tcbiomass 2022, Denver

Stable Carbon Isotope Approach for Tracking Biogenic Carbon Distribution in Bio-oil/crude Co-processing with VGO

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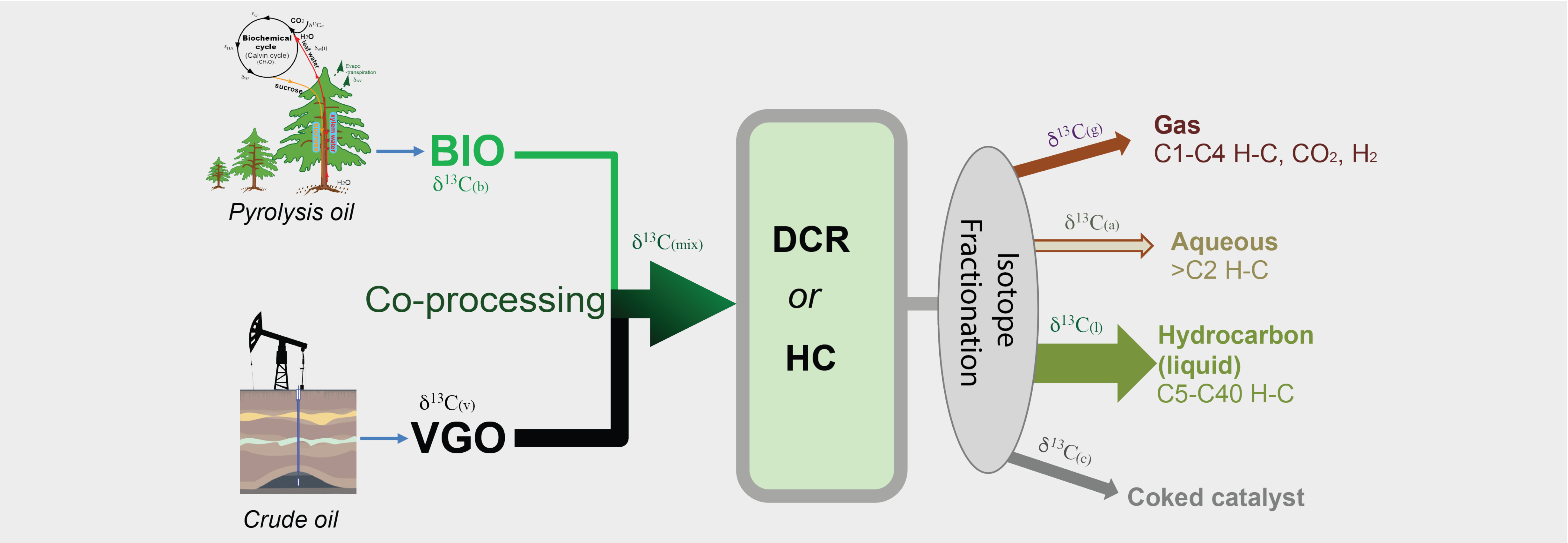
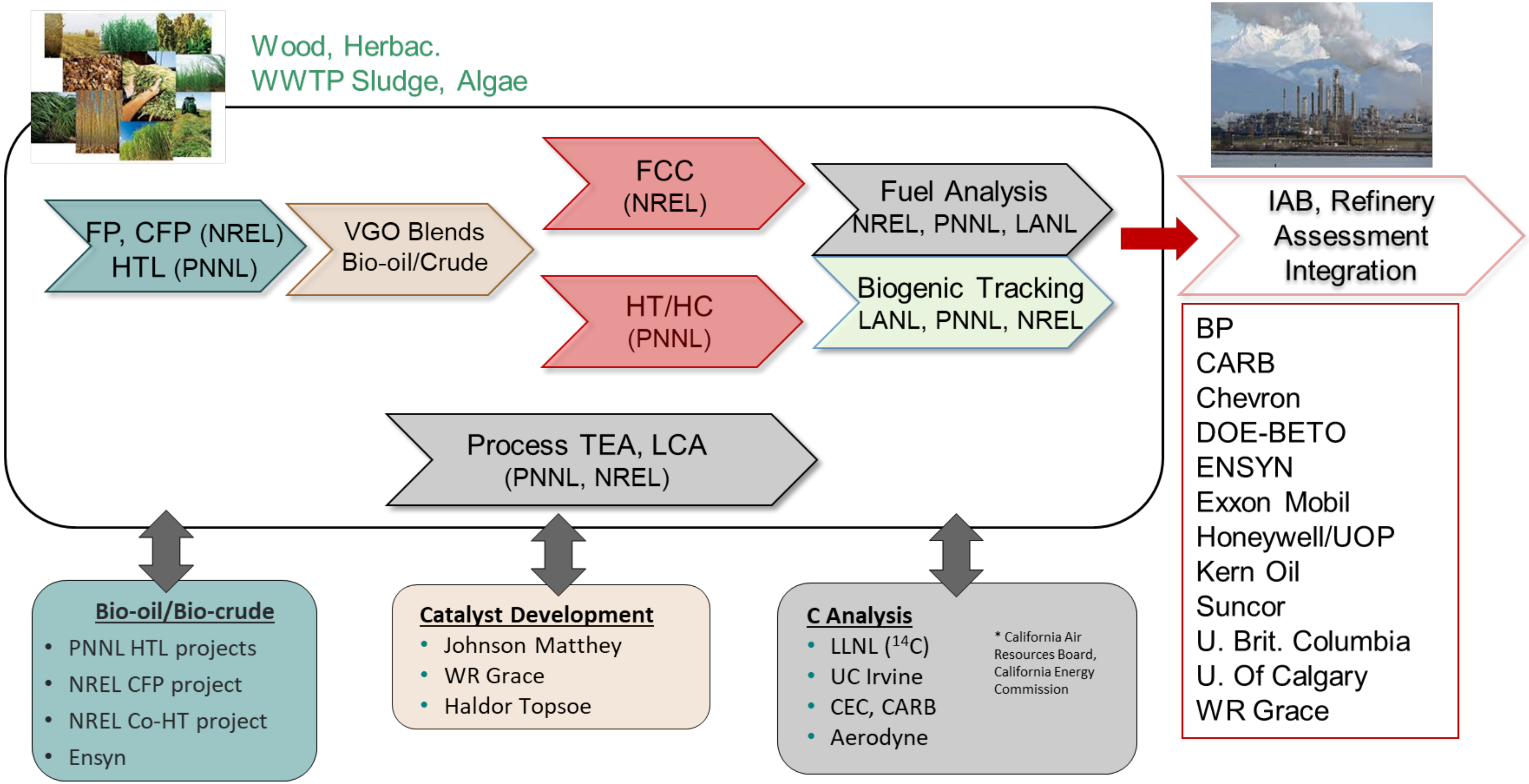


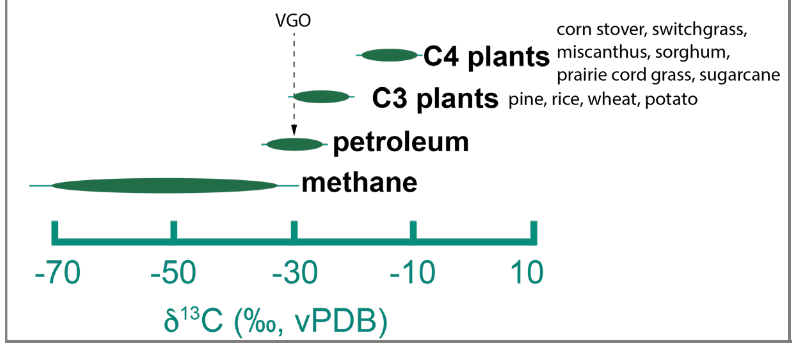
Li & Magrini-Bair et al., Fuel, 2020

A Collaborative Effort: **Bio-oil Co-processing with Refinery Streams**



April 20, 8:50: Co-Processing in Refineries of Thermal Liquefaction Products from Biomass and Waste, *by Huamin Wang, PNNL*

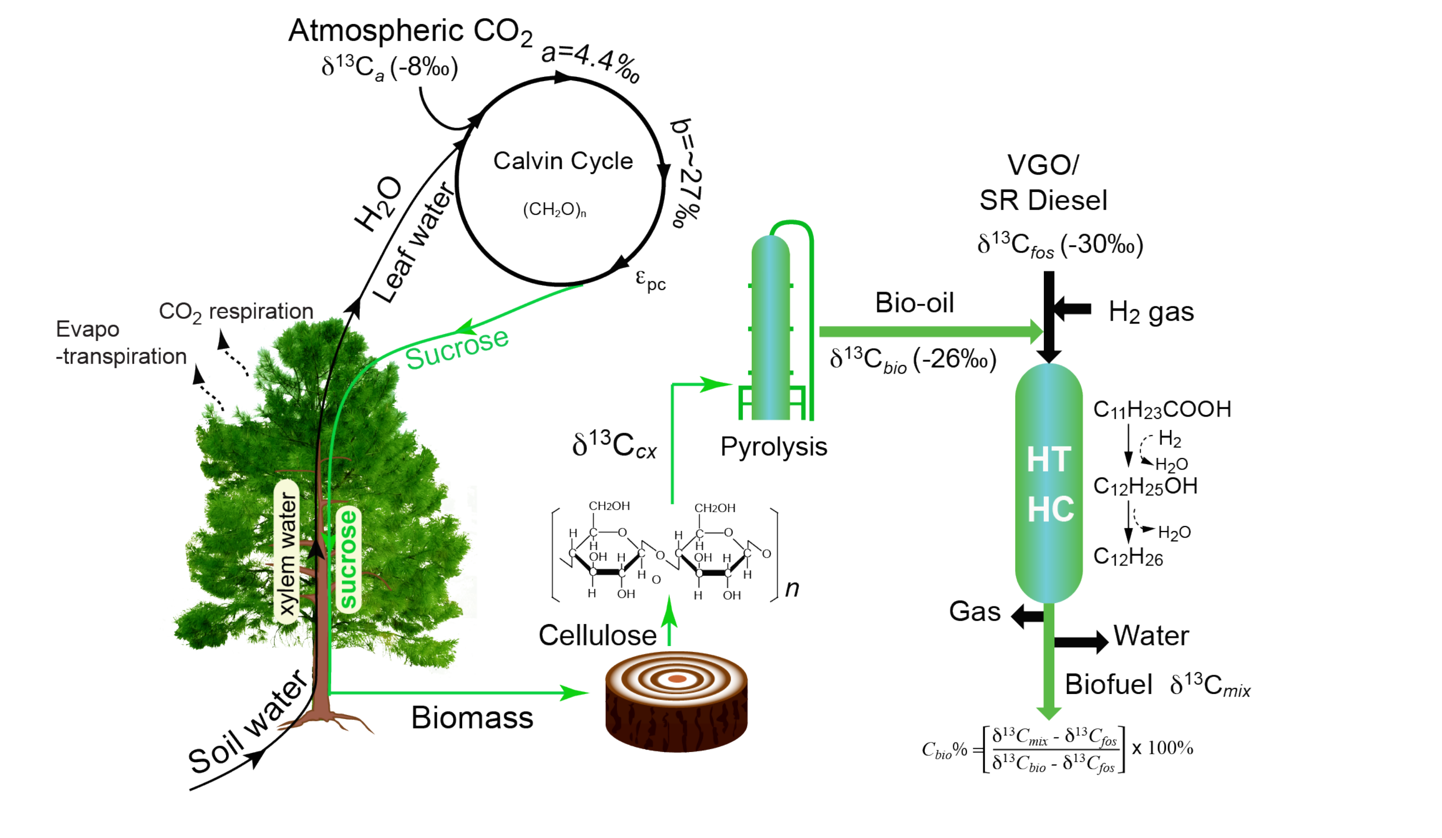
Stable Carbon Isotopes in Plants

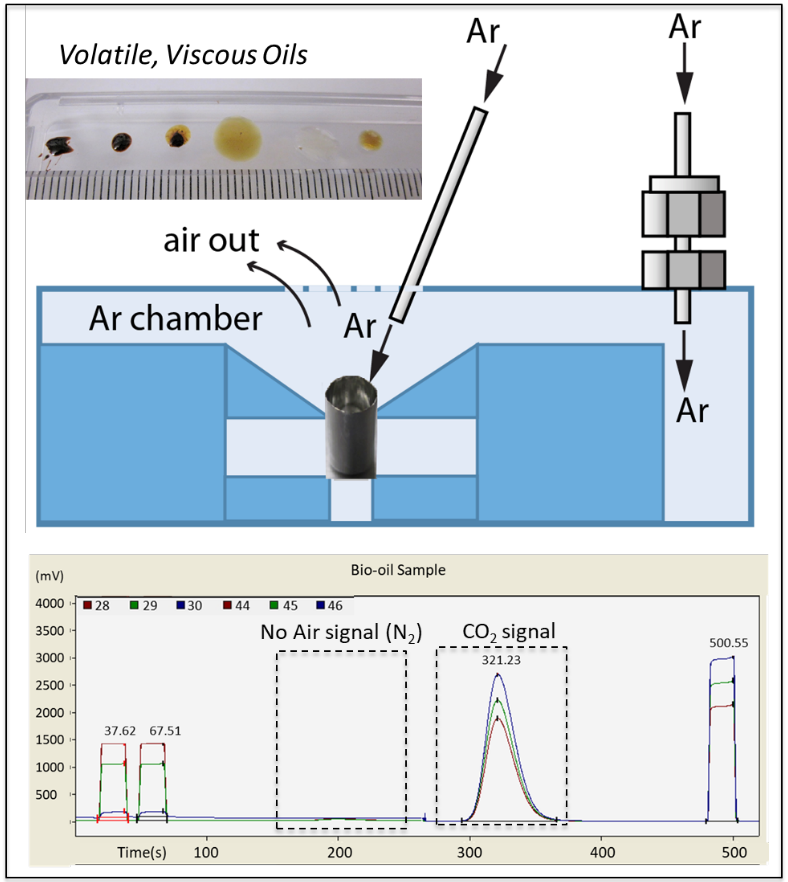


$$\delta^{13}\mathrm{C} = \left(\frac{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{sample}}}{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{standard}}} - 1 \right) \times 1000\ ‰$$

$$\delta^{13}C_c \cong \delta^{13}C_a - b + (b - a)\frac{1.6}{h_s k} + \varepsilon_{pc}$$

- Volatile, viscous samples are difficult to measure due to fractionation.
- High precision is necessary to deconvolute small blending levels
- Sealing in tin capsules under argon eliminates volatilization and prevents atmospheric contamination
- Solid standards can be run concurrently



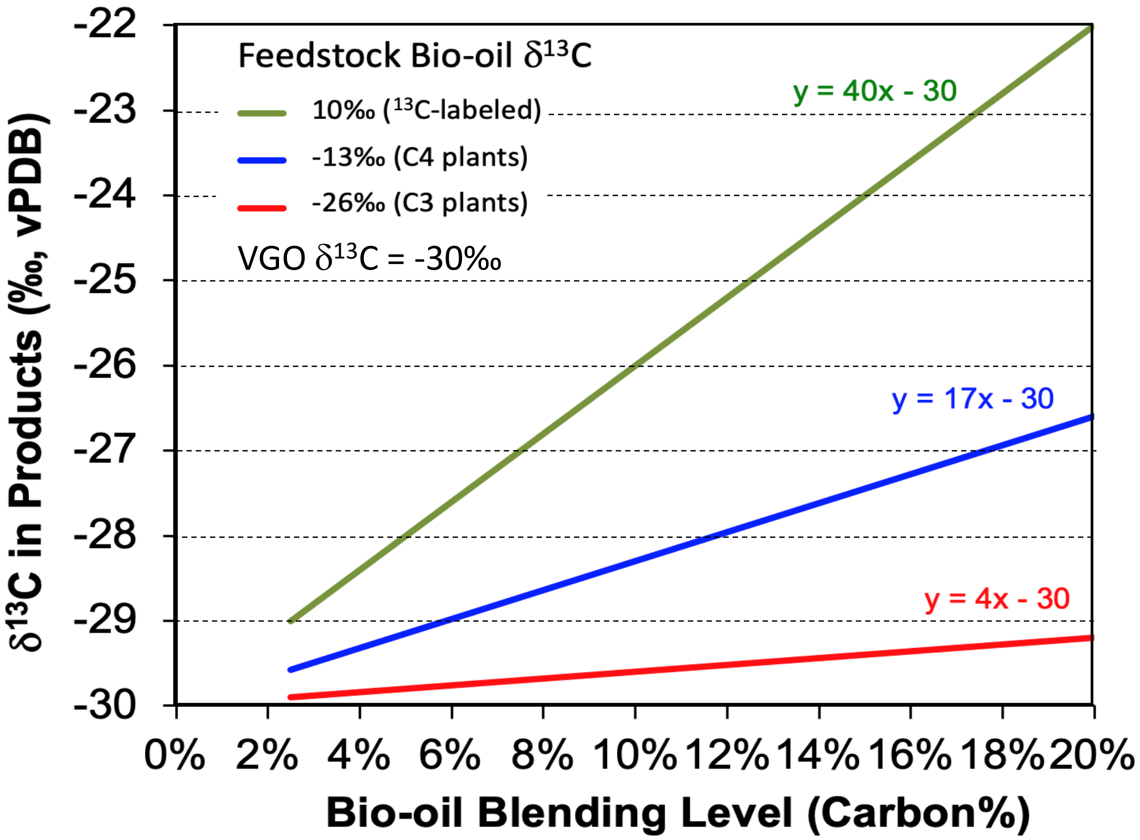


Li & Labbé et al., Chemical Geology, 2011 / Li & Wang et al., ACS Sustainable Chem. Eng., 2020

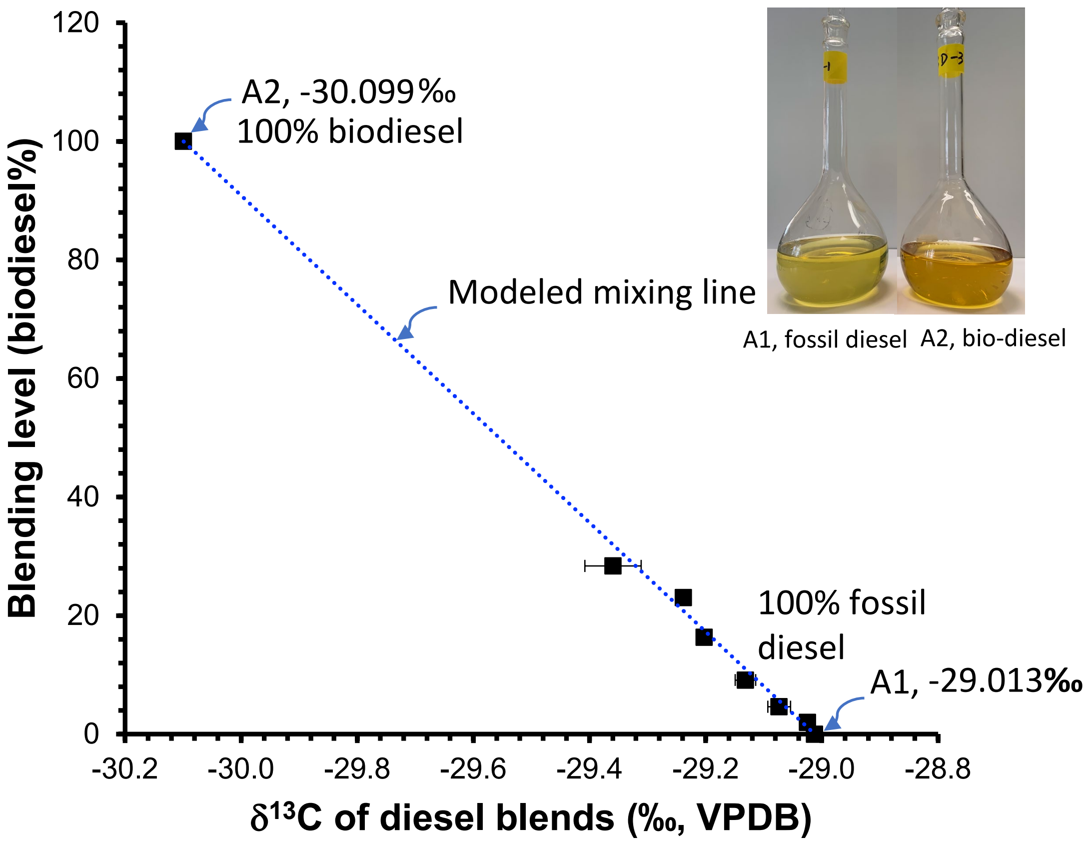
Geeza & Li et al., Energy & Fuels, 2020.

$\delta^{13}C$ Sensitivity for Biogenic C Tracking

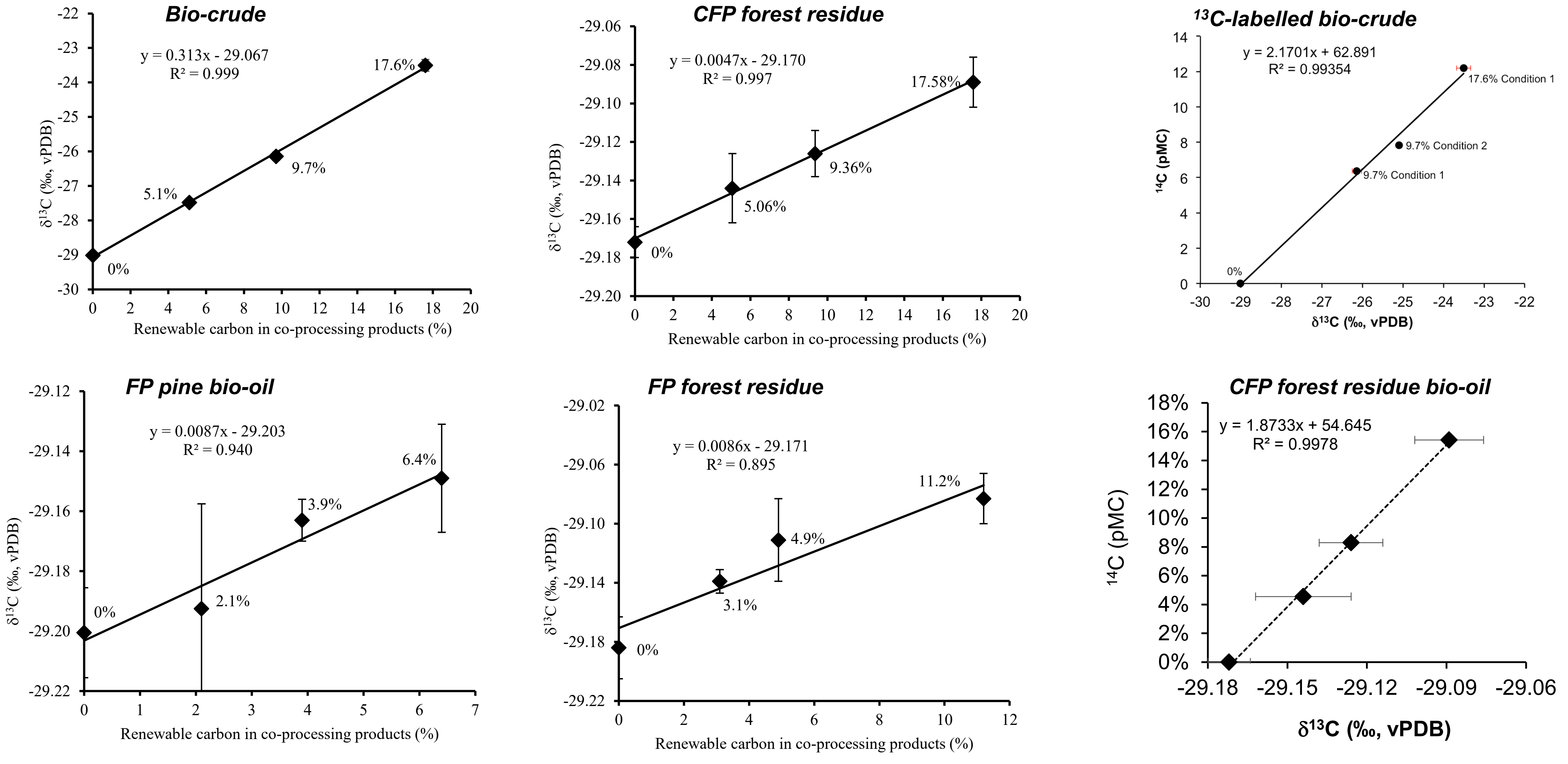
Calculated $\delta^{13}C$ in blends



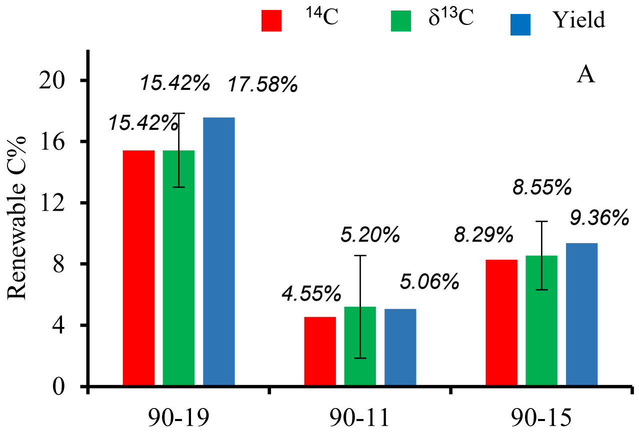
Controlled Experiment



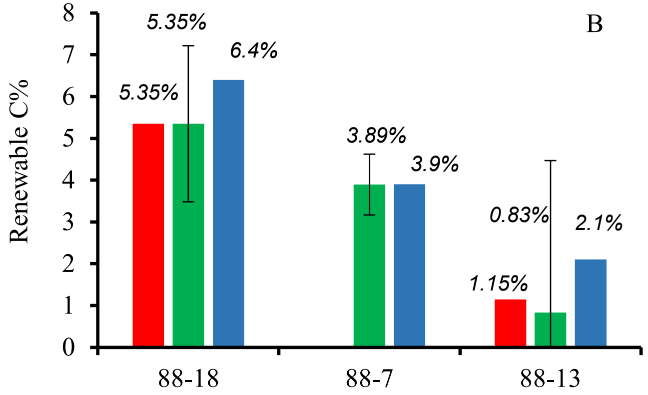
Co-processing Experiment on Blending Level and $\delta^{13}C$



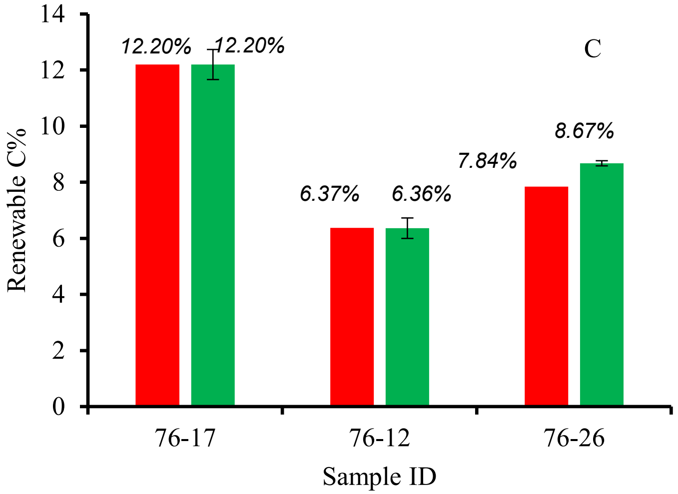
Isotope Fractionation and Quantification of Biogenic C% by $\delta^{13}C$



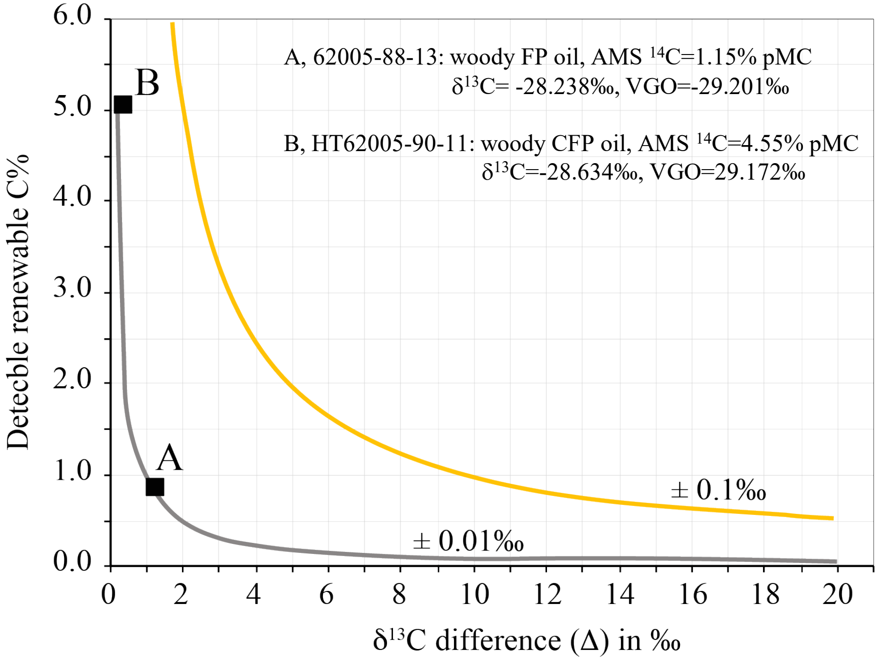
Forest residue bio-oil HC co-processing

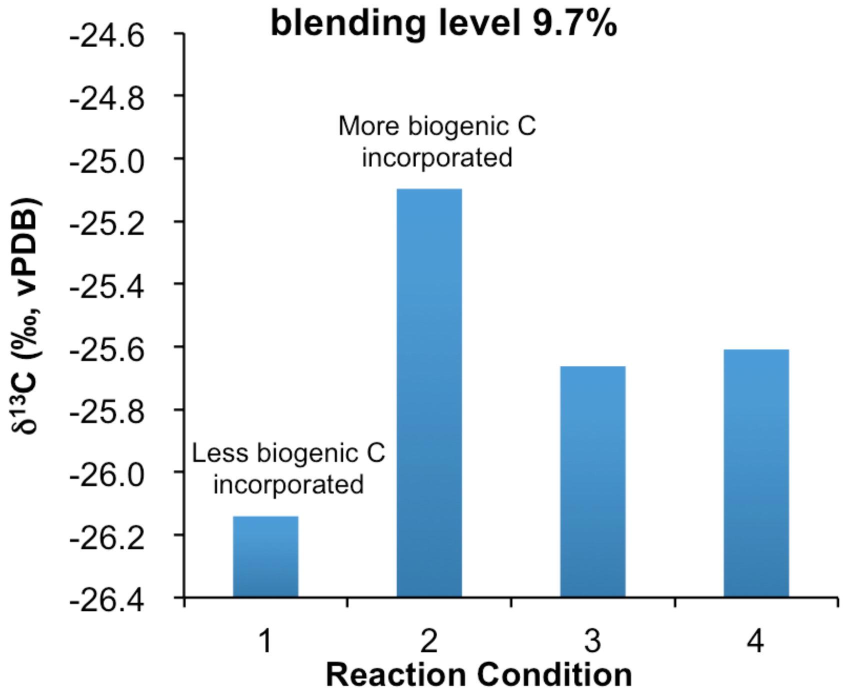


VGO + Woody biomass HC co-processing



^{13}C- labelled bio-crude

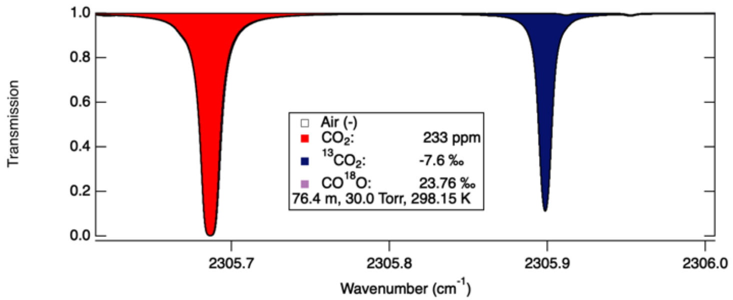




Stable C Isotope Approach for Tracking Biogenic Carbon

- High-precision $\delta^{13}C$ analysis can be a viable way to track biogenic C in bio-oil co-processing products including the feedstock derived from C3 woody biomass and guide the optimization of the co-processing parameters.
- C isotope fractionation factor is not affected by the bio-oil blending levels.
- C4 plant-derived bio-oils possess more distinct $\delta^{13}C$ values than C3 plant-derived bio-oils. It is anticipated that the use of C4 plant-derived feedstock will greatly increase the biogenic C traceability.
- Ongoing work is focused on using an optical approach for potential online detection of $\delta^{13}C$.

Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS)



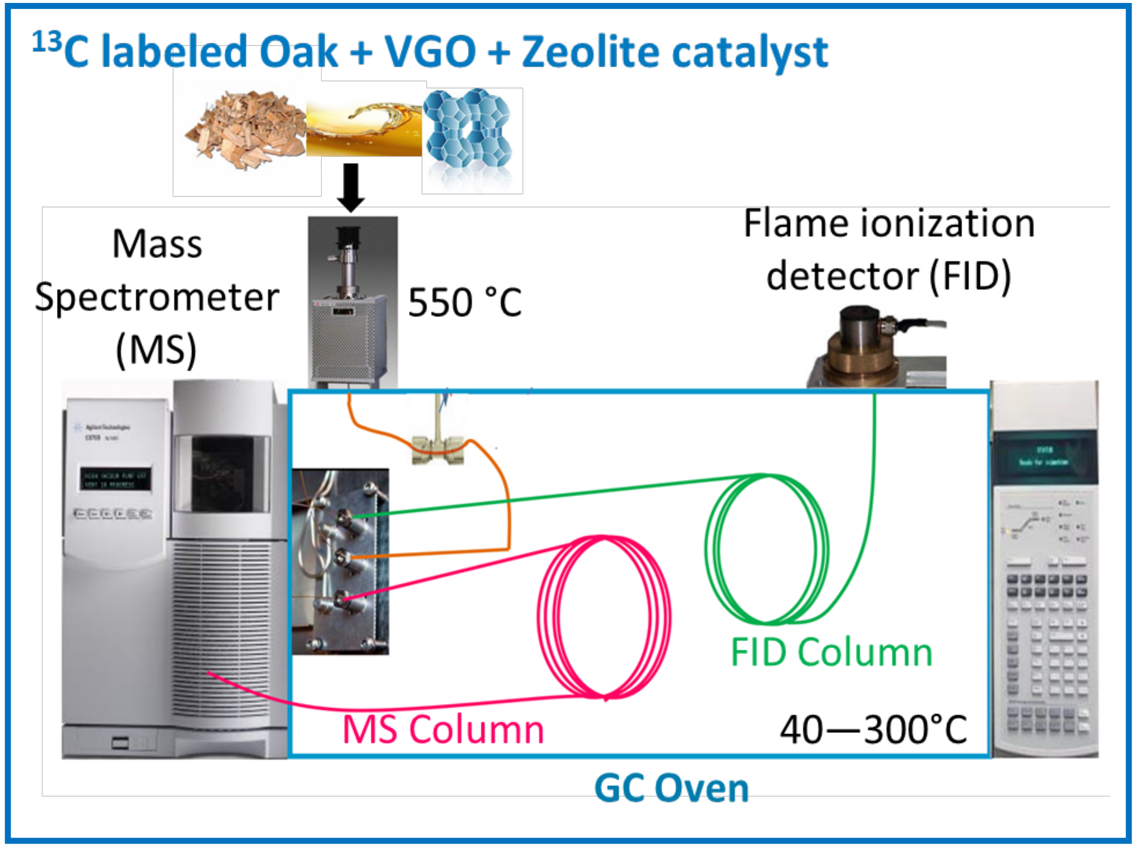
– fast, precise, potential to be online

Assess the feasibility of using optical approaches for online monitoring of $\delta^{13}C$ (‰) in low biogenic carbon transportation fuel components (0 to 10%) by comparing **TILDAS (Aerodyne)** and **IRMS (PNNL)** approaches

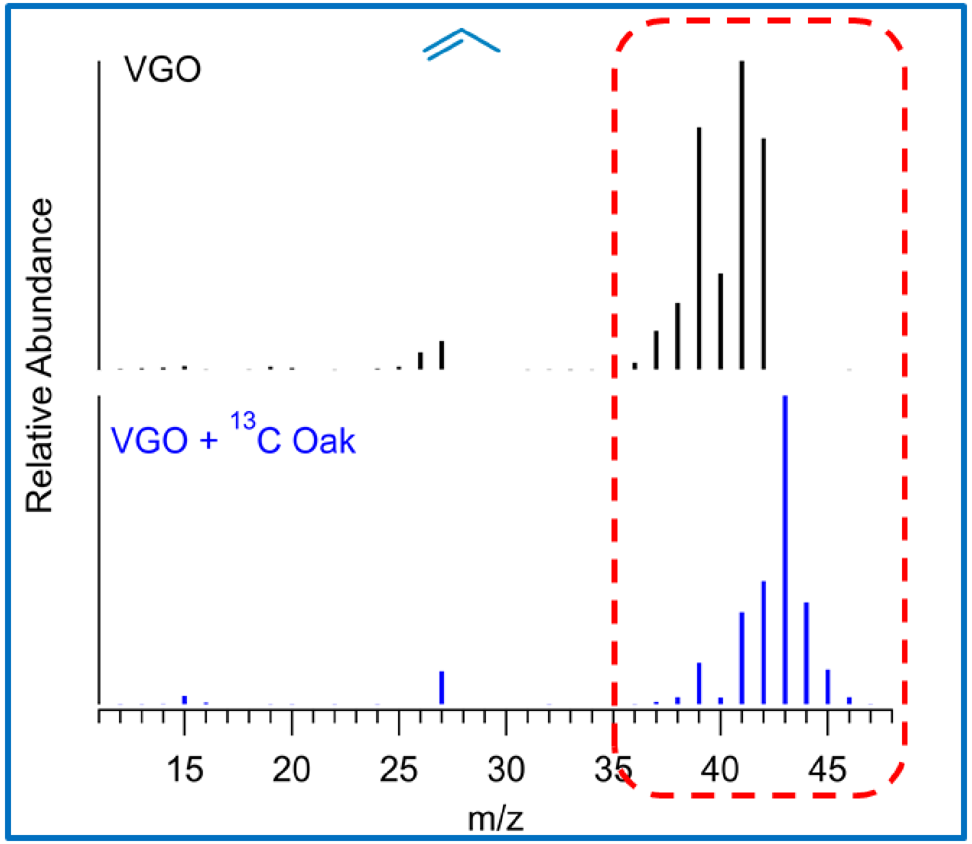
Micropyrolyzer Experiment on ^{13}C-labelled Biomass (Oak)

^{13}C-labelled Oak woody stem (^{13}C>97%): $2,142.83/gram

- Catalysts: E-cat and CP758 (ZSM-5 based catalyst)
- Feedstocks: VGO, Oak, and ^{13}C Oak



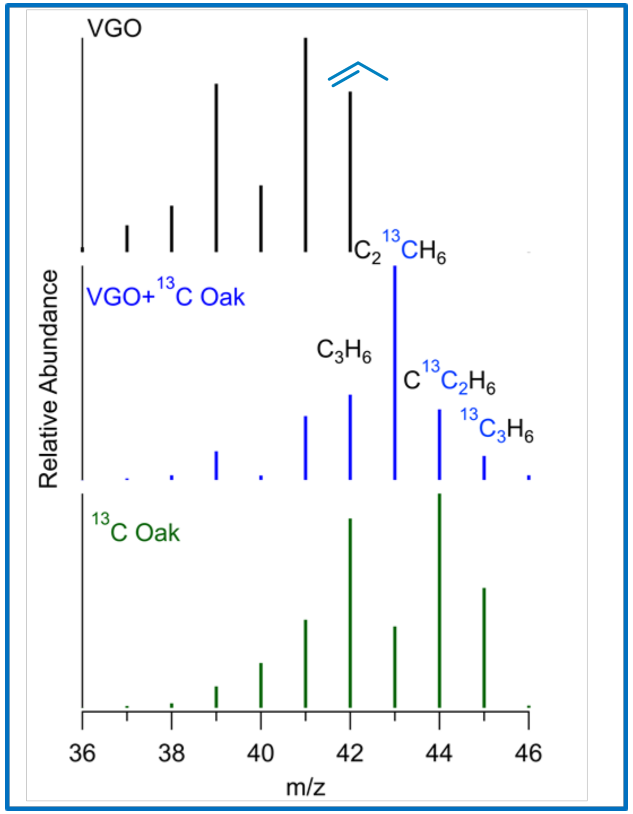
Propylene mass spectrum



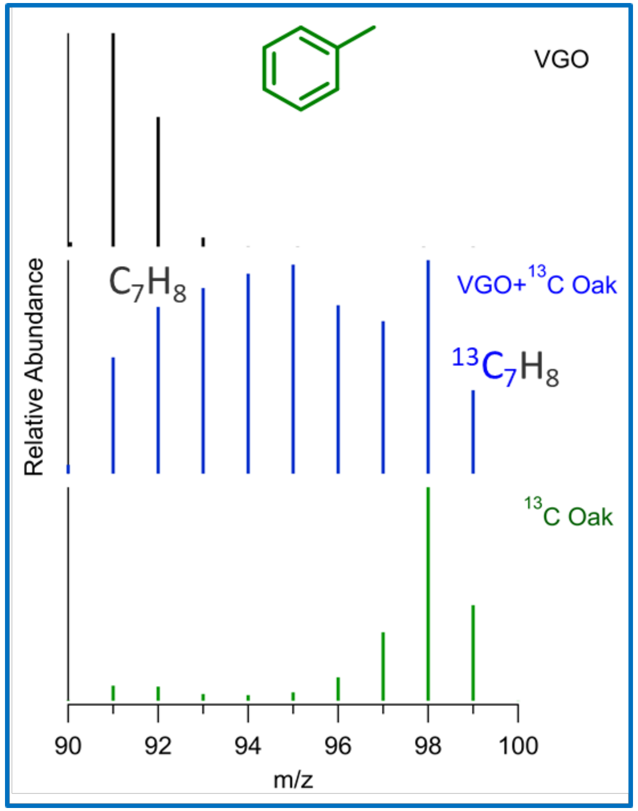
Biogenic C is incorporated into alkenes and single-ring aromatics

(found in LPG and gasoline)

Biogenic ^{13}C from Oak in Propylene



Biogenic ^{13}C from Oak in Toluene



- Biogenic carbon was extensively incorporated into alkenes (LPG) and aromatic hydrocarbons (gasoline and LCO).
- No biogenic carbon was observed in linear-alkanes; ***biogenic carbon was however incorporated into cycloalkanes***.
- All CO_2 (Dry gas) and most of the carbon laydown on the catalyst (coke) was biogenic.
- This work also shows that comprehensive catalyst development targeting both petroleum and biomass derived feeds is required to maximize the incorporation of biogenic carbon in transportation fuels.

- Propylene: We observe peaks for C_3H_6, **$C_2{}^{13}CH_6$, $C^{13}C_2H_6$, $^{13}C_3H_6$** (LPG)
- Toluene: We observe peaks for C_7H_8, **$C_6{}^{13}CH_8$ …$C^{13}C_6H_8$, $^{13}C_7H_8$** (Gasoline)
- These data suggests the so-called “hydrocarbon pool” chemistry

Mukarakate & Orton, et al., ACS Sustainable Chem. Eng. 2020

Recent Peer-reviewed Publications

James Lee, Zheng-Hua Li, Huamin Wang, Andrew E. Plymale and Charles G. Doll, **2022**. Quantification of biogenic carbon in fuel blends through LSC ^{14}C direct measurement and assessment of uncertainty. *Fuel*, JFIE-S-21-09082. https://doi.org/10.1016/j.fuel.2021.122859.

Dell'Orco, Stefano, Earl D. Christensen, Kristiina Iisa, Anne K. Starace, Abhijit Dutta, Michael S. Talmadge, Kimberly A. Magrini, and Calvin Mukarakate. **2021**. Online Biogenic Carbon Analysis Enables Refineries to Reduce Carbon Footprint during Coprocessing Biomass- and Petroleum-Derived Liquids. Analytical Chemistry, 93 (10), 4351-4360. https://doi.gorg/10.1021/acs.analchem.0c04108

Doll, CG, Plymale AE, Cooper A, Kutnyakov I, Swita M, Lemmon T, Mariefel V Olarte, Huamin Wang, **2021**. Determination of low-level biogenic gasoline, jet fuel, and diesel in blends using the direct liquid scintillation counting method for ^{14}C content. Fuel, 291:120084. https://doi.org/10.1016/j.fuel.2020.120084

Li, Zheng-Hua, Huamin Wang, Kimberly Magrini-Bair, James E. Lee, Thomas J. Geeza, Oleg V. Maltsev, Jacob P. Helper. **2020**. Quantitative Determination of Biomass-derived Renewable Carbon in Fuels from Co-processing of Bio-oils in Refinery Using a Stable Carbon Isotopic Approach. *ACS Sustainable Chemistry and Engineering*, **2020**, 8, 47, 17565–17572. https://doi.org/10.1021/acssuschemeng.0c07323

Li, Zheng-Hua, K. Magrini-Bair, H-M Wang, O. V. Maltsev, T. J. Geeza, C. I.Mora, J.E. Lee. **2020**. Tracking Renewable Carbon in Bio-oil/crude Co-processing with VGO Through $^{13}C/^{12}C$ Ratio Analysis. *Fuel*, ISSN: 0016-2361, Vol: 275, Page: 117770. https://doi.org/10.1016/j.fuel.2020.117770

Mukarakate, Calvin , Kellene Orton, Yeonjoon Kim, Stefano Dell'Orco, Carrie A. Farberow, Seonah Kim, Michael J. Watson, Robert M. Baldwin, and Kimberly A. Magrini, **2020**. Isotopic Studies for Tracking Biogenic Carbon during Co-processing of Biomass and Vacuum Gas Oil. ACS Sustainable Chemistry & Engineering 2020 8 (7), 2652-2664. https://doi.org/10.1021/acssuschemeng.9b05762

Geeza, Thomas Jeremy, Zheng-Hua Li, Oleg Vitalivich Maltsev, and James Edward Lee. **2020**. Carbon Isotope Analysis of Co-Processed Biofuels Using a Continuous-Flow Isotope Ratio Mass Spectrometer. *Energy & Fuels*, 34, 9, 11134–11142. https://doi.org/10.1021/acs.energyfuels.0c02114.

More talks about biogenic C tracking by our team….

April 21, 4:10 PM: Quantification of Biogenic Carbon in Fuel Blends through LSC ^{14}C Measurement, by James Lee et al, LANL)