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Using Separation-Enhanced Isotope Ratio Mass Spectrometry to Enable Increased Renewable Carbon Content in Transportation Fuels

Executive Summary

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Using Separation-Enhanced Isotope Ratio Mass Spectrometry to Enable Increased Renewable Carbon Content in Transportation Fuels (CRADA 525)

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Stable isotope ratio measurements using isotope ratio mass spectrometry (IRMS) have previously been shown by Los Alamos National Laboratory (LANL) to be effective for tracking co-processed biogenic carbon, with results approaching those of accelerator mass spectrometry (AMS). The lower cost of an IRMS may enable deployment to refineries, improving access and analysis turnaround times (≤2 hours) and, by extension, generate data that can allow process optimization to maximize renewable carbon in desired refinery products. This work applied chemical separation approaches as part of the IRMS analyses, enabling biogenic carbon tracking in fuel product streams by boiling point range, chemical class, or molecular compound. This work shows that IRMS results can be comparable to AMS and that IRMS has the potential to improve precision and accuracy at low blend ratios, even below those typically reported by current AMS methods. The adoption and proliferation of IRMS has the potential, through lower instrumentation cost and rapid turnaround times, to optimize refinery processes through on-site analysis.

A major outcome of this work is the similarity of the percent biocarbon value determined from the ASTM D6866 B method using AMS with those from the $\delta^{13}C$ values analyzed by IRMS for blended and co-processed samples. In the plots below, datapoints have statistical equivalence to the 1:1 line ($y = x$), indicating the percent biocarbon estimated from $\delta^{13}C$ values can be a powerful tool for the refiners.

This report is arranged into subsections that describe results obtained for each project task. Task 1 was associated with sample receipt and organization. Task 2 developed or confirmed analytical methods and standards. Task 3 analyzed the samples as received from the refiners. Under Task 4, samples were characterized and separated into saturate and aromatic fractions at CanmetENERGY, and the fractions were analyzed using two approaches at PNNL. Under Task 5, samples were sent to LANL for $\delta^{13}C$ measurements and to Beta Analytics for AMS measurements. This final report was undertaken as Task 6.

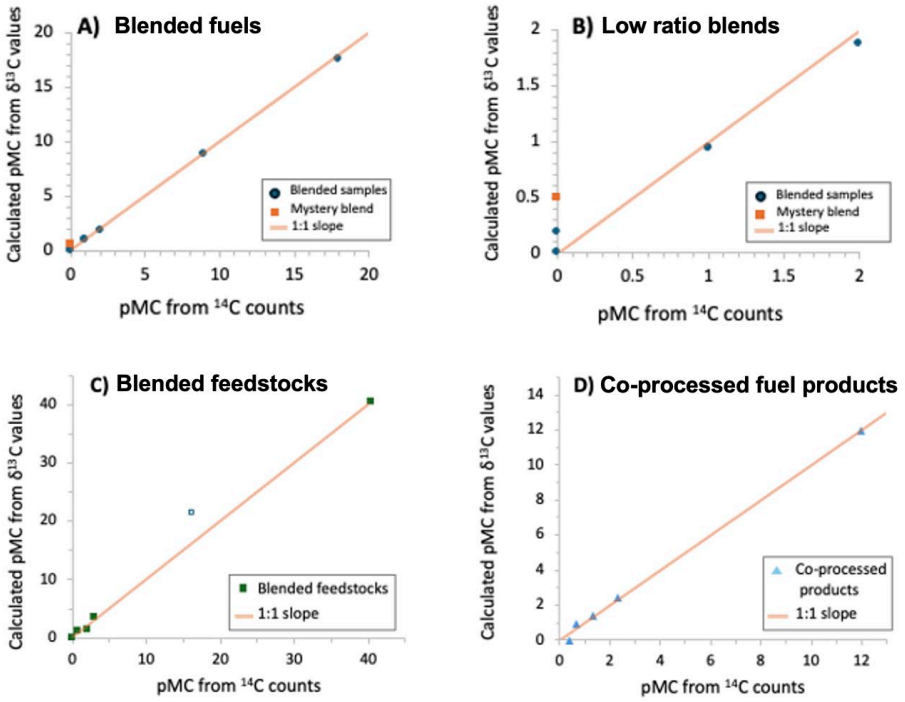

Figure ES.1. Percent modern carbon (pMC) data from ASTM D6866 B method using ^{14}C AMS measurements and calculated from $\delta^{13}C$ values analyzed via IRMS for (A and B) blended fuels and (C and D) blended feedstocks and the corresponding co-processed fuels. The orange line is the 1:1 slope ($y = x$) along which all points would plot if the methods produced identical results, and the open square in panel C is an outlier point for which the sample needs reanalysis. Abbreviations: AMS = accelerator mass spectrometry; $\delta^{13}C = ((R_{sample} / R_{standard}) - 1))$ x1 000, in per mil (‰) where R = $^{13}C/^{12}C$ ratio; IRMS = isotope ratio mass spectrometry.

Task 1 resulted in the receipt of forty-nine samples over the course of the project from three refiners and their collaborators. These samples were organized by process, identifying the feedstocks, blendstocks, and products. Because of the complexity of the various sample relationships, a series of sample schematics were produced to provide a map for datasets for each task and to identify existing gaps in the datasets. These are shown in Appendix B. These schematics were referenced throughout this project to prioritize sample analysis for percent biocarbon determination.

Because of the complexity of the IRMS measurement and the desire to ensure measurement consistency across labs and within the lab at PNNL, the Project Team developed a series of analytical standards and agreed-upon sample handling and analysis methodologies under Task 2. Sample handling and analysis methodologies were agreed upon by the Project Team and are presented in Section 5.0, where bulk samples were introduced to the combustion unit by direct injection at PNNL and by sealing in a tin capsule under an argon environment for LANL. Bulk, combustible liquids that represented the behavior of the fuel and feedstock samples were identified at PNNL as in-house standards, supplied to LANL, and used at both locations to ensure continuity in data calibrations (Experimental Section, Section 5.0). In addition, standards

with known isotopic compositions were obtained from external suppliers to correct and normalize the $\delta^{13}C$ values of bulk and compound-specific samples.

In order to obtain comparative measurements for assessing any improvements in accuracy, precision, and detection limits when separations are introduced in Task 4, it was first necessary to perform analyses of the as-received samples. This is referred to as “bulk IRMS” and comprised the work under Task 3. Fuel and feedstock samples were received in three tranches, and the bulk materials were analyzed for their $\delta^{13}C$ values via elemental-analyzer isotope ratio mass spectrometry (EA-IRMS) to provide bulk-IRMS measurements. Liquid samples were injected directly into the EA-IRMS instrument for combustion, and solid samples, such as tallow-based biofeeds, were weighed into smooth-sided tin capsules and sealed prior to being introduced into the EA-IRMS. Blend curves and assessments of linearity show that samples with small amounts of biofuel sometimes show a slightly quadratic relationship along the blending curve. When needed, quadratic models provide better precision of percent biocarbon in blind blends supplied by CanmetENERGY. The origin of the quadratic behavior is unknown; however, the nonlinearity is postulated to be related to fuel matrix effects or small variations arising during blending.

Task 4 was was conducted in two parts: the first at CanmetENERGY and the second at PNNL. Fuel samples were sent to CanmetENERGY for detailed characterization and solid-phase extractions (SPEs). Various analytical techniques including one- and two-dimensional gas chromatography (GC and GC×GC, respectively) were used to investigate the wide variation in sample hydrocarbon composition and boiling point distribution. GC with a flame ionization detector (FID) was employed to evaluate the fraction content for each sample after SPE. Normal-phase GC×GC and reverse-phase GC×GC were coupled with an FID to determine the hydrocarbon compositional fingerprint. Light naphtha samples were also resolved using paraffins, iso-paraffins, olefins, naphthenes, aromatics, oxygenates (PIONA) separation employing a GC coupled to a vacuum ultraviolet spectroscopy (VUV) detector. The three methods were compared for the more challenging, light samples and showed good agreement. Further work includes comparing the $\delta^{13}C$ values from different fractions from co-processed fuels and blended fuels with percent biocarbon values provided by GC-based separation methods for samples that span a small difference in percent biocarbon.

In the second part of Task 4, the $\delta^{13}C$ values of product and feedstock fractions provide additional information than can be obtained by the $\delta^{13}C$ value of bulk samples alone. Instead of a single data point, incorporating a bulk analysis of fractions by compound class provides an increased range of $\delta^{13}C$ values, with the resulting $\delta^{13}C$ value of the bulk sample between that of the aromatic fraction (more negative $\delta^{13}C$ value) and the saturate/paraffin fraction (less negative $\delta^{13}C$ value). The range between the fuel fractions is larger for the product than they are for the fuel feedstock, potentially indicating the incorporation of biocarbon preferentially in the saturate fraction. However, this relationship requires additional analyses for fractions of co-processed fuels originating from the same feedstocks and experiencing the same processing parameters. Ideally, these measurements would be compared with percent biogenic carbon data provided by AMS measurements.

Initial compound-specific analyses demonstrate variations among the $\delta^{13}C$ values of fuel and feedstock paraffin/saturate fractions for individual n-alkanes, suggesting a variable distribution of biocarbon for co-processed fuels across a range of compounds. Additional analyses of fuel fractions from feedstocks, blended fuels and, co-processed fuels are needed to better evaluate the distribution of biocarbon and estimate the percent biocarbon in different fractions. This analytical method could also be assessed for the potential to use a single compound to track

percent biogenic carbon instead of the need to analyze each component. If so, the time needed for analysis could be decreased.

Due to limitations in time, resources, and sample availability, it was not possible to assess the biogenic carbon distribution by fraction under different conditions (e.g., processing method or renewable feedstock type). To fully assess the biogenic carbon distribution, sample sets must include all fractions for any single processing operation, including both feedstocks and the resulting products (e.g., gas, liquid, and solid products). Additional work on the biogenic carbon distribution will depend on the sample sets supplied by industrial partners.

Task 5 comprised interlaboratory comparisons, the results of which indicate that the LANL and PNNL $\delta^{13}C$ values for the same fuel samples generally yielded similar values and therefore similar percent biocarbon estimates. Both labs noted slight quadratic curves across blend ratios, with a slightly stronger quadratic curve in the LANL data. To determine the influence(s) associated with the differences in $\delta^{13}C$ values at low blend ratios, additional sample sets and sample blends need to be analyzed for each blend curve while using the sample, matrix-matched standards for correction. At this point, the influence of sample aging during the transport of samples to LANL from PNNL cannot be distinguished from blending errors or differences in blended fuel characteristics. In addition, small differences between sampling techniques, including a generally higher standard deviation (though slight) for the LANL technique, may influence fuels differently than oils, which were the sample type for which the technique was developed. All of these effects may influence $\delta^{13}C$ values at low blend ratios.

Analytical techniques developed to distinguish neat fuels and fractions using $\delta^{13}C$ proved effective, with the results obtained in ≤2 hours and with the majority biogenic carbon content measurement aligning within 10% of the values determined by AMS. The blended feedstock set from landfill-derived material would benefit from additional analyses that account for the variation in the sample amount for the solid samples. A larger variation in the sample size can result in less-precise average $\delta^{13}C$ values from technical replicates and a higher variability from $\delta^{13}C$ analyses, making a comparison of samples less precise. Some samples would have benefited from additional analyses; however, project timelines and, in some cases, later arrival of some samples precluded those analyses. However, the current data show strong proof-of-concept that good comparisons among techniques exist and that further analyses will improve the statistics for these measurements.

This study indicates that the method of direct injection of fuel into the EA-IRMS system produced reproducibility on replicate measurements comparable to the method in which samples were encased in tin capsules sealed under an argon environment. These methods are used to avoid potential isotope fractionation of low viscosity samples that could lead to nonrepresentative $\delta^{13}C$ values. Direct injection also reduces the time needed for $\delta^{13}C$ analysis, as fuel could be directly removed from a fuel stream, injected, and data provided within ca. 10 minutes. This method of sample introduction would allow for a streamlined analysis at the facility setting.

The approach was shown to be effective since the $\delta^{13}C$ values of fuels can have high precision when measured in replicates and have been shown to provide precise estimates of the percent biocarbon. The new method of directly injecting fuel samples into the EA-IRMS system is comparable with the published method and may be more appropriate for liquid fuels as a method to minimize sample evaporation/volatilization during transfers prior to analysis. The $\delta^{13}C$ values using direct-injection EA-IRMS provide statistically similar values for the biogenic carbon content to the approved ASTM D6866 B method using ^{14}C AMS measurements. However, in

some cases, the fossil and biogenic sources can have similar $\delta^{13}C$ values depending on the source of carbon, meaning that the estimated percent biocarbon for a co-processed fuel will be less precise than for a co-processed fuel with a large range between feedstock/blendstock sources. The results suggest that the evaluation of fuel fractions can expand the range of $\delta^{13}C$ of co-processed fuels even when the co-processed feedstocks are similar, providing the potential for increased accuracy and precision, as compared to direct analysis of the parent samples.

These results contribute to a deeper understanding of the applicability of IRMS for measuring the biogenic carbon in transportation fuels. In this study, a broad evaluation of several fuel separation methods, when combined with measuring the stable carbon isotope ratios of fuels and fuel fractions, suggests that this approach can quantify the biocarbon in fuels with greater precision than analyzing the neat sample, particularly at low blending ratios.

The findings from this project are likely to encourage refiners to co-process renewable feedstocks, even when only relatively small amounts of renewables are present in the fuel. This will increase the demand for renewable feedstocks, encourage the production of additional renewable feedstocks, increase domestic job opportunities, and ultimately increase renewable content in transportation fuels. Additionally, co-processed fuels deliver fuel properties compatible with today's engines, and future fuels will be adapted to meet the requirements of new engines. This project will benefit the U.S. taxpayer by ensuring that a transition to fuels having increased renewable content will be seamless, while reducing greenhouse gas emissions through the displacement of crude oil feedstocks.

IRMS has the potential to be deployed on-site at refinery locations to provide the rapid sample analysis needed to optimize refinery operations for the incorporation of biogenic carbon in the final transportation fuel product. In addition, lab requirements and the mastery of sample processing and instrumentation, the costs of instrumentation and lab setup, and the pool of individuals with expertise make stable carbon isotope analysis and IRMS-based measurements more approachable than ^{14}C measurements via AMS in a refinery setting. While not part of this study, $\delta^{13}C$ measurements can also be made using optical spectroscopy, yielding results comparable to those obtained by IRMS, further reducing the costs for stable isotope ratio measurement, as well as instrument costs and stability over IRMS. This can only lead to an expansion of the use of $\delta^{13}C$ at refinery locations, allowing further realization of the benefits of stable isotope measurement in the field.