REPORT

ER-427

EXHAUST HYDROCARBON REACTIVITY OF VEHICLES OPERATED WITH DIFFERENT FUELS AND SIMULATED FAILURE MODES

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GENERAL MOTORS CORPORATION

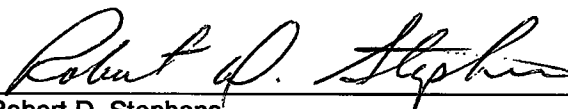DEVELOPMENT CENTER

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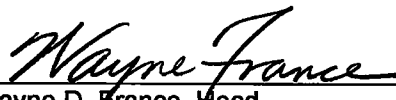
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**Intended
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Abstract

Tailpipe exhaust was collected from and speciated for two late model GM vehicles which were operated with three different fuels (Auto/Oil designations A, 18A, and F) and two simulated failure modes (stoichiometric with one spark plug disconnected or rich A/F with no spark plug disconnected). These data were collected originally as part of an evaluation of remote sensor accuracy but have been further analyzed in this report to provide initial insight into the role of fuel and vehicle operating conditions on exhaust gas reactivity. Carter incremental reactivity factors were used to determine the average incremental reactivity per carbon for the exhaust hydrocarbons and the raw fuels. It was determined that the incremental reactivities of exhaust from vehicles operated with a fuel-rich, non-misfire condition were significantly higher than the exhaust from vehicles operated with a stoichiometric A/F ratio and a simulated misfire. For fuels 18A and F, the reactivity of exhaust from the fuel rich/no misfire mode was also significantly higher than the reactivity of the raw volatilized fuel. The increased reactivities during rich operating conditions were found to be mainly due to elevated concentrations of olefinic hydrocarbons and lower concentrations of paraffinic hydrocarbons in the exhaust.

Purpose

The purpose of this research was to determine the reactivity of exhaust mixtures generated by vehicles using different fuel blends and operated with different simulated failure modes that yield high hydrocarbon emissions.

Summary

Two late model GM vehicles were operated on a chassis dynamometer with three different reformulated gasolines (Auto/Oil designations A, 18A, and F) and two different high emitting modes. Exhaust mixtures and raw fuel samples were collected and speciation analyses were performed. These data were originally collected as part of an evaluation of remote sensor accuracy, but have been further analyzed in this report to gain insight into the potential impact of fuel and vehicle operating conditions on exhaust gas reactivity. To accomplish this, Carter incremental reactivity factors were used to determine the average reactivity per carbon of the exhaust hydrocarbons. The following differences in the maximum incremental reactivity were observed:

1) Exhaust reactivity was higher during fuel rich operation than during misfire operation when using fuels 18A and A.

2) The reactivity of exhaust from vehicles operating fuel rich was higher than the reactivity of the raw fuel, when operating with either fuel 18A or F.

3) Significantly higher reactivity was observed in exhaust from vehicles using fuel 18A than fuel F, when operating fuel rich.

Significance

These data indicate that the reactivity of the exhaust volatile organic carbon of high emitters is dependent upon the type of emission control malfunction present. The importance of emission system failure mode on exhaust reactivity suggests that vehicle inspection and maintenance programs should emphasize the detection of the failure modes that lead to the most reactive exhaust gas compositions.

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Introduction

Air quality has been an ongoing concern in various parts of the U. S. for several decades. The role of automobile exhaust in the formation of tropospheric ozone was recognized in the early 1950's[1]. In Los Angeles county in the 1960's, "Rule 66" was aimed at reducing emissions of the most reactive hydrocarbons[2]. This rule was a reflection of the growing body of knowledge that indicated that not all hydrocarbons were equal in terms of their ability to react to form ozone. Since that time, a great deal of research has been done in an attempt to better understand the reactivity of vehicular emissions[3-11]. More recently, the importance of reformulated fuel on the reactivity of exhaust and evaporative emissions has been examined by the Auto/Oil Air Quality Improvement Research Program[12-18] and others research groups[19-23]. These studies have shown consistent trends in exhaust reactivities as a function of fuel component changes. Many of the recent estimates of exhaust and fuel reactivity have been based on reactivity scales developed by Carter[24,25]. Carter's reactivity factors are calculated from a photochemical model in which he has calculated the additional ozone formation that will result from addition of a small amount of volatile organic carbon (VOC) to a standard urban atmosphere. The incremental reactivity (IR) of the VOC is defined as:

$$IR = \Delta O_3 \div \Delta VOC$$

Carter has calculated lists of IRs for two standard conditions: (1) low VOC/NO_x ratios where the ozone formation is most sensitive to changes in VOC concentrations, referred to as maximum incremental reactivity (MIR), and (2) moderate VOC/NO_x ratios, where the maximum ozone formation is achieved in the standard mixture, i.e., the maximum ozone reactivity (MOR). These different scales represent the importance of the VOC-to-NO_x ratio in the ozone formation process. Values of MIR and MOR have been assigned to most VOC compounds or classes of compounds present in vehicle exhaust. The overall ΔO_3 that results from a vehicle exhaust mixture, using either MIR or MOR, can be determined as follows:

$$\Delta O3 = \Sigma\ (IR_i \cdot VOC_i) \qquad\qquad (1)$$

where IR_i represents the reactivity of each individual VOC, denoted as VOC_i. Hence, to determine the overall reactivity of an exhaust mixture, the reactivity of individual compounds and quantities of the individual exhaust compounds must be known.

The Carter reactivity factors (both MIR and MOR) 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:

$$Avg.\ R/C\ =\ \Sigma(ppmC_{each\ compound} \cdot R/C_{each\ compound})\ \div\ \Sigma(ppmC_{total}) \qquad (2)$$

The California Air Resources Board (CARB) has adopted a vehicle exhaust emissions certification standard that is based on the reactivity (MIR) of the total non-methane organic gas (NMOG) content of the exhaust. The exhaust reactivity is calculated 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 using Carter's MIR scale, relative to that formed from a standard exhaust mixture, e.g.:

$$RAF = [Average\ R/C]_{vehicle} \div [Average\ R/C]_{standard\ vehicle} \qquad (3)$$

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 average reactivity of different vehicle exhaust mixtures can be used to compare the relative ozone forming potential for different mixtures that have equivalent carbon concentrations. Currently, there is a lack of data regarding the relationship between vehicle operating conditions and exhaust reactivity. An understanding of such relationships might provide important insight into steps that could be taken to lower

atmospheric ozone levels. For certification engineers, knowledge concerning factors associated with varying RAF values might be important for the successful certification of vehicles.

Studies of on-road emissions have indicated that small fractions of the entire on-road fleet are responsible for the majority of all warm-running vehicle CO emissions[26,27]. Although HC remote sensing is not as accurate for measurements of hydrocarbons as for measurements of CO^{28}, remote sensing studies also indicate that a majority of HC emissions are caused by a small minority of all vehicles[27,29]. If a majority of HC emissions are generated by the small minority of vehicles that have a malfunction, it is very possible that these vehicles also contribute the majority of the reactive hydrocarbons that are precursors to ozone formation. Clearly, a wide variety of real-world emission system failure modes occur[30,31]. The relationship between emission system failure mode and the reactivity of exhaust is unknown. It is conceivable that exhaust reactivity is related to specific vehicle emission failure mode and that certain types of emission control system failures contribute a disproportionate fraction of the more highly reactive HC. If so, inspection and maintenance programs can be designed to emphasize the correction of failure modes that contribute disproportionately to atmospheric ozone formation.

In this study, we have analyzed the speciation of exhaust mixtures generated by two late model GM vehicles operated on a chassis dynamometer with simulated malfunction conditions[28]. 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 Improvement Research Program[32]. This study was originally conducted to evaluate the accuracy of remote sensors, but the data have been further analyzed in this report to gain insight into the potential impact of fuel and vehicle operating conditions on exhaust gas reactivity. The average MIR and MOR reactivity was determined using Carter reactivity factors as described above (2). The relationships between reactivity and test variables (vehicle, vehicle operating conditions, and fuel) were examined.

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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[28]. 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 operation[33]. 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 Program[32]. 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 vehicle, its operating conditions, the fuel utilized, the HC concentrations, and the measured average MIR and average MOR of each sample is listed in **Table I**.

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. Analysis of the samples was 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 be measured using total NMOG (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

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Table I Operating Conditions and Measured Emissions, Average MIR, and Average MOR

Sample Name[a]	Speed	A/F	Spark[b]	Fuel Type	Avg. MIR	Avg. MOR	Avg. ppmC
Bon-52601	30.1	14.7	yes	A	0.806	0.407	3717
Lum-52701	28.6	14.7	yes	A	0.761	0.410	4023
Lum-52801	28.3	14.7	yes	A	0.815	0.443	3609
Bon-52802	30.7	14.7	yes	18A	0.747	0.413	3171
Bon-60901	36.0	8.0	no	A	1.123	0.763	3345
Bon-60101	29.9	8.0	no	18A	1.221	0.770	4401
Lum-60201	29.9	10.0	no	18A	1.228	0.809	4245
Lum-60202	38.2	9.0	no	18A	1.172	0.750	6012
Bon-60301	41.0	8.0	no	F	0.993	0.610	4233
Bon-60401	35.0	8.0	no	F	1.071	0.628	4548
Lum-60402	33.1	8.0	no	F	1.067	0.609	4200
Lum-60701	39.0	10.0	no	F	1.051	0.619	3183
RFA-52601	—	—	—	A	0.843	0.758	—
RFA-61401	—	—	—	A	0.948	0.824	—
RF18A-60101	—	—	—	18A	1.000	0.815	—
RF18A-61402	—	—	—	18A	1.068	0.859	—
RFF-60901	—	—	—	F	0.780	0.613	—

[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] The average per carbon MIR and MOR was calculated via equation (2), using the reactivity factors of Carter[24].

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 $CO/CO_2/N_2$. Fuels A and 18A were tested twice and fuel F was tested once.

Results

Table I shows the samples that were speciated and the conditions under which the samples were collected. This table also shows the concentrations in total ppmC measured and the average MIR and MOR values of the samples. **Tables II and III** show the mean and standard deviation of the MIR and MOR, respectively, after segregating the samples

according to fuel, vehicle operating condition, and sample type (exhaust or volatilized fuel). These data have also been plotted in **Figures 1 and 2**, respectively and show a clear trend toward increased reactivity of exhaust during fuel rich operation relative to that

## Table II The Affect of Fuel and Operating Conditions on Average MIR

Fuel	Rich A/F No Misfire	Stoichiometric with Misfire	Raw Volatilized Fuel
A	1.123 (1)[a]	0.794 ±0.029 (3)	0.896 ± 0.074 (2)
18A	1.207 ± 0.031 (3)	0.747 (1)	1.034 ± 0.048 (2)
F	1.046 ± 0.036 (4)	———	0.780 (1)
All Fuels	1.116 ±0.085 (8)	0.782 ± 0.033 (4)	0.928 ± 0.117 (5)

[a] Numbers in parentheses indicate the number of samples tested.

Table III The Affect of Fuel and Operating Conditions on Average MOR

Fuel	Rich A/F No Misfire	Stoichiometric with Misfire	Raw Volatilized Fuel
A	0.763 (1)[a]	0.420 ± 0.020 (3)	0.791 ± 0.047 (2)
18A	0.776 ± 0.030 (3)	0.413 (1)	0.837 ± 0.031 (2)
F	0.617 ± 0.009 (4)	———	0.613 (1)
All Fuels	0.695 ± 0.085 (8)	0.418 ± 0.017 (4)	0.774 ±0.098 (5)

[a] Numbers in parenthesis indicate the number of samples tested.
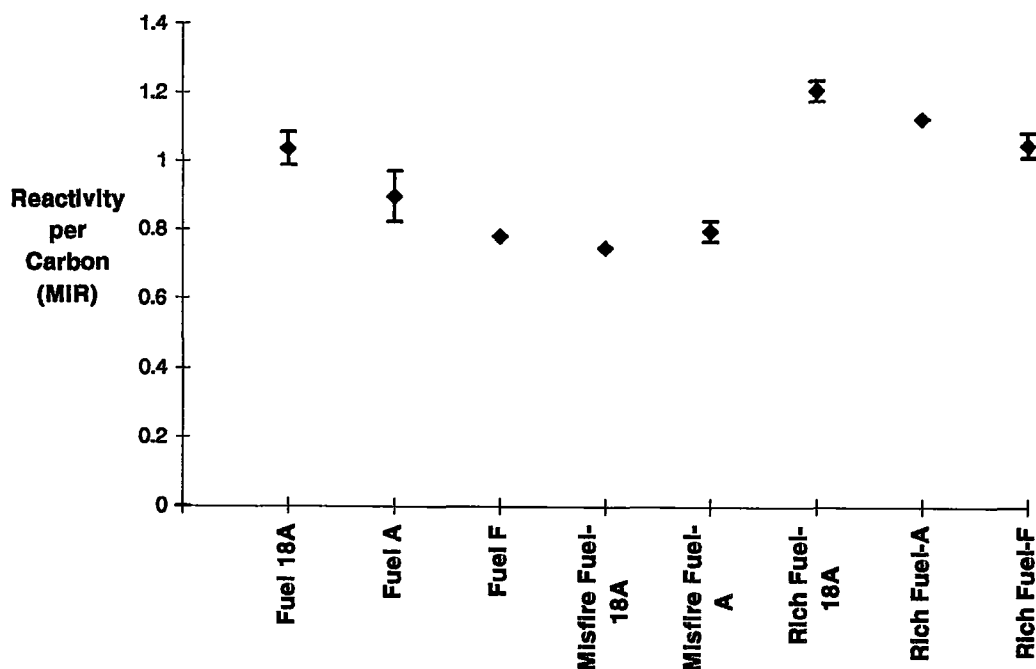
Figure 1. Mean and standard deviation of the MIR values for the exhaust and fuel samples.
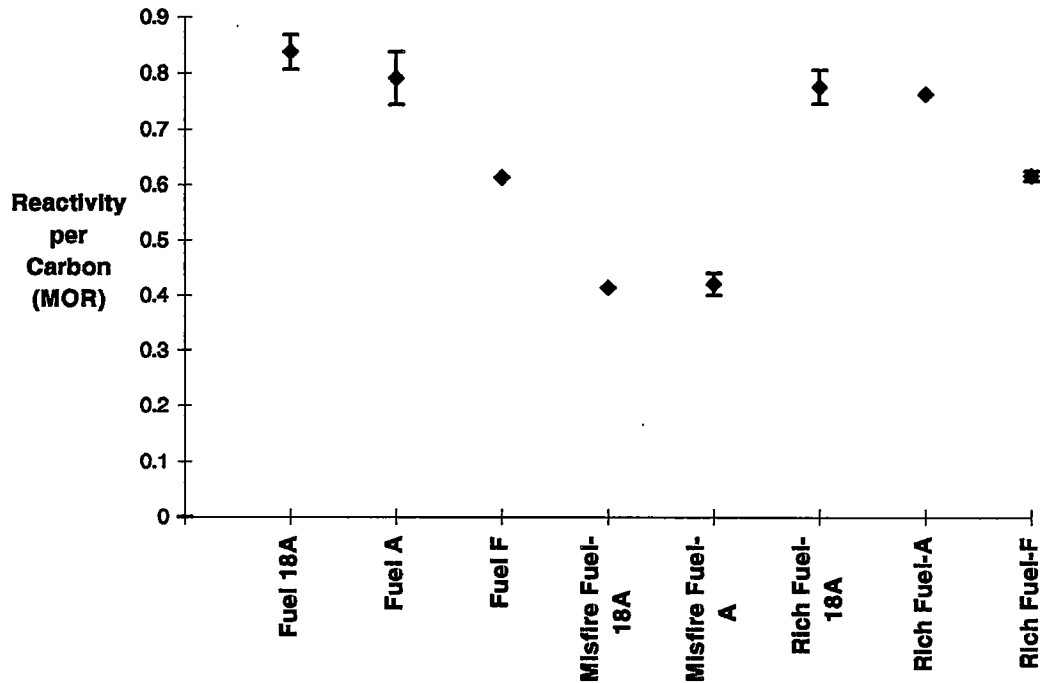
Figure 2. Mean and standard deviation of the MOR values for the fuel and exhaust samples.

which is observed during misfire conditions. In addition, the MIR data show the exhaust reactivity during fuel rich operating conditions to be higher than the reactivity of the raw fuel.

Table IV shows the mean per-carbon MIR and MOR values (averaged across all fuels), respectively, as measured for each vehicle during each operating condition. These data show no significant differences in exhaust reactivity between vehicles when using any individual fuel.

Although there is a limitation in the number of samples within some categories, the analyses of data shown in Tables II through IV indicate that statistically significant

Table IV The Affect of Vehicle and Operating Conditions on MIR and MOR

Operating Condition/Fuel	Bonneville	Lumina
Misfire MIR	0.777 ± 0.042 (2)	0.788 ± 0.038 (2)
Rich MIR	1.102 ± 0.096 (4)	1.130 ± 0.085 (4)
Misfire MOR	0.410 ± 0.004 (2)	0.426 ± 0.024 (2)
Rich MOR	0.693 ± 0.086 (4)	0.697 ± 0.098 (4)

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differences in reactivity exist at the 95th percentile confidence limit. For MIR, these differences include: (1) reactivity is higher in exhaust from vehicles operated fuel rich than exhaust from vehicles with a simulated misfire, when operated on fuels 18A and A, and (2) the reactivity of exhaust from vehicles operated fuel rich with fuel 18A or F is higher than the reactivity of the raw fuel and (3) the reactivity of exhaust from vehicles operated fuel rich with fuel 18A is higher than the exhaust reactivity of vehicles operated fuel rich with fuel F.

Statistically significant results for MOR are the same as MIR for points (1) and (3) above. In addition, raw fuel A was found to have higher reactivity than the exhaust from vehicles operated with a simulated misfire and fuel A.

The changes in reactivity as a function of operating conditions are a direct result of the chemical species present. **Table V** summarizes the fractions of total carbon that exists as each hydrocarbon type, alkane, alkene, and aromatic for each individual sample. These data are also plotted in **Figures 3, 4, and 5,** respectively, after determining the means and standard deviations for each fuel and operating condition. Methane has not been included

Table V Fractions of Hydrocarbon Type in Samples

Sample Name	Fuel Type	Spark Plug	Percent as Alkanes	Percent as Alkenes	Percent as Aromatics
Bon–60101	18A	N	14.13	28.42	33.08
Lum–60201	18A	N	17.57	29.22	35.00
Lum–60202	18A	N	15.98	29.33	31.61
Bon–60901	A	N	26.38	28.61	30.14
Bon–60301	F	N	32.15	26.89	24.68
Bon–60401	F	N	26.99	32.47	23.35
Lum–60402	F	N	24.60	33.53	21.62
Lum–60701	F	N	28.98	31.60	22.92
Bon–52802	18A	Y	50.62	18.33	25.64
Bon–52601	A	Y	54.06	19.63	20.91
Lum–52701	A	Y	64.73	15.74	15.30
Lum–52801	A	Y	60.74	18.83	15.85
RF18A-601T	18A	—	35.95	7.85	39.60
RF18A-614T	18A	—	32.09	10.44	40.51
RFA-526T	A	—	52.61	6.36	34.46
RFA-614T	A	—	47.95	10.87	36.19
RFF-609T	F	—	56.71	10.17	29.81

as an alkane in these data. **Figure 3** shows that alkanes are lower in exhaust during rich operating conditions relative to either the misfire condition or the raw fuel. **Figure 4** shows that alkenes are elevated in exhaust for either operating condition, but are most elevated when the vehicles are operating in a fuel rich condition. **Figure 5** shows that aromatic fractions are lowest during misfire conditions, followed by rich operating conditions, then raw fuel.
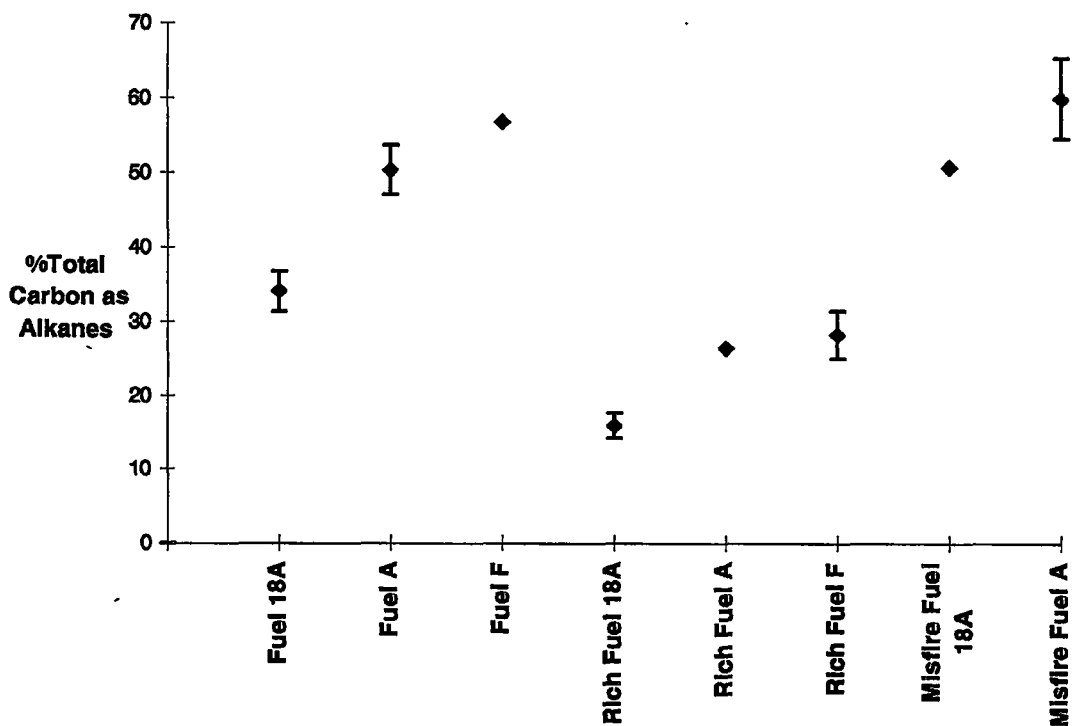
Figure 3. Mean and standard deviations of the percentages of total carbon present as alkanes in the exhaust and fuel samples.
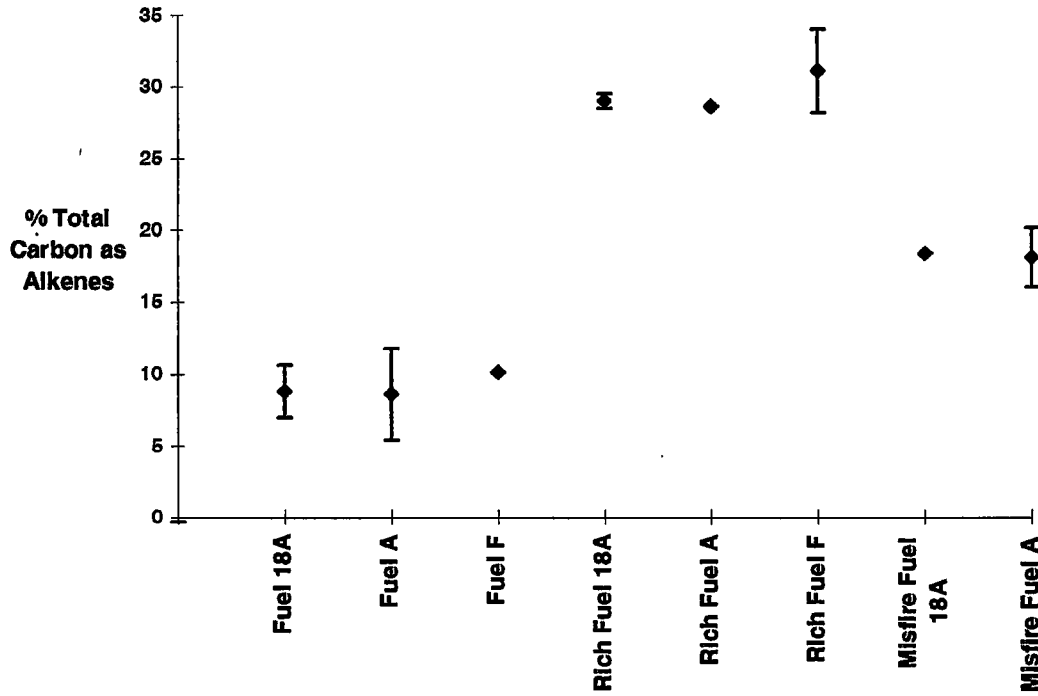
Figure 4. Mean and standard deviations of the percentages of total carbon present as alkenes in the exhaust and fuel samples.
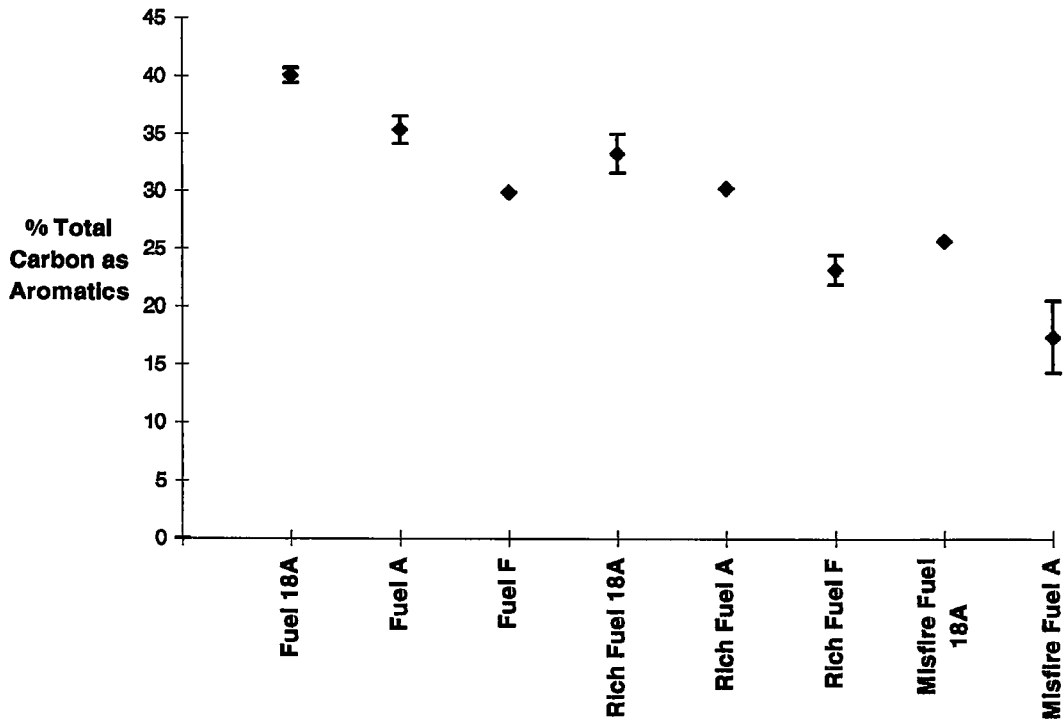
Figure 5. Mean and standard deviations of the percentages of total carbon present as aromatics in the fuel and exhaust samples.

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Table VI shows the ratios of the fractions of hydrocarbon types in the exhaust relative to the fractions in the raw fuel for each of the fuels and operating conditions used.

Table VI Exhaust/Fuel Ratios of Hydrocarbon Types

Sample Type	HC Type	Exh:Fuel Fuel 18A	Exh:Fuel Fuel A	Exh:Fuel Fuel F
Rich/No Misfire	Alkane	0.47	0.52	0.50
Stoich/Misfire	Alkane	1.49	1.19	N/A
Rich/No Misfire	Alkene	3.17	3.32	3.06
Stoich/Misfire	Alkene	2.00	2.10	N/A
Rich/No Misfire	Aromatic	0.83	0.85	0.78
Stoich/Misfire	Aromatic	0.64	0.49	N/A

As this table indicates, the rich operating condition results in lower alkane and aromatic concentrations and increased alkene concentrations in exhaust relative to the concentrations in the raw fuel. During the misfire operating conditions, the alkane and alkene concentrations are increased and the aromatic concentrations decreased, relative to the raw fuel. For all fuels (except fuel F, which was not used with the misfire condition), the rich operating condition generated higher concentrations of alkenes and aromatics, and lower concentrations of alkanes than did the misfire condition.

Previous studies conducted by the Auto/Oil Air Quality Improvement Research Program have found that the exhaust:fuel ratios of individual HC species within each HC class (alkane, alkene, or aromatic) is fairly constant, but that some compounds have anomalously high ratios[16]. We have calculated the slopes and correlation coefficients (r^2) for the relationships between exhaust component concentrations and fuel component concentrations within each HC class after separating data from each operating condition. These data are listed in **Table VII.** As was also observed during the Auto/Oil program, this analysis found that some alkane, alkene, and aromatic compounds had higher exhaust:fuel ratios than were typical for most species within a hydrocarbon class. The behavior of some of these compounds was expected because they are recognized as partial oxidation products, but the anomalous behavior of the other compounds could not be

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Table VII Regression Statistics for the Exhaust:Fuel Volumetric Concentrations of Each Species

Operating Condition	Fuel	Alkanes slope (r^2)	Aromatic[a] slope (r^2)	Alkenes[b] slope (r^2)
Misfire	18A	1.86 (0.96)	0.34 (0.86)	0.43 (0.84)[b]
Misfire	A	1.45 (0.93)	0.34 (0.83)	0.35 (0.83)[c]
Rich	18A	0.40 (0.99)	0.75 (0.99)	0.40 (0.92)[d]
Rich	A	0.48 (0.99)	0.78 (0.99)	0.45 (0.92)[e]
Rich	F	0.44 (0.99)	0.65 (1.00)	(0.69)[f]

[a] Benzene was omitted from the regression analysis.

[b] 2 methyl-1,3-butadiene, 2-methyl-1-butene, cis-2-butene, 3-methyl-1-butene, and 2-methyl-1-butene were omitted from the regression analysis.

[c] 2-methyl-1-butene was omitted from the regression analysis

[d] cis-2-butene, trans-2-butene, 2-methyl-1,3-butadiene, 2-methyl-1-butene, and cyclopentadiene were omitted from the regression analysis.

[e] 2-methyl-1-butene was omitted from the analysis.

[f] 2-methyl-propene, cis-2-butene, 2-methyl-2-butene, 1,3-butadiene, 4-methyl-cis-2-pentene, and propene were omitted from the analysis.

explained. In this study, we also find unusually high concentrations of benzene (a partial oxidation product) and several alkenes. However, for the most part, the alkene compounds that we found to have unusually high exhaust:fuel ratios were not the same compounds observed as outliers in the Auto/Oil study. Also, we found that the alkene compounds that were outliers on these regression analyses varied from fuel to fuel and from operating condition to operating condition. In our regression analyses, we have omitted these outliers and listed them as footnotes to Table VII. Typically, the exhaust:fuel concentration ratios of the alkene compounds omitted from the regression analyses were much higher than the ratios for the other alkenes. This explains the difference in the exhaust:fuel ratios listed in Table VI and the regression slopes listed in Table VII. We have calculated the fraction of total sample reactivity (both MIR and MOR) contributed by each of the compound classes and listed these data in **Table VIII**.

These data show that the reactivity of exhaust generated during the rich operating condition is a result of the increased concentrations of alkenes and decreased concentrations of alkanes, relative to the concentrations in the raw fuel. The increased reactivity of the exhaust generated during the misfire condition relative to the reactivity of

Table VIII The Fraction of Total Reactivity Due to Each Type of HC

Sample	Spark Plug	Fuel Type	Alkane MIR Frac	Alkene MIR Frac	Aromatic MIR Frac	Alkane MOR Frac	Alkene MOR Frac	Aromatic MOR Frac
Bon-52601	yes	A	0.26	0.57	0.18	0.31	0.45	0.25
Lum-52701	yes	A	0.33	0.49	0.18	0.37	0.35	0.28
Lum-52801	yes	A	0.29	0.55	0.16	0.32	0.40	0.28
Bon-52802	yes	18A	0.26	0.54	0.20	0.28	0.39	0.33
Bon-60901	no	A	0.09	0.57	0.34	0.08	0.34	0.58
Bon-60101	no	18A	0.05	0.53	0.41	0.04	0.32	0.63
Lum-60201	no	18A	0.05	0.53	0.41	0.05	0.31	0.64
Lum-60202	no	18A	0.05	0.55	0.39	0.05	0.34	0.60
Bon-60301	no	F	0.12	0.61	0.27	0.12	0.40	0.48
Bon-60401	no	F	0.09	0.68	0.23	0.09	0.47	0.43
Lum-60402	no	F	0.08	0.70	0.22	0.08	0.50	0.42
Lum-60701	no	F	0.10	0.67	0.23	0.10	0.47	0.43
RFA-52601		A	0.25	0.15	0.60	0.16	0.06	0.78
RFA-61401		A	0.20	0.23	0.57	0.13	0.09	0.77
RF18A-60101		18A	0.15	0.16	0.67	0.10	0.07	0.81
RF18A-61402		18A	0.12	0.20	0.66	0.09	0.09	0.81
RFF-60901		F	0.27	0.26	0.47	0.12	0.12	0.68

the raw fuel is due to the increased concentration of the alkenes in the exhaust relative to the concentration in the raw fuel. For the misfire condition, the increased exhaust reactivity resulting from the increase in concentration of the alkenes more than offsets the increased concentration of the low reactivity alkanes.

Overall, the main difference between the reactivity of the rich and misfire conditions is due to the increased concentrations of alkenes in the exhaust generated during fuel rich conditions relative to the concentrations in the exhaust generated during the misfire condition.

Previous analyses by the Auto/Oil Air Quality Improvement Research Program has found that the only fuel factors that significantly reduce exhaust reactivity from high emitters is a reduction in olefin content or a reduction in T_{90}[18]. Although it was not our intention to identify which fuel parameters were associated with changes in exhaust reactivity, our results are consistent with those found during the Auto/Oil study. The least reactive exhaust mixtures from each operating condition were generated from fuel F,

which has reduced levels of olefin and T_{90} relative to fuels 18A and A, as shown in **Table IX.**

Table IX Fuel Properties

Fuel	Aromatic Vol %	Olefin Vol %	T_{90}	RVP[a] psi	MTBE
A[12]	32	12	333	9	0
18A[34]	36.9	12.6	340	8.5	11.8
F[12]	20	5	280	9	0

[a] Reid Vapor Pressure

Conclusions

In this study, speciation measurements of exhaust from two different vehicles, operated with two different simulated emission control failure modes were used to evaluate reactivity, using Carter's maximum incremental reactivity (MIR) and maximum ozone reactivity (MOR). The fuels used were 18A, A, and F, as designated by the Auto/Oil Air Quality Improvement Research Program. The failure modes consisted of a simulated misfire (spark plug wire disconnected while running with stoichiometric air/fuel ratio) and commanded fuel rich operation (air/fuel ratios between 8.0 and 10.0 with all spark plug wires connected and operating normally). These data have shown that both fuel and vehicle operating condition are important factors in determining the reactivity of exhaust gas generated by high emitting vehicles.

In considering MIR, three conclusions from this study include:

1) Exhaust reactivity was higher during fuel rich operation than during misfire operation when using fuels 18A and A.

2) The reactivity of exhaust from vehicles operating fuel rich was higher than the reactivity of the raw fuel, when operating with either fuel 18A or F.

3) Significantly higher reactivity was observed from vehicles using fuel 18A than fuel F, when operating fuel rich.

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In terms of MOR, conclusions (1) and (3) also apply. In addition, the reactivity of fuel A is higher than the reactivity of exhaust generated by vehicles using fuel A, when operated with a simulated misfire.

In all samples, the relative reactivities can be explained by fractions of total exhaust carbon that are present as alkenes. The effect of operating conditions (misfire versus fuel rich) has not been previously observed, to our knowledge. The relationship between the reactivities of exhaust gases generated by using different fuels is consistent with findings previously reported by the Auto/Oil program for high emitting vehicles, i.e., that reductions in fuel olefinic content and reductions in T_{90} contribute to decreases in exhaust reactivity.

These data suggest that, for high emitting vehicles, the impact of exhaust hydrocarbons on urban ozone formation is dependent upon the type of emission control system failure involved.

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