

IMPACT OF OPERATING CONDITIONS AND FUEL COMPOSITION ON VEHICLE EMISSIONS

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INTRODUCTION

Control of exhaust hydrocarbon (HC) emissions is an important feature in the design of motor vehicles. Both the Federal Government (1990 Clean Air Act Amendments¹) and the State of California¹ instituted 25% decreases in the permitted HC emission levels in the early 1990's. The California regulations required an additional reduction in fleet-averaged, new automobile HC emissions from 0.25 gm/mile NMHC in 1993 to 0.062 gm/mile NMOG in 2003.

The Federal Clean Air Act defines specific toxic exhaust species, which may be subject to future control (e.g. benzene, butadiene, formaldehyde, acetaldehyde). California will require that the reactivity of the emissions for smog formation (the Ozone Forming Potential), rather than total HC mass, form the basis of the regulations. To meet these species-specific requirements, concentrations of individual HC species in the exhaust must be measured, and the chemistry of the emissions process must be understood better.

The bulk of the FTP (Federal Test Procedure) emissions from current vehicles occur early in either a cold start or a warm restart before the catalytic converter reaches its minimum operating temperature.² Therefore, these start-up emissions are engine-out emissions, unaffected by the catalyst. The effects of fuel composition and engine operating conditions on engine-out HC emissions (both total and individual species) are the subjects of this presentation. Initially, sources of unburned hydrocarbon emissions will be presented. The effects of fuel composition, engine operating conditions, and air/fuel mixing on these emissions will then be discussed in the context of the ability to accurately predict HC emissions from vehicles.

SOURCES OF EXHAUST HCS

Oxidation in the combustion chamber is generally an efficient process with little HC escaping combustion during fuel-lean operation. Nonetheless, unburned fuel and fuel-derived combustion products are exhausted from engines, and this section examines major sources of these emissions.^{3,4}

CREVICE VOLUMES - For all operating conditions, a principal source of HC emissions is storage of unburned fuel in crevice volumes around the piston rings (~5-7% of the intake charge). Because the entrances are narrow, the flame cannot enter these crevices, leaving the fuel in them unburned. This fuel leaves the crevices during the expansion stroke, and a large fraction of the stored HC (~50-90% depending upon operating conditions and fuel composition) is converted to CO or CO₂ in the hot burned gases within the cylinder or in the exhaust system. Thus, late cycle burn up of stored HCs affects both the total HC emissions and the concentrations of important partial combustion products such as olefins, butadiene, and benzene.

BULK GAS QUENCHING - When an engine runs fuel rich, the contributions of methane and acetylene in the exhaust rise rapidly.^{5,6} These species are present in the core gas within the cylinder after flame propagation is complete. This occurs because the low level of oxygen in the post-flame gas slows the conversion of these intermediate combustion products to CO and CO₂. Incomplete combustion during marginal operation (i.e. very fuel lean or high exhaust gas recirculation) can also increase emissions of all HC species because the flame speed is too slow to complete fuel consumption within the cylinder during the power stroke. These sources are unrelated to crevice storage but are affected by late-cycle burn-up.

WALL WETTING BY FUEL - Another important exhaust HC source arises when liquid gasoline enters the combustion chamber and strikes its walls during cold start of a port-fuel-injected (PFI) engine, producing a fuel film which does not evaporate and burn completely during flame passage.⁷ This can increase the total HC emissions early in a cold start relative to the emissions observed with prevaporized gasoline fuel, which minimizes wall wetting (see Figure 1). As the engine warms, the HC emissions from the two fueling techniques approach one another. Wall wetting increases the contribution of lower volatility species such as aromatics to the exhaust emissions. The HC emissions from this source are influenced by the design of the port, combustion chamber, and

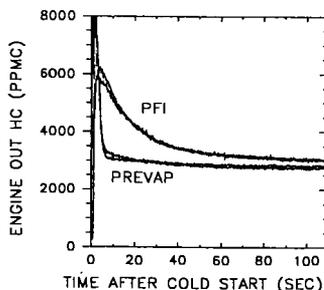


Figure 1. Total HC emissions vs time after cold start for PFI and prevaporized starts in a V8 engine.

injection system. Wall wetting does not contribute appreciably to HC emissions during warmed-up operation because fuel evaporation occurs more rapidly.

EXPERIMENT

To assess the effect of fuel composition on emissions of individual HC species, we have carried out a series of experiments in which the same single-cylinder engine was run at four operating conditions using single-component hydrocarbon fuels. The fuels tested span most classifications found in gasoline and several alternative hydrocarbon fuels: alkanes,⁸ naphthenes,⁹ olefins,¹⁰ and aromatics.^{8,9,10} Emissions from one gasoline and selected synthetic fuel mixtures were also measured^{9,10} providing information about interactions between fuel components.

A 475 cm³, port-fuel-injected, single-cylinder engine with 9:1 compression ratio was used in these experiments. The head and piston have geometries typical of modern multi-cylinder engines. The engine was run at four steady-state conditions. The baseline condition was 10% fuel-lean, 1500 rpm, mid-load, optimum spark timing, and 90°C coolant temperature. Fuel injection took place onto a closed intake valve. Additional conditions studied were: 2500 rpm; retarded spark; or 15% fuel-rich with the other parameters as defined for baseline.

Total emissions were measured by a heated, flame ionization detector (HFID) connected to the exhaust pipe by a heated sample line. Samples were also taken for gas chromatographic (GC) analysis of HCs.⁹ With the exception of benzaldehyde, MTBE, and methacrolein, oxygenated organics were not quantified. However, the measured hydrocarbon species account for approximately 90% of the organic emissions and atmospheric reactivity.

FUEL STRUCTURE EFFECTS ON TOTAL HC EMISSIONS

The total HC emissions vary with fuel structure as illustrated in Figure 2 for nine fuels even though nearly the same amount of fuel mass is stored within crevices for all fuels. The total exhaust HC emissions increase from 320 ppmC₁ [ppmC₁ = $\sum_i (\text{ppm}_i \times \text{#carbons}_i)$ for all exhaust species *i*] for ethylene fuel to ~2200 ppmC₁ for an aromatic blend (80% xylenes/ 20% ethylbenzene). Only a small portion of this increase arises because the carbon content of the inlet charge is 20% larger for the blend than for ethylene fuel as a result of the different H/C ratio. Similar trends in total HC emissions with fuel structure are observed for the other engine operating conditions.^{8,9,10} Total HC emissions from olefinic fuels are lower than those from their paraffinic analogs in all cases.¹⁰ The results in Figure 2 demonstrate that, during the exhaust stroke, burn up of fuel stored in crevices is affected by fuel structure and exerts a large influence on HC emissions.

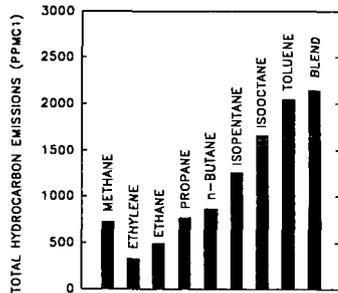


Figure 2. Effect of fuel structure on total HC emissions for nine fuels at baseline condition.

Table I. Exhaust composition as a percentage of total HC emissions for isooctane and toluene fuels.

exhaust species	ISOCTANE		TOLUENE	
	base (%)	2500 (%)	base (%)	2500 (%)
methane	1.7	4.8	0.8	1.3
ethylene	3.5	9.3	0.8	3.0
propylene	8.9	13.7		
butadiene	0.5	0.9	0.3	n.a.
isobutene	22.9	25.3		
isooctane	46.5	21.7		
benzene	0.3	0.6	5.9	11.0
benz-aldehyde			5.0	7.3
toluene			80.0	63.9
total HC (ppmC ₁)	2006	1207	2040	1320

Recent experiments¹¹ in which HC oxidation in the exhaust system was stopped by introducing a cold quench gas near the exhaust valve show that the fuel structure effect on total emissions occurs within the engine cylinder. Continuing oxidation in the exhaust system influences the individual HC species concentrations significantly and reduces the total emissions by ~40% for all fuels at baseline condition. These results illustrate the importance of burn up late in the engine cycle and in the exhaust system on HC emissions.

EXHAUST HC SPECIES

PARAFFINIC FUELS - Table I presents distributions of selected HC species (as a percentage of the total HC emissions) and the total HC emissions measured by the HFID for isooctane (2,2,4 - trimethylpentane) fuel operated at two steady-state conditions (base and 2500 rpm).⁹ Although the concentrations of specific species depend on the fuel structure,

the trends shown by isooctane fuel are typical of other straight chain and branched chain alkanes.^{8, 9, 10}

Increasing the engine speed results in a decrease in the percentage of unburned isooctane fuel (47% to 22%) in the exhaust, while the sum of the olefinic combustion products increases (43% to 56%). The total exhaust HC concentration decreases indicating an increase in burn-up of stored HCs, primarily because of higher exhaust temperatures. Similar trends with speed have been observed using a multi-cylinder engine¹² and on-road vehicles.¹³

The single cylinder engine results in Table I are similar to the species distributions obtained from two multi-cylinder engine experiments using pure isooctane fuel. In a 2.3 L 4-cylinder engine at baseline condition,⁹ the contributions of the major HC species were: methane (1.5%); ethylene (6.3%); propylene (13.5%); isobutene (28%); isooctane (48%). Shore et al¹² determined distributions from a Fiat 4-cylinder engine at 2400 rpm: methane (7%); ethylene (11.1%); propylene (12.7%); isobutene (20.5%); isooctane (23.6%). The agreement of the data in refs. 6 and 12 with the base and 2500 rpm results in Table I, respectively, is reasonably good. This indicates that HC species distributions from very different engines operated under similar conditions can resemble one another, although they are not identical.

Alkene emissions from alkane combustion can be explained qualitatively by known high temperature reactions of alkyl radicals (see ref. [10]), formed by H atom abstraction from fuel species. The primary reactions of these radicals are to break a C-C bond one removed from the free radical site (β C-C bond scission¹⁴) or a C-H bond, both forming alkenes.

AROMATIC FUELS - Table I also presents data for toluene fuel.^{8, 10} For toluene as well as for the aromatic blend,⁹ unburned fuel constitutes a much larger portion of the exhaust HC

Table II Exhaust composition as a percentage of the total HC emissions for cyclohexane and 1-hexene fuels.

exhaust species	c-HEXANE		1-HEXENE	
	base (%)	2500 (%)	base (%)	2500 (%)
methane	1.3	4.8	1.6	3.1
ethylene	23.3	31.7	24.1	37.5
propylene	5.2	6.0	11.0	12.4
butadiene	12.1	11.7	9.5	10.8
benzene	4.8	6.5	0.6	1.3
c-hexane	30.0	11.7		
c-hexene	6.2	4.0	0.5	0.5
1-hexene			36.9	12.5
total HC (ppmC ₁)	1190	575	1110	400

than for isooctane fuel and is the predominant species under all operating conditions. In addition, these experiments show that benzene, a toxic species, constitutes an appreciable fraction of the total emissions (6-11%) in contrast to isooctane fuel. This confirms that dealkylation of substituted benzenes is a significant source of benzene emission.

OLEFINIC AND CYCLIC ALKANE FUELS - Table II presents selected species measured at base condition and at 2500 RPM for 1-hexene¹⁰ and for cyclohexane⁹ fuels. These types of fuels, which have no branching groups, produce large quantities of ethylene, (which is very reactive in the atmosphere), again by β C-C bond scission reactions.^{9, 10} In addition, they emit more 1,3-butadiene than any of the other fuels tested. It is interesting to note that cyclohexane fuel produces appreciable quantities of benzene in the exhaust. The concentration of benzene is approximately one half of that emitted by

toluene fuel and 10x more than is present in the exhaust from isooctane.

ATMOSPHERIC REACTIVITY - The reactivity of individual exhaust HC species for forming photochemical smog varies widely. Olefins and highly alkylated aromatics can have reactivities 5-10 times larger than paraffinic fuels.¹⁵ As discussed above, the distribution of HC species in the exhaust changes as the fuel type and engine operating conditions change. Thus, the atmospheric reactivity of the exhaust gas, which is an important factor in the California regulations, can change significantly, and engine operating strategies different from those used in meeting total HC standards may be required. Fuel structure and operating parameter effects on reactivity are complicated as has been discussed elsewhere.¹⁶

TOXIC EMISSIONS - The brief descriptions of the species emissions for selected examples of fuel components encountered in gasoline have demonstrated that each class of fuel produces a very characteristic distribution of species in the exhaust gas. Thus, control of the emission of specific species such as the toxic compounds defined in the Clean Air Act Amendments (e. g. benzene and 1,3-butadiene) can be achieved only after identifying the likely precursors of these emissions in gasoline. Benzene is formed in substantial quantity by toluene (5% of the total emissions at baseline condition). The xylene-ethylbenzene blend produces benzene emissions at a lower level (2.5% at baseline), and also generates appreciable toluene (3.7% at baseline).⁹ Thus, these results show that reduction of benzene emissions can be achieved by reduction of aromatics in the fuel but that all alkyl-substituted benzene fuels do not produce the same amount of benzene in the exhaust.

1,3-Butadiene is a very characteristic emission from both cyclic alkane and terminal straight chain olefin fuels as shown in Table II and expanded upon in reference¹⁰ (e.g. butadiene from

1-hexene fuel is 10% of the total emissions at baseline). Little butadiene (0.7% at baseline) is formed from a branched olefin such as diisobutylene or the paraffins n-butane (0.8%) or isooctane (0.5%). Thus, these experiments have clearly identified potential sources of butadiene emission from gasoline fuel.

Table III Exhaust mole fraction (ppmC₁) of toluene for three engine operating conditions using pure toluene and a 53%/47% toluene-hexane mixture.

operating condition	toluene fuel	hexane/ toluene	predicted for mix ^a
base	1763	669	936
retarded spark	1215	408	645
fuel rich	2807	1292	1491

^a Predicted toluene mole fraction using the measured exhaust toluene for toluene fuel scaled by the known (53.1%) amount of toluene in the mix.

Table III presents the mole fraction of toluene in the exhaust for two fuels: pure toluene; and a blend of toluene with n-hexane. Based on the measured mole fraction of toluene from the pure fuel at three engine operating conditions and the known amount of toluene in the mixture, predictions of the expected exhaust toluene emission can be made. It is evident that in this case, the prediction is not as accurate. In all cases, the exhaust toluene is predicted to be substantially larger than is observed. Therefore, addition of a more volatile fuel to toluene actually reduces the emissions from the toluene in the mixture. In another experiment, a very low volatility component (1,2,4-trimethyl benzene) was added to gasoline. In this case, the emissions of all components in the gasoline, including high volatility ones (e.g. isopentane), increased relative to expectation,¹⁷ opposite to the result in Table III. Thus, it appears that if the vaporization characteristics of a fuel are changed by addition of another fuel component, the emissions may not follow a simple additivity relationship. Increasing the volatility decreases the emissions even of low volatility components. Decreasing the volatility increases the emissions even of high volatility components. In the DIB example, DIB has a volatility approximately equal to the mid-point of gasoline. Thus, the volatility of the mixture was not changed significantly from that of the base gasoline, and this may explain why additivity was observed. Similar conclusions were drawn during the AUTO/OIL Air Quality Improvement Research Program¹⁸ in which it was observed that "the presence of heavy hydrocarbons in the fuel seems to increase the mass emissions of all unreacted fuel species of a given hydrocarbon class equally, regardless of boiling point." These Auto/Oil tests were performed on a wide variety of engine designs.

SUMMARY

In this presentation, the sources of hydrocarbon emissions have been discussed, showing the importance of crevice storage, in-cylinder wall wetting by fuel, and burn-up of stored fuel late in the engine cycle in determining both total emissions and the distribution of individual species. Engine operating conditions influence exhaust HC emissions. Conditions that result in higher in-cylinder or exhaust temperatures (e.g. higher speed or retarded spark timing) result in reduced total HC emissions accompanied by an increase in the importance of partial oxidation products such as olefins. The volatility of the fuel can affect emissions of all components in a gasoline. These observations indicate that the emissions process is a complicated one that will be difficult to model with accuracy for any given vehicle. However, the experiments summarized above show that the sources of particular exhaust gas species can be evaluated effectively by pure fuel experiments. Thus, benzene is formed from substituted aromatic fuel components and from cyclic alkanes. Terminal, straight-chain olefins and cyclic alkanes form substantial amounts of butadiene. While cyclic alkanes are not normally present in large quantity in gasoline and the concentrations of olefins are being reduced, particularly in California, it is important to understand the emissions properties of all types of gasoline fuel components to avoid changing gasoline formulation in ways that will be detrimental to the environment. It is also critical to understand the effect of engine calibration (speed, spark timing, fuel/air ratio, etc) on the hydrocarbon emissions process in order to most efficiently meet government regulations, whether they are based on total HC mass or on atmospheric reactivity.

ADDITIVITY OF FUEL COMPONENTS IN A MIXTURE

- To predict HC emissions of fuel mixtures based on measured emissions from pure fuels, additivity of fuel components must be established. Ideally, if an engine is run on a 50/50 mixture of fuel components, the exhaust HC species emissions from each component would be one half of those from the pure fuel. In some cases, this is observed. As an example, when 20% diisobutylene (DIB) was added to gasoline, the emissions arising from DIB could be predicted well from the measured emissions from pure DIB and the known amount of DIB in the fuel mixture.¹⁰ However, additivity is not always observed.

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