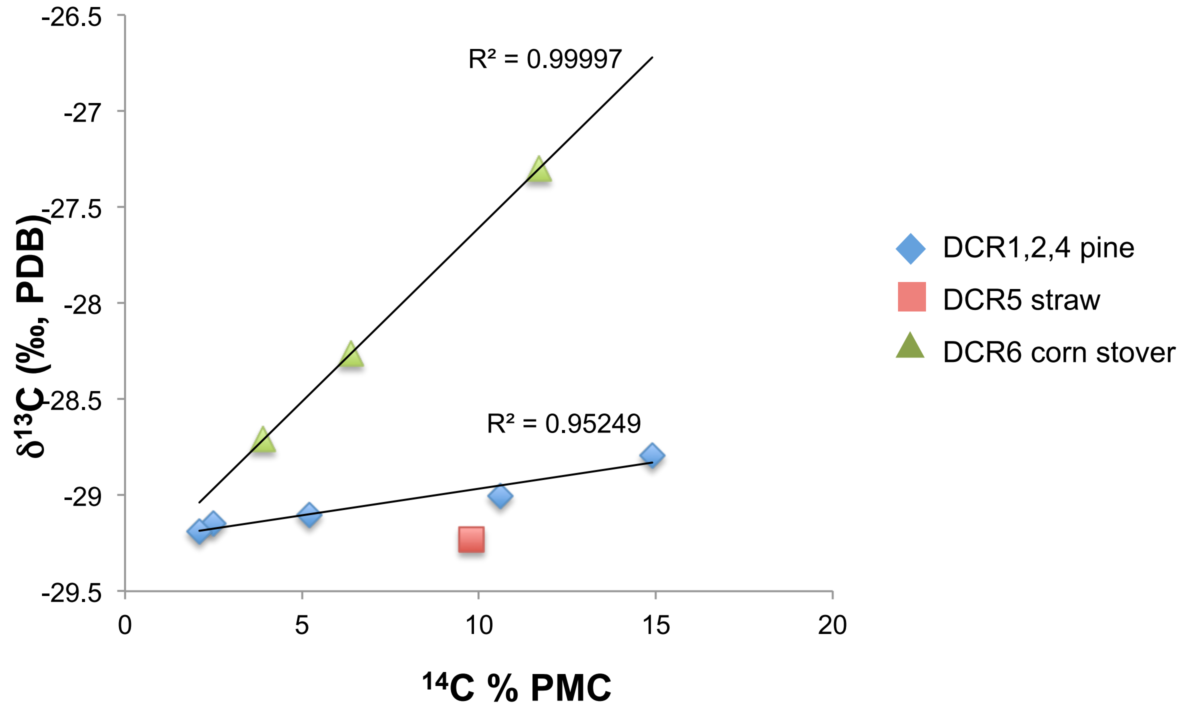

- These DCR runs were made at a given reactor T (940, 970 or 1000°C) and variable feed T (~300, 450, 575 and 700°C) to test how T affects co-processing.
- Stable isotope compositions are consistent with decreased incorporation of renewable C into syncrude as feed T increases.
- Changes in renewable C incorporation are much more sensitive to reactor T. A similar degree of incorporation is seen at 970 and 1000°C, but less is seen at 940°C.
- By comparison, VGO-only processing is affected in a minor way by reactor T, but not by feed T.

# $^{14}C$ results for DCR-4 concentration ladders




The pMC in co-processing products correlate well to the amount of bio-oil in the feed mixture (2.5 – 10 wt%), and reflect the relative apportionment of the renewable carbon to these products (more renewable C to corn stover syncrude than pine syncrude; more renewable C to syncrude relative to product gas).

# Correlation between $^{14}C$ and $\delta^{13}C$




A linear relationship between $\delta^{13}C$ values and $^{14}C$ is expected due to the mass-dependent fractionation of $^{14}C$ and $^{13}C$, relative to $^{12}C$. Details controlling the exact isotope fractionation during photosynthesis (e.g., diffusion, stomatal conductance, enzyme reactions) will cause variations around the expected mass dependent fractionation of 2.0. Greater variation would be expected for C3 (eg, pine) compared to C4 plants (eg, corn), as the results confirm. Once this relationship is established, for a given bio-oil source, it could be used as a proxy for $^{14}C$ measurements.

# Carbon Accounting Using Stable Isotopes

Because of the overlapping range in the stable C isotope compositions of fossil oils and bio-oils from C3-type feedstocks, it is widely thought that stable isotopes are not useful to track renewable carbon during co-production. In contrast, our study demonstrates the utility of stable isotopes to:

- capture a record of renewable carbon allocation between FCC products of co-processing
- record changes in carbon apportionments due to changes in reactor or feed temperature

Stable isotope trends as a function of percent bio-oil in the feed are more pronounced when the $\delta^{13}C$ of the bio-oil endmember differs greatly from the VGO (i.e., it has a C4 biomass source–corn stover, switch grass, Miscanthus, sugarcane– versus a C3 biomass source–pine, wheat, rice, potato), but trends on the latter case are significant for endmember differences of just a few permil.

The correlation between measured $^{14}C$ and $\delta^{13}C$ may be useful as an alternative to carbon accounting, but the relationship must first be established for different bio-oil sources.