

Carbonyl Formation during High Efficiency Clean Combustion of FACE Fuels

2010-01-2212

Published
10/25/2010

Samuel A. Lewis, John Storey, Charles Sluder, Kukwon Cho, Raynella Connatser and
Teresa Barone
Oak Ridge National Laboratory

Copyright © 2010 SAE International

ABSTRACT

The low temperature conditions that occur during high efficiency clean combustion (HECC) often lead to the formation of partially oxidized HC species such as aldehydes, ketones and carboxylic acids. Using the diesel fuels specified by the Fuels for Advanced Combustion Engines (FACE) working group, carbonyl species were collected from the exhaust of a light duty diesel engine operating under HECC conditions. High pressure liquid chromatography - mass spectrometry (LC-MS) was used to speciate carbonyls as large as C₉. A relationship between carbonyl species formed in the exhaust and fuel composition and properties was determined. Data were collected at the optimum fuel efficiency point for a typical road load condition. Results of the carbonyl analysis showed changes in formaldehyde and acetaldehyde formation, formation of higher molecular weight carbonyls and the formation of aromatic carbonyls. Details of these changes in carbonyl formation and discussion of formation mechanisms will be presented.

INTRODUCTION

Increasingly stringent emissions regulations for diesel engines and vehicles, as well as concern for fuel efficiency, have resulted in new developments in both emissions control technology and in-cylinder combustion strategies. Lowering engine-out NO_x and PM reduces demands on the emissions control and potentially enables more durable catalyst formulations.

Conventional approaches to diesel combustion have been plagued by a trade-off between NO_x and PM emissions. A strategy that reduced one pollutant typically increased the other. Recent theoretical and experimental studies describe combustion regimes, which exhibit simultaneous low NO_x

and PM emissions [1,2,3,4,5,6,7]. While the details of the various approaches to new combustion regimes vary somewhat, the approaches share the goal of burning the injected fuel charge in a lean pre-mixed combustion event. Formation of PM is reduced by the fuel-lean conditions in the premixed combustion. NO_x formation is avoided by use of exhaust gas recirculation (EGR) to reduce the flame temperature. Previous papers from our group describe HECC operation, associated engine performance, and regulated emissions [3,4,5,7].

In vehicle applications, HECC strategies are most often incorporated into low-load operating points due to the rapid pressure rise typically associated with the premixed combustion. HECC strategies often increase CO and HC exhaust concentration as well, and we have previously reported large increases in aldehydes and other partially oxygenated HC species not typically responsive to the total HC measurement [7,8,9].

The FACE fuel matrix, reported on elsewhere during this meeting [10], has 8 fuels that vary in cetane, aromatic content, and T₉₀, and a 9th fuel that is the centroid fuel. This study reports on unique species identified in the exhaust of an engine operating in HECC mode with the 8 FACE fuels. The influence of cetane, aromatics, and volatility on the formation of carbonyl-containing compounds and the relationship to combustion is discussed.

EXPERIMENTAL APPROACH

FUEL PROPERTIES

The eight FACE diesel fuels were selected for this study. The cetane numbers, aromatic content, and distillation values (T₈₀) for the 8 fuels were listed in Table 1. The goal of the

fuel blending was to have fuels that had a cetane percentage of 30 or 55; an aromatic percentage of 20 or 45 and distillation value (T_{90}) of 270 or 340 °C. Due to blending constraints, the Fuel 2 T_{90} was higher than the Fuel 1 T_{90} value but all other distillation values were lower, so the T_{80} values for the fuels were used for comparison purposes.

Table 1. BULK FUEL PROPERTIES OF THE EIGHT MODEL FUELS INVESTIGATED.

	CETANE NO.	AROMATIC %	T_{80} °C
FUEL 1	30	23	241
FUEL 2	28	25	234
FUEL 3	31	47	251
FUEL 4	28	48	299
FUEL 5	55	22	257
FUEL 6	54	22	316
FUEL 7	45	42	255
FUEL 8	49	44	316

ENGINE TEST PARAMETERS

In order to explore the effect of fuel properties on HECC operation, a GM 1.9-L, 4-cylinder common rail diesel engine was used. The engine was equipped with a variable geometry turbocharger (VGT), an electronic exhaust gas recirculation (EGR) valve with high pressure loop EGR (HP-EGR) cooling system. The engine was operated with a dSpace-based flexible engine control system capable of actuating the EGR valve, VGT rack position, swirl control valve (SCV), start-of-injection (SOI) timing, injection duration, fuel rail pressure, and number of injection events. The control system was set up to emulate the factory engine calibration and to allow departures from it as needed to achieve HECC operation. The engine was operated at a typical cruise point –1500 rpm, and 2.6 BMEP. Complete details of the engine and all nine FACE fuel evaluations appear in a companion paper. [11]

EXHAUST SAMPLING AND ANALYSIS FOR CARBONYLS

Exhaust species were collected using an in-house dilution system that has been described in detail previously. [9] The engine exhaust gas was diluted 7:1 with filtered ambient air and cooled to 40°C. The samples were collected on a Waters® dinitrophenyl hydrazine (DNPH) cartridge. The capped cartridges were then heated in an oven to 80°C for 12 hrs. This process gives the carboxylic acids the addition time needed to react with the DNPH. The DNPH-derivatized samples were extracted with 3 ml of acetonitrile then concentrated to a volume of 1 ml. 1 ml of water was added to each sample to improve resolution during separation. The DNPH derivatives were analyzed using a Hewlett-Packard®

1100 HPLC with UV detection. The HPLC separation was conducted using Restek® Allure C18 column. The eluent from the HPLC unit was transferred directly to a Bruker Daltonics® Esquire mass spectrometer via a 100 µm inner diameter PEEK tubing, and the hydrazone derivatives were identified using negative ion electrospray ionization mass spectrometry (ESI/MS) and ESI/MS/MS. MS/MS refers to a technique in which individual ions of interest are isolated, then fragmented, and the mass spectrum of that ion analyzed to help determine its structure. The need for the analysis to be done by both MS and MS/MS was due to the co-elution of species and the appearance of the same molecular ion for some of the carboxylic acids and hydroxycarbonyls.

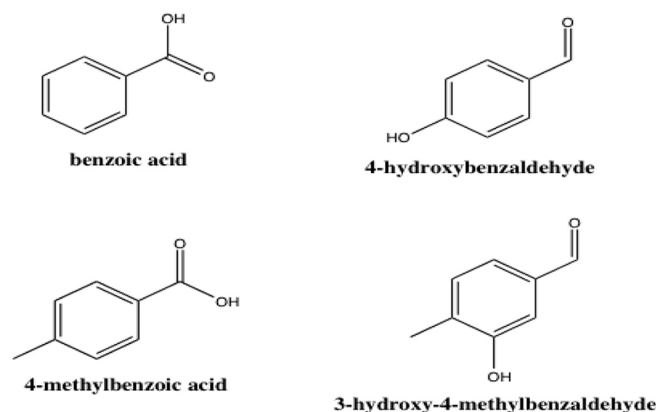


Figure 1. Congener pairs analyzed with MS/MS

Table 2. The derivatized carbonyls, carboxylic acids, and hydroxycarbonyls and their negative ion mass.

	<i>Negative ion of mass M minus a proton, H⁻ (M-H⁻)</i>
Formaldehyde	209 daltons, da
Acetaldehyde	223 da
Acrolein	235 da
Propionaldehyde	237 da
Crotonaldehyde	249 da
Methacrolein	249 da
2-Butanone / Butyraldehyde	251 da
Valeraldehyde	265 da
Cyclohexanone	277 da
Methyl isobutyl ketone	279 da
Benzaldehyde	285 da
Heptaldehyde	293 da
Octylaldehyde	307 da
Tolualdehyde	299 da
Dimethylbenzaldehyde	313 da
Formic acid	225 da
Propionic acid	253 da
Benzoic acid	301 da
Toluic acid	315 da
Hydroxybenzaldehyde	301 da
Hydroxytolualdehyde	315 da

Table 2 list the carbonyls, carboxylic acids, and hydroxycarbonyls and their negative ion mass. Of particular interest in this study were the congener pairs of benzoic acid and hydroxybenzaldehyde and 4-methylbenzoic acid and 3-hydroxy-4-methylbenzaldehyde (Fig. 1) These compounds have the same molecular weight and chemical make-up, but are different in structure.

RESULTS AND DISCUSSION

MASS SPECTRAL RESULTS

Commonly, carbonyls, hydroxycarbonyls and carboxylic acids are produced during the combustion of diesel fuel. These carboxyl and acid species are easily collected and derivatized with DNPH under acid conditions. For standard aldehyde analysis, the derivatized sample is analyzed by UV absorption. Another approach is to analyze the derivatized sample by negative ESI/MS, which produces a molecular ion minus a proton (M-H⁻) as shown in Fig. 2, which is derivatized formaldehyde. [12]

During a separation, several of the species may co-elute, which is shown in Fig. 3. Since identification by UV detection is dependent on the retention time, the assignment of the peaks in a complex sample or determining the correct peak area assignment is very difficult. This lack of selectivity results in problems in identifying the carbonyl, carboxylic acid, or hydroxycarbonyl species; however, the mass spectrum data allows the identification and integration of the areas, of each species by molecular ion and retention time.

Even using mass spectrometry other issues can arise from isobaric molecules. This is true for hydroxycarbonyl and carboxylic acids with the same base molecule. For example, when first separated, hydroxybenzaldehyde and benzoic acid both form the 301 ion, as shown in the trace in Fig. 4. Due the structural differences of these two molecules, the fragment pattern of the molecules will be distinctive. By isolating the molecular ion in MS/MS mode, the molecular ion can be fragmented into neutral molecules. This collision will produce secondary ions thus allowing the identification of the molecule. The MS/MS spectra of hydroxybenzaldehyde and benzoic acid are compared in Figs. 5 and 6.

The MS/MS data of hydroxybenzaldehyde's 301 ion shows a 163 ion present and the absence of the 167 ion as shown in Fig. 5 This 163 ion is a characteristic ion of hydroxycarbonyls and carbonyls. From the MS/MS data, benzoic acid produces a 167 ion see Fig. 6. This 167 ion is a common ion of carboxylic acids. Being able to distinguish between these groups is important in determining if the oxidation of the organic species has been to a carbonyl or to a carboxylic acid. The importance of distinguishing between benzoic acid and hydroxycarbonyls will be discussed below.

FUEL COMPARISONS

The exhaust carbonyl data is compared between the FACE fuels. In general, the low cetane fuels (1,2,3,4) gave very low smoke and higher overall HCs [11]. In these studies, when two fuels with similar aromatic and cetane numbers, but with different T₈₀ numbers, are compared, the lower T₈₀ fuel