The Relationship between Gasoline Composition and Vehicle Hydrocarbon Emissions: A Review of Current Studies and Future Research Needs

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The purpose of this paper is to review current studies concerning the relationship of fuel composition to vehicle engine-out and tail-pipe emissions and to outline future research needed in this area. A number of recent combustion experiments and vehicle studies demonstrated that reformulated gasoline can reduce vehicle engine-out, tail-pipe, running-loss, and evaporative emissions. Some of these studies were extended to understand the fundamental relationships between fuel composition and emissions. To further establish these relationships, it was necessary to develop advanced analytical methods for the qualitative and quantitative analysis of hydrocarbons in fuels and vehicle emissions. The development of real-time techniques such as Fourier transform infrared spectroscopy, laser diode spectroscopy, and atmospheric pressure ionization mass spectrometry were useful in studying the transient behavior of exhaust emissions under various engine operating conditions. Laboratory studies using specific fuels and fuel blends were carried out using pulse flame combustors, single- and multicylinder engines, and vehicle fleets. Chemometric statistical methods were used to analyze the large volumes of emissions data generated from these studies. Models were developed that were able to accurately predict tail-pipe emissions from fuel chemical and physical compositional data. Some of the primary fuel precursors for benzene, 1,3-butadiene, formaldehyde, acetaldehyde and C2-C4 alkene emissions are described. These studies demonstrated that there is a strong relationship between gasoline composition and tail-pipe emissions. — Environ Health Perspect 102(Suppl 4):3–12 (1994).

Key words: air toxics, chemometric models, emissions speciation, fuel composition, ozone precursors, reformulated fuels, vehicle emissions

Introduction

Recent studies show that the chemical composition and magnitude of vehicle exhaust emissions can be directly related to the composition of the gasoline used. The objective of this paper is to present the findings of these recent studies, to discuss the results, and to suggest research to further the knowledge in this area.

Although emissions from gasoline-powered vehicles have been reduced significantly since the 1960s, motor vehicles remain significant contributors of pollutants in 41 U.S. cities. Vehicle emissions such as hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NOx) contribute to air quality problems in some urban areas. In addition, other nonregulated emissions such as benzene, 1,3-butadiene, and polycyclic organic material (POM) are considered toxic to humans (1).

As a result of the public’s growing concern for better air quality, legislation was enacted in 1990 by the U.S. Federal Government and California to require further reduction of vehicle exhaust emissions (2). California, being at the forefront of air quality control, has established a progressive system of exhaust emission standards (Table 1). Starting in the year 1996, this system will require a phase-in of lower emission vehicles meeting the various standards. In addition to the continuous lowering of the tail-pipe emissions standards, new evaporative emission standards and testing procedures will be required beginning in 1996.

As indicated in Table 1, the primary strategy adopted by California to improve air quality is to concentrate on the reduction of ambient hydrocarbon levels, followed by NOx and CO reductions. This strategy requires that hydrocarbon emissions from future ultra low emission vehicles (ULEVs) be reduced by a factor of more than six compared to 1993 base vehicle levels.

The California Air Resources Board (CARB) adopted regulations in which the ozone-forming potential of each exhaust HC species will be used to determine the total allowable HC mass emission levels.

| Vehicle class | Emissions, g/mile |
|---------------|------------------|
|               | NMOG | CO | NOx |
| 93 Base       | 0.250 | 3.4 | 0.4 |
| TLEV          | 0.125 | 3.4 | 0.4 |
| LEV           | 0.075 | 3.4 | 0.2 |
| ULEV          | 0.040 | 1.7 | 0.2 |
| ZEV           | 0.0   | 0.0 | 0.0 |

Abbreviations: NMOG, nonmethane organic gases (adjusted for reactivity); CO, carbon monoxide; NOx, nitrogen oxides; LEV, low emissions vehicle; ULEV, ultra low emissions vehicle; ZEV, zero-emissions vehicle; TLEV, transitional low emissions vehicle.
As a result, the CARB will measure the gas-phase HC species during vehicle emissions tests in order to link the reactivity of HCs to the allowable HC emissions levels. It has been recognized that up to 170 of these gas-phase species are abundant enough in vehicle emissions to be considered as ozone precursors. More specifically, hydrocarbons and nitrogen oxides react in the presence of UV light to form ozone, a major component of photochemical smog (3-4).

It is clear that vehicles will be required to operate at lower and lower emissions levels. As a result, vehicle manufacturers and fuel suppliers will need to be aware of the impact fuels, in combination with vehicle systems, have on lowering vehicle emissions (5). This paper addresses this issue by revealing information gained through several studies. These studies include laboratory experiments using pulse flame combustors, single-cylinder and multicylinder engines, and fleet studies conducted by U.S. automotive and petroleum companies. All of these studies focus on the reformulation of gasolines and the impact they will have on a vehicle's engine-out and tail-pipe emissions.

Methodology
Several laboratory experiments, fleet studies, analytical models, and measurement techniques were used to obtain the results provided in this paper. In order to understand some of the details of spark-ignited combustion, individual experimental studies were performed using single-cylinder engines, multicylinder engines, pulse flame combustors, combustion bombs, and flame propagation apparatus. In addition to these experiments, fleet studies were performed to gather comprehensive data from vehicles. The fuels used in these experiments were formulated and controlled.

A fundamental understanding of the relationships between fuel composition and emissions required the development of several advanced analytical techniques. Speciated HC analyses required the use of gas chromatography and high-performance liquid chromatography. Also, the real-time measurement of HC species dictated the use of several methods developed in our laboratory, such as Fourier transform infrared spectroscopy, laser diode spectroscopy, and atmospheric pressure ionization mass spectrometry.

Ultimately, all the information gathered by these studies was organized to provide meaningful results. We employed chemometric methods to organize, analyze, and eventually construct a predictive emissions model. The model was then validated by comparing the model predictions to actual vehicle fleet results.

The following discusses in greater detail the methodology and equipment used in the aforementioned studies.

Experimental Equipment
Pulse-Flame Combustor
The pulse-flame combustor (PFC) (Figure 1) offers the potential for determining the combustion products of any fuel in the absence of complicating factors encountered in a reciprocating engine. The PFC has been used extensively at Ford as a source of combustion products for catalyst studies. The PFC is constructed from a 3.0-cm outside diameter quartz tube about 1 m long into which liquid fuel and air are metered via a syringe pump and mass flow controllers. The fuel and air mixture is heated to 500°C and is swept into a combustion furnace where it is heated to 800°C. The flame front from the combusted fuel propagates back to the fuel injector tip where it is quenched. The flame pulsations repeat at natural frequencies between 0.5 to 1 Hz as sequential changes of the fuel and air mixture pass into the combustor, ignite, and flash back to the injector tip (6). The combustion products can be measured, before and after a catalyst, using the analytical techniques described in this paper.

Laboratory Engines
Well-characterized single-cylinder and multicylinder engines also are used in the laboratory to help understand the effects of fuel composition on emissions. One single-cylinder engine used was a Waukesha model CFR fuel-testing engine, which was modified by adapting a multicylinder head for single-cylinder operation. It has a 0.48-L displacement volume and a compression ratio of 9:1. The engine was controlled on a dynamometer to simulate various speed and load conditions. The compression ratio, head, and piston geometry of this engine is typical of modern multicylinder engines, and the engine studies produced comparable emission profiles to those of current (1989-1991) multicylinder production engines (7).

The baseline engine condition consisted of a fuel to air (F/A) equivalence ratio (φ) of 0.90 (fuel lean), MBT (minimum spark advance before top dead center for best torque) spark timing, 1500 rpm, 90°C coolant temperature, and a load of 3.8 bar IMEP (indicated mean effective pressure). The fuel-air equivalence ratio (φ) is defined as follows:

φ = \frac{(F/A) \text{ actual}}{(F/A) \text{ stoichiometry}}

The steady-state conditions were typical of a midspeed, midload cruise with a production engine. Gaseous fuels were mixed with the inlet air upstream of the intake manifold while liquid fuels were introduced onto a closed intake valve by a fuel injector located in the intake port. In addition to the baseline condition, experiments were carried out at either 2500 rpm, MBT-12° (i.e., spark advance, retarded timing),

![Figure 1. Pulse flame combustor for laboratory studies of combustion products from single- and multicomponent fuels (8).](image-url)
or $\phi = 1.15$, while the other conditions were kept the same as baseline.

Note that the relationships between fuel composition on evaporative and running-loss emissions are not discussed in this report. The results for exhaust hydrocarbon emissions are described for engines produced since 1983 (with and without oxidation or three-way catalysts).

**Fleet Studies**

**Air Quality Improvement Research Program**

The automotive and petroleum companies are conducting a comprehensive fleet testing program, also known as the Auto/Oil program, using in-use older and current model vehicles. Phase I of this program has been completed and results have been published in several technical bulletins (8) and Society of Automotive Engineers papers (9).

In this program, 26 reformulated and two reference gasolines were tested in 20 current (1989) and 14 older (1983-1985) vehicles in phase 1. Also, two methanol blends (M10 and M85), and one industry-average fuel were tested in 19 prototype flexible fuel or variable fueled passenger vehicles. The Auto/Oil results on the effect of reformulated gasolines on total HC, CO, NO$_x$, and toxic emissions are summarized for current model (1989) vehicles in this report. These vehicles are representative of exhaust emission control technology expected to be found on vehicles throughout the first half of the 1990s.

**Fuel Blending and Use**

Several fully formulated gasoline blends were used in the fleet and combustion studies. These gasolines were comprised of 100 to 200 different hydrocarbon species present in concentrations above 0.01 wt %. These species included C$_4$-C$_{12}$ paraffins, olefins, aromatics, and selected oxygenated hydrocarbons (e.g., methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), methanol, etc.) that were added as octave boosters or to vary the fuel-oxygen concentration.

Single component fuels were used in the pulse flame combustor, while simple fuel mixtures consisting of 1 to 5 components were run in the single-cylinder and multicylinder laboratory engines. Isooctane (2,2,4-trimethylpentane) (100 octane), isoctane/n-heptane (9:1 mix—90 octane) and two simple base fuels were used to represent the isoparaffinic, high-octane hydrocarbons. Toluene (110 octane) was used to represent aromatics.

**Measurement Techniques**

**Gas Chromatography**

The details of the methods used for specification of exhaust emissions in the Auto/Oil program and laboratory studies were described in recent publications (9,10). Gas chromatography (GC) was used to measure up to 140 C$_1$-C$_{12}$ hydrocarbons and ethers in the diluted exhaust. A second GC was used to measure methanol and ethanol. This method has a detection limit of about 0.05 ppm on a per carbon basis, or ppmC (S/N = 3/1), which is equivalent to approximately 0.6 mg/mi for the Federal Test Procedure–Urban Dynamometer Driving Schedule (UDDS) cycle.

**High-performance Liquid Chromatography**

High-performance liquid chromatography (HPLC) was used for the analysis of up to 12 aldehydes and ketones with a detection limit of 0.03 ppmC (S/N = 3/1). The computer algorithm used for identification of chemical species was found to be 98% accurate above the 0.05-ppmC emission level.

The total test system precision averaged about 24, 22, 15, and 14% at the 0.5 to 1.0, 1 to 2, 2 to 10, and 10 to 40 mg/mi HC emission levels for all vehicles tested in phase I of the Auto/Oil study (10).

**Real-time Monitoring**

The real-time monitoring of selected hydrocarbon species was used in a diagnostic mode to help understand the influence of fuel composition and engine operation and control systems hardware on emissions. Three real-time techniques have been developed at Ford to address these issues.

**Fourier Transform Infrared Spectrometer**

This system was used to measure emissions of C$_1$-C$_4$ hydrocarbons, nitric oxide (NO), nitrogen dioxide (NO$_2$), nitrous oxide (N$_2$O), sulfur dioxide (SO$_2$), and hydrogen cyanide (HCN) with a response time of 3 sec and detection limits down to 100 ppb (11,12).

**Tandem Mass Spectrometer**

This system was modified to allow the real-time measurement of individual hydrocarbon species in vehicle exhaust with a response time as fast as 20 msec with detection limits as low as 1 ppb for benzene and toluene (13).

**Laser-diode Spectrometer**

This instrument was developed for the measurement of selected gas-phase species with a response time approaching 100 msec and detection limits down to 10 ppb (14).

**Data Analysis Methods**

**Chemometric Analysis**

Chemometrics is a collection of statistical analysis procedures, including principal factor analysis (PFA), that can be used for the analysis of complex chemical data sets. These statistical methods have been used since the early 1970s to determine complex relationships between variables for large chemical data sets (15). These procedures (which utilize principal component, clustering, and multivariate data analysis) have proven to be valuable tools for determining the relationships between fuel composition and engine emissions (16). In addition, such methods can be used to assess data quality and generate models to accurately predict tail-pipe emissions from detailed fuel chemical composition data.

These chemometric methods were applied to an analysis of the emissions data generated from phase I of the Auto/Oil program (17,18). From the analysis, models were developed to predict HC, CO, NO$_x$, reactivity, and toxicity of emissions as a function of the chemical composition of the fuel compared to the Auto/Oil industry average fuel. The learning set for our predictive model included HC, CO, and NO$_x$ mass emissions data from over 2000 vehicle tests, detailed exhaust specification data (up to 151 chemical components) for about 600 tests, and detailed fuel parameter data, including fuel speciation. The exhaust hydrocarbon speciation data were used to calculate reactivity using the Carter method (19) and risk weighted toxicity using U.S. Environmental Protection Agency (U.S.EPA) factors (20).

Ein"Sight software (Infometrics, Seattle, WA) was used on an IBM AT for examination of fuel chemical composition and vehicle tail-pipe emissions. In addition to the chemometric software, Lotus 1-2-3 (Lotus Development Corp., Cambridge, MA) and Excel (Microsoft Corp., Redmond, WA) were used to manipulate the data matrix and ultimately provide an interactive worksheet environment for the model. The computations involved were centered on the following steps: a) matrix arrangement of data, b) calculation of eigenvectors, eigenvalues and scalar multiples, c) clustering analysis, d) error removal, e) model
validation, and f) interactive spreadsheet development.

The fuel chemical composition data were binned to include paraffins (C1–C4, C5–C6, C7, C8, C9, ≥C10), unsaturates (C2–C4, C5–C6, C7, C8, C9, ≥C10), aromatics (C6, C7, C8, C9, ≥C10), oxygenates (ethanol, methyl tertiary-butyl ether, ethyl tertiary-butyl ether), sum of the identified class compounds (paraffins, unsaturates, aromatics, and oxygenates) and unidentified components of the fuel as the independent variables. The dependent variables selected were nonmethane hydrocarbons, carbon monoxide, nitrogen oxides, exhaust chemical reactivity as the ozone forming potential, and potency weighted toxicity (formaldehyde, acetaldehyde, benzene, and 1,3-butadiene) of the tail-pipe emissions.

Two fuel data sets (industry average and certification fuels) were removed from the learning set for model validation. The industry average fuel was formulated from the same feedstocks as the other test fuels. The certification fuel was provided from a source independent of all other fuels.

**Exhaust Hydrocarbon Distribution**

**Hydrocarbon Species Formed during Combustion**

The C1–C4 hydrocarbon species listed in Table 2 are formed during combustion and catalytic processes.

Selected HC species in the C5–C8 range (e.g., benzene, toluene, and a variety of olefins) are formed during incomplete combustion of specific fuel components. Experiments performed using single-component fuels have demonstrated that unburned fuel, typically species C5 and above, contributes approximately 50% of the total engine-out HC emissions, depending upon the fuel type and engine operating conditions.

Studies to date show that more than 95% of a gasoline vehicle's tail-pipe HC mass can be accounted for by up to 167

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**Table 2.** C1–C4 hydrocarbon species formed from the combustion of fully blended gasoline.

| Hydrocarbon Species          | % of Total Emissions |
|------------------------------|-----------------------|
| Methane                      | 10                    |
| Formaldehyde                 | 6                     |
| Ethane                       | 3                     |
| Ethylene                     | 3                     |
| Acetaldehyde                 | 3                     |
| Acetylene                    | 3                     |
| Propadiene                   | 3                     |
| Propyne                      | 3                     |

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**Figure 2.** Distribution and abundance of A) paraffins, B) olefins, C) aromatics, and D) oxygenates in tail-pipe exhaust emissions for 20 current fleet (1989) vehicles using an industry average fuel (10).
Figure 3. Real-time Fourier transform infrared analysis for \(C_5-C_{12}/C_1-C_{12}\) hydrocarbons in tail-pipe emissions for a 1990 3.0-L Ford Taurus run under the FTP UDDS test cycle.

**Hydrocarbon Emissions**

**Fuel/Air Ratio**

Hydrocarbon emissions increase rapidly as the fuel and air mixture becomes fuel rich (21–23). For example, the hydrocarbon mass emitted under rich conditions \((\phi = 1.15)\) was twice that of lean conditions \((\phi = 0.90)\), when pure toluene was used as a fuel in the single-cylinder engine (7).

The distribution of hydrocarbon products also is affected by F/A. The relative abundance of methane and acetylene increased during fuel-rich operation. The abundance of propylene and isobutene (combustion products of isooctane) remained relatively unchanged under lean conditions compared to rich conditions (7).

The presence of excess oxygen or excess hydrocarbons during combustion has a significant effect on the relative concentration of the various oxygenated hydrocarbon species emitted. As the availability of oxygen increases, the emission of hydrocarbon partial oxidation products increase. For example, the combustion of toluene in the single-cylinder engine produced 4.9 wt % and 0.64 wt % benzaldehyde emissions under lean and rich conditions, respectively (7).

For optimum three-way catalyst (TWC) efficiency, the engine should operate near stoichiometric conditions \((\phi = 1.00)\). Deviations from stoichiometry result in lean (excess oxygen - \(\phi < 1.00)\) or rich (excess fuel - \(\phi > 1.00)\) operating conditions. Under typical engine operating conditions, \((\phi)\) undergoes rapid rich and lean excursions away from the stoichiometric condition. The magnitude and duration of these excursions is dependent upon the engine control system strategy, the response of the F/A exhaust sensor, and engine operating conditions.

**Temperature**

Fundamental kinetics studies using combustion bombs and spectroscopic measurements of excited species in flames have shown that the combustion (oxidation) rate of hydrocarbons increases rapidly with temperature (21). In general, olefins produce higher flame temperatures than aromatics, and both are higher than paraffins (22). Spark retardation leads to reduced peak temperatures but increased temperatures late in the cycle and in the exhaust. NO\(_x\) decreases because of the lower peak temperature while HC\(_x\) decrease because of the increased burn-up resulting from higher late cycle and exhaust temperatures. An increase in engine speed usually results in increased combustion chamber temperatures and increased catalyst temperatures, depending upon the thermal heat transfer properties of the particular engine and exhaust system.

**Fuel Parameters Affecting Hydrocarbon Emissions**

**Fuel Molecular Weight**

Single-cylinder engine studies (7) demonstrated that the total engine-out HC emissions increased as the average molecular weight of the fuel increased (Table 3). It is interesting to note that there is a 5-fold difference in engine-out HC emissions between the worst case (toluene) and the best case (ethane), under the same engine operating conditions.

| Fuel          | HC emissions, ppmC |
|---------------|--------------------|
| Methane       | 725                |
| Ethane        | 490                |
| Propane       | 730                |
| Butane        | 860                |
| Isopentane    | 1250               |
| Isooctane     | 1980               |
| Toluene       | 2500               |

*Operating conditions: \(\phi = 0.90\) (fuel lean), 1500 rpm steady-state operation, midload.*
The main effects of reducing $T_{90}$ from 360 to 280°F on tail-pipe emissions (current fleet [1989] vehicles, Auto/Oil program).

| Emission species | % Change in emissions |
|------------------|-----------------------|
| NMHC             | $-23 \pm 2$           |
| CO               | NS                    |
| NO$_x$           | $5 \pm 2$             |
| Benzene          | $-11 \pm 6$           |
| 1,3-Butadiene    | $-37 \pm 6$           |
| Formaldehyde     | $-26 \pm 13$          |
| Acetaldehyde     | $-24 \pm 9$           |

Abbreviations: CO, carbon monoxide; NO$_x$, nitrogen oxides; NS, no significant change.

The main effects of reducing olefins from 20 to 5% (current fleet [1989] vehicles, Auto/Oil program).

| Emission species | % Change in emissions |
|------------------|-----------------------|
| NMHC             | $7 \pm 2$             |
| CO               | NS                    |
| NO$_x$           | $-6 \pm 2$            |
| Benzene          | NS                    |
| 1,3-Butadiene    | $-32 \pm 5$           |
| Formaldehyde     | NS                    |
| Acetaldehyde     | NS                    |

Abbreviations: CO, carbon monoxide; NO$_x$, nitrogen oxides; NS, no significant change.

The main effects of reducing aromatics from 45 to 20% (current fleet [1989] vehicles, Auto/Oil program).

| Emission species | % Change in emissions |
|------------------|-----------------------|
| NMHC             | $-12 \pm 2$           |
| CO               | $-13 \pm 3$           |
| NO$_x$           | NS                    |
| Benzene          | $-42 \pm 4$           |
| 1,3-Butadiene    | $11 \pm 6$            |
| Formaldehyde     | $4 \pm 4$             |
| Acetaldehyde     | $20 \pm 11$           |

Abbreviations: CO, carbon monoxide; NO$_x$, nitrogen oxides; NS, no significant change.

conditions. Similar results also were obtained by Quader using a single-cylinder engine (22).

**Fuel Volatility**

Results from the Auto/Oil program current fleet showed a 23% reduction in tail-pipe HC emissions when the $T_{90}$ of gasoline was reduced from 360 to 280°F (Table 4). $T_{90}$ is a measure of the temperature at which 90% of the fuel volatilizes during distillation. The higher HC emissions observed using a higher $T_{90}$ fuel were probably because of the combined effects of the increased absorption of the heavier hydrocarbons in oil films, on metal surfaces, and in cylinder deposits (6,7) and because of the combined effects of the slower post-flame combustion rates for these hydrocarbons, especially the heavy aromatics.

Reduction in $T_{90}$ also resulted in the reduction of 1,3-butadiene, formaldehyde and acetaldehyde (Table 4). The lower formaldehyde and acetaldehyde emissions may be the result of the reduced concentration of the heavier isoparaffins and alkyl aromatics. Partial combustion of the isoparaffins and alkyl aromatics would result in an increased formation of methyl and ethyl radicals. These radicals can undergo further reactions (especially under lean conditions) to form formaldehyde and acetaldehyde.

Other physical properties of the fuel related to volatility, Reid vapor pressure (RVP) and $T_{50}$ also can have an affect on hydrocarbon emissions. RVP and $T_{50}$ are measures of the light-end, and low to middle molecular weight fuel composition.

**Fuel Paraffin Content**

Reformulated gasolines (i.e., those resulting in lower HC and CO emissions) may contain a higher fraction of saturated HC species than typical industry-average gasolines. Hydrogen abstraction from alkanes occurs in the combustion process to form alkyl radicals (23). These alkyl radicals undergo C—C bond scission and/or H atom loss to produce alkenes. The pulse flame combustor and single-cylinder engine studies demonstrated that combustion of multien carbon alkanes produced high yields of olefins (35–60% of total hydrocarbons [THC]) (6,7). These results are consistent with other work in which pure isoctane in a fuel-injected four-cylinder engine produced olefins that accounted for 45 to 60% of the THC (24). Thus, the replacement of fuel olefins with paraffins will not necessarily reduce olefin emissions as much as expected.

When simple paraffins are substituted for olefins in the fuel, the atmospheric reactivity of the tail-pipe emissions should decrease and the nonmethene hydrocarbons (NMHC) should increase. An active catalyst will reduce olefin emissions with a high degree of efficiency (92–99%), but the catalyst is not nearly as effective in reducing the engine-out emissions of paraffins (58–90%) (23). This trend is consistent with that of the Auto/Oil program that observed an increase in NMHC of 7%, when fuel olefins were reduced from 20 to 5% (Table 5).

Branched alkanes, such as isooctane, produce higher levels of methane compared to their straight chain analogues (23). This is because of the thermal cracking of the methyl groups to form methyl radicals which rapidly add atomic hydrogen to form methane. The production of methane decreases as the combustion mixture goes lean ($\phi < 1.00$). Under lean conditions, alkyl radicals can react with excess oxygen, resulting in an increased production of aldehydes as discussed previously. Under rich conditions, formation of methane probably has little to do with the presence of methyl groups in the fuel. For example, ethylene produces approximately half as much methane as isooctane.

**Fuel Aromatics Content**

A decrease in aromatics and olefins and replacement by paraffins will result in an increased production of molecular hydrogen during combustion, primarily through the water-gas shift equilibrium (i.e., CO + $H_2O = CO_2 + H_2$). The H/C ratios of fuel aromatics and olefins are lower than those of the normal and isoparaffins. An increased hydrogen concentration in the exhaust system can affect the response of the F/A sensor, resulting in a biased F/A control in the lean direction (25) with a concurrent reduction in hydrocarbon emissions. Thus, a decrease in aromatics and/or olefins should help reduce HC emissions, assuming all other important variables remain constant. This analysis is consistent with the observed effect of a 12% decrease in HC emissions measured in the Auto/Oil program (Table 6). However, previous studies (Table 3) (7) showed that the reduction of aromatics should reduce HC emissions, regardless of any sensor effects.

Aromatic hydrocarbons have higher combustion temperatures than alkanes. Higher operating temperatures will improve combustion efficiency but can result in increased NO$_x$ emissions. Therefore, the replacement of aromatics with paraffins should result in lower engine-out NO$_x$ emissions. Such effects were observed in the single-cylinder engine emission studies (7). However, no significant change in NO$_x$ was observed when the aromatics were reduced from 45 to 20% in the Auto/Oil program (Table 6). This could be because of the slight lean bias to the F/A control noted previously with the addition of paraffins; catalytic NO$_x$ control is extremely sensitive to slight leaning effects in the exhaust gas composition.

The data in Table 6 show that the reduction of aromatics resulted in a 12 and 13% reduction of NMHC and CO emissions, respectively. There was a large reduction in
benzene emissions as expected. However, there were increases in the other three toxics due to the increased fraction of the aliphatic hydrocarbons.

**Benzene as a Function of Aromatic Fuel Content**

Many laboratory studies have focused on the effect of fuel composition on benzene emissions. Benzene is one of the major aromatic hydrocarbon species emitted in tail-pipe emissions, and it is one of the five air toxic components of interest.

The real-time measurement of benzene tail-pipe emissions for a vehicle operating under various conditions and fuel composition has yielded insight into the factors that affect the emission of benzene (13). Figure 4 shows the concentration of benzene and toluene as a function of time during a vehicle's cold-start operation using a simplified mixture of isoctane and n-heptane in 9 to 1 (v/v) proportions. During subsequent tests, either toluene or xylene were added to make up 7% of the fuel (v/v). Several conclusions can be drawn from this study. First, small amounts of both benzene and toluene were produced during combustion, even from a fuel that contained no aromatic compounds. Second, when using fuels containing toluene, the major contributor to toluene emissions was unburned fuel that escaped the emission control system before the catalyst reached an efficient operating temperature. Third, substantially more benzene was produced when toluene or xylene was added to the fuel. Fourth, benzene formation was favored over toluene formation, even from the combustion of xylene-containing fuels (which one might suspect could produce toluene as a by-product). Finally, benzene appeared to be produced primarily by the dealkylation of toluene and xylenes during combustion. Dealkylation also may occur across the catalyst.

We also found that more than 90% of the benzene and toluene emissions occurred in the first 80 sec of the FTP cycle test. It can be concluded from these experiments that the reduction of aromatics in gasoline could have a marked impact on the emission of benzene, toluene, and other aromatic fuel components.

It should be noted that cyclohexane is the only nonaromatic fuel studied to date that produced significant levels of benzene. Combustion of pure cyclohexane in the PFC (6) and a single-cylinder engine (26) produced benzene at a level of about 10 and 5% in the THC emissions, respectively. The average concentration of cyclohexane in the Auto/Oil fuels was only 0.18%. Therefore, cyclohexane would not be a significant source of benzene emissions when using these fuels.

The single-cylinder engine studies demonstrated that the contribution of toluene and alkyl aromatics to benzene emissions can be expressed by the following relationship: Total benzene = unburned benzene + (toluene) (0.06) + (C5–C3 alkyl benzenes) (0.02).

Other studies have demonstrated that the fraction (wt %) of benzene in the total HC tail-pipe emissions was relatively constant for vehicles using fuels that contained similar concentrations of aromatics and benzene. The results of these studies are summarized in Table 7.

It can be concluded that benzene emissions represent about 5 wt % of the total hydrocarbons emitted from current model

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**Table 7.** The fraction (wt % of total hydrocarbons) of benzene in tail-pipe hydrocarbon emissions in light duty gasoline vehicles.

| Vehicles tested | Benzene fraction | Reference |
|-----------------|------------------|-----------|
| 1989, 20 vehicles | 5.35             | Auto/Oil (8.9) |
| 1990, 3 vehicles | 4.85             | Auto/Oil (9) |
| 1991, 1 vehicle | 4.85             | This study |
| 1983-1989, 10 vehicles | 4.85 | Chevron (27) |
| Average         | 4.93             |           |

*Average composition of fuel used: 32% aromatics, 1.5% benzene, and 8.7 RVP. *Average composition of fuel used: 43.6% aromatics, 2.8% benzene, and 8.5 RVP.
vehicles using industry average fuels, irrespective of the vehicle manufacturer or model. These results are consistent with a study by Sigsby et al. (28) in which very little difference in the benzene emissions fraction was observed among 46 vehicles with high- and low-hydrocarbon emissions. Another study showed no significant changes in the benzene fraction with mileage accumulation (29).

### Fuel Olefin Content

Replacement of olefins with paraffins and/or aromatics should result in an increase in total HC emissions. Olefins are combusted and oxidized over the catalyst more easily than paraffins or aromatics. This is consistent with an increase of 7% in hydrocarbon emissions when olefins were reduced from 20 to 5% (Table 5).

With respect to toxic HC emissions, Auto/Oil program results have shown that a 15% reduction of fuel olefin content resulted in a 32% reduction in 1,3-butadiene. Based upon fundamental hydrocarbon thermal degradation and free radical reaction mechanisms, it is postulated that 1-pentene, 1-hexene, and cyclohexene could be significant fuel precursors for 1,3-butadiene. Laboratory studies using the single-cylinder engines and the PFC have shown that cyclohexane is a significant precursor for 1,3-butadiene emissions as well.

### Fuel Oxygenate Content

The addition of oxygenated fuel components has the effect of leaning-out the air/fuel ratio (\( \phi < 1.00 \)) during vehicle open-loop operation, which should result in reduced HC and CO emissions. During closed-loop operation, a vehicle’s oxygen sensor compensates for the fuel-oxygen ratio. Because of the generally higher H/C ratios of oxygenated hydrocarbons, there tends to be an induced lean bias to the F/A control of the type noted previously for the paraffins. The addition of the 5 to 15 vol % oxygenated fuel components also serves to reduce the concentration of fuel species (e.g., high-molecular weight aromatics) that are more difficult to oxidize. The oxygenate also compensates for the octane content reduced by removal of aromatics.

A study was carried out by Southwest Research Institute (30) in which 16% MTBE and 19% ETBE were blended into an industry-average gasoline. Isobutylene emissions increased using the MTBE and the ETBE blends. The addition of MTBE or ETBE also resulted in an increase in formaldehyde and acetaldehyde emissions, respectively. The Auto/Oil results (Table 8) for fuel MTBE are consistent with these results.

### Sulfur-containing Hydrocarbons

The sulfur-containing compounds in fuel include thiophenes, disulfides, and thiols. These compounds form sulfur dioxide and a small quantity (1–2% of total sulfur) of sulfuric acid and ammonium sulfates during combustion and catalysis. Laboratory studies demonstrated that increasing fuel sulfur raises the light-off temperature of the catalyst. This occurs because catalytically active sites are blocked by sulfur compounds (e.g., sulfide and sulfate ions) thus inhibiting both the direct oxidation and steam reforming of hydrocarbon species (31,32).

The Auto/Oil program showed that the reduction of fuel sulfur from 450 to 50 ppm reduced emissions of HC by 17%, CO by 19%, and NO\(_x\) by 8% in the 1989 current fleet vehicles (Table 9). Emission levels before the catalyst (e.g., engine-out emissions) were not affected by sulfur, so the changes appeared to be because of an improved efficiency of the catalyst (33).

There were significant reductions in benzene (21%) and acetaldehyde (35%) at
reduced sulfur fuels; however, formaldehyde emissions increased. These results suggest that the mechanisms for formation of formaldehyde and acetaldehyde are different. The adsorption of fuel sulfur on catalyst sites may result in the surface formation of formaldehyde during the oxidation of organics. A comparison of formaldehyde emissions in engine-out and tail-pipe samples should yield further insight into these processes.

Emissions Model
A predictive emissions model was generated by applying chemometric methods to the emissions data generated from phase I of the Auto/Oil program (17, 18). This model was used to predict the emissions that would be expected from the use of ARCO's ECP fuel (an experimental blend of California Phase 2 gasoline) in current model vehicles (34). The composition of this reformulated fuel was established by lowering the aromatic and olefin content and adding MTBE. The predicted and measured results are compared in Figure 5.

The difference between the observed data and model predicted values for the industry average and certification fuel were 2 to 5% hydrocarbon, 1 to 10% carbon monoxide, 2 to 7% nitrogen oxides, 3 to 9% reactivity, and 10 to 20% for toxicity. The greatest difference between the observed and predicted values came from the certification fuel, which was formulated independently from the remaining test fuels.

The predictive ability of this model for NOx, photochemical reactivity, and the emission of toxics was excellent. The model prediction compared to ARCO's data using industry average fuel as the base value for HC and CO was good. HC and CO emissions were sensitive to nonfuel test parameters such as the vehicle test fleet mix. Overall, the model performs well and affirms the quality of the learning set.

Conclusions
Laboratory and fleet vehicle studies have demonstrated that reformulated gasoline can decrease vehicle tail-pipe mass emissions and emissions reactivity when compared to current commercial gasolines. The chemometric statistical methods have been used successfully to develop models that appear to accurately predict tail-pipe emissions from detailed fuel chemical composition data. However, even though a strong relationship between fuel composition and tail-pipe emissions exists, our understanding is still deficient concerning the chemistry of the combustion process, the effect of engine design, engine operating conditions, control system strategy, and their effects on these relationships.

Approximately half of the hydrocarbon mass emitted from current model vehicles is unburned fuel. It is possible that the formulation of a less reactive fuel could directly affect the atmospheric photochemical reactivity of exhaust emissions when the unburned fuel represents a major portion of the total hydrocarbon emissions. A substantial effort is underway in the automotive industry to modify engines and improve control systems to meet ULEV levels (below 0.040 gNMOG/mi, Table 1). The effects of these engineering changes on the composition of tail-pipe emissions are only beginning to be observed. Further studies will be needed to help understand the effect of fuel composition on emissions from these ULEV systems.

Table 10 summarizes the current knowledge on the primary fuel precursors for several emission species and the four air toxics of primary interest in vehicle emissions (benzene, 1,3-butadiene, formaldehyde, and acetaldehyde). The combustion generated C2-C4 alkenes and fuel-derived aromatics are of interest because of their high photochemical reactivity. Benzene, toluene, C2-benzenes and C3-benzenes are the major fuel precursors for benzene emissions. Recent work in our laboratory suggests that the combustion of cyclohexane, methylcyclohexane and terminal olefins leads to relatively high levels of 1,3-butadiene (26, 35). Further studies using the PFC and single-cylinder engine are needed to determine the importance of other fuel species for the formation of 1,3-butadiene.

The major fuel precursors of formaldehyde also are not understood fully. Normal and isoparaffinic hydrocarbons are a major source of the C2-C4 alkenes. Therefore, an increase in fuel aromaticity (C2-C4 alkyl benzenes) should result in a decrease in these alkenes but an increase in the emission of aromatics, also highly reactive in the atmosphere.

Future Research Studies
Further studies will be needed a) to determine the effect of reformulated fuels on tail-pipe emissions from malfunctioning, in-use vehicles; b) to develop models based on emissions data generated from various independent studies that are capable of predicting the effects of fuel changes on emissions; and c) to develop real-time or rapid-integrated analytical methods that can be used to measure selected chemical species, as necessary, to help understand the synergistic effect of the fuel, engine, and emissions control system.

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