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EFFECT OF FUEL COMPOSITION ON EXHAUST EMISSIONS FROM A SPARK-IGNITION ENGINE

UNITED STATES DEPARTMENT OF THE INTERIOR

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By R. D. Fleming

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PREFACE

The experimental work reported here was done by the author in partial fulfillment of the requirements for a doctoral degree in mechanical engineering and this report was submitted as a dissertation to Purdue University, Lafayette, Ind. The research was sponsored by the U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration and the work was performed at the Bureau of Mines, Bartlesville Petroleum Research Center, Bartlesville, Okla. This information is published as a report of investigations inasmuch as the work was done as a part of the Bureau's experimental work in fuels combustion research.

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EFFECT OF FUEL COMPOSITION ON EXHAUST EMISSIONS FROM A SPARK-IGNITION ENGINE

by

R. D. Fleming[1]

ABSTRACT

A single-cylinder research engine was operated on pure hydrocarbons and simple (two-component) mixtures of pure hydrocarbons to study the effect of fuel composition on exhaust emissions from a spark-ignition engine.

Used as fuels were three pure hydrocarbons that represented the primary hydrocarbon types present in commercial motor fuels: A paraffin (2,2,4-trimethylpentane), an olefin (2,4,4-trimethylpentene-2), and an aromatic (meta-xylene). The engine was operated at the same equivalence ratio for all of the fuels used in the experiment. Exhaust gas samples were collected and quantitatively analyzed for carbon monoxide, carbon dioxide, hydrogen, nitrogen oxides, aldehydes, and hydrocarbons. Exhaust hydrocarbons were separated and quantitatively measured with a chromatographic system employing a flame-ionization detector. Unknown hydrocarbons and oxygenated materials in the exhaust were identified with a Time-of-Flight mass spectrometer coupled to a chromatographic system.

The results of the exhaust gas analyses showed that ethylbenzene, 1-methyl-3-ethylbenzene, and 1-methyl-3-vinylbenzene were more abundant in the exhausts from either 2,2,4-trimethylpentane--m-xylene or 2,4,4-trimethylpentene-2--m-xylene fuel mixtures than in exhaust produced from m-xylene. Also, the pure 2,4,4-trimethylpentene-2 fuel produced smaller amounts of C_2 to C_7 olefins in the exhaust than that produced by the pure 2,2,4-trimethylpentane fuel. The exhaust from pure m-xylene fuel contained aromatic hydrocarbons of higher molecular weight than the parent fuel. The amount of total hydrocarbon (moles of exhaust hydrocarbon per mole of fuel used) in the exhaust from the three pure fuels decreased in the following order: 2,2,4-trimethylpentane > 2,4,4-trimethylpentene-2 > m-xylene. The hydrocarbon mole-fractions of unreacted fuel in the exhausts produced from each of the pure fuels were 0.20 for 2,2,4-trimethylpentane, 0.13 for 2,4,4-trimethylpentene-2, and 0.66 for m-xylene.

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[1] Mechanical engineer, Bartlesville Petroleum Research Center, Bureau of Mines, Bartlesville, Okla.

INTRODUCTION

The gasoline-powered automobile is a major source of air pollutants in urban areas, and during the past 15 years extensive research has been performed on air pollutants from internal combustion (IC) engines. Pollutants from this source contain both toxic compounds and organic materials that may not be objectionable, per se, but do react in the atmosphere to form photochemical smog.

Atmospheric pollutants from gasoline-powered equipment originate as:

1. Crankcase blowby: Gases and vapors that under pressure escape the combustion chamber past the engine pistons and enter the crankcase.

2. Evaporative emissions: Vapor lost directly to the atmosphere from the fuel tank, carburetor, or any other part of the fuel system.

3. Exhaust emissions: Pollutants that are present in the exhaust gas stream as it is discharged into the atmosphere.

Only the exhaust source of air pollutants in the spark-ignition engine is considered in this report.

Simple, as opposed to complex, mixtures of hydrocarbons were used as fuel in this research program so that compositional interactions could be revealed in a study of manageable proportions. Fuels were formulated to provide information on fuel factors that would be significant in any move toward manufacturing reduced olefin, increased aromatic, lead-free fuel.

Most of the experimental research in this area has been performed with engines operating on full boiling-range gasolines. Gasoline is a complex mixture of many hydrocarbons representing several types. The major components are paraffins, olefins, and aromatics.

Modern automobile engines require high-octane fuels in which a high octane rating is accomplished by the addition of lead compounds. There is some evidence to indicate that lead may become a health hazard with the increasing automobile population (9, 12, 30).[2] Also, lead in gasoline prohibits further development of emission control devices such as catalytic converters. If lead compounds were to be removed from motor fuels, octane quality would have to be met in another way. One way to obtain high-octane fuel without lead compounds is to blend in large quantities of aromatics.

This research was performed at the Bureau of Mines Bartlesville Petroleum Research Center to determine exhaust emissions from an engine operated on pure hydrocarbons as fuels. The pure hydrocarbons represented were a paraffin, an olefin, and an aromatic. The effect of mixtures of these pure fuels on the exhaust emissions was then determined, with particular emphasis on unburned

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[2] Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

hydrocarbons in the exhaust. The use of a mixture of two hydrocarbons as fuel allows the identification of those combustion products, which are the result of interaction effects. Interaction products are defined as follows:

1. Those exhaust products whose quantities are either enhanced or suppressed when a second fuel component is added.

2. Any new product resulting from the fuel mixture which is not produced in the exhaust from either fuel component.

The text of this report is divided into three main parts. First, a description of the method of investigation is given; second, the experimental results are presented and discussed; and finally, the conclusions are given.

ACKNOWLEDGMENTS

The author is grateful to Professor J. R. Osborn, School of Mechanical Engineering, Purdue University, for his suggestions, recommendations, and counsel during the course of the research program. Special thanks are expressed to the members of the Fuels Combustion Research Group, Bartlesville Petroleum Research Center, for their assistance and suggestions during the execution of the experimental work.

METHOD OF INVESTIGATION

The composition of exhaust gases from a single-cylinder engine was determined experimentally with particular emphasis on exhaust hydrocarbons. The fuels used in this experiment involved three hydrocarbons--paraffin, olefin, and aromatic types. First, the engine was run with each fuel, and combustion-product composition and yield were determined. Then, 50/50 mixtures (by weight) of paraffin and olefin, paraffin and aromatic, and olefin and aromatic were used as fuels, and again combustion-product composition and yield were determined. Finally, the effect of each fuel mixture on the exhaust emission was determined from resulting data.

The engine and associated system used to produce the exhaust are described. Also described are the exhaust sampling method, the method of combustion-product identification, and the specific experiments.

The Engine System

The engine system includes (1) a standard Cooperative Fuel Research (CFR) single-cylinder, knock-testing engine with variable compression ratio cylinder, (2) a modified air-fuel induction system, and (3) a modified exhaust system.

Cooperative Fuel Research Engine

The engine used in the experiment was a single-cylinder CFR research engine with a variable compression ratio cylinder. The engine specifications for this experiment are given in table 1. The engine is coupled to a direct current dynamometer. Engine speed is controlled by adjustment of dynamometer field current in combination with a throttle valve setting that corresponds to predetermined air and fuel flow rates.

TABLE 1. - Engine specifications

Bore	inches	3.25
Stroke	do	4.50
Displacement	cubic inches	37.33
Compression ratio		8.00 to 1
Fuel system		Continuous manifold injection
Valve timing, crank angle degrees:		
Intake opens, ATC		10
Intake closes, BTC		146
Exhaust opens, ATC		140
Exhaust closes, ATC		15

Air-Fuel Induction System

Air-Intake System

Figure 1 is a schematic of the engine with associated air-inlet and exhaust systems. Inlet-air to the engine passes through a particulate filter and a temperature-controlled cooling coil, which is maintained at approximately 40° F. This provides the engine with air of constant humidity.

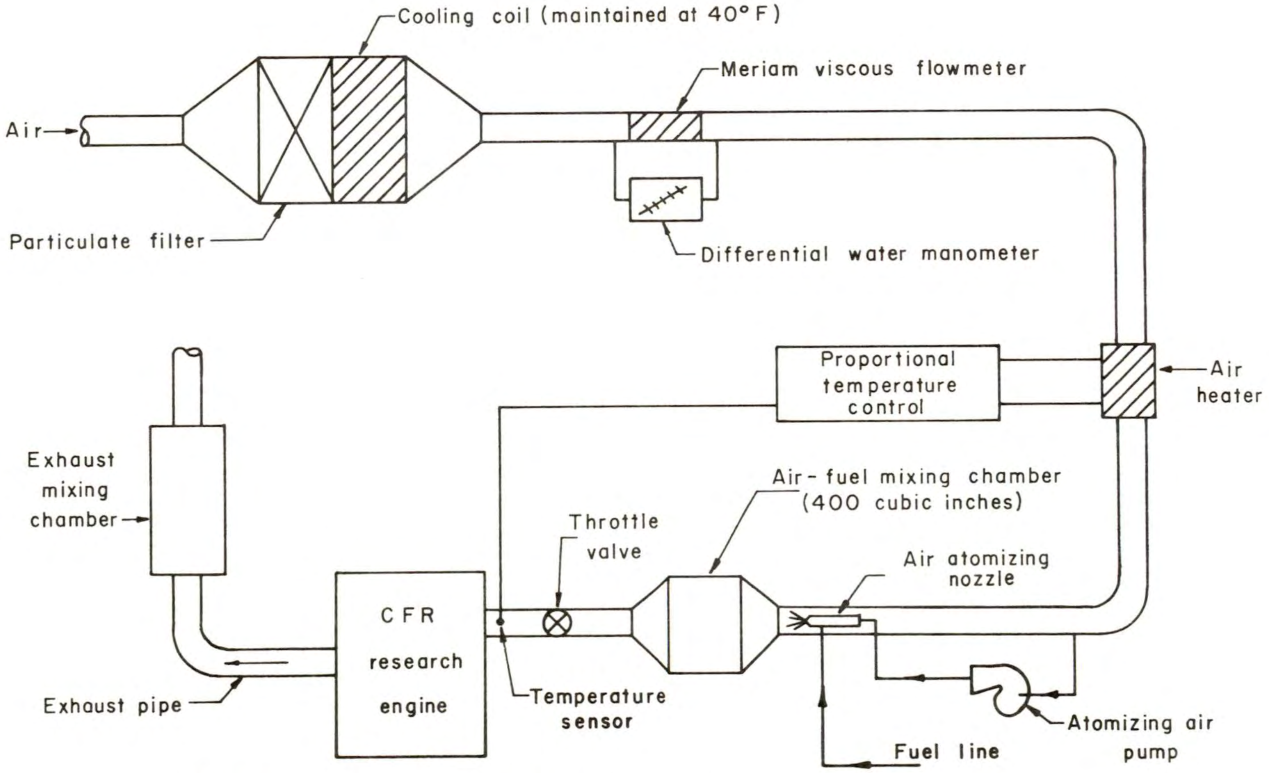

FIGURE 1. - Engine, Air-Fuel Induction System, and Exhaust System.

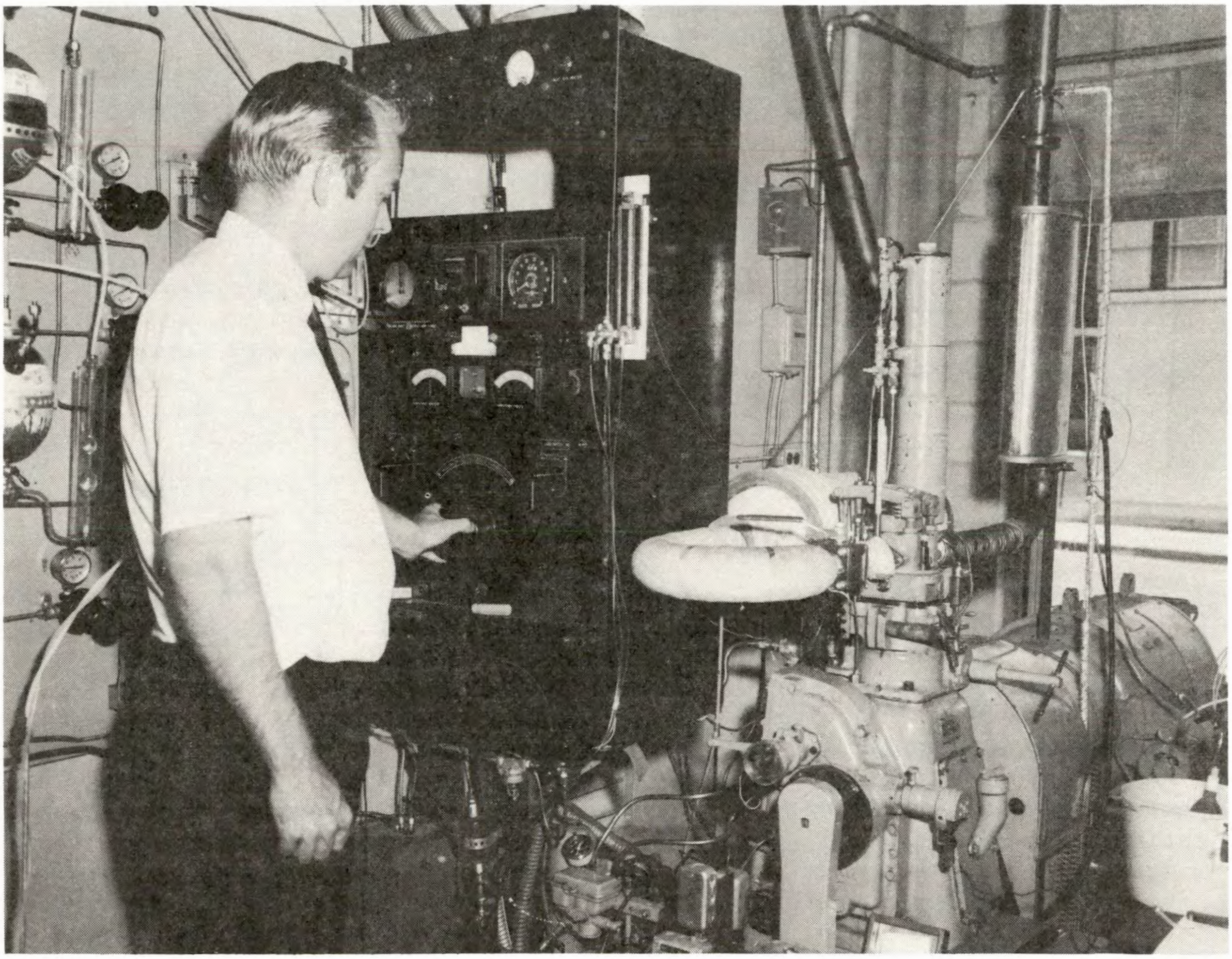

FIGURE 2. - CFR Engine Used for Exhaust Gas Study.

Airflow is measured with a Meriam[3] viscous flowmeter and controlled with a 1-1/2-in. ball valve as a throttle. The air is reheated by means of finned heating elements installed in the inlet-air duct. The heater elements are connected to a proportional temperature controller equipped with a thermistor as a temperature sensor. The sensor is installed in the intake system 2 in. from the engine intake valve. The temperature controller (fig. 1) maintains the intake air-fuel mixture at a constant predetermined temperature. A photograph of the engine is shown in figure 2.

Fuel-Metering System

Liquid fuel flow was measured volumetrically from a nitrogen-pressurized fuel-feed system (fig. 3). Fuel was introduced into the engine intake system just ahead of a 400-cu. in. mixing chamber. The mixing chamber provided a

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[3] Reference to trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

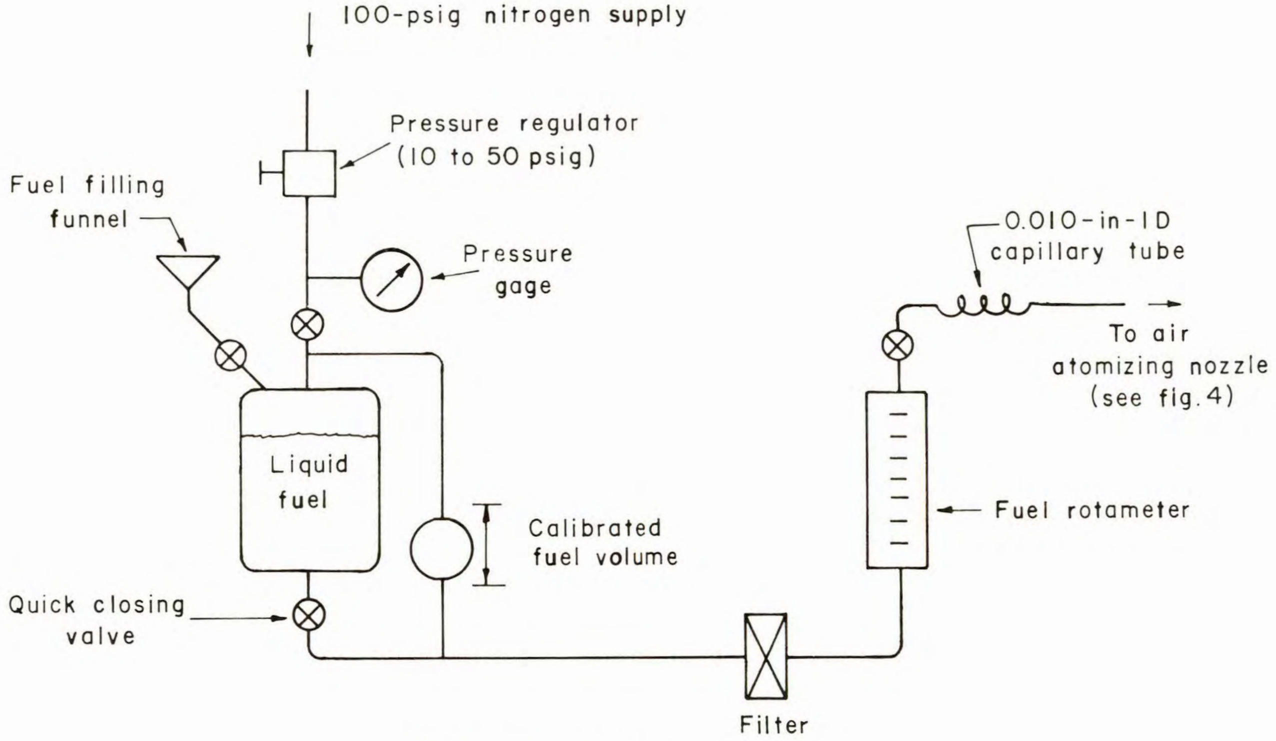

FIGURE 3. - Fuel Metering System.

residence volume to allow time for air and fuel mixing and for complete vaporization of the liquid fuel. Although a single-cylinder engine takes air-fuel mixture at an unsteady flow rate, fuel was injected into the unsteady air stream at a continuous, steady flow rate. The residence volume tended to level the effect of variation in air-fuel ratio and provided a homogeneous air-fuel mixture at the intake valve. The liquid fuel was introduced into the heated air stream by means of an air-atomizing nozzle, which produced a highly atomized fuel spray. Heated air from the intake air stream was pumped under 15 psi pressure to the atomizing nozzle; therefore, no secondary flowmeter was needed to measure airflow rate to the nozzle.

Liquid fuel rate to the nozzle was controlled by variation in nitrogen pressure above the fuel in the fuel tank (fig. 3). A short piece of 0.010-in.-ID capillary tubing in the supply line restricted the flow. About 40 psi nitrogen pressure was required to maintain the appropriate fuel-flow rate for this experiment. The approximate flow rate could be set by means of a rotameter installed in the fuel supply line. The actual flow was measured by observing the time interval required to use 10 ml of fuel from a calibrated buret. Thus, by knowing the fuel temperature, the fuel density as a function of temperature, and the volumetric flow rate, the mass flow rate could be calculated.

The Exhaust System

The engine exhaust system (fig. 1) consisted of about 4 ft of 1-1/4-in. pipe leading to a standard automotive exhaust muffler and about 10 ft of 1-1/2-in. tailpipe, which exhausted to the atmosphere.

A single-cylinder engine produces a pulsating (unsteady) flow of exhaust gas. Radial as well as longitude concentration gradients exist within the exhaust pipe (11, 20). The muffler in the exhaust system acted as a mixing chamber to give an average exhaust sample at the muffler outlet. Exhaust samples for the purpose of analysis were taken from the tailpipe 2 in. downstream of the muffler outlet.

Exhaust Sampling System

The exhaust gas sampling system is illustrated in figure 4. Exhaust samples were withdrawn from the engine exhaust system 2 in. downstream of an exhaust mixing chamber. The samples were taken from the center of the tailpipe through a 1/4-in.-OD stainless steel tube, which was heated to prevent water condensation. The exhaust subsequently passed through a pump, a viscous flowmeter, and into a sample bag (made of polyvinyl fluoride film). The entire sampling system was heated above the dew point of the exhaust gas to prevent water condensation. To dilute the exhaust, the sample bags had been filled with dry nitrogen to keep water in the vapor state, and inhibit further chemical reactions. The sample bags were covered with opaque material to minimize photosensitive reactions among the exhaust products. Nitrogen and exhaust volumes were adjusted so that the bags contained about 6 parts of nitrogen to 1 part of exhaust. The approximate volume of each bag was 50

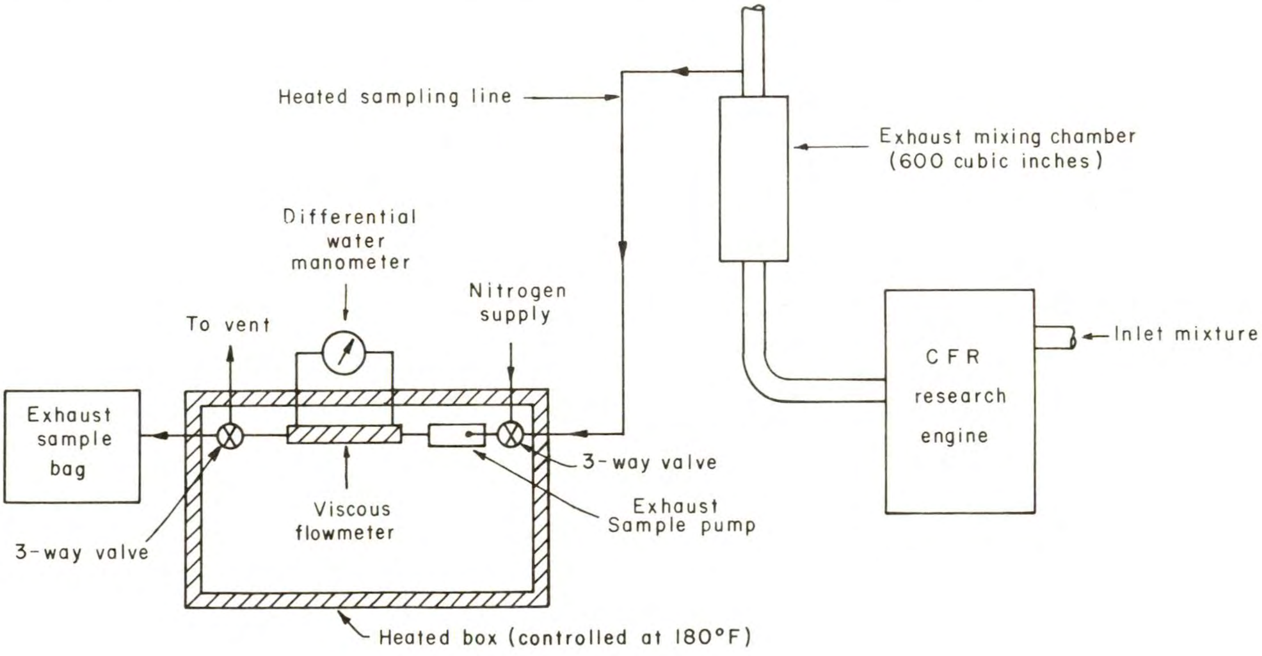

FIGURE 4. - Exhaust Gas Sampling System.

liters. During sampling, each bag was filled to about 40 liters to maximize volume-to-surface ratio and minimize surface effects; that is, the loss of combustion products to the bag surface.

Retention of water (gaseous phase) in the exhaust sample is necessary to keep oxygenated products and heavier hydrocarbons in the sample. If water condensers were placed in the sampling line, significant quantities of oxygenates and C_8 and heavier hydrocarbons would be lost along with the condensed water.

Exhaust Analysis

The combustion products measured and the type of instrument used for each measurement were as follows:

1. Carbon monoxide (CO) by nondispersive infrared (NDIR).

2. Carbon dioxide (CO_2) by NDIR.

3. Hydrogen (H_2) by gas chromatography.

4. Total hydrocarbon $[HC]_t$ by flame ionization detection.

5. Nitric oxide (NO) by NDIR.

6. Nitrogen dioxide (NO_2) by nondispersive ultraviolet (NDUV).

7. Total aldehydes (RCHO) by the 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH) method.

8. Formaldehyde (HCHO) by the chromotropic acid method.

9. Hydrocarbon components by gas chromatography.

These methods including calibration procedures and instrument theory are described in appendixes C-H.

Oxygen measurements were omitted because of the method of sampling. For the engine condition used, the oxygen concentration was about 0.8 to 1.0 percent in the undiluted exhaust gas. Since the samples were diluted by a factor of 7, the concentration of oxygen would be on the order of 0.1 percent. The oxygen instruments available were not reliable in this concentration range.

Combustion Product Identification[4]

The normal procedure for identifying unknowns in an exhaust sample analyzed with a chromatographic system is to observe the length of time each component is retained in the chromatographic column and to compare these

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[4] The method of combustion product identification was developed at the Bureau of Mines Bartlesville Petroleum Research Center by D. E. Seizinger.

retention times with that of known compounds. Some uncertainty in the identifications can result from this method, because the column may perform differently with a single component than it would if the same compound were present in a complex mixture, such as exhaust gas. Also, many compounds can elute from a chromatographic column at the same time; therefore, in this research program some additional information was obtained for more positive identification of exhaust gas components.

The components were identified with a chromatographic-system/mass-spectrometer couple. The exhaust gas components were separated with a chromatographic system, and a portion of the column effluent was fed into the mass spectrometer. Since some of the exhaust components of interest were at very low concentration in the sample, it become necessary to concentrate these components. Because the parent fuel peak in the exhaust sample represented the major component, the chromatographic column would be overloaded and poor separation would result. Thus it was necessary to fractionate the exhaust sample before it could be used in the chromatographic-system/mass-spectrometer couple.

Sample Fractionation System

The system used to fractionate the sample is shown in figure 5. The system includes the following: (1) A Biotron sampling valve equipped with a sample loop (8 in. long by 0.125-in. OD by 0.09-in. ID) packed with glass wool; (2) a Perkin-Elmer model 900 gas chromatograph equipped with flame ionization detector; (3) subambient temperature accessories, and sample effluent stream splitter (column is 2 ft long by 0.25-in. OD by 0.1875-in. ID packed with 100-120 mesh, acid-washed Chromosorb W coated with 10 percent OV 101); and a Carle model 2025 fractionation valve equipped with a sample loop 8 in. long by 0.125-in. OD by 0.093-in. ID packed with glass wool.

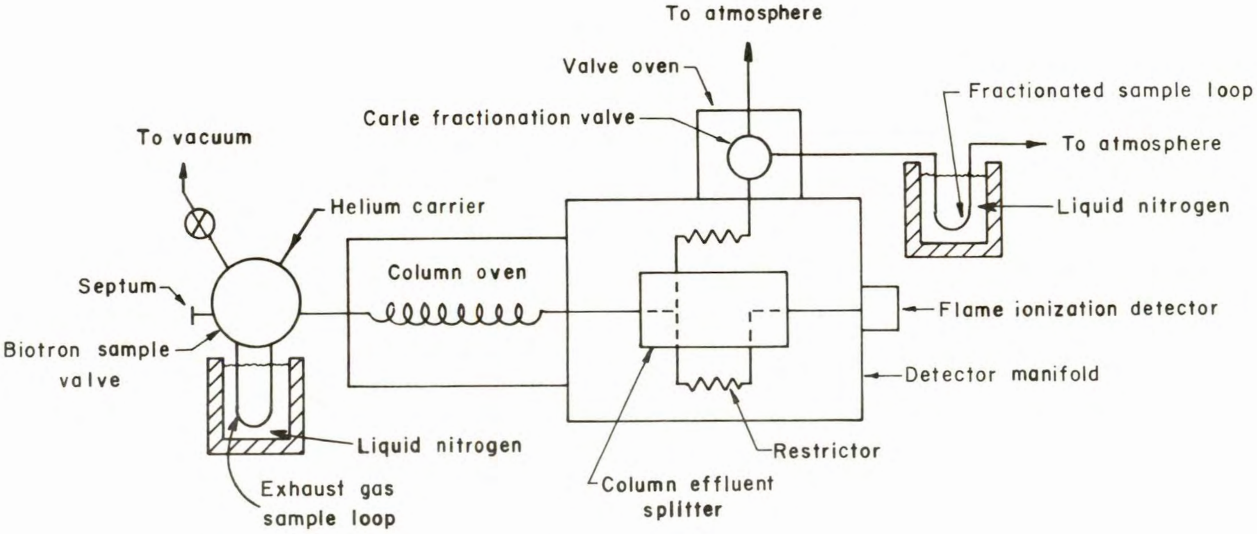

FIGURE 5. - Chromatographic System for Sample Fractionation.

Fractionation Procedure

Approximately 1 liter of nitrogen-diluted exhaust is condensed in the packed exhaust sample loop (see fig. 5) immersed in liquid nitrogen. As the sample is condensed, the noncondensable components are removed by vacuum. Following the sample concentration step, the loop is heated with hot water and the loop content is transferred to the chromatographic column. The column is linearly programed from -65° to 170° C at a rate of 8° C/min. The column effluent is split into two portions: One portion is directed to a flame ionization detector while the remaining portion is directed to the fractionation valves.

When the exhaust-gas fuel component elutes from the column, the fractionation valve is actuated to bypass the liquid-nitrogen-cooled fractionated sample loop. Thus, the exhaust-gas fuel component is removed from the sample. This circumvents future problems associated with overloading the open tubular column in the chromatographic system coupled to the mass spectrometer.

Chromatographic-System/Mass-Spectrometer Couple

The chromatographic system coupled to the mass spectrometer for peak identification is shown schematically in figure 6. The complete system includes a Biotron sampling valve, a Beckman model GC-5 gas chromatograph (equipped with flame ionization detector, temperature programer, and low-temperature accessory), and a Bendix model 12-101 Time-of-Flight mass spectrometer. The chromatographic column used was 0.01-in. ID by 0.02-in. OD by 150 ft long coated with Versilube F-50 (purchased from Perkin-Elmer Corp.).

Identification Procedure

Following the collection of the fractionated sample, as previously described, the liquid-nitrogen-cooled sample loop is transferred to the sampling valve mounted on the chromatographic system coupled to the mass

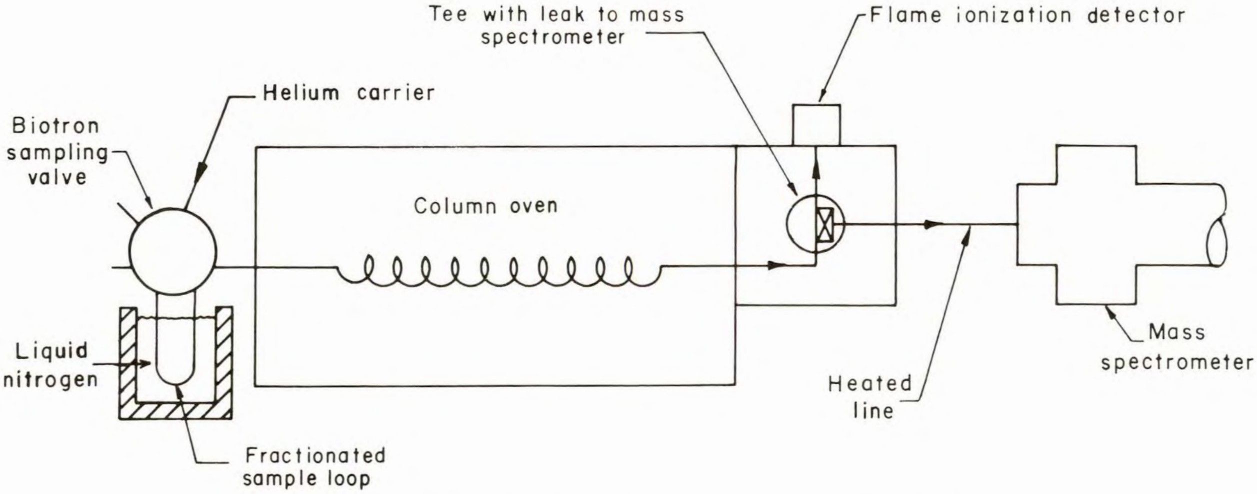

FIGURE 6. - Chromatographic-System/Mass-Sprectrometer Couple.

spectrometer. With the column oven at -60° C, the sample loop is heated with hot water and the loop content transferred to the capillary column. The open tubular column is programed from -60° to +135° C. A portion of the column effluent is directed to a flame ionization detector; the remaining portion of the stream is expanded through an orifice into a heated line leading to the mass spectrometer source. The mass spectrometer is used as a chromatographic detector using one of the four available output signals. As an exhaust component emerges, two channels are used to scan simultaneously two different mass ranges. The spectra, which are recorded with a Honeywell Viscorder, are used to identify the unknown exhaust gas components.

Fuels Used in the Experiments

The fuels used in the experimental program represent paraffin, olefin, and aromatic types. The hydrocarbons were selected to meet the following specifications:

1. All hydrocarbon components have the same number of carbon atoms per molecule.

2. Molecular weight is representative of some gasoline components.

3. The octane number is such that no antiknock fuel additive is needed to operate the engine at 8 to 1 compression ratio.

The fuels selected were 2,2,4-trimethylpentane (isooctane); 2,4,4-trimethylpentene-2; and meta-xylene. The octane numbers by research method for these pure hydrocarbons are 100, +0.3,[5] and +4.0, respectively (3). Note also that the paraffin and olefin have the same branched-chain structure. Compositional data for the hydrocarbons and the fuel mixtures are listed in table 2. The fuel AB was obtained by mixing equal weights of fuel A and fuel B. Similarly, fuels AC and BC were obtained by mixing equal weights of fuel A and fuel C, and fuel B and fuel C, respectively.

Engine Operating Conditions

The engine was operated under the conditions given in table 3 for all experiments.

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[5] This fuel has the same knocking characteristic as isooctane with 0.3 ml of tetraethyllead added. In other words, the olefin and aromatic fuels have research octane numbers greater than 100.

TABLE 2. - Fuel composition data

Fuel designation	Fuel component	Composition, mole-percent
A	2,2,4-Trimethylpentane	99.7
	2,2-Dimethylhexane[1]	.3
	2,3-Dimethylhexane[1]	Trace
	3-Methylhexane[1]	Do.
B	2,4,4-Trimethylpentene-2	96.0
	2,4,4-Trimethylpentene-1[1]	3.8
	Isooctenes[1]	.2
C	meta-Xylene	99.3
	para-Xylene[1]	.7
AB	Fuel A	49.6
	Fuel B	50.4
AC	Fuel A	48.2
	Fuel C	51.8
BC	Fuel B	48.6
	Fuel C	51.4

[1] The information on known impurities was furnished by Phillips Petroleum Co., the manufacturer.

TABLE 3. - Engine operating conditions

Speed	rpm	1,000
Airflow rate	lb/min	0.45
Equivalence ratio		1.03
Spark timing, BTC		15°
Throttle position[1]	percent	67
Intake mixture, temperature	° F	165±4
Coolant temperature	° F	211±1
Oil sump temperature	° F	140±10

[1] Engine throttle position is defined as the ratio of the actual engine air consumption (mass flow rate) to the maximum theoretical flow rate; where the theoretical flow rate is a function of atmospheric pressure, engine displacement, molecular weight of the inlet mixture, and inlet mixture temperature. The derivation of the equation to calculate throttle position is given in appendix I.

EXPERIMENTAL RESULTS AND DISCUSSION

The experiments performed in this research can be separated into two phases. First, the combustion-product composition and yield from the engine were determined for three separate pure hydrocarbon fuels. Second, the procedure was repeated with two-component fuel mixtures which were obtained by mixing the three hydrocarbons (50/50 by weight) in every possible two-way combination.

In this section the qualitative and quantitative results are given, and finally all experimental results are summarized.

Qualitative Results

Qualitative results of exhaust hydrocarbon emissions from the engine for 2,2,4-trimethylpentane (isooctane), 2,4,4-trimethylpentene-2 (DIB-2), and an isooctane and DIB-2 mixture are shown in figure 7.

The chromatographic peak areas are proportional to the concentration of hydrocarbon in terms of parts per million carbon atom (ppmC). The peak areas for C_1 and C_2 hydrocarbons cannot be compared with those of C_3 and higher hydrocarbons because a different sample size was associated with the two methods of separation. (See appendix F.)

Surprisingly, benzene and toluene appear as exhaust products from nonaromatic fuels. These materials were identified with a mass spectrometer and were observed in every exhaust sample. Therefore, there is no doubt that these products were real and did exist in the exhaust samples. The chromatographic column failed to separate benzene, 4,4-dimethyl-cis-pentene-2, and 2,4-dimethylpentane; however, mass spectra data indicated that benzene was the most prominent hydrocarbon in the three-component mixture.

The source of the benzene and toluene in the exhaust could be questioned, but the two possible sources of these aromatics are as follows:

1. Products of pyrolysis of small amounts of lubricating oil from the engine cylinder walls (because lubricating oils probably do contain compounds with aromatic rings); or

2. The aromatics could be synthesized from the paraffin or olefin or both fuels under the conditions in the combustion chamber.

The second source seems more likely for two reasons: First, the presence of significant quantities of other heavy hydrocarbons, which might come from lubricating oil, was not observed. Second, there was about 3 times more toluene in the exhaust from the olefin fuel than from the paraffin fuel. The higher level of aromatics coming from the fuel, which contains the double bond, suggests that these products are probably synthesized in the combustion chamber.

Isooctane

The major hydrocarbon products observed (fig. 7) from isooctane are methane, ethylene, ethane, acetylene, propylene, methylacetylene, isobutane, isobutylene, and unreacted fuel (isooctane).

The probable elementary reactions which account for the products are discussed. Initiation is probably by hydrogen abstraction which is thermochemically plausible. The abstraction of a hydrogen atom can yield one of the four radicals.

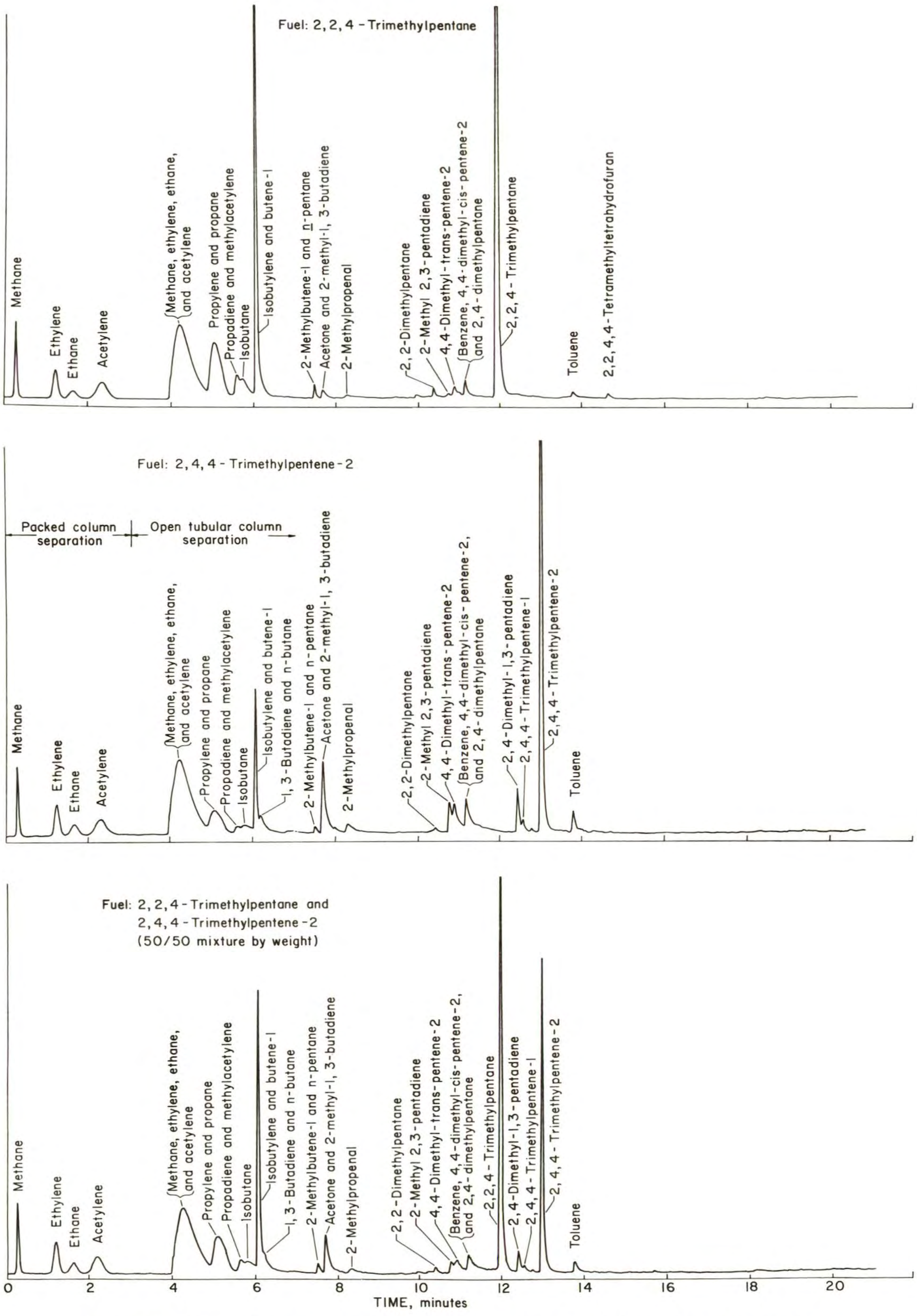
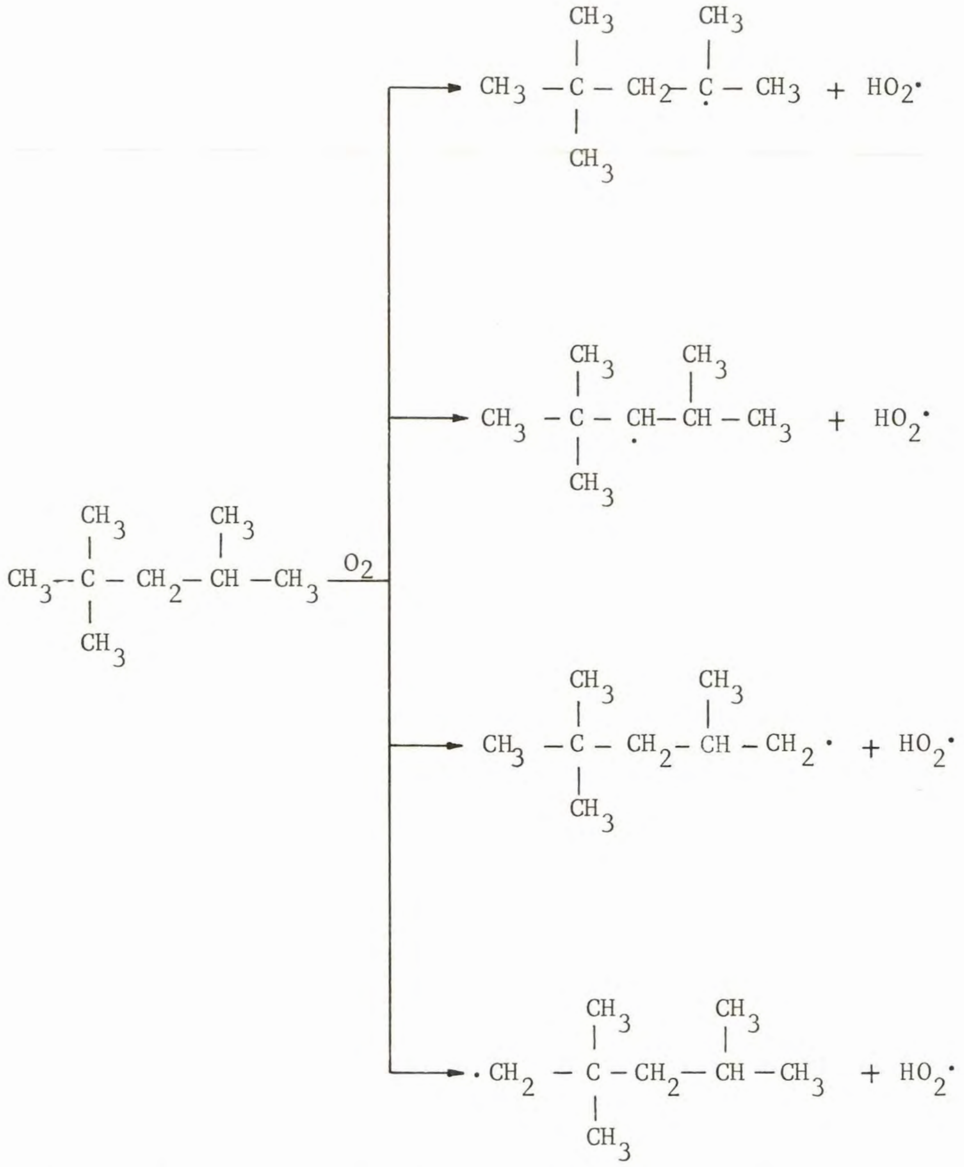


FIGURE 7. - Chromatograms Showing Exhaust Hydrocarbon Separation for Paraffin and Olefin Fuels.



$$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3 \xrightarrow{O_2} CH_3-C(CH_3)_2-CH_2-\dot{C}(CH_3)-CH_3 + HO_2\cdot \qquad (1a)$$

$$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3 \xrightarrow{O_2} CH_3-C(CH_3)_2-\dot{C}H-CH(CH_3)-CH_3 + HO_2\cdot \qquad (1b)$$

$$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3 \xrightarrow{O_2} CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_2\cdot + HO_2\cdot \qquad (1c)$$

$$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3 \xrightarrow{O_2} \cdot CH_2-C(CH_3)_2-CH_2-CH(CH_3)-CH_3 + HO_2\cdot \qquad (1d)$$

The primary fate of the isooctyl radicals must be as follows:

$$i\text{-}C_8H_{17}\cdot \longrightarrow \text{olefin + small alkyl radical} \qquad (2)$$

$$i\text{-}C_8H_{17}\cdot + O_2 \longrightarrow \text{DIB}^{6} + HO_2\cdot \qquad (3)$$

Reactions 2, 3, and 4 were proposed by Bradow and Alperstein (8).

$$i\text{-}C_8H_{17}\cdot + O_2 \longrightarrow i\text{-}C_8H_{17}\text{-}O_2\cdot \qquad (4)$$

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[6] DIB refers to diisobutylene, the mixture of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2.

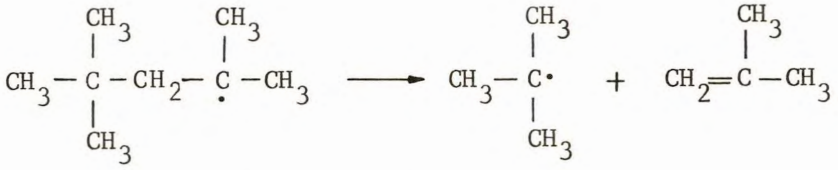
Reaction 3 is probably unimportant because DIB was not observed in the exhaust from isooctane. Reactions 2 and 4 may both be important under the conditions in the combustion chamber. Isooctyl radicals will also be formed by

$$i\text{-}C_8H_{18} + R \longrightarrow i\text{-}C_8H_{17}\cdot + RH \qquad (5)$$

where R represents $H\cdot$, $CH_3\cdot$, $HO_2\cdot$, or $OH\cdot$

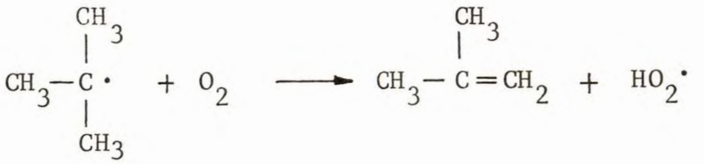
This reaction may account for some of the hydrogen and methane formed and may be the main reaction that produces water.

Isobutylene is the most abundant olefin in the exhaust from isooctane. The tertiary isooctyl radical formed in reaction 1a can decompose to form isobutylene, reaction 2:



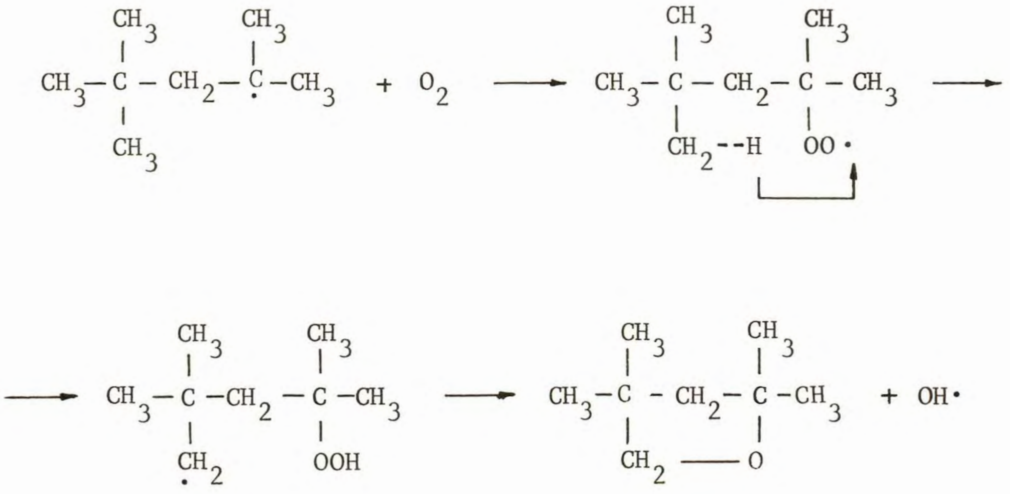
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{\cdot}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}\cdot + CH_2=\overset{CH_3}{C}-CH_3 \qquad (6)$$

The isobutyl radical may then react with O_2 to yield a second isobutylene molecule:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}\cdot + O_2 \longrightarrow CH_3-\overset{CH_3}{C}=CH_2 + HO_2\cdot \qquad (7)$$

Or the radical may abstract a hydrogen atom from another fuel molecule and form isobutane, which is observed in the exhaust. The tertiary isooctyl radical may combine with oxygen by reaction 4 and form 2,2,4,4-tetramethyltetrahydrofuran (<u>34</u>) as follows:

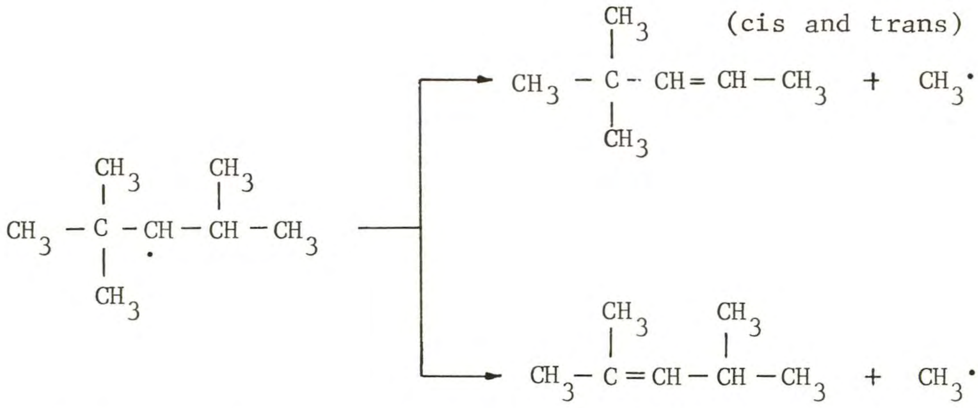


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{\cdot}{\overset{CH_3}{C}}-CH_3 + O_2 \longrightarrow CH_3-\underset{CH_2\text{--}H}{\overset{CH_3}{C}}-CH_2-\underset{OO\cdot}{\overset{CH_3}{C}}-CH_3 \longrightarrow$$

$$\longrightarrow CH_3-\underset{\cdot CH_2}{\overset{CH_3}{C}}-CH_2-\underset{OOH}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{CH_2\,-\!-}{\overset{CH_3}{C}}-CH_2-\underset{O}{\overset{CH_3}{C}}-CH_3 + OH\cdot \qquad (8)$$

A small amount of this material is observed in the exhaust from isooctane. 2,2,4,4-Tetramethyltetrahydrofuran is an intermediate product and occurs in large quantities earlier in the combustion cycle (<u>24</u>, <u>34</u>).

The secondary isooctyl radical 1b can decompose by reaction 2 to form cis and trans isomers of 4,4-dimethylpentene-2, or 2,4-dimethylpentene-2.

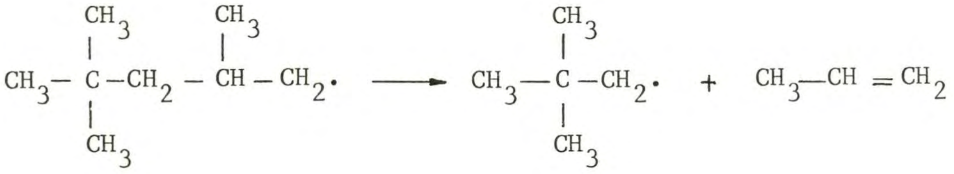


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{\cdot}{CH}-\overset{CH_3}{CH}-CH_3 \rightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH-CH_3 + CH_3\cdot \quad \text{(cis and trans)} \qquad (9a)$$

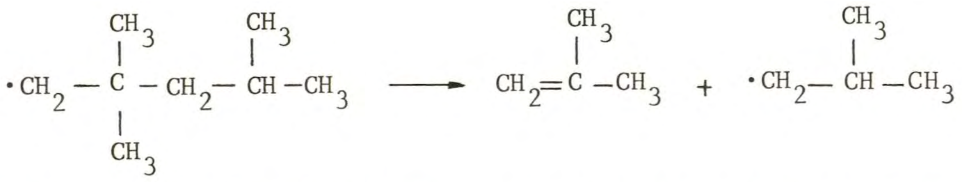
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{\cdot}{CH}-\overset{CH_3}{CH}-CH_3 \rightarrow CH_3-\overset{CH_3}{C}=CH-\overset{CH_3}{CH}-CH_3 + CH_3\cdot \qquad (9b)$$

All three of these products were observed at low concentrations in the exhaust.

Propylene and isobutylene could come from the primary isooctyl radicals 1c and 1d. By reaction 2,



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_2\cdot \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2\cdot + CH_3-CH=CH_2 \qquad (10)$$



$$\cdot CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_3 \longrightarrow CH_2=\overset{CH_3}{C}-CH_3 + \cdot CH_2-\overset{CH_3}{CH}-CH_3 \qquad (11)$$

The neopentyl radical from reaction 10 can lose methyl to yield further amounts of isobutylene. The isobutyl radical from reaction 11 can lose methyl to yield more propylene.

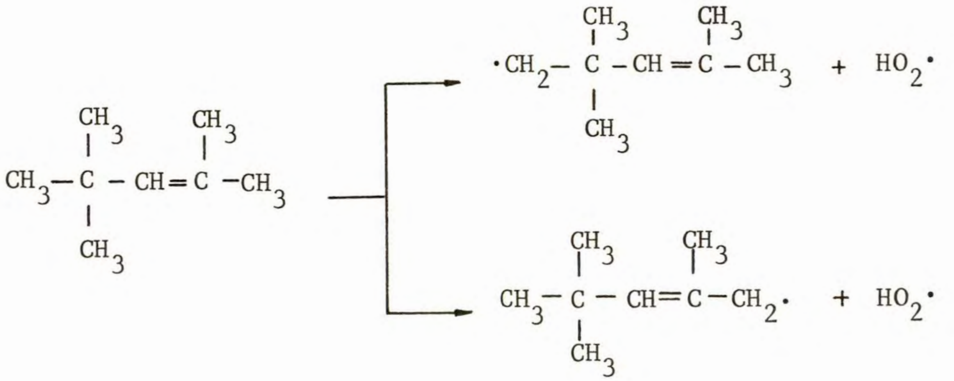
The chief source of ethylene, acetylene, propylene, and methylacetylene is probably pyrolysis reaction of fuel fragments.

2,4,4-Trimethylpentene-2

The exhaust products from 2,4,4-trimethylpentene-2 (DIB-2) (see middle part of fig. 7) are similar to those produced from isooctane with a few exceptions. DIB-2 fuel produces much less propylene, propadiene and/or methylacetylene, isobutane, and isobutylene. On the other hand much larger quantities of acetone and 2-methyl-1,3-butadiene, 2-methylpropenal, 2-methyl-2,3-pentadiene, 4,4-dimethyl-trans-pentene-2, 4,4-dimethyl-cis-pentene-2, and 2,4-dimethyl-1,3-pentadiene were observed in the exhaust from DIB-2.

Note that the 2,4,4-trimethylpentene-1 (DIB-1) shown as an exhaust product from DIB-2 fuel in figure 7 is primarily a fuel contaminate and not a product of reaction. (See table 2.)

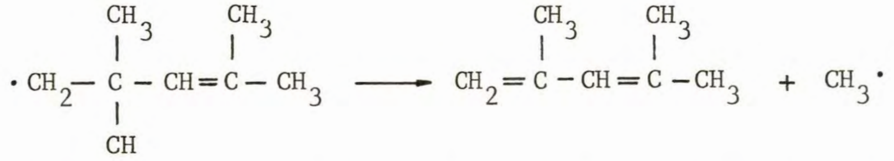
The following reactions are proposed to explain the experimental results. If the initial reaction step for the olefin fuel was assumed to be loss of a hydrogen atom, one of the two following radicals would be formed:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 \longrightarrow \cdot CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 + HO_2\cdot \tag{12a}$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_2\cdot + HO_2\cdot \tag{12b}$$

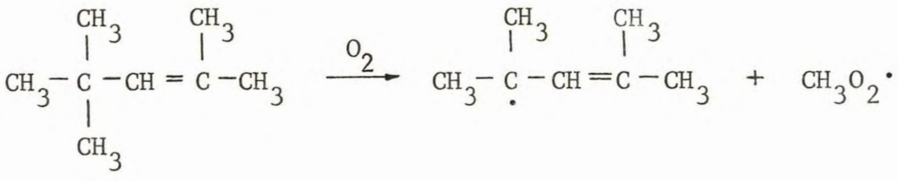
Further loss of methyl from radical 12a would yield 2,4-dimethyl-1,3-pentadiene which is observed to be present in the exhaust:



$$\cdot CH_2-\underset{CH}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 \longrightarrow CH_2=\overset{CH_3}{C}-CH=\overset{CH_3}{C}-CH_3 + CH_3\cdot \tag{13}$$

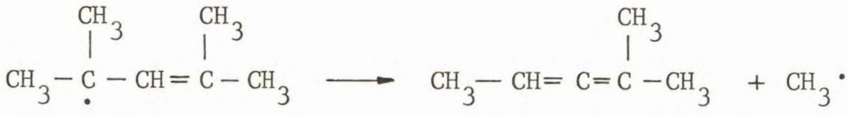
The loss of methyl from radical 12b to form 4,4-dimethyl-1,2-pentadiene would be much more difficult because of the higher bond dissociation energy. The bond dissociation energy for loss of methyl for reaction 13 is about 62 kcal and that for loss of methyl from radical 12b to form 4,4-dimethyl-1,2-pentadiene is about 109 kcal (26). The latter diolefin was not observed in the exhaust.

A more probable initial step for this olefin fuel would be the loss of methyl to form the resonance stabilized radical:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 \xrightarrow{O_2} CH_3-\underset{\cdot}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 + CH_3O_2\cdot \tag{14}$$

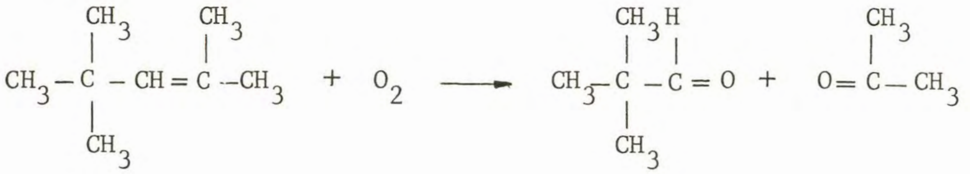
Then further hydrogen atom abstraction from any one of the methyl groups would produce 2,4-dimethyl-1,3-pentadiene. Further loss of any one of the methyl groups from this resonance stabilized radicals, and migration of a hydrogen atom would produce 2-methyl-2,3-pentadiene:



$$CH_3-\underset{\bullet}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 \longrightarrow CH_3-CH=C=\overset{CH_3}{C}-CH_3 + CH_3^{\bullet} \qquad (15)$$

Both 2,4-dimethyl-1,3-pentadiene and 2-methyl-2,3-pentadiene were found in the exhaust from DIB-2 fuel, and both of these diolefins were observed to be very reactive; they disappeared from the exhaust sample rapidly. In fact, they disappeared so rapidly that they were gone by the time a sample could be prepared for analysis by the chromatographic-system/mass-spectrometer couple. Therefore, these dienes were identified only by chromatographic column retention time. The most probable fate of these materials is reaction with the nitrogen dioxide (NO_2) in the sample (16).

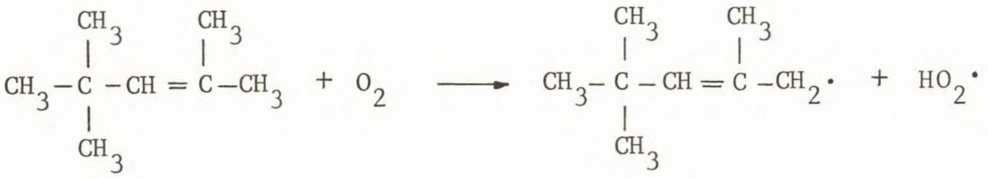
The acetone and 2-methyl-1,3-butadiene (this diene, although quite reactive did not disappear as rapidly as the dienes mentioned above) in the exhaust from DIB-2 fuel was not resolved with the chromatographic system analysis; therefore, the relative contribution of each component to the total area of this peak was not determined. The mass spectra data for this peak do show, however, that acetone is the major component of the mixture. No chemical mechanism is proposed for the formation of acetone for the DIB-2 fuel, but the results of this experiment indicate that the main source of acetone comes from the cleavage of the originally doubly bonded carbons. If so, then some 2,2-dimethylpropenal may also be present:



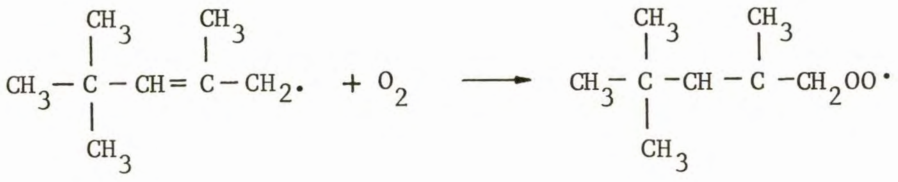
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 + O_2 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{H}{C}=O + O=\overset{CH_3}{C}-CH_3 \qquad (16)$$

This aldehyde was not isolated in this experiment, but it could have been present in the exhaust, and further decomposed later during combustion, or it may have been unresolved from some other component in the chromatogram.

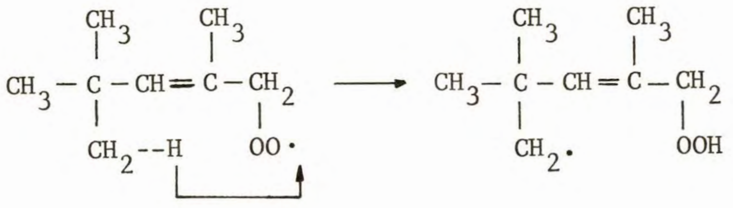
A mechanism for isobutylene and 2-methylpropenal from the DIB-2 fuel could be as follows:



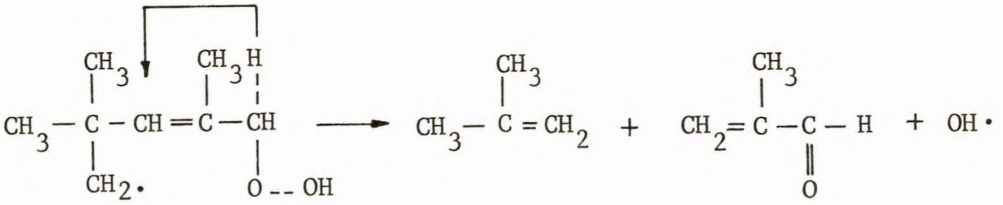
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 + O_2 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_2^{\bullet} + HO_2^{\bullet} \qquad (17a)$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_2\cdot + O_2 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH-\overset{CH_3}{C}-CH_2OO\cdot \qquad (17b)$$



$$CH_3-\underset{CH_2--H}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-\underset{OO\cdot}{CH_2} \longrightarrow CH_3-\underset{CH_2\cdot}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-\underset{OOH}{CH_2} \qquad (17c)$$



$$CH_3-\underset{CH_2\cdot}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-\underset{O--OH}{\overset{H}{CH}} \longrightarrow CH_3-\overset{CH_3}{C}=CH_2 + CH_2=\overset{CH_3}{C}-\underset{O}{\overset{}{C}}-H + OH\cdot \qquad (17d)$$

More 2-methylpropenal was observed in the exhaust from DIB-2 than in that from isooctane.

An Isooctane and 2,4,4-Trimethylpentene-2 Mixture

The qualitative results from a 50/50 mixture (by weight) of isooctane and DIB-2 are shown in the lower portion of figure 7. These results indicate that no new exhaust components appeared as a result of the fuel mixture. By observing the relative size of each chromatographic peak in the three chromatograms in figure 7, it is apparent that there are no interacting effects with the paraffin and olefin fuel mixture; that is, the results for the fuel mixture could be obtained by a linear combination of results for the paraffin fuel and olefin fuel when used separately in the engine. These results were tested statistically for interaction effects and are discussed in the section about quantitative results.

m-Xylene

The exhaust hydrocarbon separation for pure m-xylene as fuel is shown in the middle portion of figure 8. The top chromatogram in figure 8 for isooctane is the same as that in figure 7. It is repeated here for the comparison of results from isooctane, m-xylene, and the isooctane-m-xylene mixture. The latter is shown in the lower portion of figure 8.

The only nonaromatic components found in the exhaust from m-xylene were methane, ethylene, acetylene, and 2-methylpropenal.

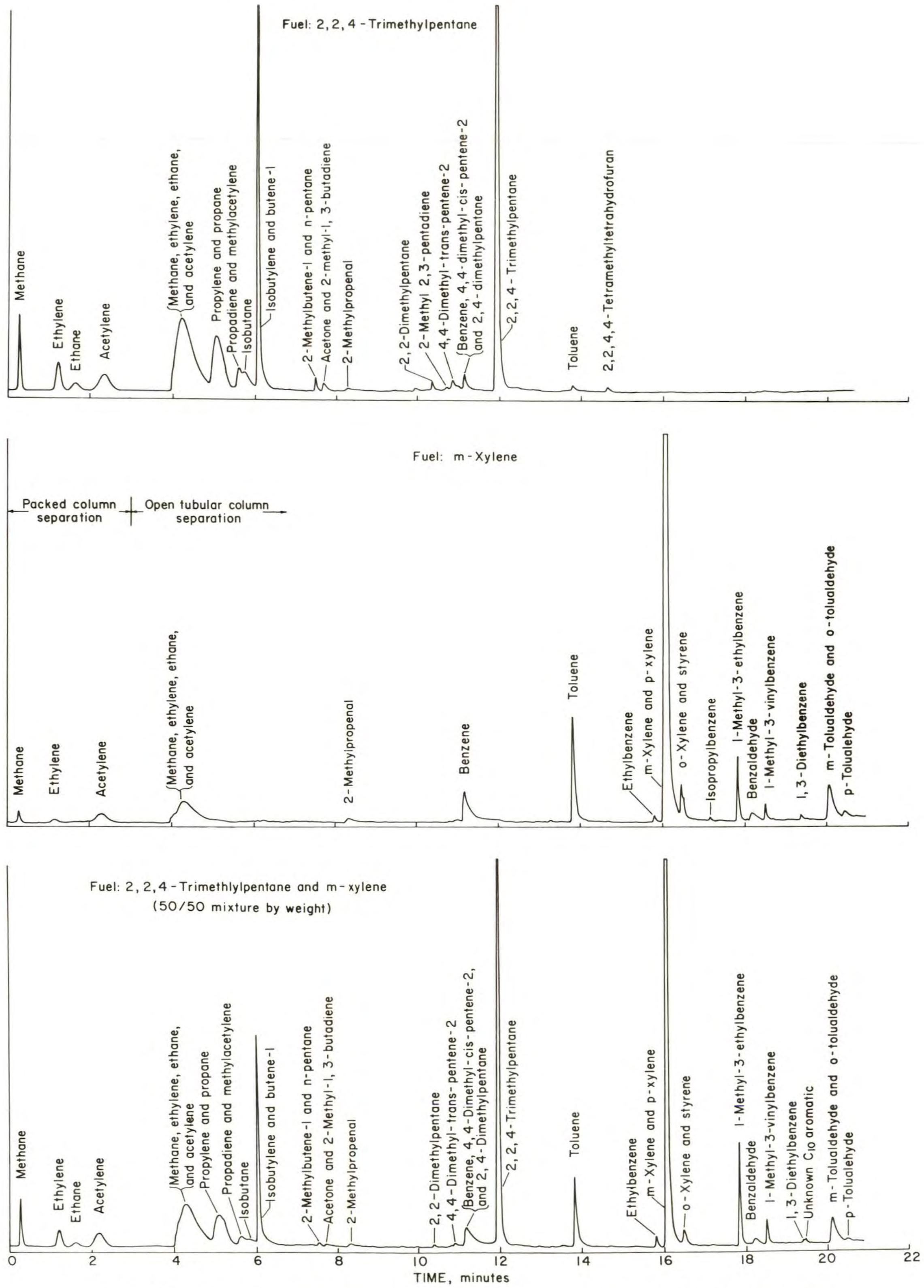
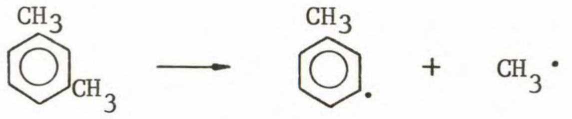


FIGURE 8. - Chromatograms Showing Exhaust Hydrocarbon Separation for Paraffin and Aromatic Fuels.

Methane probably came from the pyrolysis reaction:



(18)

The methyl radical can abstract a hydrogen atom from another fuel molecule:

(19)

This reaction can be generalized to a form analogous to reaction 5:

(20)

where R represents H·, CH_3·, HO_2·, or OH·

Ethylene and acetylene are produced by thermal decomposition of the aromatic ring. 2-Methylpropenal can come from the oxidation of fragments of the aromatic ring.

The other exhaust products associated with the m-xylene fuel are modified aromatic compounds. To form the other aromatics, the most probable first step is the abstraction of a hydrogen atom from one of the methyl groups:

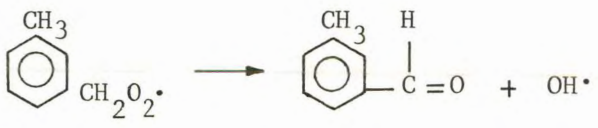
(21)

The next stage would be oxidation of this relatively stable methylbenzyl radical:

(22)

The methylbenzylperoxy radical could then decompose, abstract hydrogen from other molecules, or be oxidized further.

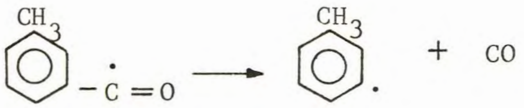
Probable reactions are as follows (13):


(23)

m-Tolualdehyde was observed in the exhaust from m-xylene. This compound could react further with oxygen as follows:


(24a)

Further decomposition of this radical would result in:


(24b)

This radical could then form toluene by


(24c)

Toluene was indeed formed and appeared in relatively large quantities. Toluene could then react by reactions similar to 21 through 24 to form benzaldehyde and benzene, which were also observed in the exhaust.

A more important reaction for the formation of toluene from m-xylene would probably be the abstraction of a methyl group as the first step:


(25a)


(25b)

Of course benzene could be formed from toluene in a similar way. Reaction 25 would probably contribute more to the formation of toluene because fewer intermediate steps are required.

1-Methyl-3-ethylbenzene is an important product from m-xylene fuel because it involves a methyl addition reaction. The first step is the abstraction of hydrogen from the fuel molecule:


(26a)


(26b)

The $CH_3C_6H_4\cdot$ radical could then form more toluene by reaction 25b. 1-Methyl-3-ethylbenzene could also come from the reaction of m-$CH_3C_6H_4CH_2\cdot$ with $CH_3\cdot$ radicals, but this reaction probably is a small contributor because methyl radicals are extremely reactive, and with the relatively high concentration of oxygen in the system, these reactive particles would be scavenged by oxygen. The absence of ethane in the exhaust also suggests a scarcity of free methyl radicals for radical-radical reaction.

Ethylbenzene can be formed from toluene by a mechanism similar to reaction 26, and can then produce styrene by loss of hydrogen under the high-temperature conditions in the combustion chamber. Trace quantities of styrene were detected, but they were not separated from o-xylene in the chromatographic system. o-Xylene can be formed by rearrangement of the m-xylene. This product did appear in the exhaust but only in relatively low concentration. It is possible that some p-xylene also was formed but could not be detected because it was not separated from m-xylene.

1-Methyl-3-vinylbenzene is a high-temperature pyrolysis product from 1-methyl-3-ethylbenzene by loss of hydrogen. Small amounts of isopropylbenzene and 1,3-diethylbenzene also appear in the exhaust from m-xylene fuel.

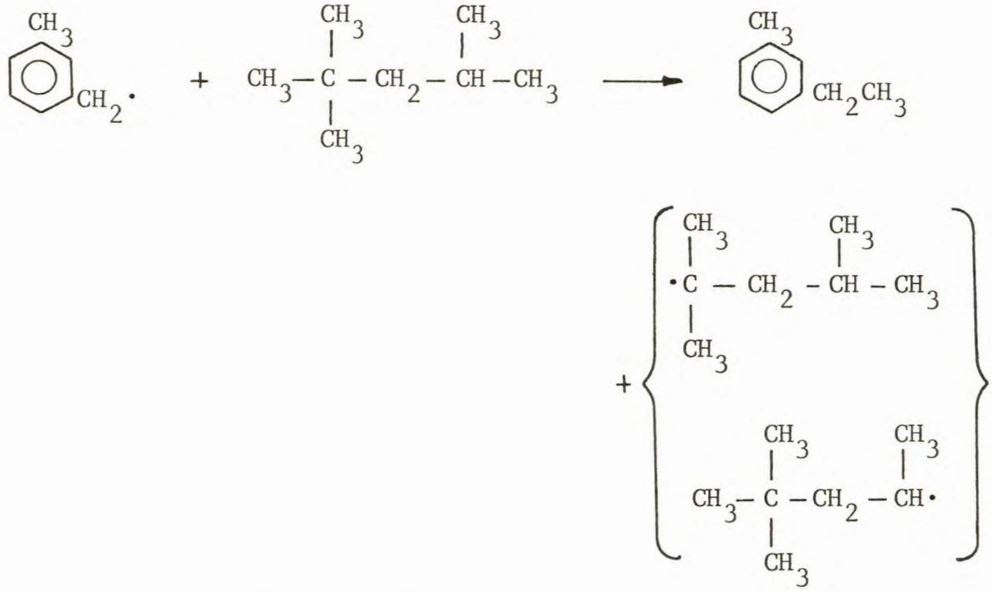
An Isooctane and m-Xylene Mixture

The exhaust hydrocarbon separation for the isooctane and m-xylene mixture is shown in the lower chromatogram in figure 8. By comparison of the three chromatograms in figure 8, it is apparent that ethylbenzene, 1-methyl-3-ethylbenzene, and 1-methyl-3-vinylbenzene are more abundant in the exhaust from paraffin-aromatic fuel than in the exhaust from the pure aromatic fuel. This effect is actually greater than it appears to be from these chromatograms because there was only about half as much aromatic in the fuel from which these exhaust products originated. This effect is defined as an interaction effect in this report, and the magnitude of this interaction effect is discussed under quantitative results.

The formation of these interaction products for the fuel mixture can be explained by a reaction similar to reaction 26, except that more than one type of fuel molecule is involved:

(27a)

(27b)



(27c)

Reaction 27b has only two methyl radicals to abstract from the m-xylene molecule. Reaction 27c has five different methyl groups which can be removed from the isooctane molecule to form 1-methyl-3-ethylbenzene. In addition to the probability factor, the carbon-carbon bond dissociation energy for removing a methyl group from isooctane is about 75 kcal, whereas that for m-xylene is about 89 kcal. Therefore, from the consideration of both probability factor and energy levels, reaction 27 should produce more 1-methyl-3-ethylbenzene than reaction 26 produces. This is in agreement with the experimental results.

A higher concentration of ethylbenzene was also found in exhaust from the paraffin-aromatic fuel than in that from pure aromatic fuel. This result can be explained by a reaction similar to reaction 27, except that toluene would be substituted for m-xylene in reaction 27a.

If 1-methyl-3-vinylbenzene and styrene are products of pyrolysis from 1-methyl-3-ethylbenzene and ethylbenzene, respectively, then higher concentrations of the latter products would be expected when higher concentrations of

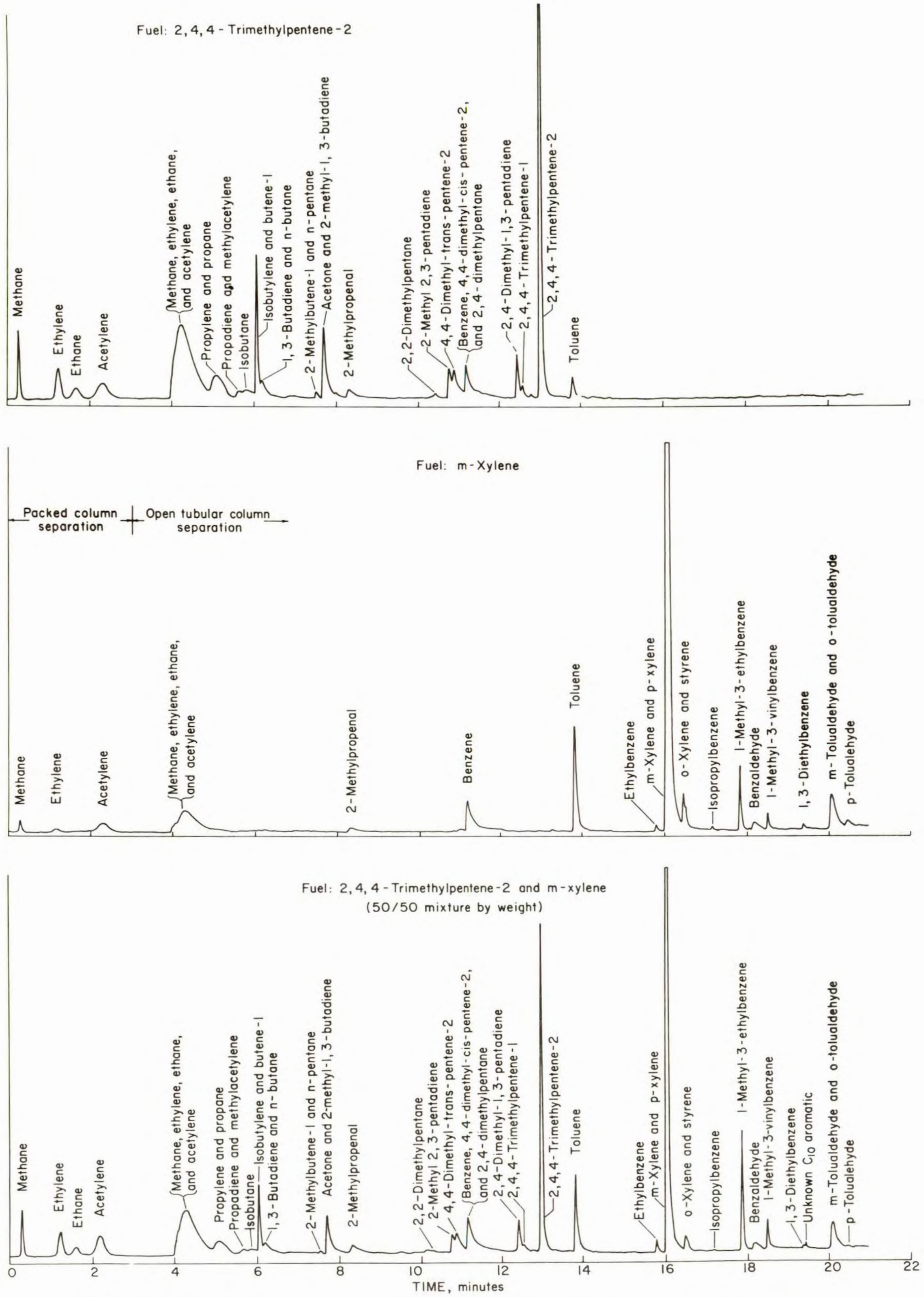


FIGURE 9. - Chromatograms Showing Exhaust Hydrocarbon Separation for Olefin and Aromatic Fuels.

1-methyl-3-ethylbenzene and ethylbenzene are observed. Figure 8 does show that the 1-methyl-3-vinylbenzene peak is larger for the fuel mixtures than it is for the pure aromatic. 1-Methyl-3-vinylbenzene was observed to increase in the exhaust when isooctane was added to m-xylene. It was impossible to determine whether or not styrene was increased by the addition of isooctane because of the o-xylene interference; that is, styrene and o-xylene were not resolved in the chromatograms, and o-xylene was a much larger contributor to the total peak area.

Styrene probably was increased when ethylbenzene was increased; however, in this experiment no increase was detected because of o-xylene interference. To support this assumption, one additional engine run was made with pure ethylbenzene as fuel. The results showed that apart from the ethylbenzene peak the largest component in the exhaust was styrene, which is consistent with the assumption that styrene is a dehydrogenation product of ethylbenzene.

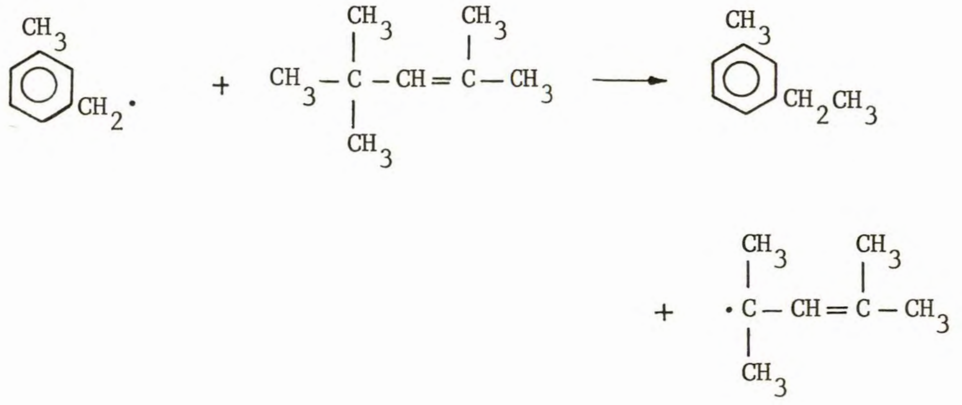
Isopropylbenzene, a very small exhaust product from m-xylene fuel, was apparently decreased with the addition of isooctane. The concentration of 1,3-diethylbenzene and another product labeled unknown C_{10} aromatic also apparently were affected by the addition of paraffin to the aromatic fuel.

A 2,4,4-Trimethylpentene-2 and m-Xylene Mixture

A chromatogram that shows the exhaust hydrocarbon separation for a DIB-2 and m-xylene mixture is illustrated in the lower part of figure 9. Chromatograms for pure DIB-2 and m-xylene fuels are reproduced from figures 7 and 8, respectively, for comparison. The results (fig. 9) for the fuel mixture are essentially what would be expected from the results of each fuel component with the exception of ethylbenzene, 1-methyl-3-ethylbenzene, and 1-methyl-3-vinylbenzene. The concentration of these products increased when DIB-2 was added to m-xylene fuel. The same result was observed for the isooctane and m-xylene mixture. The explanation for these results is similar to that given for reaction 27:

(28a)

(28b)



(28c)

The removal of a vinylic methyl group is not considered because of the high activation energy required. The bond dissociation energy of this carbon-carbon double bond is about 109 kcal (26). The allylic methyl groups are somewhat easier to abstract. The bond dissociation energy for this carbon-carbon double bond is about 62 kcal (26). Therefore, the probability factor for reaction 28c would be less than that for reaction 27c because there are only three methyl groups available for abstraction in reaction 28c as opposed to five available methyl groups in reaction 27c. On the other hand, the activation energy for reaction 28c should be less than for reaction 27c, since the bond dissociation energy for the carbon-carbon bond in reaction 27c is about 75 kcal and that for 28c is about 62 kcal.

Results indicate that the increase of 1-methyl-3-ethylbenzene in the exhaust when DIB-2 was added to the m-xylene (fig. 9) were about the same as that found for the addition of isooctane to m-xylene fuel (fig. 8). These results are consistent with those reactions 27 and 28.

Quantitative Results

Quantitative data were obtained for all of the reaction products shown in figures 7, 8, and 9 and for carbon monoxide, carbon dioxide, hydrogen, nitrogen oxides, total aldehydes, and formaldehyde. These data are summarized in tables 4, 5, and 6. The engine was run on each of the six fuels under the conditions given in table 3. The exhaust emission data in tables 4, 5, and 6 represent the average of five repetitive engine runs. The repetitive runs were made in a completely randomized manner to circumvent introducing effects due to drift in engine emission levels rather than due to fuel changes only.

Emission data are expressed as moles of exhaust product per mole of fuel introduced into the engine intake air stream. The method of calculating these emission data is given in appendix J.

The data in table 4 are arranged in groups to show the effect of fuel mixtures on exhaust products. The three columns of data represent results for isooctane, a 50/50 mixture (by weight) of isooctane and 2,4,4-trimethylpentene-2, and 2,4,4-trimethylpentene-2, respectively. Similarly, table 5 lists results from isooctane, a 50/50 mixture (by weight) of isooctane and m-xylene, and m-xylene. Table 6 lists results from

2,4,4-trimethylpentene-2, a 50/50 mixture by weight of 2,4,4-trimethylpentene-2 and m-xylene, and m-xylene, respectively.

TABLE 4. - Summary of exhaust emissions for paraffin and olefin fuels

(Moles of exhaust product/mole of fuel × 10^4)

Exhaust component	Fuels used in the engine		
	Iso-octane	Mixture of iso-octane and 2,4,4-trimethylpentene-2 (50/50 by weight)	2,4,4-Trimethylpentene-2
Carbon monoxide	1,380	1,410	1,470
Carbon dioxide	78,000	77,900	77,900
Hydrogen	430	420	420
Nitrogen oxides	2,120	2,270	2,230
Total aldehydes	17	18	18
Formaldehyde	12	12	12
Methane	35	31	37
Ethylene	17	17	20
Ethane	5	7	8
Acetylene	18	17	19
Propylene and propane	18	14	9
Propadiene and methylacetylene	3	2	2
Isobutane	2	2	2
Isobutylene and butene-1	24	18	10
1,3-Butadiene and n-butane	0	Trace	3
2-Methylbutene-1 and n-pentane	.6	.6	.5
Acetone and 2-methyl-1,3-butadiene	1	6	10
2-Methylpropenal	.1	1	2
2,2-Dimethylpentane	.5	.4	.4
2-Methyl-2,3-pentadiene	.2	.8	2
4,4-Dimethyl-trans-pentene-2	.4	2	2
Benzene,4,4-dimethyl-cis-pentene-2, and 2,4-dimethylpentane	1	3	3
2,2,4-Trimethylpentane	31	15	0
2,4-Dimethyl-1,3-pentadiene	0	.9	2
2,4,4-Trimethylpentene-1	0	.2	.4
2,4,4-Trimethylpentene-2	0	10	18
Toluene	.3	.6	.9
2,2,4,4-Tetramethyltetrahydrofuran	.1	0	0
Total hydrocarbon	156	142	139

TABLE 5. - Summary of exhaust emissions for paraffin and aromatic fuels

(Moles of exhaust product/mole of fuel × 10^4)

Exhaust component	Fuels used in the engine		
	Iso-octane	Mixture of isooctane and meta-xylene (50/50 by weight)	Meta-xylene
Carbon monoxide	1,380	1,490	1,290
Carbon dioxide	78,000	77,800	77,900
Hydrogen	430	370	210
Nitrogen oxides	2,120	2,180	2,160
Total aldehydes	17	16	13
Formaldehyde	12	10	8
Methane	35	21	8
Ethylene	17	9	4
Ethane	5	2	0
Acetylene	18	13	10
Propylene and propane	18	10	.9
Propadiene and methylacetylene	3	2	.1
Isobutane	2	1	0
Isobutylene and butene-1	24	12	.3
1,3-Butadiene and n-butane	0	0	.7
2-Methylbutene-1 and n-pentane	.6	.3	0
Acetone and 2-methyl-1,3-butadiene	1	.5	0
2-Methylpropenal	.1	.6	.6
2,2-Dimethylpentane	.5	.2	0
2-Methyl-2,3-pentadiene	.2	0	.2
4,4-Dimethyl-trans-pentene-2	.4	.2	0
Benzene, 4,4-dimethyl-cis-pentene-2, and 2,4-dimethylpentane	1	3	[1]3
2,2,4-Trimethylpentane	31	15	0
Toluene	.3	3	4
2,2,4,4-Tetramethyltetrahydrofuran	.1	0	0
Ethylbenzene	0	.2	.2
m-Xylene and p-xylene	0	36	70
o-Xylene and styrene	0	.7	2
Isopropylbenzene	0	0	.1
1-Methyl-3-ethylbenzene	0	2	1
Benzaldehyde	0	.3	.4
1-Methyl-3-vinylbenzene	0	.5	.4
1,3-Diethylbenzene	0	Trace	.1
Unknown C_{10} aromatic	0	.1	0
o-Tolualdehyde and m-tolualdehyde	0	3	3
p-Tolualdehyde	0	Trace	.08
Total hydrocarbon	156	131	106

[1] This represents benzene only when using the pure aromatic fuel.

TABLE 6. - Summary of exhaust emissions for olefin and aromatic fuels

(Moles of exhaust product/mole of fuel × 10^4)

Exhaust component	Fuels used in the engine		
	2,4,4-Trimethylpentene-2	Mixture of 2,4,4-trimethylpentene-2 and meta-xylene (50/50 by weight)	Meta-xylene
Carbon monoxide................	1,470	1,280	1,290
Carbon dioxide.................	77,900	78,100	77,900
Hydrogen.......................	420	290	210
Nitrogen oxides................	2,230	2,320	2,160
Total aldehydes................	18	16	13
Formaldehyde...................	12	10	8
Methane........................	37	22	8
Ethylene.......................	20	11	4
Ethane.........................	8	4	0
Acetylene......................	19	14	10
Propylene and propane..........	9	5	.9
Propadiene and methylacetylene.	2	.1	.1
Isobutane......................	2	1	0
Isobutylene and butene-1.......	10	4	.3
1,3-Butadiene and n-butane.....	3	1	.7
2-Methylbutene-1 and n-pentane.	.5	.1	0
Acetone and 2-methyl-1,3-butadiene....................	10	6	0
2-Methylpropenal...............	2	2	.6
2,2-Dimethylpentane............	.4	.2	0
2-Methyl-2,3-pentadiene........	2	.7	.2
4,4-Dimethyl-trans-pentene-2...	2	1	0
Benzene,4,4-dimethyl-cis-pentene-2 and 2,4-dimethylpentane..............	3	4	[1]3
2,4-Dimethyl-1,3-pentadiene....	2	.8	0
2,4,4-Trimethylpentene-1.......	.4	0	0
2,4,4-Trimethylpentene-2.......	18	9	0
Toluene........................	.9	3	4
Ethylbenzene...................	0	.3	.2
m-Xylene and p-xylene..........	0	32	70
o-Xylene and styrene...........	0	.8	2
Isopropylbenzene...............	0	0	.1
1-Methyl-3-ethylbenzene........	0	2	1
Benzaldehyde...................	0	.2	.4
1-Methyl-3-vinylbenzene........	0	.5	.4
1,3-Diethylbenzene.............	0	Trace	.1
Unknown C_{10} aromatic..........	0	.1	0
o-Tolualdehyde and m-tolualdehyde...............	0	2	3
p-Tolualdehyde.................	0	Trace	.08
Total hydrocarbon..............	139	117	106

[1] This represents benzene only when using the pure aromatic fuel.

Carbon Monoxide, Carbon Dioxide, and Hydrogen Emissions

Since the engine was operated at an air-fuel ratio slightly leaner than stoichiometric (equivalence ratio = 1.03) for each fuel, the carbon monoxide (CO) emissions were quite low. The maximum variation of CO levels for the different fuels was about 16 percent. This variation is quite small since the engine was operated at a condition in which the CO concentration was approaching zero. Thus, a small variation in equivalence ratio would result in a large change in CO concentration; that is, measured in terms of percent change.

The emission of carbon dioxide (CO_2) was about the same for all the fuels tested. This result would be expected since each fuel was run at the same equivalence ratio.

The hydrogen content in the exhaust was about the same for isooctane and 2,4,4-trimethylpentene-2, but much lower for m-xylene. This result is quite reasonable because the H/C ratio (by atoms) for m-xylene (C_8H_{10}) was much lower than isooctane (C_8H_{18}) or 2,4,4-trimethylpentene-2 (C_8H_{16}). The hydrogen content of the exhaust from the fuel mixtures is about what would be expected, based on the hydrogen content of exhausts produced from each fuel component.

Nitrogen Oxide Emissions

The only oxide of nitrogen generated in the engine combustion chamber is nitric oxide (NO). In this experiment, exhaust samples were collected in a bag and the exhaust products were analyzed a few minutes later. This time delay allowed some of the NO to oxidize to nitrogen dioxide (NO_2); thus, the samples were analyzed for both NO and NO_2. NO_2 represented an average of about 10 percent of the total nitrogen oxides in the exhaust samples at the time when NO and NO_2 were measured (about 20 minutes after sample collection). The results shown in tables 4, 5, and 6 represent the sum of NO and NO_2, which is designated as NO_x.

The NO_x emission for each of the six fuels tested in this experiment was about the same. The production of NO_x in the engine is highly dependent on flame temperature. These results indicate that about the same temperatures were reached in the combustion event for each fuel tested. The results of tables 4, 5, and 6 indicate that slightly greater than 0.2 mole of NO_x was produced for each mole of fuel used. This number may seem quite high, but the engine conditions used for this experiment would result in a maximum yield of NO_x.

Total Aldehydes and Formaldehyde Emissions

The total aldehyde and formaldehyde data given in tables 4, 5, and 6 were determined by the MBTH method and chromotropic procedures, respectively, as described in appendix G.

Total aldehyde content in the exhaust from isooctane, 2,4,4-trimethylpentne-2, and the mixture of isooctane and 2,4,4-trimethylpentene-2 was about the same. The total aldehydes produced from m-xylene were lower. However, this lower total aldehyde content for the aromatic fuel exhaust was caused by the smaller amount of formaldehyde produced from the aromatic, and also because of the lack of sensitivity of the MBTH method to aromatic aldehydes.

Formaldehyde in the exhaust was the same for the paraffin and olefin fuels but was considerably less for the exhaust from the aromatic fuel. This result was not surprising because about the only source of formaldehyde from xylene would be decomposition of a peroxy group attached to the ring, whereas the paraffin or olefin would have many other ways to form formaldehyde. Nothing unusual was found for the fuel mixtures in terms of formaldehyde emission.

Exhaust Hydrocarbon Emission

The hydrocarbons listed in tables 4, 5, and 6 are those that existed in any significant quantity in the exhaust gas samples. Among the hydrocarbons separated there are also some aldehydes and ketones, and at least one ether. The chromatographic system used for these separations is described in appendix F. This system employs a flame ionization detector (FID) whose response to hydrocarbon is proportional to the number of carbon atoms in the molecule. Thus, the mole concentration of each hydrocarbon was obtained by dividing the carbon atom concentration by the number of carbon atoms in the molecule.

The flame ionization detector does not respond to carbonyl compounds in a linear fashion; for example, formaldehyde is not detected by FID. The C_2 and higher aldehydes were detected by FID, but the response was not proportional to the number of carbon atoms. The FID's response to carbonyl compounds is unknown, but is somewhat lower than the response to hydrocarbons; therefore, the emission values given in tables 4, 5, and 6 for nonhydrocarbon compounds are slightly lower than the true values.

The primary differences in the emission characteristics (table 4) for the paraffin and olefin fuels are as follows: The paraffin fuel yielded about twice as much propylene and propane as the olefin fuels. (Although propylene and propane are unresolved in the chromatographic system, it is believed that for these fuels, the amount of propane emitted is insignificant as compared to propylene.) The isobutylene and butene-1 (this mixture is primarily isobutylene) yield is about 2.4 times greater for the paraffin fuels. The olefin fuel produced about 10 times more acetone and 2-methyl-1,3-butadiene (acetone is the main component in this mixture) than the paraffin fuels. The emission of 1,3-butadiene, 2-methyl-propenal, 2-methyl-2,3-pentadiene, 4,4-dimethyl-trans-pentene-2, 4,4-dimethyl-cis-pentene-2, and 2,4-dimethyl-1,3-pentadiene was much greater for the olefin fuel than for the paraffin fuel. The benzene, 4,4-dimethyl-cis-pentene-2, and 2,4-dimethylpentane were unresolved in the chromatographic system; therefore, the relative contribution of each of these components to the total detector response is unknown. However, the mass spectrometer analysis of this chromatographic peak showed a high contribution from benzene. Toluene, another aromatic compound which showed up in the exhaust from both paraffin and olefin fuels, was about 3 times more abundant in the olefin exhaust. Therefore, it is reasonable to assume that benzene was also greater in the olefin exhaust. These aromatic compounds are believed to be synthesized in the combustion chamber.

The abundance of unreacted fuel in the exhaust was somewhat greater for isooctane than 2,4,4-trimethylpentene-2. This would be expected since 2,4,4-trimethylpentene-2 (an olefin) is more reactive than isooctane (a paraffin). The total hydrocarbon per mole of fuel used that was emitted from the engine using isooctane (0.0156 mole) was quite a bit higher than the 0.0139 value determined for 2,4,4-trimethylpentene-2. Note that, apart from the unreacted fuel exhaust component, the olefin fuel exhaust actually contained fewer olefin products than the paraffin fuel. The amount of olefin product from the olefin fuel, not counting unreacted fuel, was 0.00509 mole of hydrocarbon per mole of fuel used as compared to 0.00632 for the paraffin fuel.

The m-xylene (table 5) produced much fewer nonaromatic exhaust components than the paraffin fuel. Of course, this was expected because the ring structure of aromatics is quite stable. The main nonaromatic hydrocarbons emitted from the engine using m-xylene as fuel were methane, ethylene, and acetylene. Acetylene was the most prominent nonaromatic which is produced from the decomposition of the benzene ring. About 76 percent of the exhaust hydrocarbons from m-xylene were aromatics. About 87 percent of the aromatics in the exhaust was unreacted m-xylene. The total hydrocarbon content of the exhaust from aromatic fuel was considerably lower than for the paraffin or olefin fuel. The hydrocarbon contents in the exhausts from the three pure fuels, in terms of moles of total hydrocarbon per mole of fuel used, were 0.0156 for isooctane, 0.0139 for 2,4,4-trimethylpentene-2, and 0.0106 for m-xylene fuel.

Interaction Products From Fuel Mixtures

The exhaust emission data obtained from fuel mixtures were investigated statistically for interaction effects. The term interaction effect is defined as follows: If the quantity of any hydrocarbon in the exhaust from a fuel mixture can be determined, within experimental error, by the linear combination of results for this same hydrocarbon in the exhausts from each fuel component, then there is no interaction effect. Those exhaust hydrocarbons that require a nonlinear relationship to predict the experimental results are called interaction products.

The results from the fuel mixture of isooctane and 2,4,4-trimethylpentene-2 (table 4) were investigated for interaction effects. The results for the fuel mixture could be predicted (within experimental error) by a straight-line relationship; therefore, no interaction effect was found for the paraffin and olefin fuel mixture.

The exhaust products from the fuel mixture of isooctane and m-xylene (table 5) were examined by statistical analysis, and no interactions were found, except for ethylbenzene, 1-methyl-3-ethylbenzene, and 1-methyl-3-vinylbenzene.

Similarly the results for the 2,4,4-trimethylpentene-2 and m-xylene mixture (table 6) were examined statistically for interaction effect. The results showed that the only interaction products were ethylbenzene, 1-methyl-3-ethylbenzene, and 1-methyl-3-vinylbenzene; therefore, the interaction products for the olefin and aromatic fuel mixture were the same as those found for the paraffin and aromatic fuel mixtures.

These results are consistent with reactions 27 and 28. The primary source of 1-methyl-3-ethylbenzene from the isooctane and m-xylene mixture is by reaction 27. Then 1-methyl-3-vinylbenzene is a thermal dehydrogenation product from 1-methyl-3-ethylbenzene. These two products are produced in a similar way from the olefin and m-xylene mixture by reaction 28. Ethylbenzene and styrene might be produced in a similar manner except toluene would be an intermediate product. Although styrene was not detected as an interaction product, the relatively large concentration of o-xylene in the exhaust probably prevented this effect from showing up (since o-xylene and styrene were unresolved by the chromatographic system).

Summary of Experimental Results

1. Benzene and toluene were found in small quantities in the exhausts produced from isooctane and 2,4,4-trimethylpentene-2 fuels.

2. The amount of nitrogen oxides produced in the engine is about the same for isooctane, 2,4,4-trimethylpentene-2, and m-xylene fuel when the engine operates at an equivalence ratio of 1.03.

3. Formaldehyde yield in the exhaust is less for m-xylene fuel than for either isooctane or 2,4,4-trimethylpentene-2 fuel.

4. The amount of total hydrocarbon (in terms of moles of hydrocarbon per mole of fuel used) in the exhaust from the three pure fuels followed the sequence: Isooctane > 2,4,4-trimethylpentene-2 > m-xylene.

5. Interaction products, in the exhausts from isooctane and m-xylene fuel mixture and a 2,4,4-trimethylpentene-2 and m-xylene fuel mixture, were ethylbenzene, 1-methyl-3-ethylbenzene, and 1-methyl-3-vinylbenzene.

Interpretation of Experimental Results

The results of this investigation are interpreted and compared with results obtained in previous investigations.

Fewer olefin products (not counting the unreacted fuel component) were found in the exhaust from 2,2,4-trimethylpentene-2 than in the exhaust from isooctane. The olefins which account for the main difference are isobutylene and propylene. (See table 4.) The relative ease of formation of isobutylene and propylene from isooctane accounts for these results. Some of the products can be explained only on the basis of initial attack on the primary hydrogen atoms of the methyl groups rather than the initial removal of a tertiary or secondary hydrogen atom. Tertiary, secondary, and primary hydrogen atoms, in that order, will usually show decreasing susceptibilities toward oxidation, but in a highly branched chain hydrocarbon where the potentially more reactive atoms are shielded, and at temperatures sufficiently high to reduce selectivity, initial reaction may be largely confined to the more strongly bonded hydrogen atoms at the exposed methyl groups.

Following initial loss of primary hydrogens the two primary isooctyl radicals are formed. These two radicals degrade according to reactions 10 and 11. Rust and Collamer (34) treated 2,2,4-trimethylpentane with oxygen in the vapor phase at 450° C and found that more than 90 percent of the primary isooctyl radical in reaction 1d decomposed by reaction 11. For 2,2,4-trimethylpentene-2, a similar mechanism would not work because of the high activation energy required for bond scission.

No proof was developed that benzene and toluene, which appeared in the exhausts from isooctane and 2,4,4-trimethylpentene-2, were synthesis products, but some evidence indicated that they probably were. For example, toluene represented about 0.2 percent of the total hydrocarbon in the exhaust from isooctane and about 0.6 percent of the total hydrocarbon in the exhaust from 2,4,4-trimethylpentene-2. This increased amount of toluene in the olefin is evidence that points toward a synthesis product rather than contamination from the engine's lubricating oil.

The amount of oxides of nitrogen in the exhaust from each of the fuels tested is not unusual because the test conditions in terms of equivalence ratio were the same for all experiments. NO_x production in the engine is highly dependent on the maximum temperature reached in the combustion chamber. The relationship of NO_x production as a function of equivalence ratio in an engine increases with increasing equivalence ratios and reaches a maximum with an equivalence ratio slightly greater than 1.0 (22). This maximum point corresponds approximately with the equivalence ratio of 1.03 used in this research.

The smaller amount of formaldehyde in the exhaust from m-xylene is explained by considering that the only source of formaldehyde is by degradation of peroxy groups on the aromatic ring. The small amounts of low molecular weight hydrocarbons in the exhaust from m-xylene indicate that once the ring is broken, the fragments are rapidly and completely oxidized. On the other hand, the paraffin or olefin fuel would produce many small alkyl radicals in pyrolysis reactions which would be expected to combine with oxygen to form low-molecular weight aldehydes and ketones. One of the major byproducts expected from these pyrolysis reactions is formaldehyde.

The amount of total hydrocarbons in the exhaust from the three pure fuels decreased in the order: Isooctane > 2,4,4-trimethylpentene-2 > m-xylene. The primary difference in the total hydrocarbons emitted from the paraffin and olefin fuels can be accounted for by the unreacted fuel components. This result would be expected because the olefin would be somewhat more reactive toward oxidation than the paraffin, once combustion has been initiated. The m-xylene exhaust results in the lowest amount of total hydrocarbon. However, about 66 percent of the unburned hydrocarbon in the exhaust from the aromatic fuel is unreacted m-xylene.

Three interaction products were observed in the exhausts from isooctane--m-xylene and 2,4,4-trimethylpentene-2--m-xylene fuel mixtures. These products were identified as ethylbenzene, 1-methyl-3-ethylbenzene, and 1-methyl-3-vinylbenzene. The increase of 1-methyl-3-ethylbenzene in the exhaust, when the paraffin or olefin is added to m-xylene, would be predicted by reactions 27 and 28. These reactions can be generalized for the fuel mixtures. Following the abstraction of a hydrogen atom from the m-xylene molecule, the reactions would be

(29)

and

(30)

where RCH_3 can be m-$CH_3C_6H_4CH_3$, i-$C_7H_{13}CH_3$, or i-$C_7H_{15}CH_3$. Reaction 30 is probably the most important reaction for the formation of 1-methyl-3-ethylbenzene because reaction 29 requires the methyl radicals which would be rapidly scavenged by oxygen. Both reactions 29 and 30 would enhance the production of 1-methyl-3-ethylbenzene if i-$C_7H_{13}CH_3$ or i-$C_7H_{15}CH_3$ were added to the m-xylene fuel. These are precisely the results observed for the isooctane--m-xylene and 2,4,4-trimethylpentene-2--m-xylene fuel mixtures. The formation of ethylbenzene would follow a similar mechanism with the toluene and benzyl radicals being intermediates. 1-Methyl-3-vinylbenzene would be the dehydrogenation product of 1-methyl-3-ethylbenzene.

The large amount of acetone produced in the exhaust from 2,4,4-trimethylpentene-2 suggests a mechanism involving oxygen attack at the carbon-carbon double bond with subsequent bond cleavage to form an aldehyde and acetone. To support this type of mechanism, the engine was run with 2,4,4-trimethylpentene-1 as fuel. The result was an increase in formaldehyde and an unknown oxygenate which could possibly correspond to 4,4-dimethyl-2-pentanone. The amount of acetone in this exhaust was about the same as that produced in 2,2,4-trimethylpentane exhaust. Further work would be necessary to identify these components and obtain proof of this type of mechanism.

Comparison of Results to Previous Studies by Others

Most previous investigations of pure hydrocarbons used as fuel in internal-combustion engines were directed toward a more fundamental understanding of the knock process in engines. Most of these studies involved a motored engine that had no flame front or a normally fired engine in which gas sampling valves were used to extract samples from the combustion chamber at various points in the combustion cycle.

The results from motored engines (7, 24, 29, 31) are difficult to compare with results from a normally fired engine. Even comparisons with results of experiments where end gases of a normally fired engine were sampled (1, 8) is difficult because many reactions occur during blowdown and the exhaust stroke.

The investigations by Ninomiya and Golovoy (28) are most nearly comparable to the results of this research than any previous studies. They found that combustion of a mixture of 25 volume-percent n-heptane in toluene produced exhaust in which ethylbenzene, styrene, and dimethylacetylene were increased by factors of 1.9, 1.9, and 2.1, respectively, as compared to emissions from pure toluene. The result of increases in ethylbenzene and styrene for a toluene--n-heptane mixture is analogous to the results in this program for the increases of 1-methyl-3-ethylbenzene and 1-methyl-3-vinylbenzene for the isooctane--m-xylene mixture. The dimethylacetylene as reported by Ninomiya and Golovoy (28) for the toluene-heptane mixture did not appear except for equivalence ratios lower than 1.1. Therefore, if the dimethylacetylene was present in the isooctane--m-xylene mixture exhaust, it probably (where the equivalence ratio is 1.03) would not be detected in this research program.

The products of combustion from isooctane reported (28) represented similar characteristics for hydrocarbon composition as the results found in this research. The results on diisobutylene (28) would not be comparable to the results for 2,4,4-trimethylpentene-2 used in this program because diisobutylene is a mixture of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 in which the predominant component is 2,4,4-trimethylpentene-1.

CONCLUSIONS

The main conclusion of this investigation on the effect of fuel composition on exhaust emissions from a spark-ignition engine is as follows:

1. When either alkanes or alkenes are added to an aromatic fuel used in an internal-combustion engine, the emission of certain alkylbenzenes and alkenylbenzenes in the exhaust will increase. The structure of alkylbenzenes and alkenylbenzenes will depend on the aromatic in the fuel. For example, if the aromatic fuel is toluene, the exhaust products that are expected to increase for alkane-aromatic or alkene-aromatic mixtures will be ethylbenzene and styrene. For o-xylene, m-xylene, and p-xylene fuels the increasing products would be o-ethyltoluene and o-vinyltoluene, m-ethyltoluene and m-vinyltoluene, and p-ethyltoluene and p-vinyltoluene, respectively.

Other conclusions are as follows:

2. Under the conditions in the combustion chamber of an internal-combustion spark-ignition engine, small amounts of aromatics may be synthesized from pure olefin and/or paraffin fuels.

3. The amount of nitrogen oxides in the exhaust is the same for isooctane, 2,4,4-trimethylpentene-2, and m-xylene when expressed as moles of exhaust product per mole of fuel input to the engine (equivalence ratio = 1.03, air intake rate constant).

4. The hydrocarbon mole-fraction of unreacted fuel in the exhaust from m-xylene was much greater than from isooctane or 2,4,4-trimethylpentene-2. From this it can be deduced that as aromatic content in fuel is increased, the hydrocarbon mole fraction of aromatic in the exhaust that represents unburned fuel increases.

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APPENDIX A.--NOMENCLATURE

Symbol	
A	Fuel designation for 2,2,4-trimethylpentane
AB	Fuel designation for 2,2,4-trimethylpentane and 2,4,4-trimethylpentene-2 mixture
AC	Fuel designation for 2,2,4-trimethylpentane and meta-xylene mixture
B	Fuel designation for 2,4,4-trimethylpentene-2
BC	Fuel designation for 2,4,4-trimethylpentene-2 and meta-xylene mixture
C	Fuel designation for meta-xylene; degrees centigrade; and carbon atom
CO	Carbon monoxide
CO_2	Carbon dioxide
e	Constant, base of natural logarithm
E	Activation energy, kcal/mole
F	Degrees Fahrenheit
F-50	(Versilube) General Electric trade name
H	Hydrogen atom
H_2	Molecular hydrogen
HC	Hydrocarbon
$[HC]_t$	Total hydrocarbon
HCHO	Formaldehyde
i	Iso
k	Constant of proportionality
m	Meta
m	Mass
$\dot{m}$	Mass rate of flow

M	Molecular weight
n	Normal
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Total oxides of nitrogen ($NO + NO_2$)
o	Ortho
O	Oxygen atom
O_2	Molecular oxygen
OV-101	Ohio Valley Chemical Co. trade name
p	Para
p	Pressure, lb/ft^2
R	Universal gas constant; radical; and degrees Rankine
rpm	Angular velocity, revolutions per minute
RCHO	Total aldehydes
s/v	Surface-to-volume ratio
T	Absolute temperature
V	Volume, ft^3
W	Moles or air; white
X	Moles of exhaust products
X•	Chain carrier
Y	Number of hydrogen atoms in fuel molecule
Z	Moles of fuel
	Benzene

Greek symbol

φ	Equivalence ratio (actual air-fuel ratio)/(stoichiometric air-fuel ratio)

Subscripts

A	Air
a	Actual
i	Any exhaust component
t	Theoretical

Abbreviations

ATC	After top center
BTC	Before top center
CFR	Cooperative Fuel Research
DIB	Diisobutylene
GC	Gas chromatograph
IC	Internal combustion
ID	Inside diameter
MBTH	3-Methyl-2-benzothioazolone hydrazone hydrochloride
NDIR	Nondispersive infrared
NDUV	Nondispersive ultraviolet
OD	Outside diameter
PE	Perkin-Elmer
ppm	Parts per million
ppmC	Parts per million carbon atom

APPENDIX B.--REVIEW OF LITERATURE

The combustion of hydrocarbon fuels in IC spark-ignition engines is a complex process, involving simultaneous heat transfer, mass transfer, and chemical reactions. Complete combustion of hydrocarbon fuel yields only carbon dioxide and water as the products of chemical reaction. Under the conditions of combustion in an IC engine, other products are also formed. These include carbon monoxide, hydrogen, and partially oxidized materials primarily of the aldehyde family. Some fuel passes through the engine unburned, and some of the fuel is chemically rearranged by pyrolysis under the thermal stress of the combustion process. The effect of this rearrangement is primarily to produce fragments of the fuel molecule; however, some new products can be formed by interaction of various fragments of the fuel molecule.

Both absolute and relative concentrations of combustion products are influenced by numerous factors. Some of the most prominent factors are as follows: (1) Ratio of weight of air to weight of fuel (air-fuel ratio) in the combustion chamber during combustion; (2) ignition timing; (3) inlet mixture density; (4) combustion-chamber geometry; and (5) the variable parameters, such as speed, load, and engine temperatures. The air-fuel ratio influences the principal combustion products more than any of the other factors.

The combustion of mixtures richer in fuel than stoichiometric produces carbon monoxide (CO) and tends to produce residual fuel in the exhaust, either unburned or partially burned. Mixtures leaner in fuel than stoichiometric produce much less CO and, usually, lower concentrations of unburned hydrocarbon. However, if the mixture is excessively lean, flame will not propagate through it properly, the engine will misfire, and hydrocarbon emissions can become quite high.

Ignition timing also greatly influences the combustion process. It governs the time available for combustion to occur before the process is disturbed by cooling in the expansion stroke or exhaust blowdown. Both air-fuel ratio and ignition timing are readily adjustable.

The shape of the combustion chamber can significantly influence hydrocarbon emissions because the surface-to-volume ratio (s/v) can vary. Scheffler (36)[1] reported that hydrocarbon concentration varied from about 275 ppm with a 4.5 s/v ratio to about 600 ppm for an 8.5 s/v ratio. The flame in the combustion chamber is quenched at the chamber surface and leaves an unburned layer of hydrocarbons, which mixes with the burned charge and escapes with the exhaust (11). Experiments with a single-cylinder engine (adapted from a 230-cu. in. six-cylinder engine) showed that small crevices formed by the piston, bore, and top compression ring were responsible for at least one-half of the exhaust hydrocarbon emissions in a clean engine; that is, the combustion chamber was free of deposits (39).

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[1] Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

Mechanisms responsible for flame propagation are heat conduction and diffusion. To determine which is more important in an engine would be difficult; actually, both may be important. Chemical reactions can be started and accelerated by a temperature increase; consequently, heat conduction from hot to cold gases is important to flame propagation. Also, the diffusion of certain active particles may be important. These active particles (free radicals and atoms), because of their energetic nature, are supposedly able to start chemical reactions in cold gases. Thus, interpretation of the quenching effect starts with the assumption that one of these two processes is more important and identifies the chamber walls as a sink for either heat or active particles. The result may be described as either a thermal or diffusional interpretation. In either case, an engine contains relatively cool walls and enough surface area for flame quenching to occur.

Note that all of the quench-zone hydrocarbons do not escape the combustion chamber during the exhaust stroke. A fraction of these gases are retained in the cylinder as residual gases and may be subsequently burned in the next cycle. Friedman (14-15) and Potter (32) correlated quench thickness with pressure and air-fuel ratio. Accordingly, Huls (19) used these data for computations to see if the experimentally observed trends in engines could be predicted. The engine combustion period was divided into 10 parts, and the hydrocarbon concentrations were computed. For the calculations, no afterburning and complete mixing of quench gases with bulk gases were assumed. Measured hydrocarbon concentrations and those calculated from measured pressures and temperatures were compared, and the comparisons showed that, with two exceptions, the calculated values were higher than the measured exhaust values. The calculated values were based on the temperature data of Friedman (15) and the pressure and quench distance data of Friedman (14). Similarly, the temperature data of Friedman (15) and the pressure and quench distance data of Potter (32) were calculated. Results of all calculations were higher than the measured exhaust hydrocarbon concentrations.

The difference previously stated can be resolved by assuming that the reactions during blowdown and the exhaust stroke follow the Arrhenius rate equation and by assuming that two-thirds of the quench volume gases leave with 95 percent of the cylinder contents of the engine (20). The rate equation (23) for the reaction of hydrocarbon (HC) is

$$\Delta[HC] = k[HC]\,[O_2]\,T^{\frac{1}{2}}\,e^{-E/RT} \qquad \text{(B-1)}$$

where the brackets represent concentration and k is a proportionality constant.

Combustion Products

The combustion products that are most important as air pollutants are carbon monoxide, oxides of nitrogen, hydrocarbons, and partial oxidation products.

Carbon Monoxide

Ideally a gasoline engine would produce exhaust products as shown in figure B-1. This graph is based on a gasoline with a stoichiometric ratio of 14.7. If the real engine is operated at a stoichiometric or leaner air-fuel ratio, the carbon monoxide becomes less than 0.5 percent (fig. B-2). These data represent the results from three different engines. Carbon monoxide is toxic and is harmful if highly concentrated in the atmosphere, but it does not influence the photochemical formation of smog.

Oxides of Nitrogen

At the temperatures normally reached in an engine combustion chamber, some of the nitrogen and oxygen combine to form nitric oxide (NO). Some of the NO is converted to nitrogen dioxide (NO_2) after the combustion cycle. Other oxides of nitrogen may be produced (10, 37) but in much smaller amounts. The aggregate of NO and NO_2 is commonly designated as NO_x. The influence of air-fuel ratio on concentration of NO_x in exhaust gas is shown in figure B-3. The amount of NO produced in the combustion chamber is highly dependent upon the temperature reached in the combustion event.

Newhall and Starkman (27) reported that the measured concentration of NO to the exhaust exceeds the chemical equilibrium value corresponding to the maximum bulk or average temperature of the combustion products. The high concentration of NO can be explained by freezing of local equilibrium concentrations formed at higher temperatures. These equilibrium concentrations must exist in the combustion chamber because no increase in the exhaust concentration of NO was observed when 5,000 ppm of NO was added to the engine air intake system (27).

Exhaust Hydrocarbons

Many exhaust hydrocarbons are formed by pyrolytic reactions, most of which are highly temperature dependent. For example, the bond dissociation energy of the benzylhydrogen is 78 kcal and that of the phenylmethyl bond is 89 kcal (38). In addition to pyrolysis reaction products, some of the hydrocarbons in the exhaust are unburned fuel components.

Combustion of Isooctane

Bradow and Alperstein (8) proposed that the first step in the combustion of isooctane is the loss of hydrogen to a chain carrier X·

$$i\text{-}C_8H_{18} + X\cdot \longrightarrow i\text{-}C_8H_{17}^{\bullet} + HX \tag{B-2}$$

to form any of the possible four isomeric isooctyl radicals. Ninomiya and Golovoy (28) observed a decrease in exhaust isooctane with increase in the equivalence ratio (equivalence ratio=$\varphi=\frac{\text{Actual air-fuel ratio}}{\text{Stoichiometric air-fuel ratio}}$), which indicates that the chain carrier X· is oxygen. As oxygen concentration in the

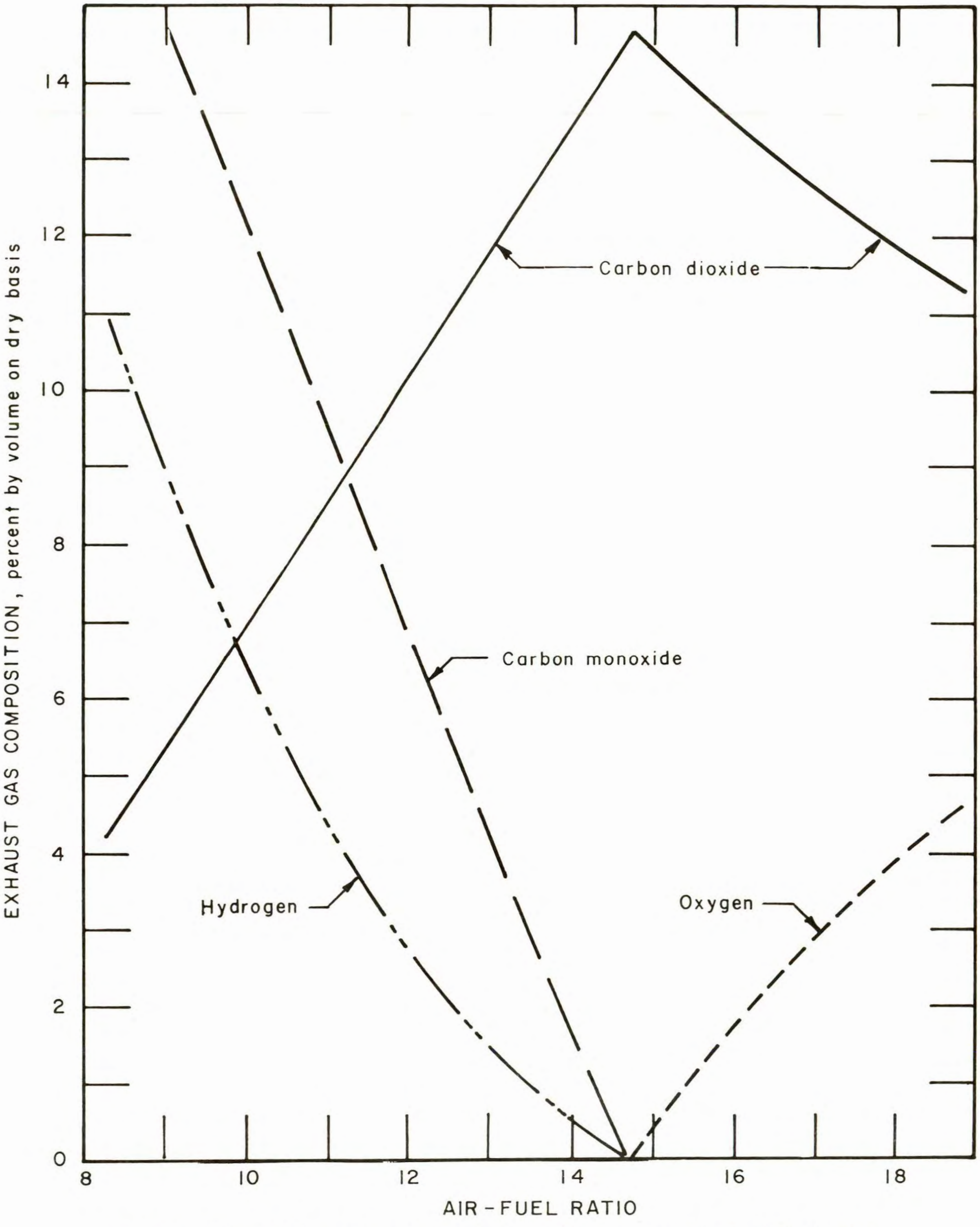


FIGURE B-1. - Relationship of Combustion Products to Air-Fuel Ratio (33).

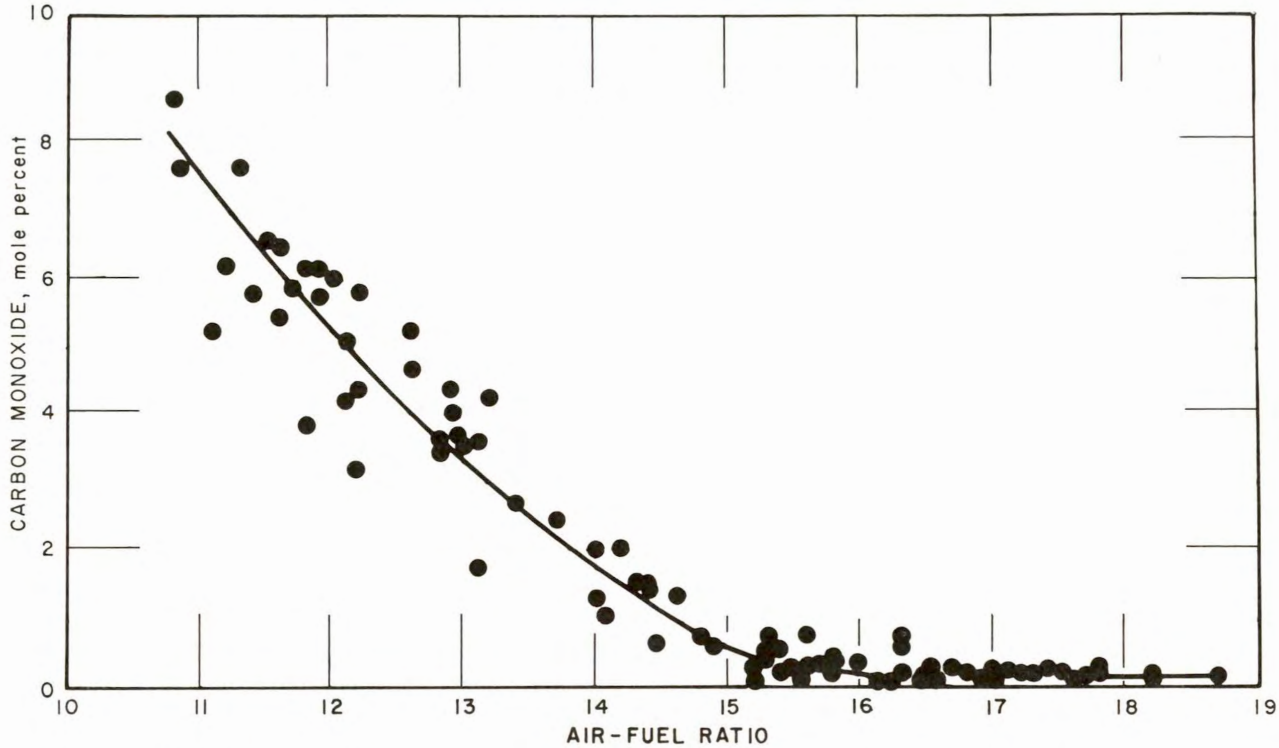
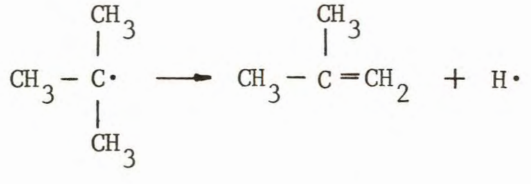


FIGURE B-2. - Effect of Air-Fuel Ratio on Exhaust Gas Carbon Monoxide Concentration (17).

chamber is increased, the conversion of isooctane to isooctyl radicals increases. Isooctyl radicals thus formed fragment to olefins and small alkyl radicals. All the four possible isomeric heptenes are observed in the exhaust (28), and as formation of isooctyl radicals increases, concentrations of heptenes in the exhaust rise with increasing equivalence ratio. Methyl radicals give rise to methane and ethane (28). As oxygen becomes more available, the oxidation of methyl radicals increases; therefore, methane and ethane in the exhaust decrease with increase in equivalence ratio.

Heptenes can undergo thermal cracking to form smaller alkyl and alkyl radicals, which can form C_2 to C_4 olefins by loss of hydrogen atoms:



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C\cdot}} \longrightarrow CH_3-\overset{\displaystyle CH_3}{C}=CH_2 + H\cdot \qquad (B\text{-}3)$$

$$CH_2=CH-\dot{C}H_2 \longrightarrow CH_2=C=CH_2 + H\cdot \qquad (B\text{-}4)$$

Reactions B-3 and B-4 are unimolecular processes with high activation energy and are sensitive to temperature changes but insensitive to oxygen concentrations. The formation of light olefins follows the temperature profile of the combustion chamber, and ethylene, propylene, propadiene, and isobutylene show maxima at an equivalence ratio of 1.0 (28).

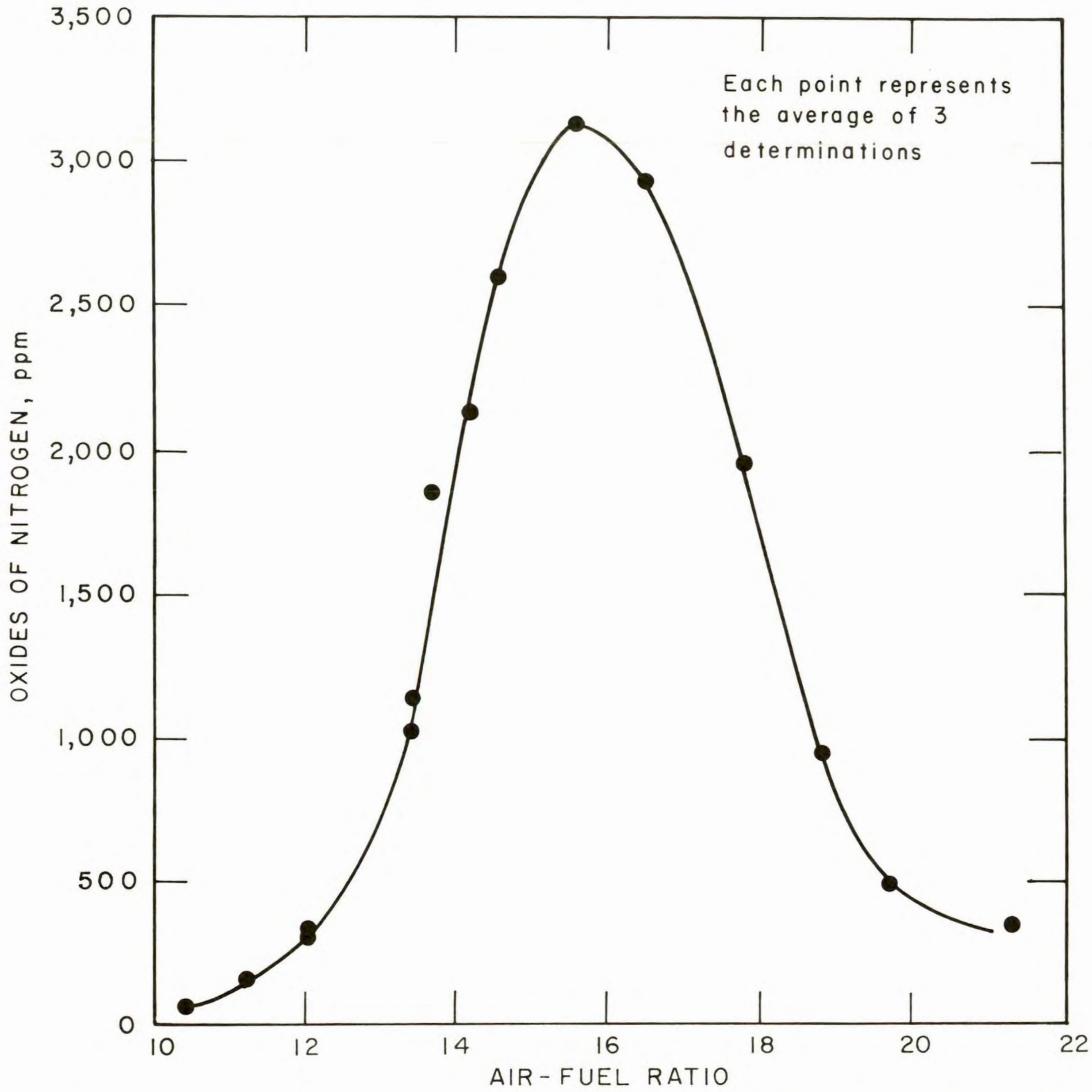


FIGURE B-3. - Influence of Air-Fuel Ratio on Concentration of NO_x in Exhaust Gas (22).

Alkyl radicals can also combine with oxygen to form peroxy radicals leading to aldehydes and ketones. As oxygen availability increases with increasing equivalence ratio, the amount of aldehydes in the exhaust increases (6).

Combustion of Diisobutylene (28)

At temperatures prevailing in the combustion chamber, combustion of diisobutylene is far more efficient than that of isooctane. For example, the fractional mole concentration of unreacted diisobutylene fuel is about 12 times smaller than unreacted isooctane in the exhaust using pure isooctane fuel under the same operating conditions. At an equivalence ratio of 1.05 the diisobutylene emission is about 4 times smaller than that of isooctane.

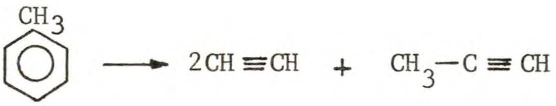
The concentration of isobutylene in the exhaust from diisobutylene at an equivalence ratio of 0.9 was 10^{-2} mole/mole of fuel, as compared to isobutylene produced from isooctane fuel (2×10^{-3} mole/mole of fuel), under the same experimental conditions.

Combustion of Toluene (28)

Toluene probably undergoes three types of competitive reactions, and each one is sensitive in a different way to changes in temperature and concentrations of other radicals, such as H and O atoms present in the combustion chamber. The following three primary decomposition reactions probably occur in the IC engine because they are noted in hot tubes (25) and under slow oxidation conditions (4-5):

(B-5)

(B-6)



(B-7)

All are highly endothermic reactions and are favored by an increase in temperature. When toluene was used as fuel, the decomposition of toluene was favored by an increase in temperature and the rate of decomposition was consistent with the decrease in fractional mole concentration of toluene in the exhaust until a minimum concentration was reached near an equivalence ratio of 1.0. As the temperature in the combustion chamber decreased when the equivalence ratio increased to values greater than 1.0, the amount of toluene increased in the exhaust.

Methane and benzene are formed by the reaction of methyl or phenyl radicals with hydrogen atoms. Benzyl radicals can combine with methyl radicals to yield ethylbenzene. As the higher temperature leads to the formation of more benzyl and methyl radicals, the concentration of ethylbenzene increases. Experiments showed that ethylbenzene concentration was a maximum at an equivalence ratio of 1.0. Further increase in equivalence ratio reduced ethylbenzene in the exhaust.

Combustion of Toluene-n-Heptane Blend (28)

When a mixture of toluene and n-heptane (75 percent toluene and 25 percent n-heptane by volume) was used as fuel, the combustion chamber temperature was observed to be the same as that of toluene. The major effect of the presence of n-heptane was a marked decrease in the fractional mole concentration of unreacted toluene in the exhaust. Evidently alkyl radicals react with toluene to produce alkylated products. The decrease of toluene in the exhaust is consistent with the observed increase of ethylbenzene, styrene, dimethylacetylene, and methane in the exhaust.

Partial Oxidation Products

Relatively little is known about partial oxidation products (18), which include aldehydes, alcohols, esters, ketones, and acid derivatives. They are often found at total concentrations of 50 to 100 ppm in the composite of typical exhaust. Formaldehyde and acetaldehyde are most prominent. Sampling and analytical procedures for these materials are not reliable.

In general, these products are intermediates in the oxidation process and may be associated with incomplete combustion. They appear in abundant quantities in the exhaust from misfiring engines; therefore, malfunctioning automobiles are a source of large quantities of these objectionable materials (21).

APPENDIX C.--DETERMINING CARBON MONOXIDE, CARBON DIOXIDE, AND NITRIC OXIDE IN EXHAUST GAS

Procedures

Standard instruments were used in analyzing exhaust gas samples for carbon monoxide (CO), carbon dioxide (CO_2), and nitric oxide (NO).

Beckman Model IR 315 infrared analyzers were used for CO, CO_2, and NO determinations. The instrument used for CO has an optimum range of 0 to 1 percent CO and uses a sample cell 3/4 in. in length. The CO_2 instrument has a range of 0 to 4 percent using a cell length of 1/8 in. The instrument for NO has an optimum range of 0 to 1,000 ppm NO and uses a 10-in. sample cell and optical filter. The optimum ranges for the infrared instruments provide an accuracy of ±1 percent of full scale or ±0.01 percent CO, ±0.04 percent CO_2, and ±10 ppm NO.

For analysis of exhaust samples, these analyzers were used within their optimum ranges. The instruments were calibrated with standard gases mixed by means of a dynamic flow system. Calibration curves were obtained for each instrument for use in the analysis of exhaust gases in bag samples. The ranges covered were 0 to 0.5 percent CO, 0 to 3 percent CO_2, and 0 to 900 ppm NO.

Before each sample analysis each instrument was zeroed with nitrogen and adjusted to a full-scale reading on its recorder and indicating meter with the appropriate calibration mixture.

Principles of Operation

The Beckman infrared analyzer automatically and continuously determines the concentration of a particular component of interest in a complex gas mixture. The analysis is based on a differential measurement of the absorption of infrared energy. To measure the differential absorption of infrared energy, the instrument uses a double-beam optical system contained in the analyzer section. A simplified functional diagram is shown in figure C-1.

Two infrared sources are used--one for the sample energy-beam, the other for the reference energy-beam. The beams are blocked simultaneously 10 times per second by a chopper (a two-segmented blade rotating at 5 revolutions per second). In the unblocked condition, part A of figure C-1, each beam passes through the associated cell and into the detector.

The sample cell is a flow-through tube that receives a continuous stream of sample. The reference cell is a sealed tube filled with a reference gas. This gas is selected for negligible absorption of infrared energy of those wavelengths absorbed by the sample component of interest.

The detector consists of two sealed compartments separated by a flexible metal diaphragm. Each compartment has an infrared-transmitting window to permit entry of the corresponding energy beam. Both chambers are filled, to the

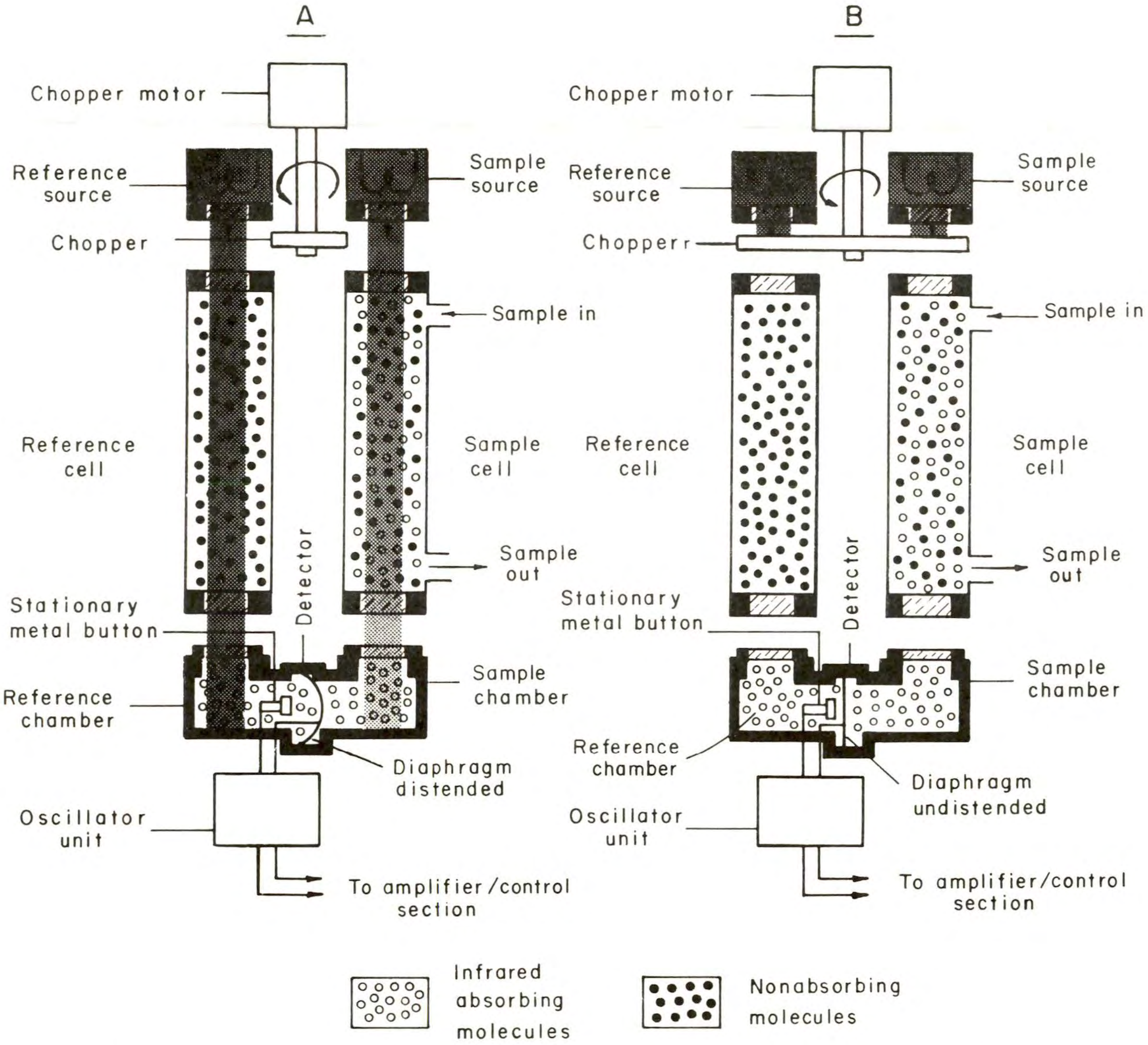


FIGURE C-1. - Functional Diagram of Infrared Analyzer. A, Beams not blocked by chopper pass through cells and into detector. B, Beams blocked by chopper do not reach detector.

same subatmospheric pressure, with the vapor of the component of interest. Use of this substance as the gas charge in the detector causes the instrument to respond only to that portion of net difference in energy due to the presence of the measured component.

In operation, the presence of the infrared-absorbing component of interest in the sample stream causes a difference in energy levels between the sample and reference sides of the system. This differential energy increment undergoes the following sequence of transformations:

1. Radiant energy: In the sample cell, part of the original energy of the sample beam is absorbed by the component of interest. In the reference cell, however, absorption of energy from the reference beam is negligible.

2. Temperature: Inside the detector, each beam heats the gas in the corresponding chamber. Gas in the reference chamber is heated more, however, since energy of the reference beam is greater.

3. Pressure: Higher temperature of gas in the reference chamber raises the pressure of this compartment above that of the sample chamber.

4. Mechanical energy: Gas pressure in the reference chamber distends diaphragm toward sample chamber. The energy increment is thus expended in flexing the diaphragm.

5. Capacitance: The diaphragm and the adjacent stationary metal button constitute a two-plate variable capacitor. Distention of the diaphragm away from the button decreases the capacitance.

When the chopper blocks the beams (as in part B of figure C-1) pressures in the two chambers equalize, and the diaphragm returns to the undistended condition. Therefore, as the chopper alternately blocks and unblocks the beams, the diaphragm pulses, thus cyclically changing detector capacitance. The detector is part of an amplitude modulation circuit that impresses the 10-Hz information signal on a 10-MHz carrier wave provided by a crystal-controlled, radiofrequency oscillator. Additional electronic circuitry in the oscillator unit demodulates and filters the resultant signal, yielding a 10-Hz signal.

The 10-Hz signal enters the amplifier/control section, where it is amplified and then rectified. The resulting dc signal is applied, through the output filter circuit, to the meter and recorder.

The meter reading is a function of the concentration of the component of interest in the sample stream. When the instrument is put into operation, it is adjusted so that a reading of zero, or any desired arbitrary reading, corresponds to a concentration of 0 percent of the component of interest, while a full-scale reading corresponds to the highest concentration in the operating range covered.

APPENDIX D.--NITROGEN DIOXIDE ANALYSIS OF EXHAUST GAS

A Beckman Model 255A ultraviolet analyzer was used to measure the nitrogen dioxide (NO_2) in the exhaust samples. The instrument was calibrated with a standard mixture of 100 ppm NO_2 in nitrogen before the analysis of each exhaust gas sample.

Principles of Operation

The Model 255A ultraviolet analyzer automatically and continuously determines the concentration of NO_2 in a gas mixture. The analysis is based on a differential measurement of the absorption of ultraviolet energy.

To measure the differential absorption of ultraviolet energy, the instrument uses a double-beam optical system contained in the analyzer section. A simplified functional diagram is shown in figure D-1.

A tungsten source lamp directs a beam of near-ultraviolet energy to a splitter for division into two equal beams, one each for the sample and reference cells. On emerging from the splitter the beams are alternately interrupted 10 times per second by a two-lobed rotating chopper blade. Thus, in the condition A of figure D-1, only the reference beam passes through the corresponding cell and arrives at the detector; in condition B, only the sample beam passes through the corresponding cell and arrives at the detector.

The sample cell is a flow-through tube that continuously receives the sample. Presence of the NO_2 in the sample cell results in absorption of energy of characteristic wavelength from the sample beam. The reference cell is a sealed tube filled with a nonabsorbing reference gas. This gas is selected for minimal absorption of near-ultraviolet energy of those wavelengths absorbed by NO_2.

On emerging from the cells, the two beams impinge alternately on the beam-combining mirror assembly, where they are directed through a bandpass color filter and onto a blue-sensitive phototube detector. The phototube receives alternate pulses of optical energy: Half have passed through the sample cell, the other half through the reference cell. The difference between the amounts of energy absorbed from the sample and reference beams during their passage through the associated cells results in generation of a 10-Hz phototube-output signal that is proportional to the concentration of NO_2 in the sample cell. This signal is applied to a two-stage, low-frequency preamplifier.

The preamplifier output signal is routed to an amplifier/control section for further amplification and phase inversion, then back into the analyzer section for synchronous rectification.

The resulting fullwave-rectified signal is returned to the amplifier/control section for filtering and additional conditioning, as required, to drive the meter and recorder.

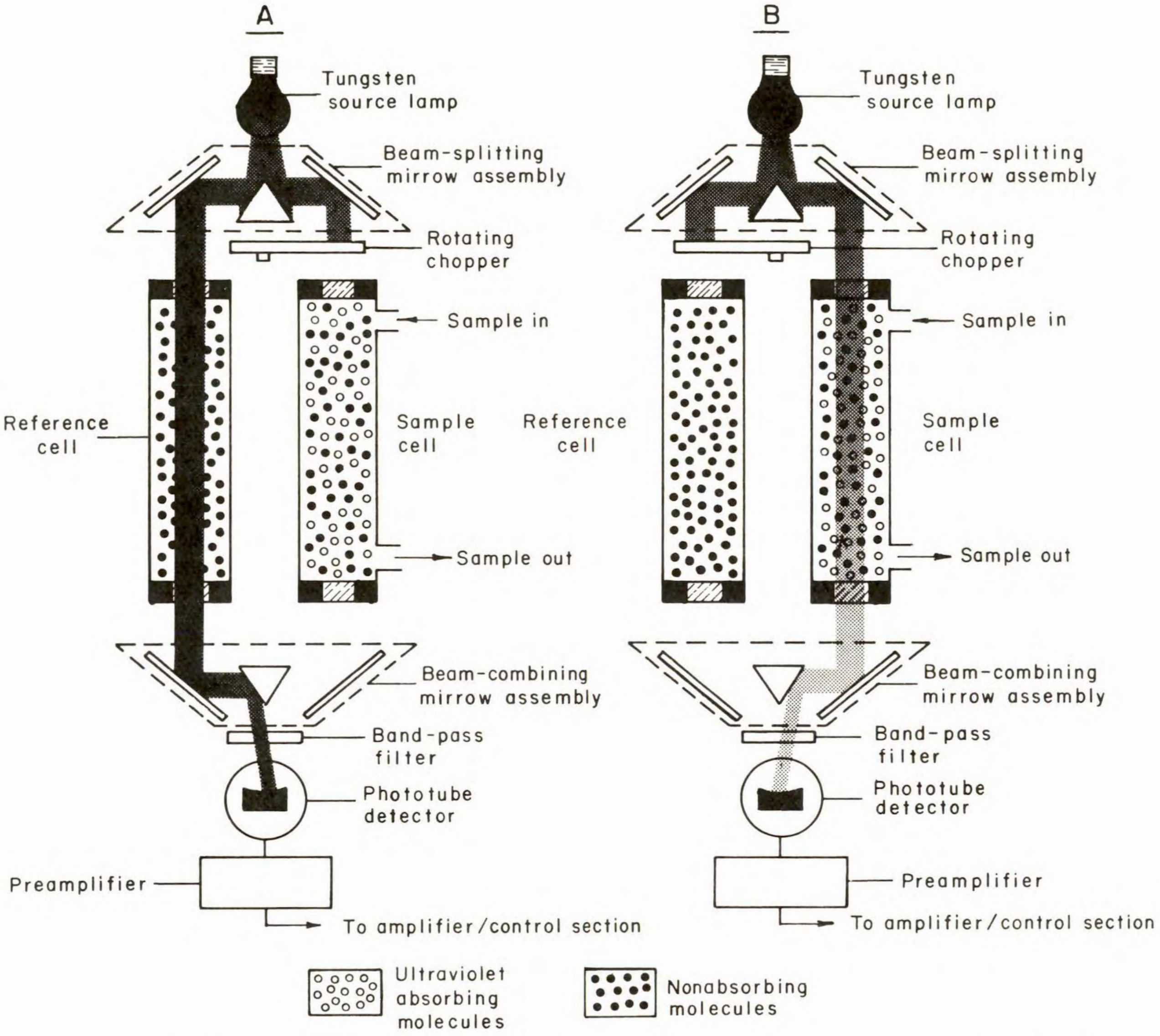


FIGURE D-1. - Functional Diagram of Ultraviolet Analyzer. A, Reference beam not blocked by chopper, passes through reference cell to detector. Sample beam blocked. B, Reference beam blocked. Sample beam not blocked by chopper, passes through sample cell to detector.

The meter reading is a function of the concentration of NO_2 in the sample stream. When the instrument is put into operation, it is adjusted so that a full-scale reading, or any desired arbitrary reading, corresponds to the highest concentration in the operating range.

APPENDIX E.--TOTAL HYDROCARBON ANALYSIS OF EXHAUST GAS

A Beckman Model 109A total hydrocarbon analyzer was used to measure the hydrocarbon content in the exhaust samples. The instrument was calibrated before each measurement using a mixture of 300 ppm of propane in nitrogen. This corresponds to 900 ppmC (parts per million carbon atom). The response of the instrument is linear in terms of ppmC; thus, only one hydrocarbon mixture is necessary for calibration.

Principles of Operation

The Beckman hydrocarbon analyzer automatically and continuously determines the hydrocarbon content of a gas stream. The instrument utilizes the flame-ionization method of detection (FID).

A hydrogen/air or a hydrogen-inert gas/air flame contains an almost negligible number of ions. Introduction of mere traces of hydrocarbons into such a flame, however, produces a large amount of ionization. This effect is the basis of the flame-ionization method of detection.

The sensing unit of the analyzer is the burner assembly--principal components are the manifold, the burner jet, and the collector.

The manifold receives the sample, fuel, and air streams; directs the sample and fuel through the burner jet and into the flame; and supplies the air around the periphery of the flame.

Electrical elements of the burner are the burner jet and the collector. The burner jet is connected to the positive terminal of a 90-v polarizing battery; the collector is connected to the negative terminal. The two polarized electrodes establish an electrostatic field in the vicinity of the flame. The field causes charged particles formed during combustion to migrate. Electrons go to the burner jet; positive ions go to the collector. Thus, a small current flows between the two electrodes.

The current generated by the burner is measured by an electrometer amplifier consisting of a modulator, an ac amplifier, a demodulator, a measuring circuit, and an output-attenuation circuit.

The current from the burner flows through a measuring resistor; this causes a dc voltage to be applied to the modulator. The modulator converts the dc voltage to a 120-Hz ac signal and applies the latter to the amplifier. The resultant amplified signal is converted to dc by the demodulator and is then filtered and applied to the output attenuator and the meter.

The internal flow system delivers sample gas, fuel gas, and air to the burner.

Since injection rate of the gas affects instrument response, the flow system is designed to provide stable flow rates to the specified valves. Each gas is supplied at an adjustable pressure to an associated capillary. From the capillary, the gas flows into the burner.

APPENDIX F.--HIGH-RESOLUTION GAS CHROMATOGRAPHIC ANALYSIS OF EXHAUST GAS

The basic unit of the chromatographic system is a Perkin-Elmer (PE) Model 900 gas chromatograph equipped with a temperature programer and a flame-ionization detector. A schematic diagram of the system is shown in figure F-1. Chromatographic separation of the hydrocarbons is accomplished through parallel use of two columns--a packed column in which the C_1 and C_2 components are resolved, and a high-resolution, open tubular column for separating the C_3 through C_{12} components.

The packed column consists of a 42-in. and a 30-in. section of 1/8-in.-OD Teflon tubing packed with Porapak Q and Porapak T, respectively. The columns were operated at room temperature with nitrogen as a carrier (nitrogen flow rate was 81 ml/min). This nitrogen stream is also used as the auxiliary stream to accelerate the flow of the open tubular column output to the detector.

The open tubular column (purchased from Perkin-Elmer Corp.) is made of 150 ft of 0.010-in.-ID (0.020-in.-OD) stainless steel tubing coated with GE

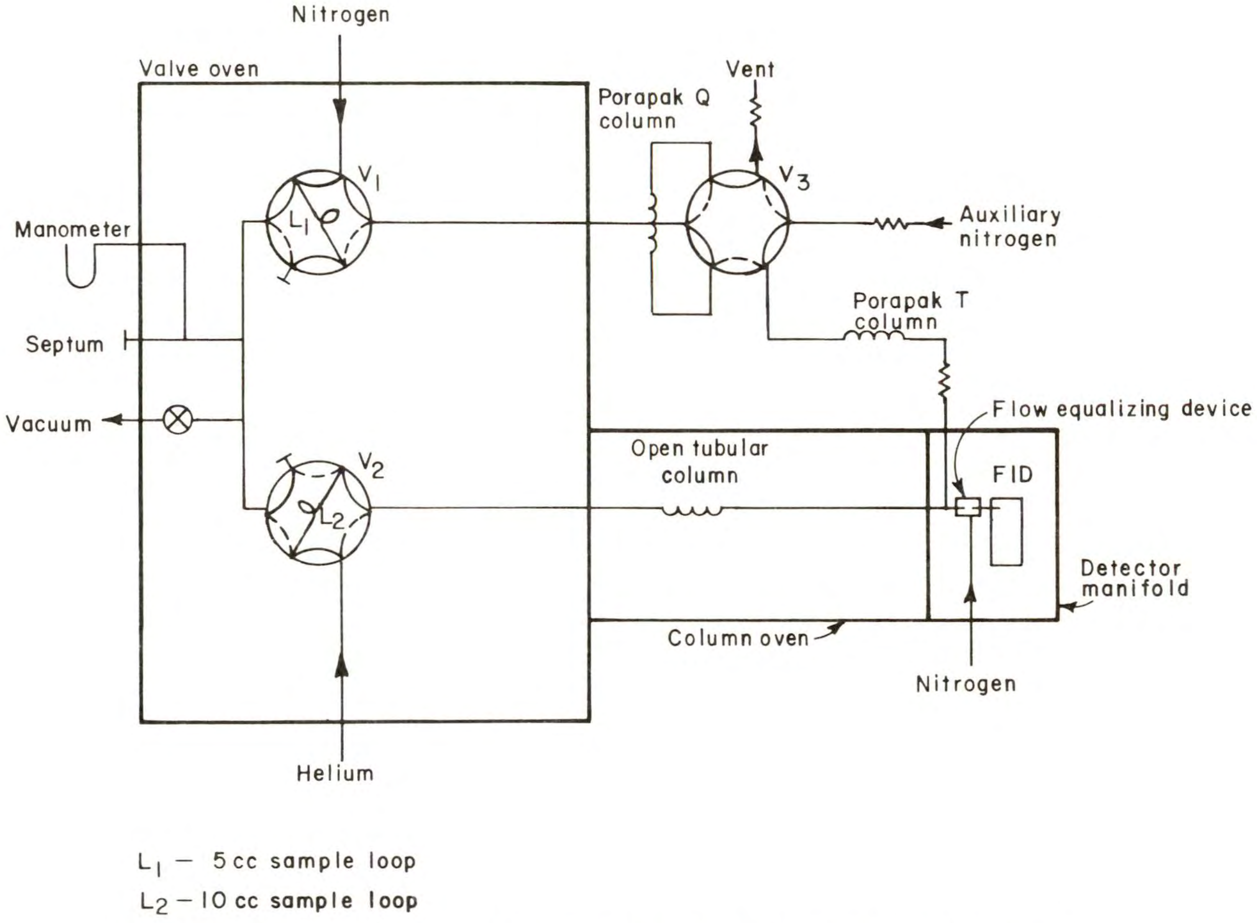
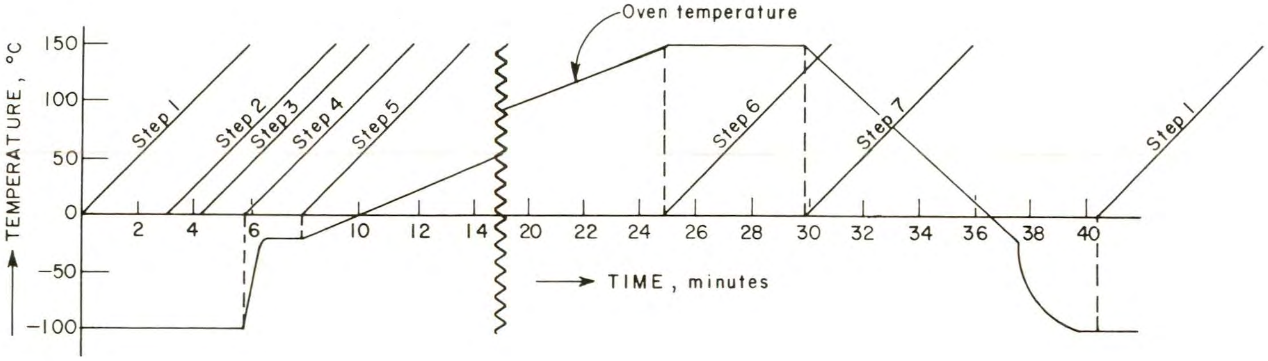


FIGURE F-1. - Chromatographic System for Analysis of Exhaust Hydrocarbons.



Step 1. Inject sample onto Porapak column. Evacuate loop 2. Open tubular column maintained at -100 °C.
Step 2. Backflush Porapak column.
Step 3. Inject sample into open tubular column. Evacuate loop 1.
Step 4. Raise oven temperature to −20°C.
Step 5. Start temperature program.
Step 6. Switch to isothermal operation at 150 °C.
Step 7. Run terminated. Automatic cooldown to −100 °C.

FIGURE F-2. - Oven Temperature Schedule and Sequence of Operations.

Versilube F-50. Temperature is programed from -100° to 135° C. The carrier is helium at a flow rate of 8.8 ml/min. An auxiliary carrier (nitrogen at 81 ml/min) is introduced at the column output to reduce residence time and increase purge effectiveness in the detector and its associated plumbing.

The sample-injection system uses two air-actuated sampling valves, each carrying a calibrated loop. The loops (5 and 10 cm^3 capacity each) are filled with sample after previous evacuation. The entire sample-injection system is enclosed in a valve oven maintained at 60° C. For analysis, the two sample loops are first charged with sample and subsequently discharged at different times into the respective carrier streams of the two columns. To enable a single detector to be used, injections to the respective columns are timed such that the C_1 and C_2 compounds will have been eluded from the first column and detected prior to emergence of sample from the second column. Subambient temperatures in the oven are attained by liquid nitrogen injection controlled by the PE-900 program controller modified to extend its use to lower subambient temperatures.[1] The temperature variation in the open tubular column oven during a complete analysis is illustrated in figure F-2. This figure also depicts the sequence for the various operation steps involved in the course of a complete analysis.

Output from the detector-electrometer is recorded on an Infotronics Model 40 tape recorder. The data subsequently are recovered in playback through a high-speed electronic integrator (Infotronics Model CRS-11 HSB/40) from which integrated area data for the individual peaks are obtained on a printout tape.

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[1] The unmodified temperature programer operates in the range -75° to 400° C. By installing a switch and a 5K-10 turnpot in series with R2003, the lower limit of the programer's temperature range can be extended to approximately -120° C. (See circuitry schematic included in Instruction Manual for PE Model 900.)

The performance of the system can be summarized briefly as follows:

a. Exhaust chromatograms showing in excess of 180 resolved peaks have been obtained. Application of subtractive techniques showed that relatively few peaks represented unresolved mixture of saturated and unsaturated hydrocarbon components.

b. Under the described operating conditions, the lowest detection limit of the method is 0.01 ppmC.

c. Total analysis time is 40 min.

APPENDIX G.--DETERMINATION OF TOTAL ALDEHYDES AND FORMALDEHYDE IN EXHAUST GAS

Total Aldehydes

Total aldehydes in the exhaust were determined by the MBTH (3-methyl-2-benzothioazolone hydrazone hydrochloride) method. The procedure was essentially the same as that prescribed by Sawicki and coworkers (35)[1] for atmospheric samples.

The procedure was to pass gaseous sample through a train of three bubblers connected in series. The bubblers contained 15 ml, 10 ml, and 25 ml of 0.4 percent MBTH reagent solution, respectively. Following absorption, the contents of the first and second bubblers were transferred into a 250-ml volumetric flask and were allowed to stand for 1 hour. The content of the third bubbler was similarly treated in a separate 250-ml volumetric flask. At the end of the 1-hour reaction period, 25 ml of 1 percent ferric chloride solution was added to each volumetric flask and the mixtures were allowed to react for 40 minutes. Acetone was then added to each flask to a final volume of 250 ml and optical densities were measured (against a blank) with a Spectronic 20 spectrophotometer.

The MBTH method was calibrated with standard liquid and gaseous aldehyde mixtures. Propionaldehyde/ethanol mixtures were prepared by mixing redistilled aldehyde with ethanol at volume ratios of 1:100 and 1:10,000. The calibration was made with liquid samples consisting of 0 to 0.5 ml of the 1:10,000 mixture and also with vaporized 0 to 0.5 ml samples of the 1:100 mixture in nitrogen.

Formaldehyde

The method used for determination of formaldehyde in exhaust samples was the chromotropic acid procedure. The method is similar to that described by Altshuller and coworkers (2).

The procedure involves passing exhaust sample through a bubbler containing absorbing solution. The absorbing liquid in the bubbler consists of 10 ml of distilled water. After passing 4.2 liters of sample through the bubbler, 2 ml of the absorbing solution are mixed with 1 ml of 10 percent (by weight) chromotropic acid solution and 20 ml of concentrated H_2SO_4. The mixture is immersed for 10 minutes in a water bath kept at about 95° C. The content is then cooled to room temperature and the optical density is measured against a blank with a Spectronic 20 spectrophotometer.

The method is calibrated using both gaseous formaldehyde blends and aqueous formaldehyde blends.

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[1] Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

APPENDIX H.--DETERMINATION OF HYDROGEN IN EXHAUST GAS

A gas chromatograph was used for the determination of hydrogen in the exhaust samples.

The separation of hydrogen from other gases in the exhaust is accomplished in a column of molecular sieve operated at 0° C using nitrogen as the carrier gas. The detector is a thermal conductivity cell.

The detector and column are maintained at 0° C by immersion in an ice-water bath.

The sample introduction system includes a six-port rotary valve with Teflon rotor equipped with a 5-ml sample loop.

The chromatograph was calibrated with a mixture of 0.1 percent hydrogen in nitrogen. It has been shown that peak height measurements are a linear function of hydrogen concentration for the range of 0 to 0.1 percent hydrogen.

APPENDIX I.--DERIVATION OF THE EQUATION TO CALCULATE ENGINE THROTTLE POSITION

Engine throttle position defined in this report is

$$\text{throttle position (percent)} = \frac{(\dot{m}_A)_a}{(\dot{m}_A)_t} \times 100 \qquad \text{(I-1)}$$

where

$(\dot{m}_A)_a$ = the actual measured engine air consumption rate in lbm/min and

$(\dot{m}_A)_t$ = the maximum possible inlet mixture consumption rate for the operating inlet temperature and engine speed.

Assumption: Inlet mixture is an ideal gas.

The ideal gas equation is

$$PV = \frac{mRT}{M} \qquad \text{(I-2)}$$

where

P = pressure (lb/ft^2, abs)

V = volume (ft^3)

m = mass (lbm)

R = universal gas constant

T = absolute temperature of inlet mixture (° R)

M = molecular weight of inlet mixture

Solving for m,

$$m = \frac{PVM}{RT}$$

If V is considered to be the displacement volume of the engine and P is the atmospheric pressure, then the mass flow rate is

$$\dot{m}_A = \frac{PVM}{RT} \times \text{(number of intake strokes per unit time)} \qquad \text{(I-3)}$$

For a 4-cycle engine the number of intake strokes per minute = rpm/2 then

$$(\dot{m}_A)_t = \frac{PVM}{RT} \times \left[\frac{\text{rpm}}{2}\right] \qquad \text{(I-4)}$$

where

$(\dot{m}_A)_t$ = maximum theoretical flow rate (that is, with no pressure drop in inlet system) of inlet mixture (lbm/min)

P = atmospheric pressure lb/ft^2 (abs)

V = engine displacement volume (ft^3)

M = molecular weight of inlet mixture

rpm = engine speed (rpm)

R = universal gas constant $\left(1545 \frac{\text{ft-lb}}{\text{lbm-mole-}^\circ\text{R}}\right)$

T = absolute temperature of inlet mixture (° R)

Substituting equation I-4 into equation I-1, the result is

$$\text{throttle position (percent)} = \frac{2(\dot{m}_A)_a RT}{PVM\,[rpm]} \times 100 \qquad \text{(I-5)}$$

In the above definition of throttle position, the total inlet system is the effective throttle. This includes the airflow meter, inlet piping, throttle valve, and the intake valve. Thus, 100 percent throttle (by this definition) cannot be achieved in the real engine.

APPENDIX J.--METHOD OF CALCULATING EXHAUST EMISSION DATA

The exhaust gas samples were analyzed for various components. The instruments used for analysis give concentration values in either percent, ppm, or ppmC by volume. Those components expressed in terms of ppm or ppmC can be converted to percent by volume by multiplying by 10^{-4}.

Since each fuel used in the experiment has the formula C_8H_y, the general combustion equation would be

$$\begin{aligned} ZC_8H_y + W[O_2 + 3.764N_2] \longrightarrow\ & X_1CO + X_2CO_2 + X_3[HC]_t \\ & + X_4O_2 + X_5H_2O + \ldots \\ & + X_nN_2 \end{aligned} \qquad \text{(J-1)}$$

where

$$X_1 + X_2 + X_3 + \ldots + X_i + \ldots + X_n = 100$$

X_i = concentration of the ith exhaust product in terms of percent by volume

X_3 = concentration of total hydrocarbon measured by FID in terms of percent by volume (carbon atom)

Z = number of moles of fuel required to produce 100 moles of exhaust

W = number of moles of air used with the Z moles of fuel to produce 100 moles of exhaust gas.

The 3.764 value is the number of moles of "apparent nitrogen" per mole of oxygen in air. The term "apparent nitrogen" refers to the entire group of inert gases in the atmosphere and therefore the molecular weight of 28.161 is used rather than the value, 28.016 for pure nitrogen.

Taking a carbon balance for equation J-1 above,

$$8Z = X_1 + X_2 + X_3 \qquad \text{(J-2)}$$

Since all the carbon in the exhaust is contained in CO, CO_2, and unburned hydrocarbon, only the first three terms are considered in a carbon balance. Since Z moles of fuel produces 100 moles of exhaust, then the concentration value of each exhaust component is equivalent to the mole fraction of each component. Therefore, for any component i, it takes Z moles of fuel to produce X_i moles of exhaust product. Thus X_i/Z represents the number of moles of exhaust component i per mole of fuel input to the engine.

Solving for Z in equation J-2,

$$Z = \frac{X_1 + X_2 + X_3}{8} \qquad (J-3)$$

The number of moles of exhaust product per mole of fuel input to the engine is as follows:

$$\frac{8X_i}{X_1 + X_2 + X_3}$$

where

X_i = measured concentration of any component i in the exhaust (percent by volume)

X_1 = measured concentration of CO in the exhaust (percent by volume)

X_2 = measured concentration of CO_2 in the exhaust (percent by volume)

X_3 = measured concentration of total hydrocarbon $[HC]_t$ by FID expressed as C_1 (percent by volume).

It should be noted that when a fuel mixture of $C_8H_{y_1}$ and $C_8H_{y_2}$ is used, one mole of fuel is defined as:

$$N_1 \, [C_8H_{y_1}] + N_2 \, [C_8H_{y_2}]$$

where

$N_1 + N_2 = 1$

N_1 = mole fraction of component 1

N_2 = mole fraction of component 2.