Quantification of biogenic carbon in fuel blends through LSC ^{14}C direct measurement and assessment of uncertainty

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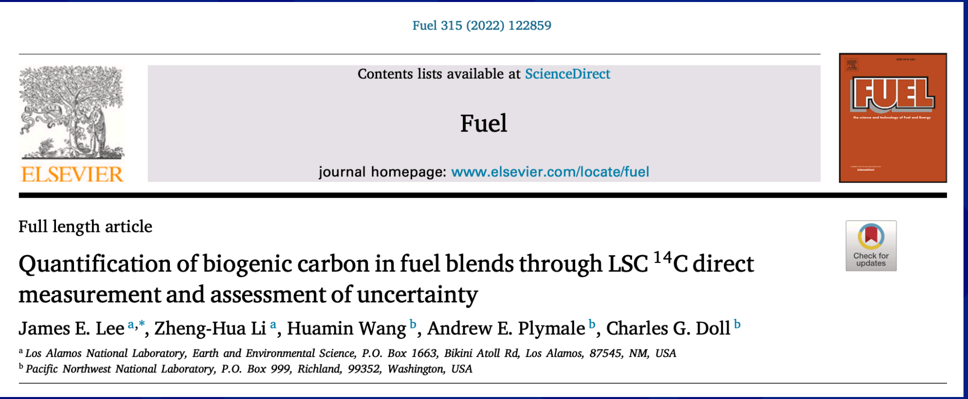
Fuel 315 (2022) 122859

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full length article

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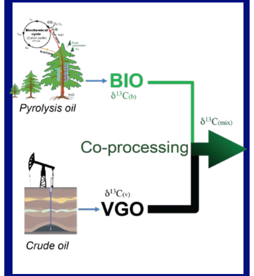
21 April 2022

LA-UR-22-23215

Presentation Overview

01

Why track biogenic Carbon



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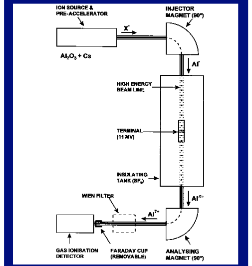
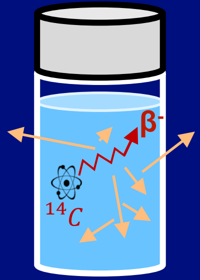
Standard Method



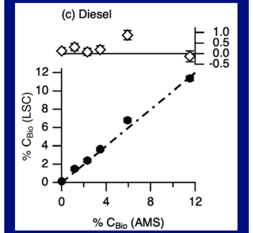
03

Direct LSC Approach



04

Results

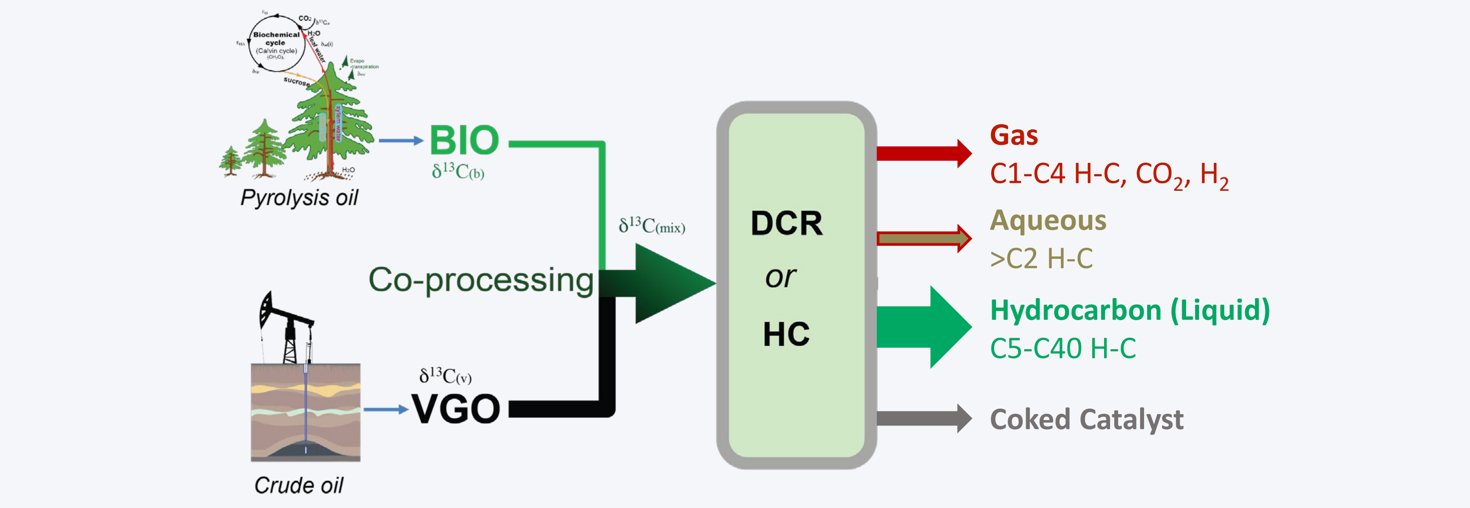


05

Future Approach

Why track biogenic Carbon?

- Co-processing of biogenic (*Pyrolysis Oil*) and fossil feedstock (*VGO*)
- Increasing biogenic blending increases waste products
- How much biogenic (renewable) carbon makes it into fuel products



How is the amount of biogenic carbon determined?

Method	Equip. Cost	Sample Cost	Time	Advantages	Disadvantages
ASTM D6866: AMS ^{14}C		$500	14 days	• Accurate • Universal for biomass	• External Analysis
ASTM D6866: LSC ^{14}C (Benzene)	<$100k	$200	1 day	• Accurate • Universal for biomass	• Technically difficult • Involves toxic/explosive chemicals
Representative Chemical (e.g. ASTM D7806)				• Fast	• Specific to feedstocks and upgrading techniques/conditions • Could be faked/cheated

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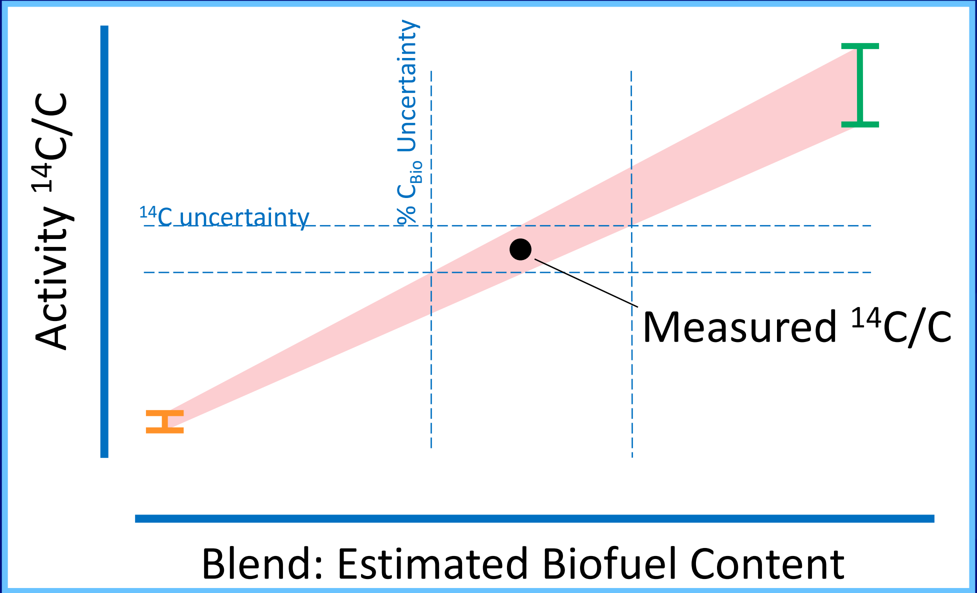
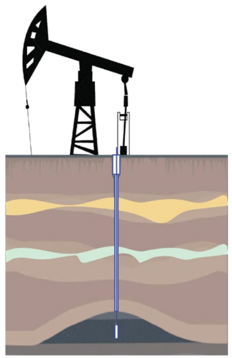
^{13}C EA-GCC-IRMS	<$300k	$10	15 min	• Fast • Applicable for most biomass	• Need to analyze feedstocks • Technical experience
LSC ^{14}C Direct	<$100k	$30	12 hours	• Technically simple • Universal for biomass	• Unknown uncertainty • Sample Color
Yield Mass Bal.				• Cheap	• Accuracy

How is the amount of biogenic carbon determined?

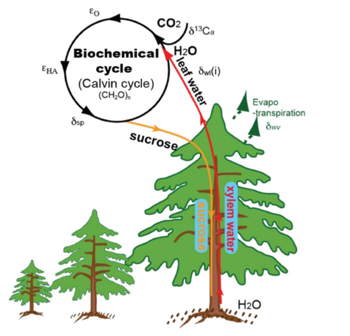
Blended Fuels



Fossil Derived Oils



$^{14}C = 0$ DPM/g

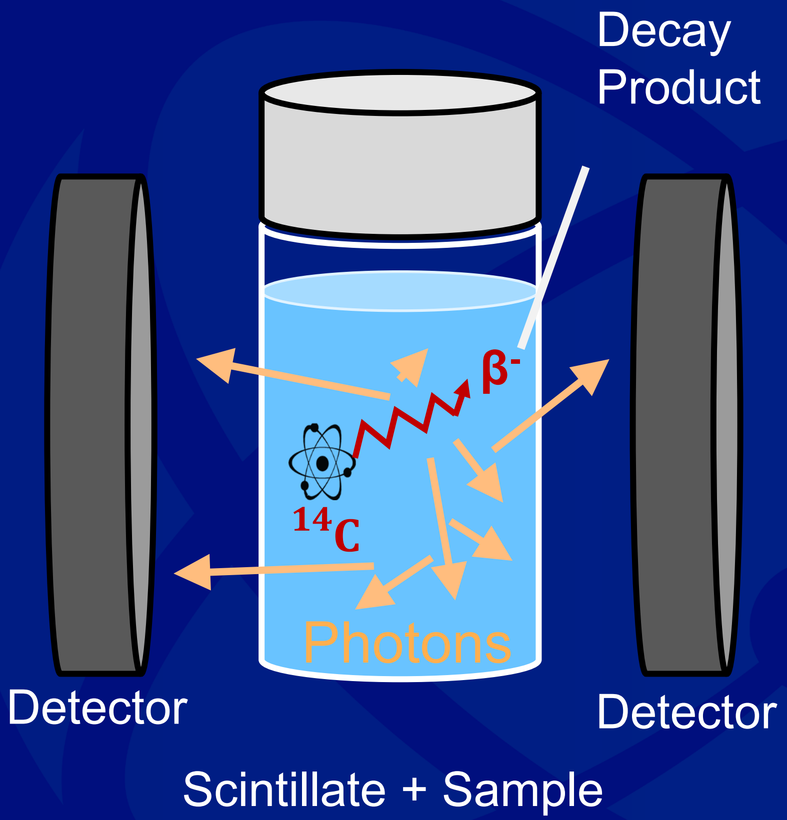


$^{14}C = 13.56^{+10-20\%}_{-5\%}$

Biogenic Oils & Fuels

^{14}C LSC Direct Measurement – It's Easy

1. Mix sample with "scintillate cocktail"
2. Radioactive atoms from sample decay
3. Photons are produced when decay products (beta particles) interact with scintillate solution
4. LSC counts:
   a. # of photon producing events
   b. LSC counts # photons during each event
   c. Create Energy Spectrum



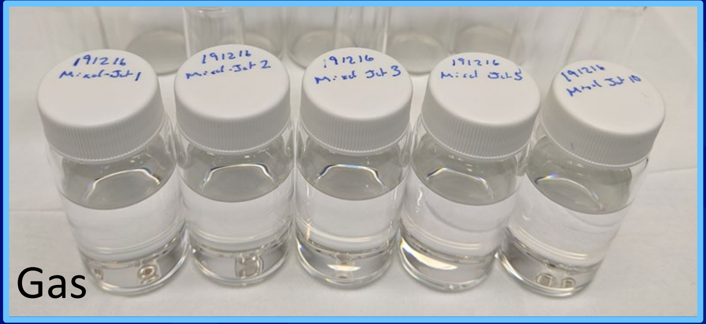
Methods for Optimizing and Testing

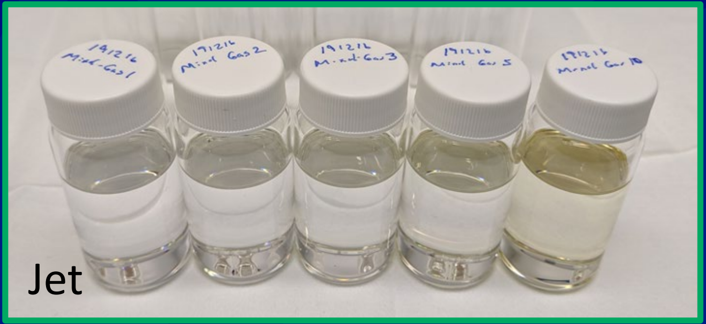
Process Optimization

- Sample Volume, Counting Period, ROI…

4 types of Biofuels blended

- PNNL HT pine saw dust fuels:
  - Gasoline (volatility < 150^{o}C)
  - Jet Fuel (150-250^{o}C)
  - Diesel (250-350^{o}C)
  - Fossil component: Toluene
  - Blends: 0%, 1%, 2%, 3%, 5%, 10%
- Commercial Diesel Blend
  - B100 + Toluene
  - Blends: 0%, 1%, 2%, 3%, 5%, 10%, 100%





Accounting for the effects of color and chemical composition

Effects of Chemical Composition

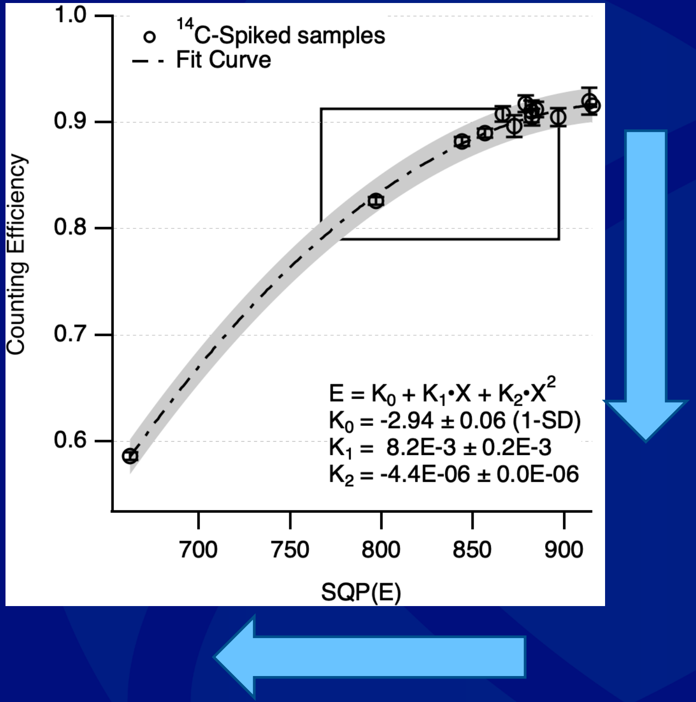
- Absorb decay energy or UV light

Effects of Color

- Absorb UV and visible light

Found: Best way to estimate 'E' is by calibration using control samples w/ similar matrix

$1\text{-}\sigma \approx 0.7\%$ (absolute)



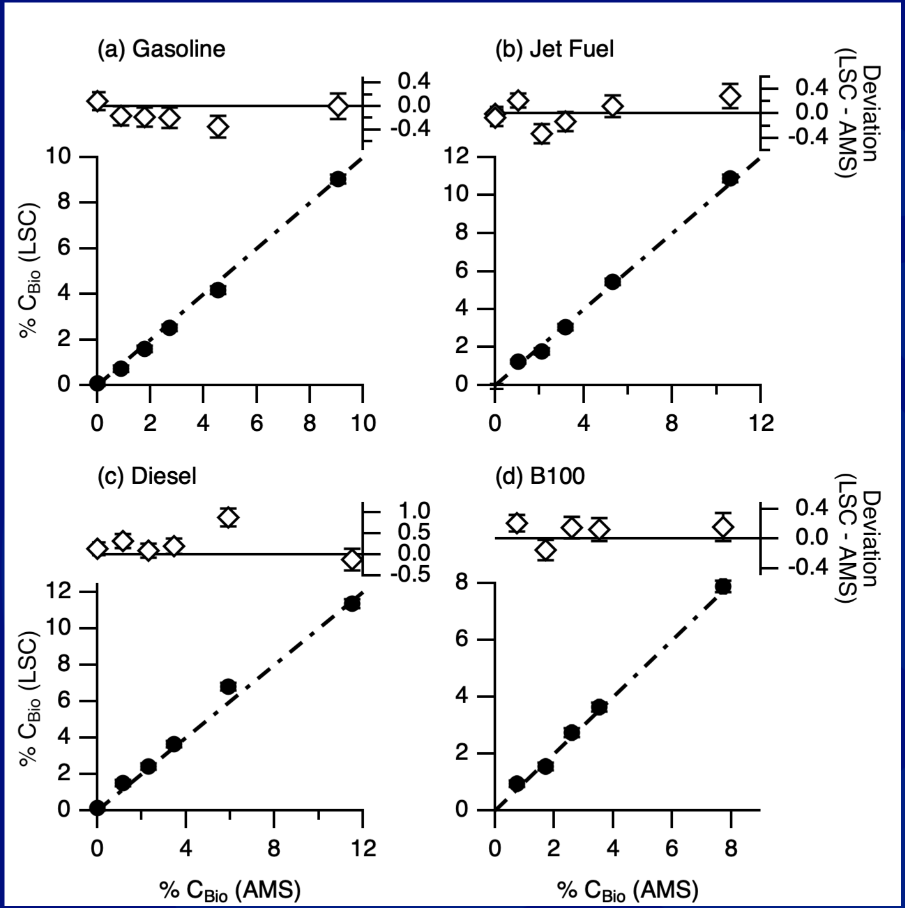
Performance of ^{14}C LSC Direct Analysis

Conditions

- 8-hour counting period
- 4-cycles of counting (total 24 hrs)
- PTFE-lined PE vials
- 5 mL of sample

Performance

- Precision: <0.2% C_{Bio}
- Accuracy: <0.5% C_{Bio}



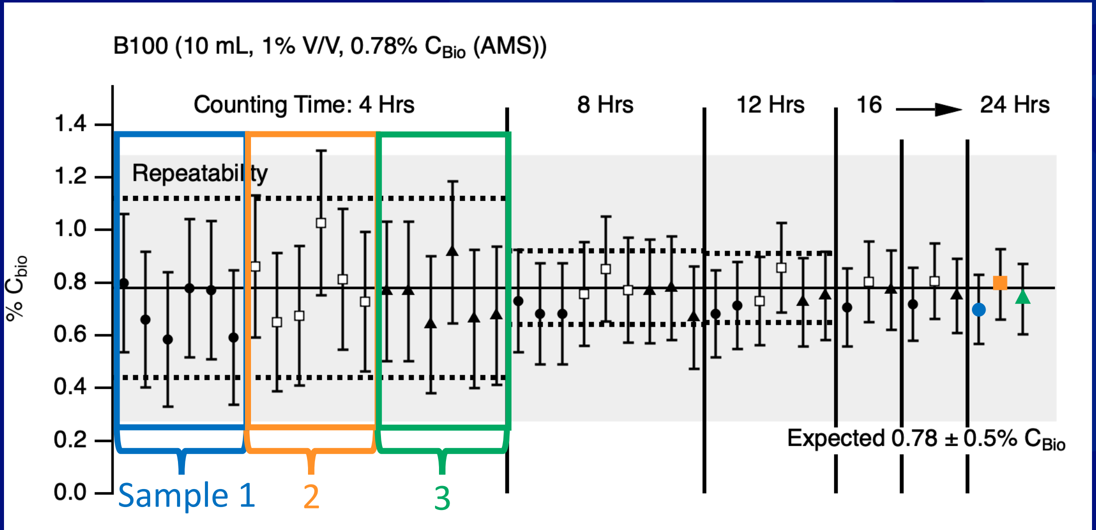
Reproducibility of the measurement

Conditions:

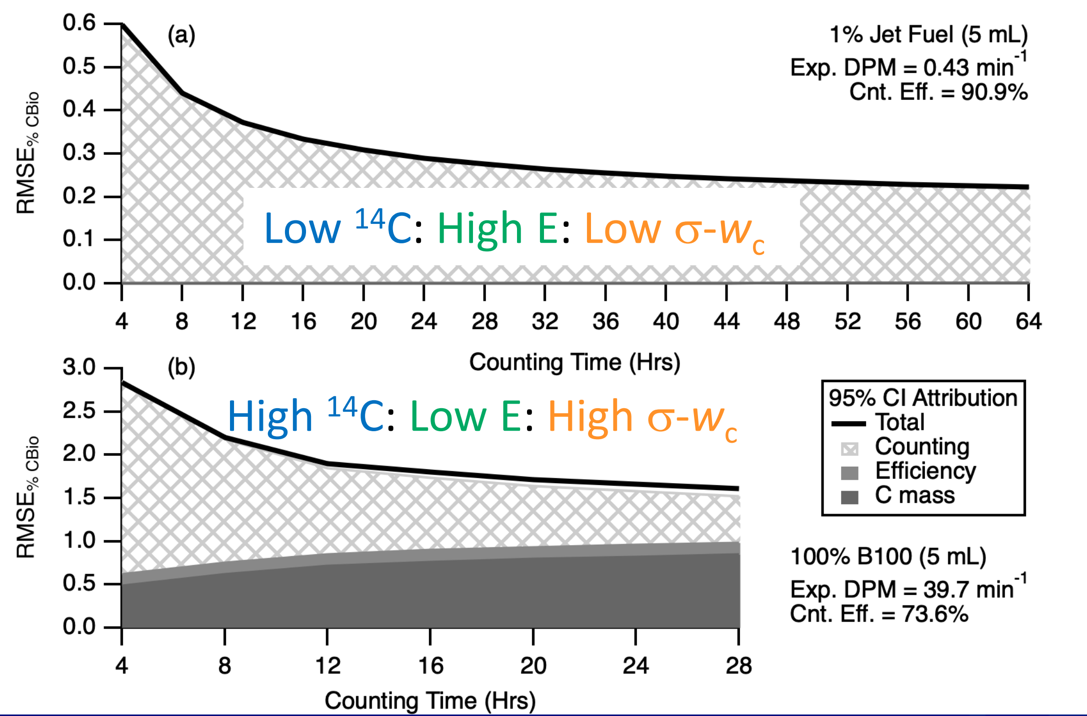
- 3 Identical samples (10 mL B100, 0.8% C)
- Count for 4 hrs, repeat 6 times
  - 8 hr count = 4 hr + 4 hr

Performance (4 hrs)

- Precision <0.25%C_{Bio}
- Repeatability ≈ 0.35 %C_{Bio}
- Decreases for longer counting periods



Source of Uncertainty in determining $\%C_{Bio}$



Uncertainty = f(V_{sample}, color, ^{14}C)

To achieve precision <1 $\%C_{bio}$

- 5 mL sample < 8 hrs
- 10 mL sample < 4 hrs

Sources of Uncertainty

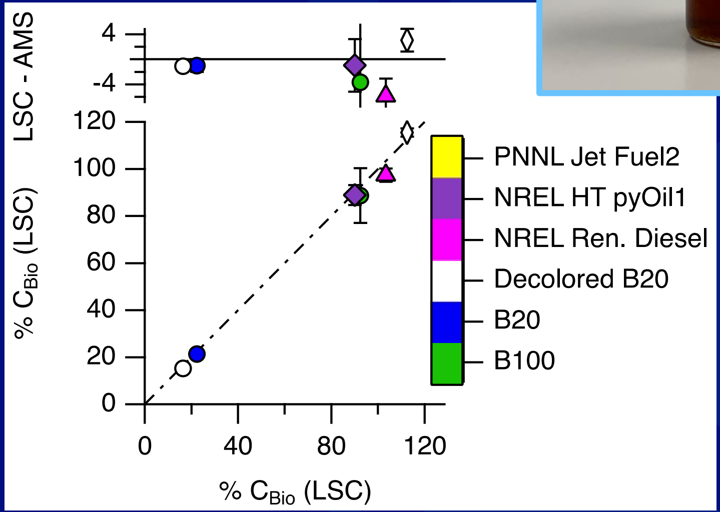
- All → Carbon Mass (σ≈0.3% abs.)
- Dark samples → Efficiency (σ≈0.7% abs.)
- Low ^{14}C → Counting and Background (σ≈0.05-0.22 min^{-1})

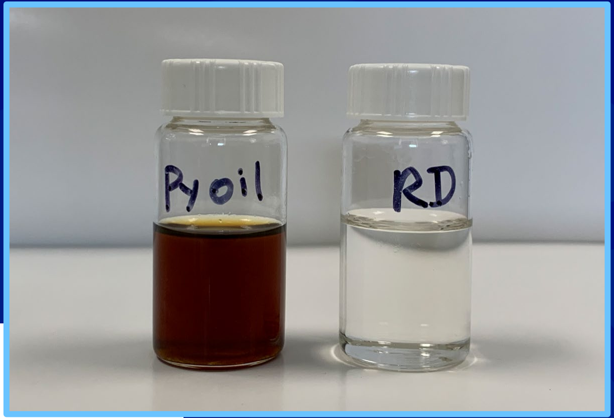
Application to Dark Colored Samples

Dilution – measuring a small quantity of sample

- HT-Pyoil (AMS = 89.04 pMC)

	1:1	19:1
Vol.	5 mL	0.5 mL
Eff.	<2%	73%
Dev.	N/A	1.0%





Limitations and Future Applications

- Color effects: exponentially more important with darker color
- C-wt %: Req’ independent measurement
- Liquid samples only

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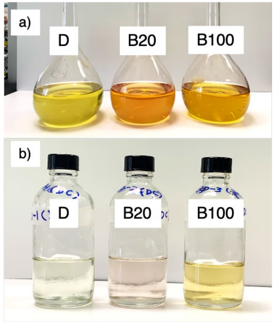
Decolorization Techniques:
Absorbents, Ozonization, bleaching



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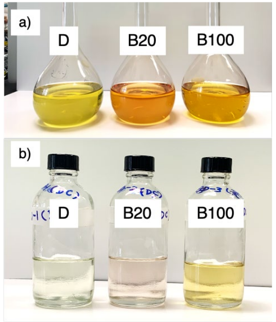
Limitations and Future Applications

- Color effects: exponentially more important with darker color
- C-wt %: Req' independent measurement
- Liquid samples only

CO_2 Conversion-Absorption: Consistent medium, Known C-wt %

Decolorization Techniques: Absorbents, Ozonization, bleaching



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Extra Slides

- Math

Direct LSC Approach – It's Easy

Analytical Steps to determine $\%C_{bio}$

1) Amount of ^{14}C: $D_{sample} = \frac{C_{sample} - C_{bkgd}}{E}$

2) Amount Carbon: $m_C = m_{sample} * w_C$

3) Biogenic Carbon Fraction: $\%C_{bio} = 100 \cdot \frac{D_{sample}/m_C}{A_{modern} \cdot REF}$

Variable Cheat-Sheet

C_{sample}	Sample Count Rate
C_{bkgd}	Background Noise
E	Counting Efficiency
m_{sample}	Sample Mass
w_C	Carbon Mass Fraction
A_{modern}	14C Content of Pre-Industrial Wood
REF	Modifier