

REPORT

ER-430

A TECHNIQUE FOR THE RAPID ESTIMATION OF VEHICLE EXHAUST GAS REACTIVITY

Robert D. Stephens
Environmental Research Department

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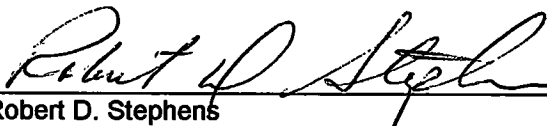
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Purpose

The purpose of this research was to determine if a commercial NDIR, used in conjunction with a Flame Ionization Detector, could be used to estimate the reactivity of exhaust hydrocarbons.

Summary

Two late model GM vehicles were operated on a chassis dynamometer with three different fuels and two different high emitting failure modes. The three fuels were A, 18A, and F, as formulated for the Auto/Oil Air Quality Improvement Research Program. The high emitting modes were either (1) commanded low air/fuel ratio (A/F) or (2) stoichiometric A/F with one spark plug wire disconnected. The fuels and the exhaust from the vehicles were speciated via GC and the reactivity was determined using maximum incremental reactivity factors, as determined by Carter. Hydrocarbon (HC) concentrations for the exhaust and raw fuel/N₂ mixtures were also measured via a non-dispersive infrared (NDIR) analyzer and a Flame Ionization Detector (FID). Previous studies have determined that NDIRs respond primarily to the alkanes in raw fuel and exhaust HC mixtures, and that the reactivity of such mixtures is primarily due to the alkenes and aromatics in the mixture. This study has shown that the difference between readings acquired by an NDIR and the FID is well correlated to the exhaust reactivity.

Significance

The California Air Resources Board has adopted a new car certification standard that is based upon the reactivity of the exhaust hydrocarbons. This study shows that exhaust gas reactivity can be quickly estimated by using non-dispersive infrared analyzer measurements in conjunction with Flame Ionization Detector measurements of total hydrocarbons. This technique could potentially allow a real-time estimation of exhaust reactivity.

Introduction

The California Air Resources Board (CARB) has adopted a vehicle exhaust emissions certification standard that is based on the maximum incremental reactivity (MIR) of the total non-methane organic gas (NMOG) in the exhaust. The MIR reactivity scale is based upon the work of Carter¹, and provides an estimate of the reactivity of many of the individual compounds or classes of compounds present in vehicle exhaust. To determine the overall reactivity of an exhaust mixture, the reactivity of individual compounds and quantities of the individual exhaust compounds must be known. For new vehicle certification purposes, the State of California will set emissions standards that are based upon the composite FTP gram-per-mile (gpm) emissions of NMOG multiplied by an overall reactivity adjustment factor (RAF). The RAF is used to estimate the amount of ozone that is formed from the NMOG in a given exhaust mixture relative to the ozone that would be formed from a standard exhaust mixture, as calculated using the Carter MIR scale.

The decision to adopt a reactivity-based standard is an acknowledgment that ozone formation is dependent not only upon the overall mass of emissions, but also dependent upon the relative reactivity of the individual hydrocarbons present.

The Carter MIR reactivity factors and the measured concentration of each carbon species in the exhaust can also be used to estimate the overall reactivity of an exhaust mixture, on a per-carbon basis (R/C), via the following equation:

$$\text{Avg. R/C} = \frac{\sum(\text{ppmC}_{\text{each compound}} \cdot \text{R/C}_{\text{each compound}})}{\sum(\text{ppmC}_{\text{total}})} \quad (1)$$

where R/C represents the MIR on a per-carbon basis.

In previous studies we have analyzed the speciation and reactivity of exhaust mixtures generated by two late model GM vehicles operated on a chassis dynamometer with simulated malfunction conditions^{2,3}. The vehicles were operated in cruise modes with three different fuels and with either of two operating conditions, (a) stoichiometric with a simulated misfire (a sparkplug wire disconnected) or (b) rich air/fuel ratio (A/F) and all sparkplugs operating normally. The fuels utilized consisted of A, 18A, and F, as formulated for the Auto/Oil Air Quality Research Program⁴. After speciation was performed, the average MIR reactivity was determined using Carter reactivity factors as described above (1).

Previous studies have shown that non-dispersive infrared analyzers (NDIR) have a widely variable response to different HC compounds^{5,6}. Our studies have shown that NDIRs respond primarily to the alkane compounds in exhaust mixtures². We have also shown that the speciation and reactivity of exhaust is dependent upon the vehicle operating mode and that the majority of reactivity is due to the alkenes and aromatics present in an exhaust mixture³. As a result of these findings, it seemed probable that the error in an NDIR measurement of exhaust HC would be correlated to the fractions of alkenes and aromatics (i.e., the highly reactive compounds) in the exhaust.

In this study, we have analyzed the correlation between the NDIR response factor and the exhaust reactivity, as determined via equation (1). For these analyses, the NDIR response factor is defined as:

$$\text{NDIR Response Factor} = \text{HC}(\text{as measured via NDIR}) \div \text{HC}(\text{as measured via FID}) \quad (2)$$

We suggest that this correlation can be used as a means to rapidly estimate exhaust gas reactivity. As such, exhaust gas measurements via FID and NDIR provide the development engineer with the necessary tool to evaluate the impact of engine/catalyst parameters on exhaust reactivity. This method of estimating exhaust gas per-carbon-reactivity has the potential to assist the development engineer in meeting future reactivity based emissions standards in California.

Experimental

Exhaust samples were collected from a 1991 Chevrolet Lumina equipped with a 3.1 liter V-6 engine, and a 1989 Pontiac Bonneville equipped with a 3800 (3.8 liter) V-6 engine. Both vehicles were operated in a cruise mode on a chassis dynamometer. The vehicles were each equipped with an interface to the assembly line diagnostic link (ALDL) which allowed for variable commanded air/fuel (A/F) ratio operation⁷. Each vehicle was run twice with each of three different fuels. The fuels utilized were designated as type A, 18A, and F, as formulated for the Auto/Oil Air Quality Improvement Research Program⁴. Fuel A is a blend mixed to represent industry average fuel, fuel 18A is an oxygenated fuel containing MTBE, and fuel F is a low aromatic fuel. The vehicles were operated in either of two conditions: (a) a simulated misfire (via disconnection of one spark plug wire) with stoichiometric A/F ratio, or (b) fuel rich operation with all spark plugs operating normally.

The exhaust samples were collected through cold traps to lower the humidity of the samples. Hence, the concentrations of species that are highly water soluble would have been decreased in the collected samples relative to their concentration in the exhaust. Speciation analyses of the samples were performed with a Varian model 3600 gas chromatograph equipped with a flame ionization detector. Because of the sampling and measurement technique, most oxygenated species that might have been present in the exhaust were not measured. As a result, we consider these analyses to be based on total hydrocarbons, although our analyses include the reactivity of benzaldehyde and MTBE, as measured via the GC. For the fuels we have studied, the distinction between total hydrocarbons and total organic gas is probably only relevant for exhaust samples generated during vehicle operation with fuel 18A, i.e., the MTBE containing fuel. We expect the reactivities for exhausts generated from fuels A and F to be nearly equal to the reactivities that would have been determined based upon measurements of total organic gas (i.e., HC plus oxygenates) because the oxygenate concentrations in these exhaust mixtures should be low. For exhaust mixtures from vehicles using fuel 18A (which contains MTBE), we have probably somewhat underestimated the average reactivity because the oxygenate reactivities are typically higher than the average HC reactivity.

Volatilized samples of raw fuel were also speciated. These samples were prepared by injection of liquid fuel into teflon bags containing mixtures of CO/CO₂/N₂. Fuels A and 18A were tested twice and fuel F was tested once.

NDIR measurements of the exhaust and raw fuel samples were analyzed using both commercial NDIR instruments and a remote sensor designed and built at GM R&D^{8,9}. The commercial NDIR instruments consisted of a Siemens Ultramat-22P and a Horiba MEXA-324GE. For the commercial instruments, measurements were performed

by drawing the samples through the instruments via a sampling pump. For the remote sensor measurements, the samples were pressurized and sprayed into the infrared beam to simulate the actual on-road operation of the sensor. The data reported here were obtained via the remote sensor, however we will also refer to the measurements performed via the commercial instruments.

Results

It is generally recognized that FIDs provide a reasonably accurate measure of total HC in complex mixtures. Except for oxygenated HCs, FIDs respond in a linear fashion with the total number of C atoms in a sample. As mentioned earlier, NDIRs respond primarily to the alkane compounds in a sample². Consequently, the difference in the response of the two instruments should provide a reasonably good measure of the alkenes and aromatics in an HC mixture. Since previous analysis has indicated that the majority of reactivity can be attributed to the alkenes and aromatics in exhaust mixtures³, the NDIR response factor should be indicative of the reactivity of the mixture.

The samples analyzed in this study are summarized in **Table I**, where we have listed the vehicle operating conditions, the fuel utilized, the measured HC concentrations, the average per-carbon MIR, and the NDIR response factor measured for each sample. A plot of the

Table I Sample and Reactivity Data

<u>Sample Name^a</u>	<u>Speed</u>	<u>A/F</u>	<u>Spark Plug^b</u>	<u>Fuel Type</u>	<u>NDIR R.F.^c</u>	<u>ppmC (FID)</u>	<u>Avg. MIR/C^d</u>
Bon-52601	30.1	14.7	yes	A	0.55	3717	0.806
Lum-52701	28.6	14.7	yes	A	0.61	4023	0.761
Lum-52801	28.3	14.7	yes	A	0.61	3609	0.815
Bon-52802	30.7	14.7	yes	18A	0.62	3171	0.747
Bon-60901	36.0	8.0	no	A	0.37	3345	1.123
Bon-60101	29.9	8.0	no	18A	0.23	4401	1.221
Lum-60201	29.9	10.0	no	18A	0.38	4245	1.228
Lum-60202	38.2	9.0	no	18A	0.30	6012	1.172
Bon-60301	41.0	8.0	no	F	0.53	4233	0.993
Bon-60401	35.0	8.0	no	F	0.39	4548	1.071
Lum-60402	33.1	8.0	no	F	0.46	4200	1.067
Lum-60701	39.0	10.0	no	F	0.48	3183	1.051
RFA-52601	---	---	---	A	0.48	---	0.843
RFA-61401	---	---	---	A	0.49	---	0.948
RF18A-60101	---	---	---	18A	0.49	---	1.000
RF18A-61402	---	---	---	18A	0.44	---	1.068
RFF-60901	---	---	---	F	0.56	---	0.780

^a Speciation analyses were performed on raw fuel samples, designated with an “RF” prefix, and vehicle exhaust samples from a Bonneville (Bon) and a Lumina (Lum).

^b For some tests a spark plug was disconnected (yes) to simulate a misfire condition.

^c NDIR response factor (R.F.) is defined via equation (3).

^d The average per carbon MIR and MOR was calculated via equation (2), using the reactivity factors of Carter¹.

average MIR in the sample as a function of the remote sensor NDIR response factor is shown in **Figure 1**. These data show that there is a reasonable correlation ($R^2 = 0.82$) between the average MIR/C of each sample and the measured NDIR response factor. We will use the terms “reactivity” and “per-carbon-reactivity” interchangeably throughout the remainder of this report.

Our analyses indicate that, for the samples analyzed in this study, the alkanes contributed, on average, 16.2% (with a standard deviation of 9.6%) of the total exhaust reactivity. Samples analyzed from the Auto/Oil Air Quality Improvement Research Program indicate that alkanes in the exhaust of vehicles operated with fuels A and F contributed approximately 12% and 16%, respectively, of the total exhaust reactivity. The fraction of total reactivity due to alkanes in exhaust from vehicles operated with other reformulated fuels used during the Auto/Oil program did not differ significantly from these values. This suggests that exhaust generated from vehicles using these other reformulated fuels will have similar trends in the relationship between NDIR response factor and exhaust reactivity.

Since the alkanes are typically the least reactive hydrocarbon compounds, an increase in alkane fraction corresponds to a decrease in reactivity. In other words, an increase in alkane fraction corresponds to a decrease in the fraction of the more reactive alkene and aromatic compounds, which have low NDIR response factors. Consequently, there is an inverse relationship between NDIR response factor and per-carbon reactivity because the NDIR response factor increases as the alkane fraction of total HC in the sample increases.

The regression statistics obtained from the relationship shown in Figure 1 yield uncertainties (one standard deviation) in the intercept and slope of 0.079 (5%) and 0.165 (12.3%), respectively.

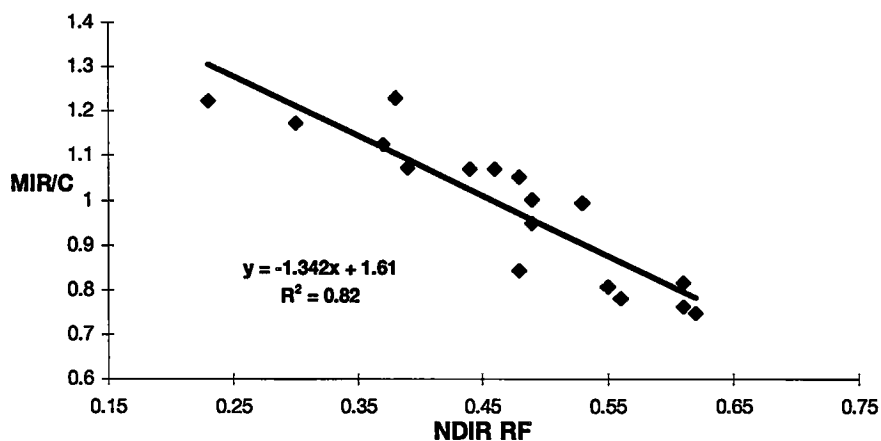


Figure 1. The relationship between per-carbon-reactivity(MIR/C) and NDIR Response Factor.

Discussion

Since vehicle exhaust consists of over one-hundred different hydrocarbon compounds, each with its own unique infrared absorption spectrum, the relationship between reactivity and NDIR response factor will be a function of several factors. These factors include (1) the bandwidth and band center of the infrared filter used by the NDIR and (2) the mixture of HCs present. Although we do not know the wavelengths used by commercial NDIR instrumentation, our analysis indicates that the correlation between reactivity and the commercial NDIR response factors was lower ($R^2 = 0.73$ for the Seimans and $R^2 = 0.71$ for the Horiba) than was observed with the remote sensor NDIR. The variability in this correlation is probably a function of the NDIR infrared filter bandwidth and band center. Clearly, there will be a bandwidth and band center that will yield an optimum correlation between response factor and reactivity. These wavelengths would likely correspond to the portion of the spectrum where alkanes contribute the predominant fraction of total infrared absorbance for the majority of exhaust mixtures.

An alternative to NDIR for these measurements is available. Fourier transform infrared spectrometry (FTIR) could be utilized. With this approach, all wavelengths are measured simultaneously, hence an experimental study could be undertaken to identify the optimal wavelengths for the correlation. Other research groups are also exploring techniques aimed at measuring exhaust reactivity directly via an FTIR measurement. For example the American Industry/Government Emissions Research program has a subcommittee conducting research in this area.

Conclusions

By using a FID and an NDIR, the reactivity of an exhaust mixture can be estimated. This is accomplished with a three step process. First, the HC concentration of the exhaust is measured using each instrument. Next, the NDIR response factor is determined via equation (2). Finally, the estimated MIR/C is determined via the relationship shown in Figure 1:

$$\text{Estimated MIR/C} = -1.342(\text{NDIR RF}) + 1.613 \quad (4)$$

Or, more simply, as follows:

$$\text{Estimated MIR/C} = -1.342 (\text{HC}_{\text{NDIR}} + \text{HC}_{\text{FID}}) + 1.613 \quad (5)$$

In practice, the application of this technique will probably be limited by the HC sensitivity of the NDIR used. Sensitivity of such instruments can be optimized by increasing the sample optical pathlength and/or increasing the signal averaging time used to perform the measurement. Using either of these approaches to optimize sensitivity will decrease the time response of the NDIR measurement.

Acknowledgments

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