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Isotopic Tracing Of Fuel Components In Particulate Matter From A Compression Ignition Engine Fueled With Ethanol-In-Diesel Blends

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Accelerator Mass Spectrometry (AMS) was used to investigate the relative contribution to diesel engine particulate matter (PM) from the ethanol and diesel fractions of blended fuels. Four test fuel blends and a control diesel fuel baseline were investigated. The test fuels were comprised of ¹⁴C depleted diesel fuel mixed with contemporary grain ethanol (>400 the ¹⁴C concentration of diesel). An emulsifier (Span 85) or cosolvent (butyl alcohol) was used to facilitate mixing. The experimental test engine was a 1993 Cummins B5.9 diesel rated at 175 hp at 2500 rpm. Test fuels were run at steady-state conditions of 1600 rpm and 210 ft-lbs, and PM samples were collected on quartz filters following dilution of engine exhaust in a mini-dilution tunnel. AMS analysis of the filter samples showed that the ethanol contributed less to PM relative to its fraction in the fuel blend. For the emulsified blends, 6.4% and 10.3% contributions to PM were observed for 11.5% and 23.0% ethanol fuels, respectively. For the cosolvent blends, even lower contributions were observed (3.8% and 6.3% contributions to PM for 12.5% and 25.0% ethanol fuels, respectively). The distribution of the oxygen, not just the quantity, was an important factor in reducing PM emissions.

INTRODUCTION

Dependence on foreign petroleum sources, price fluctuations on international petroleum markets, domestic agriculture policy and politics, and concerns for environmental and human health are driving research into the use of non-conventional, cleaner-burning fuels for internal combustion engines. Oxygenated fuels in compression-ignition (diesel) engines reduce particulate matter (PM) while also improving or maintaining acceptable levels of other regulated emissions (NO_x, HC and CO) [1-8,13]. The mechanisms through which oxygenates reduce PM, however, are not fully understood. Beyond changes in combustion chemistry, the influence of thermophysical properties on fuel injection and fuel-air mixing can play a significant role.

Gross measurements of PM, NO_x, HC, SO₂ and CO in emissions are straightforward means for measuring gross effects. Isotope tracing is an obvious way to follow specific fuel components in the emissions. In most cases, stable isotope tracing is impractical. Stable isotopes have an inherent background level which affects sensitivity. In general, the relatively high natural background requires very high enrichment of the stable isotope in the fuel component. Achieving a sufficient quantity of enriched isotope fuel component would be very expensive. Radioisotopes are much rarer so the natural background is much lower. Carbon-14 labeled fuels have been traced

in combustion systems [14-16], but the detection of decay counting is not efficient for long-lived radiocarbon (half-life ~5730 years). Counting 0.1% of the decays of a ^{14}C sample takes 8.3 years.

We used accelerator mass spectrometry (AMS) to investigate the relative contribution of fuel components on diesel engine PM emissions. The carbon isotope ratio of soot (the carbonaceous component of PM) indicated the ethanol and diesel fractions of blended fuels residing in the emitted PM. Rather than waiting for radioactive decay, AMS counts electrostatically accelerated nuclei (32.5 MeV for $^{14}\text{C}^{4+}$) in a simple particle detector [9]. AMS is a tandem mass spectrometry method with a charge changing disassociation cell between the mass spectrometry elements. Molecular isobars are completely disassociated in the charge changing process and any atomic isobars are discriminated in the detector. AMS is particularly efficient in detecting long-lived isotopes ($10\text{ y} < t_{1/2} < 100\text{ My}$). The rarity of long-lived radioisotopes yields a much lower background than that achievable with stable isotopes. For example, the naturally occurring carbon isotopic abundances are: ^{12}C (98.9%), ^{13}C (1.1%), and ^{14}C ($1.2 \times 10^{-10}\%$). The natural background of ^{14}C is 10 orders of magnitude lower than the rare stable isotope ^{13}C and AMS achieves limits of quantitation for ^{14}C below $1 \times 10^{-18}\text{ mol}$ in individual samples ($\text{LOQ} < 1\text{ amol } ^{14}\text{C} / \text{mg C}$). The decrease in background yields much greater sensitivity for ^{14}C AMS over ^{13}C MS.

MATERIALS AND METHODS

A 1993 Cummins B5.9 rated at 175 hp (131 kW) served as the experimental test engine (see specifications in Table 1). The engine employs a mechanically-governed in-line fuel injection pump capable of injection pressures up to 115 MPa. No modifications were made to the test engine to optimize for operation on the test fuels.

Table 1. Cummins B5.9 engine specifications.

Model year	1993
Displacement	5.88 liters (359 in ³)
Configuration	6-cylinder inline
Bore	102 mm (4.02 in)
Stroke	120 mm (4.72 in)
Compression ratio	17.6:1
Horsepower rating	175 hp @ 2500 rpm
Torque rating	420 ft-lb @ 1600 rpm
Aspiration	turbocharged and aftercooled
Injection timing (fixed)	11.5° BTDC

In this study, contemporary grain ethanol served as an isotopic tracer in petroleum derived (old carbon) diesel fuel. The high quality ethanol (low water content) was manufactured by Midwest Grain Products, Pekin, IL. The diesel was a CARB-certified No. 2 diesel fuel obtained from

Golden Gate Petroleum, Hayward, CA. Properties of ethanol and the diesel test fuel are shown in Table 2.

Table 2. Ethanol and diesel fuel properties.

Fuel	Ethanol ^a	Diesel ^b
Density (kg/L)	0.7923	0.8473
Cetane number	<5	49.1
Sulfur (ppm)	-	98
SFC total aromatics (wt. %)	-	16.32
SFC PNA's (wt. %)	-	4.09
Nitrogen	-	< 5 ppm
Boiling point (°C)	78	-
Distillation by D86 (°C)		
IBP	-	173
10%	-	237
50%	-	299
90%	-	336
95%	-	347
EP	-	358
Lower heating value (MJ/L)	21.2	35.4

^a from literature sources

^b as determined by fuel analysis

Since the solubility of ethanol in diesel fuel is limited, either an emulsifier (Span 85, also known as sorbitan trioleate) or a cosolvent (n-butanol) was used to stabilize 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. The Span 85 and n-butanol were obtained from Spectrum Quality Products, Inc.; the DTBP was obtained from Pfaltz & Bauer. The four different ethanol-in-diesel blends investigated are shown in Table 3. A high-speed, high-shear mixer (Greenco Model 1-LV Homomixer) was used to prepare the emulsified blends.

Table 3. Test fuel blends (components listed in percent by volume).

Fuel Blend	Diesel	Ethanol	SPAN 85	n-butanol	DTBP
A	72.0	23.0	4.0	-	1.0
B	70.0	25.0	-	4.0	1.0
C	83.5	11.5	4.0	-	1.0
D	82.5	12.5	-	4.0	1.0

All fuel blend components were converted to AMS samples using the disposable tube method [10] typically employed elevated biological tracers. The ¹⁴C content of all fuel components was measured at the Center for AMS at Lawrence Livermore National Laboratory.

Prior to beginning any experiments, lab facilities were checked for fixed and aerosol ^{14}C contamination with AMS analyzed swipes and fullerene soot aerosol monitors [17]. During the experiments, a steady-state engine speed-load condition of 1600 rpm and 210 ft-lbs (285 N-m) was used and measurements were made for PM, NO_x , HC and CO emissions, as well as for fuel consumption. Gaseous emissions (NO_x , HC and CO) were monitored using Horiba Instruments emissions analyzers and fuel consumption was measured via a load cell mounted under the fuel tank. PM was determined using a mini-dilution tunnel and gravimetric filter paper measurements.

In preparation for AMS analysis, the filters were baked at 900 °C for 2 h prior to loading to remove carbon residue and stored in sealed plastic bags after cooling. The filters (Pallflex Tissuquarz 2500QAT-UP) were conditioned overnight in petri dishes and weighed before and after PM loading on a Mettler UM3 microbalance. Filters were then sealed in plastic bags prior to preparation as AMS samples. Because of the limited quantity of contemporary grain ethanol obtained and time needed to collect sufficient PM mass for AMS analysis (~ 30 min. of engine operation), only one filter was collected for each test fuel.

Filters were cut into 2 or 3 pieces for AMS measurement of isotope ratios. Isotope ratios were measured to within 1-8%. Relative uncertainties were governed primarily by counting statistics. The samples with very low ^{14}C content had larger uncertainties. AMS measures the isotope concentration of unknown samples relative to those of known standards. In these experiments we normalized to four identically prepared standards of Australian National University Sucrose [11].

AMS sample preparation includes two steps. First samples are placed in evacuated quartz tubes with CuO and combusted at 900°C to CO_2 and H_2O . The water is frozen in the combustion tube using a dry ice-isopropyl alcohol bath and the CO_2 is cryogenically transferred to the reduction tube containing TiH_2 and Zn catalyst. The CO_2 is reduced to graphite in individual sealed tubes. The graphite is loaded into aluminum sample holders which are placed in a 64-place sample wheel for use in the AMS ion source. The volatile fuel blend components were frozen in the combustion tube by placing the exterior of the tube in liquid nitrogen prior to evacuation.

RESULTS AND DISCUSSION

Brake-specific emissions and fuel consumption results from the baseline diesel fuel and the four test fuel blends are shown in Table 4. A graphical representation of PM and NO_x emissions is shown in Figure 1. As anticipated, the general trend was towards lower PM emissions with higher levels of oxygenate (note that the cosolvent n-butanol is itself also an oxygenate), although an anomaly exists in that fuel blend C produced a 10% increase in PM. The data also indicates that the homogeneous cosolvent blends are more effective at reducing PM emissions compared to the emulsified blends. NO_x emissions from the ethanol-in-diesel blends were 22% to 27% lower than that of the baseline diesel and did not show large variation across the different blends. Emissions of both HC and CO increased, but remained very low as is typical with diesel engine combustion. Fuel consumption was higher with the test fuel blends due to the lower energy density of ethanol.

Table 4. Brake-specific emissions and fuel consumption results (g/kW-hr).

FUEL	Diesel	Blend A	Blend B	Blend C	Blend D
PM	0.032	0.025	0.012	0.035	0.029
NOx	6.28	4.58	4.90	4.92	4.88
HC	0.084	0.160	0.172	0.203	0.224
CO	0.312	0.517	0.625	0.358	0.371
bsfc	230	249	270	261	256

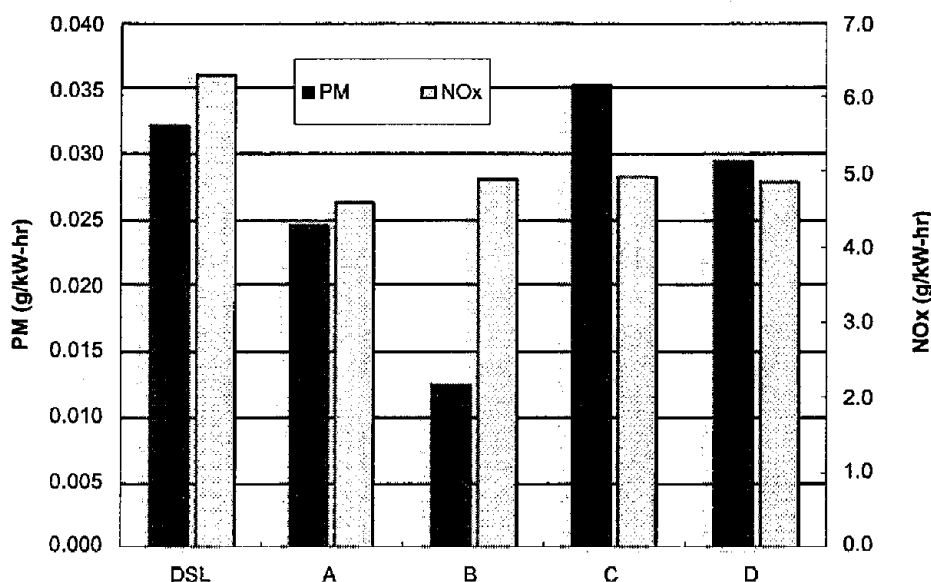


Figure 1. Brake-specific emissions of PM and NO_x.

Isotope ratios of the fuel components are reported in Table 5. The ¹⁴C content of the petroleum derived components are low, but not as low as expected. The cryogenic procedure used in packaging the volatile fuel components likely trapped some atmospheric CO₂ into the sample. The sealed tube sample prep method used here is typically used for biological tracing samples, not radiocarbon dating. The elevated background due to the multiple tube method is unimportant in its typical application. The emulsifier, Span 85, has a contemporary ¹⁴C content, indicating it is derived from biological products.

Improvements in background and quantitation of the petroleum components is easily obtainable by switching to the AMS method typically used in high precision radiocarbon dating [18,19]. Our measurements of the ¹⁴C content of NIST SRM 2975 diesel soot using the high precision, low background sample prep method are typically less than 0.10 amol ¹⁴C / mg C. We have achieved backgrounds half this ratio, only 50 zeptomole ¹⁴C / mg C.

Table 5. Carbon-14 content of fuel components.

COMPONENT	amol ¹⁴ C / mg C
Diesel	0.26
Ethanol	109
n-butanol	0.31
Span 85	109
DTBP	0.17

Measured isotope ratios (IR) contain contributions from all the components (and possibly more) shown in Eq. 1.

$$IR_{\text{sample}} = \frac{{}^{14}C_{\text{diesel}} + {}^{14}C_{\text{ethanol}} + {}^{14}C_{\text{absorbed}} + {}^{14}C_{\text{emulsifier}} + {}^{14}C_{\text{cosolvent}} + {}^{14}C_{\text{additives}}}{C_{\text{diesel}} + C_{\text{ethanol}} + C_{\text{absorbed}} + C_{\text{emulsifier}} + C_{\text{cosolvent}} + C_{\text{additives}}} \quad (1)$$

In practice we try to reduce the number of terms of this equation by limiting the number of components or rendering some terms negligible through judicious choice of compounds or experimental conditions. Through the use of appropriate controls we determined the contributions of the various components in Eq. 1. Traditional tracer experiments depend on radioactive decay for detection and are usually dominated by a highly labeled tracer with very small mass. In our case, the labeled tracer was not radioactive in the traditional sense and contributed a significant amount of carbon in the measured isotope ratio. We sought to determine the mass of tracer ethanol in the soot and need to consider the products of carbon mass and the isotope ratios. The total carbon mass is expressed in Eq. 2.

$$M_{\text{sample}} = M_{\text{diesel}} + M_{\text{ethanol}} + M_{\text{absorbed}} + M_{\text{emulsifier}} + M_{\text{cosolvent}} + M_{\text{additive}} \quad (2)$$

The product of the isotope ratio and carbon mass of each sample is the sum of the product of each component as described in Eq. 3.

$$IR_{\text{sample}} M_{\text{sample}} = \sum_{i=\text{component}} IR_i M_i \quad (3)$$

Equations 2 and 3 can be solved to determine the mass contributions of each component with knowledge of the isotope ratios of the components and a series of controls adding each component to the fuel mixture.

The isotope ratios of the filter samples loaded with PM from the fuel blends and the associated controls were elevated due to the absorption of atmospheric CO₂ and other carbon compounds on the soot during equilibration. Atmospheric CO₂ has approximately the same ¹⁴C content as ethanol, 109 amol ¹⁴C / mg C. The quantity of absorbed carbon depends on the surface area of the soot and length of time spent equilibrating in the atmosphere. It should scale with the mass of soot

deposited on the filters when equilibration times are constant. Separate control blanks were collected for soot samples from fuel blends A and B and from blends C and D. Assuming that all the sorbed carbon was contemporary, the mass of carbon absorbed with the separate sets of filters were 2.4% and 4.2% for blends A and B and blends C and D, respectively. These values for mass fraction of absorbed atmospheric carbon were propagated in the soot samples obtained from the fuel blends and the controls that included emulsifier or cosolvent without the ethanol.

Equations 2 and 3 were used to solve for the fractional mass of carbon in the soot from the emulsifier and ethanol. The mass fraction of carbon in the soot was not measured so all isotope measurements are expressed as fractions of soot carbon rather than absolute numbers. Since the ^{14}C content of the cosolvent and ignition improver were essentially the same as the diesel fuel, their contributions to the carbon soot mass could not be determined in our limited experiment. Either n-butanol or DTBP could be traced if desired, but we were not interested in obtaining isotope labeled material for this purpose. Our interest was primarily in tracing the ethanol. The contributions of the ethanol to the carbon mass in the soot is displayed in Table 6. Since the emulsifier is only 4% by volume in blends A and C, its contribution to the carbon mass is not large.

As the data in Table 6 shows, ethanol contributed less to soot than did the diesel in all of the test fuel blends. Results also indicate that the percent of fuel ethanol contributing to soot is higher for the emulsified blends A and C compared to the cosolvent blends B and D. The reduction in ethanol derived soot in the cosolvent blends is greater than one would expect from just the increased amount of oxygen due to the butanol. Along with the brake-specific emissions data, this suggests that the chemical mechanisms that inhibit soot formation and/or promote soot oxidation are different depending on the nature in which ethanol is blended with the diesel fuel.

Table 6. Contributions of ethanol to carbon soot mass. Fuel blends A and C used the emulsifier Span 85 while Blends B and D used n-butanol as a cosolvent.

Fuel blend	Ethanol volume % (fuel)	Ethanol carbon mass % (fuel)	Ethanol carbon mass % (soot)	Fuel oxygen mass %
A	23.0	15	8.6	8.2
B	25.0	16	6.3	9.2
C	11.5	7	4.7	4.4
D	12.5	8	3.8	5.0

CONCLUSIONS

Gravimetric filter paper measurements and isotopic tracing of PM reveal that ethanol-in-diesel blends reduce PM emissions from compression-ignition engines in a manner which results in a lower ethanol contribution to soot relative to its fraction in the fuel blend. Experimental results also indicate that homogeneous blends of ethanol and diesel behave differently than emulsified blends and yield lower PM emissions.

This study also demonstrated the power of using AMS to perform isotope tracing without using any specially labeled material. No radioactive material was used in any part of these experiments. Therefore, no mixed wastes (radioactive and hazardous) were generated, greatly simplifying disposal [12]. In practice, one could label any fuel additive or component and follow its fate in particulate emissions or exhaust gases. The sub-attomole sensitivity of ^{14}C -AMS can be used to separate components of exhaust gases (e.g., hydrocarbons, CO, CO₂) and quantify fuel stock contributions. Particulate separators can also be used to look at the fate of fuel components in different sized soot emissions.

Ethanol was selected as an oxygenate in this example because it was readily available with an appropriate ^{14}C content and it is a politically popular alternative to fossil fuels. It may not be the best alternative oxygenate due to its resemblance to acetylene and other known soot precursors. Ongoing experiments in which we separate volatile/non-volatile fractions and soluble/non-soluble fractions of soot prior to AMS analyses will improve our understanding of the combustion processes. Additional work to capture and separate CO₂ and CO in exhaust gases will provide valuable data for validation of combustion modeling.

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