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Measuring the Effect of Fuel Structure and Blend Distribution on Diesel Emissions Using Isotope Tracing

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Isotopic Tracing of Fuel Components in Particulate and Gaseous Emissions from Diesel Engines using Accelerator Mass Spectrometry
LDRD Final Report for 01-ERI-007
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The attached paper," Measuring the Effect of Fuel Structure and Blend Distribution on Diesel Emissions Using Isotope Tracing," to be submitted to the annual meeting of the Western States Section of the Combustion Institute and UCRL-PROC-201918 "Investigation of HCCI Combustion of Diethyl Ether and Ethanol Mixtures Using Carbon 14 Tracing and Numerical Simulations" constitute the final report for LDRD-ERI-007, Isotopic Tracing of Fuel Components in Particulate and Gaseous Emissions from Diesel Engines using Accelerator Mass Spectrometry. The papers describe how ^{14}C-AMS was developed to trace molecules in fuels to emission products. Experimental results were compared to chemical kinetic model predictions. A.S. (Ed) Cheng, a graduate student of Prof. Robert Dibble (Mechanical Engineering, UC-Berkley), received his Ph.D. based in part on his work on this project. Dr. Cheng is now on the faculty at California State University, Sacramento. A second graduate student in Prof. Dibble's group, Hunter Mack, is using the technique in studying a new combustion regime and is supported through funds from DOE.

We successfully demonstrated differences in the emission products of fuel molecules depending on how they were mixed (homogeneous vs. heterogeneous) that is beyond the capability of current models. These experiments have led to support from DOE Office of FreedomCAR and Vehicle Technologies Program and a collaboration with the Combustion Research Facility at Sandia National Laboratories in Livermore, CA. Also, the energy and automotive industries have approached us about using the technique to examine specific problems that have been difficult to address due to lack of sensitive measurement techniques. Prior to this LDRD project and the papers it has generated, the automotive and energy industries were unaware of isotope tracing with "non-radiactive" levels of carbon-14. The demonstration of molecular site specific tracing in engines is opening research questions that previously not asked because no measurement technique could address them.

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Measuring the Effect of Fuel Structure and Blend Distribution on Diesel Emissions Using Isotope Tracing

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Abstract

Carbon atoms occupying specific positions within fuel molecules can be labeled and followed in emissions. Renewable bio-derived fuels possess a natural uniform carbon-14 (^{14}C) tracer several orders of magnitude above petroleum-derived fuels. These fuels can be used to specify sources of carbon in particulate matter (PM) or other emissions. Differences in emissions from variations in the distribution of a fuel component within a blend can also be measured. Using Accelerator Mass Spectrometry (AMS), we traced fuel components with biological $^{14}C/C$ levels of 1 part in 10^{12} against a ^{14}C-free petroleum background in PM and CO_2. Different carbon atoms in the ester structure of the diesel oxygenate dibutyl maleate displayed far different propensities to produce PM. Homogeneous cosolvent and heterogeneous emulsified ethanol-in-diesel blends produced significantly different PM despite having the same oxygen content in the fuel. Emulsified blends produced PM with significantly more volatile species. Although ethanol-derived carbon was less likely to produce PM than diesel fuel, it formed non-volatile structures when it resided in PM. The contribution of lubrication oil to PM was determined by measuring an isotopic difference between 100% bio-diesel and the PM it produced. Data produced by the experiments provides validation for combustion models.

Introduction

Chemical pathways of combustion can be identified through tracing and measurement of unusual isotopes. Radioisotopes are specific and distinctive because they are extremely rare in natural materials. A radioisotope-labeled compound may have a very high abundance-to-background ratio, but poor signal-to-noise in the isotope detector may obscure this property. Detector sensitivity must increase as the radioactivity of the isotope of interest decreases. Short-lived radioisotopes can be efficiently detected by their decay but produce high radiation hazards in the laboratory. Radioisotopes with long half lives (e.g., ^{14}C half life = 5730 y) are inefficiently detected by measuring decays.

Rare stable isotopes can be used as tracers to avoid issues associated radioactivity but specificity of the label can be lost with the higher natural background. The rare stable isotope of carbon, ^{13}C, occurs naturally at 1.1% while the natural abundance of ^{14}C due to cosmic radiation is 1.2 parts in 10^{12}. The ten orders of magnitude difference in natural background of these carbon isotopes significantly impacts ease of measuring an isotope signal.

Researchers in the mid-1980s labeled fuel components with ^{14}C and traced the isotope to PM or soot from a diesel engine [1] or diffusion flame [1,2] using a decay-counting technique. These experiments required special radioactive test facilities to contain the large amounts of volatile radioactive compounds needed for decay counting and housing a radioactive engine. In addition to generating a significant amount of radioactive and mixed wastes, high level radioactive tracing can never be used in a realistic combustion environment.

An alternative technique to decay counting, accelerator mass spectrometry (AMS), is an isotope-ratio measurement method developed in the late 1970s as a powerful tool for tracing long-lived radioisotopes in chronometry in the earth sciences and archaeology [3]. The high sensitivity of AMS allows the specificity of the ^{14}C atom to be used while avoiding radiological issues. Furthermore, AMS detection permits tracing with actual combustion systems in a realistic setting such as road vehicles in conventional dynamometer facilities. Samples prepared for ^{14}C analysis are combusted to CO_2 and then reduced to graphite for use in the AMS ion source. The technique separates individual nuclei by mass and then counts them rather than waiting for radioactive decay, allowing measurement of more than 100 ^{14}C samples per day.

The contemporary quantity of ^{14}C in living things (1.2 parts in 10^{12} C or 110 fmol ^{14}C/ g C) is highly elevated compared to the quantity of ^{14}C in petroleum-derived products (< 1 part in 10^{15}). Accordingly, components of bio-derived fuels contain elevated ^{14}C as compared to fossil fuels and are labeled uniformly throughout a molecule. This isotopic elevation is sufficient to trace the fate of bio-derived fuel components in emission products without the use of radioactive materials. The most common bio-fuels are ethanol, bio-diesel and bio-gas for natural gas. The complications of licensing and radioactive waste disposal are completely avoided by exploiting the sensitivity of AMS to measure the "non-radioactive" levels of ^{14}C in bio-derived fuels. Another approach to labeling a fuel is to purchase ^{14}C-labeled material and dilute it with petroleum-derived material to yield a contemporary level of ^{14}C. Custom radiolabeled molecules have the ^{14}C in a specific position within the molecule and place the label in nearly every molecule. The added specificity of position allows investigation of effects of molecular structure on emissions. In each case, the virtual absence of ^{14}C in petroleum-based fuels gives a very low ^{14}C background that makes tracing fuel components practical.

If mechanisms of soot formation are understood, then combustion modeling can be used to evaluate possible changes in fuel formulation and suggest possible fuel components that can improve combustion and reduce PM and other emissions. Combustion modeling assumes that large molecules break down into small components and then build up again during soot formation. If all carbon atoms behave similarly, then there should be little or no difference in the contribution of carbon from aromatics, cyclo-alkanes,

alkanes or oxygenated species in the PM emissions. AMS allows the labeling of specific carbon atoms within fuel components, tracing the carbon atoms, and testing this hypothesis. The influence of neighboring atoms on the mechanisms by which a particular fuel molecule breaks into fragments can be studied. Furthermore, the propensity of specific molecular structures within fuel molecules (e.g., carbon-carbon double bonds, carbon-oxygen double bonds, carbon-hydroxyl structures) to form specific emission products can be measured.

Researchers at Southwest Research Institute (SwRI) showed that the addition of the oxygenate dimethoxymethane to diesel fuel not only reduced total PM emissions, but also increased the volatile organic fraction (VOF) of the PM [4,5]. A fuel formulation that significantly shifts PM to the VOF can be as valuable in reducing emissions as a variation that drops total PM by simplifying emission treatment. AMS can be used to distinguish the ^{14}C signal in the PM after it has been separated into VOF and non-volatile fraction (NVF) to help determine the chemical pathways by which fuel oxygenation affects PM composition.

The methods described below for tracing fuel components in the emissions of diesel engines can be applied to any combustion system. Any molecule containing carbon can be labeled with ^{14}C. Although only recently applied to studies of engine combustion processes [6-10], the techniques for measuring the ^{14}C concentrations of PM and CO_2 by AMS are straightforward and routine.

Facilities

Emission samples were collected from a fleet diesel engine at the University of California at Berkeley (UCB) and an optical research engine at Sandia National Laboratories (SNL). The facilities provide complimentary capabilities for collecting data and examining combustion mechanisms.

The UCB engine is a 1993 Cummins B5.9, a 6 cylinder 5.9 liter turbocharged and aftercooled diesel engine rated at 175 bhp. Fuel injection is achieved with a Bosch P7100 PE type inline pump capable of injection pressures of up to 115 MPa. No modifications were made to the engine or fuel injection system to optimize for operation on the test fuels. The engine was operated at steady-state conditions of 1600 rpm and 285 N-m. Diluted exhaust was drawn through each filter for 10 minutes.

The SNL alternative fuels optical engine laboratory features a single-cylinder version of a modern-technology, Caterpillar 4-stroke direct injection (DI) diesel engine. This engine has been modified by SNL to provide extensive optical access into the combustion chamber as well as precise control of operating parameters [11,12]. The engine is based on the Caterpillar 3176/C-10 platform (350 bhp version) used in heavy-duty trucking, but utilizes a near-production HEUI-A fuel-injection system. In addition to standard cylinder-pressure-based diagnostic capabilities, windows in the upper periphery of the cylinder liner and in the piston crown enable in-cylinder combustion processes to be studied using advanced laser/imaging diagnostics.

The SNL engine was operated in a skip-fired mode, with one combustion event every 12th engine cycle. The skip-fired operation mode was selected to reduce the risk of a window failure and to reduce ring wear because the upper piston ring pack is not lubricated. A 1200-rpm, moderate-load (8.00 bar gross indicated mean effective pressure) operating condition was studied, and injection timing was optimized such that the engine operated at peak efficiency. A minimum of 72 fires were required to deposit sufficient soot for isotopic analysis. In practice, however, collecting PM over 216 fires produced a larger sample that was easier to process and analyze by AMS.

AMS is an isotope ratio mass spectrometry technique where $^{14}C/^{13}C$ ratios of the unknowns are normalized to measurements of 4-6 identically prepared standards of known isotope concentration.

Typical samples are placed in quartz combustion tubes with excess copper oxide (CuO), evacuated and combusted to CO_2. The evolved CO_2 is purified, trapped, and converted to graphite in the presence of cobalt or iron catalyst in individual reactors [14]. The AMS sample prep method accommodates samples containing between 0.05 and 10 mg carbon. Samples containing 0.2-2 mg carbon are preferred for obtaining higher measurement precision and lower systemic backgrounds. All graphite targets were measured at the Center for AMS at LLNL [13]. A general description of how AMS works is available in the literature [3]. Approximately 15000 ^{14}C-AMS samples are measured annually at LLNL with 2-3 measurement days per week.

Materials and Methods

The ^{14}C content of all major fuel components and lubrication oils must be measured prior to use. In our application, diesel fuel was not separated into components for individual measurements; its isotopic content was measured with the full additive and detergent commercial package added by the manufacturer.

The fuels used in the UCB Cummins engine were baseline diesel fuel and blends of diesel with bio-derived ethanol or biodiesel. The ethanol-diesel blends contained the same total oxygen concentration (7.0 mass %). Table 1 lists fuel blends and ^{14}C content of the major constituents in the UCB ethanol-diesel blended fuels. Because ethanol is soluble in diesel fuel in only small quantities, either an emulsifier (Span 85, i.e. sorbitan trioleate) or a cosolvent (n-butanol) was used to prepare the ethanol-in-diesel blends. An ignition improver, di-tert-butyl peroxide (DTBP), was also used to compensate for the low cetane number of ethanol and to give all blends the same cetane number (49.2) as the baseline diesel. The ^{14}C content of this diesel fuel is higher than expected for a petroleum product, probably due to small amounts of contemporary carbon detergents. The isotopic content of the lubrication oil was at instrument background. The contemporary carbon from the ethanol is the tracer in these fuels. Since the ethanol is bio-derived, it is uniformly labeled; each carbon atom in the ethanol molecule is equally labeled with ^{14}C. The emulsifier is also derived from a biological source.

Table 1. UCB test fuel blend components (volume %) and their ^{14}C content (amol ^{14}C/ mg C).

Fuel Component	**Emulsified Blend**	**Cosolvent Blend**	**^{14}C Content**
Diesel	76.0	77.0	0.33
Ethanol	18.5	18.0	107
SPAN 85	4.0	-	110
n-butanol	-	3.5	0.09
DTBP	1.5	1.5	0.01

The baseline diesel fuel (D2) used in the tests was a CARB-certified no. 2 diesel fuel with a sulfur content of 125 ppm. Additional baseline diesel fuel properties are available [9]. The biodiesel was vegetable oil-derived and met published ASTM fuel specifications [15]; the specifications include a minimum cetane number of 47. A representative composition of the biodiesel fuel, as provided by the manufacturer (Cytoculture International, Inc.) is given in Table 2.

In addition to the baseline diesel and neat biodiesel (B100), blends of 20% biodiesel (B20) and 50% biodiesel (B50), by volume, were prepared for testing. The ^{14}C content of all four test fuels were measured before engine testing began; results are listed in Table 3. As expected, the ^{14}C content of the biodiesel was much larger than that of the baseline diesel fuel. The oxygen content of each test fuel is also indicated in Table 3.

Table 2. Representative composition of biodiesel fuel.

Compound	**% by mass**
Methyl linoleate CAS 112-63-0 $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2CH_3$	55.4
Methyl oleate CAS 112-62-9 $C_{17}H_{33}CO_2CH_3$	21.3
Methyl palmitate CAS 112-39-0 $C_{15}H_{31}CO_2CH_3$	11.8
Methyl linolenate CAS 301-00-8 $CH_3(CH_2CH{=}CH)_3(CH_2)_7CO_2CH_3$	7.5
Methyl stearate CAS 112-61-8 $C_{17}H_{35}CO_2CH_3$	4.0

Table 3. Experimental test fuels.

Test fuel	**Designation**	**^{14}C content (amol ^{14}C/mg C)**	**Oxygen content (% by mass)**
Baseline diesel	D2	0.0783	0.0
20% biodiesel	B20	20.2	2.3
50% biodiesel	B50	50.2	5.6
100% (neat) biodiesel	B100	103	11.0

For the SNL engine, the ^{14}C concentration of all fuel components and the lubrication oil were checked by AMS and confirmed to be of petroleum origin ($^{14}C/C$ ratios $<10^{-15}$). The fuel used in this study was blended from an oxygenated hydrocarbon, dibutyl maleate (DBM) (88.0 vol%); a paraffinic hydrocarbon, n-hexadecane (7.0%) ; and an ignition improver, 2-ethylhexyl nitrate (5.0%). The ignition improver was required to achieve the desired ignition delay of 400 μs under the desired operating conditions (900 K and 60 bar at TDC when motored at 1200 rpm). The high concentration of DBM in the fuel was selected to optically study the combustion of the oxygenated hydrocarbon without the complication of high dilution in a conventional diesel fuel. Combustion of this fuel blend has been examined in detail at SNL [12]. A poly-isobutylene lubrication oil that cracked at ~570K was used so that any unburned lube oil deposited on filters during non-fired cycles could be easily removed from filters through heating.

The DBM fuel blend spiked with radiolabeled DBM in different positions; [maleate-1,4-^{14}C]- DBM or [maleate-2,3-^{14}C]- DBM. Separate batches of fuel contained tracer ^{14}C in the 1 and 4 carbon positions or the 2 and 3 positions of the maleate (see Fig. 1). Several microliters of tracer were used to spike the fuel and obtain fuel containing 90 fmol ^{14}C/ g C, approximately 85% the ^{14}C found in living organisms.

All PM samples were collected on Gelman Sciences PALLFLEX tissuquartz 2500QAT-UP membrane filters. These quartz filters were pre-combusted at 1173 K for 3 h to remove all carbon residue and allowed to cool to 300 K in the furnace before removal.

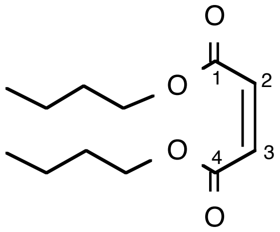

Figure 1: DBM molecule with the carbon atoms of the maleate numbered

Combustion gas samples were collected in Tedlar bags after the filters on each engine. The bags were maintained at temperatures between 290-300 K and processed within several days of collection. Water, sulfur dioxide, and unburned fuel were removed using a dry ice-isopropanol cold trap. The CO_2 was then cryogenically condensed in a liquid nitrogen cold trap and non-condensable gases (NO_x) were removed. The CO_2 was then moved to a graphitization head [14] for conversion to an AMS graphite sample.

Beyond measuring total PM emissions, we sought to determine partitioning of the PM. In practice, the criteria for this separation are operationally defined by the investigator. Depending on the field of the investigator, the separation of PM carbon is commonly described by the following pairs: elemental and organic carbon, soluble organic fraction (SOF) and insoluble organic fraction (IOF), or volatile organic fraction (VOF) and non-volatile organic fraction (NVF). We prefer the VOF/NVF nomenclature because it reflects the process we use and the physical properties employed in any realistic exhaust treatment scheme.

Loaded UCB filters were cut in half with a clean stainless steel scissors. One half was cut into strips and placed in a quartz combustion tube with CuO oxidizer to combust to CO_2. The combusted sample was then converted to an AMS graphite sample [14]. These samples are measurements of the total carbon in the PM. The other half filter was heated to 613K for 2 h in a furnace and then allowed to cool to room temperature to remove the VOF. The VOF is estimated by measuring the difference in mass of the two half filters. This procedure to remove the VOF was developed to obtain consistent isotope ratios and mass fraction of the NVF from National Institute of Standards and Technology (NIST) standard reference material (SRM). NIST SRM 2975 (diesel soot) and SRM 1649a (urban dust) are the closest NIST SRMs to exhaust PM. The filters loaded with PM lose mass during the thermal separation and the soot deposits are noticeably lighter in color. The remaining carbon is the NVOF. The filters with NVF are then prepared as AMS samples with the usual procedure [14].

Whole SNL filters (both skip-fired and motored controls) were heated to 613K for 2 h in a furnace and allowed to cool to room temperature. The heating effectively removed uncombusted lube oil deposited on the filters during the motored cycles in addition to the VOF. After cooling, the filters were cut into strips, placed in quartz combustion tubes with CuO and combusted to CO_2 as above. Every fourth filter was not heat treated and analyzed ‘as is’ to evaluate the effectiveness of the pretreatment. Combustion gas samples were collected in Tedlar bags after the filter holder.

Traditional gravimetric measurements of filters can be misleading for several reasons. It is difficult to measure 100 μg variations in a 100 mg filter. Furthermore, the filters are fragile and it is easy to lose small pieces on the soot-free border when handling with forceps. The PM deposited on quartz filters has very high specific surface area and readily absorbs water and other molecules from the vapor phase. An alternative technique for quantifying carbon utilizes the CO_2 pressure from the completely combusted sample measured during the AMS graphite preparation method.

The isotope ratio of the sample, R_{sample}, is calculated from the measured isotope ratios of the sample, $R_{sample(meas)}$, the average of the measured standards, $R_{stand(meas)}$, and the known isotope ratio of the standard, R_{stand}, shown in Eq.1.

$$R_{sample} = \frac{R_{sample(meas)}}{R_{s\tan d(meas)}} R_{s\tan d} \qquad (1)$$

The measured ratio of ^{14}C to total C for each sample (R_{sample}) is described below. The concentration of the ^{14}C labeled fuel component is $^{14}C_{tracer}/C_{tracer}$. The contributions from the fuel and additives to the measured ratio are $^{14}C_{fuel}/C_{fuel}$ and $^{14}C_{add}/C_{add}$, respectively. The background contribution is $^{14}C_{bk}/C_{bk}$ and the possibility of contamination to the sample is indicated as $^{14}C_{uk}/C_{uk}$.

$$R_{sample} = \frac{^{14}C_{tracer} + {}^{14}C_{fuel} + {}^{14}C_{add} + {}^{14}C_{bk} + {}^{14}C_{uk}}{C_{tracer} + C_{fuel} + C_{add} + C_{bk} + C_{uk}} \qquad (2)$$

In theory, all the components in Eq.2 need to be determined by a series of control experiments. In practice some components can be minimized by experimental design. In the case of PM samples, the ^{14}C terms of petroleum derived fuel components are insignificant, only a biologically-derived additive (e.g., SPAN 85) contributes to the ^{14}C content. The $^{14}C_{bk}$ component is a systemic background associated with sample prep and well known. It is hoped that C_{uk} is eliminated and C_{bk} is consistently measured in blanks and baseline diesel samples.

The denominator of Eq.2 is an expression for the total carbon mass of the sample. The product of the isotope ratio and carbon mass is the quantity of ^{14}C in the sample. The ^{14}C in the measured sample comes from the fuel components, whose isotope ratios we measure. The relative contribution of the tracer to the PM ^{14}C content can then be calculated by subtracting the sum of the contributions of the non-tracer fuel components from the total ^{14}C in the sample. The carbon mass of the tracer, C_{tracer}, in the PM is determined by dividing the tracer ^{14}C content, $^{14}C_{tracer}$, by the tracer ^{14}C concentration, R_{tracer}, (Eq.3).

$$C_{tracer} = \frac{^{14}C_{tracer}}{R_{tracer}} \qquad (3)$$

The fraction of PM mass attributable to the tracer, F_{tracer}, is then the ratio of C_{tracer} to sample carbon mass, C_{sample}, (Eq.4).

$$F_{tracer} = \frac{C_{tracer}}{C_{sample}} \tag{4}$$

Results And Discussion

Ethanol-Diesel Blends. The baseline diesel, homogeneous cosolvent and herterogeneous emulsified blends produced very different emissions. Combustion modeling did not predict these differences because the chemical kinetic models do not account for the heterogeneity of the fuel. The homogeneous cosolvent blend (described in Table 1) reduced total PM emissions to 71% of the baseline diesel level while the heterogeneous emulsified blend actually experienced a 14% increase in total PM mass measured gravimetrically. The carbon mass in the PM generated from the cosolvent and emulsified blends was almost identical when measured from CO_2 pressure during AMS sample graphitization. NO_x emissions from the ethanol-in-diesel blends were 89% that of the baseline diesel for both blends, probably due to lower combustion temperature. Emissions of both HC and CO increased, but remained very low as is typical with diesel engine combustion. With our fixed load operation, fuel consumption was higher with the test fuel blends due to the lower energy density of ethanol.

The CO_2 pressures measured from half filters during the production of graphite for AMS analysis provide an accurate measure of carbon mass. The partitioning of carbon in the VOF and NVF for the different fuel is shown in Figure 2. The baseline diesel and cosolvent blend both have roughly 55% VOF in this trial. The emulsified blend had a much larger more variable VOF, 75-90%.

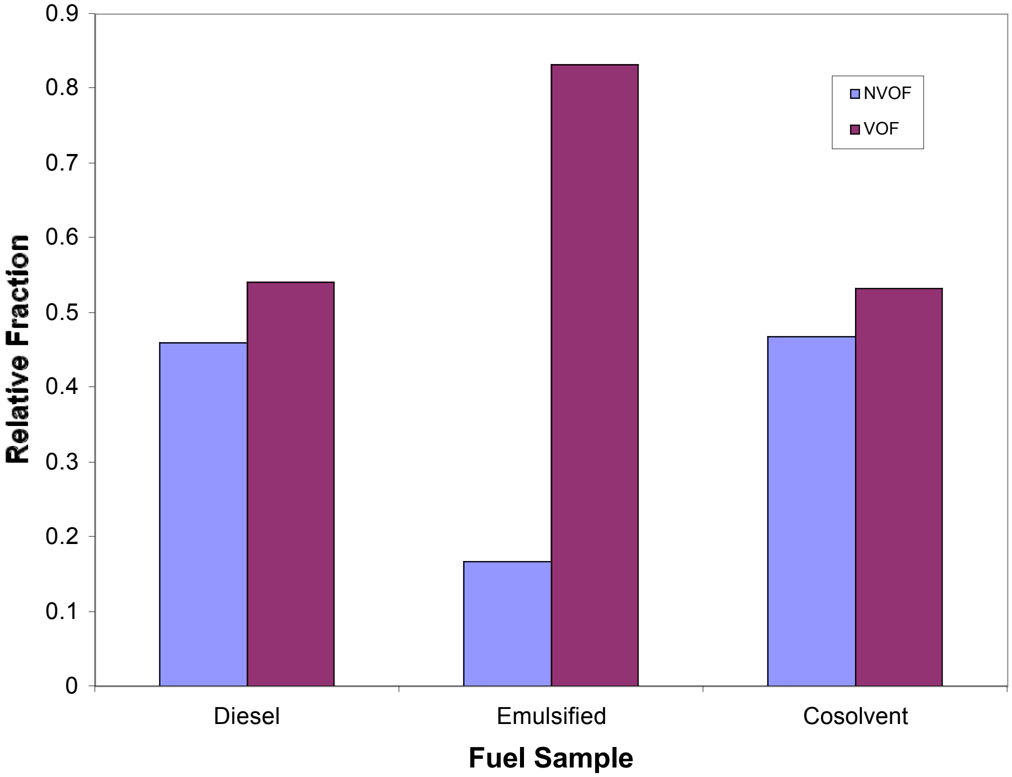

Figure 2. Partitioning of PM carbon between VOF and NVOF on filters loaded with baseline diesel , emulsified blend and cosolvent blend fuels. Baseline diesel VOF/NVOF partitioning varied by ~2% among replicate samples. The emulsified blend experienced much larger variations of ~10%.

When viewed in conjunction with the brake-specific emissions, the large VOF of the emulsified blend yields a brake-specific PM NVF only 23% that of diesel assuming 80% VOF from the emulsified blend. The cosolvent blend yields a brake-specific PM NVF 32% that of diesel assuming 55% VOF partition. The NVF PM is more resistant to exhaust oxidation, so driving more PM into the VOF may be more effective than simple PM mass reduction in reducing emissions.

The ^{14}C content of the ethanol provides the tracer for determining the fate of the ethanol-derived carbon in the engine emissions. The ^{14}C signal from the bio-derived ethanol in the PM was easily measured above the isotope level of the baseline diesel. Blank filters used to measure the carbon mass and isotopic content of the ambient environment absorbed approximately 25 □g carbon with a ^{14}C content about 50% of bio-derived plants. In a half filter this background accounted for 0.5 amol of ^{14}C. Filters loaded with PM from running baseline diesel also absorbed approximately 0.4 amol of ^{14}C between loading and AMS sample processing. Since fresh soot is more absorbent than aged soot, it is reasonable to assume most of this ^{14}C was absorbed in the engine lab where the ambient ^{14}C content is 50% that of contemporary plants as measured from blank filters. This absorbed mass is approximately 10 □g. Finally, the ^{14}C content of the diesel fuel is 0.3 amol ^{14}C / mg C. This level is higher than expected for a petroleum-derived material. Commercial diesel fuel contains a variety of additives, some of which may have bio-derived carbon, that slightly elevate the^{14}C above a single petroleum derived molecule (e.g. n-butanol in this study). The PM collected from the baseline diesel fuels contained about 1.2 amol ^{14}C / mg C. The thermal treatment to remove the VOF cut this background level to 0.7 amol ^{14}C / mg C.

Several trends were observed among the samples analyzed for ^{14}C content of total carbon PM. The total carbon PM for the cosolvnet blend had a lower ^{14}C concentration than that of the emulsified blend. Compared to the isotope content of the CO_2 from each fuel, the cosolvent blend produced PM with a ^{14}C concentration ~35% that of the CO_2 while the emulsified blend produced PM with a ^{14}C concentration ~40-45% that of the CO_2. The carbon mass generated by cosolvent and emulsified blends were almost identicle.

The trend that ethanol-derived carbon was less likely than diesel fuel-derived carbon to be found in the PM is not surprising. If the difference between CO_2 and PM partitioning were due only to the stability of the C-O bond in the ethanol, the reduction in PM ^{14}C content would likely be closer to 50%: the carbon attached to the oxygen would all be oxidized to CO_2 while the other carbon would behave like the diesel-derived carbon. Since the difference is greater, the carbon not adjacent to the oxygen in ethanol does not combust like the diesel fuel. It may be preferentially oxidized to CO_2 or there may be a significant contribution of ethanol-derived carbon in small volatile aldehydes formed during combustion. Techniques to separate and measure isotopic content of semi-volatile compounds are being investigated. The contemporary emulsifier could not entirely account for the higher ^{14}C content of the emulsified blend PM.

Carbon mass measured by CO_2 pressure from combusted half filters was the same for cosolvent and emulsified blends. The emulsified blend produced PM with higher mass but did not contain more carbon. Furthermore, much of this larger mass was volatile. The combination of no carbon and volatility of the PM, and the possibility of unburned emulsifier in the PM suggest that the higher PM mass may be due to absorbed water.

For the cosolvent blend, 63-87% of the ethanol-derived carbon in the PM resided in the NVF. In the case of the cosolvent blend, it appears that the ethanol-derived carbon resides primarily in the building blocks of soot rather than in condensed volatiles on the surface of the PM. The tendency of ethanol to produce acetylene and other soot precursors during combustion is supported by this data. For the emulsified blend, 20-35% of the ^{14}C in the PM resided in the NVF. Some of the loss of ^{14}C to the VOF for the emulsified blend appears to be associated with the emulsifier. Control experiments in which emulsifier was added to diesel without ethanol indicated that emulsifier-derived carbon resided mostly in the VOF.

Since the majority of the carbon from the fuel is fully combusted, the isotope ratio of the collected CO_2 reflects the isotopic content of the fuel. The CO_2 from the emulsified blend has more ^{14}C than the cosolvent blend as expected due to use of a contemporary emulsifier. The CO_2 contained 17 amol ^{14}C/g C and 13 amol ^{14}C/g C, mirroring the isotopic content of the emulsified and cosolvent UCB fuels.

Biodiesel-Diesel Blends. Addition of biodiesel had little effect on the performance of test engine [9]. Engine out NO_x increased slightly due to slightly advanced ignition. The addition of oxygen in the biodiesel contributed to lower CO, PM and unburned hydrocarbon emissions compared to baseline diesel. The 100% biodiesel fuel produced the most interesting results. The total PM (gravimetric) emissions from B100 were slightly higher than the baseline diesel but the NVF was only 34% that of conventional diesel fuel.

The B100 fuel also provided an opportunity to determine the contribution of lubrication oil to PM [10]. A depression in the ^{14}C content of the NVF PM with respect to the fuel was attributed the petroleum-derived lubrication oil. Measurements of the isotopic content of the fuel completed on separate days were consistently at the contemporary ^{14}C content of 103 amol ^{14}C / mg C. Table 4 summarizes the results indicating that lubrication oil contributed 4% of the carbon in NVOF PM.

Table 4. Summary of lubrication oil contribution to NVOF. The uncertainties in the averages are 1 standard deviation.

Filter	**NVF (amol ^{14}C / mg C)**	**Fraction NVF From Lube Oil**
1	98.1 ± 0.6	4.8%
2	98.1 ± 0.3	4.8%
3	98.2 ± 0.4	4.8%
4	100.5 ± 0.6	2.4%
Average	98.7 ± 1.2	4 ± 1%

The isotope content of CO_2 in combustion gas samples of B100 (102 ± 0.5 amol ^{14}C / mg C) was slightly depressed from that of the fuel samples (103 ± 0.5 amol ^{14}C / mg C). Dilution of the exhaust with the ambient air in the dilution tunnel accounted for the depression. The ambient air at the UCB Combustion Lab has a depressed ^{14}C ratio, typically ~60% the contemporary value of 103 amol ^{14}C / mg C. The ambient CO_2 concentration was measured at 380 ppm. These values for the ambient CO_2 are common in urban areas with high vehicle traffic. When the uncertainties in the measurements of fuel and CO_2 are considered, the contribution of lubrication oil to CO_2 was not significant.

In this study, the depression in isotope ratio was used to determine the contribution of lubrication oil to PM. The approach was successful due to the relatively large (4%) contribution of lubrication oil to NVF. It was a direct measurement of carbon from the lubrication oil under the speed and load used. It would probably be difficult to apply the procedure to engine operation under light loads due to the low PM levels produced.

Ideally, a uniformly labeled lubrication oil would be used as a tracer with conventional fuel. The advantage is that the contribution of the lubrication oil to the PM would be easier to measure. Our approach here measured small differences in the contemporary ^{14}C background. In essence, we measured a small difference between two big numbers. Because AMS measurement precision is 5 parts per 1000, we are confident that the depression in isotope content in the PM was due to the consumption of lubrication oil. The limitation of measuring the difference of two large numbers prevented the determination of lubrication oil in exhaust CO$_2$.

A suitably labeled lubrication oil would be a much better tracer. Lubrication oil labeled at 10-50 times the contemporary ^{14}C concentration would still not be a radioactive material [16], but its small contribution would be easier to measure against the ^{14}C-free petroleum background of a conventional fuel. Here we would measure a small signal against an the instrumental background. If lube oil were labeled at 10 times the contemporary ^{14}C level and 2% of the PM were due to lubrication oil carbon, the PM would have a ^{14}C concentration of 20 amol ^{14}C / mg, a value 200 times above instrumental background. This is a huge signal for AMS and gives us approximately two orders of magnitude in usable signal to noise. A lubrication oil suitably labeled would allow measurements of lube oil transport in exhaust at virtually all operation modes. Furthermore, labeled lubrication oil would enable PM size separation and apportionment of carbon to fuel or lubrication oil. Apportionment could continue to specific compounds separated and identified by gas chromatography and then quantified by AMS.

DBM Structural Tracing. All filters from the SNL experiments were loaded with a significant amount of carbon. Unfortunately, much of it was unburned lubrication oil. The lube oil deposition decreased over the course of a day, but the total carbon remained significant on filters collected with motored cycles only. Using the poly-isobutylene lubrication oil with the low cracking temperature (~570K) removed the large carbon background on the filters. The motored only filters had insufficient carbon (0-5 µg) to produce an AMS sample. The heating procedure to remove the VOF did not visibly reduce the deposited soot.

The ^{14}C content of the motored and skip-fired PM samples was almost identical and 3 orders of magnitude smaller than the bulk fuel, indicating that effectively all of the labeled carbon in the DBM was combusted to CO$_2$ that passed through the PM collection filter (Fig. 3).

The absence of ^{14}C from the filters in general (and from the PM in particular) indicates that the labeled carbon atom in the DBM, the 1,4 maleate position, is thoroughly oxidized to CO$_2$ (see Fig. 3). The 2,3 maleate position is no more sooty than an average carbon atoms in the fuel, despite having a carbon-carbon double bond. The double bond between the 2 and 3 carbon positions is a structure likely to produce soot precursors. By selectively labeling specific carbon atoms in a fuel, the tendency of neighboring atoms to influence the sites of molecular cleavage during combustion can be interrogated. The deposition of the tracer into different emission products depends upon the molecular fragments formed during combustion. This type of data can help combustion modelers construct and refine chemical-kinetic combustion mechanisms.

The addition of oxygen to diesel fuel reduces the production of PM. The effectiveness of the oxygen varies. We saw earlier that emulsified and homogeneous blends of ethanol-in-diesel produced PM emissions with different properties. Likewise, the distribution of oxygen within fuel molecules influences the effectiveness of the oxygen in decreasing PM. Carbon-oxygen bonds are very stable during combustion. Typically, any carbon bonded to an oxygen does not form soot. The fuel breaks into 1-2 carbon fragments. The carbon-oxygen double bond C=O of the 1,4 maleate carbon does not break and may frequently form CO directly. Virtually all CO is further oxidized to CO2 in the lean combustion conditions of diesels. There is evidence that the 1,4 maleate carbon retains both oxygen atoms bonded to it, however. It then makes CO$_2$ directly during combustion. Direct production of CO$_2$ is not desirable.

The point of putting oxygen in the fuel is to make as much CO as possible during the early stages of combustion. When a single carbon atom grabs two oxygen atoms, the soot reduction potential of the fuel is diminished.

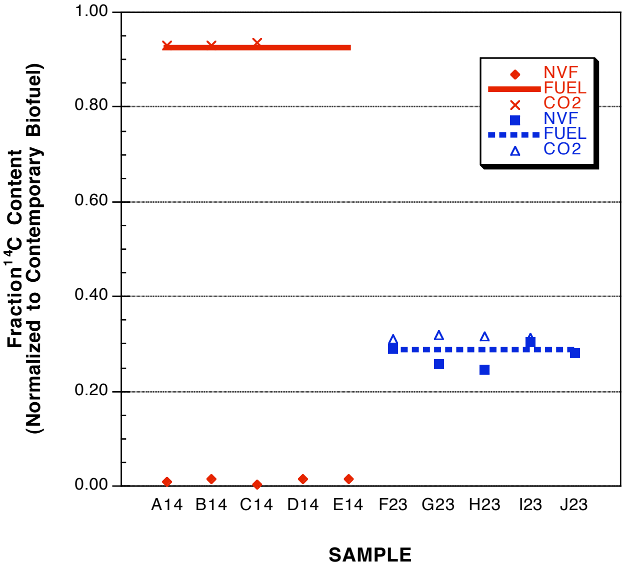

Figure 3. Carbon-14 content of the fuel, NVF PM, and CO_2 from 1,4 maleate and 2,3 maleate labeled DBM, numbers 14 and 23 in the sample names, respectively. Fraction ^{14}C content is the concentration of ^{14}C relative to the modern level in a biofuel, roughly 100 amol ^{14}C / mg C.

Conclusion

AMS provides a means of following the fate of carbon in specific compounds from the fuel to the emissions from any combustion source. Selective labeling of specific carbon atoms within a fuel component provides direct experimental evidence of the behavior of different chemical groups during combustion. In addition to providing data validation to combustion modelers, the data provides insights into which chemical structures within fuels and additives most greatly influence emissions.

The almost complete lack of ^{14}C in the PM collected with the DBM fuel labeled in the 1,4 maleate position suggests that the carbon-oxygen double bond does not break during combustion. Experiments designed to examine the influence of neighboring atoms on the carbon atoms in other chemical structures are underway.

The ease of using the contemporary tracer carbon in ethanol demonstrated the simple application to tracing bio-derived components of blended fuels. Although the majority of the ethanol-derived carbon was fully oxidized, more ethanol-derived carbon appeared in the PM than one might expect for a molecule containing so much oxygen. The data points to potential problems of using oxygenates which form unsaturated C_2 fragments during combustion. The differences in the PM produced with cosolvent and emulsified blends suggests that the distribution of oxygen in the fuel, not just its content, significantly affects PM production.

The extension of carbon isotope tracer analysis from engines to industrial combustors is straightforward. Methods for analyzing PM and CO_2 are well established. Sample size limitations in engines should not be a problem for larger combustors, so the analysis of less common chemical species in emissions should be easier. Basic chemical separation techniques could be implemented to isolate and analyze CO, small acids (e.g., formic and acetic) and aldhydes produced in combustion. Measuring these products can validate and improve combustion models and provide information on the effectiveness of combustors and emission control devices. AMS enables carbon isotope tracing in actual systems without the complications of radioactive materials.

AMS provides a means of following the fate of carbon in specific compounds from the fuel or oil to the emissions from diesel engines. The sensitivity and precision of ^{14}C-AMS overcame the limitations of using a labeled fuel to measure consumption of lubrication oil. Production of a universally labeled lubrication oil, preferably by polymerization of a small labeled base to produce uniformly labeled PAOs, is needed to thoroughly measure the transport of lubrication oil in the combustion chamber and out the exhaust head at all operation modes. A labeled lube oil will also enable particle size separation and apportionment to fuel or oil. The debate over the source of nano-particles could be quickly addressed.

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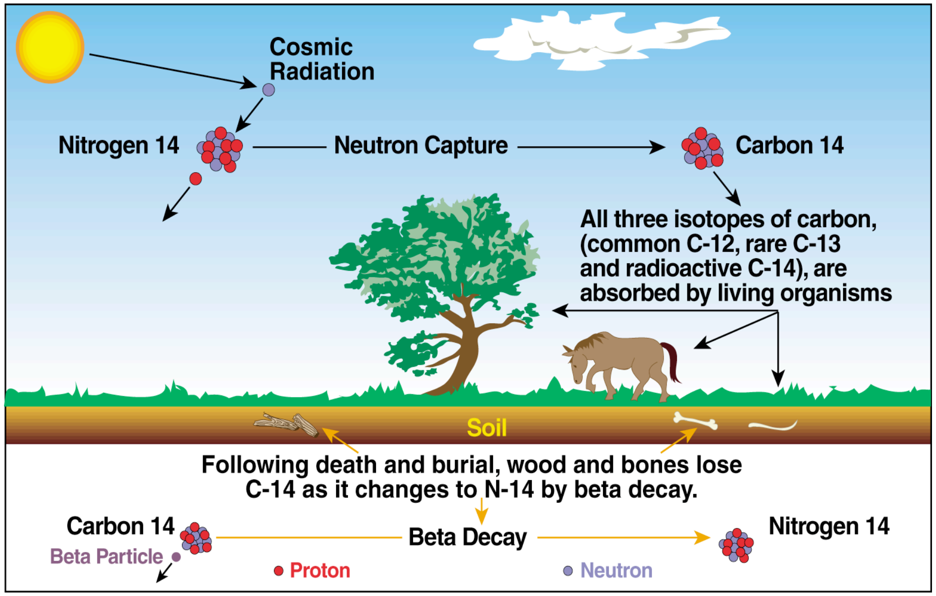
All living things are naturally labeled with low levels of Carbon-14 produced in the atmosphere

- Cosmic rays naturally produce C-14 in the atmosphere.
- C-14 is quickly oxidized to CO_2 and incorporated into all plants and animals
- C-14 is radioactive (half-life = 5730 years).
- When a plant or animal dies, it no longer replaces its carbon.

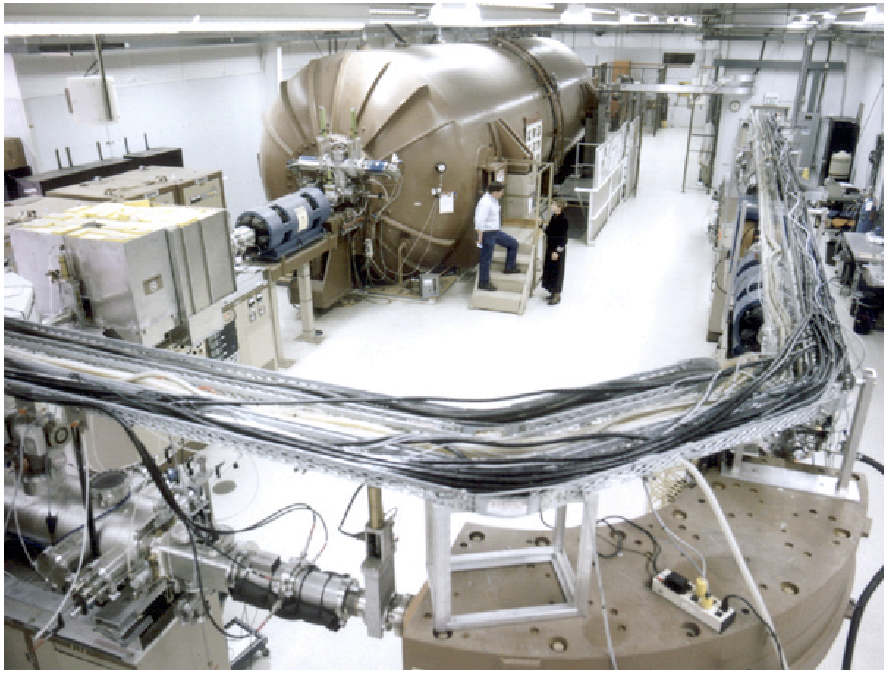


- Renewable fuels (ethanol, biodiesel, biogas) are universally labeled (C-14 distributed evenly throughout the molecules).
- Fossil fuels are essentially C-14 free since the carbon has been "dead" and isolated for more than 60,000 years (> 10 half-lives).

We exploit techniques developed for radiocarbon dating to trace natural C-14 levels from fuels to emissions against a C-14 free petroleum background.

Isotope label needed to follow fuel carbon in specific molecular structures through the combustion process

- Combustion breaks fuel molecules into 1-2 carbon fragments, destroying molecular signatures
- All isotopes of carbon follow the same reaction chemistry
  - Chemistry governed by electron configurations unique to each element
  - Nuclear mass provides a label for tracing
- Exploit the unique signature of ^{14}C to follow carbon atoms through the combustion process

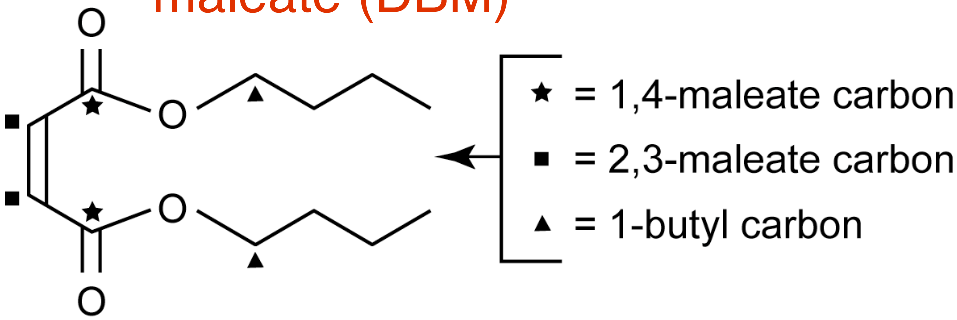


- Accelerator Mass Spectrometry counts individual C-14 atoms
- "Non-radioactive" levels of C-14 can be used in any conventional engine lab, dynamometer facility, or open road test.

Position of carbon within a fuel molecule affects its distribution in combustion products

- Custom synthesis of C-14 labeled fuel molecules allows placement of label in a specific molecular position
  - Custom synthesis places label in nearly every molecule
  - Dilute highly labeled tracer to C-14 level of biofuel to keep fuel nonradioactive
- Tracer does not affect global properties of fuel
  - Picoliters of tracer per liter of fuel
  - Tracer is member of chemical class common in fuel
  - Tracer distributes uniformly throughout fuel

Carbon atom tracing applied to the Diesel oxygenate dibutyl maleate (DBM)



★ = 1,4-maleate carbon

■ = 2,3-maleate carbon

▲ = 1-butyl carbon

- 1,4 maleate carbon does not make soot
- 2,3 maleate carbon less sooty than predicted despite soot precursor carbon-carbon double bond.
- 1-butyl carbon retains adjacent oxygen 10% of the time
- Direct production of CO_2 by 1,4 maleate carbon wastes fuel oxygen