analytical chemistry

pubs.acs.org/ac

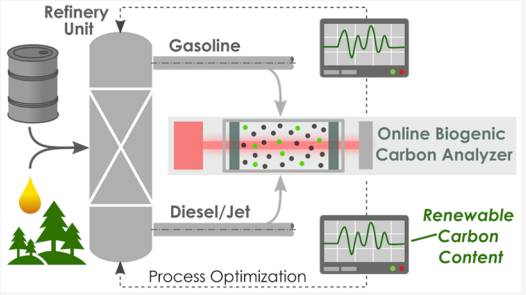
Perspective

Online Biogenic Carbon Analysis Enables Refineries to Reduce Carbon Footprint during Coprocessing Biomass- and Petroleum-Derived Liquids

Stefano Dell'Orco, Earl D. Christensen, Kristiina Iisa, Anne K. Starace, Abhijit Dutta, Michael S. Talmadge, Kimberly A. Magrini, and Calvin Mukarakate*

Cite This: https://dx.doi.org/10.1021/acs.analchem.0c04108

ABSTRACT: To mitigate green-house gas (GHG) emissions, governments around the world are enacting legislation to reduce carbon intensity in transportation fuels. Coprocessing biomass and petroleum-derived liquids in existing refineries is a near-term, cost-effective approach for introducing renewable carbon in fuels and enabling refineries to meet regulatory mandates. However, coprocessing biomass-derived liquids in refineries results in variable degrees of biogenic carbon incorporation, necessitating accurate quantification to verify compliance with mandates. Existing refinery control and instrumentation systems lack the means to measure renewable carbon accurately, reliably, and quickly. Thus, accurate measurement of biogenic carbon is key to ensuring refineries meet regulatory mandates. In this Perspective, we present existing methods for measuring biogenic carbon, point out their challenges, and discuss the need for new online analytical capabilities to measure biogenic carbon in fuel intermediates.



The transportation sector is a major contributor to global greenhouse gas (GHG) emissions and demand for transportation is expected to increase due to growth in world population and economies of developing countries. As such, governments are enacting policies and incentives to limit GHG emissions. In the U.S., the renewable fuel standard (RFS) aims to increase the share of renewable fuel to 36 billion gallons by 2022.[1] Individual states in the U.S. enacted additional mandates such as low carbon fuel standards (LCFS) or alternative fuel standards (AFS).[2] Airlines for America (A4A) set a goal of cutting CO_2 emissions in half by 2050.[3] In Europe, the Renewable Energy Directive II (RED II) mandated a renewable fuels increase to 14% by 2030.[4] Coprocessing bioderived liquids (BDL) with petroleum-derived liquids in existing refineries is a relatively low-cost approach for adding renewable carbon to the transportation sector. During coprocessing, biogenic carbon can end up in either desirable products or side products (Figure 1). Accurate quantification of biogenic carbon in gasoline, diesel, and jet fuels is a key barrier that needs addressing for demonstrating compliance with renewable carbon mandates and GHG reduction.

Over the last 10−20 years, several technologies have been developed to convert biomass into fuels. Lignocellulosic biomass is attractive for biofuel production as it is abundant, with an estimated global production of 182 billion tonnes per year, of which 7 billion tonnes are currently harvested for energy production.[5] This renewable resource can be converted to liquid intermediates[6,7] using fast pyrolysis (FP), which is capable of producing up to 80 wt % liquid yield.[7] However, FP oil is unsuitable as a transportation fuel due to high oxygen and water contents, poor stability, and acidity. Vapor or liquid upgrading can improve the quality of FP bio-oils. Hydrotreating (HT) FP oils or catalytic fast pyrolysis (CFP) of biomass to produce CFP oil, followed by HT are commonly suggested approaches for producing hydrocarbon liquids.[8−16] Petroleum refineries could potentially dedicate whole upgrading sections, such as hydrotreaters to biointermediates; however, this is an uneconomical approach given that the capacity of existing hydrotreaters is approximately an order of magnitude larger than current production of bio-oils in FP plants.[17] Thus, existing petroleum refinery infrastructure would be more economically utilized with a mixture of biomass- and petroleum-derived feedstocks.

Identifying suitable insertion points for BDL is key to successful implementation of coprocessing. BDL vary considerably in composition, for example, FP bio-oils contain 36−55

Received: September 29, 2020
Accepted: February 16, 2021

https://dx.doi.org/10.1021/acs.analchem.0c04108
Anal. Chem. XXXX, XXX, XXX−XXX

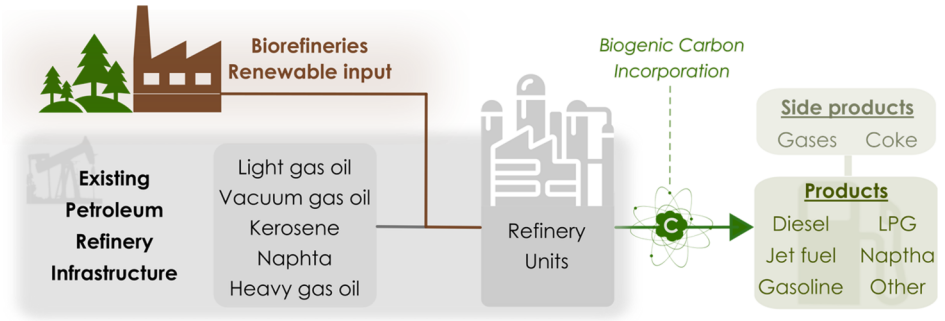
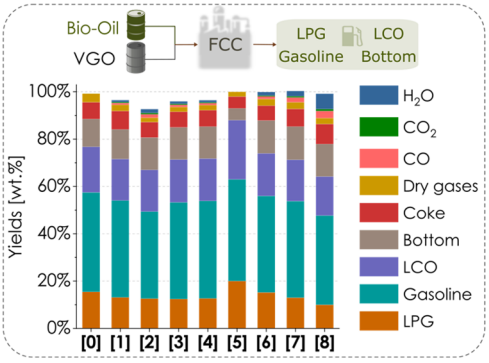


Figure 1. General scheme of coprocessing fossil and renewable sources in existing petroleum refineries.



ID	Bio-Oil type	Bio-Oil: VGO ratio	Conversion [wt.%]*	Reference
[0]	VGO	0:100	66-71%	45,46,29,47,48 (avg.)
[1]	CFP	10:90	70.1%	45
[2]	FP	10:90	69.2%	46
[3]	HDO	10:90	69.1%	46
[4]	HDO	10:90	69.6	46
[5]	HDO	10:90	66-71%	29
[6]	FP	10:90	68.5%	47
[7]	FP	20:80	75.5%	47
[8]	FP	5:95	68.1%	48

Figure 2. Products yields derived from selected studies on coprocessing VGO and BDL [1],[45] [2, 3, 4],[46] [5],[29] [6, 7],[47] [8].[48] *Conversion defined as the sum of the yields of products (e.g., dry gas, LPG, gasoline, etc.) measured during coprocessing BDL and VGO mixtures.

wt % oxygen and have acid numbers of 40 to >100 mg KOH/g, while CFP or HT oils can have <1−25 wt % oxygen and <1−50 mg KOH/g.[18−24] The properties of the BDL impact the choice of insertion location and the most suitable unit operations should be selected accordingly. Previous reports identified hydrotreaters/hydrocrackers (HT/HC) or fluid catalytic crackers (FCC) as suitable for BDL.[17,25,26] Unlike FCC, HC/HT do not have in situ catalyst regeneration making them nonideal to accept higher amounts of oxygenated species that may cause more rapid catalysts deactivation.[25,26] A recent review reported challenges and opportunities for coprocessing FP, CFP, and HT-FP oils with vacuum gas oil (VGO) in an FCC and concluded this technology is viable after minor reactor modifications.[27]

Several reports cited in that review demonstrated that coprocessing bio-oils in an FCC led to increased yields of nonfuel products compared to VGO alone, indicating that all biogenic carbon fed into the process does not necessarily end up in desirable fuels. Thus, it is critical to determine the destination of biogenic carbon during coprocessing to evaluate true GHG impacts on transportation fuels. The fate of biogenic carbon in coprocessed products can be determined by intentionally labeling carbon in one of the feeds or using radiocarbon analysis[28−30] to differentiate between fossil and modern carbon.[31−36] Relatively simple mass, carbon, and energy balances have also been used to account for biogenic carbon incorporation.[37] Radiocarbon analysis is a widely accepted technique that has been adopted as an ASTM standard (D6866-20)[38] and is approved by U.S. regulatory agencies; United States Department of Agriculture (USDA) and the Environmental Protection Agency (EPA), for verifying biobased carbon content.[39] Although traditional radiocarbon analysis techniques are well-established and fairly robust, they have inherent limitations in terms of costs, complexity, precision, and analysis time. These analytical techniques are unsuitable for real-time process monitoring in a refinery. To assist in process optimization for renewable carbon utilization and accelerate adoption of coprocessing renewable feedstocks, targeted efforts are needed to develop online/in-field measurements of biogenic carbon at refinery sites. This Perspective reviews current analytical techniques for quantifying biogenic carbon and discusses shortcomings, pain points, and opportunities for developing advanced rapid online analytical methods. We will first review state-of-the-art methods and then propose potential solutions for online measurements, while also identifying the most appropriate measurement locations in refineries.

■ COPROCESSING IN REFINERY UNITS

As noted above, refineries have potential to accept BDL in three main units: HT, HC, and FCC.[25,26] HTs eliminate heteroatoms via catalysis at high hydrogen pressure and temperature, while HCs reduce molecular weights while consuming hydrogen.[40] FCCs upgrade heavier distillates (e.g., VGO) without the need for hydrogen. FCCs can tolerate higher feed oxygen compared to HT and can adapt more easily to feedstock variability.[41,42] An FCC as a point of insertion for BDL may be attractive given relative feedstock flexibility and lack of hydrogen (which is costly), but lower carbon efficiencies may offset those benefits. The choice of insertion point is also related to local market considerations: FCCs primarily produce gasoline range hydrocarbons while HCs mainly produce diesel and kerosene.[43] In the U.S., the Department of Energy estimated that 8 billion gallons of biomass-derived fuels can be produced in the 110 currently

https://dx.doi.org/10.1021/acs.analchem.0c04108
Anal. Chem. XXXX, XXX, XXX−XXX

active domestic FCC units; therefore, it is possible to foresee utilization of this technology in the midterm.[44]

Laboratory and pilot scale studies have evaluated the feasibility of coprocessing BDL with VGO in an FCC,[29,41,45−49] while fewer studies investigated the possibility of cohydroprocessing BDL, mainly for lipids.[50] A recent review summarized results from coprocessing three different types of BDL: FP, CFP, and hydrodeoxygenated (HDO) oils with VGO in an FCC.[27] Cracking VGO in an FCC generally produces ∼50% gasoline-range hydrocarbons, plus liquefied petroleum gas (LPG), light cycle oil (LCO), heavy cycle oil (HCO), coke and a mixture of light hydrocarbons.[51,52] FCC product distributions from coprocessing were found to vary based on the BDL type or blend percentage. Figure 2 shows product yields from selected FCC coprocessing reports. VGO was coprocessed with 10 wt % each of FP, CFP and two types of HDO.[45,46] The addition of FP reduced gasoline yield compared to the base case. However, higher gasoline yields were obtained with CFP or HDO compared to FP. For all BDL tested, a higher amount of CO and CO_2 than for VGO only was observed due to the presence of oxygenated species in BDL. In another study, similar gasoline yields were reported when coprocessing HDO/VGO, though higher amounts of LPG and LCO were produced, while a reduced amount of HCO was recovered.[29,53] These experiments were carried out in laboratory-scale fixed bed quartz reactors. Pilot-scale coprocessing conducted with various FP:VGO blends (5:95, 10:90, and 20:80), produced similar gasoline yields, low LPG formation, and increased coke compared to the baseline with just VGO.[47,48] In contrast, a reduction in coke formation was observed during coprocessing FP or HT compared to baseline in another study.[46] Coprocessing partially upgraded BDL (e.g., CFP or HDO) in a microactivity reactor gave slightly higher total yields of liquid products and similar coke yields compared to coprocessing FP.[49] These data (Figure 2) show that introducing BDL in an FCC impacts the yield and composition of products but is not enough to determine the renewable carbon content in finished fuels.

To determine the fate of biogenic carbon previous works showed the possibility of using techniques involving carbon isotopes detection. One report,[29] estimated renewable carbon distribution in products from coprocessing VGO and BDLs in FCC using ^{14}C radiocarbon analysis while another study[28] evaluated the biogenic carbon incorporation in a microscale reactor by cofeeding ^{13}C-labeled oak pyrolysis with VGO over an FCC catalyst. The results showed that biogenic carbon was incorporated into alkenes, cycloalkanes, and aromatic hydrocarbons but not into linear alkenes.

Additionally, both studies found that CO_2 and coke generated was composed of biogenic carbon. From a refinery scale-up perspective, biogenic carbon tracking is needed to optimize renewable carbon incorporation in desirable products. Thus, measuring biogenic carbon directly in refinery units would facilitate process design improvements, as well as enhance understanding of reaction pathways for optimizing catalyst formulations. Most importantly, it would be possible to consistently track renewable carbon in fuel products to demonstrate compliance with the U.S. Renewable Identification Numbers (RINs) system to obtain credit for introducing renewable energy into the market.[54,55]

ESTABLISHED METHODS FOR MEASURING BIOGENIC CARBON

Techniques for measuring renewable carbon are provided in the International Sustainability and Carbon Certification Guidance (ISCC 203-01).[56] Some basic approaches involve comparing yields during coprocessing and baseline cases. One approach is based on measurement of overall mass yields while another (and more detailed approach) is based on carbon yields, accounting for CO and CO_2. Similarly, energy balance can be used, considering biointermediates have a diminished heating value due to presence of oxygen compared to hydrocarbon feedstocks; this data is then used to proportionally calculate the percentage of biogenic energetic share in the final products.[37,57] These indirect approaches have evident advantages in terms of implementation and simplicity, as mass and energy balances are a fundamental concept of process design engineering. However, these cannot be easily generalized since coprocessing yields are highly feedstock and process dependent. From a research and optimization point of view, these methods do not give information on the reaction pathways that are useful to both process and catalyst optimization. Moreover, the introduction of oxygenated compounds may change reaction mechanisms, making results from the baseline case invalid.

Renewable carbon can be measured directly to provide more accurate and agnostic evaluations. These techniques involve the measurement of carbon isotopes, ^{12}C, ^{13}C, and ^{14}C, and their ratios. The atmosphere contains stable ^{12}C and ^{13}C together with a much smaller fraction of unstable ^{14}C (natural abundance in parts per trillion), all in the form of carbon dioxide. Carbon dioxide is continuously consumed by plant matter, with an uptake of all three isotopes. After death, carbon is no longer consumed and the amount of ^{14}C begins to decrease relative to plant matter. The rate of radioactive decay is a constant−half-life of 5720 ± 47 years for ^{14}C.[58] Fossil sources, being hundreds of millions of years old, do not contain any measurable ^{14}C, and therefore, the biogenic content of any mixture of fossil and modern carbon sources can be correlated to the ^{14}C content.[58,59]

Offline Carbon Isotope Measurement Techniques. Several methods for measuring carbon isotopes have been developed to determine the amount of biobased carbon in solid, liquid, and gaseous samples. ASTM adopted the standard method D6866 in 2004 (current version D6866-20) for verifying biogenic carbon in a wide range of materials.[60] Two methods are included: accelerator mass spectrometry (AMS, D6866 Method B) and liquid scintillation counting (LSC, D6866 Method C). The US EPA, under the RFS, has approved the use of this standard to evaluate the bioderived portion of fuels.[39]

Accelerator Mass Spectrometry. The theory and detailed review of AMS can be found elsewhere.[61,62] Briefly, samples are ionized, accelerated, and separated to be counted in a Faraday collector. AMS directly counts the amount of ^{14}C, ^{13}C, and ^{12}C in a given sample, determining the ^{14}C to ^{12}C ratio directly. Prior to ionization, the sample is converted either to carbon dioxide or to graphite obtained by catalytic reduction of carbon dioxide.[63−65] The salient feature of AMS is its extraordinarily high resolving power, capable of differentiating ^{14}N from ^{14}C at extremely low concentrations. Selected cofeeding studies that utilized D6866 Method B[29,45−48] are summarized in Table 1. An interesting feature

https://dx.doi.org/10.1021/acs.analchem.0c04108
Anal. Chem. XXXX, XXX, XXX−XXX

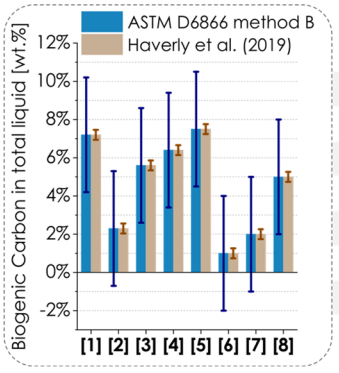
Table 1. Biogenic Carbon Content Measured by ^{14}C Radiocarbon Analysis, with AMS (According to ASTM D6866 Method B) in Selected Studies

Feedstock			FCC Products: Biogenic Carbon Content [wt %]							
type of pyrolysis oil	bio-oil-VGO ratio [wt %]	bio-oil oxygen content	total liquid	LPG	gasoline	LCO	bottom	coke	dry gases	ref
CFP	10:90	19.5	7.2−7.3		7.0−7.1	7.3−7.4	7.6−7.7			45
FP	10:90	51.0	2.3		2	2.5	2.6			46
HDO 1	10:90	39.2	5.6		5.3	5.9	6.2			46
HDO 2	10:90	27.4	6.4		6.1	6.3	6.8			46
HDO	10:90	21.0	7.5		7.2			15.8	11.9	29
FP	5:95	50.7	1							48
FP	10:90	51.1	2							47
FP	20:80		5		3−5	5	6			47

of these data is a dependency on bio-oil type. Coprocessing CFP or HT led to higher biogenic carbon incorporation than with FP.[45,46] In addition, coprocessing two different HT oils, one mildly hydrotreated (HDO 1) and the other severely hydrotreated (HDO 2), demonstrated an increase in biogenic carbon with severity of hydrotreating, which corresponds to reduced oxygenate content.[46] These results emphasize the importance of an accurate biogenic carbon evaluation to directly account for incorporation, especially at refinery sites.

A potentially challenging aspect of applying this standard method is the stated precision: ±3 wt % absolute. This may have a large impact on data interpretation for percent modern carbon (pMC) concentrations relevant to coprocessing shown in Table 1. It should be noted this uncertainty statement was not derived from an official ASTM interlaboratory study but was taken from a somewhat limited evaluation of precision of both AMS and LSC on a wide range of products.[64] Particularly, AMS was not applied to lower concentrations but was focused on a range relevant to the USDA biopreferred program, (≥25% biogenic carbon).[64,66] Precision of this method for liquid fuels, particularly at concentrations relevant to coprocessing, was not established.

A more recent study investigated AMS precision on fuels containing biogenic carbon in the range of 0 to 10% at four laboratories.[67] The results showed a lower absolute measurement error, indicating a 95% confidence interval of ±0.26 wt % as well as a detection limit of 0.40 wt %. To illustrate the impacts on data interpretation, the error bars depicted in Figure 3 show biogenic carbon uncertainty calculated using the stated precision of D6866 and that derived in this recent study.[67] It is evident the stated precision would result in uncertainties that are possibly greater than the measured biogenic content in some studies; however, the more recent evaluation of relevant products and concentrations shows this method is capable of accurately tracking biogenic carbon during coprocessing. Any advanced methods would ideally meet or exceed the precision and accuracy of this technique.



ID	BC Incorporation (avg.)	Reference
[1]	82.9%	45
[2]	45.2%	46
[3]	86.4%	46
[4]	84.2%	46
[5]	91.0%	29
[6]	39.8%	47
[7]	38.3%	47
[8]	45.3%	48

Figure 3. Coprocessing pyrolysis oil and VGO: Biogenic carbon incorporation in total-liquid for literature data. Error bars refer to absolute precision stated in ASTM D6866 Method B (±3 wt %)[38] and in a more recent report (0.26 wt %):[67] [1],[45] [2, 3, 4],[46] [5],[29] [6, 7],[47] [8].[48]

Liquid Scintillation Counting. LSC is much less complex and costly than AMS for measuring radiocarbon. There are multiple techniques for sample preparation for LSC, though D6866 only covers benzene synthesis. Two alternatives have been studied and applied to mixtures containing biogenic carbon: CO_2 absorption and direct counting. Details of method preparation will not be described in detail here, but it is noted that more in-depth preparation, such as benzene synthesis, improves accuracy and limit of detection but adds cost, complexity, and time. CO_2 absorption is less expensive and complex but is also less accurate than benzene synthesis.[68,69] A much simpler approach, only suitable for liquid samples, is direct counting without any sample preparation.[70−72] All these techniques involve a liquid scintillation counter to detect byproducts from the radioactive decay of ^{14}C. The energy of the decay byproducts is converted to photons by a "cocktail" solution and further detected and amplified by the counter.[32,62,64] Although significantly more straightforward, the precision of direct counting is poor by comparison because of quenching properties related to different colors of the liquid that lead to loss of counts. Different products require their own baseline analysis to determine quenching effects. The accuracy and limit of detection of this technique is related to the amount of time over which signal is collected. A previous study[73] showed that increasing the counting time improved precision (0.2% absolute for 2% of biogenic content with 180 min of counting time), comparable with AMS[67] and LSC-benzene. Direct LSC has been used to track biogenic carbon in a wide range of fuel blends, ethanol/gasoline, diesel, HVO, and FAME,[71,74,75] and better results were obtained with higher biogenic concentrations. As noted, biogenic content of FCC coprocessing outputs may be at relatively low percentages (<10 wt %) and applying this technique requires long analysis times.

■ ADVANCED METHODS FOR TRACKING BIOGENIC CARBON

AMS and LSC methods described above are well established for differentiating renewable carbon. However, there are several aspects that make these techniques complex and expensive both in terms of equipment costs and analysis time,

https://dx.doi.org/10.1021/acs.analchem.0c04108
Anal. Chem. XXXX, XXX, XXX−XXX

thus limiting applicability at refinery sites. To directly measure biogenic carbon during coprocessing, new techniques will need to be developed. The ideal analytical apparatus would be implementable online on an FCC, HT, or HC; points where process feedback is maximized. Online analytical techniques have been previously investigated for the determination of other radionuclides (e.g., ^{90}Sr, ^{99}Tc, and actinides)[62] or applied for monitoring catalytic conversions.[76,77] A new biogenic carbon analysis method should exhibit reduced overall analysis time and reduced sample preparation steps compared to the standard AMS or LSC-benzene analyses. Although AMS is widely considered the standard method with the highest precision, it requires large, highly sophisticated, and expensive analytical facilities with high operating costs. Recently, some efforts have been made to make AMS more economical by reducing equipment size and associated costs.[78−83] Several emerging analytical alternatives have shown potential to address these challenges and may be applicable in coprocessing.

δ^{13}C-Isotope Ratio Mass Spectrometry. Measurement of ^{13}C/^{12}C isotope ratio is expressed in the form of δ^{13}C through the equation provided below:

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

The amount of ^{13}C depends mainly on organic source and geographical origin. Minute differences in isotope ratios can be used to determine region of origin as well as modern vs fossil carbon source.[84,85] Generally, classes of materials, such as plants and petroleum products have different average δ^{13}C values. Measuring δ^{13}C values of a mixture's components, such as VGO and a specific BDL, can be used to develop a mixing model that can be used to determine the percentage of each in the mixture as well as their products from coprocessing. This measurement can be carried out by much simpler equipment than AMS, such as an elemental analyzer gas-source isotope ratio mass spectrometer (EA-IRMS or IRMS), nuclear magnetic resonance spectroscopy (NMR),[86−88] or cavity ring down spectroscopy (CRDS).[89−91] Compared to the other techniques, IRMS has the highest precision and can potentially be used as a standalone system to differentiate carbon sources.[92] Potential advantages of IRMS are lower cost than AMS and faster analysis time than LSC. ^{13}C/^{12}C ratio has been used to measure renewable carbon content in biodiesel blends with petroleum-derived diesel.[35,36] A recent report[93] used this method to measure biogenic carbon during coprocessing in a pilot scale FCC. Promising results were obtained in terms of precision and detection limit. The precision obtained with this method was ±0.013‰, and the uncertainty decreased with greater difference in isotopic ratios between petroleum and BDL feeds. While the biogenic carbon detection limit observed was approximately 0.3% when a 4‰ difference in δ^{13}C was measured between bio-oil and petroleum feeds, it increased when this difference was reduced due to similar δ^{13}C signal between the feedstocks.

Biogenic carbon contents from this study were compared with D6866 Method B, showing strong correlation (R^2 = 0.998). A limitation stated by the authors is overlapping δ^{13}C values between some modern carbon sources and petroleum feedstocks. Stable carbon isotope ratios in plants are related to photosynthetic pathways for carbon fixation and plants are categorized in two families: C_3 plants, such as trees, rice, soybean, cotton, and cold-season grass, or C_4 plants, such as corn stover, switchgrass, warm-season grass, miscanthus, and sugar cane.[94−97] δ^{13}C of petroleum sources have been reported in the range −34 to −24‰ depending on the source, while the values for C_3 and C_4 are in the range −30 to −22‰ and −18 to −13‰, respectively.[84,93,98−100] As shown in Figure 4, the

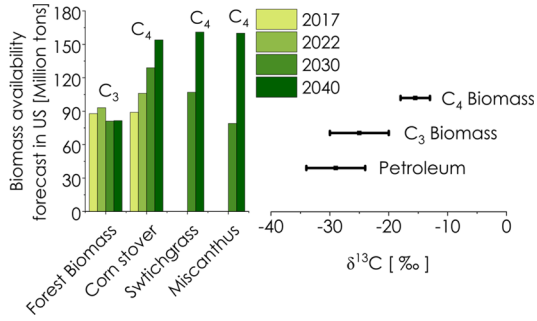


Figure 4. (left) Biomass availability forecast comprising forest and agricultural residues.[102] (right) δ^{13}C ranges; comparison of petroleum sources with C_3 and C_4 biomasses.[84,98,99]

range of δ^{13}C values for C_3 plants largely overlaps with that of petroleum fossil sources (e.g., VGO), while for C_4 plants the range of values is clearly separated from fossil sources. As described by the authors,[93] the method measures δ^{13}C of each single blend unit (bio-oil and VGO), estimating the fractionation in the coprocessing unit. Then, the δ^{13}C of the end products is measured calculating the blending level through a mixing model. In coprocessing BDL, it would be easier to differentiate the δ^{13}C of the biogenic portion when C_4 plants are used as biomass sources, while with C_3 plants, a tolerable isotopic difference is needed (i.e., about 4−5‰) with current measurement precision. It should be noted that the δ^{13}C method depends on the individual sources and while the range of possible isotopic values for C_3 plants and VGO overlaps, it has the potential for differentiating small blending levels from VGO as demonstrated in a recent report.[101]

This method could succeed in refineries, especially with BDL mainly from agricultural residues, such as the ones specified. Observing future forecasts of U.S. biomass availability for energy purposes (Figure 4), some C_4 plants (agricultural residues of corn stover, switchgrass, and miscanthus) would reach higher amounts than C_3 biomass by 2040. However, woody biomass (C_3) are the most researched feedstocks for FP and CFP because they are less difficult to feed into reactors, produce high bio-oil yields, and have low inorganic content compared to agricultural (C_4) plants.[20,103] Despite potential advantages of δ^{13}C as a method for tracking renewable carbon in coprocessing, widespread adoption would be straightforward only in the scenario of using C_4 derived BDL. With C_3 type, in some cases, petroleum feeds would be indistinguishable from BDL in terms of δ^{13}C, limiting application flexibility.

Optical and Laser Techniques for ^{14}C Detection. Optical and laser techniques for ^{14}C detection and quantification have been proposed as advanced methods for measuring biogenic carbon.[104,105] Optical detection of carbon isotopes, such as ^{14}C, has shown some issues, especially when high precision and low limits of detection are required. A limitation being susceptibility of spectroscopic detectors to

https://dx.doi.org/10.1021/acs.analchem.0c04108
Anal. Chem. XXXX, XXX, XXX−XXX

physical interference from background signals, thus, requiring chemical or physical sample preparation to improve precision.

Some of these methods require complete combustion of the sample to form CO_2. Nevertheless, ^{14}C can be directly detected without any other chemical modification. Complete combustion may also be needed to prevent fouling of the optics and eliminate some interferences. Researchers in several laboratories have studied solutions to improve precision of optical technologies, using different approaches. Optical ^{14}C detection based on saturated-absorption cavity ring-down (SCAR) spectroscopy was demonstrated in previous reports.[106−108] More recent studies demonstrated the possibility of SCAR in achieving precision closer to that of AMS.[109] Limitations reported with SCAR are mainly related to the complex and nonlinear nature of the analysis.[110−112] Other studies have demonstrated significant improvement in precision using mid-infrared $^{14}C^{16}O_2$ spectrometers based on cavity ring-down spectroscopy (CRDS) for several applications.[112−114]

One report demonstrated that CRDS obtained accurate measurements of ^{14}C compared to AMS, even in the presence of interferences from biological samples.[114] This work identified interferences, such as other CO_2 isotopes or nitrous oxides that limited spectrometer sensitivity and the study highlighted that a pMC fraction of >1 would be ideal to achieve significant accuracy. Further investigations,[89] using a laser-based mid-infrared CRDS detected ^{14}C in samples with pMC fraction <1. Another group[115] applied mid-infrared CRDS together with an advanced sampling system to analyze atmospheric $^{14}CO_2$ in an online setup. With this system the authors were able to differentiate between ^{14}C contained directly in the form of $^{14}CO_2$ and ^{14}C derived from the combustion of $^{14}CH_4$. Another optical ^{14}C detection method, intracavity optogalvanic spectroscopy (ICOGS),[116] provided the foundation for potential applications in several fields that require very low detection limits by replacing AMS with a simpler, less expensive and faster technique. This method works with a fixed frequency stabilized $^{14}CO_2$ laser and combines four different techniques previously studied: laser assisted ratio analyzer (LARA), optogalvanic spectroscopy, optical impedance spectroscopy and laser intracavity absorption spectroscopy.[117] A later study[118] was able to replicate these initial results and resolve issues found by other authors around the repeatability of the results and the absorption background due to $^{13}CO_2$ and $^{12}CO_2$.[117,119−121] It was demonstrated that a precision of 1% is achievable by ICOGS with a few minutes of analysis, although calibration can be challenging.[105] The main advantage of SCAR, CRDS, and ICOGS optical techniques for ^{14}C detection is the possibility of real-time analysis. Samples need to be oxidized to CO_2 that can be further directed to the optical isotope spectrometer; thus, direct online measurement of refinery unit outputs are possible with limited sample preparation and potentially preconcentration.

REFINERY BENEFITS FOR ONLINE BIOGENIC CARBON ANALYZERS

The major objectives of refiners considering alternative feedstocks like BDL are to (1) maintain safe and reliable operations throughout the refinery, (2) maximize refinery profitability with feedstock processing margins and applicable policy incentives, and (3) strategically improve the refinery's overall environmental sustainability profile. New online analyzers would further contribute to operational risk mitigation and contribute significantly to improving refiner's ability to both quantify and monitor renewable carbon in fuels and optimize overall refinery profitability.

Online refinery stream analyzers would be integrated into a refinery's distributed control system (DCS), where operating personnel interact continuously with the control system for process monitoring to facilitate response to changing process trends, alarms, upset conditions, etc. Online biogenic carbon analyzer data can contribute to advanced notifications for abnormal trends or operating range exceedances. For example, if online renewable carbon content in a process stream decreased in absence of other operational changes like a feedstock change (i.e., different VGO or bio-oil composition), this may indicate that bio-oil flow issues like plugging upstream of the FCC unit, over cracking or coking are occurring. Some of these issues would not be captured by conventional control variables. Refiners can utilize online analyzers in this way to reduce risk of operational upsets while coprocessing. Therefore, online techniques for determining the fraction of biogenic carbon in product streams are highly desirable. Currently, online analytics are integral to refinery operations for compliance with regulations, maintenance of smooth operation, and enabling rapid product distribution adjustments. In the US, the EPA requires the measurement of carbon dioxide, methane, and nitrous oxide emissions (40 CFR (Code of Federal Regulations) 98, subpart Y), as well as sulfur emissions (40 CFR 60, Subpart Ja), all of which can be performed with online process mass spectrometry.[122] Online distillation analyzers are used to monitor product quality.[123] Non-dispersive infrared (NDIR) analyzers are commonly used throughout refineries for process monitoring.[124] Because of peak overlap, they are coupled with multivariate statistical analysis, such as PLS, PCA, and MCR.[125] Given that other refinery online analytical tools are already in place, online biogenic carbon measurement could be a practical route to analyzing the renewable carbon fraction in products from coprocessing and could help drive coprocessing renewable intermediate organic streams into the fuel production chain.

In addition, today's refineries have sufficient instrumentation to perform detailed mass balance-based yield calculations and quantify product yield impacts resulting from changes in unit operations including new feedstocks. However, current refinery control and instrumentation systems lack the means to measure renewable carbon contents accurately, reliably, and quickly. Renewable carbon contents would be required inputs for biofuel product allocation calculations applied for quantifying applicable policy incentives. With the data provided by online biogenic carbon analyzers, refiners would have the capability to optimize refinery economics for coprocessing scenarios by considering margin impacts from yields, measured, and calculated by existing refinery instrumentation and from policy credits, measured, and calculated with biogenic carbon data. Figure 5 shows a simple example of how a refinery might assess both yield (blue line) and potential policy credits from coprocessing biomass-derived feedstocks (red line) to maximize total profitability (black line and triangular data point). Without reliable means to quantify biogenic carbon, a major component of the optimization data is missing.

The data reported through the DCS is also saved in a data historian for future investigations, data analysis, and reporting. With the data reported and historized, the refinery technical

https://dx.doi.org/10.1021/acs.analchem.0c04108
Anal. Chem. XXXX, XXX, XXX−XXX

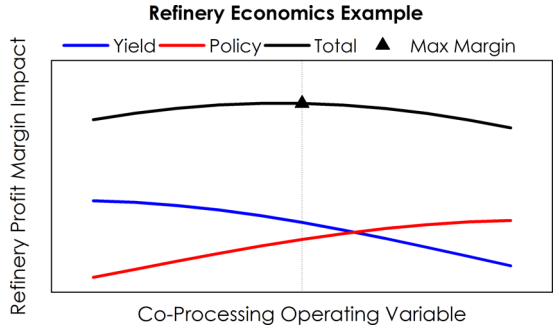


Figure 5. Example showing how refiners can utilize online analyzers to maximize overall refinery economics with coprocessing.

and environmental teams can easily access and apply it for certification or compliance-related reports. This data can also be combined with the rest of the historical plant data and integrated in refinery analysis tools like process simulations and optimization models. With these tools, refiners can further evaluate biogenic carbon distribution and utilization in the refinery. Ultimately, with tools like online biogenic carbon analyzers, refiners can quantify and track progress in reducing overall facility carbon intensity. In the initial commercial phases of coprocessing, it is likely that bio-oil concentrations in refinery unit feedstocks will be less than 5 wt % to minimize risk to reliable operations and considering BDL availability.[27] This means that quantifying biogenic carbon in gasoline, diesel, and jet fuel blend pools collected from all refinery unit operations will require extremely sensitive analytical tools due to increased dilution from petroleum derived finished fuels. There are also strong drivers for accurate online analytical methods that can be installed on the product streams of refinery unit operations in which coprocessing BDL is conducted. Coprocessing examples for straight-run diesel oil HT and FCC in Figure 6 highlight streams where online biogenic carbon analyzers could be installed. Refiners would likely prioritize installation of analyzers for quantifying biogenic carbon in fuel blendstocks like "diesel" from the hydrotreater and "naphtha" and "LCO" from the FCC. In addition, refiners may also consider adding analyzers to

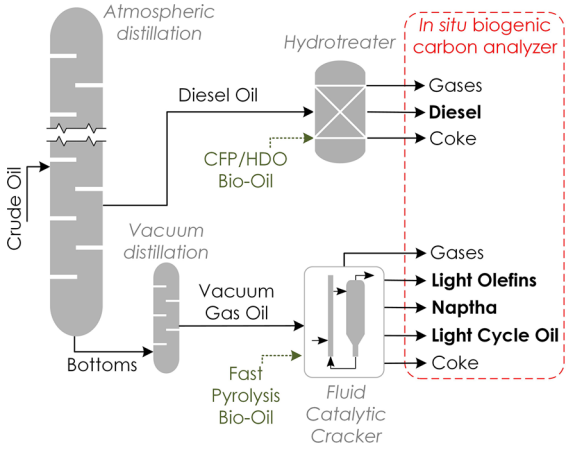


Figure 6. Simplified schematic showing insertion points for different bio-oils in existing refineries and possible positions for coupling biogenic carbon analyzer to accurately measure renewable fuels in finished fuels.

petrochemical products like propylene "LPG" if incentives for renewable plastics evolve from future policy.

On the basis of the current coprocessing research, it is likely that CFP oils or heavily upgraded oils would be coprocessed in hydroprocessing units and FP oil and partial upgraded bio-oils would be coprocessed in FCC or residuum FCC units. In refinery unit operations, where online analyzers are installed on unit product streams, a slip stream of each product can be combusted to generate $^{12}CO_2$, $^{13}CO_2$, and $^{14}CO_2$. The ratio of the isotopes can be used to calculate biogenic carbon incorporated in the refinery intermediate stream and, by volumetric blending calculations, in the finished fuel products. Online analyzers are nothing new for refineries who routinely utilize them for safety, process control, process optimization, product quality control, and continuous monitoring of major emissions sources. An optimal online biogenic carbon analyzer should be inexpensive, accurate, reliable, easy to maintain, and enable rapid analytical results. Reliable and accurate devices for measuring renewable carbon contents in blended finished products would address a major technology gap associated with coprocessing BDL in existing refining infrastructure and facilitate more rapid adoption of the coprocessing technology.

AUTHOR INFORMATION

Corresponding Author

Calvin Mukarakate − *Catalytic Carbon Transformation and Scale-up Center, National Renewable Energy Laboratory, Golden, Colorado 80401-3393, United States;* orcid.org/0000-0002-3919-7977; Email: Calvin.Mukarakate@nrel.gov

Authors

Stefano Dell'Orco − *Department of Industrial Engineering, University of Florence, 50135 Florence, Italy; Catalytic Carbon Transformation and Scale-up Center, National Renewable Energy Laboratory, Golden, Colorado 80401-3393, United States*

Earl D. Christensen − *Catalytic Carbon Transformation and Scale-up Center, National Renewable Energy Laboratory, Golden, Colorado 80401-3393, United States*

Kristiina Iisa − *Catalytic Carbon Transformation and Scale-up Center, National Renewable Energy Laboratory, Golden, Colorado 80401-3393, United States;* orcid.org/0000-0003-1326-901X

Anne K. Starace − *Catalytic Carbon Transformation and Scale-up Center, National Renewable Energy Laboratory, Golden, Colorado 80401-3393, United States*

Abhijit Dutta − *Catalytic Carbon Transformation and Scale-up Center, National Renewable Energy Laboratory, Golden, Colorado 80401-3393, United States;* orcid.org/0000-0003-4258-7287

Michael S. Talmadge − *Catalytic Carbon Transformation and Scale-up Center, National Renewable Energy Laboratory, Golden, Colorado 80401-3393, United States*

Kimberly A. Magrini − *Catalytic Carbon Transformation and Scale-up Center, National Renewable Energy Laboratory, Golden, Colorado 80401-3393, United States;* orcid.org/0000-0002-0216-7424

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.analchem.0c04108

https://dx.doi.org/10.1021/acs.analchem.0c04108
Anal. Chem. XXXX, XXX, XXX−XXX

Notes

The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was authored in part by the National Renewable Energy Laboratory, managed and operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding was provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. We thank Thomas J. Geeza from Los Alamos National Laboratory for editing the Perspective and for stimulating discussions.

■ REFERENCES

(1) EPA. *Renewable Fuel Standard Program*. https://www.epa.gov/renewable-fuel-standard-program (accessed 2020-07-01).
(2) *California Air Resources Board*. https://ww2.arb.ca.gov/ (accessed 2020-07-01).
(3) *Airlines For America*. https://www.airlines.org/# (accessed 2020-07-01).
(4) *Renewable Energy—Recast to 2030 (RED II) EU Science Hub*. https://ec.europa.eu/jrc/en/jec/renewable-energy-recast-2030-red-ii (accessed 2020-05-18).
(5) Dahmen, N.; Lewandowski, I.; Zibek, S.; Weidtmann, A. *GCB Bioenergy* **2019**, *11* (1), 107−117.
(6) Bridgwater, A. V. *Biomass Bioenergy* **2012**, *38*, 68−94.
(7) Bridgwater, A. V.; Peacocke, G. V. C. *Renewable Sustainable Energy Rev.* **2000**, *4* (1), 1−73.
(8) Iisa, K.; French, R. J.; Orton, K. A.; Dutta, A.; Schaidle, J. A. *Fuel* **2017**, *207*, 413−422.
(9) Griffin, M. B.; Iisa, K.; Wang, H.; Dutta, A.; Orton, K. A.; French, R. J.; Santosa, D. M.; Wilson, N.; Christensen, E.; Nash, C.; Van Allsburg, K. M.; Baddour, F. G.; Ruddy, D. A.; Tan, E. C. D.; Cai, H.; Mukarakate, C.; Schaidle, J. A. *Energy Environ. Sci.* **2018**, *11* (10), 2904−2918.
(10) Liu, C.; Wang, H.; Karim, A. M.; Sun, J.; Wang, Y. *Chem. Soc. Rev.* **2014**, *43* (22), 7594−7623.
(11) Ruddy, D. A.; Schaidle, J. A.; Ferrell, J. R.; Wang, J.; Moens, L.; Hensley, J. E. *Green Chem.* **2014**, *16*, 454−490.
(12) Elliott, D. C. *Curr. Opin. Chem. Eng.* **2015**, *9*, 59−65.
(13) Wildschut, J.; Mahfud, F. H.; Venderbosch, R. H.; Heeres, H. J. *Ind. Eng. Chem. Res.* **2009**, *48*, 10324−10334.
(14) Zacher, A. H.; Olarte, M. V.; Santosa, D. M.; Elliott, D. C.; Jones, S. B. *Green Chem.* **2014**, *16* (2), 491−515.
(15) Mahadevan, R.; Adhikari, S.; Shakya, R.; Wang, K.; Dayton, D.; Lehrich, M.; Taylor, S. E. *Energy Fuels* **2016**, *30* (4), 3045−3056.
(16) Peterson, B.; Engtrakul, C.; Wilson, A. N.; Dell'Orco, S.; Orton, K. A.; Deutch, S.; Yung, M. M.; Starace, A. K.; Parent, Y.; Chiaramonti, D.; Magrini, K. A. *ACS Sustainable Chem. Eng.* **2019**, *7* (17), 14941−14952.
(17) Karatzos, S.; Mcmillan, J.; Saddler, J. *Potential and Challenges of Drop-in Biofuels*, A Report by IEA Bioenergy Task 39; IEA, 2014.
(18) Patel, A.; Agrawal, B.; Rawal, B. R. *Energy Sources, Part A* **2020**, *42* (13), 1649−1661.
(19) Iisa, K.; French, R. J.; Orton, K. A.; Yung, M. M.; Johnson, D. K.; Ten Dam, J.; Watson, M. J.; Nimlos, M. R. *Energy Fuels* **2016**, *30* (3), 2144−2157.
(20) Howe, D.; Westover, T.; Carpenter, D.; Santosa, D.; Emerson, R.; Deutch, S.; Starace, A.; Kutnyakov, I.; Lukins, C. *Energy Fuels* **2015**, *29* (5), 3188−3197.
(21) Oasmaa, A.; Czernik, S. *Energy Fuels* **1999**, *13* (4), 914−921.
(22) Iisa, K.; Robichaud, D. J.; Watson, M. J.; Ten Dam, J.; Dutta, A.; Mukarakate, C.; Kim, S.; Nimlos, M. R.; Baldwin, R. M. *Green Chem.* **2018**, *20* (3), 567−582.
(23) Black, S.; Ferrell, J. R. *RSC Adv.* **2020**, *10* (17), 10046−10054.
(24) Black, S.; Ferrell, J. R. *Energy Fuels* **2016**, *30* (2), 1071−1077.
(25) Freeman, C. J.; Jones, S. B.; Padmaperuma, A. B.; Santosa, D. M.; Valkenburg, C.; Shinn, J. *Initial Assessment of U.S. Refineries for Purposes of Potential Bio-Based Oil Insertions*, PNNL-22432; Pacific Northwest National Laboratory, 2013. .
(26) van Dyk, S.; Su, J.; Mcmillan, J. D.; Saddler, J. *Biofuels, Bioprod. Biorefin.* **2019**, *13* (3), 760−775.
(27) Stefanidis, S. D.; Kalogiannis, K. G.; Lappas, A. A. *Wiley Interdiscip. Rev.: Energy Environ.* **2018**, *7* (3), 1−18.
(28) Mukarakate, C.; Orton, K.; Kim, Y.; Dell'orco, S.; Farberow, C. A.; Kim, S.; Watson, M. J.; Baldwin, R. M.; Magrini, K. A. *ACS Sustainable Chem. Eng.* **2020**, *8* (7), 2652−2664.
(29) Fogassy, G.; Thegarid, N.; Schuurman, Y.; Mirodatos, C. *Green Chem.* **2012**, *14* (5), 1367.
(30) Corma, A.; Huber, G. W.; Sauvanaud, L.; O'Connor, P. *J. Catal.* **2007**, *247* (2), 307−327.
(31) Dijs, I. J.; van der Windt, E.; Kaihola, L.; van der Borg, K. *Radiocarbon* **2006**, *48* (3), 315−323.
(32) Edler, R. *The Use of Liquid Scintillation Counting Technology for the Determination of Biogenic Materials*; Eikenberg, J., Jäggi, M., Beer, H., B, H., Eds.; Arizona Board of Regents, University of Arizona, 2009.
(33) Norton, G. A.; Cline, A. M.; Thompson, G. C. *Fuel* **2012**, *96*, 284−290.
(34) Telloli, C.; Rizzo, A.; Canducci, C.; Bartolomei, P. *Radiocarbon* **2019**, *61* (6), 1973−1981.
(35) dos Santos, V. H. J. M.; Ramos, A. S.; Pires, J. P.; de M. Engelmann, P.; Lourega, R. V.; Ketzer, J. M. M.; Rodrigues, L. F. *Chemom. Intell. Lab. Syst.* **2017**, *161*, 70−78.
(36) dos Santos, V. H. J. M.; Ketzer, J. M. M.; Rodrigues, L. F. *Energy Fuels* **2017**, *31* (1), 523−532.
(37) Schimmel, M.; Toop, G.; Alberici, S.; Koper, M. *Determining the Renewability of Co-Processed Fuels*, Final Report; Utrecht, Netherlands, 2018.
(38) ASTM International. *Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis* ASTM D6866-20; ASTM International: West Conshohocken, PA, 2020; pp 1−19. DOI: 10.1520/D6866-20.
(39) U.S. Environmental Protection Agency. *Federal Register* **2006**, *71*, 14669−14904.
(40) Deniz, Uner. *Advances in Refining Catalysis*; CRC Press, 2017.
(41) de Miguel Mercader, F.; Groeneveld, M. J.; Kersten, S. R. A.; Way, N. W. J.; Schaverien, C. J.; Hogendoorn, J. A. *Appl. Catal., B* **2010**, *96* (1−2), 57−66.
(42) Agblevor, F. A.; Mante, O.; McClung, R.; Oyama, S. T. *Biomass Bioenergy* **2012**, *45*, 130−137.
(43) Fuels Europe. *Religious Education* **2017**, *13* (3), 252−254, DOI: 10.1080/0034408180130314.
(44) U.S. Department of Energy. *New Pilot Plant Demonstrates the Potential to Co-Process Biomass Streams with Petroleum*. https://www.energy.gov/eere/bioenergy/articles/new-pilot-plant-demonstrates-potential-co-process-biomass-streams-petroleum (accessed 2020-04-15).
(45) Wang, C.; Li, M.; Fang, Y. *Ind. Eng. Chem. Res.* **2016**, *55* (12), 3525−3534.
(46) Wang, C.; Venderbosch, R.; Fang, Y. *Fuel Process. Technol.* **2018**, *181* (July), 157−165.
(47) Pinho, A. D. R.; De Almeida, M. B. B.; Mendes, F. L.; Ximenes, V. L.; Casavechia, L. C. *Fuel Process. Technol.* **2015**, *131*, 159−166.

https://dx.doi.org/10.1021/acs.analchem.0c04108
Anal. Chem. XXXX, XXX, XXX−XXX

(48) de Rezende Pinho, A. R.; de Almeida, M. B. B.; Mendes, F. L.; Casavechia, L. C.; Talmadge, M. S.; Kinchin, C. M.; Chum, H. L. *Fuel* **2017**, *188*, 462−473.
(49) Lindfors, C.; Paasikallio, V.; Kuoppala, E.; Reinikainen, M.; Oasmaa, A.; Solantausta, Y. Y. *Energy Fuels* **2015**, *29* (6), 3707−3714.
(50) Bezergianni, S.; Dimitriadis, A.; Kikhtyanin, O.; Kubicka, D. *Prog. Energy Combust. Sci.* **2018**, *68*, 29−64.
(51) Chen, Y. M. *Powder Technol.* **2006**, *163* (1−2), 2−8.
(52) Vogt, E. T. C.; Weckhuysen, B. M. *Chem. Soc. Rev.* **2015**, *44* (20), 7342−7370.
(53) Fogassy, G.; Thegarid, N.; Toussaint, G.; van Veen, A. C.; Schuurman, Y.; Mirodatos, C. *Appl. Catal., B* **2010**, *96* (3−4), 476−485.
(54) Renewable Fuel Standard Program ,US EPA. *Renewable Identification Numbers (RINs) under the Renewable Fuel Standard Program*. https://www.epa.gov/renewable-fuel-standard-program/renewable-identification-numbers-rins-under-renewable-fuel-standard (accessed 2020-07-06).
(55) Mcphail, L.; Westcott, P.; Lutman, H. USDA - A Report from the Economic Research Service: The Renewable Identification Number System and U. S. Biofuel Mandates. 2011.
(56) *Guidance for the Certification of Co-Processing*ISCC 203-01; ISCC System GmbH, 2017.
(57) *Co-Processing of Biogenic Feedstocks in Petroleum Refineries*; California Air Resources Board, 2017.
(58) Libby, W. F.; Anderson, E. C.; Arnold, J. R. *Science (Washington, DC, U. S.)* **1949**, *109* (2827), 227−228.
(59) Taylor, R. E. Radiocarbon Dating. In *Chronometric Dating in Archaeology. Advances in Archaeological and Museum Science*; Taylor, R. E.; Aitken, M. J., Eds.; Springer: Boston, MA, 1997; Vol. 2.
(60) Measuring Biogenic Carbon Content Testing through ASTM D6866. *Beta Analytic Testing Laboratory*. https://www.betalabservices.com/renewable-carbon/astmd6866.html (accessed 2020-05-01).
(61) Fifield, L. K. *Rep. Prog. Phys.* **1999**, *62* (8), 1223−1274.
(62) Hou, X.; Roos, P. *Anal. Chim. Acta* **2008**, *608* (2), 105−139.
(63) Accelerator Mass Spectrometry, C14 Dating, What is AMS? *Beta Analytic Testing Laboratory*. https://www.radiocarbon.com/accelerator-mass-spectrometry.htm (accessed 2020-12-10).
(64) Norton, G. A.; Devlin, S. L. *Bioresour. Technol.* **2006**, *97* (16), 2084−2090.
(65) Hut, G.; Ostlund, H. G.; van der Borg, K. *Radiocarbon* **1986**, *28* (2A), 186−190.
(66) U.S. Department of Agriculture. Product Categories. *BioPreferred*. https://www.biopreferred.gov/BioPreferred/faces/pages/ProductCategories.xhtml (accessed 2021-01-08).
(67) Haverly, M. R.; Fenwick, S. R.; Patterson, F. P. K.; Slade, D. A. *Fuel* **2019**, *237*, 1108−1111.
(68) Qureshi, R. M.; Aravena, R.; Fritz, P.; Drimmie, R. *Appl. Geochem.* **1989**, *4* (6), 625−633.
(69) Woo, H. J.; Chun, S. K.; Cho, S. Y.; Kim, Y. S.; Kang, D. W.; Kim, E. H. *J. Radioanal. Nucl. Chem.* **1999**, *239* (3), 649−655.
(70) Bronic, I. K.; Baresic, J.; Horvatincic, N.; Sironic, A. *Radiat. Phys. Chem.* **2017**, *137*, 248−253.
(71) Doll, C. G.; Wright, C. W.; Morley, S. M.; Wright, B. W. *Appl. Radiat. Isot.* **2017**, *122*, 215−221.
(72) Edler, R.; Kaihola, L. *Nukleonika* **2010**, *55* (1), 127−131.
(73) Norton, G. A.; Woodruff, M. X. *J. Am. Oil Chem. Soc.* **2012**, *89* (5), 797−803.
(74) Kristof, R.; Logar, J. K. *Talanta* **2013**, *111*, 183−188.
(75) Kristof, R.; Hirsch, M.; Kozar Logar, J. *Appl. Radiat. Isot.* **2014**, *93*, 101−105.
(76) Lo, J. G.; Chao, K. J.; Shio-Jin, S. *Int. J. Radiat. Appl. Instrumentation. Part* **1987**, *38* (9), 689−693.
(77) Sarkadi-Pribóczki, E.; Kumar, N.; Salmi, T.; Kovács, Z.; Murzin, D. Y. *Catal. Lett.* **2004**, *93* (1/2), 101−107.
(78) Ognibene, T. J.; Bench, G.; Brown, T. A.; Peaslee, G. F.; Vogel, J. S. *Int. J. Mass Spectrom.* **2002**, *218* (3), 255−264.
(79) Schulze-König, T.; Dueker, S. R.; Giacomo, J.; Suter, M.; Vogel, J. S.; Synal, H. A. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2010**, *268* (7−8), 891−894.
(80) Bard, E.; Tuna, T.; Fagault, Y.; Bonvalot, L.; Wacker, L.; Fahrni, S.; Synal, H. A. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2015**, *361*, 80−86.
(81) Salehpour, M.; Håkansson, K.; Possnert, G.; Wacker, L.; Synal, H. A. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2016**, *371*, 360−364.
(82) Lee, S. H.; Park, S. H.; Kong, M. J.; Kim, Y. S. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2020**, *465*, 15−18.
(83) Santos, G. M.; Southon, J. R.; Griffin, S.; Beaupre, S. R.; Druffel, E. R. M. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *259* (1), 293−302.
(84) Peters, K. E.; Moldowan, J. M.; Schoell, M.; Hempkins, W. B. *Org. Geochem.* **1986**, *10* (1−3), 17−27.
(85) Rashmi, D.; Shree, P.; Singh, D. K. *Food Control* **2017**, *79*, 169−176.
(86) Botosoa, E. P.; Caytan, E.; Silvestre, V.; Robins, R. J.; Akoka, S.; et al. *J. Am. Chem. Soc.* **2008**, *130* (2), 414−415.
(87) Pironti, C.; Cucciniello, R.; Camin, F.; Tonon, A.; Motta, O.; Proto, A. *Anal. Chem.* **2017**, *89* (21), 11413−11418.
(88) Martin, G. J.; Martin, M. L. *Annu. Rep. NMR Spectrosc.* **1995**, *31* (C), 81−104.
(89) Fleisher, A. J.; Long, D. A.; Liu, Q.; Gameson, L.; Hodges, J. T. *J. Phys. Chem. Lett.* **2017**, *8* (18), 4550−4556.
(90) Crosson, E. R.; Ricci, K. N.; Richman, B. A.; Chilese, F. C.; Owano, T. G.; Provencal, R. A.; Todd, M. W.; Glasser, J.; Kachanov, A. A.; Paldus, B. A.; Spence, T. G.; Zare, R. N. *Anal. Chem.* **2002**, *74* (9), 2003−2007.
(91) Zare, R. N.; Kuramoto, D. S.; Haase, C.; Tan, S. M.; Crosson, E. R.; Saad, N. M. R. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106* (27), 10928−10932.
(92) Lancet, M. S.; Winschel, R. A.; Burke, F. P.; Burke, P. *Fuel* **1993**, *72* (8), 1209−1217.
(93) Li, Z.; Magrini-Bair, K.; Wang, H.; Maltsev, O. V.; Geeza, T. J.; Mora, C. I.; Lee, J. E. *Fuel* **2020**, *275*, 117770.
(94) Monson, R. K.; Edwards, G. E.; Ku, M. S. B. *BioScience* **1984**, *34* (9), 563−566.
(95) Sage, R. F.; Christin, P. A.; Edwards, E. J. *J. Exp. Bot.* **2011**, *62* (9), 3155−3169.
(96) Ehleringer, J. R.; Cerling, T. E. *Encycl. Glob. Environ. Chang. earth Syst. Biol. Ecol. Dimens. Glob. Environ. Chang.* **2002**, *2*, 186−190.
(97) Cerling, T. E.; Wang, Y.; Quade, J. *Nature* **1993**, *361* (6410), 344−345.
(98) Kohn, M. J. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107* (46), 19691−19695.
(99) O'Leary, M. H. *BioScience* **1988**, *38* (5), 328−336.
(100) Coplen, T. B.; Böhlke, J. K.; De Bievre, P.; Ding, T.; Holden, N. E.; Hopple, J. A.; Krouse, H. R.; Lamberty, A.; Peiser, H. S.; Révész, K.; Rieder, S. E.; Rosman, K. J. R.; Roth, E.; Taylor, P. D. P.; Vocke, R. D.; Xiao, Y. K. *Pure Appl. Chem.* **2002**, *74* (10), 1987−2017.
(101) Geeza, T. J.; Li, Z.; Maltsev, O. V.; Lee, J. E. *Energy Fuels* **2020**, *34*, 11134.
(102) Langholtz, M.; Stokes, B.; Eaton, L. *Ind. Biotechnol.* **2016**, *12* (5), 282−289.
(103) Carpenter, D.; Westover, T. L.; Czernik, S.; Jablonski, W. *Green Chem.* **2014**, *16*, 384−406.
(104) Zare, R. N. *Nature* **2012**, *482*, 312−313.
(105) Murnick, D. E. *J. Labelled Compd. Radiopharm.* **2019**, *62* (11), 768−775.
(106) Giusfredi, G.; Galli, I.; Mazzotti, D.; Cancio, P.; De Natale, P. *J. Opt. Soc. Am. B* **2015**, *32* (10), 2223.
(107) Giusfredi, G.; Bartalini, S.; Borri, S.; Cancio, P.; Galli, I.; Mazzotti, D.; De Natale, P. *Phys. Rev. Lett.* **2010**, *104* (11), 1−4.
(108) Cancio, P.; Bartalini, S.; Borri, S.; Galli, I.; Gagliardi, G.; Giusfredi, G.; Maddaloni, P.; Malara, P.; Mazzotti, D.; De Natale, P. *Appl. Phys. B: Lasers Opt.* **2011**, *102* (2), 255−269.

https://dx.doi.org/10.1021/acs.analchem.0c04108
Anal. Chem. XXXX, XXX, XXX−XXX

(109) Galli, I.; Bartalini, S.; Ballerini, R.; Barucci, M.; Cancio, P.; De Pas, M.; Giusfredi, G.; Mazzotti, D.; Akikusa, N.; De Natale, P. *Optica* **2016**, *3* (4), 385−388.
(110) Lehmann, K. K. *Appl. Phys. B: Lasers Opt.* **2014**, *116* (1), 147−155.
(111) Sadiek, I.; Friedrichs, G. *Phys. Chem. Chem. Phys.* **2016**, *18* (33), 22978−22989.
(112) Genoud, G.; Vainio, M.; Phillips, H.; Dean, J.; Merimaa, M. *Opt. Lett.* **2015**, *40* (7), 1342.
(113) Galli, I.; Pastor, P. C.; Di Lonardo, G.; Fusina, L.; Giusfredi, G.; Mazzotti, D.; Tamassia, F.; De Natale, P. *Mol. Phys.* **2011**, *109* (17−18), 2267−2272.
(114) McCartt, A. D.; Ognibene, T. J.; Bench, G.; Turteltaub, K. W. *Anal. Chem.* **2016**, *88* (17), 8714−8719.
(115) Genoud, G.; Lehmuskoski, J.; Bell, S.; Palonen, V.; Oinonen, M.; Koskinen-Soivi, M.-L.; Reinikainen, M. *Anal. Chem.* **2019**, *91*, 12315−12320.
(116) Murnick, D. E.; Dogru, O.; Ilkmen, E. *Anal. Chem.* **2008**, *80* (13), 4820−4824.
(117) Persson, A.; Eilers, G.; Ryderfors, L.; Mukhtar, E.; Possnert, G.; Salehpour, M. *Anal. Chem.* **2013**, *85* (14), 6790−6798.
(118) Marino, B. D. V. *Near Surface Leakage Monitoring for the Verification and Accounting of Geologic Carbon Sequestration Using a Field Ready 14C Isotopic Analyzer*; Office of Scientific and Technical Information: United States, 2014.
(119) Carson, C. G.; Stute, M.; Ji, Y.; Polle, R.; Reboul, A.; Lackner, K. S. *Radiocarbon* **2016**, *58* (1), 213−225.
(120) Paul, D.; Meijer, H. A. J. *Anal. Chem.* **2015**, *87* (17), 9025−9032.
(121) Eilers, G.; Persson, A.; Gustavsson, C.; Ryderfors, L.; Mukhtar, E.; Possnert, G.; Salehpour, M. *Radiocarbon* **2013**, *55* (2), 237−250.
(122) Lewis, G. *Fast On-Line Monitoring of Flare Gases with the Prima PRO Process Mass Spectrometer*; Thermo Fisher Scientific: Winsford, Cheshire, U.K., 2015.
(123) Komulainen, T.; Sourander, M.; Jämsä-Jounela, S. L. *Comput. Chem. Eng.* **2004**, *28* (12), 2611−2619.
(124) Espinosa, A.; Lambert, D. *Hydrocarb. Process.* **1995**, *72* (2), 86.
(125) Chung, H. *Appl. Spectrosc. Rev.* **2007**, *42* (3), 251−285.

https://dx.doi.org/10.1021/acs.analchem.0c04108
Anal. Chem. XXXX, XXX, XXX−XXX