

**FUEL COMPONENT EFFECTS ON HYDROCARBON  
EMISSIONS FROM A SPARK-IGNITION ENGINE**

by

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# FUEL COMPONENT EFFECTS ON HYDROCARBON EMISSIONS FROM A SPARK-IGNITION ENGINE

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Submitted to the Department of Mechanical Engineering on April 24, 1998  
in partial fulfillment of the requirements for the Degree of  
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## ABSTRACT

A fuel component perturbation experiment was performed in order to determine the sensitivity of the engine-out emission levels of two olefins, 2-methylpropene (2MP) and 1,3-butadiene, to selected fuel components. In this experiment, a base fuel was perturbed with the following four major fuel components: MTBE, toluene, m,p-xylene, and iso-octane. For each of these components, new fuel mixtures were blended by increasing the percent volume of that particular component by three different increments. A spark-ignition engine was run at steady-state using these different fuel blends plus a baseline fuel with no perturbation. Samples were collected and analyzed using gas chromatography methods. Different hydrocarbon exhaust species were identified and quantified, and trends in any of these species were noted.

The final results do indicate increasing trends in 2MP from the MTBE- and iso-octane- perturbed fuel blends. The sensitivity factor for the fuel MTBE/exhaust 2MP relationship was found to be approximately  $3.582 \times 10^{-5} \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol MTBE})$  using normalized data and  $3.598 \times 10^{-5} \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol MTBE})$  using data corrected by an offset factor. For the iso-octane fuel mixture, the sensitivity was  $3.287 \times 10^{-5} \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol iso-oct})$  using normalized data and  $3.500 \times 10^{-5} \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol iso-oct})$  using data corrected by an offset factor. Perturbing the fuel with the aromatics did not have any noticeable effects on the exhaust hydrocarbon species. However, the exhaust samples from these fuel blends were also used in determining the MTBE and iso-octane sensitivities. By increasing the aromatic percent volumes, the percent volumes of MTBE and iso-octane in the fuel mixtures decreased. Neither MTBE, toluene, m,p-xylene, nor iso-octane had any noticeable effect on the levels of 1,3-butadiene in the exhaust.

Thesis Advisor: Professor Wai K. Cheng  
Associate Professor of Mechanical Engineering



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## TABLE OF CONTENTS

ABSTRACT .....	3
ACKNOWLEDGMENTS .....	5
TABLE OF CONTENTS .....	7
LIST OF FIGURES .....	9
LIST OF TABLES.....	11
CHAPTER 1: INTRODUCTION.....	13
1.1 Background .....	13
1.2 Typical Spark-Ignition Engine Emissions .....	14
1.3 The Auto/Oil Air Quality Improvement Research Program .....	15
1.4 The Importance of 1,3-Butadiene Emissions.....	18
1.5 Objectives.....	18
CHAPTER 2: SELECTION OF FUEL COMPONENTS TO BE PERTURBED.....	21
2.1 Auto/Oil Study.....	21
2.2 General Effect of Aromatics, MTBE, and Olefins in Fuel.....	21
2.3 Fuel Effects on 1,3-Butadiene Exhaust Emissions.....	22
2.4 Fuel Components to be Perturbed.....	23
CHAPTER 3: EXPERIMENTAL DESIGN AND PROCEDURE.....	25
3.1 Engine Specifications and Operating Parameters .....	25
3.2 Fuel Specifications .....	27
3.3 Fuel Perturbations.....	27
3.4 Fuel System .....	28
3.5 Exhaust Gas Sampling Unit.....	30
CHAPTER 4: HYDROCARBON ANALYSIS PROCEDURE .....	35
4.1 Gas Chromatography using a Flame Ionization Detector .....	35
4.1.1 Flame Ionization Detector .....	35
4.1.2 Calibration of the GC Analyzer .....	36
4.2 Identification of Species .....	37
4.3 Calculation of Species Concentration.....	38
4.4 Hydrocarbon Analyzer .....	38
4.5 Uncertainty Analysis.....	39

CHAPTER 5: ANALYSIS OF GAS CHROMATOGRAPH DATA.....	41
5.1 Sensitivity of the Exhaust Fuel Species .....	41
5.2 Trends in 2-Methylpropene .....	44
5.3 Trends in 1,3-Butadiene .....	50
CHAPTER 6: PRODUCT FORMATION CHEMISTRY .....	53
6.1 2-Methylpropene from MTBE.....	53
6.2 2-Methylpropene from Iso-octane .....	54
CHAPTER 7: SUMMARY AND CONCLUSIONS .....	57
REFERENCES .....	59
APPENDIX A: COMPOSITION OF FUELS USED IN AUTO/OIL .....	61
APPENDIX B: FUEL SPECIFICATIONS .....	63
APPENDIX C: EXHAUST SAMPLE PROPERTIES .....	65
APPENDIX D: PERCENT VOLUMES AND NEW HC INDICES .....	71



## LIST OF FIGURES

Figure 1.1	Paraffin exhaust levels versus paraffin % weight in fuel. ....	16
Figure 1.2	Aromatic exhaust levels versus aromatic % weight in fuel. ....	17
Figure 1.3	Olefin exhaust levels versus olefin % weight in fuel. ....	17
Figure 3.1	Removable Pump/Filter/Fuel System. ....	29
Figure 3.2	Single cylinder of exhaust gas sampling unit. ....	31
Figure 3.3	Components for measuring the pressure of exhaust gas and diluting the sample. ....	32
Figure 5.1	MTBE sensitivity. ....	42
Figure 5.2	Toluene sensitivity. ....	43
Figure 5.3	m,p-Xylene sensitivity. ....	43
Figure 5.4	Iso-octane sensitivity. ....	44
Figure 5.5	2-Methylpropene exhaust concentrations versus % volume MTBE in fuel. ....	45
Figure 5.6	2-Methylpropene exhaust concentrations versus % volume iso-octane in fuel. ....	45
Figure 5.7	2-Methylpropene exhaust concentrations versus % volume toluene in fuel. ....	46
Figure 5.8	2-Methylpropene exhaust concentrations versus % volume m,p-xylene in fuel. ....	47
Figure 5.9	Calculated 2MP HC Index vs. Normalized Measured 2MP HC Index. ....	49
Figure 5.10	Calculated 2MP HC Index vs. Offset Measured 2MP HC Index. ....	49
Figure 5.11	1,3-Butadiene exhaust concentrations versus % volume MTBE in fuel. ....	51
Figure 5.12	1,3-Butadiene exhaust concentrations versus the % volume toluene in fuel. ....	51
Figure 5.13	1,3-Butadiene exhaust concentrations versus the % volume m,p-xylene in fuel. ....	52
Figure 5.14	1,3-Butadiene exhaust concentrations versus the % volume iso-octane in fuel. ....	52



## LIST OF TABLES

Table 1.1	Hydrocarbon composition of spark-ignition engine exhaust. ....	15
Table 2.1	Main effects of changes in fuel variable on mass exhaust emissions.....	22
Table 3.1	Summary of engine specifications and operating parameters. ....	25
Table 3.2	Major fuel components of California Phase II Certification gasoline. ....	27
Table 3.3	Different mixtures and their perturbation % volumes.....	28
Table 4.1	Jensen <i>et al.</i> 's Method 2 used to separate C <sub>4</sub> -C <sub>12</sub> hydrocarbons.....	35
Table 4.2	Comparison of total HC concentrations for different fuel mixtures. ....	39
Table 4.3	Exhaust species standard deviations and total uncertainties in concentration .....	40
	measurements.	
Table 5.1	Equations for different fuel mixtures: % weight of component in fuel vs. HC.....	41
	index of the component in the exhaust.	
Table A.1	Composition of fuels used in Auto/Oil study.....	61
Table C.1	MTBE-perturbed fuel mixture.....	65
Table C.2	Toluene-perturbed fuel mixture.....	66
Table C.3	m,p-Xylene-perturbed fuel mixture. ....	67
Table C.4	Iso-octane-perturbed fuel mixture. ....	69
Table D.1	Percent volumes and new HC Indices .....	71



# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Air pollution has been a serious problem since the onset of the Industrial Revolution, though the causes and the constituents of today's air pollution versus those in the late 1800's are extremely different. Most of today's air pollution consists of carbon monoxide (CO), hydrocarbons (HC), oxides of nitrogen (NO<sub>x</sub>), sulfur oxides, particulate matter (PM), and lead [1]. Certain HCs are critical because they cause serious environmental and health problems. The EPA has identified the following HCs as toxic: benzene, 1,3-butadiene, formaldehyde, and acetaldehyde [2]. Toxic air pollutants from vehicle emissions contribute significantly to the elevated cancer risks in urban centers - up to more than one in 1,000 over a 70-year lifetime of exposure [3]. In certain areas of the United States, over 50% of the public's total exposure to toxic air contaminants comes from benzene and 1,3-butadiene found in automobile exhaust [4]. Hence, vehicle emissions constitute serious health concerns.

In addition to being toxic, hydrocarbons can react with NO<sub>x</sub> in the presence of sunlight to form ozone, the primary ingredient for smog. Ozone is a criteria pollutant which is defined by the Clean Air Act (CAA) as an air pollutant "which causes or contributes to air pollution which may reasonably be anticipated to endanger public health or welfare," and "[whose] presence ... in the ambient air results from numerous or diverse mobile or stationary sources" [5]. The most common health-related problem due to ozone is a decrease in pulmonary and/or respiratory function in individuals which can result in chronic asthma or emphysema. This is because ozone reacts rapidly with bio-organic compounds containing double bonds, many of which are functionally and structurally essential [6]. Smog affects general public welfare in the form of limited visibility, damaged architectural structures and art forms, and injured vegetation. These negative effects clearly illustrate the need to reduce the level of ozone precursors emitted into the air.

In 1990, 33% of all the hydrocarbon emissions came from combustion processes of mobile sources [7]. Because of this significant amount, stringent regulations have been developed to control HC emissions from automobiles. HC emissions come from gasoline components which vaporize from the fuel or are formed as products of incomplete combustion within the internal combustion engine. Thus, the Clean Air Act regulates automobile emissions, mandates cleaner gasoline, and requires the use of clean-fueled vehicles in some of the nation's most polluted cities.

A significant portion of HC emissions from the automobile engine are captured and oxidized by the catalytic converter. At high temperatures, the catalyst's efficiency can reach up to 99% for hydrocarbons [8]. However, the catalyst needs to be warmed up to above 250°C to be effective. This and other limitations on the catalysts motivate scientists and researchers to develop new techniques to reduce the amount of escaping HC emissions before the catalyst is warmed up fully. Therefore, the identification and quantification of engine-out (i.e. before the catalyst) or raw emissions are of particular interest in research studies. The findings elucidate the chemical reactions that occur and the pathways that different compounds follow from the initial fuel input to the final hydrocarbon emissions. Understanding these processes is essential for controlling pollutant levels. The focus of this thesis is the analysis of the fuel component effects on hydrocarbon emissions to determine which components in the fuel produce specific HC emissions.

## **1.2 Typical Spark-Ignition Engine Emissions**

A spark-ignition engine operating under normal steady-state conditions will yield engine-out HC emissions in the range of 1,000 to 3,000 ppmC1 (i.e. mole fraction of HC multiplied by the number of carbon atoms per HC molecule). This is approximately 1% to 2.5% of the fuel flow into the engine. These HC emissions are caused by the following processes: flame quenching at the combustion chamber walls, unburned mixture filling and emptying crevice volumes and escaping the combustion process, absorption of fuel vapor into oil layers and desorption during expansion and exhaust strokes, and poor combustion quality. The poor combustion quality occurs when the A/F ratio, EGR, and spark timing result in an environment not favorable to flame propagation. For example, if the mixture is too rich, HC emissions

increase due to the increase in unreacted or partially reacted fuel. However, HC emissions can also increase due to very lean mixtures which cause incomplete combustion or misfiring during the engine's operating cycles [8].

Engine exhaust gases contain a wide variety of hydrocarbon emissions due to incomplete combustion. Table 1.1 lists an average breakdown of emissions by class of the hydrocarbons from a spark-ignition engine with and without a catalytic converter:

Table 1.1. Hydrocarbon composition of spark-ignition engine exhaust.

	Percent of total HC			
	Paraffins	Olefins	Acetylene	Aromatics
Without catalyst	33	27	8	32
With catalyst	57	15	2	26

Some of these hydrocarbon emissions are relatively unreactive and do not participate significantly in the formation of smog. Others are major components in smog-forming chemistry. Fuel composition plays a major role in exhaust emission composition. Fuels with high aromatic and/or olefin levels result in higher concentrations of hydrocarbons that react in the photochemical smog reactions. Many of these organic compounds found in the exhaust are not initially in the fuel, which means significant pyrolysis and synthesis of different compounds take place during the combustion process [8].

### 1.3 The Auto/Oil Air Quality Improvement Research Program (Auto/Oil or AQIRP)

The Auto/Oil Air Quality Improvement Research Program (Auto/Oil) is a cooperative program initiated by automotive and petroleum companies. Its objective is to conduct research to generate data on the potential reductions in vehicle emissions and improvements in air quality by testing reformulated gasoline, various alternative fuels, and developments in automotive technology. The objective of the current study - to examine the fuel component effects on non-fuel olefin emissions - was motivated by the results of the Auto/Oil Program and attempts to explain the Auto/Oil vehicle test data through detailed laboratory scale/engine/dynamometer experiments. The Auto/Oil data pertinent to the current study are summarized in the following paragraphs.

Phase I of this program examined total vehicle emissions from two fleets of vehicles using reformulated gasolines with varying paraffin, aromatic, olefin, oxygenate, and sulfur contents. Twenty-six gasoline formulations were used on thirty-four different vehicles [9]. The emissions data were analyzed to determine any general effects of fuel composition on mass emissions of hydrocarbons. The results indicated that the majority of paraffinic and aromatic exhaust species were actually “feed-through” or unreacted parts of the fuel. Figures 1.1 and 1.2 are graphs of the Auto/Oil data that illustrate the linear relationship and zero-intercept at the y-axis which supports the feed-through conclusion [10]. The offsets for the smaller paraffins, such as methane and ethane, and for benzene suggest that these particular HCs are also products of incomplete combustion. However, data for the unsaturated HCs indicate that ethene, ethyne, propene, 1,3-butadiene, and 2-methylpropene are olefin compounds in the exhaust that are not initially in the fuel. Therefore, they must be products of incomplete combustion. Figure 1.3 shows the olefin emission levels as a function of the amount of that component found in the fuel or if the component is not found in the fuel, then the concentration levels are simply indicated along the y-axis.

Figure 1.1. Paraffin exhaust levels versus paraffin % weight in fuel.

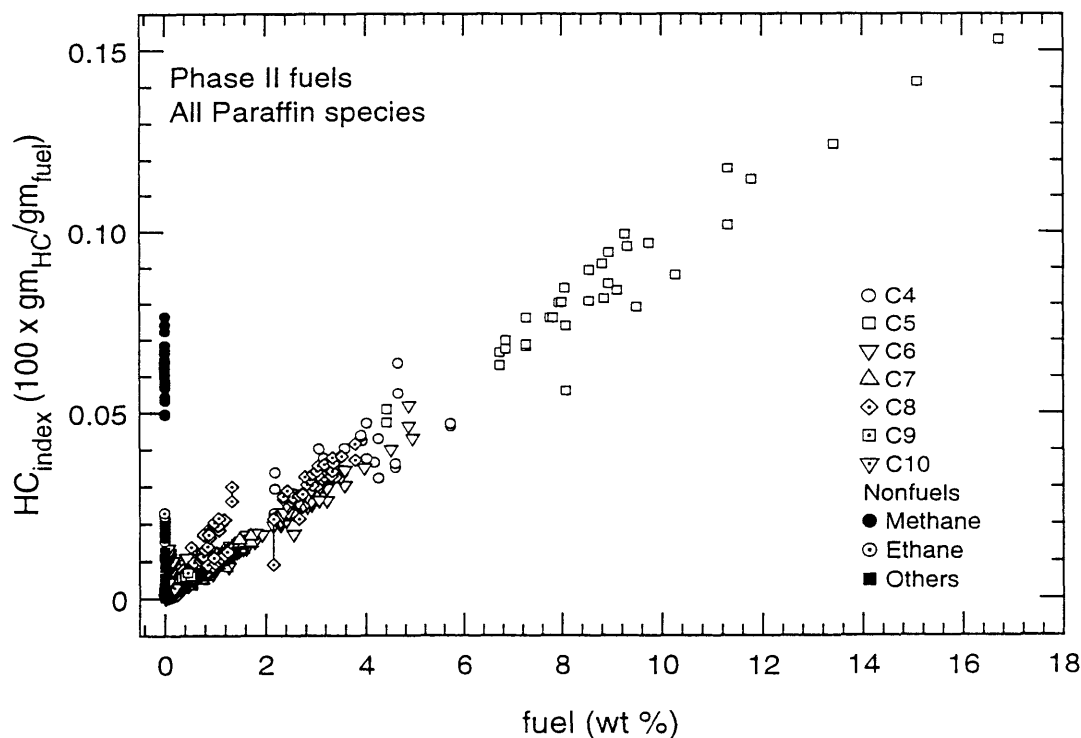




Figure 1.2. Aromatic exhaust levels versus aromatic % weight in fuel.

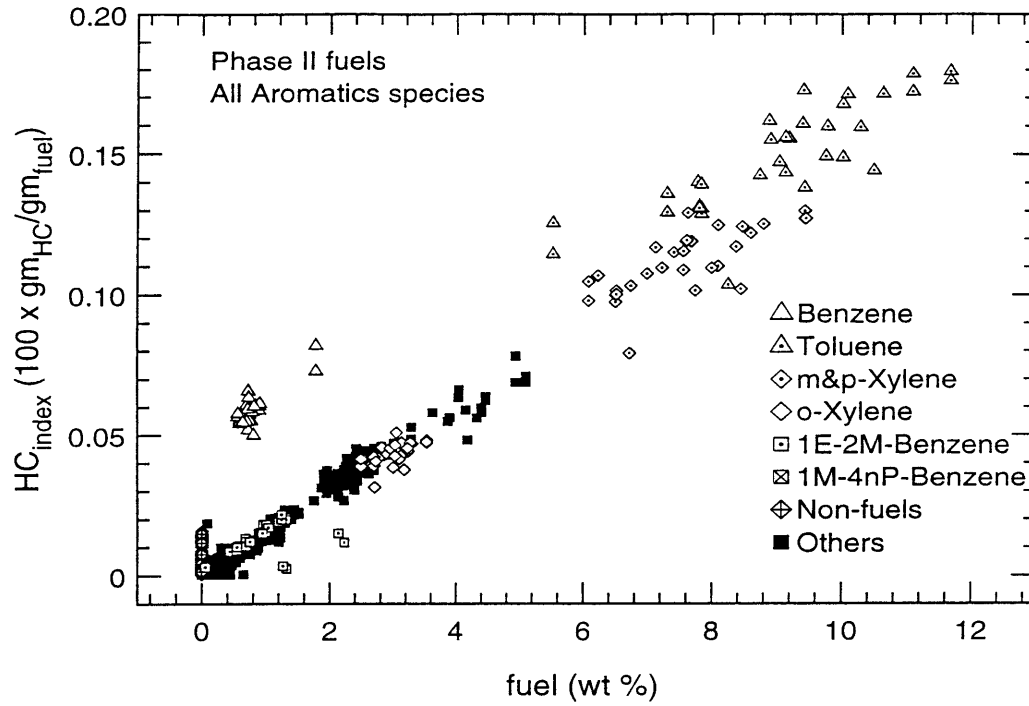
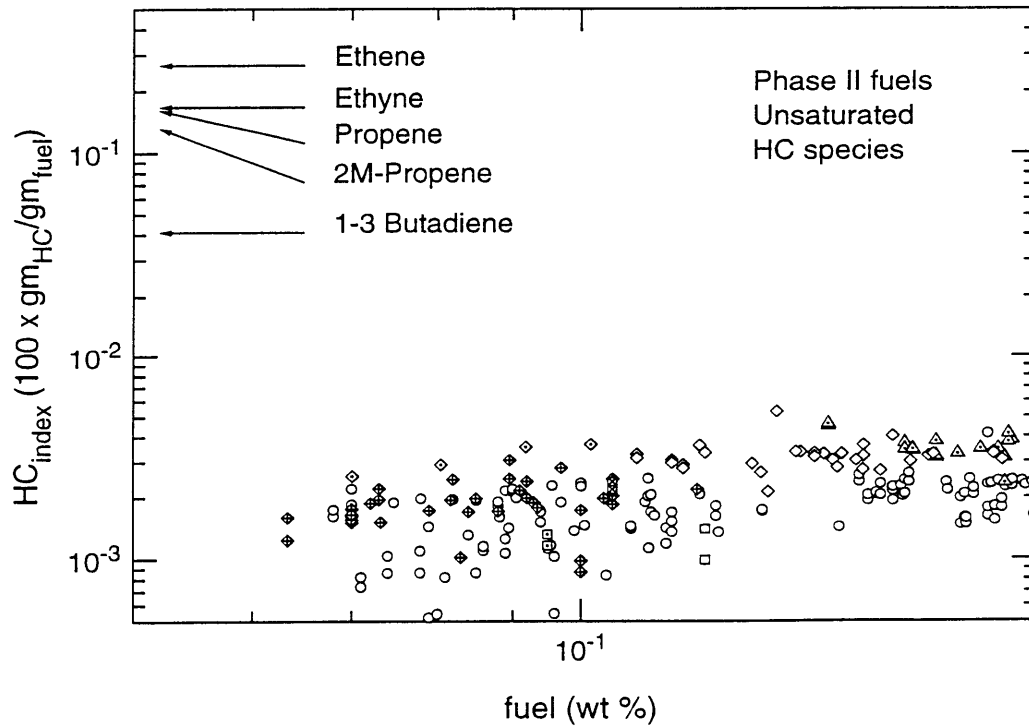


Figure 1.3. Olefin exhaust levels versus olefin % weight in fuel.



The Auto/Oil data also indicate that about 29% of the total HC emissions are olefin emissions. This corresponds closely with the 27% for olefins in Table 1.1. Olefins are especially important because they have especially high ozone-forming potentials, ranging from 5.3 to 10.9 g<sub>ozone</sub>/g<sub>HC</sub> [11]. The smaller unsaturated compounds, ethene, ethyne, and propene, can be formed from many different fuel components and through many different pathways as a result of partial oxidation. It is difficult to relate them to any one specific fuel specie. Therefore, the focus of this project is to study the fuel component effects on the next most abundant engine-out exhaust olefins: 2-methylpropene and 1,3-butadiene, the latter being both a significant and toxic emittant.

#### **1.4 The Importance of 1,3-Butadiene Emissions**

In terms of mass, the total toxic emissions are generally dominated by benzene. However, weighting the mass emission rates by the relative risk factors used by the EPA or the California Air Resources Board considerably increases the significance of the low 1,3-butadiene emissions relative to other toxic species. 1,3-Butadiene accounts for only up to 7% of the total toxic mass emitted by spark-ignition engines. However, this small amount of mass accounts for up to 72% of the toxicity, according to EPA's relative risk factors [12]. In fact, 1,3-butadiene accounts for 12% of the EPA estimated total cancer cases from outdoor exposure. This is why the production of 1,3-butadiene is of particular interest for this project.

#### **1.5 Objectives**

The previous work in the Auto/Oil Program includes much data on emissions versus the type of fuel used and composition. The twenty-six different fuels used vary greatly with regards to their compositions. In order to determine which fuel components affect which exhaust emissions, the first objective was to perform a detailed analysis of the Auto/Oil data, tracing the exhaust levels of 2-methylpropene and 1,3-butadiene specifically. Using the fuel component information from the first objective, the second objective was to perturb a base fuel with different fuel components at three different levels and determine the sensitivity of the exhaust species to the level of the perturbed component in the

fuel. Any increasing or decreasing trends in 2-methylpropene or 1,3-butadiene in the exhaust was to be tracked. The final objective was to quantify any noticeable sensitivities of these two exhaust components to the perturbed fuel species and explain the chemistry that took place to cause these trends.



## CHAPTER 2

### SELECTION OF FUEL COMPONENTS TO BE PERTURBED

#### 2.1 Auto/Oil Study

The results from the Auto/Oil study were examined and used as a guide to select the fuel components to be perturbed. One of the studies of the Auto/Oil program tested two fleets of vehicles: 20 from 1989 and 14 from 1983-1985 [13]. The exhaust emissions were captured, identified, and quantified for each gasoline composition. Eighteen different gasolines with varying amounts of aromatics, olefins, and MTBE were used. The 90 percent distillation temperature also varied for different fuels, but that particular property was not examined for this experiment. Mass exhaust emissions of HCs, non-methane HCs (NMHCs), CO, and NO<sub>x</sub> were all affected by changes in the fuel composition. The gross properties such as total aromatics were controlled. No attempt was made to control the detailed species present in the test fuels. See Appendix A for the fuel compositions used in this Auto/Oil study. Only 2 levels of each variable were studied. Therefore, analysis of the data from the Auto/Oil study did not estimate curvature or second order effects. All statistical models used in the program were linear in the fuel variable and in combinations of fuel variables.

#### 2.2 General Effect of Aromatics, MTBE, and Olefins in Fuel

The hydrocarbon emissions are of more interest than CO and NO<sub>x</sub> emissions for this project, so they will be the focus of this discussion. For the more current fleet, Hochhauser *et al.* found that individually reducing aromatics or increasing MTBE resulted in lower overall HC emissions. Lowering olefins increased HC emissions [13]. Changing the fuel variables had similar effects on the NMHC emissions except for the effect of changing aromatics. Reducing the amount of fuel aromatics reduced NMHC by 12% but reduced total HC emissions by only 6.5%. This is because high aromatic fuels produce

exhaust methane than low aromatic fuels. In order to reduce the amount of aromatics in the fuel, the amount of paraffins were increased. The data suggests that high paraffin fuels produce more exhaust methane than low paraffin fuels.

The same tests were performed on the older fleet as well. The change in the MTBE level in the fuels used on the older fleet had similar effects as on the more current fleet. However, reducing the aromatic level in the fuel increased the HC exhaust emissions, which differs from the results on the more current fleet. Reducing the olefin content reduced HC emissions only when the aromatic fuel content was high. The NMHC response was very similar to that of the HC emissions. Table 2.1 lists the specific increases and decreases in HC and NMHC as the level of aromatics, MTBE, and olefins were changed [13].

Table 2.1. Main effects of changes in fuel variable on mass exhaust emissions.

		Change in Fuel Variable (by mass)		
Emission Constituent		Aromatics 45% to 20%	MTBE 0% to 15%	Olefins 20% to 5%
New Fleet	HC	-6.5±1.9	-5.5±1.9	5.8±2.0
	NMHC	-11.6±1.9	-6.4±2.0	7.1±2.1
Older Fleet	HC	13.6±3.2	-9.1±2.9	5.7±3.0
	NMHC	10.5±3.6	-9.0±3.3	6.9±3.5

### 2.3 Fuel Effects on 1,3-Butadiene Exhaust Emissions

1,3-Butadiene is a straight-chain di-olefinic (double bonds between 2 pairs of carbon atoms) hydrocarbon with a molecular formula of C<sub>4</sub>H<sub>6</sub>. It is not found in gasoline as a fuel component but appears in exhaust emissions as a partial oxidation product of certain fuel components. Even though it is a hydrocarbon, its trends in emission levels differ from the overall exhaust HC trends. For the current fleet, the average 1,3-butadiene emission rate for all of the fuels was 0.94 mg/mi (0.54% wt). Increasing the MTBE by 15% reduced the 1,3-butadiene levels by 7% except when the fuel contained high levels of aromatics. At high aromatic levels, 1,3-butadiene levels also increased with an increase in MTBE. Reducing the fuel olefin content by 75% lowered exhaust 1,3-butadiene by 31%. Reducing the fuel

aromatic content by 56% increased the 1,3-butadiene emissions by 10% but only when MTBE was present in the fuel. When examining a single component of the hydrocarbon emissions, the fuel variance effects depend on more than just the change in a single type of fuel component. For example, the effect may depend on the fuel oxygenate level as well as the aromatic level. For the older fleet, the average 1,3-butadiene emissions rate was 1.8 mg/mi (0.39% wt), which was 1.9 times higher than that of the current fleet. The fuel mixture with high levels of MTBE and olefins had a 1,3-butadiene emission rate of 3.0 mg/mi, where the fuel mixture with low MTBE and low olefins had a rate of 0.93 mg/mi.

#### **2.4 Fuel Components to be Perturbed**

It was difficult to determine exactly what kinds of trends existed in the Auto/Oil study's 2-methylpropene and 1,3-butadiene exhaust levels with respect to each type of fuel component (aromatics, olefins, oxygenates). 2-Methylpropene was not examined specifically in previous studies and was simply lumped together with the HC emissions. 1,3-Butadiene received special attention due to its toxicity. However, its trends with respect to a single fuel component were not specifically determined. Although HC emissions decreased with an increase in MTBE, the level of exhaust 1,3-butadiene, which is also an HC, depended on the quantities of other fuel components. The inconsistency of the percent volumes of the remaining fuel components prevented making a definite fuel component trend for the 1,3-butadiene emissions. Therefore, aromatics and oxygenates were natural candidates for fuel components to be perturbed in order to study 1,3-butadiene exhaust level concentrations. Major fuel components were especially key candidates because perturbing the minor ones would most likely not have had a particularly noticeable effect in the exhaust levels of individual species. Therefore, MTBE, toluene, and m,p-xylene were chosen as fuel components to be perturbed. Also, during the inspection of the major fuel components, it was observed that 2,2,4-trimethylpentane (iso-octane) was a major fuel component. It is a paraffin, but according to Westbrook and Dryer, its oxidation can result in 2-methylpropene, one of the olefin exhaust species examined for this project [14]. Therefore, iso-octane was also chosen as one of the fuel components to perturb.





## CHAPTER 3

### EXPERIMENTAL DESIGN AND PROCEDURE

To obtain the sensitivity of the speciated engine exhaust emission levels to the fuel species, a number of tests were run on a spark-ignition engine using a fuel for which the composition was perturbed by adding different quantities of selected components. To analyze the exhaust species, it was necessary to develop a set-up where exhaust samples could be captured and stored easily without any significant chemical reactions taking place over the course of a day. It was also necessary to be able to swap fuels quickly without contaminating the fuel so that all of the tests with one perturbed fuel component mixture could be performed in one day. The engine, the fuel properties, the fueling system, and the exhaust sampling and storage system are described below.

#### 3.1 Engine Specifications and Operating Parameters

The engine from which all the samples were collected was a Nissan SR20DE engine, a commercial two-liter four-cylinder spark-ignition engine. The SR20DE is a 16-valved DOHC in-line four-cylinder engine with two branches of intake and exhaust ports for each cylinder. The following table lists the engine specifications:

Table 3.1. Summary of engine specifications and operating parameters

Model	Nissan SR20DE 4-stroke
Type	4-cylinder, 4 valves/cylinder, DOHC, pent-roof, spark plug located at center
Bore x Stroke	86 mm x 86 mm
Compression Ratio	9.5
Clearance Volume	58.8 cm <sup>3</sup>
Displacement	1.998 liters (499 cm <sup>3</sup> /cylinder)
Valve Timing	IVO: 13 BTC IVC: 55 ABC EVO: 57 BBC EVC: 3 ATC

Valve Diameter	intake: 34 mm exhaust: 30 mm
Maximum Torque	18.2 kg m @ 4850 RPM
Maximum Power	140 hp @ 6400 RPM
Injection Timing	30 BTC
Spark Timing	27 BTC
Equivalence Ratio	1.0
RPM	1500
Intake Manifold Pressure	0.4 bar
Coolant Temperature	75°C - 85°C
Exhaust Temperature	530°C - 540°C

This engine had been modified for single cylinder operation in order to eliminate any cylinder-to-cylinder uncertainty that might have developed with four-cylinder use. Injection of fuel and combustion occur only in one active cylinder. The distributor has been replaced by a separate electronic ignition controller for the active cylinder. The exhaust runner of the active cylinder was separated from those of the disabled cylinders in order to obtain correct readings of the fuel-to-air equivalence ratio from the Horiba oxygen sensor located downstream of the exhaust port.

The engine was coupled to a dynamometer, which consists of an induction motor with a DC current driven clutch and an Eddy current brake. The dynamometer controller maintained the engine at a constant speed of 1500 RPM. The throttle position was set to maintain an intake manifold pressure of 0.4 bar. The amount of fuel injected was adjusted so that the air-to-fuel equivalence ratio ( $\phi$ ) was always  $1.0 \pm 0.005$ . These conditions are representative of steady state for a normally-operating automotive engine operating at light load and medium speed.

For the ease of temperature control, the engine coolant, oil, and fuel were cooled by separate water-cooled heat exchangers. There was no control of the air temperature which was equal to the ambient temperature of the test cell ( $\sim 22^\circ\text{C}$ ). The samples were collected while the engine was running at steady-state conditions. For the first test of the day, the engine required approximately 30 minutes to fully warm up. The subsequent runs took the engine 10 to 15 minutes to reach steady-state operating conditions. The exhaust samples were collected when the exhaust temperatures generally ranged between  $530^\circ\text{C}$  to  $540^\circ\text{C}$ , and the coolant temperatures between  $75^\circ\text{C}$  to  $85^\circ\text{C}$ .

### 3.2 Fuel Specifications

The fuel chosen was to be representative of what is being used today and what will more commonly be in use in the future. Federal requirements mandate a Phase II fuel to be used by the year 2000 [15]. Therefore, the fuel selected for this project was California Phase II Certification Gasoline, purchased from Phillips Chemical Company. Appendix B includes a list of its specifications. Also, MTBE is a major fuel component in this blend, and since one of the fuel components to be perturbed needed to be an oxygenate, the California Phase II Certification Gasoline was an ideal fuel to perturb. Table 3.2 lists the major constituents of this fuel.

Table 3.2. Major fuel components of California Phase II Certification gasoline.

Fuel Component	% vol
MTBE	12.8
2-Methylbutane	9.8
2,2,4-Trimethylpentane	7.0
Toluene	6.6
m,p-Xylene	5.3
2,3-Dimethylpentane	4.9
2,3-Dimethylbutane	3.4
Others	50.2

### 3.3 Fuel Perturbations

For each set of tests, a particular fuel component was chosen to be perturbed. Fuel mixtures were made for three different leveled perturbations by adding the selected fuel component to the original fuel to increase the percent volume of the selected. The data sets contain exhaust information from these three different perturbation levels plus a baseline with no perturbation. Table 3.3 shows the different fuel components which were perturbed and their corresponding percent volumes in the fuel at the different levels of perturbation. Note that when the amount of the selected component is increased, there is a corresponding decrease in the percentages of the rest of the components because of the dilution effect.

Table 3.3. Different mixtures and their perturbation % volumes.

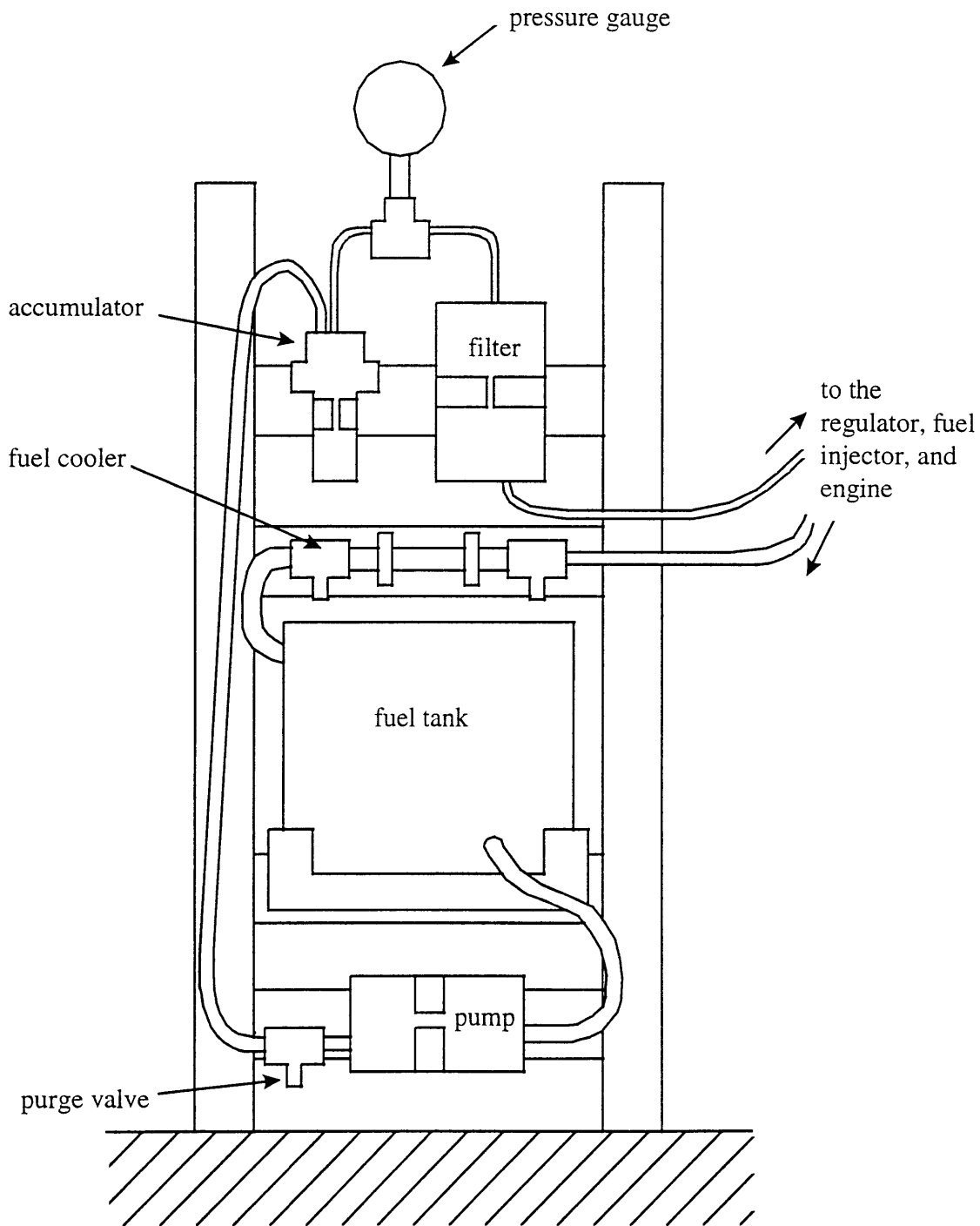
Perturbed Fuel Component	Total % Volume in Mixture			
	Baseline None added	First perturbation	Second Perturbation	Third Perturbation
MTBE	12.79	21.74	25.48	29.01
Toluene	6.64	11.76	16.38	20.53
m,p-Xylene	5.34	9.9	14.04	17.82
2,2,4 TriMethylpentane	7.01	14.84	21.46	26.58

### 3.4 Fuel System

The fuel system was designed so that all of the components through which liquid fuel flowed could easily be removed and replaced by a separate set of identical components. This was to avoid cross contamination of the different fuel mixtures. See Figure 3.1 for the removable fuel system. The fuel flowed from the storage tank, through the pump, accumulator, filter, regulator, and then back to the storage tank. All of these items, including the fuel injector, could be removed and replaced each time a new mixture was to be tested.

Once a full set of tests (baseline, first, second, and third-level perturbations) was run on the engine, each removable fuel system needed to be purged before introducing a different fuel blend with a new perturbing fuel component. This cleansing process was done by pouring a small amount of the new mixture into the fuel system, operating the pump so that the new mixture would flow through the entire system, and emptying the fuel from the system through the purge valve. This procedure was repeated to make sure that the previous mixture was as fully removed from the system as possible. Finally, a third amount of the new mixture was introduced into the fuel tank, making the set-up ready for new tests.

Figure 3.1. Removable Pump/Filter/Fuel System.



### 3.5 Exhaust Gas Sampling Unit

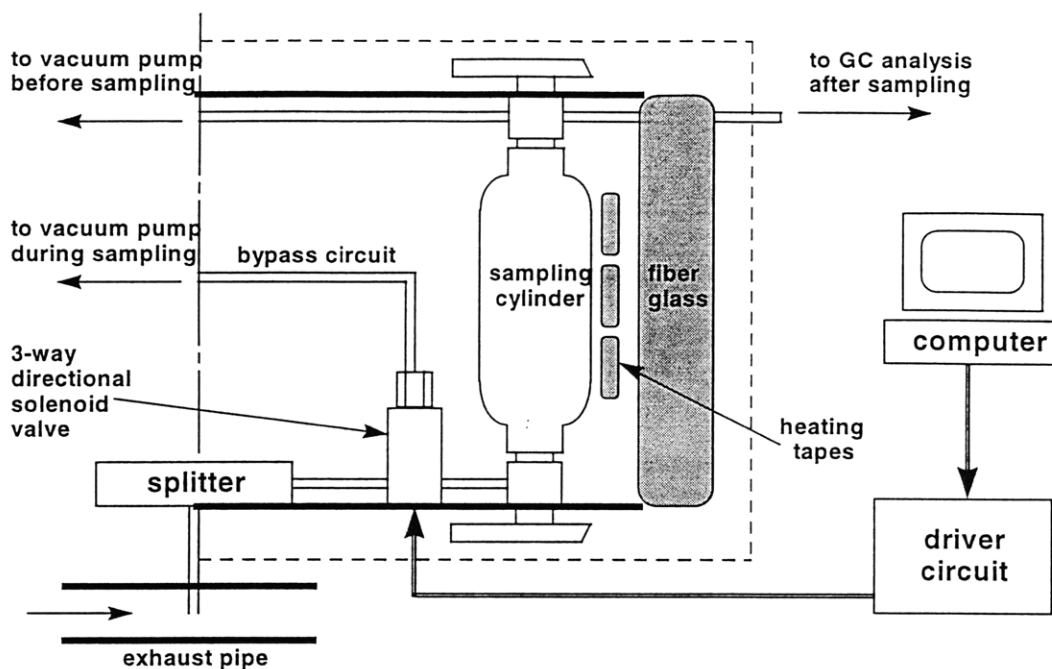
The equipment used to capture and store the exhaust samples was designed and built by Kuo-Chiang Chen, a previous Ph.D. student who worked on a project that also required the collection of exhaust samples [16]. The following were the design requirements for the exhaust gas sampling unit for this project:

- 1) Storage units needed to be able to store exhaust gas samples for gas chromatography analysis.
- 2) The amount of exhaust gas sample captured by the sampling unit needed to be sufficient for the GC analysis procedure. The GC analyzer required at least 5 cubic centimeters of exhaust sample for each analysis process.
- 3) The time delay between the inlet of exhaust gas sample to the storage unit of the sampling system needed to be small in order to avoid post-combustion oxidation so that the evolution of hydrocarbon emissions could be correctly interpreted.
- 4) The storage units could not allow chemical reactions to occur that would significantly alter the composition of hydrocarbon levels before the GC analysis could be performed.

These design requirements were very similar to those of Chen's experiment. Therefore, his exhaust gas sampling unit capable of storing sixteen samples was used. Figure 3.2 illustrates one of the 16 sampling cylinders and the components associated with it.

A sampling tube that extended to the center of the exhaust runner placed approximately 30 centimeters after the opening of the exhaust valve was used to transport exhaust to the sampling unit. The space from the exhaust valve to the sampling location was roughly equal to the engine displacement volume. The sampling location was chosen to provide enough space and time for the exhaust gas of one cycle to be fully mixed so that representative, cycle-averaged samples could be collected. The other end of the tube was connected to a splitter which was used to divide the sample gas into 16 parts. Each of these parts flowed either to the sampling cylinder or through the bypass circuit. Before the sampling process, all of the sampling cylinders were connected to a central pipe that was connected to a vacuum pump. All of the cylinders were completely evacuated, making the pressure within each of the cylinders as close to zero as possible.

Figure 3.2. Single cylinder of exhaust gas sampling unit.



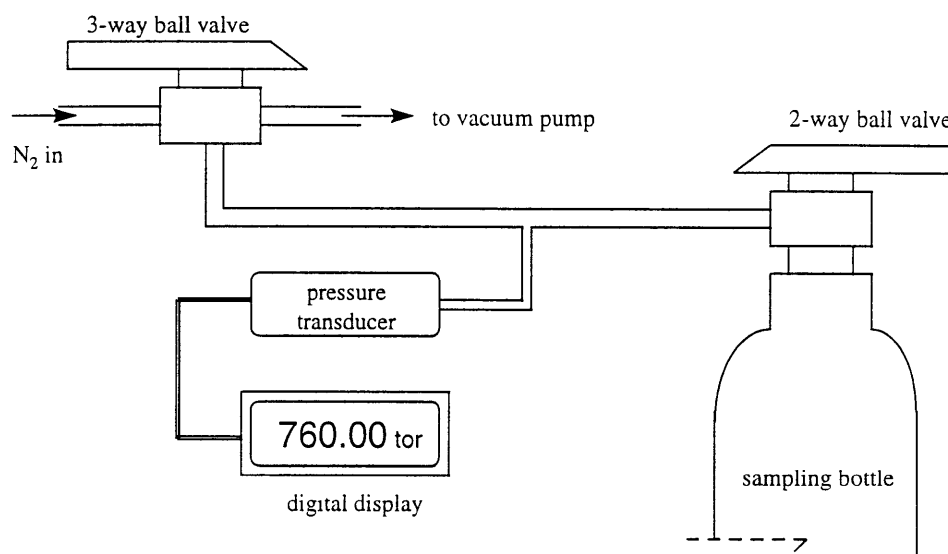
The direction of the flow from the splitter was controlled by a fast-acting three-way directional solenoid valve, which was turned on and off by the computer. The bypass circuit was connected to a vacuum pump, which caused the exhaust to flow from the exhaust runner through the splitter. When the solenoid valve was not energized, the exhaust gas was directed to the bypass circuit and then out of the vacuum pump. When the solenoid valve was energized, the pressure difference between the sampling cylinder and the splitter caused a sample of exhaust to be sucked into the sampling cylinder.

The duration which the solenoid valve was energized was 1 second. This 1 second interval, which corresponds to 25 firing cycles, was chosen in order to obtain a fairly homogeneous exhaust sample. A digital/AD/DA IO board and a modified computer code originally written by Chen were used to energize each solenoid valve for the appropriate time. The duration the solenoid valve was energized was timed by a real time clock (Intel 8254). The digital signal of the sampling events from the computer was amplified by the driver circuit which provided 24-volt DC current to each solenoid valve.

The sample was stored in the sampling cylinder and diluted with nitrogen through the top three-way ball valves. Nitrogen was added to the exhaust sample for the following reasons: 1) it was needed in

order to increase the pressure within the sampling cylinder to levels high enough so that the gas chromatograph (GC) analyzer could accept a sample, 2) nitrogen is a relatively inert gas in comparison to the components that make up exhaust and was used to try to keep any further chemical reactions from taking place during the storage time, 3) because the sample was stored at higher than atmospheric pressure, if there were any minor leaks in any of the sampling cylinders, some of the diluted sample would leak out rather than air leak in which would have changed the HC concentration of the sample. Figure 3.3 illustrates the set-up used to dilute the sample. Typical values for the dilution ratio ranged from 10-15.

Figure 3.3. Components for measuring the pressure of exhaust gas and diluting the sample.



First, the 2-way ball valve was closed while the 3-way ball valve was directed to the vacuum pump until the line in between the 2-way ball valve and the 3-way ball valve was completely evacuated. The 3-way ball valve was closed while the 2-way ball valve was opened to measure the pressure of just the sample inside the cylinder. This pressure generally ranged from 50 to 100 torr. After this pressure was recorded, the 3-way ball valve was directed towards the nitrogen supply, and nitrogen was slowly forced into the cylinder until the pressure transducer read some value between 800 and 1,000 torr. The new pressure



divided by the initial pressure was the dilution ratio used when calculating the concentration of the different components in the exhaust.

The design of this apparatus tried to minimize the length of the sampling loop and maximize the flow speed in order to minimize the transport time of the sample from the sampling point to the sampling cylinder. However, the physical space and fitting all of the necessary tubing and components within the sampling unit was a constraint. Stainless steel, 0.125 inch OD tubing (0.05 inch ID) was used in the loop from where the sample was collected to the sampling cylinder as a compromise between increasing the flow speed of the exhaust but keeping the tubing big enough to prevent water and heavy hydrocarbon condensation. For this configuration, the transport time of the sample from the sampling point to the sampling cylinder was approximately 0.05 seconds. This timing, measured using the bypass flow rate (flow rate of the pump) and the dimensions of the sampling tubing and exhaust runners, was on the same order of magnitude as the timing of one engine cycle.

All of the components of the sampling units were covered by two 0.1875 inch aluminum plates at the top and bottom of the sampling unit and surrounded by 1.25 inch fiberglass insulation. Heating tape was also installed within the sampling unit to prevent condensation of hydrocarbons or water from the exhaust while flowing through the bypass circuit or during storage. However, the temperature at which any of the exhaust species would condense at such low partial pressures within the sampling cylinder was so low that the heating tape was not needed for this experiment.



## CHAPTER 4

### HYDROCARBON ANALYSIS PROCEDURE

#### 4.1 Gas Chromatography using a Flame Ionization Detector

A gas chromatography (GC) analysis was used to identify and quantify the different species within the exhaust. There are a number of different options for this type of GC analysis. However, for this experiment, a single flame ionization detector (FID) was used because of its availability, cost, and success in similar types of experiments. The flame ionization detector's insensitivity to water and carbon disulfide makes it ideal for analyzing organic compounds. In the FID, a carrier gas such as helium, flows through an electrode gap and the organic compounds from the sample being analyzed are ionized by a hydrogen flame. The presence of charged particles within the electrode gap causes a current to flow across the gas and through a measuring resistor. A voltage jump serves as the output and corresponds to the number of carbon atoms in the compound flowing through the FID at the moment.

A 5890 Hewlett-Packard GC Analyzer was used to perform the analysis of the samples. The appropriate column installed in the analyzer was a J&W Scientific DB-1 with a 60 meter length, 0.32 millimeter inner diameter, 1 micrometer film thickness. Table 4.1 describes the heating method used to elute the different compounds through the column [17].

Table 4.1. Temperature programming in Jensen *et al.*'s Method 2 used to separate C<sub>4</sub>-C<sub>12</sub> hydrocarbons.

Temperature (°C)	Temperature Change Rate	Time (sec)	Cumulative (sec)
-80	0.01 min	0.6 sec	0.6 sec
-80 to -50	20°C/min	90 sec	90.6 sec
-50	2.5 min	150 sec	240.6 sec
-50 to 250	6°C/min	3000 sec	3240.6 sec

The carrier gas flowed through the column continuously, and a 5 millimeter plug of the nitrogen-diluted sample was injected into the column from the sample cylinder at a particular pressure. This pressure was recorded and used later to normalize the concentration values. The different compounds that made up the exhaust sample flowed through the column at different flow rates due to their interaction with the film coated on the inside of the column. When a particular component finally reached the end of the column, it entered the FID, a voltage output and its magnitude were recorded by an integrator connected to the output of the GC analyzer, and the time it took for that particular exhaust species to travel to the end of the column from when the sample was injected was recorded. By the end of a run, a series of voltage peaks made up a chromatogram. The timing of each of the voltage peaks was used to identify the different exhaust components. This will be explained in Section 4.2. The area under the peak corresponded to the total number of C-C bonds that were broken for the particular exhaust species. This number was used to determine the actual concentration of the compound in the exhaust.

#### 4.1.2 Calibration of the GC Analyzer

The first procedure of the day was to run the calibration gas through the GC analyzer. The calibration gas consisted of 22 different hydrocarbons with known concentrations. A sensitivity coefficient was determined by dividing the known concentration of the component in the calibration gas and the pressure at which the cal gas was injected by the normalized area under the signal corresponding to that component as follows:

$$\text{norm sens coeff} = \frac{(\text{PPMC1 of component in cal gas}) \times (\text{injection pressure of cal gas})}{(\text{area under peak})} \quad (4.1)$$

where norm sens coeff stands for normalized sensitivity coefficient, PPMC1 is the known mole fraction value specified by the gas manufacturer, injection pressure is the injection pressure of the calibration gas, and area under the peak is the direct value given by the integrator for the area under the voltage peak for a specific component in the cal gas. This sensitivity coefficient represented ppmC1/area count. This was done for all the components in the calibration gas. Usually two calibration samples were run through the GC analyzer at the beginning of the day. Afterwards, one calibration run was performed after every four sample runs to make sure that the sensitivity coefficients were consistent throughout a given day.

The sensitivity coefficients for the HC species eluted between the ethane and toluene peaks remained nearly constant during the duration of a day. They may have varied up to 9% between different runs, but this compares relatively well to Jensen's *et al.* measurements whose sensitivity coefficients differed by up to 8% for their HC species [17]. However, methane, ethylene, and the heavier HC components, such as toluene and m,p-xylene, tended to have fluctuating sensitivity coefficients of up to a factor of 2. For methane and ethylene, these variations were due to the method used. This particular method does not clearly separate the first two lighter HC components well. Therefore, it was difficult for the integrator to tell if the change in voltage corresponded to methane or ethylene. A different heating method would have separated methane and ethylene more clearly. It would have been too time-consuming for each sample to be tested twice, using two different methods. Because neither methane nor ethylene exhaust levels were of great concern for this project, only the heating method for separating the hydrocarbons larger than ethylene was run for each sample.

The cause of the variations in the heavier hydrocarbons is still unclear. One hypothesis is that the heavier HC species may have condensed on part of the plumbing. However, 2-methylpropene and 1,3-butadiene are both lighter-end HC species. Since this project dealt with the concentration levels of these two species in particular, the variation in the heavier HC species did not affect the results of this project.

## 4.2 Identification of Species

After the calibration runs, a plug of gas from the sampling cylinders was injected and run through the GC analyzer, and a chromatogram was produced from the sample. The resulting chromatogram had many more voltage peaks than for the calibration gas since there were so many more different components in the exhaust. A method for identifying the species not found in the cal gas was needed. Jensen *et al.* determined and tabulated the order and timing in which HC compounds elute for the heating method used in this procedure. Reference [17] includes the tabulated retention indices for different hydrocarbons for the particular heating method used in this experiment. This particular method was used because of its clear separation of C<sub>4</sub>-C<sub>12</sub> hydrocarbons. Using this tabulated HC library, the different species could be identified using the following linear interpolation equation for retention time [18]:

$$\frac{RI}{100} = n + \left[ \frac{t_{unk} - t_n}{t_{n+1} - t_n} \right] \quad (4.2)$$

where RI is the retention index for the unknown species,  $t_{unk}$  is the retention time of the unknown species,  $n$  is the carbon number of the last n-paraffin that elutes prior to the unknown species,  $t_n$  is the retention time of that paraffin, and  $t_{n+1}$  is the retention time for the next n-paraffin to elute. Once all of the retention indices were determined, they were paired with those found by Jensen *et al.* and matched with the corresponding hydrocarbon species.

### 4.3 Calculation of Species Concentration

In order to determine the concentration of the exhaust species that were also in the calibration gas, the sensitivity coefficient was used in the following equation:

$$\text{exhaust PPMC1} = \frac{(\text{area under peak}) \times (\text{norm sens coeff}) \times (\text{dilution ratio})}{(\text{injection pressure of sample})} \quad (4.3)$$

where the exhaust PPMC1 is the concentration of the particular hydrocarbon being analyzed, the area under peak is the direct value given by the integrator of the component in the exhaust, the norm sens coeff is from equation 4.1, the dilution ratio is the factor by which the original exhaust sample was diluted with nitrogen, and the injection pressure of the sample is the pressure of the plug of sample before it is sent into the column. For species that were not in the calibration gas, the sensitivity coefficient of the HC that eluted close to the same time was used when calculating concentration levels. Theoretically, the GC's FID should produce a constant sensitivity coefficient for all species. Since a variance of up to only 9% was found, using a neighboring component's sensitivity coefficient was deemed valid. For the heavier HCs whose sensitivity coefficients seemed to vary a fair amount, the most consistent sensitivity coefficient during the testing period, usually that of heptane or hexane, was used to calculate the concentration. Appendix C contains all of the % volume, % weight, dilution ratio, and PPMC1 data acquired during this experiment.

### 4.4 Hydrocarbon Analyzer

To make sure that the concentration numbers lied within the appropriate range of values, a Rosemount 402 Hydrocarbon Analyzer was used to measure HC concentrations as well. This instrument

was not used to distinguish the concentration levels of each exhaust specie. It yielded a number that represented total PPMC1 of all the HC's in the exhaust and served to confirm the numbers from the GC analyzer.

The Rosemount HC Analyzer also used an FID to measure HC levels. The flame had to be lit and the analyzer needed to warm up for about an hour. Before each sample was taken, the analyzer was calibrated using nitrogen as the zero gas and 1478 PPMC3 (propane) as the span or calibration gas. A pump was used to transport the exhaust through a heated line and then to the FID. The FID outputted a fairly instantaneous PPMC3 reading which was converted to PPMC1 simply by multiplying it by 3. Table 4.2 compares the hydrocarbon concentrations from the Rosemount Analyzer versus the GC analyzer.

Table 4.2. Comparison of total HC concentrations for different fuel mixtures.

	Total HC PPMC1			Total HC PPMC1	
	GC Analyzer	Rosemount Analyzer		GC Analyzer	Rosemount Analyzer
<u>MTBE</u>			<u>m,p-Xylene</u>		
Baseline	1500	2601	Baseline	1667	2967
First Perturbation	1681	2409	First Perturbation	1805	3102
Second Perturbation	972	2226	Second Perturbation	1866	3051
Third Perturbation	1752	2352	Third Perturbation	1742	2835
<u>2,2,4 Trimethylpentane</u>			<u>Toluene</u>		
Baseline	2459	2442	Baseline	2698	3006
First Perturbation	2384	2158	First Perturbation	2921	3180
Second Perturbation	2443	2370	Second Perturbation	2722	2949
Third Perturbation	2171	2429	Third Perturbation	2824	3009

For most of the tests, the total HC count from the HC analyzer was significantly higher than that from the GC analyzer. This was to be expected because the HC count from the GC analyzer only includes the area under major peaks whereas the count from the HC analyzer includes all the hydrocarbons in the exhaust. Had the HC count from the GC analyzer been greater than that from the Rosemount HC analyzer, this would have indicated an error in the testing procedure or the analysis of the GC data.

#### 4.5 Uncertainty Analysis

There were a number of parameters that affected the species concentration results. These parameters affected the concentration in ways that are difficult to quantify. Therefore, the following

method was used to determine the standard deviations and uncertainties for the species concentration levels. A baseline fuel was tested for each set of perturbed fuels. The standard deviations for the major exhaust components from the baseline fuels were determined for each set of perturbed fuels by calculating the average, squaring the difference from the average for each sample, summing these squares, and taking the square root. The largest standard deviation was considered representative of the standard deviation for that species for all of the different fuel mixtures. See Table 4.3 for the standard deviations and the resulting 95% confidence interval size, assuming a normal random distribution.

Table 4.3. Exhaust species standard deviations and total uncertainties in concentration measurements.

Exhaust Component	Standard Deviation, $\sigma$ (PPMC1)	Total Uncertainty, $1.96 \sigma$ (PPMC1)	Coefficient of Variation $\sigma/(\text{mean})$
Propane	38	74	0.20
2-Methylpropene	32	63	0.17
1,3-Butadiene	12	24	1.11
Butane	5	10	0.32
Pentane	6	12	0.29
Hexane	3	6	0.17
2,2,4 Trimethylpentane	28	55	0.23
Heptane	6	12	0.20
Toluene	53	104	0.19
m,p-Xylene	35	69	0.21



## CHAPTER 5

### ANALYSIS OF GAS CHROMATOGRAPH DATA

This chapter examines the data obtained from the GC analyzer; in particular, the trends for 2-methylpropene and 1,3-butadiene exhaust levels with respect to the different perturbed fuel mixtures are evaluated.

#### 5.1 Sensitivity of the Exhaust Fuel Species

The Auto/Oil program carried out a study where the sensitivities of exhaust fuel component emission indices versus percent weight in the fuel for MTBE, toluene, m,p-xylene, and iso-octane were determined. The emission index is defined as the exhaust fuel species mass percentage of the total fuel mass input into the engine. For this experiment, these slopes were plotted and calculated for these four fuel components in order to make sure that the test procedure and data analysis were accurate. Table 5.1 lists the different sensitivity equations calculated from this experiment and from the Auto/Oil data for the different fuel components.

Table 5.1. Equations for different fuel mixtures: % weight of component in fuel vs. HC index of the component in the exhaust.

Perturbed component	<u>Equation for Species HC Index (%) in Exhaust vs. % Weight</u>	
	Calculated from experiment	Calculated from Auto/Oil Data
MTBE	$y = 0.0066x$	$y = 0.0085x$
Toluene	$y = 0.0171x + 0.0779$	$y = 0.0147x + 0.016$
m,p-Xylene	$y = 0.0180x + 0.0695$	$y = 0.0147x$
Iso-octane	$y = 0.0075x + 0.0563$	$y = 0.0098x$

For these equations, y is the HC Index (%) for the perturbed component, and x is the percent weight of the perturbed component in the fuel mixture. Note that the perturbations which were measured as volume

percentages have been converted to weight fractions/percentages via density values. This conversion was done in order to compare the sensitivities determined by the Auto/Oil program, which are all in percent weight. The differences in the y-intercepts were most likely due to the following differences between the Auto/Oil study and this particular study: the remaining fuel composition, the type of engine used, and the experimental procedure. Consistency in the sensitivities and not necessarily in the y-intercepts serves as a representative indicator as to whether the experiment was carried out properly. The table shows that the slope values differ by 14% to 23%. This suggests that the test procedure and data analysis used in this project produced results similar to those obtained in the Auto-Oil program. Figures 5.1 - 5.4 shows the different slopes, equations where the x value is in %, and  $R^2$  values for the linear relationships obtained from the results of this experiment. These concentration values were plotted against % weight in order to compare it with the Auto/Oil data, but the remaining analysis was done in % volume.

Figure 5.1. MTBE sensitivity

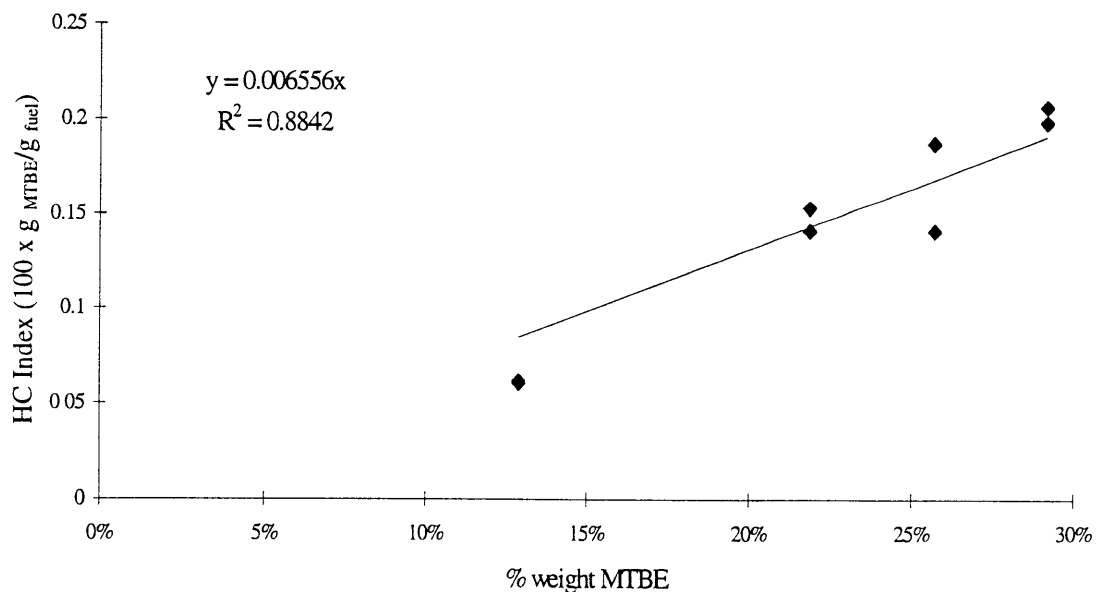


Figure 5.2. Toluene sensitivity.

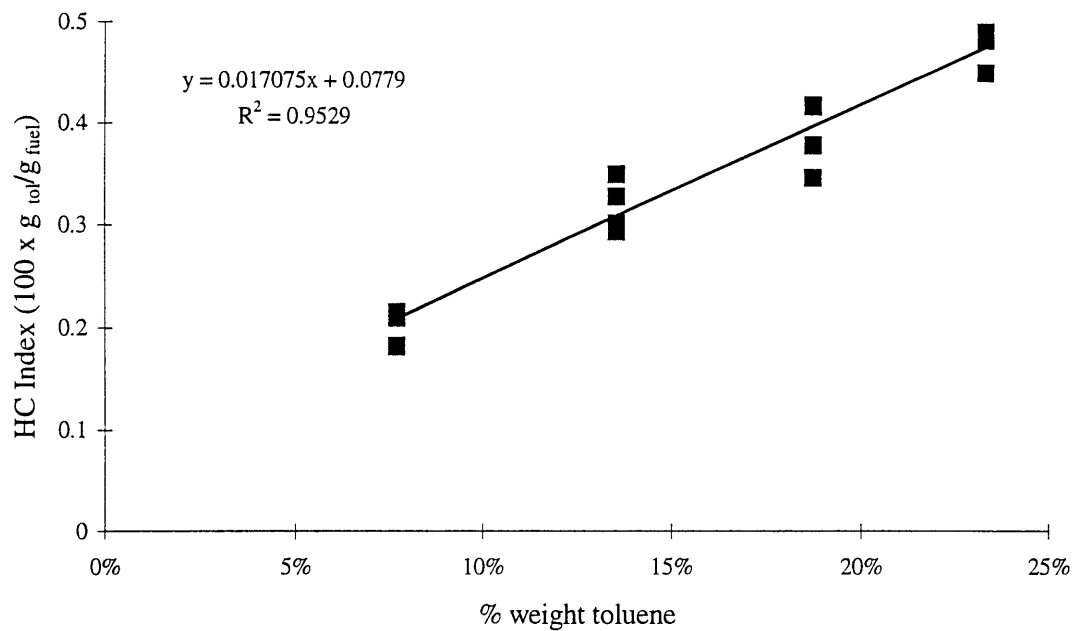


Figure 5.3. m,p-Xylene sensitivity.

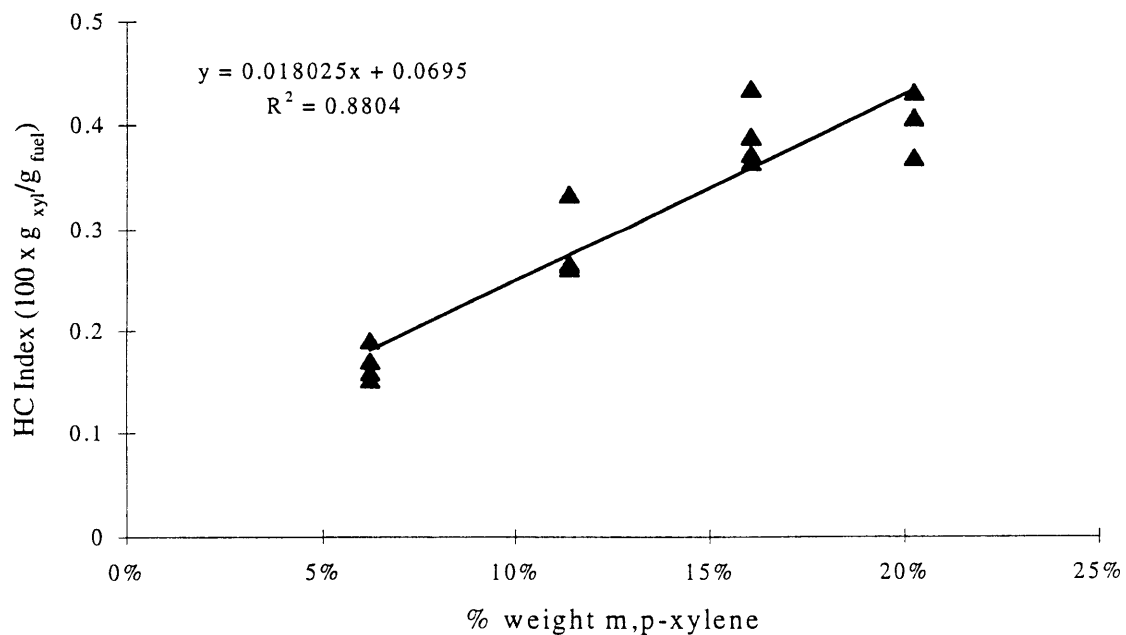
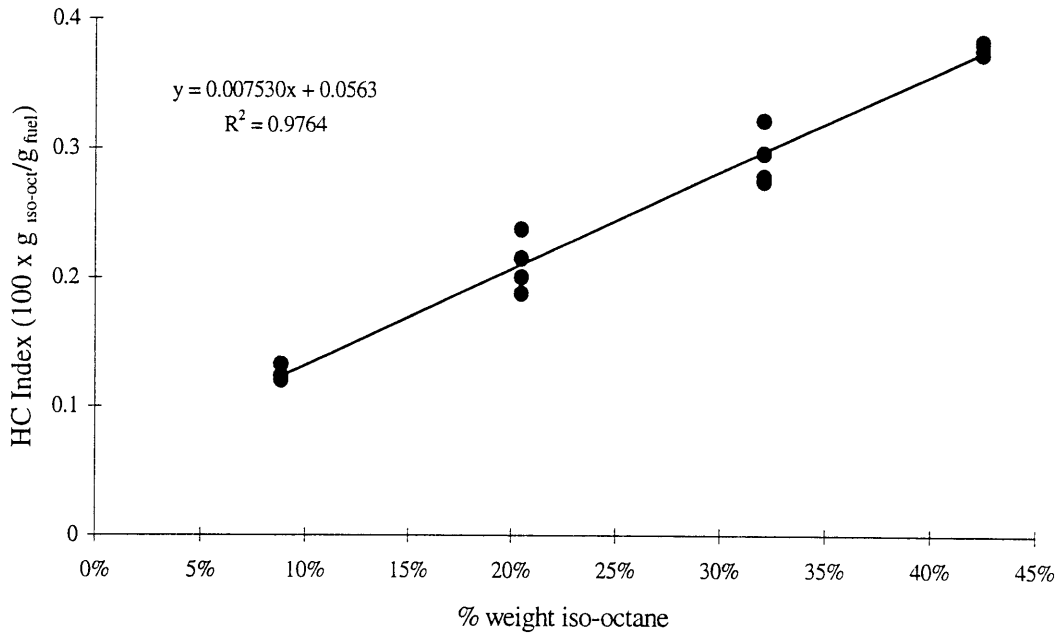


Figure 5.4. Iso-octane sensitivity.



## 5.2 Trends in 2-Methylpropene

The 2-methylpropene HC indices versus the percent volume of MTBE and iso-octane in the fuel are shown in Figures 5.5 and 5.6, respectively. The results clearly indicate increasing trends in exhaust 2-methylpropene concentrations versus both fuel components. The effects caused by the MTBE and the iso-octane perturbations displacing the other fuel components are not considered yet. These effects will be included later in an overall analysis of all the data points together.

Figure 5.5. 2-Methylpropene exhaust concentrations versus % volume MTBE in fuel.

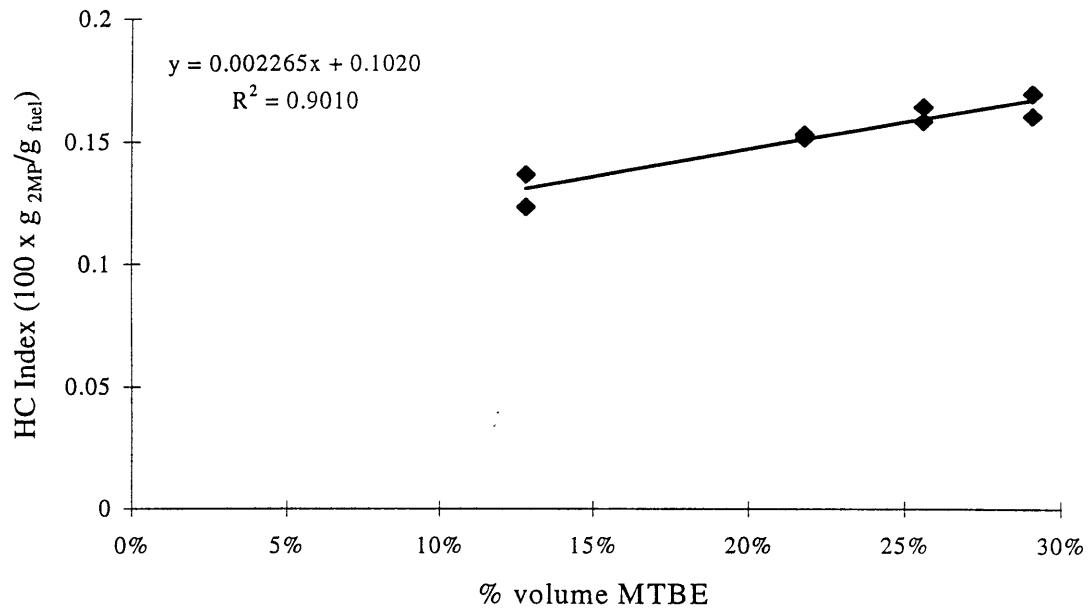
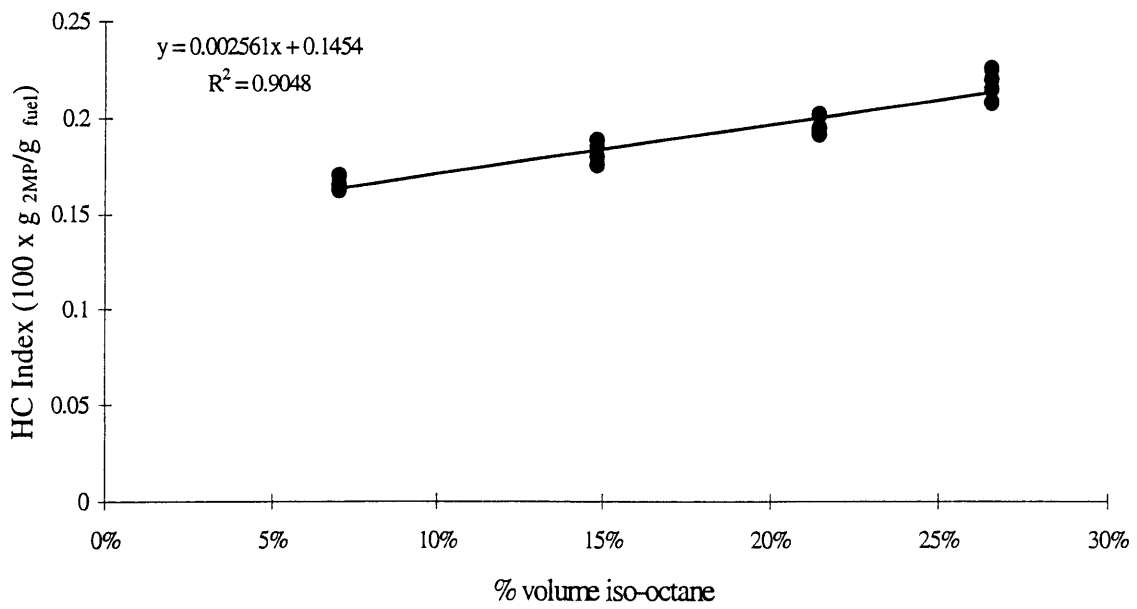


Figure 5.6. 2-Methylpropene exhaust concentrations versus % volume iso-octane in fuel.



Toluene and m,p-xylene were also used to perturb the fuel. Figures 5.7 and 5.8 show a decrease in the amount of 2-methylpropene in the exhaust. One hypothesis that this result may suggest is that the increase in the aromatics may inhibit the production of 2-methylpropene. However, increasing the percent volume of the aromatics in the fuel mixtures displaced the % volumes of MTBE, iso-octane, and other components in the initial fuel mixture, such as paraffins larger than butane, that might contribute to the formation of 2-methylpropene. Excluding the perturbed component, the % volume of the different fuel components relative to each other remained the same as the absolute % volume of the fuel components decreased. This means that the absolute % volumes of the components that produce 2-methylpropene in the aromatic fuel mixtures were not as high as in the fuel mixtures perturbed with MTBE or iso-octane. Therefore, another hypothesis is that decreasing the absolute % volumes of MTBE, iso-octane, and fuel components other than the aromatics may have caused the decrease in exhaust 2-methylpropene levels seen in Figures 5.7 and 5.8.

Figure 5.7. 2-Methylpropene exhaust concentrations versus % volume toluene in fuel.

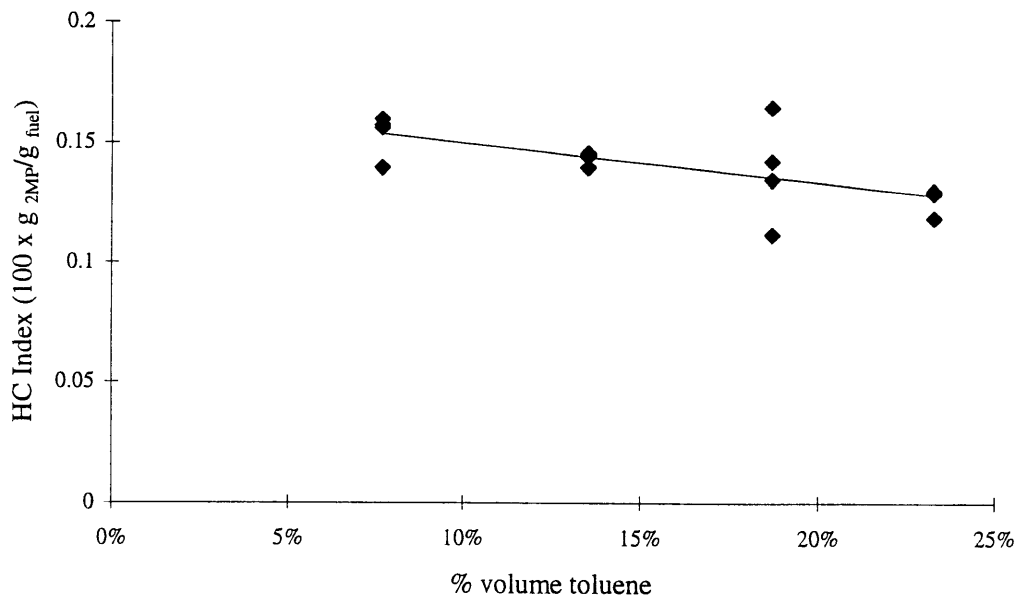
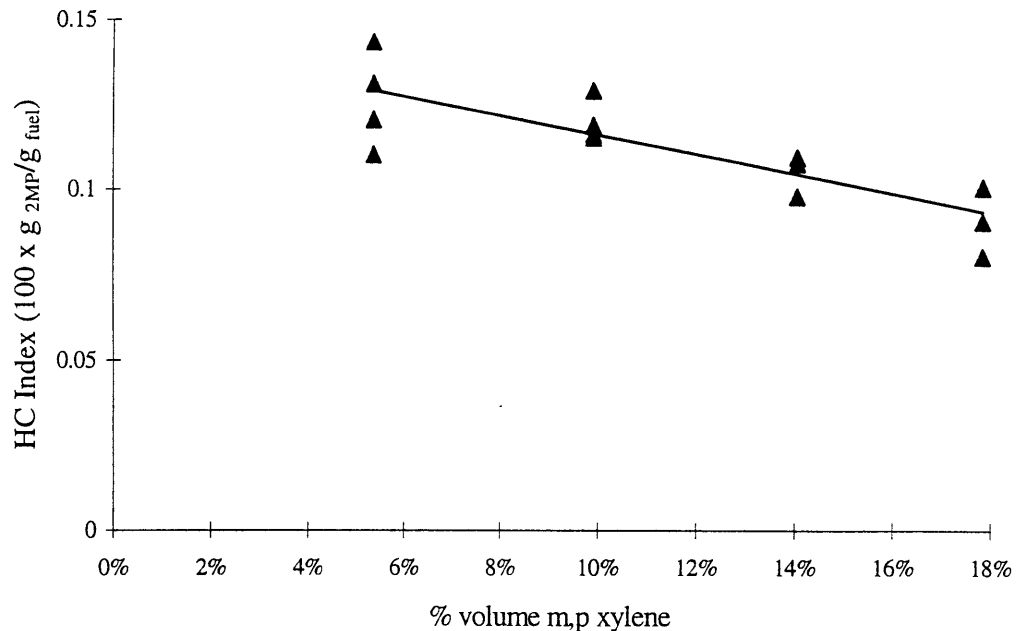


Figure 5.8. 2-Methylpropene exhaust concentrations versus % volume m,p-xylene in fuel.



One way to check if the displaced fuel was the cause for the decrease in 2-methylpropene exhaust levels was to see if the 2-methylpropene levels depended on all three percent volumes : % volume of MTBE, % volume of iso-octane, and % volume of paraffins larger than butane. This relationship could be modeled as the equation of a straight line such as  $y=m_1x_1+m_2x_2+m_3x_3$ , where  $y$  is the HC Index of the 2-methylpropene in the exhaust,  $m_1$  is the sensitivity of 2-methylpropene to MTBE,  $x_1$  is the % volume of MTBE in the fuel mixture,  $m_2$  is the sensitivity of 2-methylpropene to iso-octane,  $x_2$  is the % volume of iso-octane,  $m_3$  is the sensitivity of 2-methylpropene to the paraffins larger than butane, and  $x_3$  is the % volume of these paraffins. The  $m_1$ ,  $m_2$ , and  $m_3$  values were determined by performing the following steps:

1. The percent volumes of MTBE, iso-octane, and paraffins larger than butane (excluding iso-octane) were calculated for each of the fuel mixtures.
2. The different % volumes for every data point was put into a matrix consisting of 56 rows (each row representing a separate test) and three columns (each column representing the % volume for either MTBE, iso-octane, or paraffins larger than butane).

3. Two separate methods were used to correct for the day-to-day differences that may have occurred when taking exhaust samples on different days. An average HC index value was determined for the baseline fuel (no perturbation) since a baseline run was performed for each group of mixtures. The first method was to use this average HC index to normalize the rest of the HC indices for each set of runs. Another method was to determine what the offset set was for each of the fuel mixtures with respect this is average HC index, and account for this offset in the HC index values. The normalized/offset HC indices were put into a 56 x 1 matrix. See Appendix D for the data used in these matrices.
4. MATLAB was used to manipulate the matrices in order find the best least squares fit values for  $m_1$ ,  $m_2$ , and  $m_3$ . The sensitivities found are as follows:

For the normalized 2-methylpropene HC indices:

$$\begin{aligned}
 m_1 &= 0.00003852 \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of MTBE}) \\
 m_2 &= 0.00003287 \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of iso-octane}) \\
 m_3 &= 0.00001506 \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of paraffins larger than butane})
 \end{aligned}$$

For the offset 2-methylpropene HC indices:

$$\begin{aligned}
 m_1 &= 0.00003598 \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of MTBE}) \\
 m_2 &= 0.00003500 \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of iso-octane}) \\
 m_3 &= 0.00001562 \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of paraffins larger than butane})
 \end{aligned}$$

These  $m$  values between the normalized and offset HC indices do not vary by more than 7%.

5. New HC index values were calculated using these sensitivities in the  $y=m_1x_1+m_2x_2+m_3x_3$  equation. These were plotted against the normalized/offset measured values for 2-methylpropene. The linearity of the  $y=x$  line demonstrates how well the calculated  $m_1$ ,  $m_2$ , and  $m_3$  represent the actual sensitivity of 2-methylpropene with respect to MTBE, iso-octane, and paraffins larger than butane. Aside from seven data points, Figures 5.9 and 5.10 show the HC index values do not lie more than 7% away from the  $y=x$  line. This indicates that these  $m_1$ ,  $m_2$ , and  $m_3$  values are representative of the sensitivities of 2-methylpropene to the three different fuel components.



Figure 5.9. Calculated 2MP HC Index vs. Normalized Measured 2MP HC Index.

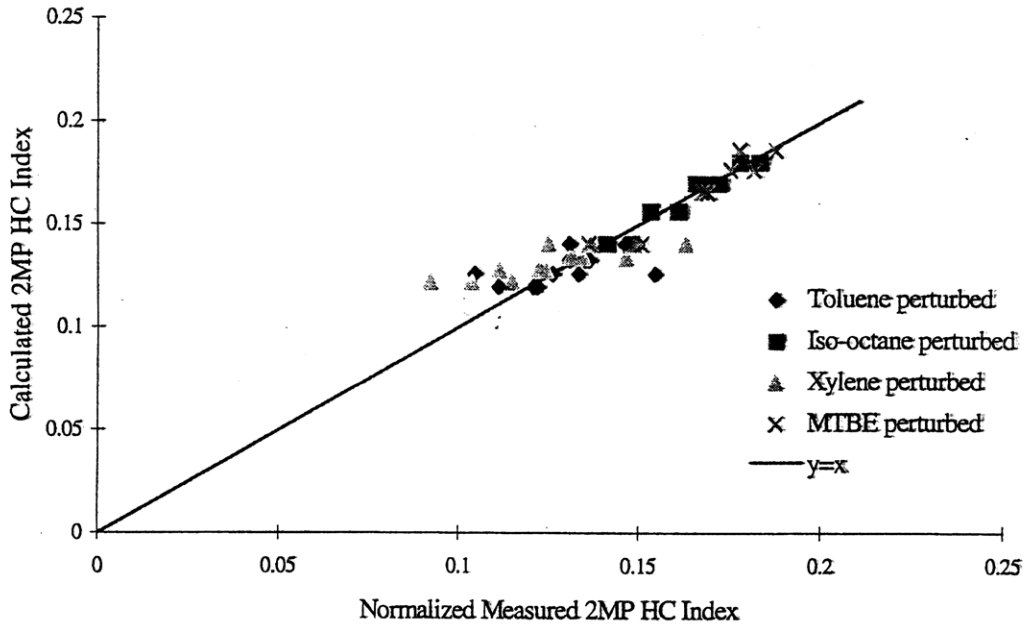
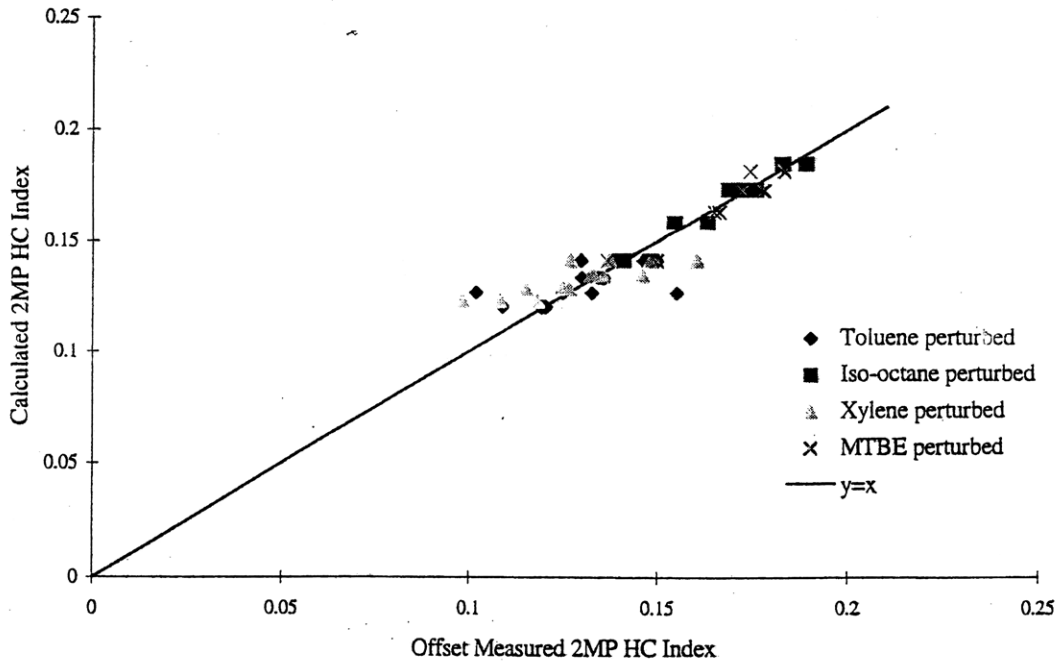


Figure 5.10. Calculated 2MP HC Index vs. Offset Measured 2MP HC Index.



### 5.3 Trends in 1,3-Butadiene

The results do not indicate any noticeable trends for 1,3-butadiene versus perturbations in MTBE, toluene, m,p-xylene, nor iso-octane. Figures 5.11 - 5.14 illustrate the scatter of the results. A major problem with trying to measure the amount of 1,3-butadiene in the exhaust was that the 1,3-butadiene reacted relatively quickly with the other exhaust components compared to the time scales at which the exhaust samples were tested. According to Kaiser *et al.*, if  $\phi = 1.0$  while the exhaust samples were collected, the 1,3-butadiene loss rate may have been up to 1.5% per hour after the first hour [19]. The GC analysis should have been carried out within approximately 1-2 hours after sampling. However, due to the nature of this project's set-up, this was not possible. The engine where the samples were collected and the GC analyzer were in two different locations. Therefore, the exhaust samples were always run through the GC analyzer the day after the samples were collected. This could have resulted in up to a 35% reduction in the amount of 1,3-butadiene that was measured versus what was actually captured, depending on when the sample was collected and tested. Since the different level perturbation exhaust samples were captured at different times and the samples were run through the GC at various times, it was difficult to precisely account for the 1.5% per hour reduction. The times through which the samples were sent through the GC were recorded, and the data on Figures 5.11-5.14 attempts to account for this hourly reduction by factoring in the percent reduced over an estimated elapsed time. Even with this hourly reduction correction, the results suggest no trend between the four different perturbed fuel components and exhaust 1,3-butadiene.

The 1.5% hourly reduction needs to be confirmed using the apparatus in this particular test set-up. One way to test this would be to simply collect many exhaust samples using unperturbed fuel, and run the samples through the GC analyzer every hour for a given period of time. This should give the 1,3-butadiene reduction rate for the given test equipment. One way to avoid having to apply a reduction rate to the 1,3-butadiene levels would be to have many GC analyzers available to test the exhaust samples immediately after they are collected. However, due to financial, space, and time constraints, this was not an option.

Figure 5.11. 1,3-Butadiene exhaust concentrations versus % volume MTBE in fuel.

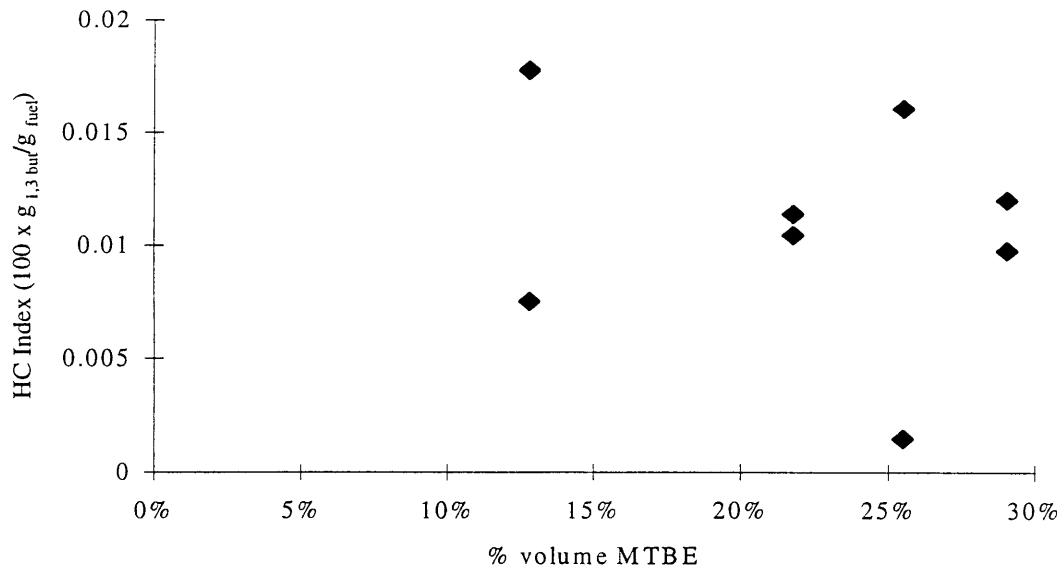


Figure 5.12. 1,3-Butadiene exhaust concentrations versus the % volume toluene in fuel.

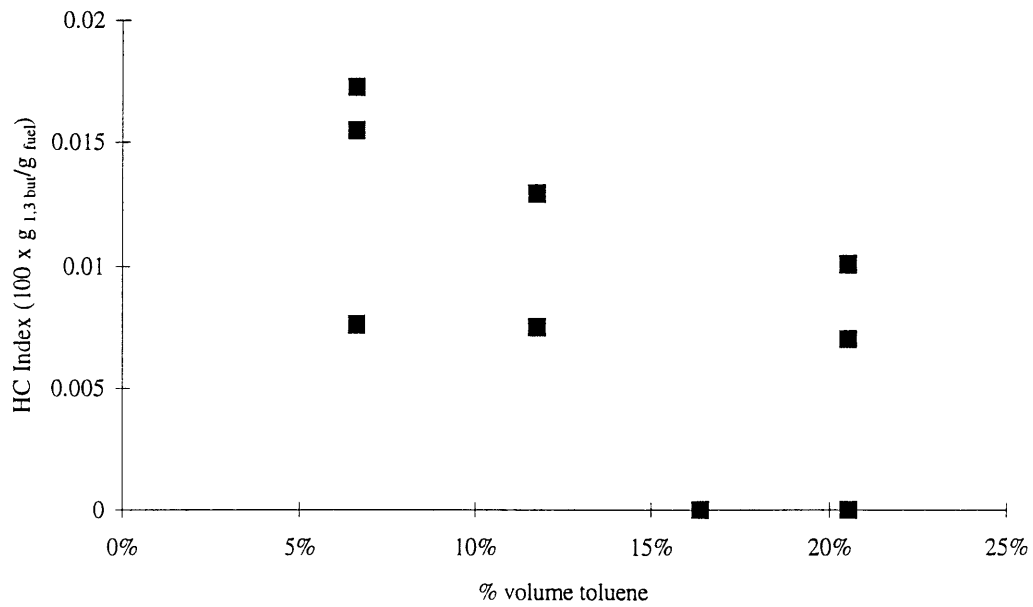


Figure 5.13. 1,3-Butadiene exhaust concentrations versus the % volume m,p-xylene in fuel.

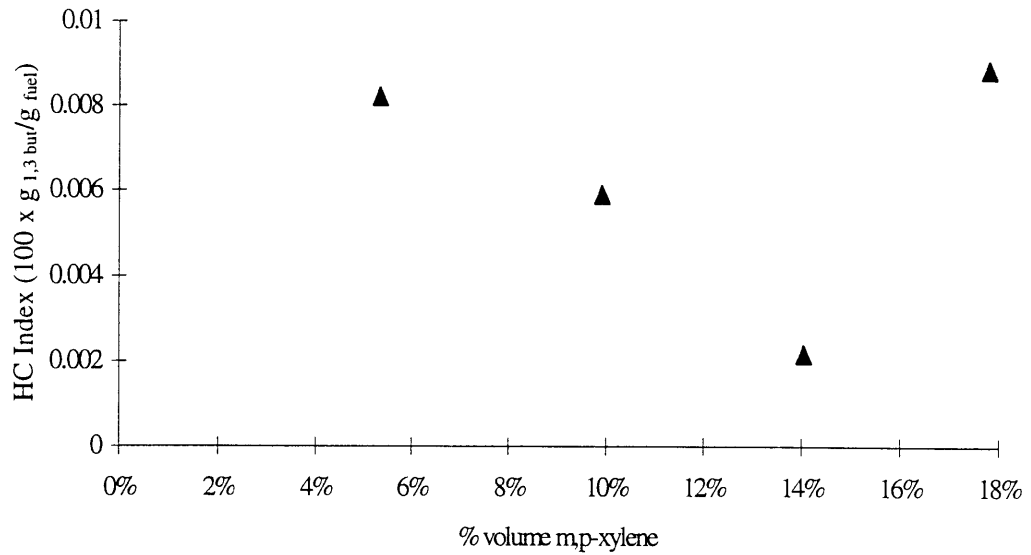
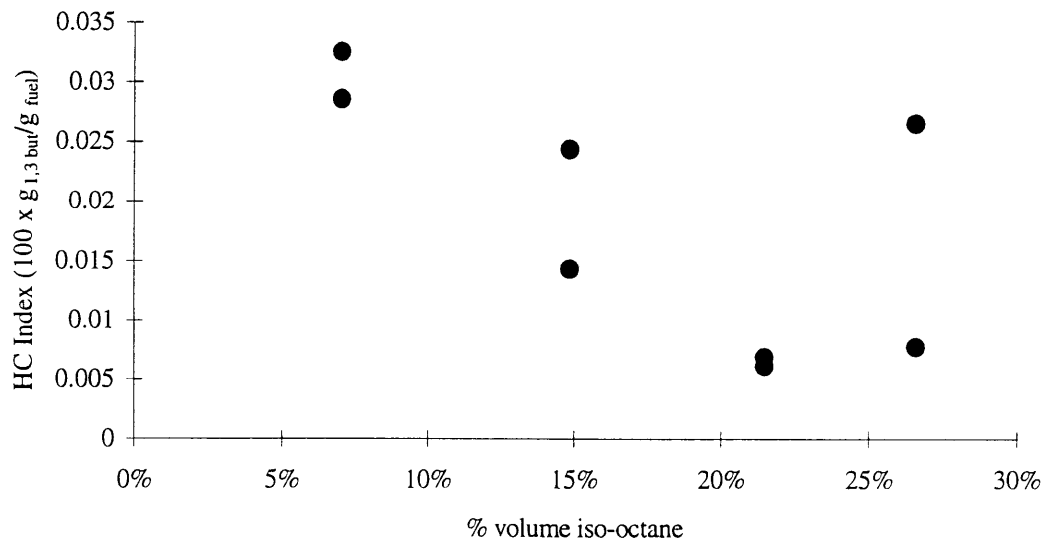


Figure 5.14. 1,3-Butadiene exhaust concentrations versus the % volume iso-octane in fuel.



## CHAPTER 6

### PRODUCT FORMATION CHEMISTRY

In an ideal combustion process, all of the fuel hydrocarbons would react only with the oxygen in the air, producing only water and carbon dioxide under lean to stoichiometric conditions, and hydrogen and carbon monoxide under rich conditions. In practice, there are many products of incomplete combustion, such as 2-methylpropene. The results from this project are consistent with the oxidation chemistry of MTBE and iso-octane. The processes that take place which finally produce 2-methylpropene are described in the following sections.

#### 6.1 2-Methylpropene from MTBE

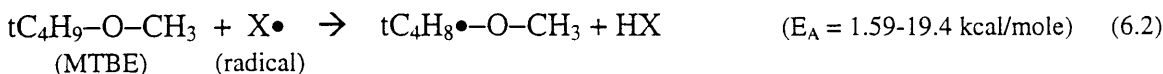
According to Curran *et al.* [20], there are three different ways in which 2-methylpropene can be formed from MTBE. One of the ways is a simple decomposition reaction if the amount of available energy is high enough. The dissociation reaction, which has an activation energy of 59,000 calories per mole, is



However, this activation energy is higher than that of other reactions that occur with MTBE. Therefore, this dissociation reaction most likely contributes the least amount of 2-methylpropene to the exhaust out of all the reactions.

Another process that produces 2-methylpropene is initiated when a radical, either an H, O, OH, CH<sub>3</sub>, or HO<sub>2</sub> abstracts a hydrogen atom from the t-butyl group of the MTBE molecule. The remaining radical then undergoes β-scission to produce 2-methylpropene, formaldehyde, and a free hydrogen radical.

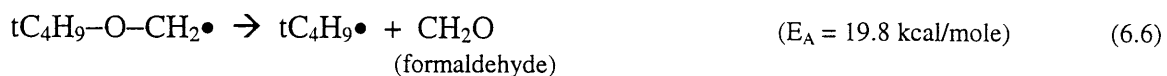
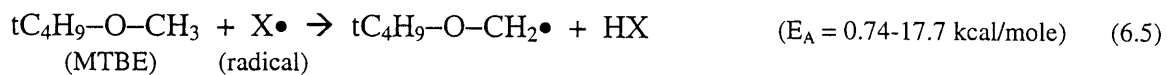
The following reactions occur when the hydrogen atom is abstracted from the t-butyl group:





where the t denotes a tertiary carbon structure, and the i indicates an isomer arrangement of the carbon atoms in the compound. Depending on what the X• radical is, the activation energy for reaction 6.2 ranges between 1,590 and 19,400 cal/mole. Reaction 6.3 has an activation energy of 24,800 cal/mole.

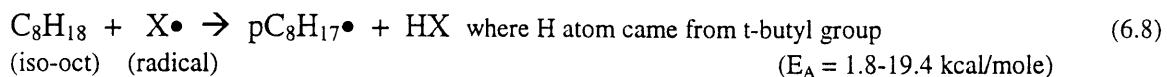
However, if the H atom is abstracted from the methyl group rather than from the t-butyl group, the following reactions occur instead:



The activation energy for reaction 6.5 ranges between 739 and 17,700 cal/mole, depending on X•. Reaction 6.6 has an activation energy of 19,800 cal/mole.

## 6.2 2-Methylpropene from Iso-octane

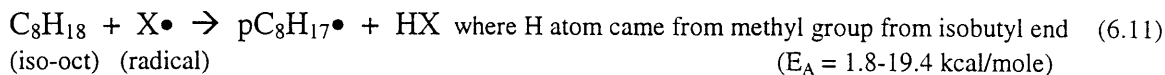
Axelsson *et al.* [21] did a study on the chemical kinetics of the oxidation of iso-octane by using applications of numerical modeling of n-butane, iso-butane and n-pentane. This was used here to determine how 2-methylpropene is produced from iso-octane. There are three different principal alkyl decomposition paths that lead to the production of 2-methylpropene. Similar to the kinetics for MTBE, the reactions are first set off when a radical abstracts a hydrogen atom from the iso-octane molecule. If the abstracted hydrogen atom comes from the t-butyl group, the following reactions take place:





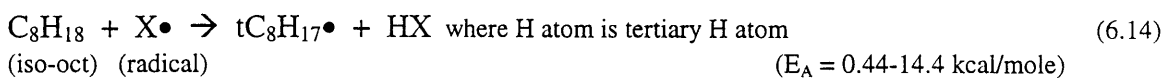
Depending on what the X• radical is, the activation energy for reaction 6.8 ranges between 1,810 and 19,400 cal/mole. Reaction 6.9 has an activation energy of 29,500 cal/mole.

However, if the radical abstracts a hydrogen atom from a methyl group from the isobutyl end of the molecule, the following reactions take place:



The activation energies for 6.11 and 6.12 are the same as for reactions 6.8 and 6.9.

The radical can also abstract the tertiary hydrogen atom from the isobutyl group. This would lead to the following chain of reactions:



The activation energy for reaction 6.14 ranges between 443 and 14,400 cal/mole. The activation energy for reaction 6.15 is 29,000 cal/mole.

There are obvious similarities between the product formation of 2-methylpropene from MTBE and from iso-octane. Because the activation energies for MTBE oxidation reactions are of the same order of magnitude for iso-octane oxidation reactions, it is difficult to determine which component produces 2-methylpropene. Chapter 6 results indicate that the sensitivities are very similar: for the sensitivities found using normalized HC indices, the 2-methylpropene sensitivity to MTBE was 17% greater than the sensitivity to iso-octane, and for the offset HC indices, the MTBE sensitivity was only 3% greater than the iso-octane sensitivity. For the California Phase II fuel used in this study, MTBE made up 12.79% by

volume whereas iso-octane made up only 7.01%. Therefore, more of the 2-methylpropene found in the exhaust was most likely a result of the incomplete combustion of MTBE rather than that of iso-octane.



## CHAPTER 7

### SUMMARY AND CONCLUSIONS

In this study, an experimental method was developed to determine the fuel component effects on the make-up of the exhaust emissions in a spark-ignition engine. For this methodology, a base fuel was perturbed with certain fuel components one at a time, and engine exhaust samples were collected when using these perturbed fuel blends. These exhaust samples were collected while the engine was running at steady-state and then analyzed using a gas chromatograph analyzer. This analysis identified the different species in the exhaust as well as quantified the exhaust concentration of the particular exhaust species. Using this information, the sensitivities of these concentrations to selected fuel components were determined.

The perturbed fuel components had the following effects on the exhaust:

1. Increasing the amount of a particular component in the fuel resulted in an increase in the amount of that component found in the exhaust. The sensitivity factor of the fuel MTBE on the exhaust MTBE was found to be  $6.56 \text{ E} \times 10^{-5} \text{ g}_{\text{MTBE}}/(\text{g}_{\text{fuel}} \times \% \text{ wt MTBE})$ . For toluene, it was  $1.71 \text{ E} \times 10^{-4} \text{ g}_{\text{tol}}/(\text{g}_{\text{fuel}} \times \% \text{ wt tol})$ . The sensitivity for m,p-xylene was  $1.80 \times 10^{-4} \text{ g}_{\text{m,p-xy}}/(\text{g}_{\text{fuel}} \times \% \text{ wt m,p-xy})$ . And for iso-octane, the sensitivity was determined to be  $7.53 \times 10^{-5} \text{ g}_{\text{iso-oct}}/(\text{g}_{\text{fuel}} \times \% \text{ wt iso-oct})$ . These values are in agreement with those found in the Auto/Oil study with a percent difference of up to 29%.
2. The amount of 2-methylpropene found in the exhaust increased with increasing amounts of MTBE in the fuel. The concentration of 2-methylpropene jumped from 161 ppmC1 to 222 ppmC1 as the % volume of MTBE was increased from 12.8 to 29.0, respectively. The sensitivity factor for this relationship, ignoring the displaced fuel effect, was found to be approximately  $2.27 \times 10^{-5} \text{ g}_{\text{2MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol MTBE})$ .
3. The increase in fuel MTBE did not have any noticeable effects on any of the exhaust species concentrations other than on MTBE and 2-methylpropene levels.

4. Exhaust 2-methylpropene also increased with increasing amounts of iso-octane. The 2-methylpropene concentration increased from 201 ppmC1 to 266 ppmC1 as the % volume of iso-octane was increased from 7.01 to 26.58. Ignoring the displaced fuel effect, the sensitivity factor of iso-octane in the fuel to 2-methylpropene in the exhaust was  $2.56 \times 10^{-5} \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol iso-oct})$ .
5. Iso-octane did not have any noticeable effects on any of the exhaust species concentrations other than on iso-octane and 2-methylpropene levels.
6. There were no noticeable trends of 2-methylpropene levels in the exhaust relative to the amounts of toluene or m,p-xylene in the fuel. However, decreasing % volume of the original fuel mixture, thus decreasing the % volume of MTBE and iso-octane in the fuel blend, resulted in a decreasing amount of 2-methylpropene in the exhaust.
7. The best least squares fit values for 2-methylpropene sensitivities to MTBE, iso-octane, and paraffins larger than butane ( $m_1$ ,  $m_2$ , and  $m_3$ ), which incorporate the displaced fuel effect, were found to be as follows:

For the normalized 2-methylpropene HC indices:

$$\begin{aligned}
 m_1 &= 3.852 \times 10^{-5} \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of MTBE}) \\
 m_2 &= 3.287 \times 10^{-5} \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of iso-octane}) \\
 m_3 &= 1.506 \times 10^{-5} \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of paraffins larger than butane})
 \end{aligned}$$

For the offset 2-methylpropene HC indices:

$$\begin{aligned}
 m_1 &= 3.598 \times 10^{-5} \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of MTBE}) \\
 m_2 &= 3.500 \times 10^{-5} \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of iso-octane}) \\
 m_3 &= 1.562 \times 10^{-5} \text{ g}_{2\text{MP}}/(\text{g}_{\text{fuel}} \times \% \text{ vol of paraffins larger than butane})
 \end{aligned}$$

8. Neither MTBE, toluene, m,p-xylene, nor iso-octane seemed to have any noticeable effect on the levels of 1,3-butadiene in the exhaust. Factoring in the reaction rate of 1,3-butadiene did not “clean up” the wide scatter of 1,3-butadiene levels in the exhaust. Therefore, the conclusion is that there is no trend of 1,3-butadiene in the exhaust relative to the amounts of MTBE, toluene, m,p-xylene, or iso-octane in the fuel.

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## APPENDIX A

**TABLE A.1. COMPOSITION OF FUELS USED IN AUTO/OIL PROGRAM**

Fuel Mixture Code	Aromatics % vol	MTBE % vol	Olefins % vol	T90 °F	RVP PSI	Benzene % vol
A	32.0	0	9.2	330	8.7	1.5
B	29.9	0	4.6	309	8.7	0.5
C	43.8	15.4	3.3	288	8.7	1.3
D	20.7	0	22.3	357	8.5	1.5
E	43.7	14.8	17.2	357	8.7	1.4
F	20.0	1	3.2	279	8.8	1.5
G	44.3	0	17.4	286	8.8	1.4
H	20.2	14.6	20.2	286	8.5	1.5
I	42.9	0	4.1	353	8.9	1.3
J	21.4	14.9	4.0	356	8.6	1.3
K	45.7	0	4.9	294	8.8	1.5
L	47.8	0	17.7	357	8.5	1.4
M	18.0	14.5	21.8	356	8.7	1.5
N	21.4	13.9	5.7	292	8.8	1.4
O	16.7	14.6	19.3	283	8.6	1.4
P	20.3	0	18.3	284	8.5	1.5
Q	21.5	0	4.8	357	8.6	1.5
R	46.0	15.2	4.0	354	8.4	1.4



## APPENDIX B

### FUEL SPECIFICATIONS

PHILLIPS CHEMICAL COMPANY, CALIFORNIA PHASE II CERTIFICATION FUEL, LOT W-615

<u>TESTS</u>	<u>RESULTS</u>	<u>SPECIFICATIONS</u>	<u>METHOD</u>
Specific Gravity, 60/60 F	0.7380		ASTM D-4052
API Gravity	59.74		ASTM D-1298
Corrosion, 3 hrs @ 50°C	1a	1 Max	ASTM D-130
Phosphorous, gm/US gal	0.000	0.005 Max	ASTM D-3231
Sulfur, ppm	32.5	30-40	ASTM D-2622
Multi-Substituted Alkyl Aromatics	14	12-14	CARB DHA
MTBE, LV%	10.92	10.8-11.2	
Carbon, wt%	84.3		PHILLIPS
Hydrogen, wt%	13.7		PHILLIPS
Oxidation Stability (min)	1400+	1400 Min	ASTM D-525
Existent Gums, mg/100ml, washed	<0.10	<5	ASTM D-381
Reid Vapor Pressure	6.9	6.7-7.0	ASTM D-323
TEL (ml/gal)	<0.00	0.005 Max	ASTM D-3237
Benzene Content, LV%	0.95	0.8-1.0	ASTM D-4815
Net Heat of Combustion, BTU/lb	18156		ASTM D-3338

<u>DISTILLATION, °F</u>		<u>ASTM D-86</u>
IBP	101	
5%	130	
10%	139	130-150
20%	153	
30%	168	
40%	185	
50%	203	200-210
60%	223	
70%	242	
80%	265	
90%	300	290-300
95%	328	
EP	379	390 Max
Loss	0.9	
Residue	1.0	2.0 Max

<u>HYDROCARBON TYPE, % VOLUME</u>	<u>Uncorrected</u>	<u>Corrected</u>	<u>ASTM D-1319 Spec</u>
Aromatics	27.2	24.2	22-25
Olefins	6.5	5.8	4-6
Saturates	66.3		
Research Octane Number	96.48		ASTM D-2699
Motor Octane Number	86.97		ASTM D-2700
Antiknock Index	91.7	91 Min	
Sensitivity	9.51	7.5 Min	





## APPENDIX C

### EXHAUST SAMPLE PROPERTIES

The following tables are sample properties and corresponding exhaust concentrations for different fuel mixtures.

**Table C.1. MTBE-perturbed fuel mixture.**

Sample Cylinder #	Perturbation size (x's orig vol)	Dilution Ratio	Total % vol MTBE	Additional % vol MTBE	Total % wt MTBE
1	0	12.27	12.79	0.00	12.88
2	0	12.05	12.79	0.00	12.88
5	2	10.49	29.02	18.61	29.19
8	2	10.55	29.02	18.61	29.19
10	1	10.67	21.74	10.26	21.88
12	1	10.59	21.74	10.26	21.88
14	1.5	10.85	25.55	14.64	25.70
16	1.5	10.61	25.55	14.64	25.70

All concentration levels are in PPMC1.

Cylinder #	Methane	Ethene	Ethane	Propane	2-MP	1,3-But	Butane	Pentane
1	79.87	94.33	83.26	134.36	177.94	18.30	7.16	17.90
2	117.84	121.56	112.62	167.25	160.85	7.40	13.70	19.55
5	87.44	112.85	101.28	153.94	209.84	9.95	9.38	17.06
8	95.93	114.26	108.81	147.97	221.64	11.33	10.10	20.18
10	81.19	111.08	101.78	157.23	197.58	10.44	12.21	17.50
12	85.55	114.78	108.09	166.60	199.39	10.88	10.98	19.42
14	10.81	17.48	15.34	27.21	214.50	1.44	1.72	3.84
16	73.47	86.78	76.59	123.60	163.69	16.84	6.59	16.47

Cylinder #	MTBE	Hexane	Benzene	2,2,4-TMP	Heptane	Toluene	Octane	m,p-Xyl
1	63.83	13.05	62.14	89.14	14.70	191.26	6.10	174.43
2	64.71	15.25	85.96	129.32	21.80	265.79	8.70	212.52
5	209.32	11.98	77.10	104.25	16.96	230.48	7.89	216.06
8	217.78	14.09	81.56	109.28	18.32	243.00	8.15	229.70
10	148.60	13.53	77.18	110.62	18.60	234.14	8.24	199.83
12	161.49	13.26	80.10	115.29	11.36	250.90	8.78	221.35
14	197.41	2.09	12.18	18.37	2.99	38.74	1.36	35.12
16	148.12	12.01	57.16	82.00	13.52	175.95	5.61	160.46

\* Only eight of the sixteen samples were analyzed using the GC due to time constraints on this particular day.

**Table C.2. Toluene-perturbed fuel mixture.**

Sample Cylinder #	Perturbation size (x's orig vol)	Dilution Ratio	Total % vol toluene	Additional % vol tol	Total % wt tol
1	0	9.98	6.61	0.00	7.68
2	0	10.44	6.61	0.00	7.68
3	0	10.34	6.61	0.00	7.68
4	0	10.88	6.61	0.00	7.68
5	3	10.65	20.53	14.91	23.28
6	3	9.70	20.53	14.91	23.28
7	3	10.71	20.53	14.91	23.28
8	3	10.08	20.53	14.91	23.28
9	2	10.98	16.38	10.46	18.70
10	2	9.22	16.38	10.46	18.70
11	2	10.37	16.38	10.46	18.70
12	2	10.83	16.38	10.46	18.70
13	1	10.94	11.76	5.52	13.54
14	1	10.88	11.76	5.52	13.54
15	1	10.46	11.76	5.52	13.54
16	1	10.89	11.76	5.52	13.54

All concentration levels are in PPMC1.

Cylinder #	Methane	Ethene	Ethane	Propane	2-MP	1,3-But	Butane	Pentane
1	69.21	164.99	129.78	204.10	181.99	23.73	19.26	26.39
2	57.21	181.39	139.99	204.00	204.84	0.00	19.22	28.77
3	52.61	180.03	131.80	197.91	207.96	10.41	18.45	29.25
4	57.01	179.35	137.55	194.47	203.47	21.28	20.68	29.86
5	40.26	147.42	117.97	186.78	169.84	0.00	18.48	22.69
6	41.70	139.98	116.69	164.00	168.54	13.89	13.85	22.65
7	42.66	154.69	126.31	165.01	168.29	0.00	9.22	26.58
8	45.41	138.74	120.80	149.10	154.54	9.63	16.57	21.98
9	48.02	163.89	140.17	183.35	185.55	0.00	15.33	24.98
10	41.11	132.88	106.42	148.90	145.33	0.00	9.34	19.55
11	48.86	161.96	131.92	168.89	175.81	0.00	9.53	24.50
12	53.54	162.61	141.39	243.45	214.70	0.00	34.14	41.65
13	60.98	182.40	132.68	210.73	182.20	0.00	14.41	23.07
14	68.46	196.98	141.66	192.10	188.02	17.79	11.30	24.76
15	63.70	195.58	140.16	191.93	189.36	10.28	15.99	23.48
16	69.84	197.12	143.84	188.47	189.73	17.78	17.48	24.41

**Toluene-perturbed fuel mixture (continued).**

Cylinder #	MTBE	Hexane	Benzene	2,2,4-TMP	Heptane	Toluene	Octane	m,p-Xyl
1	4.43	26.69	245.27	157.78	39.70	231.25	24.31	138.09
2	3.62	30.61	268.41	187.98	47.64	273.09	29.08	170.82
3	4.48	28.79	268.93	186.97	44.72	266.52	28.39	171.45
4	3.76	28.05	274.88	186.69	47.01	271.05	30.17	185.30
5	0.00	19.80	287.47	144.51	37.25	612.57	20.15	139.79
6	3.38	25.48	315.88	146.69	37.86	623.10	23.75	144.77
7	3.57	24.04	317.13	143.33	36.42	614.01	22.36	151.16
8	0.00	22.60	297.05	133.14	35.29	571.53	14.78	299.12
9	3.66	25.23	317.72	151.34	38.28	530.34	24.40	168.40
10	0.00	21.26	263.18	127.56	32.05	440.33	21.18	138.88
11	3.66	24.86	313.80	155.00	39.72	529.23	25.22	168.29
12	0.00	44.45	333.66	154.84	56.10	480.76	21.32	202.94
13	3.83	23.60	303.68	151.56	37.60	372.58	23.49	154.13
14	5.57	26.05	336.60	168.82	43.63	416.36	26.59	176.13
15	4.29	25.40	319.88	159.11	38.91	382.36	20.30	158.31
16	3.72	27.35	352.28	168.24	42.25	444.44	27.70	203.94

**Table C.3. m,p-Xylene-perturbed fuel mixture.**

Sample Cylinder #	Perturbation size (x's orig vol)	Dilution Ratio	Total % vol m,p-xylene	Additional % vol xyl	Total % wt xyl
1	3	10.68	17.82	13.18	20.25
2	3	10.77	17.82	13.18	20.25
4	3	10.54	17.82	13.18	20.25
5	2	10.19	14.04	9.19	16.05
6	2	10.03	14.04	9.19	16.05
7	2	10.05	14.04	9.19	16.05
8	2	10.11	14.04	9.19	16.05
9	1	10.22	9.90	4.82	11.40
10	1	9.86	9.90	4.82	11.40
11	1	10.24	9.90	4.82	11.40
12	1	10.69	9.90	4.82	11.40
13	0	10.74	5.34	0.00	6.20
14	0	11.46	5.34	0.00	6.20
15	0	10.64	5.34	0.00	6.20
16	0	12.47	5.34	0.00	6.20

**m,p-Xylene-perturbed fuel mixture (continued).**

All concentration levels are in PPMC1.

Cylinder #	Methane	Ethene	Ethane	Propane	2-MP	1,3-But	Butane	Pentane
1	42.21	99.56	89.48	120.04	105.48	12.18	10.76	17.42
2	42.15	118.34	103.67	160.63	131.83	0.00	11.84	21.76
4	37.92	108.35	93.97	137.00	118.80	0.00	11.12	19.34
5	35.28	113.59	101.74	160.32	140.50	0.00	13.57	20.69
6	33.49	113.64	102.77	164.20	142.76	0.00	14.04	21.05
7	34.76	108.52	99.21	154.66	127.74	2.98	12.02	19.00
8	35.50	116.66	107.18	164.52	140.78	0.00	13.40	21.54
9	35.87	122.41	104.52	176.77	154.53	8.09	14.47	17.10
10	33.23	118.49	99.86	175.94	151.29	0.00	15.19	23.80
11	37.06	123.89	109.51	178.77	150.04	0.00	12.02	23.34
12	36.20	132.53	111.94	192.98	168.00	0.00	15.00	27.23
13	34.25	127.69	106.42	186.59	156.80	0.00	13.40	24.25
14	47.04	145.73	130.39	201.76	170.55	0.00	14.28	25.22
15	42.31	122.03	108.78	164.79	143.38	11.27	15.18	19.70
16	38.37	145.39	118.04	215.33	186.70	0.00	17.21	28.58

Cylinder #	MTBE	Hexane	Benzene	2,2,4-TMP	Heptane	Toluene	Octane	m,p-Xyl
1		14.81	78.18	91.78	16.55	258.12	6.99	516.69
2		16.28	86.25	111.64	19.38	305.44	7.53	604.71
4		15.87	84.29	104.66	17.69	285.14	7.04	570.32
5		18.53	87.25	127.92	21.22	351.82	9.52	608.76
6		14.80	85.43	118.75	20.11	321.43	8.34	510.69
7		15.62	81.58	113.35	18.30	319.45	8.94	544.86
8		15.94	85.27	121.54	20.40	326.59	8.64	521.57
9		15.92	83.26	129.94	21.21	329.65	8.90	370.12
10		15.48	82.83	125.57	20.80	322.87	8.88	365.49
11		15.14	83.62	124.33	20.49	325.34	8.58	373.21
12		17.82	94.42	147.72	24.49	393.60	10.76	467.22
13		19.13	77.85	126.93	20.46	280.27	8.46	213.08
14		18.36	89.65	141.94	20.55	316.79	8.55	238.83
15		15.22	77.76	126.92	21.25	290.45	8.40	223.38
16		18.70	94.17	152.17	25.04	343.54	21.63	266.59

**Table C.4. Iso-octane-perturbed fuel mixture.**

Sample Cylinder #	Perturbation size (x's orig vol)	Dilution Ratio	Total % vol iso-octane	Additional % vol iso	Total % wt iso
1	0	15.78	7.01	0.00	8.86
2	0	15.62	7.01	0.00	8.86
3	0	15.05	7.01	0.00	8.86
4	0	15.39	7.01	0.00	8.86
5	3	14.72	26.58	21.05	42.51
6	3	14.31	26.58	21.05	42.51
7	3	11.65	26.58	21.05	42.51
8	3	14.36	26.58	21.05	42.51
9	1	12.68	14.84	8.43	20.47
10	1	14.38	14.84	8.43	20.47
11	1	13.35	14.84	8.43	20.47
12	1	13.67	14.84	8.43	20.47
13	2	13.83	21.46	15.54	32.09
14	2	13.16	21.46	15.54	32.09
15	2	12.09	21.46	15.54	32.09

All concentration levels are in PPMC1.

Cylinder #	Methane	Ethene	Ethane	Propane	2-MP	1,3-But	Butane	Pentane
1	35.05	157.81	178.64	171.98	204.22		14.96	24.67
2	49.46	157.40	190.25	217.52	209.85	24.01	15.63	27.52
4	40.39	183.12	217.74	200.70	200.89	29.41	15.40	26.58
5	42.24	126.16	152.45	169.97	215.02	22.99	9.36	15.10
6	81.51	234.38	110.29	191.77	265.78		12.21	18.46
7	57.59	122.42	125.12	157.94	197.13	7.14	8.41	16.91
8	37.68	134.63	164.84	198.30	257.43		9.61	20.08
9	32.08	151.93	164.70	209.08	228.28	22.76	13.23	22.11
10	49.84	144.95	176.34	202.16	232.61		13.54	22.91
11	52.92	138.16	165.99	198.20	216.85	12.23	13.49	21.19
12	84.15	251.98	118.03	198.73	222.15			20.80
13	51.19	128.56	173.66	203.48	239.64		11.02	20.88
14	48.17	146.72	181.77	212.47	249.21		11.83	23.12
15	74.72	151.01	174.83	216.28	241.01	5.50	11.53	23.20
16	70.21	145.21	156.24	200.43	236.99	5.71	11.77	20.88

**Iso-octane-perturbed fuel mixture (continued).**

Cylinder #	MTBE	Hexane	Benzene	2,2,4-TMP	Heptane	Toluene	Octane	m,p-Xyl
1		18.29	77.32	171.90	23.55	305.42	9.68	254.53
2		19.06	82.52	160.59	25.15	326.99	10.65	284.27
4		18.15	81.39	156.15	24.42	321.81	9.60	284.18
5		11.29	53.92	357.85	13.53	194.31	5.68	171.51
6		13.34	66.03	491.18	16.82	230.47	6.93	201.50
7		10.78	50.24	345.84	13.29	182.66	6.06	184.40
8		13.42	63.48	496.84	17.04	234.59	7.79	245.70
9		15.59	71.94	260.48	20.45	282.66	9.10	249.35
10		17.42	73.56	309.04	21.59	293.33	10.03	263.15
11		14.57	69.83	244.19	19.59	270.74	8.72	245.39
12		16.04	70.91	279.49	20.03	270.30	9.33	236.86
13		13.99	66.09	385.59	18.55	262.52	8.92	240.62
14		14.67	70.77	418.77	20.09	283.44	8.73	250.69
15		14.54	69.17	357.64	19.20	269.66	8.81	239.79
16		14.68	68.25	362.30	17.30	270.69	8.63	234.16

## APPENDIX D

**TABLE D.1. PERCENT VOLUMES AND NEW HC INDICES**

	% vol MTBE	% vol iso-octane	% vol paraffins	Experimental HC Index calculated from GC analyzer data	Averaged HC Index	New normalized HC Index	Calculated normalized HC Index using determined sensitivities	New offset HC Index	Calculated offset HC Index using determined sensitivities
Toluene perturbed mixture	0.1208	0.0662	0.4275	0.1456	0.1438	0.1365	0.1327	0.1360	0.1334
	0.1208	0.0662	0.4275	0.1453	0.1438	0.1362	0.1327	0.1357	0.1334
	0.1208	0.0662	0.4275	0.1443	0.1438	0.1352	0.1327	0.1347	0.1334
	0.1208	0.0662	0.4275	0.1398	0.1438	0.1310	0.1327	0.1302	0.1334
	0.1145	0.0628	0.4052	0.1648	0.1385	0.1544	0.1258	0.1551	0.1265
	0.1145	0.0628	0.4052	0.1349	0.1385	0.1264	0.1258	0.1253	0.1265
	0.1145	0.0628	0.4052	0.1115	0.1385	0.1045	0.1258	0.1019	0.1265
	0.1145	0.0628	0.4052	0.1424	0.1385	0.1335	0.1258	0.1328	0.1265
	0.1088	0.0596	0.3850	0.1186	0.1269	0.1111	0.1195	0.1090	0.1201
	0.1088	0.0596	0.3850	0.1292	0.1269	0.1210	0.1195	0.1195	0.1201
	0.1088	0.0596	0.3850	0.1294	0.1269	0.1212	0.1195	0.1197	0.1201
	0.1088	0.0596	0.3850	0.1304	0.1269	0.1222	0.1195	0.1207	0.1201
	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1562</b>	<b>0.1532</b>	<b>0.1463</b>	<b>0.1405</b>	<b>0.1465</b>	<b>0.1412</b>
	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1596</b>	<b>0.1532</b>	<b>0.1496</b>	<b>0.1405</b>	<b>0.1500</b>	<b>0.1412</b>
	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1572</b>	<b>0.1532</b>	<b>0.1473</b>	<b>0.1405</b>	<b>0.1476</b>	<b>0.1412</b>
<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1397</b>	<b>0.1532</b>	<b>0.1309</b>	<b>0.1405</b>	<b>0.1300</b>	<b>0.1412</b>	
Iso-oct perturbed mixture	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1619</b>	<b>0.1648</b>	<b>0.1410</b>	<b>0.1405</b>	<b>0.1406</b>	<b>0.1412</b>
	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1699</b>	<b>0.1648</b>	<b>0.1480</b>	<b>0.1405</b>	<b>0.1486</b>	<b>0.1412</b>
	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>		<b>0.1648</b>		<b>0.1405</b>		<b>0.1412</b>
	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1626</b>	<b>0.1648</b>	<b>0.1416</b>	<b>0.1405</b>	<b>0.1414</b>	<b>0.1412</b>
	0.1010	0.2658	0.3572	0.2102	0.2074	0.1831	0.1801	0.1890	0.1852
	0.1010	0.2658	0.3572	0.2107	0.2074	0.1835	0.1801	0.1894	0.1852
	0.1010	0.2658	0.3572	0.2045	0.2074	0.1781	0.1801	0.1833	0.1852
	0.1010	0.2658	0.3572	0.2040	0.2074	0.1777	0.1801	0.1828	0.1852
	0.1171	0.1484	0.4144	0.1848	0.1802	0.1609	0.1563	0.1635	0.1588
	0.1171	0.1484	0.4144	0.1844	0.1802	0.1606	0.1563	0.1631	0.1588
	0.1171	0.1484	0.4144	0.1755	0.1802	0.1529	0.1563	0.1543	0.1588
	0.1171	0.1484	0.4144	0.1761	0.1802	0.1534	0.1563	0.1548	0.1588
	0.1080	0.2146	0.3822	0.1899	0.1936	0.1654	0.1697	0.1687	0.1737
	0.1080	0.2146	0.3822	0.1975	0.1936	0.1720	0.1697	0.1763	0.1737
	0.1080	0.2146	0.3822	0.1951	0.1936	0.1699	0.1697	0.1738	0.1737
0.1080	0.2146	0.3822	0.1918	0.1936	0.1671	0.1697	0.1706	0.1737	

\*values in bold are for baseline mixtures with no perturbation

	% vol MTBE	% vol iso-octane	% vol paraffins	Experimental HC Index calculated from GC analyzer data	Averaged HC Index	New normalized HC Index	Calculated normalized HC Index using determined sensitivities	New offset HC Index	Calculated offset HC Index using determined sensitivities
Xylene perturbed mixture	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1433</b>	<b>0.1261</b>	<b>0.1630</b>	<b>0.1405</b>	<b>0.1607</b>	<b>0.1412</b>
	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1100</b>	<b>0.1261</b>	<b>0.1252</b>	<b>0.1405</b>	<b>0.1274</b>	<b>0.1412</b>
	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1309</b>	<b>0.1261</b>	<b>0.1489</b>	<b>0.1405</b>	<b>0.1483</b>	<b>0.1412</b>
	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1203</b>	<b>0.1261</b>	<b>0.1369</b>	<b>0.1405</b>	<b>0.1377</b>	<b>0.1412</b>
	0.1217	0.0667	0.4307	0.1289	0.1197	0.1467	0.1337	0.1463	0.1344
	0.1217	0.0667	0.4307	0.1152	0.1197	0.1310	0.1337	0.1325	0.1344
	0.1217	0.0667	0.4307	0.1161	0.1197	0.1321	0.1337	0.1335	0.1344
	0.1217	0.0667	0.4307	0.1186	0.1197	0.1349	0.1337	0.1360	0.1344
	0.1161	0.0637	0.4109	0.1080	0.1059	0.1229	0.1275	0.1254	0.1283
	0.1161	0.0637	0.4109	0.0980	0.1059	0.1116	0.1275	0.1154	0.1283
	0.1161	0.0637	0.4109	0.1096	0.1059	0.1247	0.1275	0.1269	0.1283
	0.1161	0.0637	0.4109	0.1078	0.1059	0.1227	0.1275	0.1252	0.1283
	0.1110	0.0609	0.3929	0.0912	0.0911	0.1037	0.1219	0.1086	0.1226
	0.1110	0.0609	0.3929	0.1012	0.0911	0.1151	0.1219	0.1186	0.1226
	0.1110	0.0609	0.3929	0.0810	0.0911	0.0921	0.1219	0.0983	0.1226
0.1110	0.0609	0.3929		0.0911		0.1219		0.1226	
MTBE perturbed mixture	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1366</b>	<b>0.1300</b>	<b>0.1508</b>	<b>0.1405</b>	<b>0.1501</b>	<b>0.1412</b>
	<b>0.1279</b>	<b>0.0701</b>	<b>0.4525</b>	<b>0.1235</b>	<b>0.1300</b>	<b>0.1363</b>	<b>0.1405</b>	<b>0.1370</b>	<b>0.1412</b>
	0.2902	0.0571	0.3683	0.1611	0.1656	0.1778	0.1860	0.1746	0.1819
	0.2902	0.0571	0.3683	0.1701	0.1656	0.1878	0.1860	0.1836	0.1819
	0.2174	0.0629	0.4061	0.1516	0.1523	0.1674	0.1656	0.1652	0.1637
	0.2174	0.0629	0.4061	0.1530	0.1523	0.1689	0.1656	0.1665	0.1637
	0.2555	0.0598	0.3863	0.1646	0.1617	0.1817	0.1763	0.1781	0.1732
	0.2555	0.0598	0.3863	0.1588	0.1617	0.1753	0.1763	0.1723	0.1732

Avg 2methylpropene HC Index for unperturbed fuel = 0.1435 (100 x g<sub>HC</sub>/g<sub>fuel</sub>)

Fuel Mixture	Normalizing factor using avg HC	Offset value using avg HC
Toluene	0.9371	-0.0096
Iso-octane	0.8710	-0.0213
m,p-Xylene	1.1378	0.0107
MTBE	1.1040	0.0135
	Using normalized data	Using offset data
MTBE	m1 = 0.3852	0.3598
iso-oct	m2 = 0.3287	0.3500
others	m3 = 0.1506	0.1562