U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

Webinar

Biogenic Carbon Tracking and Measurement in Co-processing of Biogenic Feeds in Petroleum Refineries

September 27th, 2023

Presenters:

Dr. Zhenghua Li, Los Alamos National Laboratory

Dr. Sophie B. Lehmann, Pacific Northwest National Laboratory

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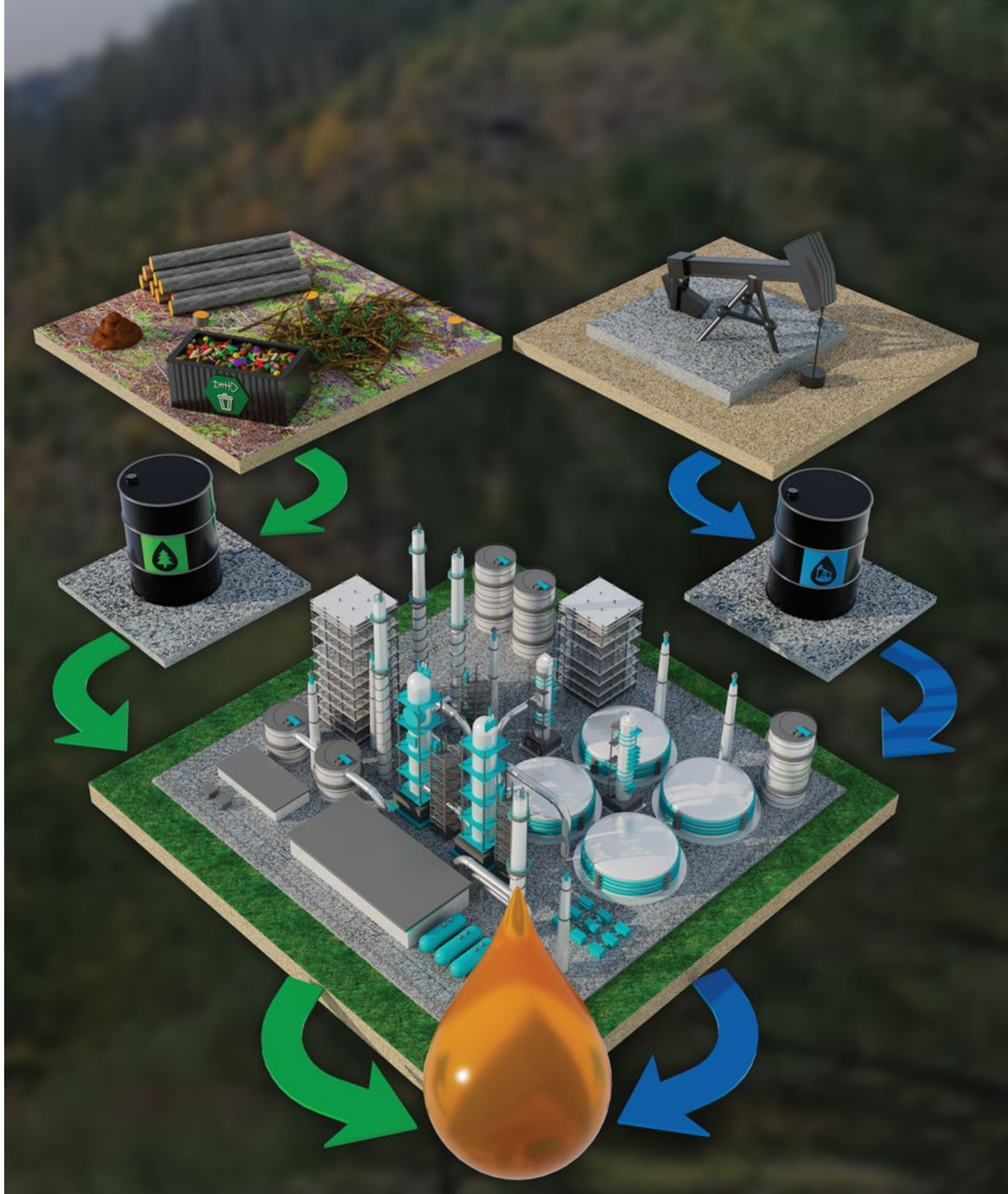
Pacific Northwest NATIONAL LABORATORY



Agenda

This Webinar (9/27/2023)

- Housekeeping
- Overview of BETO
- Biogenic Carbon Tracking and Measurement by LSC ^{14}C and IRMS $\delta^{13}C$ in Co-processing
- Laser Spectroscopy and Stable Carbon Isotopes for Tracking Biocarbon
- Q&A

Last Week's Webinar (9/20/2023)

- Co-processing Fast Pyrolysis Bio-Oils and Hydrothermal Liquefaction Bio-crudes in Fluid Catalytic Cracking and Hydroprocessing in Refineries

→ More GHG reductions, faster!

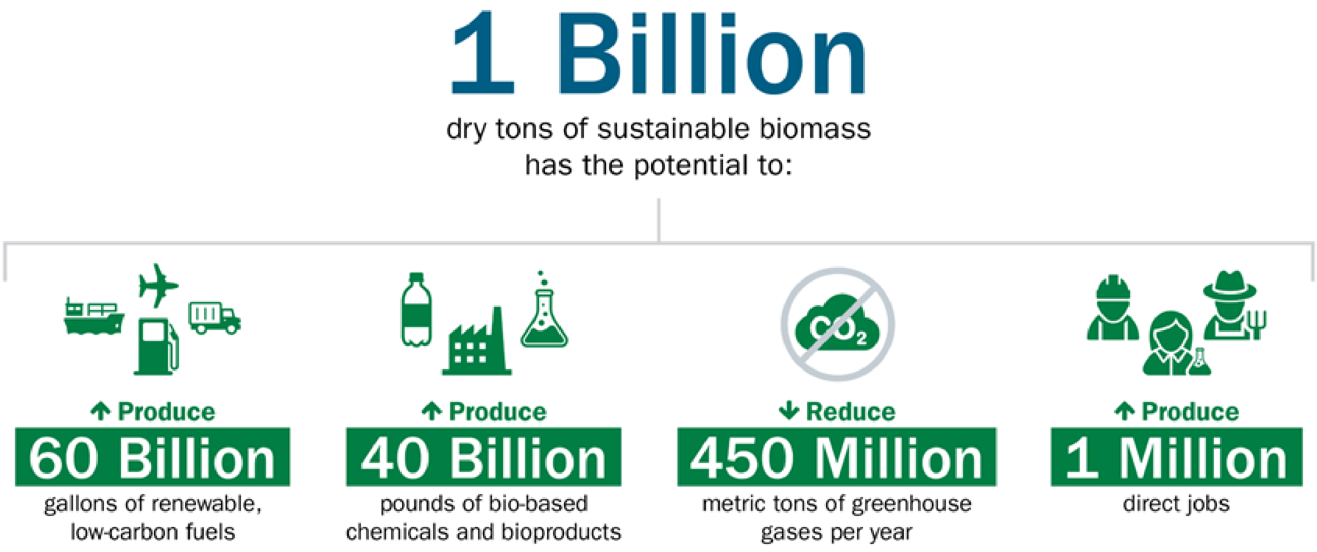
→ Focusing on Sustainable Aviation Fuel (SAF) and other strategic transportation fuels

BETO 2023 Multi-Year Program Plan

Sustainable Aviation Fuel Grand Challenge Roadmap

U.S. National Blueprint for Transportation Decarbonization

→ Unlocking the potential of the full range of renewable carbon resources



Bioenergy Technologies Office Program Areas

Renewable Carbon Resources

Feedstock

Conversion Technologies

Conversion

Systems Development and Integration

Systems

Data, Modeling, and Analysis

Data

- Support 3 billion gallons SAF by 2030
- Support 35 billion gallons SAF by 2050
- Cost-effective SAF and other strategic fuels with at least 70% greenhouse gas reductions
- Decarbonization of chemicals

Today's Presenters

Dr. Zhenghua Li

Senior Scientist

Los Alamos National Laboratory

Dr. Sophie B. Lehmann

Scientist

Pacific Northwest National Laboratory

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Biogenic Carbon Tracking and Measurement by LSC ^{14}C and IRMS $\delta^{13}C$ in Co-processing

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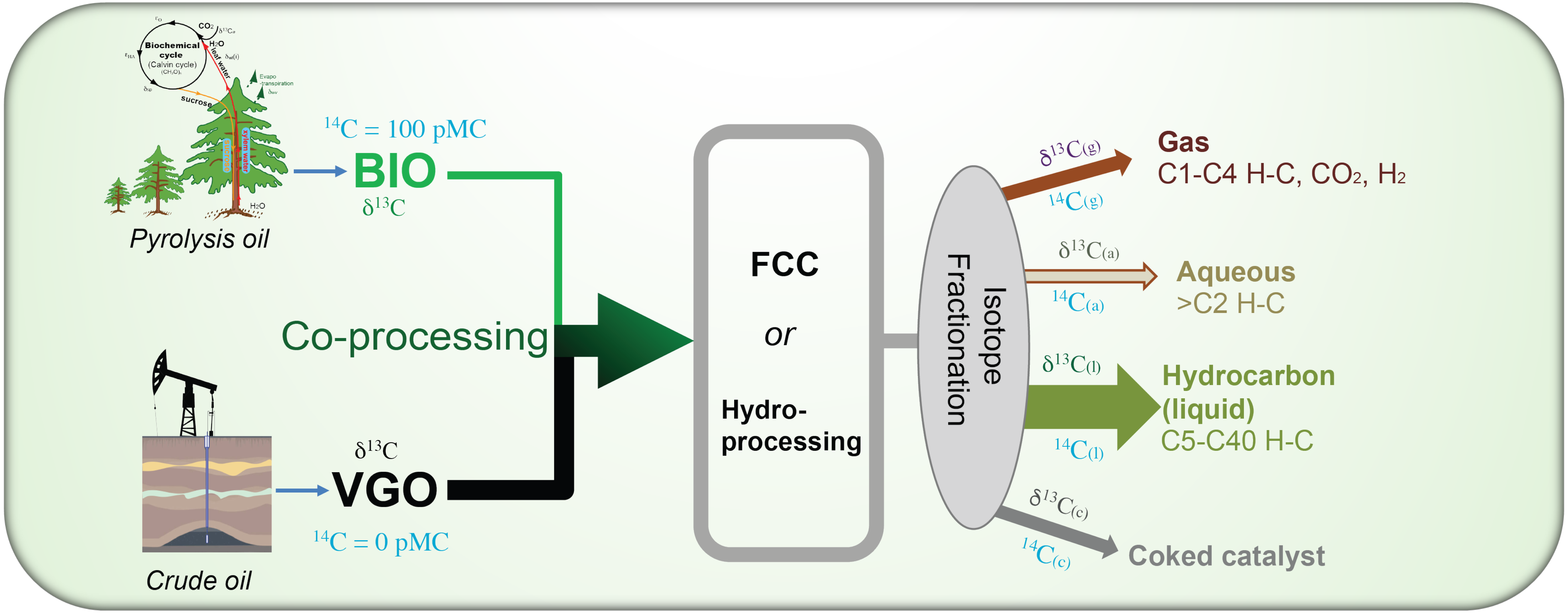
LSC: Liquid Scintillation Counting; IRMS: Isotope Ratio Mass Spectrometry



pMC: Percent Modern Carbon ^{14}C: radiocarbon isotope $\delta^{13}C$: stable carbon isotope ratio

- Petroleum contains ^{12}C and ^{13}C but not ^{14}C. Modern vegetation contains ^{12}C, ^{13}C, and ^{14}C.
- Modern vegetation contains 100 pMC ^{14}C (100% biogenic carbon).
- Fossil fuel contains 0 pMC ^{14}C due to ^{14}C decay with half-life=5,730-year (0% biogenic carbon)

Radiocarbon ^{14}C Formation and Determination of Biogenic Carbon by Measuring Radioactive Decay Activity (A)

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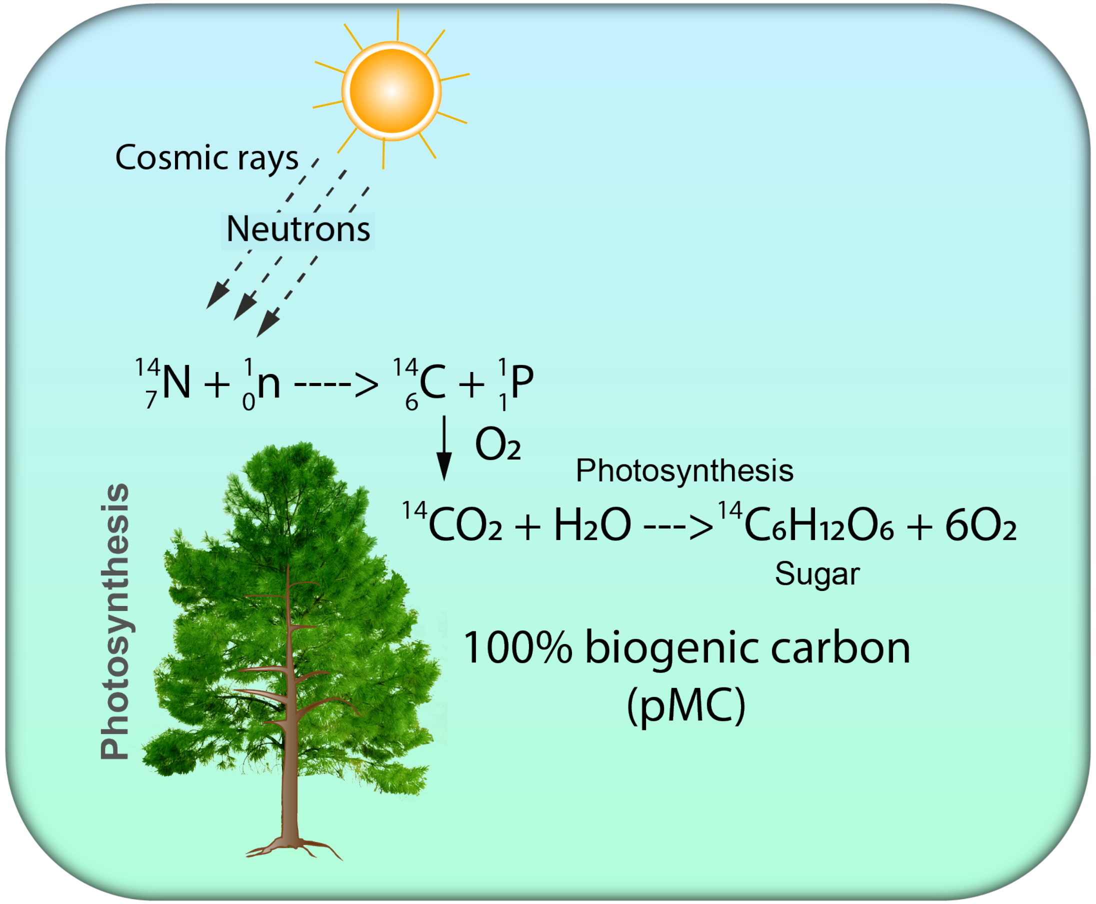

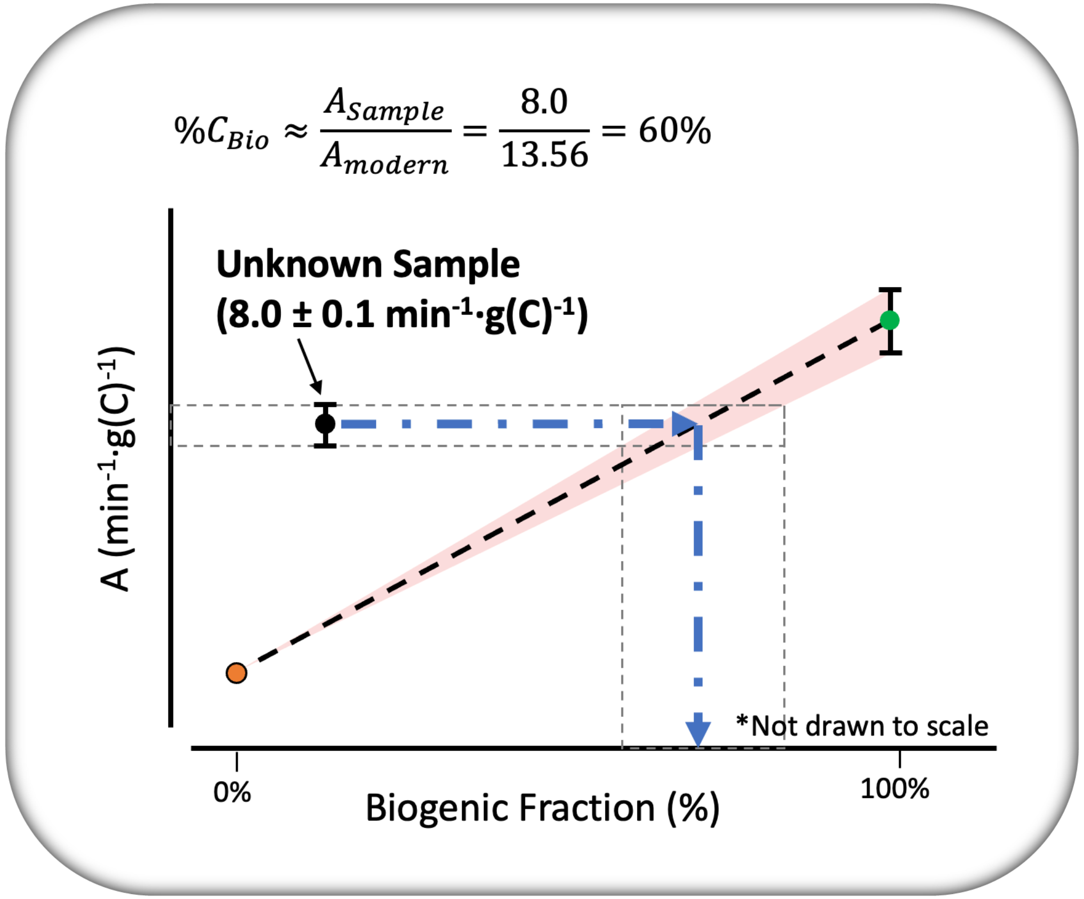

- ^{14}C is produced by cosmic rays and incorporated in plants through photosynthesis
- Biogenic C content is determined by measuring ^{14}C activity (A) in plants.
- Petroleum A is zero, while modern plant A is 13.56 (100% biogenic carbon)

Using LSC ^{14}C to Track Biogenic Carbon in Co-processing

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LANL Liquid Scintillation Counting (LSC)

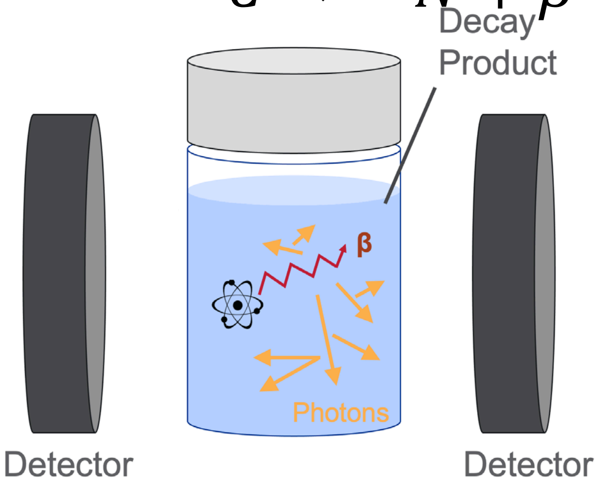
Quantulus^{TM} GCT 6220

Quantulus^{TM} 1220

HiDex 300SL

Small footprint

$$^{14}C \rightarrow {}^{14}N + \beta^-$$



^{14}N: nitrogen isotope. β^-: beta particle emission

__LSC Analysis__
- Mix sample with scintillate
- Scintillate produces photons when decay occurs
- Number of photons emitted are related to energy of decay products
- PMTs detect amount of photons

__LSC Complications__
- Scintillate can produce photons semi-randomly (Background)
- Photons “blocked” by color and/or chemical makeup of sample (Efficiency)

Using LSC ^{14}C to Track Biogenic Carbon in Co-processing

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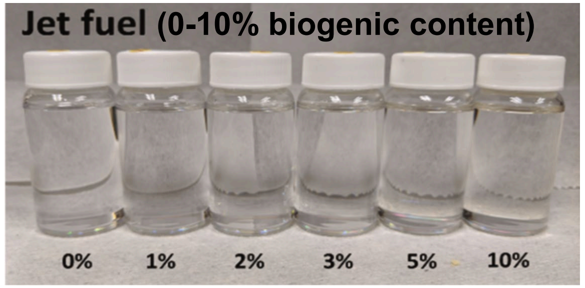
1. Near-clear fuels (petroleum jet fuel blended with SAF)

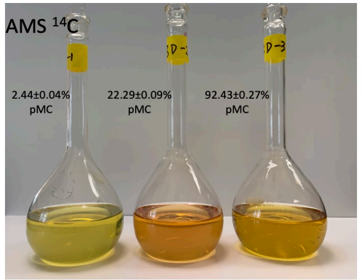


Direct LSC Measurement

Optimized data range, counting time, and data interpretation. Achieved +/-0.4 % points relative to ASTM 6866 (^{14}C AMS) in the range of 1-10% biocarbon. *Lee & Li et al 2022 (Fuel)*

Liquid Scintillation Counter

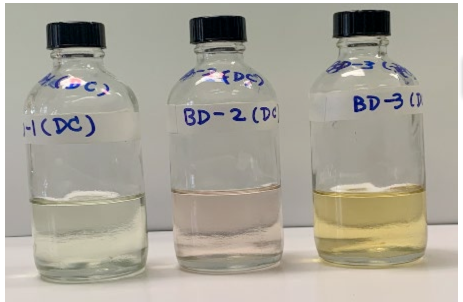
2. Lightly colored fuels (petroleum diesel and petroleum diesel/biodiesel blend, and B100 biodiesel)



B0 B20 B100

Decolorization

Adsorbents



LSC Measurement

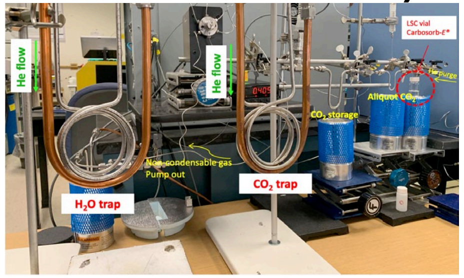
Decolorized fuels can be analyzed in LSC, but decolorization reduced biogenic carbon. *Lee & Li et al 2022 (Energy & Fuel)*

LSC Measurement

3. Dark fuels, and solids (bio intermediates and feeds)

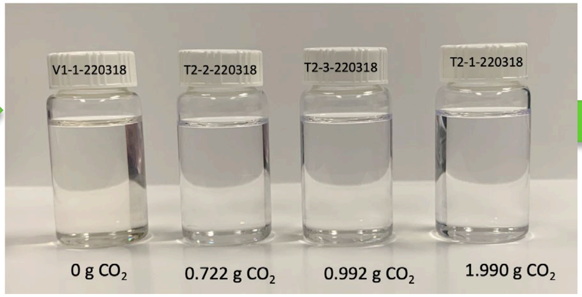
CO_2 Conversion

Oxy-combustion



CO_2 capture

In absorbent/ scintillate



Direct LSC measurement of near-clear samples of petroleum fuels blended with biofuels works

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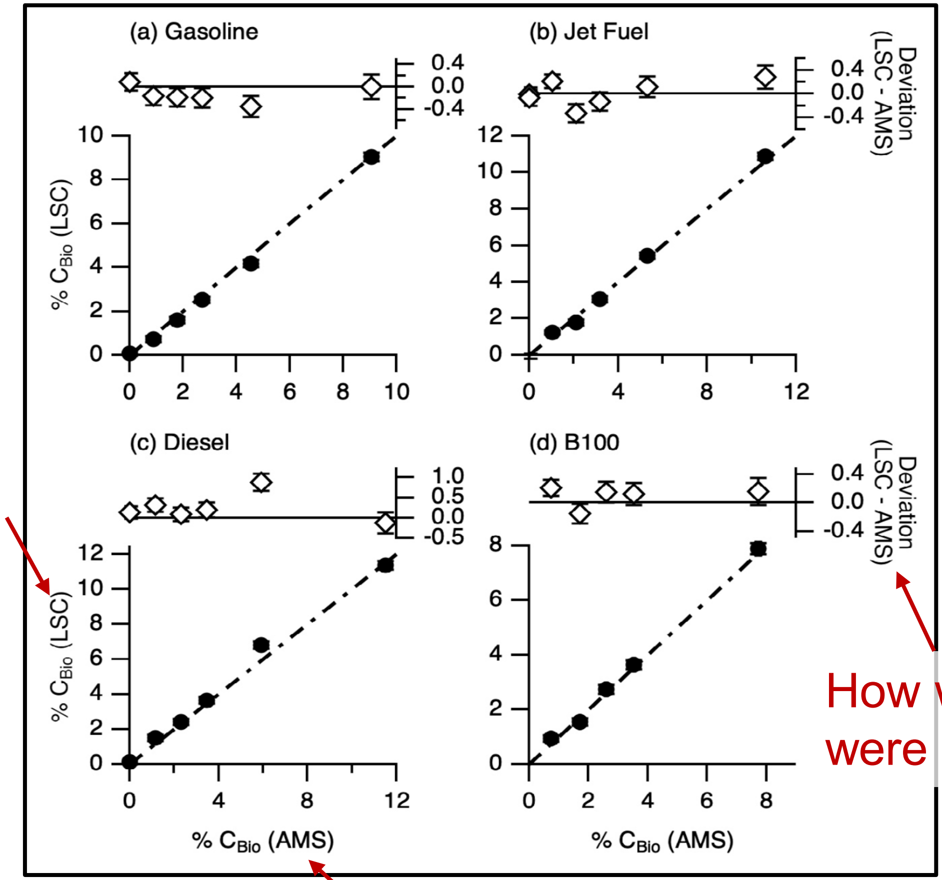
Correlation between LSC and AMS



LSC Measured

How wrong we were in % C_{bio}

"True" (ASTM-D6866)

Direct Measurement Method

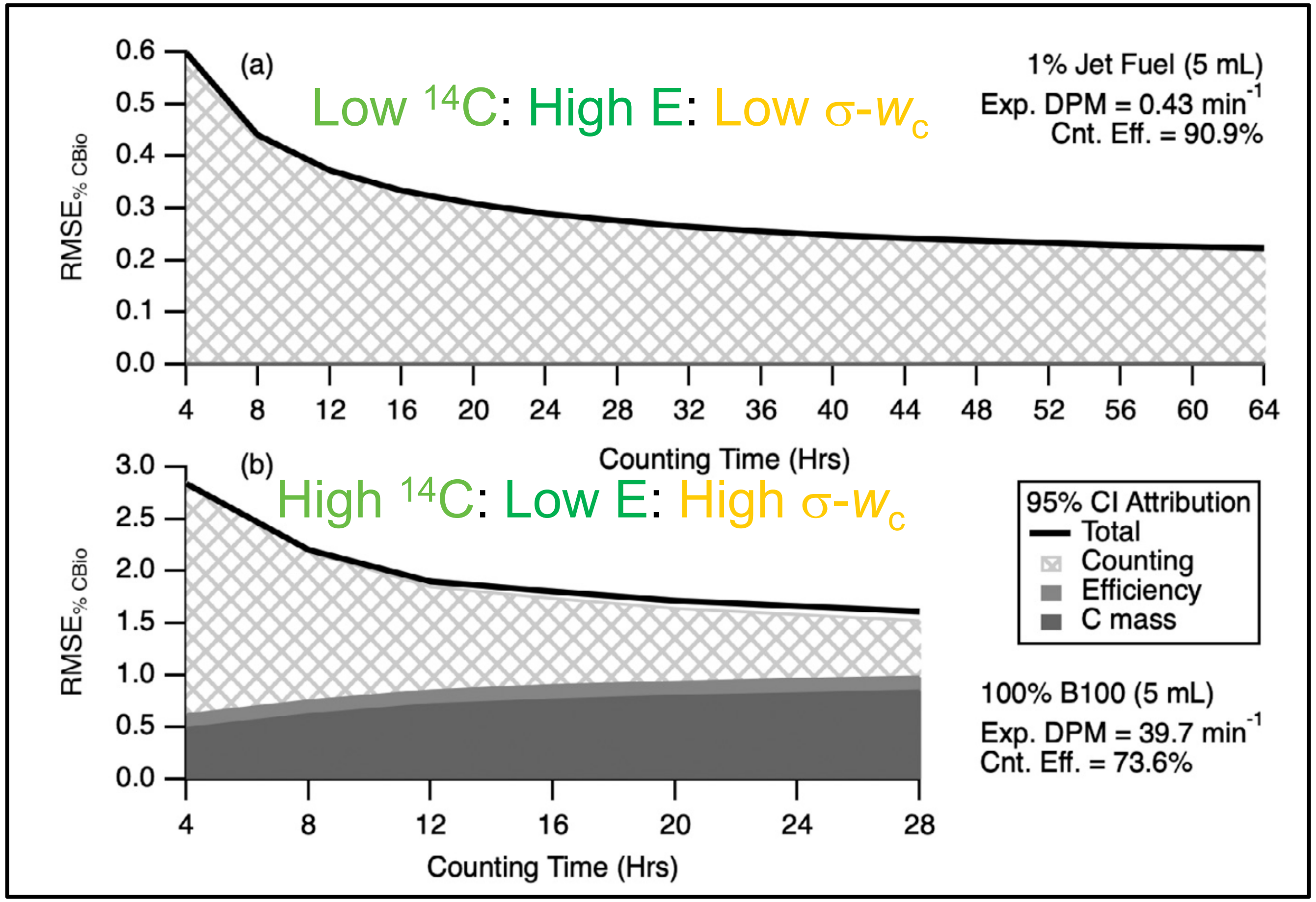
- "No Prep" approach: no sample preparation is needed, mixing fuel with scintillator directly.

Results

- Very small errors
- Accuracy better than 0.4%
- Counting Efficiency > ~80%

Lee & Li et al. 2022 (Fuel)

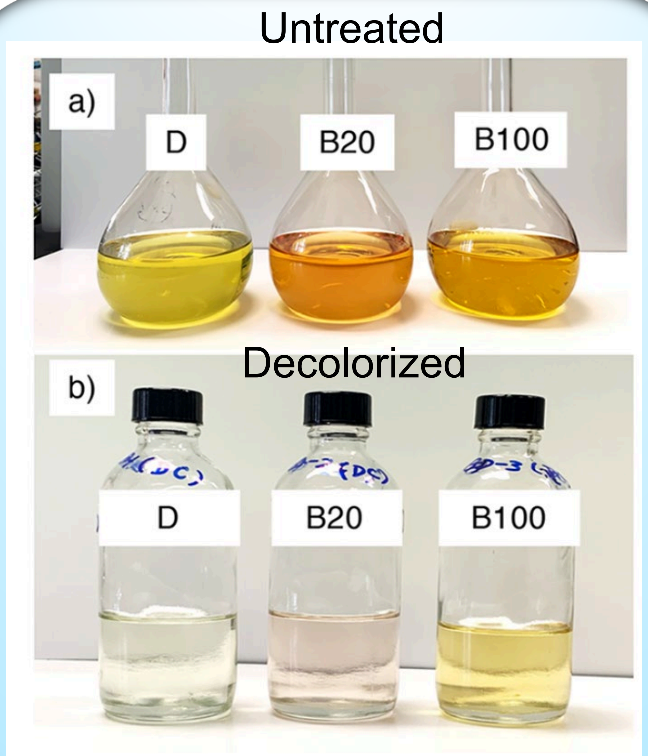
Attribution of Uncertainty for Determining Biogenic Carbon by Direct Measurement

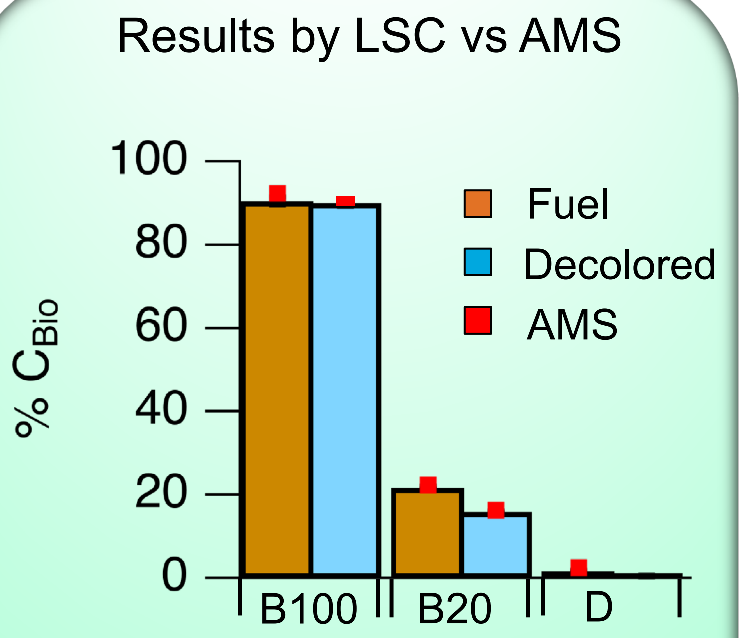


- Longer counting time, smaller uncertainty (RMSE: Root-Mean-Square Error).
- Uncertainty depends on the following fuel properties
  - Low biogenic carbon and high counting efficiency results in low uncertainty
  - High biogenic carbon and low counting efficiency results in high uncertainty
  - Higher carbon fraction means higher ^{14}C and thus higher counting efficiency.
  - Darker samples exhibit less counting efficiency, thus larger uncertainty.
- Uncertainty for the high-efficiency sample is negligible.

Lee & Li et al. 2022 (Fuel)

Diesel Decolorization of Petroleum/biofuel Blends Reduced Quench by Over 60%

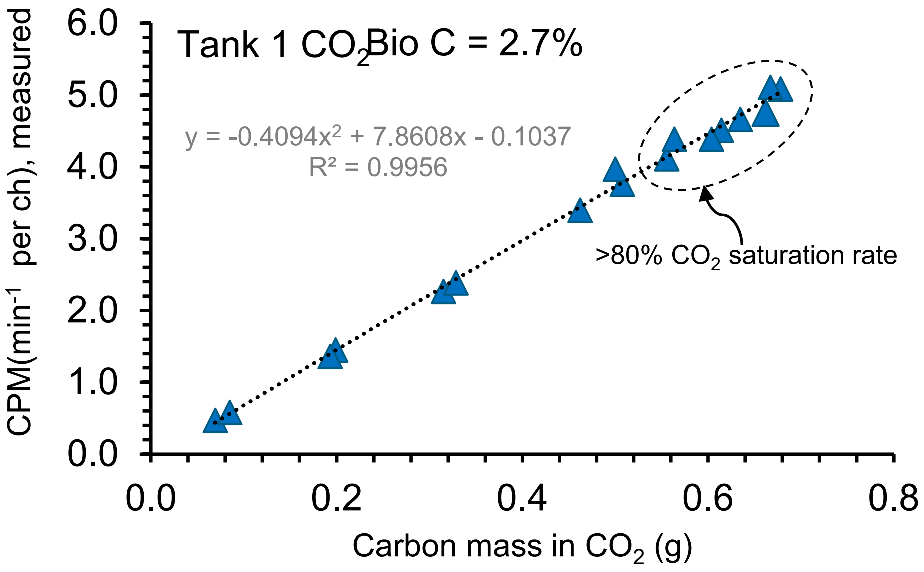


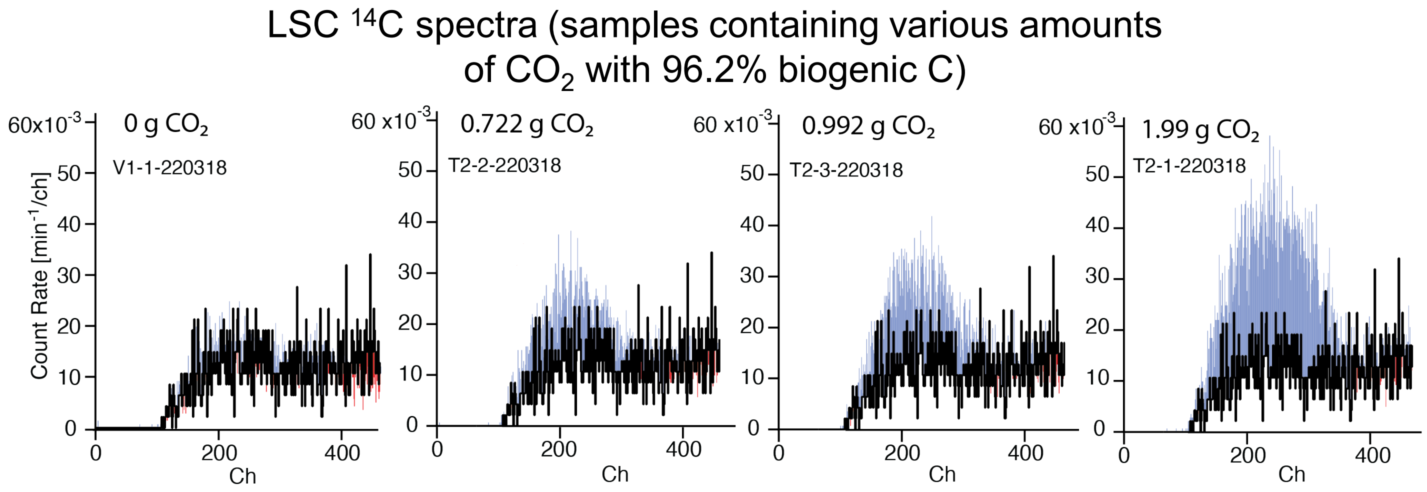


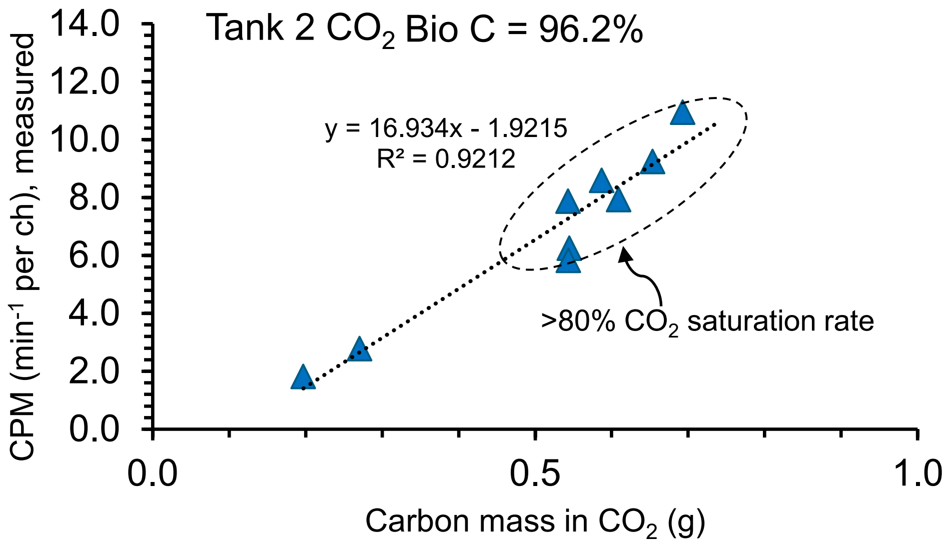
D: petroleum Diesel B20: bio-Diesel with 20% biogenic carbon B100: bio-Diesel with 100% biogenic carbon

- Investigated different techniques: Adsorbents, Catalytic, Oxidation. Adsorbents w/ Clay and Silica Gel was most effective.
- Decolorization reduced uncertainty w/out affecting $\%C_{Bio}$ interpretation for B100.
- Decoloring preferentially removed biogenic carbon in B20. We do not expect blended, co-processed samples to be affected by this artifact.

CO_2 Conversion: Development of Calibration Line







- Two tank CO_2 gases with very different biogenic carbon content are used to develop the calibration curves.
- Quantitative absorption of CO_2 in amine has been achieved.
- Very low ^{14}C signal (0.1 g C with 2.7% Bio C) can be meaningfully detected through CO_2-Amine capture.

Verification of Calibration Line for Biogenic Carbon Measurement in Solid Biomass and CO_2 Gas Samples

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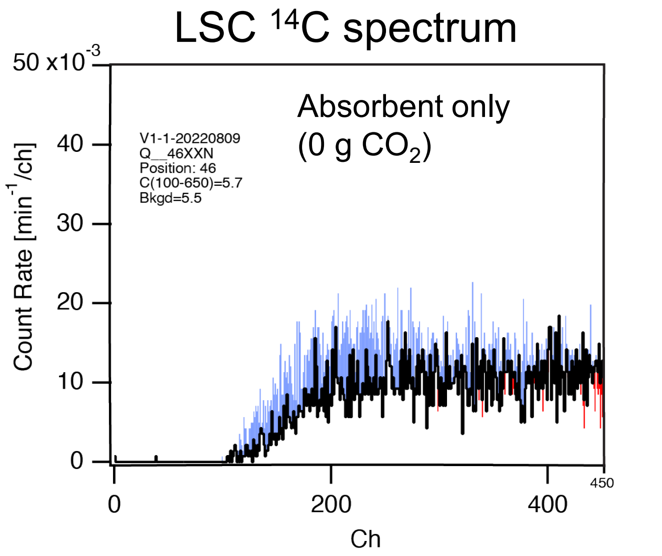
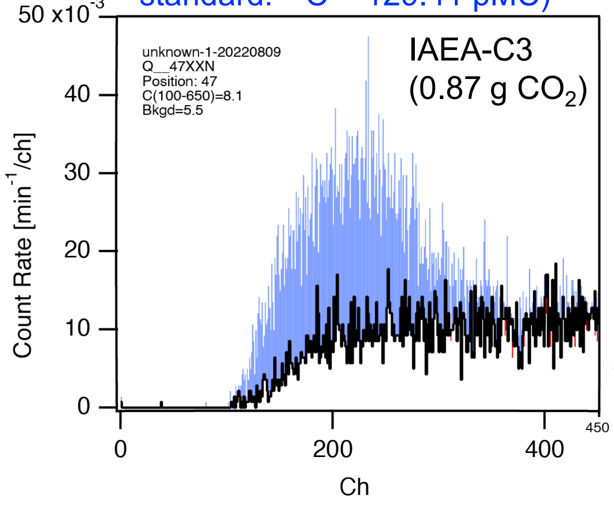
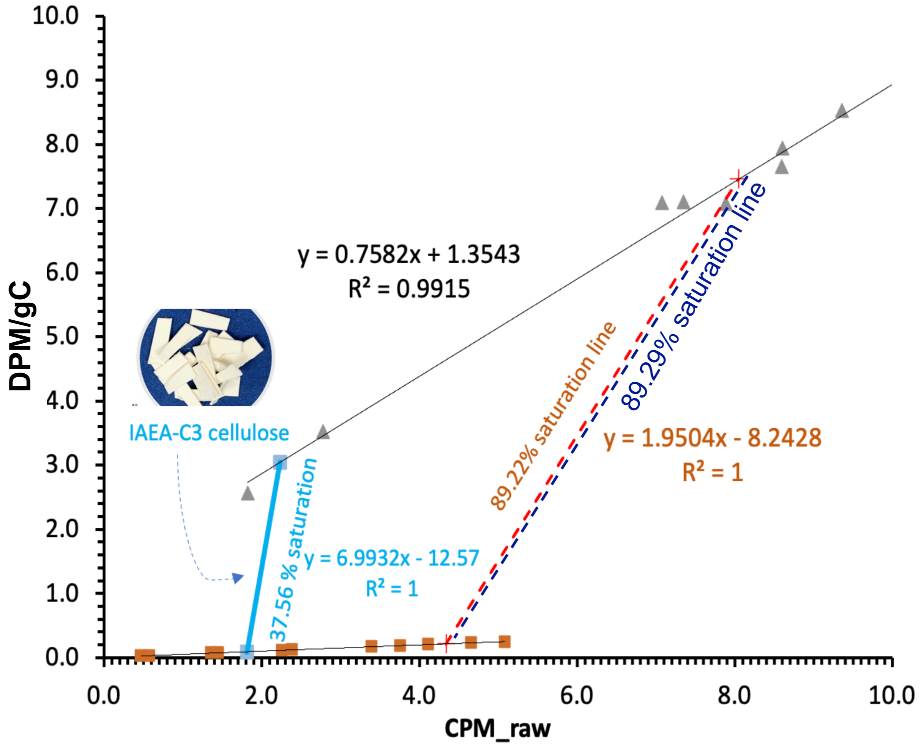


IAEA-C3 cellulose (international ^{14}C standard: ^{14}C = 129.41 pMC)





Sample ID	Saturation rate	CO_2 (g)	Bio C%, LSC	Expected %
IAEA-C3	37.56%	0.87	130.87	129.41
CO_2 gas 1	89.22%	2.222	76.9	75.9
CO2 gas 2	89.29%	2.171	48.1	47.3

- CO_2 conversion method works for all types of fuels and feedstock (clear, moderately colored, dark, and solid).
- Future work:
  - ➢ Test fuels with low biogenic carbon content and repeatability.
  - ➢ Reduce instrument background noise (currently ~3 cpm at Los Alamos).
  - ➢ Develop high capacity CO_2 absorption media.

Biogenic Carbon Tracking Through IRMS $\delta^{13}C$ Analysis

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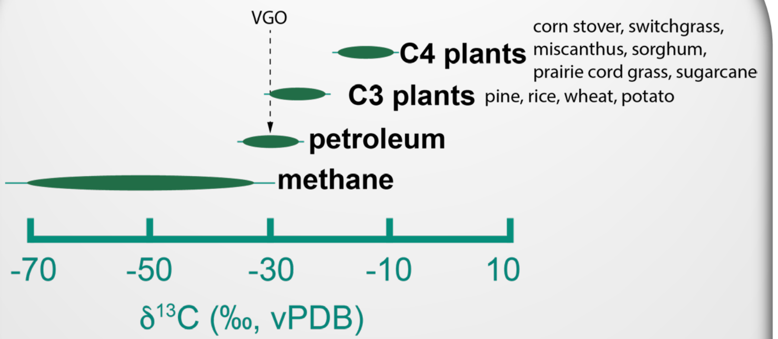
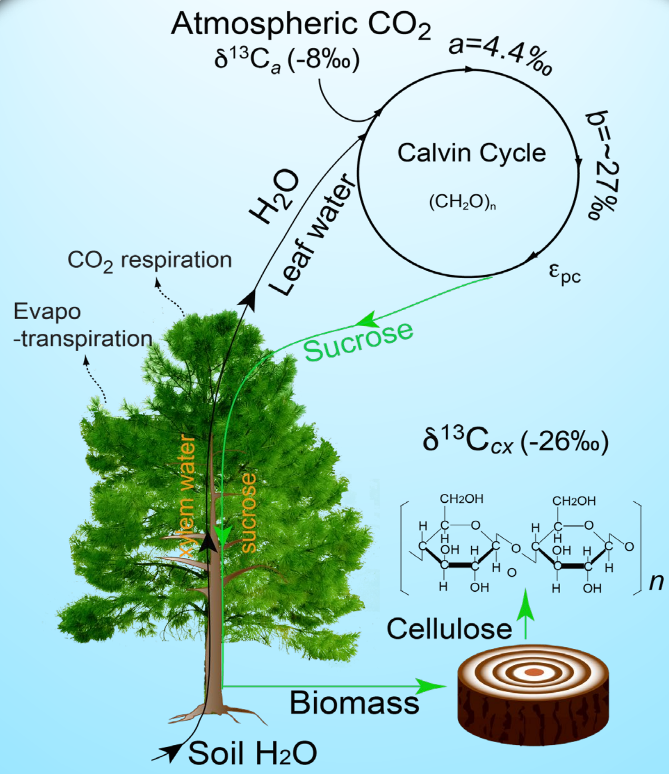


$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1 \right] \times 1000 \text{ ‰}$$

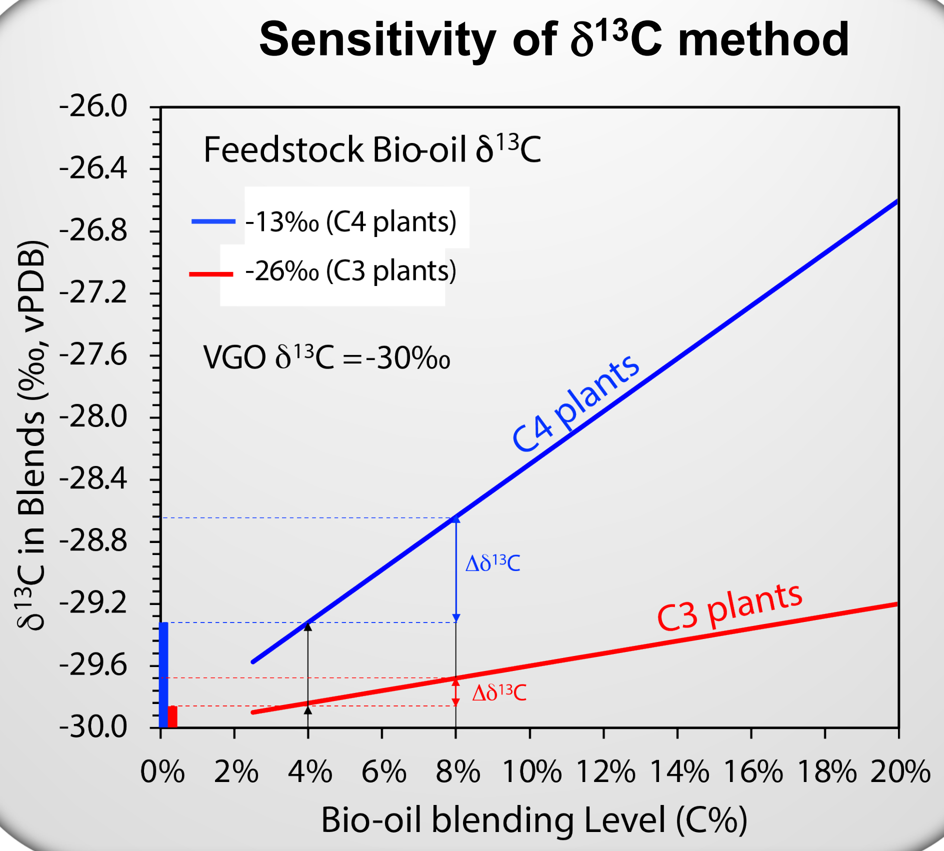


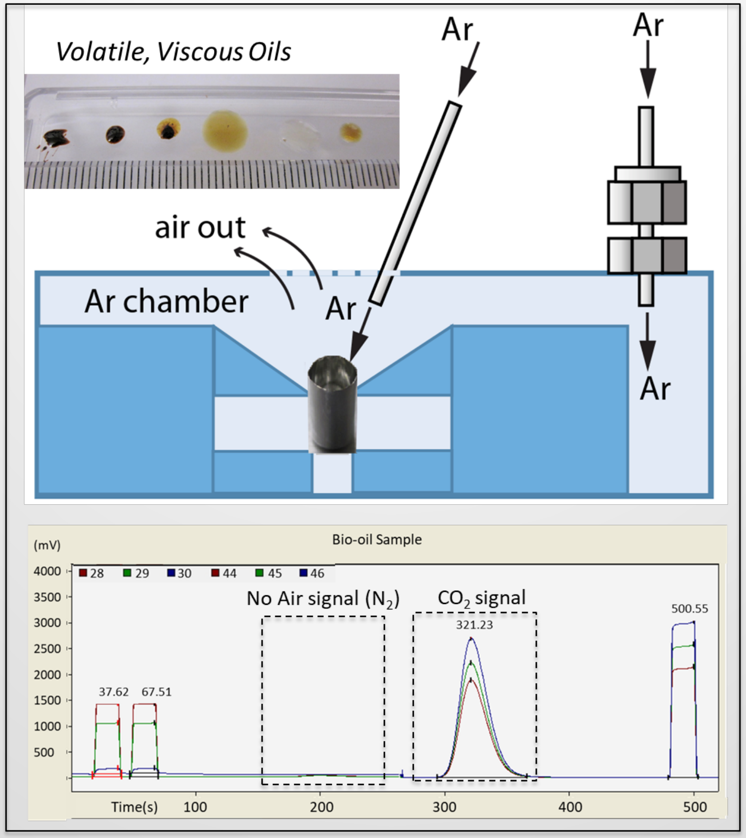
C3 plant photosynthesis

Stable Isotope Mass Spectrometry (IRMS)
-- *small footprint*

- Stable carbon method is based on $\delta^{13}C$ difference between two feedstocks.
- C4 plant-derived bio-oil has better traceability for biogenic carbon distribution.
- $\delta^{13}C$ can be easily measured using a IRMS.

Sensitivity of δ13C for Tracking Biogenic Carbon and Sample Preparation Protocol

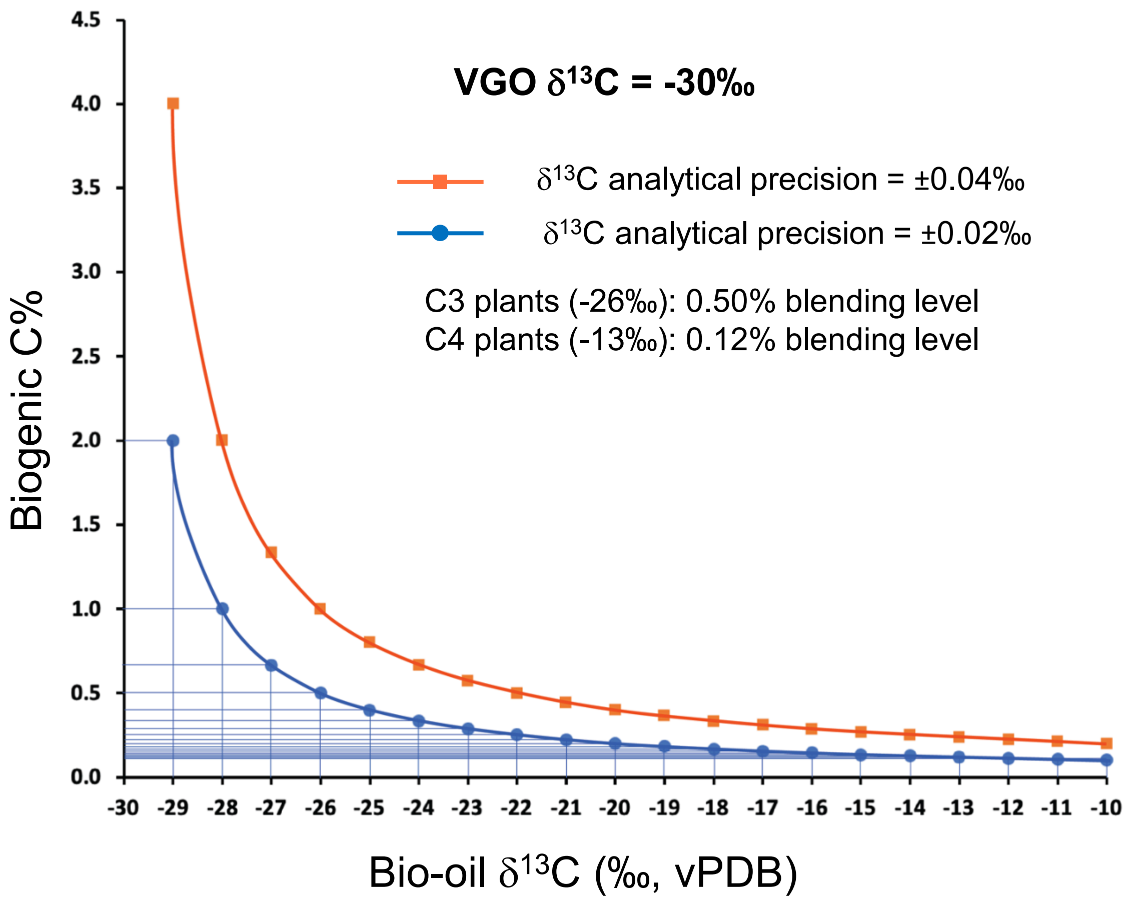


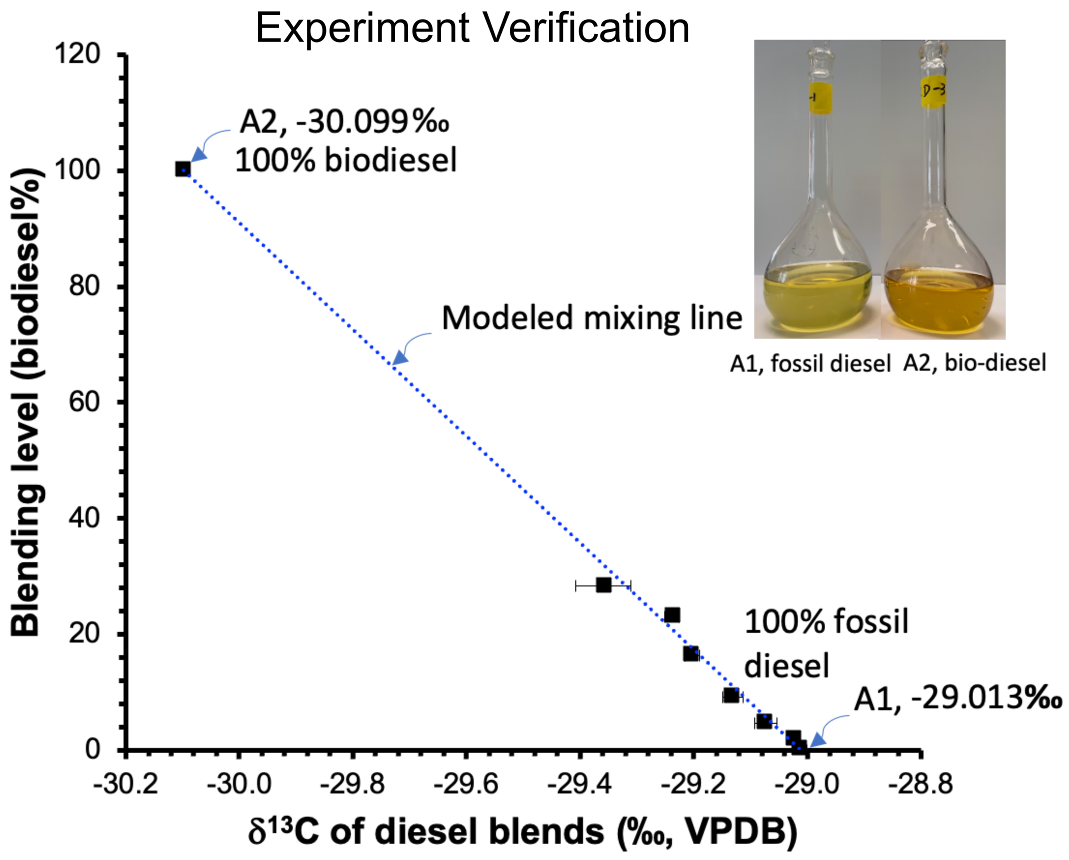


- Volatile, viscous samples are difficult to measure due to fractionation.
- Sealing in tin capsules under argon eliminates volatilization and prevents atmospheric contamination
- Solid standards can be run concurrently

Geeza & Li et al. 2020 (Fuel)

Limit of Detection of δ13C Method for Biogenic Carbon Measurement



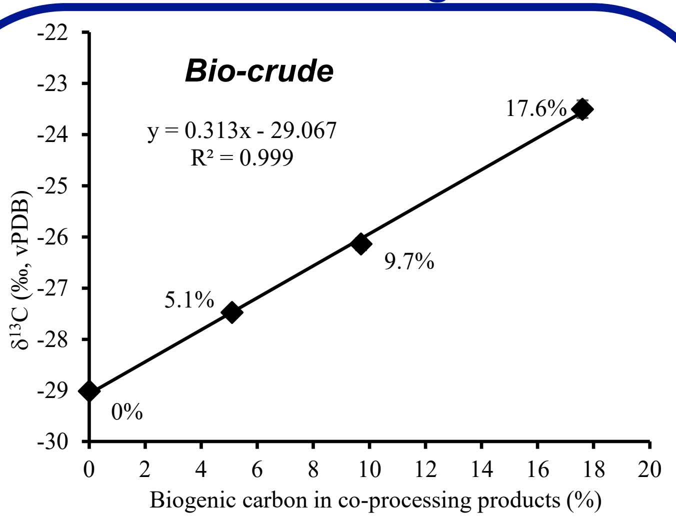


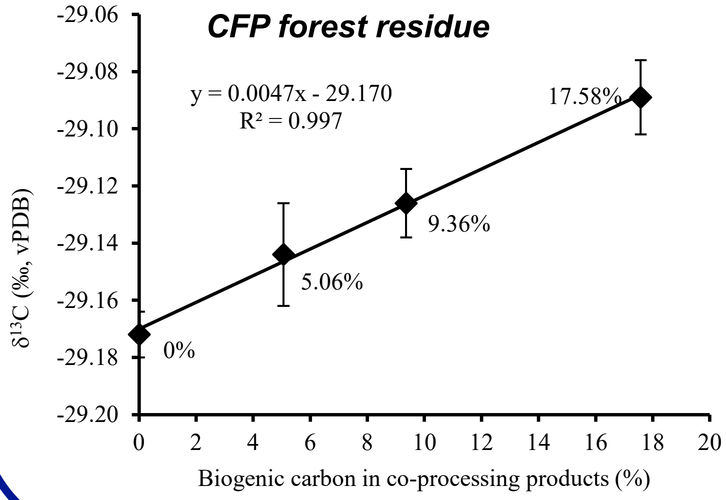
$$C_{bio}\% = \left[\frac{\delta^{13}C_{mix} - \delta^{13}C_{fos}}{\delta^{13}C_{bio} - \delta^{13}C_{fos}}\right] \times 100\%$$

- Limit of Detection depends on analytical uncertainty.
- 0.5% blending level can be detected for C3 plant-derived bio-oil.
- 0.12% blending level can be detected for C4 plant-derived bio-oil.

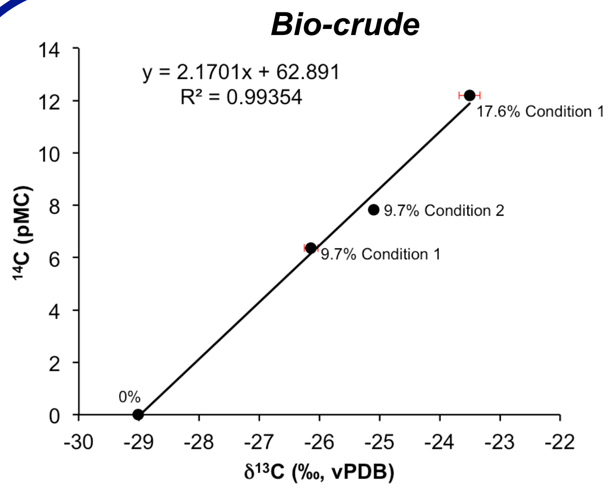
Significant Correlation Between Biogenic C% and δ13C in Co-processed Products Revealed

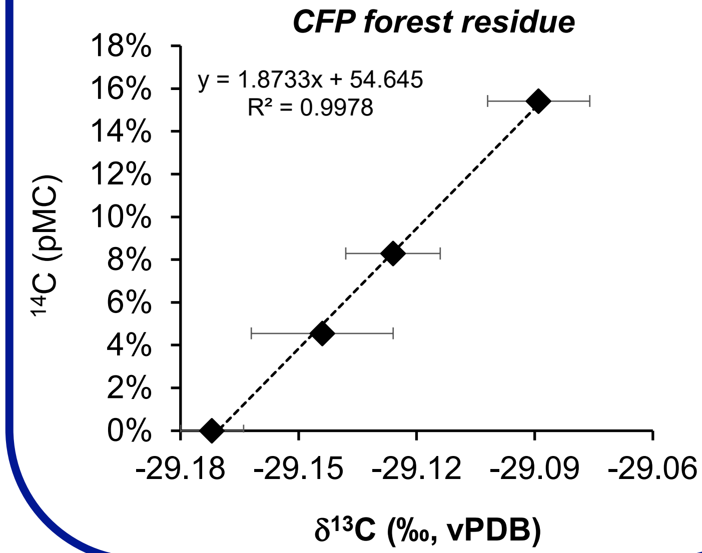
$\delta^{13}C$ and biogenic C%





AMS ^{14}C verification

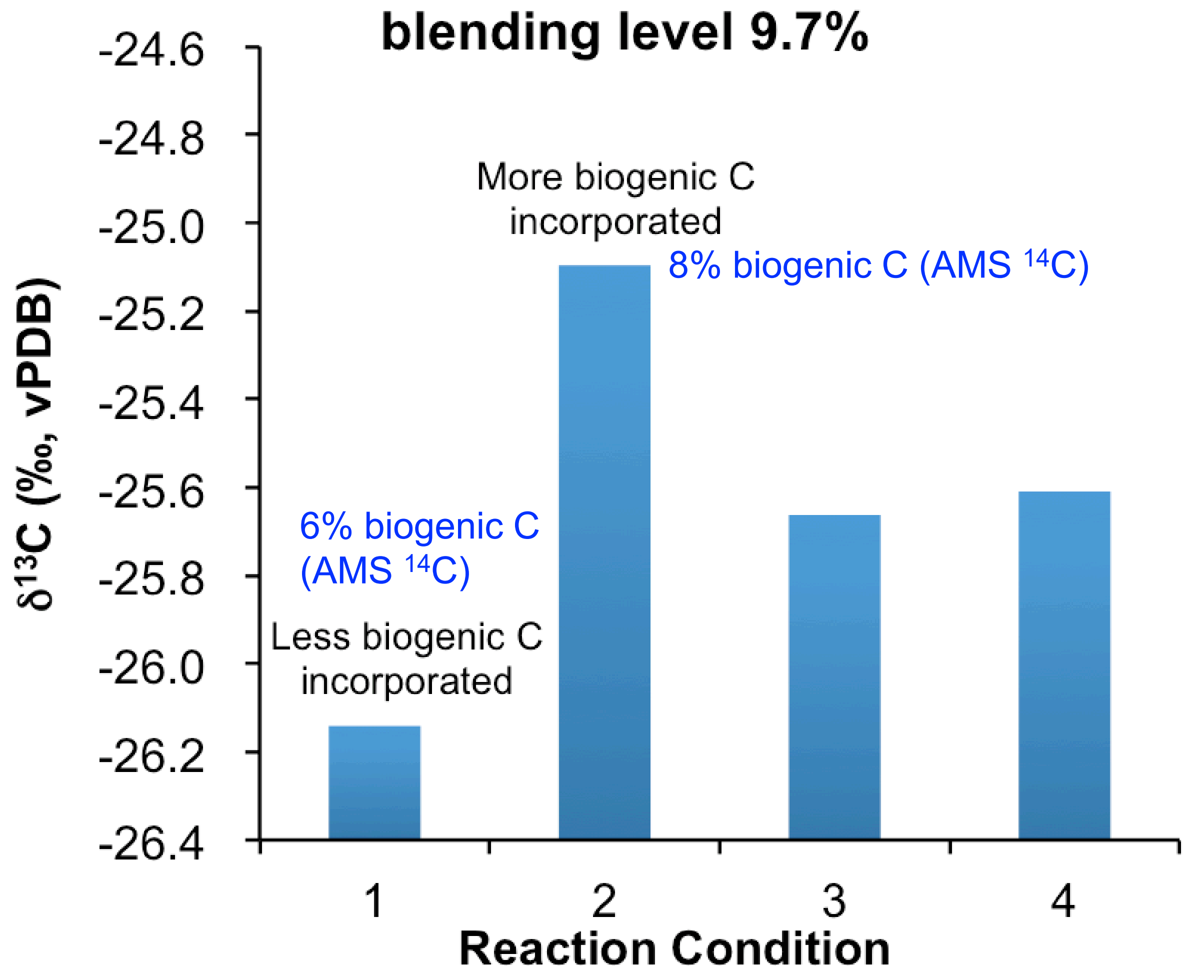




- Conducted co-processing experiments on bio-crude, FP, and CFP bio-oil.
- High precision $\delta^{13}C$ analysis revealed significant correlation with biogenic C% in co-processed products.
- $\delta^{13}C$ applicability for biogenic C tracking is confirmed by ^{14}C AMS method.

Li and Magrini et al. 2020 (Fuel)

Optimal Co-processing Condition Revealed by $\delta^{13}C$ Analysis



- Bio-crude co-processing with VGO at the same blending level (9.7%) under different co-processing reaction conditions (T, P, WHSV, H_2/VGO).
- Reaction Condition 2 shows the highest biogenic carbon incorporation.
- $\delta^{13}C$ analysis can be used to guide the optimization of co-processing parameters.

Li and Wang et al. 2021 (ACS SCE)

Quantification of Biogenic Carbon in Co-processed Products by δ^{13}C Analysis

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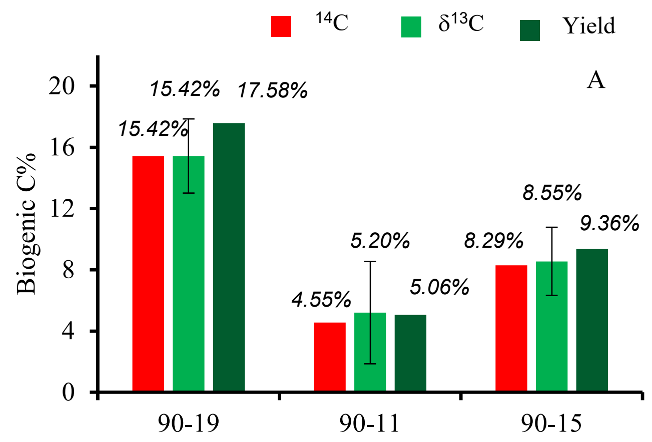
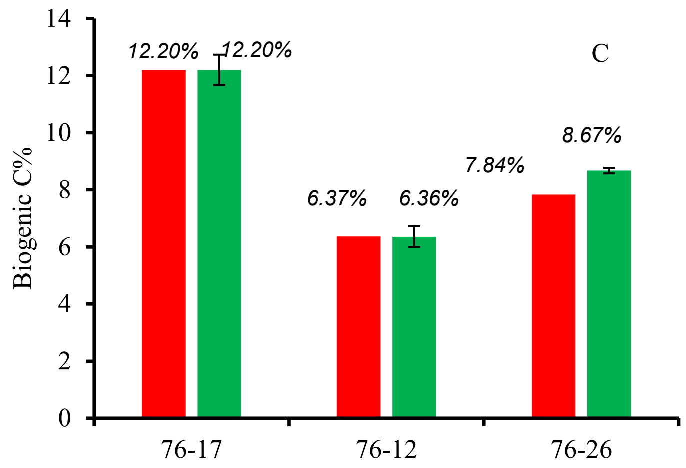
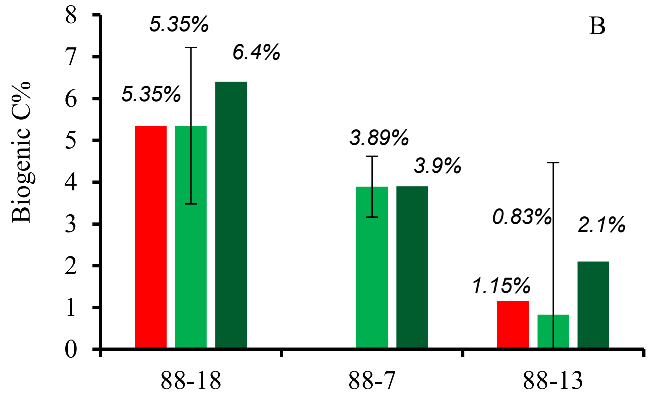


Forest residue bio-oil co-processing



Bio-crude co-processing



VGO + Woody biomass co-processing

- Quantification of biogenic carbon in co-processed products can be achieved through δ^{13}C analysis. Large uncertainty for quantifying C3-plant co-processing.
- C isotope fractionation factor is not affected by the bio-oil blending levels in co-processing.
- δ^{13}C analysis can be a viable way to track biogenic C in co-processing, **but feedstocks must be available for δ^{13}C analysis**.

Li and Wang et al. 2021 (ACS SCE)

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Senior Scientist

Los Alamos National Laboratory

Dr. Sophie B. Lehmann

Scientist

Pacific Northwest National Laboratory

Pacific Northwest
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Optical approach for tracking biocarbon in a refinery setting using $\delta^{13}C$ values

Interest of application

- *Interest from Industry Advisory Board*
- *Fast, reliable, and inexpensive biocarbon trackers*
- *Onsite and near real time analytical methods*
- *Low blend ratios of biocarbon*

Application of Optical Spectroscopy to Co-Processing

Overarching objective

- Can optical spectroscopy monitor $\delta^{13}C$ as well as isotope ratio mass spectrometry?
  - Transportation fuels
  - Low biocarbon ratios (0% to 10%)

- Can optical spectroscopy be adapted for refinery applications?
  - Challenging environment
  - Near real time measurements

$\delta^{13}C$ can be used for Tracking Biocarbon

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Natural abundance

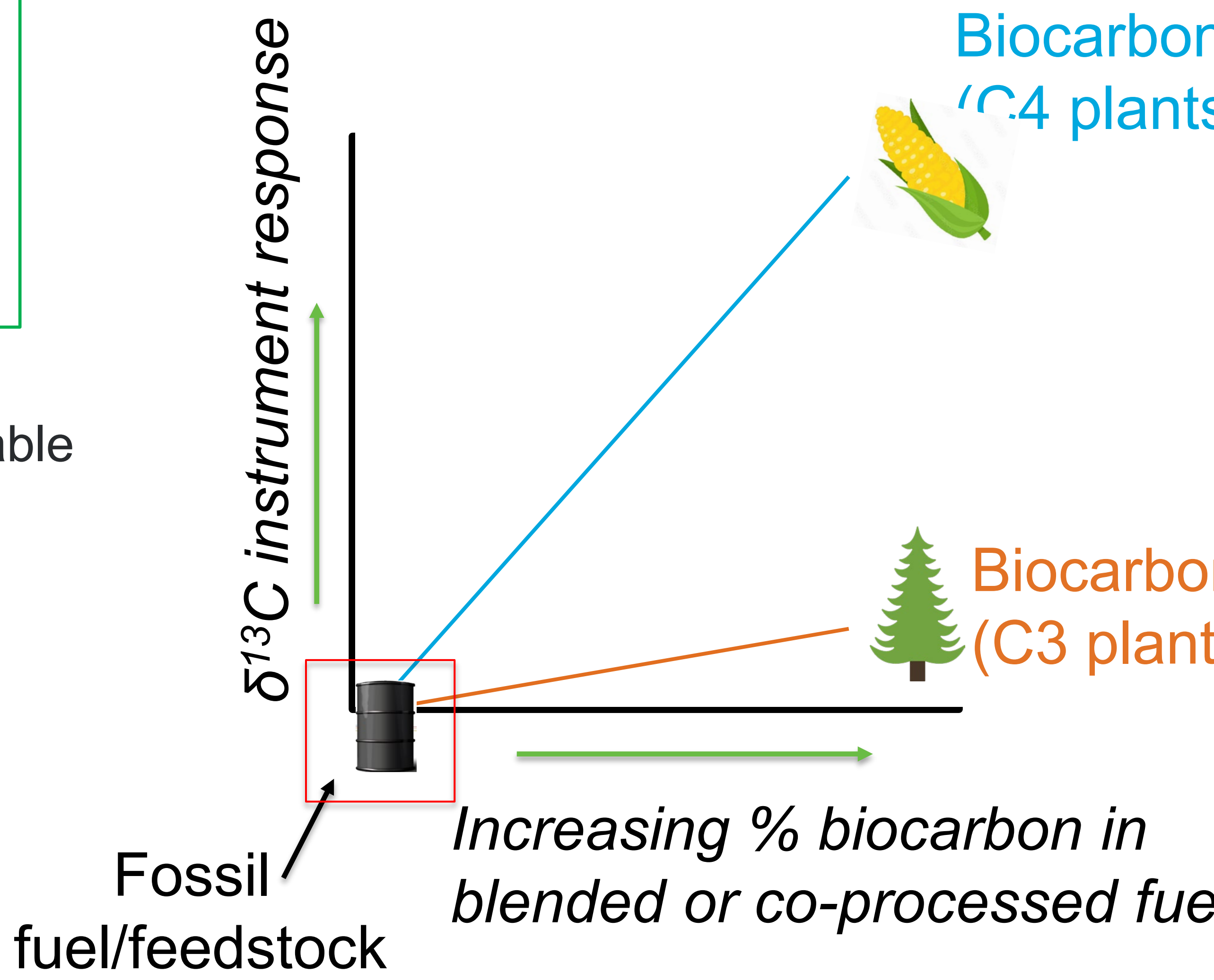
^{12}C: 98.89 %
^{13}C: 1.108 %
^{14}C: 1 x 10^{-10} %

$\delta^{13}C$ is a ratio of ratios

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

- Measured $\delta^{13}C$ correlates with percent renewable carbon in blended and co-processed fuels (i.e., linear relationship)

- $\delta^{13}C$ data can help monitor and optimize incorporation of biocarbon during coprocessing (e.g., prevention of loss to gas phase or coke)



Instrumentation for $\delta^{13}C$ Measurements

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Isotope Ratio Mass Spectrometry (IRMS)

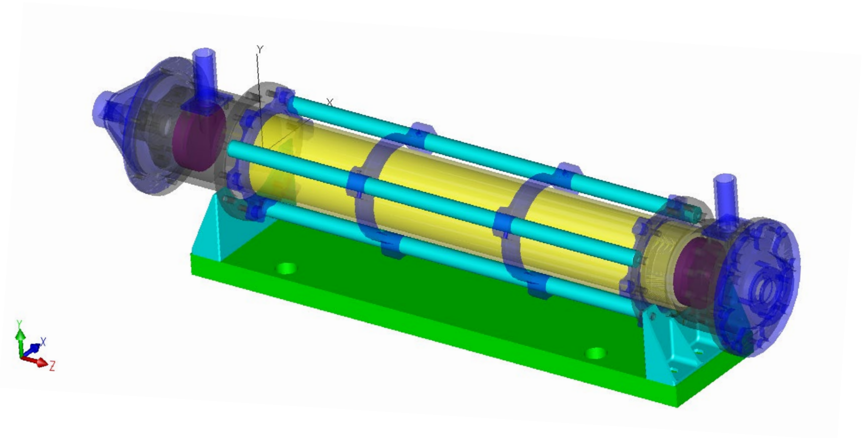
- Gold standard for $\delta^{13}C$ measurements
- High precision
- Collection to data time: ~1 to 2 days
    - Analysis time: 30 minutes
- More expensive laboratory setup
- Stable laboratory environment needed
- Larger instrument (101 cm x 135 cm x 136 cm)

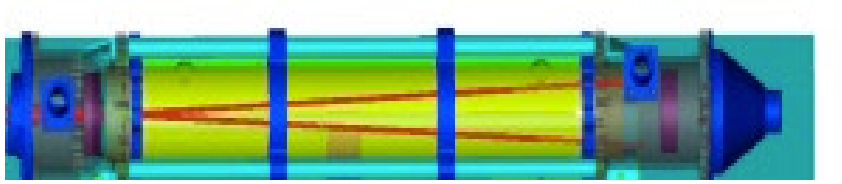
Optical Spectroscopy (TILDAS)

- Less expensive
- High precision
- Collection to data time: 20 to 60 minutes
- Smaller footprint (44 cm x 66 cm x 27 cm)
- Rugged design, field deployable
- Potential for online analysis & automation

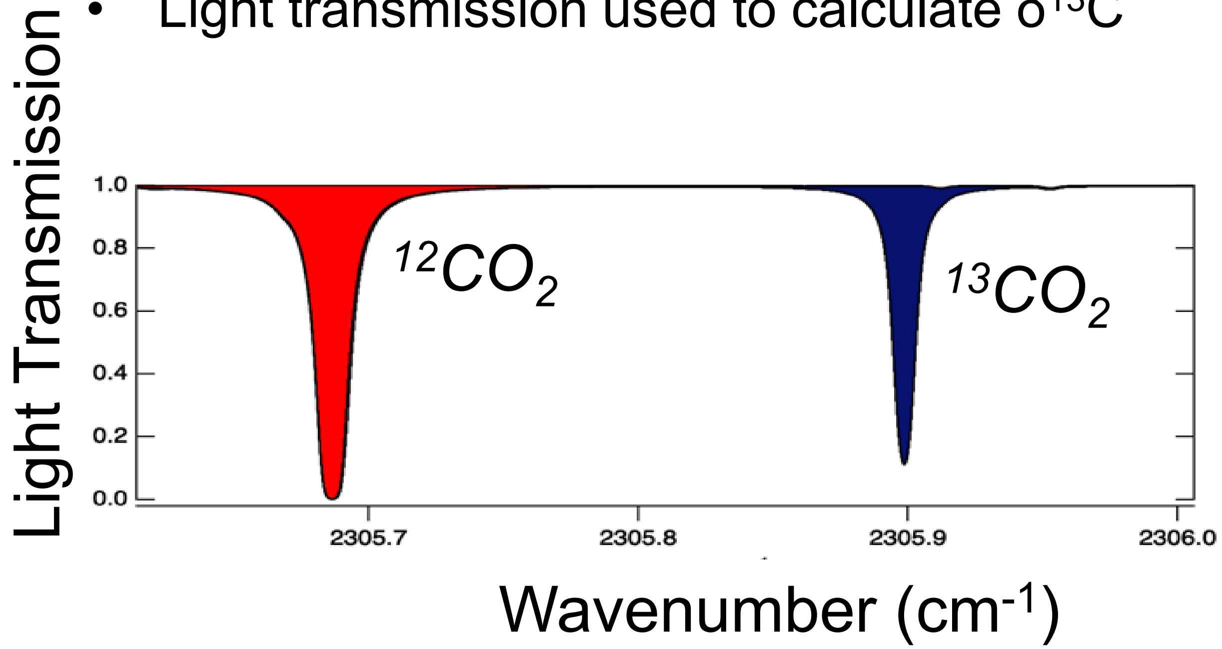
Optical Spectroscopy: Principles of TILDAS Operation

Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS)





- Sample converted to CO_2 by combustion
  - *Solid, liquid, gas samples are possible*
- Light absorption measured as wavelength
- Light transmission used to calculate $\delta^{13}C$



Method Development: Sample Preparation and Analysis

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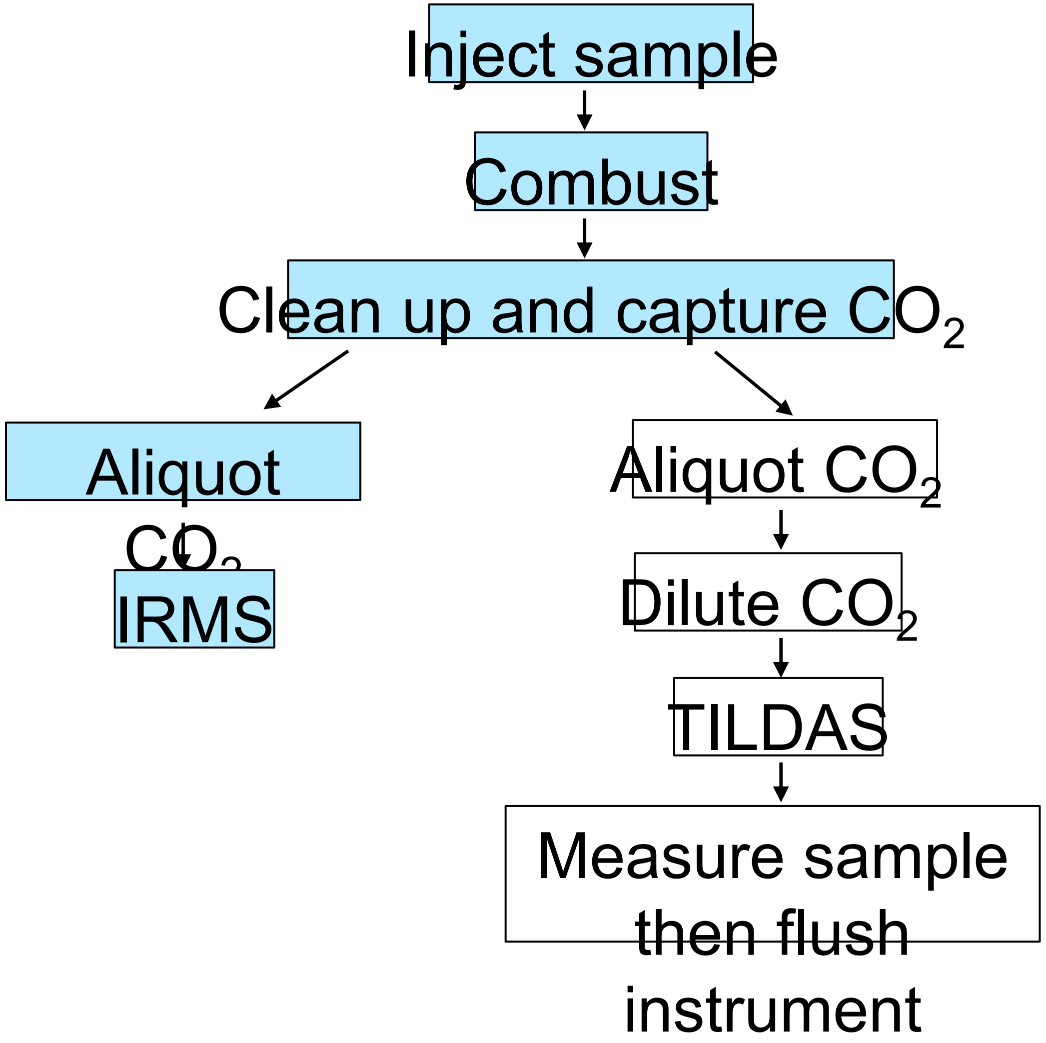
Can optical spectroscopy monitor $\delta^{13}C$ as well as isotope ratio mass spectrometry?

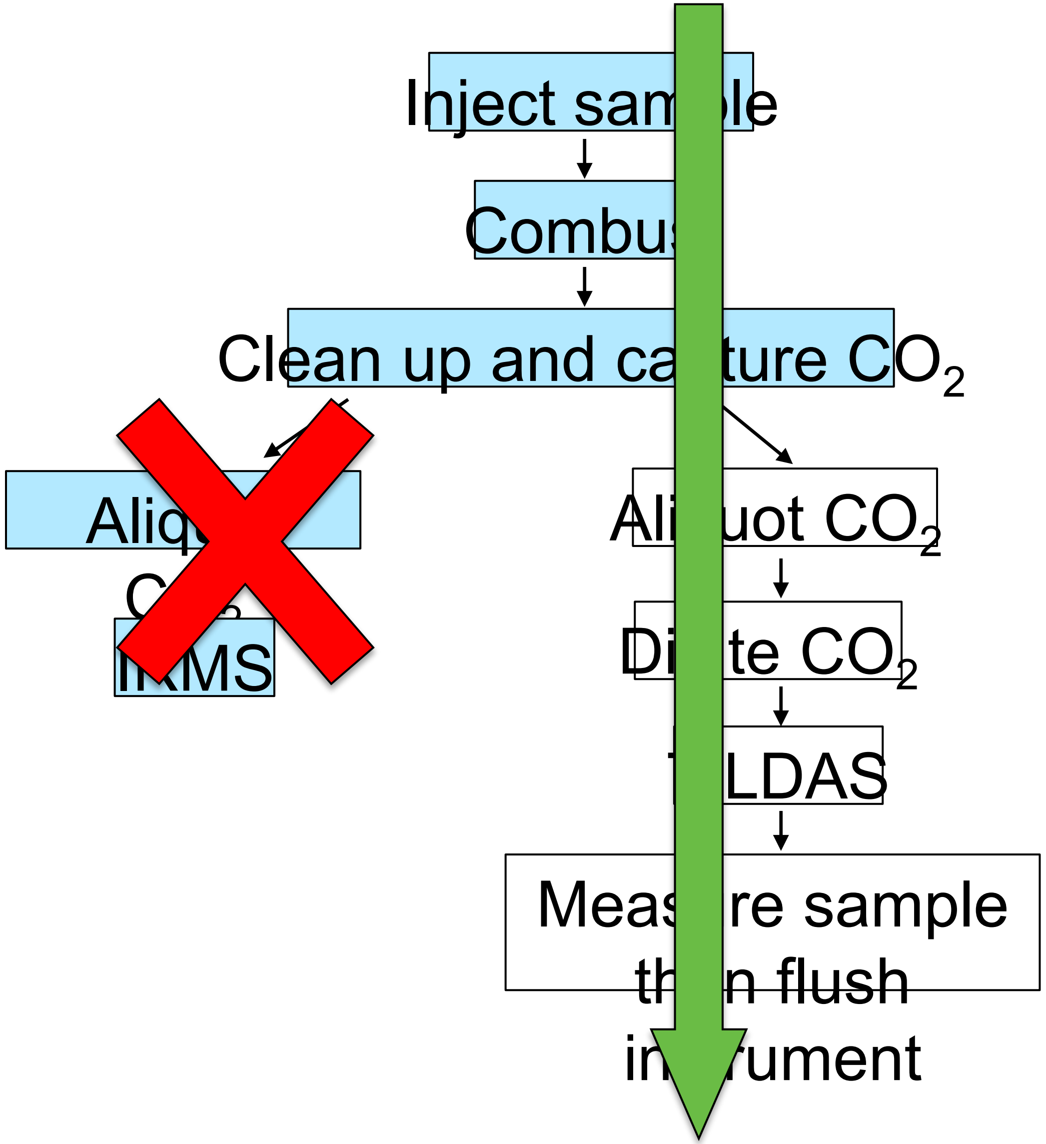
- Transportation fuels
- Low biocarbon ratios (0% to 10%)



Method Development: Optimizing Sample Preparation and Analysi

Can optical spectroscopy be adapted for refinery applications?

- Challenging environment
- Near real time measurements



TILDAS δ13C Data are Comparable to IRMS Data at Low Blend Ratios

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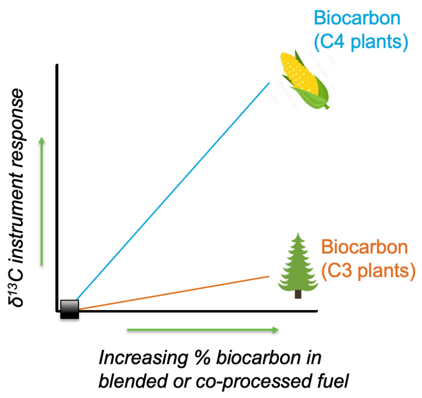

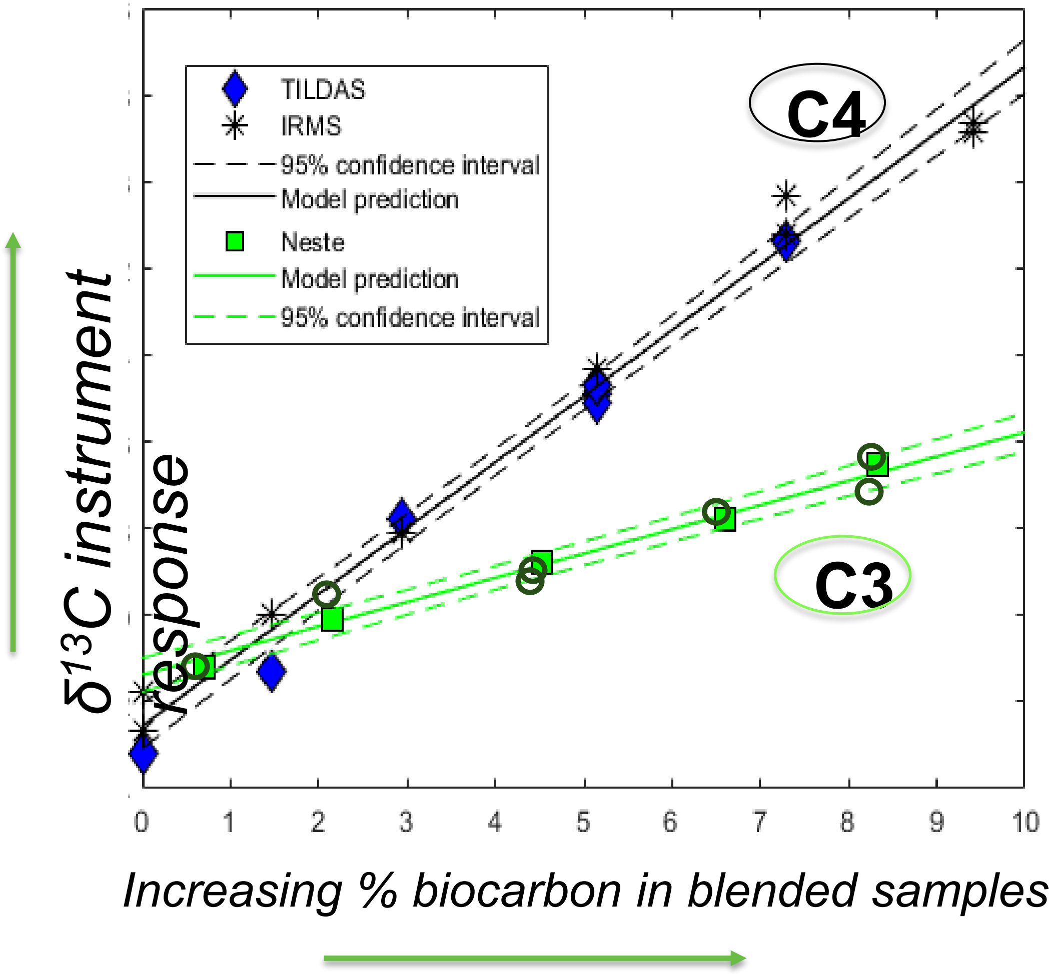

- Fossil fuel and biofuel blended at low biocarbon ratios (0% - 10%).
- Strong correlation between methods
  - R^2 close to one
  - Tight 95% confidence intervals
- ***TILDAS and IRMS yield similar results for tracking low levels of biocarbon in transportation fuels***

Optical Spectroscopy in the Refinery Setting

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- **Some instrument requirements for measuring $\delta^{13}C$ at a refinery**
  - ✓ Stable, onsite/near real time method
  - ✓ Complete sample preparation and sample analysis
  - ✓ Consistent, high precision measurements
  - ✓ Ideally inexpensive, fast, and automated analytical system

- **Project status**
  - TILDAS has the potential for near real time analysis
  - Integrating sample preparation and TILDAS to simulate near real time measurements
  - More development needed before deployment
  - Need to partner for insights on how this method can best be employed at refineries

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Agenda

This Webinar (9/27/2023)

- Housekeeping
- Overview of BETO
- Biogenic Carbon Tracking and Measurement by LSC ^{14}C and IRMS $\delta^{13}C$ in Co-processing

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- Laser Spectroscopy and Stable Carbon Isotopes for Tracking Biocarbon

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- Q&A

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