

Decolorization of Biofuels and Biofuel Blends for Biogenic Carbon Quantification with Liquid Scintillation Radiocarbon Direct Measurement

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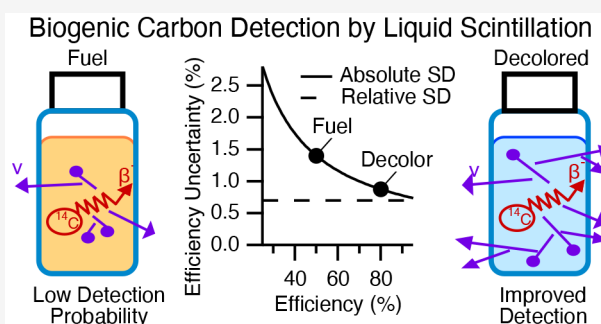
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ABSTRACT: Radiocarbon activity of fuels is a direct analog to the biogenic fraction of carbon in the fuel. The amount of radiocarbon in a fuel sample may be determined by liquid scintillation direct analysis if the sample is relatively transparent to ultraviolet light. However, many biofuels are colorful which adversely affects the counting efficiency of this technique and therefore the precision which the biofuel blend level may be determined. In such cases, decolorization may be an approach to improve measurement precision. Here, we present the effectiveness of several decolorization techniques for different fuel types. For some fuels, decolorization impacted the radiocarbon content of the sample; therefore, caution is necessary to ensure reliable assessment of biofuel blend levels.



INTRODUCTION

Quantifying the percent of biobased carbon ($\%C_{Bio}$) in fuels is essential for adoption and certification of biofuel products.¹ Commonly, blended fuel products are produced by combining refined biofuels with refined petroleum fuels, e.g., bioethanol with gasoline or biodiesel with fossil diesel. In coprocessing systems, where bioderived fats, oils, and greases are upgraded with fossil vacuum gas oils, tracking of biobased carbon can help optimize processing conditions and quantify the amount of biobased carbon converted to fuel.² Radiocarbon-based techniques offer the most universal approach to determining $\%C_{Bio}$. However, the two standard radiocarbon-based methods either require external analysis (ASTM D6866-20³ Method B: Accelerator Mass Spectrometer) or involve chemical conversion of the fuel to benzene that has health and safety hazards related to handling of highly flammable and carcinogenic materials (ASTM D6866-20³ Method C: Liquid Scintillation Counting).

Although not an ASTM accepted method, direct analysis of fuels with liquid scintillation counters (LSCs) has been shown to be precise and accurate in quantifying $\%C_{Bio}$.^{4,5} Direct analysis simply involves dispensing the sample into a vial and adding the scintillation cocktail for preparation for counting. This approach is more accessible but has two limitations. First, the direct analysis approach requires two separate measurements to determine (1) the amount of ^{14}C in the sample and (2) the total carbon mass of the sample.⁵ Second, the detection efficiency of the LSC is reduced if the sample is not colorless, as is common with biofuels, and must be determined either

through empirical parametrizations or through an internal spike process. Scintillation based spectroscopy depends on converting energy from decay radiation (beta particles) to light. Photons are produced through a series of reactions which multiply emissions and shift electromagnetic wavelength, primarily in the ultraviolet (UV) range. If the sample material can absorb energy at these wavelengths, then it will inhibit detection of decay events by the LSC photomultiplier tubes. This effect is called chemical quench and color quench, depending on which stage of reactions is disrupted.

To reduce the negative effects of quench, ASTM D6866-20³ Method C instructs users to convert the sample fuel to benzene; a material translucent to the emission energy spectra of the scintillate cocktail. As mentioned, this is a time-consuming, laborious, and potentially hazardous process. Alternative approaches include diluting the sample in an optically clear liquid (e.g., toluene)⁵ and fuel conversion to CO_2 .^{6–8} Diluting the fuel will reduce the color intensity but also reduces the sample size of biogenic carbon which negatively affects the precision of ^{14}C determination. Conversion of the fuel to CO_2 (followed by absorption of that CO_2 into an amine solution) also has a limited sample size

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(1.6–2.5 g CO₂), and the precision of this technique is currently not adequate for low blend-level fuels.^{9,10}

In this study, we explored another approach, decolorization of the fuel. Decolorization is the process of removing or degrading color-causing molecules or sections of molecules, i.e., chromophores. In organic molecules, color is often related to conjugated π -bonds in benzene-ring structures such as occurs in aromatics which are a common component in petroleum fuels. Colored components can also be naturally occurring in fats and oils as antioxidants. Oils derived from lignocellulosic biomass (bio-oils or pyrolysis oils) can also have very dark colors.¹¹ Hydroprocessing of fats and oils form *n*-paraffins which are then upgraded via isomerization for use as fuels, which are mostly colorless.¹² However, the aromatic structure of lignin in lignocellulosic biomass is largely retained in the monomers and dimers present in bio-oils derived via pyrolysis, which can become color-inducing aromatic hydrocarbons during hydroprocessing to fuels.¹³ The color and color intensity of the processed biofuel will depend on the biogenic carbon source and processing to make fuels.

In this manuscript, we test several decolorization techniques describing the techniques used, their effectiveness of removing color, and their impact on interpreting %C_{Bio} for first generation biofuel blends (i.e., fatty acid methyl esters and fossil diesel). The goal is to broaden the range of fuel types that the LSC direct measurement technique may be applicable to for biobased carbon tracking.

SAMPLE FUELS

Three types of fuel samples were used to test the decolorization techniques. All three were commercially purchased and sold as diesel, B20 (20% biodiesel blend), and B100 (100% biodiesel). These are blends that were mixed following refining of the biogenic and fossil fuels and chosen as readily available sources of renewable carbon containing fuels. It should be noted that biodiesel (long chain monoalkyl esters of fats and oils) will not necessarily contain the same chromophores encountered in coprocessed products. The decolorization approaches here should be further evaluated in the products of cofeeding fats and greases as well as bio-oils to test applicability of the techniques to developing technologies.

DECOLORIZATION TECHNIQUES

Adsorbents. Reduction of color may be accomplished by the addition of selective adsorbents such as silica gel,^{14–16} activated carbon,¹⁴ or various clays such as montmorillonite.^{17,18} These adsorbents have a high specific surface area and pore sizes which preferentially adsorb pigments^{14,17–20} which in biodiesel likely include carotenoids and chlorophylls.²¹ When the adsorbents are removed from solution, the color inducing molecules are also removed.¹⁶ Sometimes a mixture of adsorbents is used or an additional component (e.g., aluminum oxide) to improve adsorption.¹⁵ The latter reference suggests gravitational flow of the sample through a glass chromatography column packed with a layer of silica gel and a layer of aluminum oxide.

Here, we directly mixed silica gel and aluminum oxide with a fuel sample in a 20 mL glass LSC vial (method “Si+Al₂O₃”). Approximately 4.5 g of silica gel (Silica Gel 60, 0.040–0.063 mm, Millipore, 109385) and 7.5 g of aluminum oxide flakes (aluminum oxide 90 active basic, Millipore, 101076) were added to 15 mL of fuel. The sample was shaken and allowed to sit for 24 h. We then filtered the sample through a 0.02 μ m Whatman type filter (Whatman, 6809-2002) to remove the particulate adsorbents. The same process was followed using activated carbon (Alltech, 577, 2.4 g) and using bone char (20 \times 60 mesh, Charcoal House C-541, 3.5 g per 10 mL fuel) in

place of silica gel and aluminum oxide. Diesel fuel was used to test all three adsorbents.

A two-stage decolorization was also tested. This process used montmorillonite clay (Montmorillonite K10 powder, Sigma-Aldrich, 69866, 2.4 g) as a primary treatment. The fuel-clay slurry was placed on a hot plate at 60° with a glass stirring rod for 30 min and then left at room temperature overnight. Clay particulates were then removed with a centrifuge (12,000 rpm for 30 min). Silica gel and aluminum oxide were added as a secondary treatment (20 g of aluminum oxide and 10 g of silica gel). The fuel slurry was again placed on a hot plate, stirred, and allowed to sit at room temperature overnight. Silica gel and alumina oxide were removed via centrifuge.

Photo-oxidation. Oxygenation of chromophores breaks molecular bonds (π -bonds) causing ring cleavage (dearomatization) and reduces the molecules' ability to absorb light.^{22,23} Reactive oxygen species (ROS), such as hydroxyl (OH⁻), for oxygenation have been supplied through ozonization,²⁴ by addition of hydrogen peroxide,^{25–27} by addition of benzoyl peroxide,²⁸ and by water–air oxygenation.²⁹ Visible or UV light is used to produce ROS via a photolytic reaction. Frequently, catalysts such as titanium dioxide, silver nanoparticles, or gold nanoparticles are used to further promote formation of ROS.^{23,30–33}

We first prepared a baseline sample of approximately 15 mL of diesel in a 20 mL glass LSC vial. This sample was allowed to sit in a window sill for approximately 24 h. Two more samples were prepared similar to the baseline sunlight sample but with the addition of a photocatalyst: either copper wire (Copper Fine Wires Reduced 4 \times 0.5 mm, Elementar, 05 000 699)³⁴ or silver wool (Silver Wool 0.05 mm Fine Wire, Elementar, 22 131 365). The photocatalysts were to promote auto-oxidation with the small amount of oxygenated species in the fuels. The sample vial was gently shaken to mix the media with the fuel and then allowed to sit for approximately 24 h. The catalyst materials and all other particulates were removed with a 0.02 μ m Whatman syringe filter.

Efficacy of UV light was tested with the addition of another photocatalyst, titanium dioxide (Titanium(IV) Oxide, Supelco, TX0685-1). Titanium dioxide has a wide band gap and does not photochemically react in visible light but is a strong photocatalyst when excited by UV radiation. For this sample, 15 mL of diesel was mixed with 0.10 g of titanium dioxide. The sample was exposed to UV light (254 nm, 4000 μ W·cm⁻² at 2.5 cm distance) inside a foil lined box for 8 h.

Lastly, we supplied ozone using an ozone generator to a diesel sample mixed with a titanium dioxide photocatalyst and exposed to UV light. The sample was sealed in a 40 mL vial with a septum lid. Ozone flowed through a needle puncturing the septum and bubbled through the sample with a flow rate of approximately 1 lpm. A second needle punctured through the septum allowed for pressure regulation. The sample was exposed to ozone flow and UV light for 4 h and then left overnight.

Ozonization without catalysts and addition of hydrogen peroxide were also tested but not quantified. No visible change in the fuel color was observed with these approaches.

FUEL SAMPLE ANALYSIS

Spectrophotometry. Sample color was determined using spectrophotometry using an Agilent G1115 in the range of 370–1100 nm wavelength. Light absorption was scanned in 1 nm resolution with a total scan time of 5 s. Each sample was scanned a minimum of three times. Toluene, a common reference for liquid scintillation counters, was used as a reference material for the absorption spectrum. The reference spectrum was measured between each fuel sample. A single 10 mm path length quartz cuvette was used for all samples, including the reference samples.

Six decolorization methods were applied to diesel fuel samples and measured with spectrophotometry: sunlight, ozonization, Si+Al₂O₃, activated carbon, bone char, sunlight

+ copper wire, and sunlight + silver wool. Additionally, unmodified diesel fuel was also measured to determine the impact of the decolorization techniques. We quantified color removal with the parameter “decolorization efficiency” (DE) at several wavelengths (λ):

$$DE(\lambda) = 100 \cdot \frac{Abs_{fuel}(\lambda) - Abs_{decolor}(\lambda)}{Abs_{fuel}(\lambda)} \quad (1)$$

Absorption (Abs) is the fraction of light that is absorbed along the optical path length and is equal to one-minus-transmittance ($Abs = 1 - T$). Transmittance values are the measured light intensity (I) at a specific wavelength relative to the intensity through the reference material ($T = I/I_{ref}$). It is possible that more light passes through the sample than through the toluene reference which would result in Abs to be less than 0, T to be greater than 1, and DE to be interpreted as greater than 100%.

Liquid Scintillation Spectrometry. A liquid scintillation direct-measurement technique was used to determine the liquid scintillation counting efficiency (E) and ^{14}C content and uncertainty.⁵ Samples were measured with a PerkinElmer Quantulus 1220 instrument. A sample volume of 10 mL was mixed with 10 mL of Ultima Gold F scintillation cocktail (PerkinElmer, PN 6013171, Batch 78-21061). Sample quantity was determined by mass. Each sample was counted for a total of 24 h (6 repeats of 4-h periods). A 10 mL toluene sample was used to determine the background count rate.

Counting efficiency was determined using a parallel-sample internal-spike method.⁵ In this method, two identical samples are prepared. The first sample provides the count rate of the fuel (C_{fuel} min⁻¹). The second sample is spiked with 1 mL of solution of ^{14}C -internal spike organic solvent (PerkinElmer, PN 120-122, Batch 2020A) dissolved in Ultima Gold F in place of 1 mL of the scintillation cocktail. This spike quantity can be precisely weighed and the solution activity (count rate per mass solution, min⁻¹·g(solution)⁻¹, A_{spike}) determined by independent measurement. The spike activity was approximately 1000 min⁻¹·g(solution)⁻¹. The counting efficiency (E) was then calculated as

$$E = \frac{C_{spike} - C_{fuel}}{A_{spike} \cdot m_{spike}} \cdot E_{std} \quad (2)$$

where C_{spike} is the count rate of the spiked sample, m_{spike} is the mass of the spike solution added, and E_{std} is the absolute counting efficiency as determined by a PerkinElmer sealed ^{14}C standard.

Fuel samples for LSC analysis include unmodified commercial fuels and decolored fuels. The decolorization process used for these samples was the two-stage montmorillonite and Si+Al₂O₃ treatment. The decolorization process was applied to diesel, B20, and B100 fuel samples.

Sample fuel activity (decay rate per mass carbon, min⁻¹·g(C)⁻¹) was also determined for all LSC samples measured following Lee et al.⁵ The sample carbon mass fraction (w_{fuel} g(C)·g(fuel)⁻¹) was determined using an elemental analyzer system following methods described in Geeza et al.³⁵ The fuel activity is calculated as

$$A_{fuel} = \frac{C_{fuel} - C_{Bkgd}}{E \cdot w_{fuel} \cdot m_{fuel}} \quad (3)$$

The ^{14}C content of a fuel is expressed in terms of percent modern carbon (pMC), where the activity of modern carbon

(A_{modern}) is defined as 13.56 min⁻¹·g(C)⁻¹ which is the decay rate of 1 g of carbon from wood from the year 1890.^{3,36} The ^{14}C content of a fuel sample (P_{fuel}) is

$$P_{fuel} = 100 \cdot \frac{A_{fuel}}{A_{modern}} \quad (4)$$

Accelerator Mass Spectrometry. The current gold standard for determining ^{14}C content is by accelerator mass spectrometry (AMS).^{2,9} ASTM D6866-2³ describes the use of AMS for determining biocarbon content in fuel blends. Samples of unmodified diesel, B20, and B100 and decolored B20 were analyzed by Beta Analytic Testing Laboratory (Miami, FL, USA) following ASTM D6866-20.³

Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy (GC-VUV). Untreated and decolored diesel and B20 samples were analyzed for bulk hydrocarbon classes and fatty acid methyl ester (FAME) content via ASTM D8368-22³⁷ at the National Renewable Energy Laboratory (Golden, CO). This method is the standard technique for analyzing renewable diesel fuels produced through transesterification, where fats, greases, and oils are converted to fatty acids which describes most currently available commercial renewable diesel fuels and diesel blends.³⁸

FAME content is the summation of individual fatty acid methyl esters and is usually reported as % volume. Uncertainty of these results is better than 1.7%. The applicable range of FAME content for this method is 1–21.6% volume. The B100 and decolored B100 samples are outside of this range and were not analyzed with this technique.

In FAME-based diesel fuels, fossil methanol is used for transesterification which results in a fraction of carbon in renewable diesel derived from fossil carbon.²¹ The fossil fraction will vary depending on the molecular weight of triglycerides used to produce FAME. Here, we assume that renewable diesel is comprised of 95% modern carbon^{21,39} in order to compare results to AMS results.

RESULTS AND DISCUSSION

Spectrophotometric Determination of Color. Scintillation-based detectors detect decay events when the decay energy is transferred to produce photons in the scintillate cocktail. The primary fluor in the Ultima Gold F cocktail, 2,5-diphenyloxazole (PPO), absorbs energy in the 250–350 nm wavelength band and re-emits energy in the 325–450 nm band. A second transfer occurs with the secondary fluor, *p*-bis(*o*-methylstyryl)benzene (bis-MSB). The absorption spectrum of bis-MSB is 250–400 nm with re-emission focused at 400–430 nm.⁴⁰ The sensitivity of the instrument photomultiplier tubes (PMTs) is optimized for the emission spectra of bis-MSB. Absorption of energy by the sample at any of these frequency bands will reduce the counting efficiency.

The absorption spectra of diesel fuel show that diesel had a high absorbance at wavelengths below 380 nm with generally decreasing absorbance at higher wavelengths. A local maximum in absorbance is observed at around 445 nm (Figure 1a). Absorbance at these wavelengths disrupts the energy transfer between the primary and secondary fluors as well as detection by the PMTs. The lowest absorption of decolored samples, across spectra, was produced by decolorization by adsorbents (Si+Al₂O₃, activated carbon, and bone char). Visual inspection of the decolored samples supported this observation (Figure

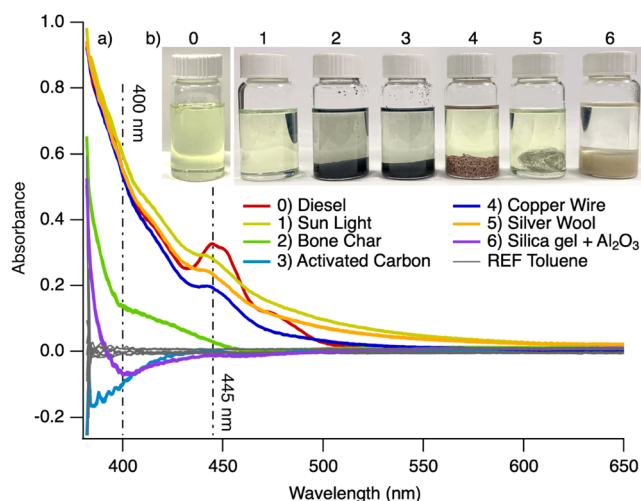


Figure 1. Measured and qualitative impact of various decolorization techniques on commercial diesel. (a) Absorption spectra of diesel and decolorized diesel samples. (b) Photographs of diesel fuel and decolorized diesel samples prior to removal of decolorization media.

1b). For the Si+Al₂O₃ treatment, decolorization appeared to occur within a few minutes. It is important to note that visual assessment is imperfect since the visible light spectrum (approximately 380–750 nm) only partially overlaps with the primary bands important for LSC analysis (<250–500 nm).

Here, we describe the reduction of sample color at two characteristic wavelengths. The first wavelength at 445 nm corresponds to a local peak in the diesel absorption spectra. The second wavelength at 400 nm is the peak emission of bis-MSB and peak sensitivity of the liquid scintillation counter. Previously, it has been suggested to quantify decolorization at 375 nm⁴¹ or at 410 nm.¹⁸ The shorter wavelength, 375 nm, is important for energy transfer between the primary and secondary fluors but is near the edge of detection for the spectrophotometer. As shown in Figure 1, absorbance at 400 nm was much higher than at 410 nm, and 400 nm is more influential to counting efficiency due to higher light emission by bisMSB at this wavelength and higher sensitivity of the PMT.

Effectiveness of the decolorization techniques is shown in Figure 2. The Si+Al₂O₃ technique nearly completely removed the color at 375 (not shown), 400, and 445 nm. Activated carbon had similar efficacy above 90% decolorization efficiency for 400 and 445 nm. Bone char had high decolorization efficiency for 445 nm but was less effective at 400 nm. Oxidation techniques (sunlight, copper wire, and silver wool) were not effective at removing color, particularly at 400 nm. While sunlight did slightly decrease color intensity at 445 nm, the absorption peak was broadened and seemed to increase color intensity across other wavelengths.

LSC Counting Efficiency. Efficacy of decolorization was also determined by quantifying the increase in LSC counting efficiency (*E*). Si+Al₂O₃ treatment was the most effective technique at removing color in spectrophotometric analysis. This approach was built upon with a two-stage adsorbent decolorization as described earlier. Photographic results of the decolorization process are shown in Figure 3. LSC counting efficiency was determined with a parallel-sample internal spike method.

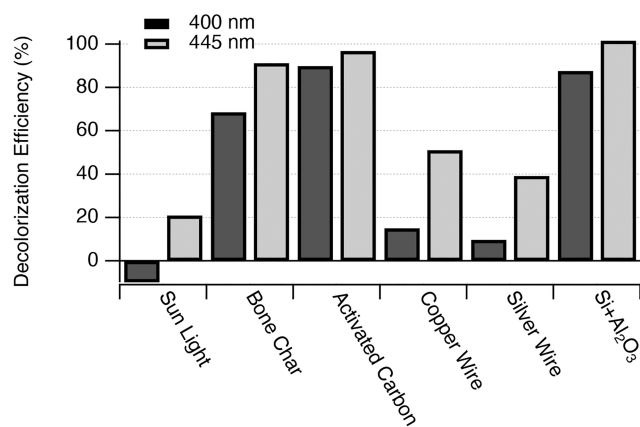


Figure 2. Decolorization efficiency (DE) of various decolorization techniques. DE is calculated at two wavelengths corresponding to an absorption peak of unmodified diesel at 445 nm and peak emission wavelength of bis-MSB at 400 nm.

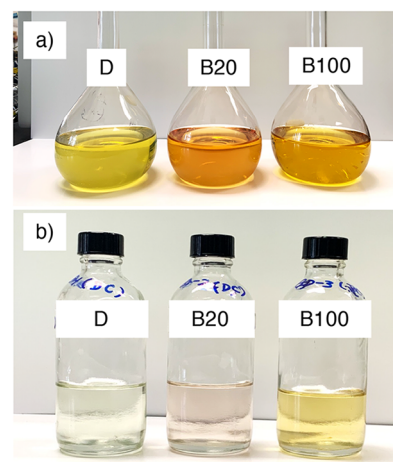


Figure 3. Photographs of (a) unmodified diesel (D), B20, and B100 fuel samples and (b) decolorized diesel, B20, and B100 fuel samples used for LSC analysis. The decolorization technique for these samples was the two-stage silica gel and aluminum oxide and montmorillonite process.

Counting efficiency was as follows: unmodified diesel fuel, 53.5%; unmodified B20, 60.7%; and unmodified B100, only 22.6% (Table 1). All of the tested fuels are considered to be highly quenched.

The two-stage decolorization technique had a significant impact on increasing LSC counting efficiency (Table 1). The most dramatic increase was observed for the very highly quenched B100 fuel, increasing *E* from 22.6 to 69.0%.

Table 1. Counting Efficiency of Fuel Samples and Decolorized Fuel Samples^a

	sample efficiency ± SD (%)	decolorized efficiency ± SD (%)
diesel	53.5 ± 0.2	80.5 ± 0.4
B20	60.6 ± 0.2	83.8 ± 0.4
B100	22.6 ± 0.1	69.0 ± 0.3

^aCounting efficiency was determined with a parallel sample, internal spike technique.⁵ Decolorized samples have been treated with a two-stage technique: first with montmorillonite clay and then with silica gel and aluminum oxide.

However, the increase in E did not decrease the uncertainty in determining P_{fuel} (Table 2). Analytically, this uncertainty is

Table 2. Biogenic Carbon Percent of Fuel Samples and Decolored Fuel Samples as Determined by AMS D6866-20, LSC Direct Analysis, and GC-VUV D8368-22

	method	Fuel %C _{Bio} ± SD	Decolored %C _{Bio} ± SD	Δ %C _{Bio} ± SD ^a
diesel	AMS	2.44 ± 0.04		
	LSC	1.6 ± 0.02	0.4 ± 0.1	-1.2 ± 0.2
	GC-VUV	2.6	0.1	-2.5
B20	AMS	22.34 ± 0.10	16.3 ± 0.09	-6.01 ± 0.13
	LSC	21.7 ± 0.2	15.9 ± 0.2	-5.8 ± 0.3
	GC-VUV	22.5	16.7	-5.8
B100	AMS	92.40 ± 0.27		
	LSC	90.6 ± 0.9	90.0 ± 0.8	-0.5 ± 1.2

^aThe difference in the biogenic carbon percent of the fuel sample and the decolored sample is due to the decolorization process.

dominated by the uncertainty of the count rate of the fuel sample and background sample (background count rate of approximately $3.5 \pm 0.03 \text{ min}^{-1}$). The parallel-sample internal spike technique may under-represent uncertainty in E that could be related to unequal preparation of the parallel samples, homogeneity of the spike solution, imperfections of vials, or some other process. In Lee et al.,⁵ we used a quench curve to determine E , and the fit of this curve had an uncertainty of approximately 0.7% absolute (1 standard deviation). This value may be a more holistic estimate of uncertainty and would imply an improvement in relative uncertainty of %C_{Bio} from approximately 3% to 1%.

Biogenic Carbon Percent Results. Results of ¹⁴C analysis by AMS and by the LSC direct analysis technique and of GC-VUV FAME analysis are provided in Table 2. Overall, we see good agreement between the three methods.

These analyses show that these fuels contained 2%, 22%, and 92% biogenic carbon for diesel, B20, and B100, respectively. The standard specification for diesel fuel in the US allows for up to 5% biodiesel,⁴² and it is common for fuel producers to add a small quantity of biodiesel. The measured blend level of the B20 sample is higher than the stated blend level but is not outside of the observed variance.⁴³ The result for the B100 sample being lower than 100% is partially related to the use of methanol in the production of fatty acid esters as previously discussed. The mass percent of this nonrenewable carbon accounts for roughly 5 wt % on average^{21,39} which does not fully account for the low biogenic carbon.

In the B100 sample, which is nominally 100% biodiesel, the decolored sample was found to contain the same ¹⁴C content as the unmodified sample. This observation implies that the removal of color-inducing chemical species did not affect the inferred biogenic fraction because the removed species contained the same ¹⁴C content as the bulk biodiesel fuel.

However, both the diesel and B20 samples were likely blended at the terminal, prior to being offered for sale at the commercial station. In these samples, we saw a large decrease in %C_{Bio} content of 1 and 6% for diesel and B20, respectively. While decolorization of these samples drastically reduced color intensity, we also observe a significant removal of biogenic carbon in both the reduction in ¹⁴C content and FAME. This implies that biogenic molecules are preferentially adsorbed

relative to fossil hydrocarbon diesel. Chromophores are expected to account for a small fraction of the fuel composition, less than the inferred decrease in biogenic content. It is not clear whether chromophores are preferentially removed in comparison to other biogenic molecules or whether there could be an optimal quantity of adsorbent to reduce bias because fuels will vary in blend levels and in composition of the biogenic fuel.

For fuels blended outside the refinery, we do not recommend adsorption-based decolorization techniques due to this process altering the biogenic carbon content in the blend. This is a major hurdle for adoption of an LSC direct analysis technique for verification purposes, as currently this is how most commercial biofuel blends are blended.³⁸

Ongoing research has focused on the coprocessing of bioderived fats, oils, and greases with fossil vacuum gas oils which will also benefit from more accessible ¹⁴C-based approaches for determining %C_{Bio} for process control. Since processing occurs at high temperature (700–900 °C), it would be expected that the refined fuels are isotopically homogeneous. In addition, the resulting renewable carbon would be in the form of hydrocarbons which would not be preferentially adsorbed, as may be the case with ester based biofuels. Decolorization may therefore be applicable to coprocessed fuels without altering the fuel ¹⁴C content but should be tested.

CONCLUSION

We discuss several techniques to remove color from fuel samples in order to improve the precision of the LSC direct measurement techniques and to broaden the types of samples applicable to these techniques. Decolorization using common adsorbent materials, specifically by addition of silica gel to the fuel, effectively reduced the sample color intensity, increased LSC counting efficiency, and had great potential to increase the precision of determining %C_{Bio}. Visually, immersion of silica gel into the fuel sample removed color within a few minutes requiring minimal additional preparation time and complexity.

However, decolorization of samples can potentially bias %C_{Bio} results by preferentially removing biogenic carbon from the blend. Likely, this fractionation was due to blending of refined biofuel and fossil fuel products. We still expect decolorization to be applicable to coprocessed fuels due to the high temperatures during processing (700–900 °C) that should promote isotopic homogeneity. Although a technique to degrade chromophores is preferred since it would not remove carbon from the sample, none of the techniques that were tested were effective.

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Notes

The authors declare no competing financial interest.

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