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# Speciated Measurements and Calculated Reactivities of Vehicle Exhaust Emissions from Conventional and Reformulated Gasolines

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Exhaust emissions were characterized from 19 vehicles tested with two fuels: a typical Los Angeles premium gasoline and a reformulated premium gasoline. The reformulated fuel had lower vapor pressure and distillation temperatures than the reference fuel and contained 11 vol % methyl-*tert*-butyl ether (MTBE). Total volatile organic compounds (VOC) emissions were reduced with the reformulated fuel by 6% across the 19 vehicles, but aldehyde and alkene emissions were increased. The reactivity of exhaust emissions was estimated by applying maximum incremental reactivity (MIR) factors to the speciated emission profiles. Total reactivity (g of ozone/mile) varied linearly with emission rate across all vehicles. Mass-normalized reactivity (g of ozone/g of non-methane organic gases) was not different for the two fuels but did vary somewhat from vehicle to vehicle. On average, mass-normalized reactivity was reduced slightly in progressing from older to newer technology types. Relative to fuel compositions, exhaust compositions were depleted in alkanes and aromatics but enriched in alkenes and carbonyls. The alkene enrichment resulted from combustion-produced C<sub>2</sub>-C<sub>4</sub> species and was responsible for much of the overall reactivity of the emissions.

## Introduction

For many years, hydrocarbons (HC) from motor vehicles have been regulated pollutants. Historically, emissions standards have addressed only the mass of total hydrocarbons (THC) or nonmethane hydrocarbons (NMHC). Consequently, methodologies for measuring THC and NMHC have been established and are now in common use.

A primary reason for these regulations is that vehicular HC emissions are major contributors to the formation of tropospheric ozone. Ozone is a constituent in photochemical smog and represents a public health concern in many urban areas.

As a group, all HC (except methane) are considered ozone precursors. Yet, there are vast differences in propensity to form ozone among the several hundred HC species which comprise vehicle exhaust (1-3). This ozone-formation potential is what is meant by the term "reactivity".

At present, there is interest in modifying fuel compositions and emissions control systems to affect a decrease in reactivity, as well as a decrease in mass of emissions. Recently, the California Air Resources Board (CARB) adopted regulations by which the reactivity of vehicle exhaust emissions will be used to determine their allowable mass (4).

Such reactivity assessments require detailed, speciated analysis of HC and carbonyl compounds in vehicle exhaust. This paper describes speciation procedures we have developed and their use in determining emission profiles. Ozone-formation potentials were calculated by applying reactivity factors to the emission profiles. The factors we used are maximum incremental reactivity (MIR) factors, which are calculated from computer model simulations (5). Similar use of MIR factors to calculate the reactivity of

Table I. Identification and Inspection Data for Test Fuels

	ref fuel <sup>a</sup>	reform. fuel
RVP, psi	8.5	7.5
API gravity	53.3	54.2
sulfur, ppm	143.0	121.0
antiknock index, (R + M)/2	91.7	92.1
composition, vol. % by FIA (ASTM D1319) <sup>b</sup>		
aromatics	43.6	35.6
alkenes	6.8	5.5
alkanes	49.1	47.9
MTBE, vol %	0.5	11.0
oxygen, wt %	0.12	2.11
hydrogen, wt %	12.0	11.9
D86 distillation, °F		
% evaporated		
5	119	123
10	140	135
20	170	150
30	196	165
40	217	182
50	235	204
60	251	231
70	267	256
80	291	282
90	318	311
95	340	333
end point	400	400
driveability index <sup>c</sup>	1232	1125

<sup>a</sup> Reference fuel is Los Angeles average premium gasoline.

<sup>b</sup> Adjusted for presence of MTBE. <sup>c</sup> Driveability index,  $1.5 T_{10} + 3.0 T_{50} + T_{90}$ , where  $T_{xx}$  = °F at percent evaporated.

vehicle emissions has been reported before (6-11). Despite many uncertainties regarding the derivation and use of MIR factors, this approach is consistent with the recently adopted CARB regulations (4).

## Program Design

This test program was designed to assess the exhaust emissions benefits which could be achieved by means of a fuel reformulation strategy that involved reduced Reid vapor pressure (RVP), reduced driveability index (DI), and addition of an oxygenate. Criteria pollutant results (THC, CO, and NO<sub>x</sub>) were reported previously (12). They showed this reformulation strategy to provide modest emission reductions for THC (5-18%) and CO (11-21%) but no change for NO<sub>x</sub>. This paper focuses on the noncriteria pollutants.

**Test Fuels.** The two gasolines used in this study are described in Table I. The reference fuel was blended from refinery components to match the average properties of premium-grade gasolines in southern California. The targeted properties were based upon results of a monitoring program conducted in 1987-1989 whereby service station samples from Los Angeles and San Diego were routinely obtained. The recipe for this reference fuel was created using a computer program developed for refinery blending. The finished blend had an RVP of 8.5 psi, a DI value of 1232, and contained approximately 0.5% methyl-*tert*-butyl ether (MTBE). This fuel differed in some respects (higher

Table II. Vehicle Identification

emission system	vehicle no.	year	make and model	engine size, L	engine type	fuel system <sup>a</sup>	mileage
nuncatalyst	1	1970	Chevy Custom (pickup)	5.7	V-8	carb	104 000
	15	1971	Plymouth Duster	3.7	I-6	carb	146 000
	69	1978	Honda Accord	1.6	I-4	carb	119 000
	90	1978	Datsun 510	1.6	I-4	carb	136 000
oxidation catalyst	2	1976	Ford Pinto	2.8	V-6	carb	82 000
	7	1978	Toyota Corona	2.2	I-4	carb	114 000
	38	1975	Olds Cutlass	5.7	V-8	carb	139 000
	41	1982	Datsun King Cab (pickup)	2.2	I-4	carb	111 000
	111	1978	Datsun B-210	1.4	I-4	carb	110 000
three-way catalyst	19	1984	Toyota Camry	2.0	I-4	PFI	61 000
	29	1984	Dodge Ramcharger <sup>b</sup>	5.2	V-8	carb	55 000
	30	1983	Ford Futura <sup>b</sup>	2.3	I-4	carb	129 000
	82	1983	Chevy Caprice <sup>b</sup>	5.0	V-8	carb	72 000
	83	1990	Honda Accord	2.2	I-4	PFI	9 000
adaptive-learning	16	1989	Ford Ranger	2.9	V-6	PFI	11 000
	18	1986	Ford Mustang <sup>b</sup>	2.3	I-4	carb	46 000
	44	1988	Olds Calais	2.5	I-4	TBI	46 000
	150	1989	Chevy Celebrity	2.8	V-6	PFI	12 000
	378	1989	Plymouth Acclaim	2.5	I-4	TBI	14 000

<sup>a</sup> Carb, carburetor; TBI, throttle body injected; PFI, port fuel injected. <sup>b</sup> Contained dual-bed catalyst.

aromatics, higher DI, and lower sulfur) from the "industry average" reference fuel used in the Auto/Oil Air Quality Improvement Research Program (13).

The reformulated gasoline was blended to match most properties of the reference fuel, except for RVP, DI, and MTBE content. Relative to the reference fuel, the RVP of the reformulated fuel was reduced by 1 psi (to 7.5), the DI was reduced by about 100 (to 1125), and the MTBE content was increased (to 11 vol%).

**Test Vehicles.** The 19 vehicles used in the test program are identified in Table II. They were obtained from several sources, including rental agencies, carpools, and company employees. The vehicles were selected to encompass the four major emissions control technologies which comprise the current fleet. These four, in order of increasing sophistication, are nuncatalyst (NC), oxidation catalyst (OX), three-way catalyst (3W), and three-way catalyst with adaptive learning (AL). The presence of AL technology was not apparent by visual inspection of the vehicles but was confirmed by referring to shop manuals.

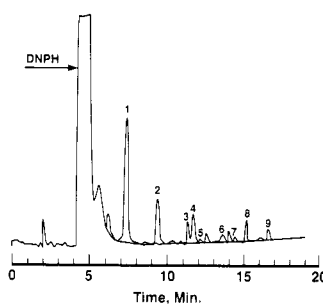
### Emissions Test Procedures

All vehicle emissions tests were conducted at Chevron Research and Technology Co. (CRTC) in Richmond, CA. The 1975 EPA Federal Test Procedure (FTP) was followed at 75 °F. Criteria pollutants (THC, CO, and NO<sub>x</sub>) were measured using standard methodologies.

Each vehicle/fuel combination was tested at least twice, but speciated measurements were generally made for only a single test. To be consistent with normal FTP practice, separate emissions samples for speciated measurements were collected from the cold start, stabilized, and hot start portions of the FTP test (bags 1, 2, and 3, respectively).

Carbonyl compounds were collected by bubbling a portion of the vehicle's diluted exhaust (approximately 2 L/min) through a pair of impingers, each of which contained 25 mL of an acetonitrile solution containing 0.3 mg/mL of 2,4-dinitrophenylhydrazine (DNPH). These sampling conditions have been documented previously (14). Subsequent analysis of the carbonyl-DNPH derivatives was done using high-performance liquid chromatography (HPLC). The HPLC conditions and representative chromatograms are shown in Figure 1. The method detection limit (MDL) (15, 16) for the DNPH derivatives was approximately 0.05 µg/mL. Under typical

### Cold Start Emissions Sample

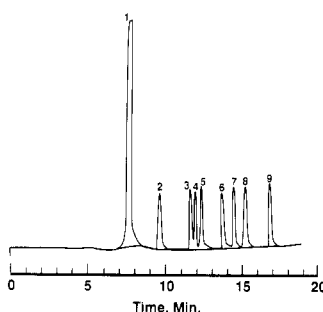


### HPLC Conditions:

Column: 25 cm x 4.6 mm Zorbax C<sub>18</sub>, 5µ  
Flow Rate: 1.0 ml/min.  
Temperature: 40 °C  
Detector: UV-Vis; λ = 360 nm  
Injection Volume: 15 µL  
Solvent Composition, % of Total:

Time, Min.	Water	CH <sub>3</sub> CN	CH <sub>3</sub> OH
0.0	40	27	33
15.0	0	5	95
18.0	0	5	95
19.0	40	27	33

### Calibration Solution



### Composition of Calibration Solution:

Peak No.	Compound	Conc., µg/mL (in CH <sub>3</sub> CN)
1	Formaldehyde-DNPH	19.602
2	Acetaldehyde-DNPH	2.268
3	Acrolein-DNPH	2.114
4	Acetone-DNPH	2.166
5	Propionaldehyde-DNPH	2.200
6	Crotonaldehyde-DNPH	1.858
7	Methyl Ethyl Ketone-DNPH	2.298
8	Benzaldehyde-DNPH	2.056
9	Tolualdehyde-DNPH	2.236

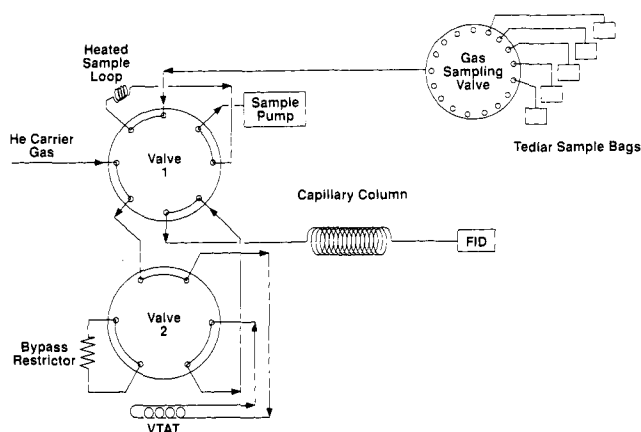
Figure 1. HPLC analysis of carbonyl compounds in vehicle exhaust emissions.

test conditions, this translates to an aldehyde emission rate of about 0.3 mg/mi.

Hydrocarbons for speciated measurements were collected in 3-L Tedlar bags and analyzed by capillary gas chromatography (GC). These small bags were filled from the 100-L bags that were routinely used for criteria pollutant measurements. The sampling point for filling the GC bags was immediately prior to the standard bench analyzers. Thus, the samples analyzed by GC were identical to those analyzed for criteria pollutants. This equivalence was verified by analyzing some samples from both 3-L and 100-L bags.

### Hydrocarbon Speciation Procedures

GC has evolved as the method of choice for analysis of C<sub>1</sub>-C<sub>12</sub> hydrocarbon constituents in vehicle exhaust



**Figure 2.** Plumbing diagram of GC system for speciated hydrocarbon measurements. Configuration shown is for start of run (filling sample loop).

emissions (11, 17–25). However, many procedures described in the literature rely upon multiple columns with column switching and back-flushing techniques. These complexities make it difficult to use the procedures in routine analysis of vehicle emissions.

Several single-column GC procedures for speciated HC analysis have recently been reported (23–25). Our procedure is similar in its reliance upon a single column, but has the advantage of sample preconcentration, which improves the detection limit.

**GC Equipment and Conditions.** All GC analyses were performed using a Varian Model 3400 gas chromatograph (Varian Associates, Sunnyvale, CA). The chromatograph was equipped with an automatic gas sampling valve, a variable temperature adsorption trap (VTAT), and a flame ionization detector (FID). Control of instrument param-

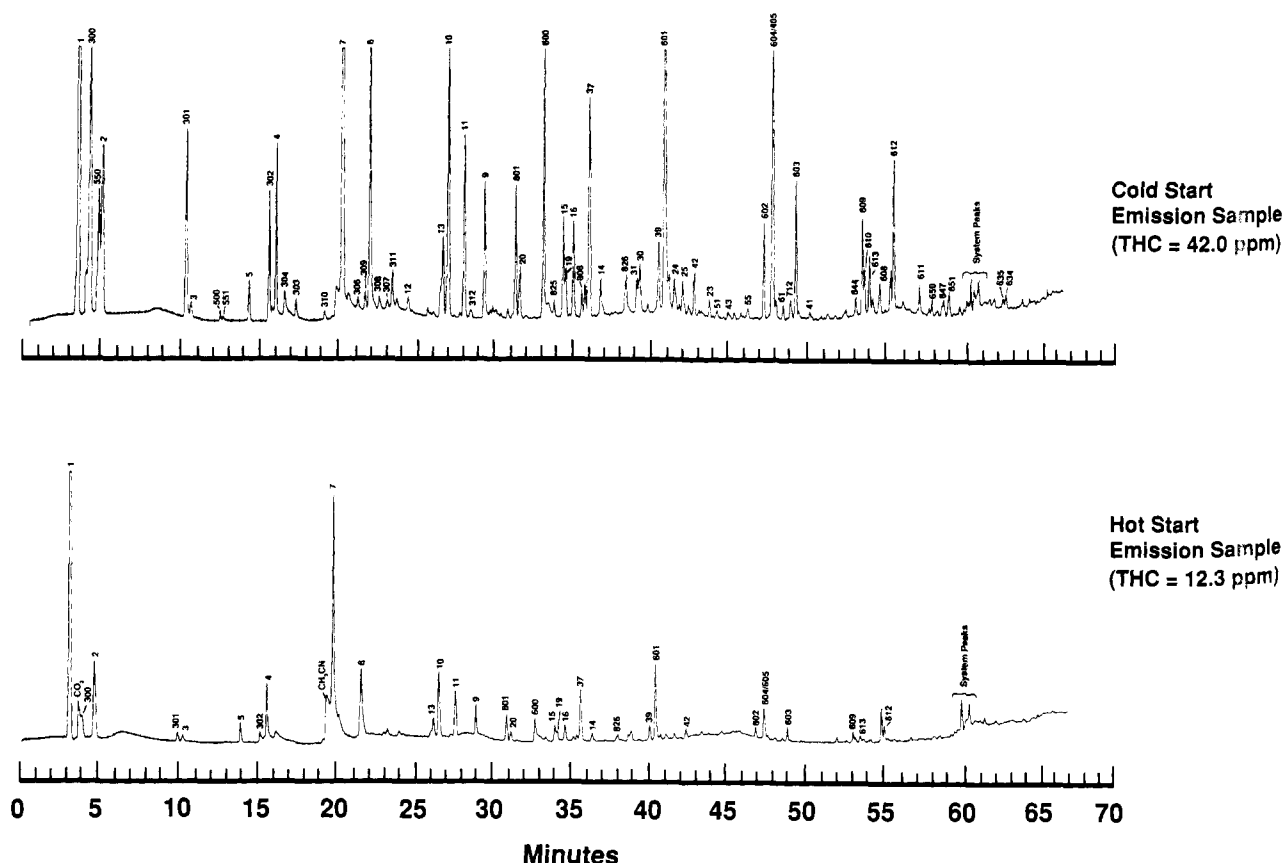
eters was accomplished by an on-board microprocessor. Data collection and manipulation were done with a Varian DS654 data station.

The analytical column used in the GC was a J&W DB-1 60 × 0.32 mm (3- $\mu$ m film) fused-silica capillary column (J&W Scientific, Folsom, CA). The unusually thick film in this column was advantageous for resolving the light hydrocarbons ( $C_1$ – $C_3$ ). The VTAT column consisted of a 3 ft × 1/16 in. stainless steel tube; the middle 2-ft section was packed with Chromosorb 106 (60/80 mesh).

All GC operating conditions are summarized in Table III. Conditions used to introduce the emissions samples into the GC are illustrated in Figure 2. A portable pump was used to draw a bag sample through the heated 5.0-mL sample loop. By means of valve switching, carrier gas was used to sweep the contents of the sample loop into the cold VTAT. Once loaded, the VTAT was isolated from the carrier gas stream (by means of valve switching) and rapidly heated to desorb the sample. A final valve rotation was used to back-flush the desorbed sample from the VTAT into the analytical column. Further details regarding use of the VTAT can be found in the literature (26).

**Compound Identification.** HC compound identification was assigned by comparing retention times of chromatographic peaks from emission samples with those from known standard mixtures. Our compound dictionary, which includes 100 hydrocarbon species, is shown in Table IV.

Representative chromatograms of cold-start (bag 1) and hot-start (bag 3) emissions samples are shown in Figure 3. As is typical with catalyst-equipped vehicles, the concentrations of HC species are much lower in the hot-start sample than the cold-start sample. Stabilized samples (bag 2) generally contain even lower concentrations.



**Figure 3.** GC analysis of emission samples from gasoline vehicle. GC conditions are shown in Table III. Peak identifications are shown in Table IV.

**Table III. GC Conditions for Speciated Hydrocarbon Measurements**

Gas Chromatographic Conditions	
column type	60 m × 0.32 mm i.d. fused-silica DB-1
film thickness	3 μm
carrier gas	He at 4.0 mL/min (~32 cm/s)
make-up gas	He at 30 mL/min
detector	FID held at 260 °C
switching valve temp	100 °C
column temp program	-60 °C; hold 5 min 8 °C/min to 20 °C; hold 3 min 3 °C/min to 155 °C; hold 0 min 20 °C/min to 215 °C; hold 5 min

Sampling Conditions	
sample pump	SKC Model 222
sampling rate	30 mL/min
sampling time	4-6 min
sample loop	5.0 mL; hold at 80 °C
automatic gas sampling valve	Model Valco A16

Sample Concentration Conditions  
gas samples were concentrated by means of a variable temperature adsorption trap (VTAT) built into the Varian 3400 gas chromatograph  
VTAT column: 2 ft × 1/16 in. stainless steel packed with Chromosorb 106 (60/80 mesh)  
GC carrier gas used to flush sample from loop into VTAT  
VTAT temperature program

time, min	temp, °C	direction of flow through VTAT
0-4	-60	forward
4-5	-60→160	no flow
5-8	160	no flow
>8	160	reverse

Since acetonitrile was used to collect aldehyde emissions, it was often present as a contaminant in the FTP bags. However, the GC peak due to acetonitrile (retention time of approximately 19.5 min) was not included when calculating VOC concentrations or reactivities.

**Compound Quantification.** Total hydrocarbon (THC) concentrations in vehicle exhaust are routinely measured using a flame ionization detector (FID) which is calibrated with a propane standard. It is assumed that all hydrocarbons (except methane) give the same FID response (on a per-carbon basis) as does propane. To be consistent with conventional THC measurement technology, the GC FID detector was also calibrated with propane. The same response factor was assumed for all other compounds except MTBE, which is known to give substantially lower response. (We measured MTBE's detector response to be 86% as great as propane's response on a per-carbon basis.)

The actual detector responses of several HC compounds were measured as part of our routine calibration procedures. Calibration was done daily by analyzing a 21-component standard gas mixture which contained a variety of alkanes, alkenes, and aromatics (Scott Specialty Gases, cylinder CLM-1526). Based upon 32 replicate analyses, the measured detector responses for toluene and xylenes were 10% lower than that of propane. All other constituents (<C<sub>11</sub>) gave responses equivalent to propane's response.

Total hydrocarbon emission levels measured by GC were compared with those measured by the conventional bench FID technique. When expressed on a gram per mile basis, the GC results from the 40 emissions tests in this program averaged 97% of the bench FID results (with a standard deviation of 6%). No difference was observed between the two fuels.

**Detection Limit.** To estimate the GC detection limit, we repeatedly measured the concentration of two trace

impurities in the Scott calibration mixture CLM-1526: 2-methylpropane and ethylbenzene. The MDL of each compound was calculated to be 0.007 ppm C. Based upon this assessment, the detection limit for any well-resolved hydrocarbon was estimated to be approximately 0.01 ppm C. Under our vehicle test conditions, this corresponds to an emission rate detection limit of approximately 0.2 mg/mi.

**Coelutions.** With materials as complex as vehicle emissions, some coelutions are unavoidable. In most cases, peak identifications were assigned to match the compound that we believe to predominate. In three exceptional cases, mathematical procedures were used to resolve coeluting pairs. These resolutions were based upon the assumption that the relative amounts of two similar compounds remain constant in the fuel and exhaust. [This assumption has been shown to be correct for the pair of *m*-xylene/*p*-xylene (27).] The three exceptional coelution cases are described below.

**1. Toluene and 2,3,3-Trimethylpentane.** The relative amounts of 2,3,3- and 2,3,4-trimethylpentane were measured in the fuels and applied to the exhaust. When emission samples were analyzed, 2,3,4-trimethylpentane was measured directly, 2,3,3-trimethylpentane was calculated, and toluene was quantified by difference.

**2. Benzene and 1-Methylcyclopentene.** The relative amounts of cyclopentene and 1-methylcyclopentene were determined from analysis of the fuels. In exhaust analysis, cyclopentene was measured directly, 1-methylcyclopentene was calculated, and benzene was determined by difference. (In all emission samples, benzene predominated over 1-methylcyclopentene—generally comprising ≥95% of the total coeluting peak.)

**3. MTBE and 2,3-Dimethylbutane.** This coelution problem only existed in cases where MTBE was present in the fuel. When this occurred, the relative amounts of 2,3-dimethylbutane and 3-methylpentane were measured in the fuel. In exhaust analysis, 3-methylpentane was measured directly, 2,3-dimethylbutane was calculated, and MTBE was determined by difference.

#### Data Analysis Procedures

**Chromatographic Data.** All chromatograms (both GC and HPLC) were visually inspected and corrected as needed (peak start and stop, baseline definition, peak identification, etc.). The corrected chromatographic files were then transferred to a personal computer where species concentrations, emission rates, and reactivities were calculated.

**Emissions Data.** Exhaust emission levels produced from the reference fuel were defined to be the baseline. Emission levels produced from the reformulated fuel were then compared to the baseline on a percentage basis. For each vehicle, the fuel effect was defined to be (reformulated fuel emission rate - reference fuel emission rate)/(reference fuel emission rate) × 100. According to this definition, a negative value indicates an emissions benefit for the reformulated fuel. The percentage effects for all vehicles were grouped and compared to determine the average effects and confidence intervals for the fleet. This statistical approach is identical to that used in analysis of the criteria emissions results (12).

In most cases, speciated emissions measurements were made on only one test of each vehicle/fuel combination. In the few cases where multiple tests were speciated, the results were arithmetically averaged to provide a single value for use in subsequent data analysis. Repeat tests generally showed very similar species profiles, with the total amount of VOC varying by 5-20%. This is similar

Table IV. Hydrocarbon Dictionary for DB-1 GC Column<sup>a</sup>

peak no. <sup>b</sup>	compd name	CAS No.	retention index <sup>c</sup>	peak no. <sup>b</sup>	compd name	CAS No.	retention index <sup>c</sup>
1	methane	00074-82-8	100.0	31	2,5-dimethylhexane	00592-13-2	734.9
300	ethylene	00074-85-1	158.8	30	2,4-dimethylhexane	00589-43-5	737.2
550	acetylene	00074-86-2	189.6	817	1,2,4-trimethylcyclopentane	02815-58-9	745.1
2	ethane	00074-84-0	200.0	39	2,3,4-trimethylpentane	00565-75-3	754.3
301	propylene	00115-07-1	295.8	38	2,3,3-trimethylpentane	00560-21-4	759.7
3	propane	00074-98-6	300.0	601	toluene	00108-88-3	760.1
500	allene	00463-49-0	337.6	29	2,3-dimethylhexane	00584-94-1	764.4
551	propyne	00074-99-7	342.5	24	2-methylheptane	00592-27-8	769.1
5	2-methylpropane	00075-28-5	372.6	25	3-methylheptane	00589-81-1	776.5
305	2-methylpropene	00115-11-7	392.7	42	2,2,5-trimethylhexane	03522-94-9	786.7
302	1-butene	00106-98-9	393.4	23	<i>n</i> -octane	00111-65-9	800.0
502	1,3-butadiene	00106-99-0	397.9	51	2,4,4-trimethylhexane	16747-30-1	808.2
4	<i>n</i> -butane	00106-97-8	400.0	43	2,3,5-trimethylhexane	01069-53-0	819.7
1000	methanol	00067-56-1	404.5	52	2,4-dimethylheptane	02213-23-2	826.3
304	<i>trans</i> -2-butene	00624-64-6	410.9	55	3,5-dimethylheptane	00926-82-9	839.3
303	<i>cis</i> -2-butene	00590-18-1	424.5	602	ethylbenzene	00100-41-4	856.0
1003	ethanol	00064-17-5	454.5	604	<i>m</i> -xylene	00108-38-3	863.8
310	3-methyl-1-butene	00563-45-1	456.2	605	<i>p</i> -xylene	00106-42-3	864.4
7	2-methylbutane	00078-78-4	474.0	60	2-methyloctane	03221-61-2	867.8
306	1-pentene	00109-67-1	489.0	61	3-methyloctane	02216-33-3	874.9
6	<i>n</i> -pentane	00109-66-0	500.0	712	styrene	00100-42-5	881.8
308	<i>trans</i> -2-pentene	00646-04-8	508.8	603	<i>o</i> -xylene	00095-47-6	887.0
311	2-methyl-2-butene	00513-35-9	521.7	41	<i>n</i> -nonane	00111-84-2	900.0
12	2,2-dimethylbutane	00075-83-2	536.8	607	cumene	00098-82-8	920.4
450	cyclopentene	00142-29-0	554.2	644	<i>n</i> -propylbenzene	00103-65-1	950.5
319	4-methyl-1-pentene	00691-37-2	557.6	609	1-ethyl-3-methylbenzene	00620-14-4	957.3
800	cyclopentane	00287-92-3	564.6	610	1-ethyl-4-methylbenzene	00622-96-8	959.6
13	2,3-dimethylbutane	00079-29-8	566.7	613	1,3,5-trimethylbenzene	00108-67-8	964.9
1412	MTBE	01634-04-4	567.1	86	4-methylnonane	17301-94-9	968.3
10	2-methylpentane	00107-83-5	571.2	608	1-ethyl-2-methylbenzene	00611-14-3	976.0
11	3-methylpentane	00096-14-0	584.3	85	3-methylnonane	05911-04-6	981.7
312	1-hexene	00592-41-6	589.5	612	1,2,4-trimethylbenzene	00095-63-6	990.2
9	<i>n</i> -hexane	00110-54-3	600.0	100	<i>n</i> -decane	00124-18-5	1000.0
314	<i>trans</i> -2-hexene	04050-45-7	604.8	611	1,2,3-trimethylbenzene	00576-73-8	1020.2
322	3-methyl- <i>trans</i> -2-pentene	00616-12-6	607.9	650	indan	00496-11-7	1034.5
320	2-methyl-2-pentene	00625-27-4	611.2	646	1,3-diethylbenzene	00141-93-5	1045.4
313	<i>cis</i> -2-hexene	07688-21-3	615.4	647	1-methyl-3-propylbenzene	01074-43-7	1047.8
321	3-methyl- <i>cis</i> -2-pentene	00922-62-3	622.1	651	1,2-diethylbenzene	00135-01-3	1054.4
801	methylcyclopentane	00096-37-7	629.3	653	1-methyl-2-propylbenzene	01074-17-5	1066.5
20	2,4-dimethylpentane	00108-08-7	632.8	654	1,4-dimethyl-2-ethylbenzene	01758-88-9	1074.3
451	1-methylcyclopentene	00693-89-0	652.3	655	1,3-dimethyl-4-ethylbenzene	00874-41-9	1076.9
600	benzene	00071-43-2	653.6	656	1,2-dimethyl-4-ethylbenzene	00934-80-5	1082.4
825	cyclohexane	00110-82-7	663.0	657	1,3-dimethyl-2-ethylbenzene	02870-04-4	1086.2
15	2-methylhexane	00591-76-4	670.1	101	<i>n</i> -undecane	01120-21-4	1100.0
19	2,3-dimethylpentane	00565-59-3	672.3	635	1,2,4,5-tetramethylbenzene	00095-93-2	1121.7
16	3-methylhexane	00589-34-4	678.5	634	1,2,3,5-tetramethylbenzene	00527-53-7	1126.9
806	<i>cis</i> -1,3-dimethylcyclopentane	02532-58-3	685.1	7800	methylindan A	27133-93-3	1152.5
807	<i>trans</i> -1,3-dimethylcyclopentane	00822-50-4	687.8	7801	methylindan B	27133-93-3	1163.9
37	2,2,4-trimethylpentane	00540-84-1	690.8	714	naphthalene	00091-20-3	1192.4
14	<i>n</i> -heptane	00142-82-5	700.0	102	dodecane	00112-40-3	1200.0
826	methylcyclohexane	00108-87-2	725.0				

<sup>a</sup> GC conditions shown in Table III. <sup>b</sup> Peak number is based on an in-house nomenclature system, which was developed to characterize gasolines. <sup>c</sup> Retention index,  $100[(\log X_i - \log X_{n_z})/(\log X_{n_{z+1}} - \log X_{n_z})] + 100Z$  where  $z$  is the number of carbon atoms in *n*-paraffin which immediately precedes peak  $i$ ;  $X_i$  is the retention time of peak  $i$ ;  $X_{n_z}$  is the retention time of *n*-paraffin (having  $z$  carbon atoms) which precedes peak  $i$ ;  $X_{n_{z+1}}$  is the retention time of *n*-paraffin (having  $z + 1$  carbon atoms) which follows peak  $i$ .

to the total HC variability measured by bench FID.

### Results and Discussion

**Non-Methane Organic Gases (NMOG) and Reactivity.** Total exhaust emissions of volatile organic compounds (VOC) were determined by summing the individual emission rates of all hydrocarbons, ethers, and carbonyls. NMOG emissions were then calculated by subtracting methane from the VOC results. The NMOG emission rates from each vehicle/fuel combination are listed in Table V.

The total reactivity (g of ozone/mi) of each emissions sample is listed in Table VI. The FTP-weighted results are further illustrated in Figure 4, where total reactivity is plotted versus NMOG emission rate. For each vehicle technology type, total reactivity was highly correlated with

NMOG emission rate ( $r^2 \geq 0.95$ ).

Mass-normalized reactivity (g of ozone/g of NMOG) was calculated by dividing the total reactivity by the NMOG emission rate of each sample. Figure 5 shows the normalized reactivity of FTP-weighted emissions from each vehicle/fuel combination. The differences in reactivity between the two fuels were very slight. Somewhat larger reactivity differences occurred from vehicle to vehicle. An effect of vehicle technology type is also apparent. On average, a slight reduction in normalized reactivity occurred in progressing from older to newer technologies (NC > OX > 3W > AL). Of all vehicles tested, emissions having the lowest normalized reactivity were produced by vehicle 18 (1986 Ford Mustang). This vehicle was equipped with a dual-bed catalyst—as were vehicles 29, 30, and 82, which also produced emissions having lower than av-

Table V. NMOG Emissions Results (g/mi)

vehicle category	car no.	FTP bag 1		FTP bag 2		FTP bag 3		FTP composite	
		ref fuel	reform. fuel	ref fuel	reform. fuel	ref fuel	reform. fuel	ref fuel	reform. fuel
noncatalyst	1	2.063	2.047	1.433	1.218	1.291	1.277	1.524	1.406
	15	16.468	14.661	3.512	3.191	2.819	2.561	5.992	5.387
	69	3.526	3.967	0.231	0.221	0.858	0.750	1.080	1.138
	90	4.039	3.720	3.354	3.338	2.589	2.579	3.286	3.209
oxidation catalyst	2	1.716	1.507	0.719	0.868	0.985	0.965	0.998	1.026
	7	0.490	0.509	0.088	0.112	0.163	0.174	0.191	0.211
	38	1.102	0.892	0.341	0.353	0.610	0.528	0.572	0.512
	41	0.931	0.898	0.139	0.161	0.158	0.183	0.307	0.318
3-way catalyst	111	1.350	1.394	0.244	0.228	0.397	0.383	0.515	0.511
	19	0.840	0.691	0.039	0.036	0.085	0.090	0.217	0.186
	29	1.124	0.962	0.222	0.181	0.639	0.407	0.523	0.404
	30	1.302	1.102	0.087	0.092	0.226	0.204	0.375	0.331
adaptive learning	82	1.135	0.590	0.195	0.111	0.315	0.271	0.423	0.253
	83	0.851	0.523	0.044	0.055	0.077	0.080	0.220	0.159
	16	0.544	0.479	0.018	0.079	0.097	0.155	0.148	0.183
	18	1.232	1.254	0.261	0.319	0.572	0.592	0.547	0.586
	44	0.540	0.532	0.159	0.138	0.264	0.252	0.263	0.251
	150	1.060	0.982	0.241	0.195	0.447	0.418	0.467	0.420
	378	0.548	0.512	0.040	0.041	0.132	0.133	0.170	0.164

Table VI. Total Reactivity Results (g of ozone/mi)<sup>a</sup>

vehicle category	car no.	FTP bag 1		FTP bag 2		FTP bag 3		FTP composite	
		ref fuel	reform. fuel	ref fuel	reform. fuel	ref fuel	reform. fuel	ref fuel	reform. fuel
noncatalyst	1	6.029	5.709	4.613	3.928	3.995	3.920	4.736	4.295
	15	45.293	38.917	11.858	10.813	9.357	8.557	18.065	16.000
	69	11.286	12.332	0.783	0.777	2.948	2.617	3.535	3.664
	90	12.761	11.783	10.496	10.241	8.242	8.062	10.346	9.962
oxidation catalyst	2	5.258	4.691	2.111	2.591	2.861	2.952	2.967	3.124
	7	1.508	1.601	0.322	0.397	0.570	0.545	0.634	0.685
	38	3.109	2.564	0.892	0.897	1.517	1.419	1.522	1.385
	41	2.796	2.745	0.327	0.425	0.362	0.446	0.844	0.907
3-way catalyst	111	3.709	3.866	0.500	0.541	0.992	0.966	1.299	1.343
	19	2.349	2.000	0.097	0.079	0.200	0.214	0.590	0.513
	29	3.282	2.793	0.575	0.426	1.847	1.158	1.481	1.115
	30	3.937	3.419	0.156	0.140	0.419	0.388	1.006	0.885
adaptive learning	82	2.691	1.638	0.367	0.213	0.798	0.650	0.966	0.627
	83	2.723	1.641	0.113	0.142	0.184	0.184	0.672	0.464
	16	1.531	1.338	0.061	0.191	0.277	0.354	0.422	0.474
	18	2.985	3.290	0.412	0.557	1.229	1.296	1.166	1.322
	44	1.510	1.567	0.404	0.324	0.636	0.620	0.685	0.662
	150	3.310	2.950	0.426	0.387	1.135	1.070	1.218	1.107
	378	1.577	1.463	0.063	0.079	0.355	0.341	0.457	0.438

<sup>a</sup> Calculated using MIR factors (from ref 5).

erage reactivity. This beneficial effect of dual-bed catalyst systems has been observed in other research programs conducted in-house.

Normalized reactivity also varied with FTP bag. Figure 6 depicts average normalized reactivity from each vehicle technology type for each phase of the FTP test. On average, reactivity was highest in bag 1, lowest in bag 2, and intermediate in bag 3. The aforementioned decrease in reactivity with increasingly modern vehicles was most pronounced in bags 2 and 3, but was almost nonexistent in bag 1. Presumably, the more efficient catalyst operation during bags 2 and 3 is responsible for these reactivity changes.

The effects of changing from reference fuel to reformulated fuel upon the normalized reactivity of exhaust emissions were also assessed statistically. Figure 7 shows the average percentage change in reactivity for each FTP bag from each vehicle technology. All effects were small (generally less than 5%) and most were not statistically significant.

Considering only the FTP-composite emissions, the largest reactivity changes resulting from the reformulated gasoline occurred with the OX vehicles (2.0% increase, but

not statistically significant) and the NC vehicles (1.6% decrease). The other vehicle types (as well as the entire test fleet) exhibited no difference in reactivity between the two fuels.

**Average Exhaust Profiles.** Average profiles of FTP-weighted exhaust emissions were calculated for each vehicle technology type on each fuel. These profiles (which are arithmetic averages of the speciated results for all vehicles of a given technology type) are listed in Table VII. The profiles are further abbreviated and shown graphically in Figure 8. (The bars in this figure do not total 100% since unidentified compounds are not included.)

An obvious difference in these profiles was due to MTBE, which was present only in emissions from the reformulated fuel. However, MTBE's contribution to the exhaust mass was much less than its contribution to fuel mass—particularly in catalyst-equipped vehicles. In comparison with most fuel constituents, MTBE was preferentially reduced.

Other differences between fuel and exhaust compositions were observed. For instance, methane and carbonyls comprised significant fractions of exhaust, but were completely absent from the fuel. Also, the aromatic fractions

Table VII. Speciated Exhaust Emission Mass Profiles<sup>a</sup>

	FTP-weighted emission rates, mg/mi							
	nuncatalyst		oxidation catalyst		3-way catalyst		adaptive learning	
	ref fuel	reform. fuel	ref fuel	reform. fuel	ref fuel	reform. fuel	ref fuel	reform. fuel
methane	188.07	156.04	66.70	57.70	73.42	66.67	65.72	67.64
ethane	21.35	20.28	13.24	12.05	15.50	13.82	11.59	11.37
propane	5.79	1.74	3.33	1.32	2.52	1.04	2.75	1.27
C <sub>4</sub> alkanes	54.31	27.60	17.65	10.10	11.81	5.77	13.23	9.36
C <sub>5</sub> alkanes	103.52	135.70	28.11	42.48	20.06	22.53	24.56	34.19
C <sub>6</sub> alkanes	121.48	136.72	27.87	35.27	21.29	18.79	23.72	28.76
C <sub>7</sub> alkanes	105.18	81.59	21.44	18.93	15.87	8.86	17.03	15.03
C <sub>8</sub> alkanes	196.67	119.05	37.12	26.92	26.40	12.18	29.63	21.95
C <sub>9+</sub> alkanes	66.08	30.32	11.32	5.48	8.01	3.08	9.36	5.24
cycloalkanes	35.87	40.78	8.06	10.70	5.85	5.20	6.89	8.34
total alkanes (minus methane)	710.23	593.78	168.14	163.24	127.31	91.27	138.75	135.53
ethene	223.37	203.95	47.62	46.37	22.24	18.71	19.51	19.91
propene	110.06	97.74	17.39	16.50	11.01	8.85	8.72	8.06
C <sub>4</sub> alkenes	75.49	95.07	8.09	18.29	7.25	9.40	5.25	10.10
C <sub>5</sub> alkenes	40.59	35.52	3.48	3.73	3.42	2.56	1.97	2.12
C <sub>6+</sub> alkenes	21.83	20.19	2.32	2.59	2.35	1.35	1.11	0.98
total alkenes	471.33	452.47	78.90	87.49	46.27	40.88	36.56	41.16
benzene	156.18	138.48	27.57	25.01	19.39	15.69	19.77	20.39
toluene	338.36	314.14	51.00	44.13	36.62	26.14	29.98	29.67
C <sub>8</sub> aromatics	425.84	380.44	52.27	47.07	42.38	29.03	35.01	32.40
C <sub>9</sub> aromatics	281.03	241.59	32.28	28.72	26.93	18.11	22.36	19.48
C <sub>10+</sub> aromatics	91.04	67.16	5.49	5.86	7.37	4.40	4.57	4.01
total aromatics	1292.45	1141.82	168.60	150.79	132.70	93.37	111.69	105.96
acetylene	209.69	177.10	15.37	13.36	7.38	4.21	2.84	3.01
propyne + allene	19.21	20.25	0.88	1.22	0.69	0.53	0.38	0.31
1,3-butadiene	2.96	1.81	0.02	0.33	0.07	0.05	0.00	0.14
formaldehyde	73.25	85.24	28.50	35.83	7.27	7.61	4.87	8.43
acetaldehyde	19.74	21.72	11.15	11.76	4.43	3.64	3.07	4.71
acrolein	11.62	13.20	3.74	3.75	1.11	0.74	0.81	1.16
other carbonyls	69.89	78.57	23.69	25.59	11.11	11.08	4.62	8.05
total carbonyls	174.50	198.73	67.08	76.94	23.93	23.07	17.31	22.35
unidentified HC	79.67	58.87	15.29	10.40	11.65	8.04	10.55	9.12
MTBE	10.50	130.30	2.43	11.83	1.42	4.59	0.84	3.16
total VOC, g/mi	3.159	2.941	0.583	0.573	0.425	0.333	0.385	0.388
total NMOG, g/mi	2.971	2.785	0.517	0.516	0.351	0.267	0.319	0.321

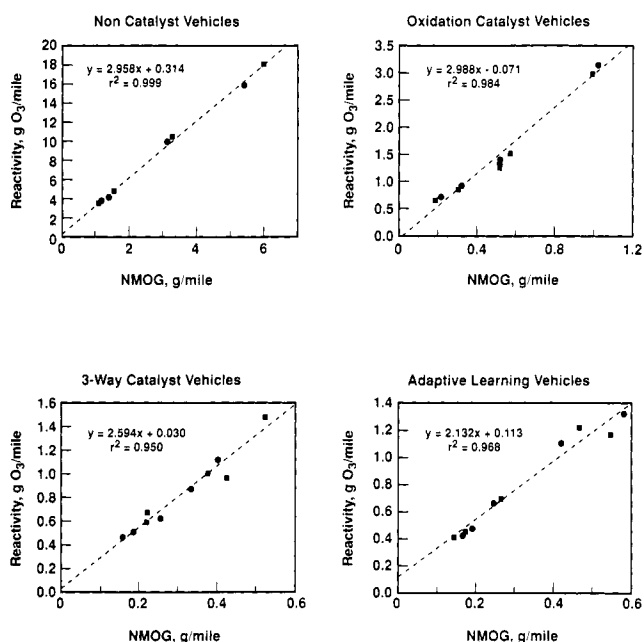
<sup>a</sup> Average results from all vehicles.

Figure 4. Total reactivity versus NMOG emission rates for FTP-weighted emissions. Dashed lines were generated from regression analyses. (■) reference fuel; (●) reformulated fuel.

of exhaust were decreased while the alkene fractions were increased relative to the fuel. Furthermore, the exhaust

alkene components were predominantly C<sub>2</sub>–C<sub>4</sub>, while the fuel alkenes were predominantly C<sub>5</sub>–C<sub>7</sub>.

Compositional effects of vehicle technology type were also seen. For example, the exhaust methane fraction increased with newer vehicles, while the carbonyl fraction was largest in exhaust from oxidation catalyst vehicles.

When expressed on a reactivity basis, the emission profiles were quite different. These reactivity profiles are listed in Table VIII and summarized graphically in Figure 8. Because of its extremely low reactivity factor, the large mass fraction of methane corresponds to a negligible reactivity fraction. Similarly, the other alkanes and MTBE had greatly reduced contributions on a reactivity basis. In contrast, the contribution of alkenes, aromatics, and carbonyls to total reactivity were enhanced relative to their mass.

**Fuel Effects upon VOC Constituents.** The effects of changing from reference fuel to reformulated fuel upon the emission rates of several VOC constituents were calculated in a manner analogous to that used for assessing reactivity effects. The results are depicted in Figure 9.

On average, total VOC emissions from all vehicles were reduced 6% by use of the reformulated fuel. The 3W vehicles showed the greatest effect, with a reduction of 21%. Results from the other vehicle categories were not significant at the 90% confidence level, although slight reductions were measured from the NC and OX vehicles and slight increases from the AL vehicles. NMOG emis-



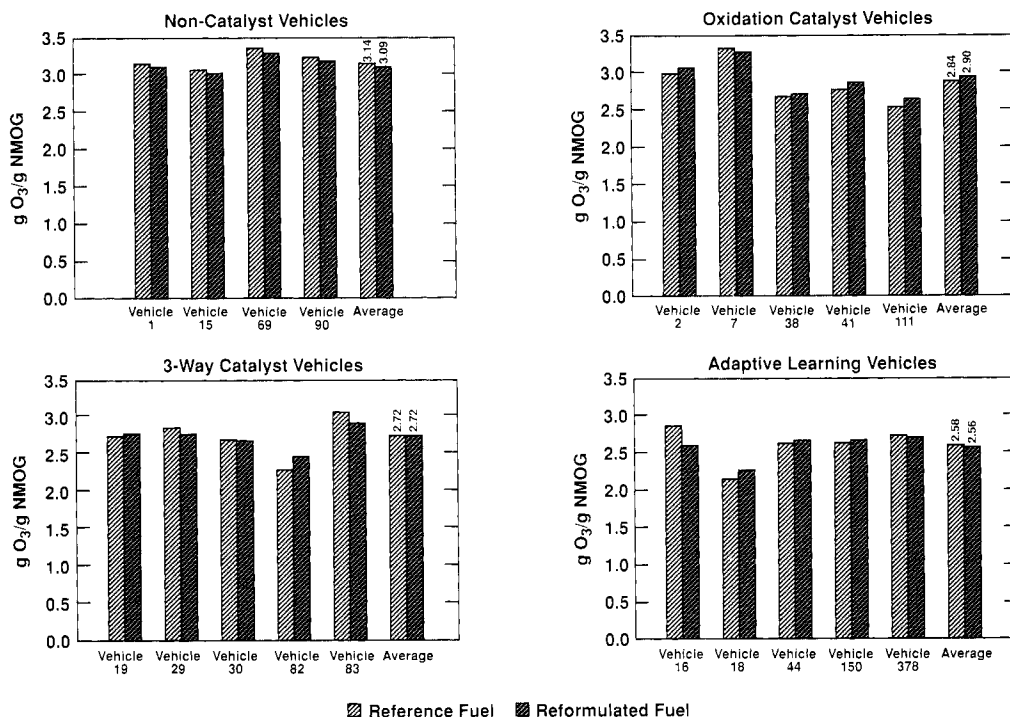


Figure 5. NMOG-normalized reactivity of FTP-weighted emissions from each vehicle.

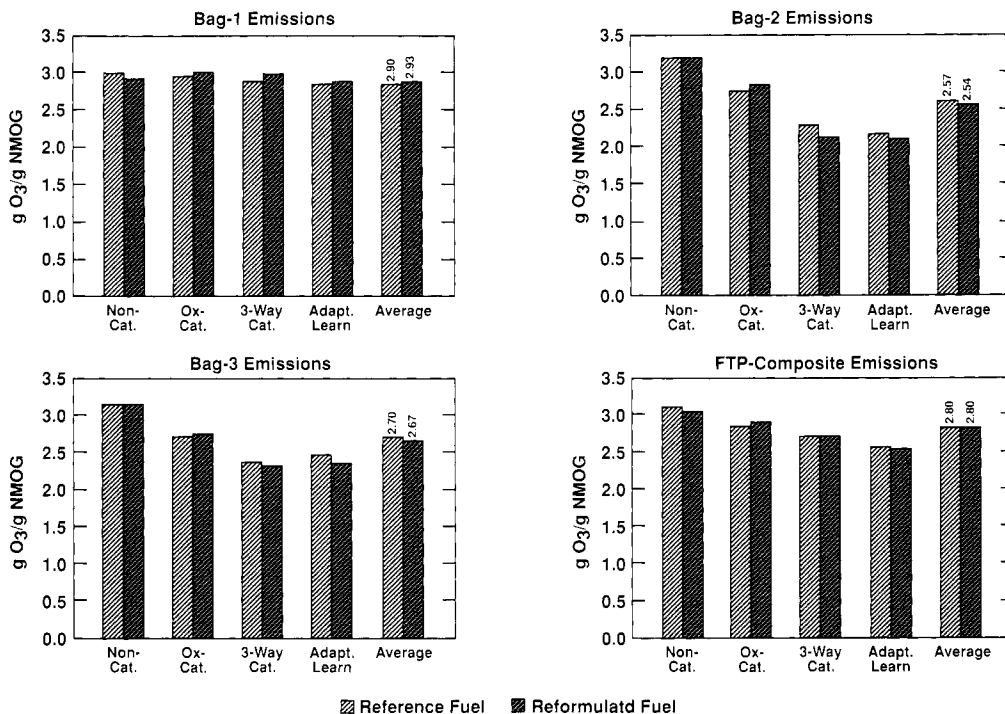


Figure 6. Variation in NMOG-normalized reactivity by FTP bag.

sions results were virtually identical to the VOC results.

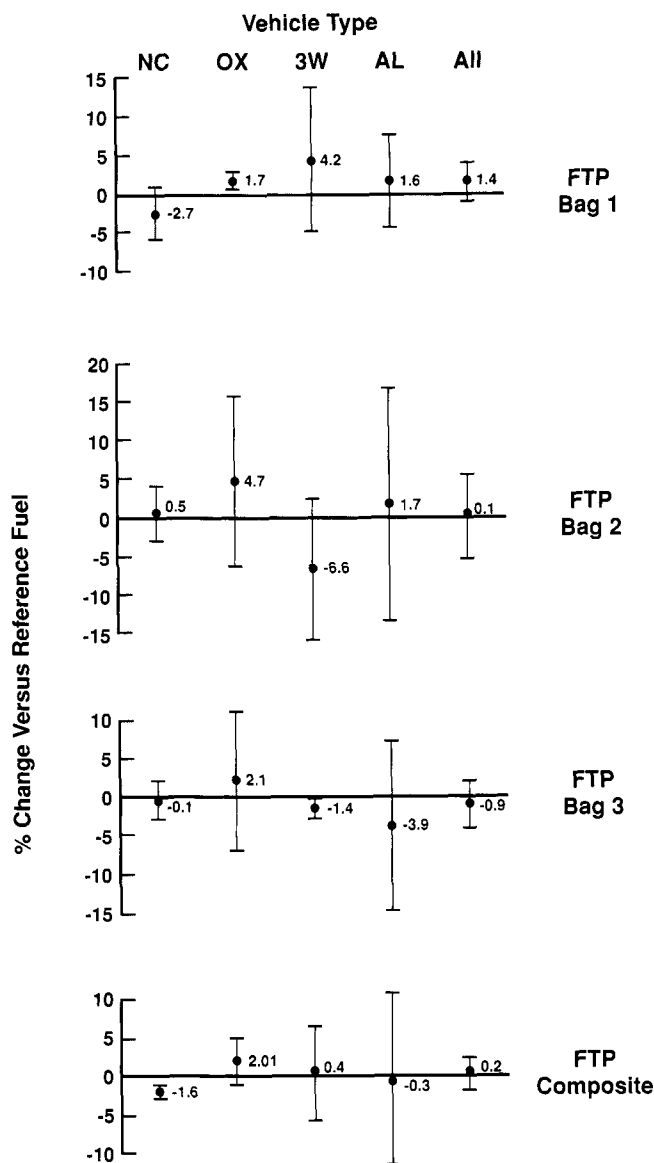
Total carbonyl emissions were increased by use of the reformulated fuel in three of four vehicle categories. This is attributed in part to MTBE, which has been reported to increase formaldehyde emissions (9, 28). As shown in Figure 9, formaldehyde increases were measured in all four vehicle categories. The largest increase (29%) occurred with OX vehicles. This effect of enhanced formaldehyde emissions from OX vehicles has been observed previously (28).

The fuel effects upon total alkene emissions were mixed among the four vehicle categories. Reformulated fuel increased alkene emissions from OX and AL vehicles, but decreased alkenes from NC and 3W vehicles. However,

even where alkene reductions occurred, they were of lesser magnitude than the reductions of total VOC. Thus, on a percentage basis, alkene emissions increased with use of reformulated fuel in all vehicle categories.

Much of this alkene increase is also attributed to use of MTBE, which serves as a precursor for isobutene formation. As Figure 9 shows, isobutene emissions were greatly increased by use of reformulated fuel in all vehicle categories. (Since 1-butene and isobutene were not chromatographically separated, the sum of these two is reported.)

The total aromatics content of the reformulated fuel was slightly lower than that of the reference fuel (36% versus 44%). Consistent with this, lower emission rates of aromatics were produced by the reformulated fuel. Figure



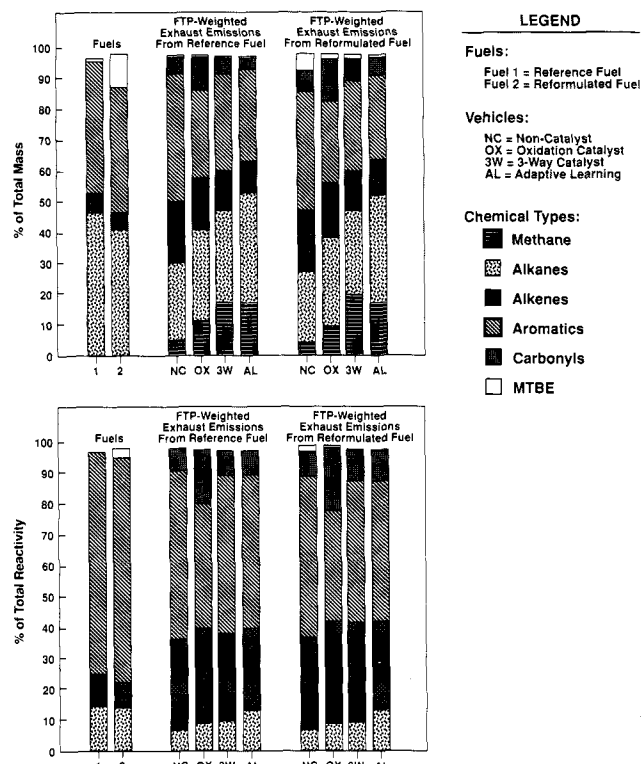
**Figure 7.** Effect of reformulated fuel upon NMOG-normalized reactivity of exhaust emissions—average percent difference versus reference fuel. Error bars represent 95% confidence intervals.

9 shows these reductions occurred in all vehicle categories and averaged 14%. The different fuel effects observed from one vehicle category to the next mirrored the changes in total VOC.

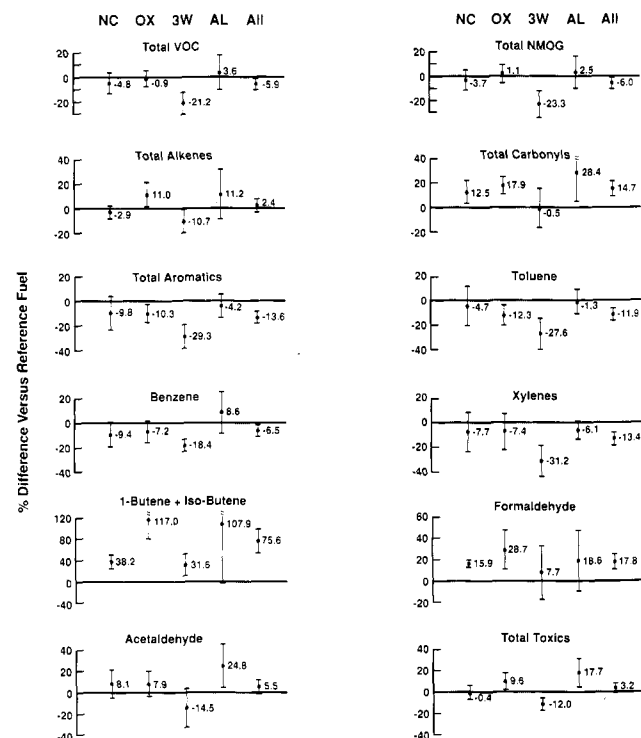
The fuel effects upon benzene emissions were similar to the effects upon total VOC. On average, the reformulated fuel gave a 7% reduction in benzene emissions, comparable to the 6% VOC reduction. Somewhat greater reductions in toluene and xylene emission rates were observed (12% and 13%, respectively).

The aromatic fractions of the fuels and emissions are compared in Table IX. From all vehicle categories, benzene was enriched in exhaust as compared to the fuel, while the other aromatics were depleted. Furthermore, this depletion of the higher aromatics was more extreme in catalyst-equipped vehicles than in noncatalyst vehicles.

**Fuel Effects Upon Toxics.** As stipulated in the 1990 Amendments to the Federal Clean Air Act, emissions of toxics from motor vehicles consist of benzene, formaldehyde, acetaldehyde, 1,3-butadiene, and polycyclic organic matter (POM). In this program, all but POM were measured. However, due to GC limitations (detection limits and resolution problems) 1,3-butadiene was reliably measured only in emission samples from NC vehicles.



**Figure 8.** Apportionment of VOC mass and reactivity by chemical type.



**Figure 9.** Effect of reformulated fuel upon FTP-weighted emission rates of selected VOC species. Error bars represent 90% confidence intervals.

Based upon literature reports, emission rates of 1,3-butadiene from the other vehicle categories are estimated at 1–3 mg/mi (28, 29).

The average FTP-weighted results of exhaust toxics are shown in Figure 10. There were large differences among the four vehicle technology types, with lesser differences between fuels. In every case, significant levels of benzene, formaldehyde, and acetaldehyde were present. From OX vehicles, the aldehydes comprised over 50% of the total

Table VIII. Speciated Exhaust Emission Reactivity Profiles<sup>a</sup>

	total reactivity of FTP-weighted emissions, mg of ozone/mi							
	nuncatalyst		oxidation catalyst		3-way catalyst		adaptive learning	
	ref fuel	reform. fuel	ref fuel	reform. fuel	ref fuel	reform. fuel	ref fuel	reform. fuel
methane	1.92	1.59	0.68	0.59	0.75	0.68	0.67	0.69
ethane	3.14	2.98	1.95	1.77	2.28	2.03	1.70	1.67
propane	1.91	0.57	1.10	0.44	0.83	0.34	0.91	0.42
C <sub>4</sub> alkanes	37.50	18.67	12.27	6.94	8.26	3.95	9.33	6.43
C <sub>5</sub> alkanes	85.59	105.82	23.61	33.57	16.42	17.82	20.45	26.97
C <sub>6</sub> alkanes	98.54	108.87	22.93	28.43	17.11	14.77	19.31	23.15
C <sub>7</sub> alkanes	88.35	66.14	18.21	15.48	13.46	7.25	14.42	12.31
C <sub>8</sub> alkanes	138.06	83.05	26.07	18.83	18.52	8.49	20.78	15.33
C <sub>9+</sub> alkanes	40.68	17.21	7.24	3.38	5.05	1.81	5.96	3.14
cycloalkanes	54.73	62.21	12.43	16.36	8.97	7.98	10.52	12.73
total alkanes (minus methane)	548.49	465.52	125.82	125.19	90.90	64.45	103.39	102.16
ethene	1183.84	1080.94	252.37	245.78	117.90	99.19	103.42	105.52
propene	726.41	645.09	114.76	108.89	72.67	58.44	57.58	53.19
C <sub>4</sub> alkenes	422.29	515.33	43.72	98.43	39.22	49.98	27.90	53.56
C <sub>5</sub> alkenes	198.31	169.64	16.19	17.01	16.53	11.52	9.43	10.26
C <sub>6+</sub> alkenes	99.45	81.46	10.36	10.32	10.80	5.52	4.84	3.98
total alkenes	2630.29	2492.45	437.39	480.44	257.12	224.65	203.16	226.51
benzene	43.73	38.77	7.72	7.00	5.43	4.39	5.54	5.71
toluene	642.89	596.87	96.89	83.85	69.57	49.66	56.96	56.38
C <sub>8</sub> aromatics	2108.84	1914.76	257.86	236.14	207.66	144.29	171.45	162.09
C <sub>9</sub> aromatics	1686.65	1474.21	192.23	172.90	161.99	110.29	132.78	116.68
C <sub>10+</sub> aromatics	477.97	353.04	28.87	31.05	38.48	23.06	24.21	21.01
total aromatics	4960.08	4377.66	583.57	530.95	483.12	331.69	390.94	361.87
acetylene	77.59	65.53	5.69	4.94	2.73	1.56	1.05	1.11
propyne + allene	86.51	91.88	5.17	6.89	3.73	2.97	2.42	2.03
1,3-butadiene	22.82	13.92	0.16	2.57	0.50	0.35	0.00	1.06
formaldehyde	454.17	528.48	176.68	222.16	45.10	47.17	30.22	52.28
acetaldehyde	75.02	82.55	42.38	44.70	16.83	13.85	11.67	17.90
acrolein	53.43	60.71	17.20	17.24	5.13	3.39	3.72	5.33
other carbonyls	47.26	52.98	17.41	17.83	6.19	5.68	1.77	3.88
total carbonyls	629.88	724.72	253.66	301.94	73.24	70.08	59.98	79.39
unidentified HC	205.87	152.12	39.51	26.88	30.10	20.79	27.27	23.58
MTBE	7.35	91.21	1.70	8.28	0.99	3.21	0.59	2.21
total react, g of ozone/mi	9.171	8.481	1.453	1.489	0.943	0.721	0.789	0.801
norm react, g of O <sub>3</sub> /g of NMOG	3.136	3.087	2.844	2.896	2.716	2.717	2.576	2.558

<sup>a</sup> Average results from all vehicles.

Table IX. Aromatic Fractions of Fuels and Exhaust Emissions

compound	wt % of fuel <sup>a</sup>	wt % of VOC from FTP-weighted exhaust			
		NC	OX	3W	AL
Reference Fuel					
benzene	2.78	4.94	4.73	4.56	5.14
toluene	13.59	10.71	8.75	8.62	7.79
xylenes	13.96	13.48	8.97	9.97	9.09
C <sub>9+</sub> aromatics	19.68	11.78	6.48	8.07	6.99
Reformulated Fuel					
benzene	2.87	4.71	4.36	4.71	5.26
toluene	10.94	10.68	7.70	7.85	7.65
xylenes	13.06	12.94	8.21	8.72	8.35
C <sub>9+</sub> aromatics	17.92	10.50	6.03	6.76	6.05

<sup>a</sup> From GC analysis.

toxics, while benzene was predominant from the other three vehicle types.

Statistical analyses (summarized in Figure 9) showed that the reformulated fuel reduced total toxics from 3W vehicles (by 12%) but increased toxics from OX and AL vehicles (by 10% and 18%, respectively). These effects upon total toxics result from the combined effects of the individual toxic species. For instance, the total toxics reduction from 3W vehicles is primarily a consequence of the large benzene reductions from these vehicles. From

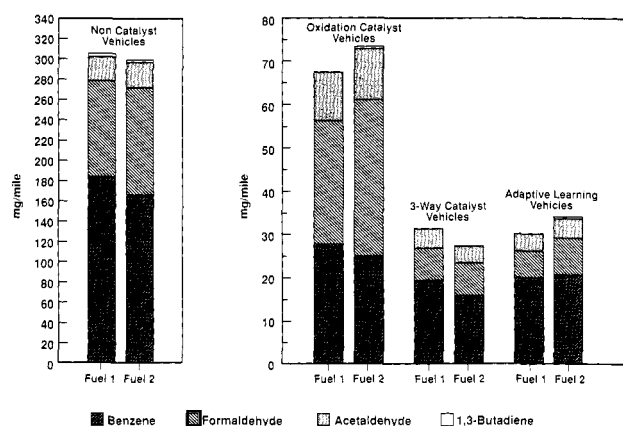


Figure 10. Average FTP-weighted emission rates of toxic species. fuel 1, reference fuel; fuel 2, reformulated fuel.

OX vehicles, increased aldehyde emissions offset the benzene decrease, resulting in a net increase of total toxics.

### Summary and Conclusions

In this program, the emissions impacts of replacing an average southern California premium-grade gasoline with a reformulated gasoline were assessed. Exhaust emissions were measured from 19 vehicles tested on both fuels. The results showed no statistically significant difference in NMOG-normalized reactivity of emissions from the two

fuels. Yet, due to a reduction in mass emission rates, a net reactivity benefit could be imputed to the reformulated fuel. This is consistent with results of other published studies involving reformulated gasolines (10, 29, 30).

Slight differences in normalized reactivity were observed among the four vehicle categories tested. On average, reactivity was reduced in progressing from older to newer technology types. These reductions were especially evident in bag 2 and bag 3 emission samples, but not in bag 1 (cold-start) samples.

Some changes in emissions profiles were observed among the different vehicle categories. For instance, aldehydes comprised nearly twice as large a fraction of the exhaust emissions from OX vehicles as compared with other vehicle types. The MTBE content of emissions was much higher from NC vehicles than from other vehicle types.

Relative to the fuel compositions, exhaust compositions were depleted in alkanes and aromatics, but enriched in alkenes and carbonyls. Furthermore, the alkenes were primarily C<sub>2</sub>-C<sub>4</sub> species, which were not present in the fuel but produced during combustion. When expressed on a reactivity basis, this enrichment of alkenes and carbonyls was even more significant.

These changes between the composition of fuel and exhaust have important implications for fuel reformulation strategies. Expected beneficial effects of substituting low-reactivity components for high-reactivity components in the fuel may be offset by changes in the exhaust. In this study, for example, MTBE (which has very low reactivity) was used. However, emissions of highly-reactive alkenes and aldehydes were found to increase from the MTBE-containing reformulated fuel. Thus, the net change in reactivity of the exhaust emissions was insignificant.

#### Acknowledgments

This test program resulted from the combined efforts of numerous individuals. The following contributions are acknowledged: Messrs. J. A. Cembura, C. P. Cronin, and W. E. Warren conducted the day-to-day operations of vehicle emissions testing; Ms. A. N. Tiedemann and Ms. H. A. Fruhlinger-Goode conducted all speciated analyses of hydrocarbon and aldehyde emission species; and Mr. J. A. Gething was responsible for the overall design and management of the program.

**Registry No.** MTBE, 1634-04-4; CH<sub>4</sub>, 74-82-8; CH<sub>3</sub>CH<sub>3</sub>, 74-84-0; CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>, 74-98-6; H<sub>2</sub>C=CH<sub>2</sub>, 74-85-1; H<sub>2</sub>C=CHCH<sub>3</sub>, 115-07-1; C<sub>6</sub>H<sub>6</sub>, 71-43-2; CH<sub>3</sub>Ph, 108-88-3; HC≡CH, 74-86-2; HC≡CCH<sub>3</sub>, 74-99-7; allene, 463-49-0; 1,3-butadiene, 106-99-0; formaldehyde, 50-00-0; acrolein, 107-02-8; acetaldehyde, 75-07-0; xylene, 1330-20-7; ozone, 10028-15-6.

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Received for review July 25, 1991. Revised manuscript received December 6, 1991. Accepted February 12, 1992.