Determination of Biodiesel Blending Percentages Using Natural Abundance Radiocarbon Analysis: Testing the Accuracy of Retail Biodiesel Blends

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Blends of biodiesel and petrodiesel are being used increasingly worldwide. Due to several factors, inaccurate blending of these two mixtures can occur. To test the accuracy of biodiesel blending, we developed and validated a radiocarbon-based method and then analyzed a variety of retail biodiesel blends. Error propagation analysis demonstrated that this method calculates absolute blend content with ± 1% accuracy, even when real-world variability in the component biodiesel and petrodiesel sources is taken into account. We independently confirmed this accuracy using known endmembers and prepared mixtures. This is the only published method that directly quantifies the carbon of recent biological origin in biodiesel blends. Consequently, it robustly handles realistic chemical variability in biological source materials and provides unequivocal apportionment of renewable versus nonrenewable carbon in a sample fuel blend. Analysis of retail biodiesel blends acquired in 2006 in the United States revealed that inaccurate blending happens frequently. Only one out of ten retail samples passed the specifications that the United States Department of Defense requires for blends that are 20% biodiesel (v/v; referred to as B20).

Introduction

With the rapid rise in the price of crude oil, projected decreases in oil supplies, and increasing concerns about climate change, alternative fuels have gained interest (*1*). One option is biodiesel, which is a mixture of fatty acid methyl esters (FAMEs) prepared from the transesterification of animal fats and vegetable oils with methanol (*2*). Proponents of biodiesel emphasize its ability to enhance engine lubrication, decrease emissions of aerosols and SO_2, and decrease dependence on foreign oil imports for many countries (*1, 3*).

It also has a higher flash point, which allows for safer handling (*3*), and it has been proposed as a partial strategy for controlling CO_2 emissions because it is partly carbon neutral (*1, 4*).

The chain length and degree of unsaturation in FAMEs varies in animal fats and vegetable oils (*5*). Most biodiesels are mixtures of methyl hexadecanoate (C_{16} FAME), methyl octadecanoate (C_{18} FAME), and C_{18} FAMEs with one, two, or three double bonds (referred to as $C_{18:1}$, $C_{18:2}$, or $C_{18:3}$ FAMEs, respectively), but they may also include FAMEs ranging from C_8 to C_{22}. A mixture of 100% FAMEs is called B100.

Biodiesel blends are formulated with B100 and petrodiesel on a volume/volume (v/v) basis to yield B2 (2% biodiesel mixed with 98% petrodiesel) to B99.9. They are available in the United States at over 1000 distributors and prepared by private consumers or user groups. Unfortunately, inaccurate blends can occur (*6, 7*). For example, since B100 is slightly denser than petrodiesel, stratification and hence insufficient mixing can result when the two liquids are combined (*6*). Inaccurately prepared blends, especially when the biodiesel content is greater than expected, can be problematic (*7*). For vehicles built prior to 1993, long-term usage of high biodiesel blends can damage hoses and gaskets (*6*). The cloud points of biodiesel blends are also temperature sensitive. For example, they have been measured at −22, −17, and 3 C° for B2, B20, and B100 products, respectively (*6*). Hence, in cold regions with improperly prepared blends, FAMEs may freeze and then clog filters (*6*). Inaccurate blending can also affect how tax rebates or reductions are determined. Most vehicle manufacturers recommend against using biodiesel blends greater than B20.

Knothe (*8*) recently reviewed a variety of methods developed for determining blend percentages (*9–17*). They include saponification number (*9*), ester number (*10*), infrared spectroscopy (IR) (*9–12, 17*), near-infrared spectroscopy (NIR) (*11–13*), ¹H nuclear magnetic resonance spectroscopy (NMR) (*13*), gas chromatography (*14*), and liquid chromatography (*15, 16*). These methods have important limitations. In particular, spectroscopic and saponification methods rely on calibration curves using several different blending ratios (*9–17*). With the exception of ref (*11*), these calibrations assume that the biodiesel component has the same FAME average molecular weight across all fuel blends; however, biodiesel FAME average molecular weight varies significantly across different source organisms (*18*). Additionally, spectroscopic and wet chemistry (saponification and ester number) methods measure the presence of the carbonyl group in the FAMEs, and this secondary chemical property may not comprehensively select for recent biological materials. For example, FAME mixtures yielded by transesterification of jojoba oils may contain significant amounts (∼20% by mass) of long-chain alcohols (*19*), which are undetected with current spectroscopic and chemical methods, but will contribute to the biological mass and thermal value of the fuel. Finally, most methods have been only tested for a limited range of blend percentages (*9, 10, 12, 15–17*). Notably, the only officially recognized standard, European Standard 14078 (*17*), measures the carbonyl group via IR and is specified for the B1.7 to B22.7 range.

We hypothesized that a method based on the natural radiocarbon (¹⁴C) abundance of biodiesel blends would overcome many of the restrictions of previous methods. We aimed to develop a method that (1) accurately determines blending ratios on a v/v basis over the range of B0 to B100; (2) requires little or no *a priori* knowledge of the types of B100 or petrodiesel components used to prepare the blend;

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and therefore (3) does not require mixture calibration curves. Radiocarbon is produced in the atmosphere by collisions between cosmic-ray neutrons and ^{14}N, after which it is quickly oxidized to CO_2 (20). Plants take up the $^{14}CO_2$ for photosynthesis, and consequently they reflect "modern" levels of ^{14}C (20, 21). Once assimilation of ^{14}C ceases, levels of ^{14}C decrease through radioactive decay with a half-life of 5730 years. The remaining ^{14}C can be detected in materials as old as ~50,000 years. Hence, petroleum, which forms over millions of years, contains no detectable ^{14}C. Therefore, ^{14}C is an ideal tracer for tracing the biological component of biodiesel in blends because all recent natural products are effectively prelabeled with ^{14}C. Measurement of ^{14}C is available at numerous laboratories, and blend percentages can then be determined via mass balance calculations.

Here, we describe a ^{14}C-based method to determine biodiesel blend percentages. To develop the method, we measured the ^{14}C content of several materials: fats and oils often used to produce B100, several different B100s, pure petrodiesels, and prepared biodiesel blends with known mixture ratios. After carefully validating the method, we evaluated more than 20 biodiesel blends purchased from retailers around the United States.

Materials and Methods

Obtaining and Preparing the Fuel Mixtures Used in This Experiment. We obtained biodiesel blends, as well as fats, oils, and other samples from around the United States mainly during the spring and summer of 2006. The locations and times of collection are listed in Table 1. From two biodiesel distributors, we collected numerous samples over several months in order to gauge the variability of their products. Based on discussions with the retailers, most were independent companies that prepared modest volumes of biodiesel blends on-site.

Stable Carbon and Radiocarbon Analysis. Stable carbon and ^{14}C analysis of organic carbon is described in detail in ref (22). Briefly, each sample was quantitatively converted from organic carbon into CO_2 and then graphite. On a small fraction of the CO_2, the stable carbon isotope ratios (δ^{13}C) were determined via isotope ratio mass spectrometry. The ^{14}C content of the graphite was measured by accelerator mass spectrometry (AMS) at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility in Woods Hole, MA (22). In this study, all ^{14}C measurements are normalized to δ^{13}C values of −25‰ and expressed with the Δ^{14}C nomenclature, which is the per mille (‰) deviation from the international ^{14}C standard, National Institute of Technology (NIST) Standard Reference Material 4990B "*Oxalic Acid I*". The latter was isolated from a crop of sugar beet grown in 1955 (23). (See also Supporting Information Figure S1).

The uncertainty of the measured ^{14}C value of each sample was important for evaluating the precision of subsequent calculations. For example, one biodiesel blend was analyzed twice over a several month period and the values were within 1‰ of each other (Table 1). In general, measurement precision varies with respect to ^{14}C content. To assign an uncertainty for any given ^{14}C value, we relied on the analysis of standards over the past two years at the NOSAMS facility. For example, standards that have values near −950 and 0‰ have uncertainties that are approximately 1 and 4‰, respectively.

Determination of v/v Biodiesel Blend Percentages Based on the Measured Δ^{14}C. We determined that the v/v blend percentage of biodiesel in a realistic fuel mixture could be estimated based on its ^{14}C content, as follows. First, we apportioned the carbon of the fuel blend with respect to the modern (biological) component and fossil (petrodiesel) component using Δ^{14}C mass balance:

$$\Delta^{14}C_{mixture} = F_{C,bio}\Delta^{14}C_{bio} + (1 - F_{C,bio})\Delta^{14}C_{petro} \qquad (1)$$

where $\Delta^{14}C_{mixture}$ is the measured ^{14}C content of the biodiesel blend via AMS. We assigned $\Delta^{14}C_{bio}$ as the average measured value of several retail fat and oil sources used in biodiesel preparations (62 ± 7‰; Table 1), and we confirmed that this was consistent with modern corn $\Delta^{14}C_{bio}$ levels in North America (an average range of 55 to 66‰, collected in 2004) (24). The $\Delta^{14}C_{petro}$ was fixed at a value −1000‰, consistent with measurements of petroleum endmembers (Table 1). Finally, $F_{C,bio}$ is the mass fraction of the total mixture carbon that is derived from biological components.

Rearranging eq 1, $F_{C,bio}$ can be expressed as

$$F_{C,bio} = \frac{\Delta^{14}C_{mixture} - \Delta^{14}C_{petro}}{\Delta^{14}C_{bio} - \Delta^{14}C_{petro}} \qquad (2)$$

Equation 2 shows that the proportion of biological carbon in the sample fuel blend ($F_{C,bio}$) can be easily determined based on the measured $\Delta^{14}C_{mixture}$ of the sample and the *a priori* known $\Delta^{14}C_{bio}$ and $\Delta^{14}C_{petro}$ values of the endmember materials. We assumed that $\Delta^{14}C_{petro}$ (−1000‰) and $\Delta^{14}C_{bio}$ (62 ± 7‰) represent reasonably constant endmembers, such that variation in $F_{C,bio}$ is fully explained by the measured $\Delta^{14}C_{mixture}$ value. (As explained in the subsequent section, we also assessed the uncertainty propagating from this assumption.) Notably, in current B100 production practice in the United States and Europe, the transesterification step from fats to FAMEs utilizes fossil methanol. For example, for a C_{18} FAME, 18/19 of the carbon (fatty chain) is from fats and oils and the other 1/19 (methyl carbon) is petroleum-derived; this was corroborated by numerous ^{14}C analyses of industrial methanol (see Results and Discussion for more detail). In order to relate $F_{C,bio}$ more precisely to the B100 endmember, we defined

$$F_{C,B100} = \frac{F_{C,bio}}{R_{C,bio/B100}} \qquad (3)$$

where $F_{C,B100}$ is the mass fraction of B100 carbon in the biodiesel blend, and $R_{C,bio/B100}$ is the ratio of biological carbon to total carbon in the pure component B100. We parameterized $R_{C,bio/B100}$ based on the compositions of different FAMEs sources that were measured in our laboratory and found in the literature (Table 2).

The blend percentage (v/v) of B100 (B*) in a fuel blend may be calculated as

$$B^* = 100\frac{V_{B100}}{V_{B100} + V_{petro}} \qquad (4)$$

where V_{B100} and V_{petro} are the extensive volumes of the biological and petroleum-based components, respectively, in a control volume of fuel blend. The individual component volumes can be expressed as

$$V_x = \frac{m_{C,x} + m_{H,x} + m_{O,x}}{\rho_x} \qquad (5a)$$

$$= \frac{m_{C,x}}{\rho_x}\left(1 + \frac{m_{H,x}}{m_{C,x}} + \frac{m_{O,x}}{m_{C,x}}\right) \qquad (5b)$$

where $m_{C,x}$, $m_{H,x}$, and $m_{O,x}$ are the total masses of carbon, hydrogen, and oxygen, respectively, for component x in the blend control volume, and ρ_x is the density of component x. For notation simplicity, we defined

$$\theta_{C,B100} = \left(1 + \frac{m_{H,B100}}{m_{C,B100}} + \frac{m_{O,B100}}{m_{C,B100}}\right) \qquad (6)$$

$$\theta_{C,petro} = \left(1 + \frac{m_{H,petro}}{m_{C,petro}}\right) \qquad (7)$$

where $\theta_{C,B100}$ and $\theta_{C,petro}$ characterize the mass abundances of hydrogen and oxygen relative to carbon in the biological and petroleum-based components, respectively. Combining eqs 4–7 and rearranging, the calculated v/v blend percentage of a biodiesel, B*, can be rewritten as

$$B^* = \frac{100}{1 + \frac{\rho_{B100}}{\rho_{petro}} \frac{\theta_{C,petro}}{\theta_{C,B100}} \frac{m_{C,petro}}{m_{C,B100}}} \qquad (8)$$

Recognizing that $m_{C,petro}/m_{C,B100} = (R_{C,bio/B100}/F_{C,bio} - 1)$, eq 8 can be expressed as

$$B^* = \frac{100}{1 + \frac{\rho_{B100}}{\rho_{petro}} \frac{\theta_{C,petro}}{\theta_{C,B100}} \left(\frac{R_{C,bio/B100}}{F_{C,bio}} - 1\right)} \qquad (9)$$

where ρ_{B100}, ρ_{petro}, $\theta_{C,B100}$, $\theta_{C,petro}$, and $R_{C,bio/B100}$ are properties of the two pure component liquids (B100 and petrodiesel), and thus $F_{C,bio}$ controls the calculated blend content, B*. We parameterized ρ_{B100}, ρ_{petro}, $\theta_{C,B100}$, $\theta_{C,petro}$, and $R_{C,bio/B100}$ using the averaged values that we calculated from a data compilation of retail B100 and petrodiesel products, based on literature surveys and our own laboratory measurements (Table 2). Hence eq 9 does not require calibration to a designated normative fuel blend; rather, it is parameterized with pure-component properties that are relatively stable for a wide range of source materials. We therefore hypothesized that eq 9 could accurately estimate the biodiesel content of any realistic fuel blend based simply on the measured $F_{C,bio}$ value (eq 2).

Uncertainty Analyses of Estimated v/v Biodiesel Percentage of Retail Blends. We evaluated the accuracy of eq 9 for realistic commercial blends using two types of tests, assuming that the only information available is a single $\Delta^{14}C_{mixture}$ measurement of an unknown fuel blend. First, we tested the predictive accuracy of eq 9 for several mixtures in each of the following categories: (1) pure retail petrodiesel; (2) retail B99.9s and B100s; and (3) biodiesel blends of B2.00, B4.97, B20.0, and B69.8, which we prepared ourselves by mixing B100 with petrodiesel (Table 1). Second, we conducted an error propagation analysis based on our data compilation of endmember properties and detailed knowledge of the $\Delta^{14}C$ measurement error. We characterized the real-world variabilities and uncertainties of all of the parameters used in eqs 2 and 9 (Table 2). For example, we assumed that the biodiesel source material may easily range from a low molecular weight mixture (coconut, average molecular weight corresponding to $\sim C_{13}$ FAME) to a high molecular weight mixture (industrial rapeseed, average molecular weight of $\sim C_{20}$ FAME). Then we calculated the first-order Taylor expansions of parameter perturbations for eqs 2 and 9, which allowed us to estimate the accumulated error of the calculated B* that propagates from the input parameter uncertainties and variabilities (35). Ideally, we expected to find consistency between the predictive capability trial results (test 1) and the error propagation analysis results (test 2) of eq 9.

Results and Discussion

The 5730-yr half-life of ^{14}C makes it ideal for identifying the biological carbon (modern levels of ^{14}C) in fats, biodiesel, and biodiesel blends relative to fossil carbon in petrodiesel. Shown in Table 1 are the results from the isotopic analyses of samples in this study. Briefly, we observed $\Delta^{14}C$ values that spanned from -1000 to $+73‰$, thereby encompassing a complete range in fossil and modern carbon end points,

respectively. Refer to the Supporting Information (Table S1 and Figure S2) regarding the $\delta^{13}C$ values of each sample.

Conversion of Fats and Oils to FAMEs. Animal fats and vegetable oils, the main source of biodiesel, had $\Delta^{14}C$ values that were $62‰ \pm 7‰$ (Table 1). This is consistent with the average range ($55–66‰$) of $\Delta^{14}C$ values of CO_2 across the North American atmosphere in 2004 as recorded by corn (24) (see also Supporting Information Figure S1). Thus, the fats and oils analyzed in this study were derived from very recent biological materials.

A dramatic shift in $\Delta^{14}C$ values was observed in the fats and oils to the FAMEs in B99.9 and B100—a result of the transesterification step with fossil methanol. This is consistent with studies in our laboratory, where we find that industrial methanol is consistently ^{14}C free. (Also refer to Supporting Information Figure S3.) Hence, most of the carbon in a typical biodiesel (e.g., 18/19 for C_{18} FAME) is from fats and oils ($+62‰$), whereas a small fraction (1/19) is actually petroleum-derived ($-1000‰$). Based on the relative abundances of FAMEs in the analysis of fats from different oils that we have measured and found in the literature (Table 2), a typical B100 should have $\Delta^{14}C$ values $\sim 3‰$. This estimate is consistent with observed values for four B100s ($-3 \pm 20‰$; Table 1). Note that the observed variability in the retail B100 $\Delta^{14}C$ values ($\pm 20‰$) is significantly higher than would be expected based simply on measurement errors ($\pm 4‰$) or variability of either endmember ($\pm 7‰$ for fats; $\pm 1‰$ for petrodiesel). The observed $\Delta^{14}C$ variability in the B100 samples may result from residual petrodiesel (or fossil components) in the tanks that were used to prepare the blends, the location of the FAMEs' agricultural source, or the presence of excess methanol. The presence of residual petrodiesel or methanol would lower the $\Delta^{14}C$ value of the B100. Methanol content in B100 is indirectly measured in the United States with the American Society for Testing and Materials Standards (ASTM) D6751-07A biodiesel method via the sample's flash point (36). ASTM specifications require a minimum value of 130.0 °C, which roughly corresponds to a maximum limit of 0.1% methanol. Using data from ref (24), and based on the ^{14}C analysis of corn in 2004, the geographic variability of $\Delta^{14}C$ is likely $\pm 10‰$ in FAMEs from North America, although urban locations may be more depleted ($\sim 20‰$) due to local fossil emissions. However, urban regions host little farming, so they should rarely contribute bias to the $\Delta^{14}C$ value of FAMEs in biodiesels. With these available factors, consider the B100 from Indiana, which had the lowest $\Delta^{14}C$ value, $-31.2‰$ (Table 1). If this sample was within the ASTM specifications, then the $\Delta^{14}C$ deviation from the B100 average ($+3‰$) could not be explained by either excess methanol or agricultural location. It is more likely that this sample was contaminated by residual petroleum. Noting that other retailers may unintentionally combine their B100 with small amounts of residual petroleum, we chose to include the Indiana B100 sample when evaluating the realistic accuracy of our method.

Using ^{14}C to Determine Biodiesel Blend Percentage. We found that eq 9 could appraise the v/v biodiesel percentage of fuel blends using only ^{14}C content as a measurement input and assuming no specific knowledge about the particular endmember liquids used to blend the sample (Table 1). We parameterized eq 9 using simple averages of ρ_{B100}, ρ_{petro}, $\theta_{C,B100}$, $\theta_{C,petro}$, and $R_{C,bio/B100}$ property values from a broad range of retail petrodiesels and B100s (Table 2). Employing these input parameters, eq 9 simplified to

$$B^* = \frac{100}{\frac{0.869}{F_{C,bio}} + 0.0813} \qquad (10)$$

where the lumped parameters, 0.869 and 0.0813, are dimensionless. For clarity, we used the notation "B*" to indicate

TABLE 1. Radiocarbon (Δ^{14}C) Content and B* (from *10*) of Samples Analyzed in This Study (All Samples Acquired in 2006 unless Noted Otherwise)

sample source	month acquired	Δ^{14}C (‰)	biodiesel (v/v)	calculated B* (v/v)
Fat Source endmembers				
used vegetable oil (N. Carolina restaurant)	April	59.1	NA[a]	NA[a]
new fry oil (Massachusetts restaurant A)	May	54.6	NA	NA
used fry oil (Massachusetts restaurant A)	May	73.5	NA	NA
bacon grease (Massachusetts restaurant B)	June	58.8	NA	NA
new Crisco soybean (store bought)	Sept	62.2	NA	NA
Petrodiesel endmembers				
Bouchard 65 barge[b]	Oct 1974[b]	−999.9	0[c]	0.01 ± 0.02
Massachusetts distributor A	Nov	−1000	0[d]	0.00 ± 0.02
removed from truck driving petrodiesel only	March 2007	−999.5	0[c]	0.05 ± 0.02
Commercial B99.9s and B100s				
California distributor A	June	−10.1	99.9[d]	98.6 ± 0.9
Massachusetts distributor A	Nov	−1.71	99.9[d]	99.4 ± 0.9
California distributor B	July	8.29	99.9[d]	100 ± 0.9
California distributor B	July	10.3	99.9[d]	101 ± 0.9
California distributor B	August	11.6	99.9[d]	101 ± 0.9
Indiana distributor A	April	−31.2	100[d]	96.7 ± 0.9
Massachusetts distributor A	June	9.88	100[d]	100 ± 0.9
Massachusetts distributor A	Sept	−4.92	100[d]	99.1 ± 0.9
California distributor C	June	15.3	100[d]	101 ± 0.9
Blends we prepared by mixing Bouchard 65 with Massachusetts distributor A B100; June (see above)				
known laboratory mix	NA	−983	2.00[e]	1.9 ± 0.2
known laboratory mix	NA	−956	4.97[e]	4.8 ± 0.2
known laboratory mix	NA	−818	20.0[e]	19.4 ± 0.6
known laboratory mix	NA	−331	69.8[e]	68.5 ± 1
Commercial biodiesel blends ranging from B2 to B20				
Minnesota distributor A	June	−979	2[d]	2.3 ± 0.2
Minnesota distributor B	June	−980	2[d]	2.2 ± 0.2
Minnesota distributor C	June	−981	2[d]	2.0 ± 0.2
Minnesota distributor D	June	−976	2[d]	2.6 ± 0.2
Indiana distributor A	April	−954	5[d]	4.9 ± 0.2
North Carolina	April	−953	5[d]	5.1 ± 0.2
Massachusetts distributor B	June	−968	5[d]	3.5 ± 0.2
Indiana distributor B	April	−869	15[d]	14.0 ± 0.5
Massachusetts distributor A	May	−855	20[d]	15.5 ± 0.6
Massachusetts distributor A	June	−901	20[d]	10.7 ± 0.4
Massachusetts distributor A	Sept	−269	20[d]	74.4 ± 1
Massachusetts distributor A	Nov	−904	20[d]	10.4 ± 0.4
Massachusetts distributor B	June	−840	20[d]	17.2 ± 0.6
Massachusetts distributor C	April	−843	20[d]	16.8 ± 0.6
Massachusetts distributor C	June	−795	20[d]	21.8 ± 0.7
Massachusetts distributor C	Sept	−796	20[d]	21.8 ± 0.7
Massachusetts distributor C	Nov	−810	20[d]	20.3 ± 0.7
Tennessee (replicate *i*)	May	−852	20[d]	15.8 ± 0.6
Tennessee (replicate *ii*)	May	−851	20[d]	15.9 ± 0.6
Postretail "Personal user" blends				
Massachusetts personal A self-mixed from retail endmembers of petrodiesel and B100	May	−900	20[c]	10.7 ± 0.4
Massachusetts personal B self-mixed from retail endmembers of petrodiesel and B100	May	−424	70[c]	59.5 ± 1
Massachusetts personal A supply (stored in owners supply jug and purchased from a retailer)	May	−3.43	100[c]	99.3 ± 0.9
Massachusetts personal B (collected from tank of vehicle and purchased from a retailer)	March 2007	−862	20[c]	14.8 ± 0.5

[a] Not applicable. [b] This oil was collected from a hold in the barge *Bouchard 65* after it spilled product in Buzzards Bay, MA in October 1974. [c] Expected biodiesel content. [d] Advertised biodiesel content. [e] Known biodiesel percentage based on laboratory preparations.

calculated blend content, whereas the prefix "B" indicates expected or advertised blend content from retailers or personal stocks. We tested the predictive capability of eq 10 against 3 petrodiesel products, 4 retail B100s, 5 retail B99.9s, and our own preparations of B2.00, B4.97, B20.0, and B69.8. For these 16 samples, eq 10 exhibited a root-mean-squared-error (rmse) of 1.05% in the calculated blend percentage of the biodiesel (Figure 1a; Table 1). We chose these 16 samples because they represented the full range of endmembers and

known prepared mixtures. Again, no prepared mixtures were used to calibrate the method; rather, they were used to validate it. Hence, the method parameterization and method validation were completely independent. This differs from current spectroscopic and chromatographic methods, which calibrate with prepared blends and then validate against prepared blends that are similar to the calibration set (see the Advantages and Disadvantages section for more details).

TABLE 2. A Survey of Petrodiesel and B100 Properties[a]

property	symbol	mean	standard deviation	n
petrodiesel density	ρ_{petro}	0.843	0.023	21
B100 density	ρ_{B100}	0.877	0.007	7
petrodiesel C/H ratio	$m_{C,petro}/m_{H,petro}$	6.60	0.60	7
B100 C/H ratio	$m_{C,B100}/m_{H,B100}$	6.38	0.16	5
B100 C/O ratio[b]	$m_{C,B100}/m_{O,B100}$	6.79	0.96	5
B100 ratio of bio/total carbon[b]	$R_{C,bio/B100}$	0.946	0.006	11

[a] These values were obtained from measurements performed in our laboratory, reports (6, 18), published manuscripts (25–29), Certificates of Authorization (30–34), and the gray literature. Our goal was to ensure that input parameters reflected a broad range of sources such that the resulting variability in the parameter values would represent realistic field variability, including one residual fuel oil included in the petrodiesel density and C/H ratios (32). The densities listed were measured at temperatures from 15 to 20 °C or not stated in the source. [b] The biodiesel endmembers represented the full range of values found for different sources, ranging from coconut (average molecular weight corresponding to C_{13} FAME) to industrial rapeseed (average molecular weight corresponding to C_{20} FAME).
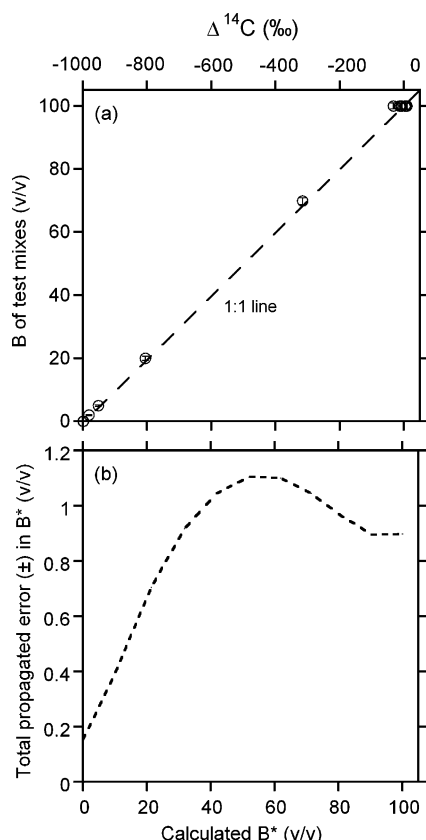

FIGURE 1. Reliability of the ^{14}C-based method for calculating biodiesel content. (a) Comparison of calculated (B*) versus known biodiesel blend percentage (B value) for prepared blends. This reflects a validation of eq 10, which was independently parameterized from pure component properties, not fitted to measurements of prepared mixtures. (b) Total propagated error in B* as a function of B*, accounting for ^{14}C measurement error and assuming wide variability in the properties of the component petrodiesel and biodiesel sources.

Uncertainty Analysis of Calculated Biodiesel Blend Percentage. To interrogate further the expected accuracy of eq 10 in the face of real world variability, we conducted a thorough error-propagation analysis. We estimated the compounded uncertainty resulting from the following: the analytical error of the $\Delta^{14}C_{mixture}$ measurement; the observed $\Delta^{14}C_{bio}$ variability (i.e., for the fat and oil sources in Table 1); and the realistic variabilities of ρ_{B100}, ρ_{petro}, $\theta_{C,B100}$, $\theta_{C,petro}$, and $R_{C,bio/B100}$ (Table 2). This resulted in an expected cumulative error that was ± 1% or less in the absolute B* blend value (Figure 2).
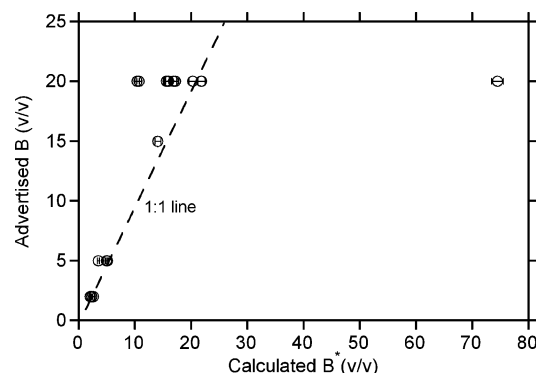

FIGURE 2. Advertised biodiesel percentage versus calculated B*. Only B2 to B20 samples are presented, but data for all samples are provided in Table 1. Error bars for B* are the total propagated error as shown in Figure 1b.

The expected error based on the propagation analysis was consistent with the observed error trends that we found for the 16 test samples, and these are listed together in Table 1. The *origin* of the error in B* depended on the blend content. For B0 (pure petrodiesel) to B3 mixtures, the uncertainty in B* primarily arises from the uncertainty in the measured $\Delta^{14}C_{mixture}$ value; for mixtures ranging from B3 to B75 mixtures, the B* error is dominated by variability in ρ_{petro}; finally, for the B75 to B100 range, the B* error is driven by uncertainty in the endmember $\Delta^{14}C_{bio}$ value. Although the C/O ratio of biodiesel exhibited the largest absolute variability of the input parameters (Table 2), the calculated B* was not very sensitive to this term.

Notably, real-world variability in ρ_{petro} affects the accuracy of any mass fraction-based method for determining biodiesel content. Hence this error affects several currently published methods (9–11, 14). Although ρ_{petro} was the largest driver of uncertainty for our radiocarbon-based blend determinations in the B20 to B70 range, we found that these previous methods did not account for ρ_{petro} variability in their accuracy assessments.

Analysis of Advertised Biodiesel Blends. We calculated B* from the $\Delta^{14}C$ values along with eqs 2 and 10 (Table 1; Figure 2). Briefly, a comparison of advertised and calculated blend content (B vs B* values) revealed discrepancies ranging from 0 to 54% in the absolute blend level. Since the expected standard error of the analysis method is ± 1% in absolute blend content (or less), we concluded that most of these differences likely result from erroneous preparations of the advertised blends.

The four B2 samples from Minnesota ranged from B*2.0 to B*2.6, indicating that these blends had been reasonably prepared. Similarly, the advertised B99.9s and B100s were consistent with the B* value, except for the previously

discussed B100 sample from Indiana (B*96.7). The largest discrepancies were found for the B20s. Six of these samples were lower than expected and ranged from B*10.4 to B*17.2. Hence, we found that B20 blends could be inadequately prepared at levels 50% below advertised. The four samples that were above the expected B20 content were more interesting. Three of them were sold by Massachusetts Distributor C and close to advertised values (B*20.3, B*21.8, and B*21.8). The fourth was a significant outlier at B*74.4. It is important to note that for the ten B20 samples that we analyzed, only one of them, Massachusetts Distributor C collected in June (B*20), would pass the B20 ± 1 requirement for B20s sold to the United States Department of Defense (37).

Massachusetts Distributor A had the most erratic B* values for advertised B20 samples—three were 25−50% below expected and one was 270% greater (B*74; Table 1). Although gas chromatography may be used for accurate blend measurements (14), we analyzed the entire set of Massachusetts Distributor A and C B20 samples by GC-FID as well as standard solutions for qualitative comparisons only. These analyses were able to confirm, based on visual inspection of the chromatograms, that the advertised Massachusetts Distributor A Sept. B20 sample was mostly constituted of FAMEs and was therefore improperly prepared; hence the GC-FID results were consistent with the ^{14}C-calculated B*74.4 (See Supporting Information Figure S4). When we first received this unusual data point, we contacted Distributor A and told them of this problem. Two months later, we collected one more sample from this distributor and it had a value of B*10.4. This indicates that even after informing the retailer of mixing problems, it continued to occur.

To test the biodiesel and biodiesel blends of postretail preparations, we acquired four different samples from individuals (Table 1). Two were blends believed to be a B20 and a B70 that were mixed by the users after they had purchased retail petrodiesel and B100. The other two were retail B20 and B100 that the owners had. The two user-blended samples prepared by two different individuals (Personal A and B; Table 1) exhibited as poor accuracy as the retail blends. While these individuals thought they were making a B20 and B70, they actually made a B*10.7 and B*59.5, respectively, indicating that the inaccuracies observed in the retail blends can also occur when individuals prepared biodiesel blends with their own endmembers. The retail sample B20 that the individual (Personal B taken from fuel tank) purchased was also much lower than expected with B*14.8. However, the B100 (Personal A supply jug) was determined to be B*99.3.

As biodiesel blend consumption increases, it is essential that the advertised blend be accurate, for fairness to the consumer, performance of the vehicle, tax regulations, and emissions (See Supporting Information Figure S5) and carbon-cycling studies. Currently, preparations of biodiesel blends can occur at numerous levels of distribution. Based on discussions with the retailers (when possible), most of the samples that we collected in 2006 were prepared by the actual retailer with splash blending of the two endmembers.

Notably, a 2004 federal survey of 50 fleets using B20 across the United States observed inaccuracies in blends that were comparable to the discrepancies reported here (7). The samples from the Federal survey were collected from producers who sold more than one million gallons per year. Approximately two-thirds of the samples were 18−20% biodiesel. However, the remaining samples ranged from 7 to 98%, indicating severe blending inaccuracies. We were motivated to complement the federal study by considering small-scale retailers in 2006. Our results indicate that the conclusions and recommendations from the 2004 study

(published in October 2005) were not available to or considered by small-scale retailers.

Advantages and Disadvantages of Radiocarbon-Based Blend Determinations. Radiocarbon-based biodiesel blend determination poses some important advantages over existing methods, including the European Standard method EN 14078 (IR-based; (17)). First, the present method is the only approach that has demonstrated ± 1% accuracy over the entire v/v blending range (0−100%) while also accounting for all real world variability in all of the input parameters. For example, we found that variability in the petrodiesel end-member density (ρ_{petro}) was an important contributor to the error of the method, and although many existing methods are vulnerable to this source of error, no previous study has characterized it. Second, with the exception of Oliveira et al. (11), IR, NMR, and saponification-based methods assume that the biodiesel component is constituted of 100% FAMEs having a designated average molecular weight. However, different biodiesel sources may have very different FAME average molecular weights; a typical value is ~290 g mol^{-1} (canola biodiesel), but it may range from 228 g mol^{-1} (coconut biodiesel) to 326 g mol^{-1} (industrial rapeseed) (18). Oliveira et al. (11) intentionally did consider a broad molecular weight range of biodiesel sources, but their calibration procedure is labor intensive, complicated, and requires many fitted parameters. EN 14078 measures the abundance of FAME ester groups, thereby assuming that the calibration mixture and test mixture have the same FAME average molecular weight. The calibration standard for EN 14078 must only pass the requirements of EN 14214, which is the automotive fuel standard for B100 (38). Hence, if an analyst calibrated EN 14078 using canola biodiesel, we estimate that this method would incorrectly diagnose B20 samples of coconut biodiesel and industrial rapeseed biodiesel as B26 and B18, respectively. By comparison we calculated estimate that the ^{14}C approach would exhibit ±1 error in the B* values for these samples. Moreover, some biodiesel preparations may contain significant quantities of non-FAME components (e.g., jojoba B100 may contain ~20% long-chain alcohols (19)), and EN 14078 would fail to account for these entirely. The present method is much less sensitive to variability in the chemical composition of the source materials, because it directly measures the most abundant ingredient: carbon. Third, the present method requires no calibration, which again reflects the robustness and broad applicability of the approach. Consequently, no standard preparations are necessary. Only a fuel blend sample must be sent to a commercial or university laboratory equipped to perform ^{14}C analysis by either AMS or radiogenic counting. The resulting Δ^{14}C value can be plugged into eq 2 and then eq 10.

Radiocarbon-based measurement of recent (bio) versus fossil (petro) carbon is the only method that directly apportions the renewable versus nonrenewable carbon in fuels, represented by the fraction $F_{C,bio}$. This enables us to connect the renewable carbon composition of fuels with the renewable carbon composition of CO_2 emissions and other carbonaceous species. See Supporting Information Figure S5.

The cost and turn-around-time of ^{14}C analysis are the main disadvantages of the present method. Such measurements can take weeks and cost several hundred dollars. However, new developments in continuous-flow AMS may shorten analysis times to days and reduce costs to less than a hundred dollars (39). Additionally, we assumed that all of the B100 was a product of the transesterification of fats and oil with fossil methanol. It is possible that other alcohols, including modern sources of alcohols, could be used. However, fossil methanol is almost exclusively used in the United States and Europe. This assumption is consistent with our mass balance calculations and data shown in Supporting

Information Figure S3. If B100 practices do change to other alcohols or sources of methanol, our approach would require only slight adjustments to the input $\theta_{C,B100}$, and $R_{C,bio/B100}$ values.

Acknowledgments

Supporting Information Available

Table listing the $\delta^{13}C$ of the samples; five figures containing information pertaining to (1) the ^{14}C content of CO_2 in the Northern Hemisphere, (2) a comparison between $\delta^{13}C$ and ^{14}C values of the fat and oils in this study, (3) the transition in ^{14}C content from the fat and oils in this study to B99s and B100s, (4) the gas chromatograms of select B20 samples, and (5) a comparison between the biodiesel content of fuels and the fraction of biomass carbon in the CO_2 emitted from the same vehicles. This information is available free of charge via the Internet at http://pubs.acs.org.

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ES071814J