Final Report

Effects of Ethanol and Volatility Parameters on Exhaust Emissions

CRC Project No. E-67

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Table of Contents

List of Figures

List of Tables

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Executive Summary

Regulations on the composition of gasoline for environmental and other initiatives continue to play an important role in the production of gasoline. Predictions of the effects of changes in fuel properties on vehicle emissions are incorporated in the Environmental Protection Agency's (EPA's) Complex Model and the California Air Resources Board's (CARB's) Predictive Model. Oxygenate content and fuel volatility (distillation) variables are important parameters when determining the emission reduction potential of new fuels and these properties are included in the models used by EPA and CARB. Although the effects of fuel volatility and oxygenates on emissions have been extensively studied in the past, data on the effects of these fuel properties on the latest-technology vehicles – those certified to California's Low-Emission Vehicle (LEV), Ultra-Low-Emission Vehicle (ULEV), and Super-Ultra-Low-Emission Vehicle (SULEV) standards – are quite limited.

The goal of the present project is to expand the database of information available on the impacts of gasoline volatility parameters and ethanol content on exhaust emissions. This program includes a test fleet with the newest technology vehicles and a comprehensive set of test fuels with varying ethanol content and mid-range and back-end volatility. For this study, 12 California-certified LEV to SULEV vehicles, with an even split between passenger cars and light-duty trucks, were tested on a 12 fuel test matrix. The 12 fuels were designed with independently varying levels of ethanol concentration (0 volume %, 5.7 volume %, and 10 volume %), T_{50} (195°F, 215°F, and 235°F), and T_{90} (295°F, 330°F, and 355°F). The fuel matrix was designed to represent both non-oxygenated and oxygenated fuels available in California and the rest of the US. Vehicles were tested with catalysts that were bench-aged to an equivalent of 100,000 miles. Measurements included regulated exhaust emissions (non-methane hydrocarbons (NMHC), carbon monoxide (CO), and oxides of nitrogen (NO_x)), fuel consumption, as well as detailed non-methane organic gas (NMOG) speciation for a subset of four fuels. Complete randomization of the fuels testing order resulted in a more statistically-robust dataset for analysis.

The final analysis of project data estimated regression coefficients for the fuel effects, with the levels of ethanol, T_{50}, and T_{90} used as continuous variables. Models predicting emissions and fuel consumption from first order effects, second order effects, and interactions of the fuel parameters were derived.

Key findings are as follows:

Regulated Emissions and Fuel Consumption

- NMHC:
    - There was a statistically significant interaction between ethanol and T_{90}. The interaction showed that NMHC emissions increased with increasing ethanol content at the mid-point and high level of T_{90}, but were unaffected at the low T_{90} level. Looked at another way, NMHC emissions increased with increasing T_{90} at

the mid-point and high level of ethanol, but were unaffected by T_{90} at the zero level of ethanol.
- NMHC emissions increased with increasing T_{50}. The percentage increases in NMHC emissions in going from the low and mid-point level for T_{50} to the high T_{50} level were 36 and 25%, respectively.

- CO:
  - There was a statistically significant interaction between ethanol and T_{50}. The interaction showed that CO emissions decreased as ethanol content was increased from the low to the mid-point level for all levels of T_{50}. However, increasing ethanol content from the mid-point to the high level produced little to no change in CO for the low and mid-point levels of T_{50}, and increased CO at the high level of T_{50}. Looked at another way, CO emissions increased with increasing T_{50} at the mid-point and high levels of ethanol, but were unaffected by T_{50} at the zero level of ethanol.
  - CO emissions decreased with increasing T_{90}. The percentage decreases in CO emissions in going from the low and mid-point level for T_{90} to the high T_{90} level were 24% and 7%, respectively.

- NO_x:
  - There was a statistically significant interaction between ethanol and T_{50}. The interaction showed that NO_x emissions increase with increasing ethanol content at the low level of T_{50}. At the mid-point level of T_{50}, NO_x emissions are largely unaffected as ethanol content is increased from the zero to the mid-point level, but increase as ethanol is increased to the high level. At the high level of T_{50}, NO_x emissions are largely unaffected by ethanol content. Looked at another way, NO_x emissions decreased with increasing T_{50} at the high level of ethanol, but were largely unaffected by T_{50} at the zero and mid-point levels of ethanol.

- Fuel Consumption:
  - Fleet average fuel consumption increased by 1.4% when ethanol content was increased from the zero to the high level.
  - Fleet average fuel consumption decreased by 1.2% when T_{50} was increased from the low to the high level.
  - Fleet average fuel consumption decreased by 0.6% when T_{90} was increased from the low to the high level.

In the fuel set used in this work, 10% ethanol tended to decrease volumetric heat content by 2.2%.

NMOG and Toxics Emissions

Detailed speciation measurements were performed for a subset of four fuels with target T_{90} = 355°F in order to evaluate the fuel effects of ethanol and T_{50} on NMOG and the four mobile source air toxics: benzene, 1,3-butadiene, formaldehyde and acetaldehyde. Key findings are as follows:

- NMOG:
    - NMOG emissions increased by 14% when ethanol content was increased from the zero to the high level.
    - NMOG emissions increased by 35% when T_{50} was increased from the low to the high level.

- Formaldehyde:
    - Formaldehyde emissions increased by 23% when T_{50} was increased from the low to the high level.

- Acetaldehyde:
    - Acetaldehyde emissions increased by 73% when ethanol content was increased from the zero level to the high level.

- Benzene:
    - Benzene emissions increased by 18% when ethanol content was increased from the zero to the high level.
    - Benzene emissions increased by 38% when T_{50} was increased from the low to the high level.

- 1,3-butadiene:
    - 1,3-butadiene emissions increased by 22% when ethanol content was increased from the zero to the high level.
    - 1,3-butadiene emissions increased by 56% when T_{50} was increased from the low to the high level.

The effects of ethanol and T_{50} on NMOG and mobile source toxics described above were only observed for the subset of fuels having the high level of T_{90}. The results of this study do not permit any conclusions as to what effects ethanol or T_{50} might have had on NMOG or toxics emissions for fuels having low or mid-point T_{90} levels.

1. Introduction

As vehicle and fuel technologies continue to meet more stringent emission standards, it is useful to understand the effects of fuel properties on the emissions and performance of vehicles. Over the years, the impact of fuel properties on vehicle emissions has been the subject of numerous studies and programs. Data from these earlier programs have been used in the development of regulations for fuel properties. These data also have been incorporated into the Environmental Protection Agency's (EPA's) Complex Model and the California Air Resources Board's (CARB's) Predictive Model to estimate the effects of changes in fuel properties on vehicle emissions. Although the database on the emissions impact of fuel properties is large, data on the effects of fuel properties on the latest technology vehicles – those certified to California's Low-Emission Vehicle (LEV), Ultra-Low-Emission Vehicle (ULEV), and Super-Ultra-Low-Emission Vehicle (SULEV) standards – is more limited. In the future, these vehicle technologies will account for an increasing share of the emissions of the in-use vehicle fleet.

Today, regulatory agencies continue to consider changes in gasoline composition regulations in response to environmental and other initiatives. Oxygenate content and fuel volatility are two parameters that are considered to be important in determining the emission reduction potential of new fuels. Both properties are included in the models used by EPA and CARB. Many states have banned methyl t-butyl ether (MTBE), leading to greater use of ethanol (EtOH). The Renewable Fuel Standard (RFS) adopted as part of the federal Energy Policy Act of 2005 requires significant and increasing volumes of renewables to blended into the transportation fuel pool between 2006 and 2012, much of which is likely to be ethanol.

The effects of fuel volatility and ethanol/oxygenates on emissions have been investigated extensively in past studies [1-12]. These studies have shown some general trends of how these properties affect emissions. The reduction of T_{50} and T_{90} and the corresponding reduction of heavy fuel hydrocarbon compounds have generally been found to reduce exhaust hydrocarbon emissions [2,3,5,8]. Ethanol and other oxygenates typically have been found to reduce total hydrocarbon (THC) and carbon monoxide (CO) emissions [1,2,7-9,11,12]. Increases in oxides of nitrogen (NO_x) have been observed for oxygenates in some studies, although this observation is not consistent over all test fleets [1,2,7-9,11,12]. While these studies provide important information, there is relatively limited data on how these fuel parameters will affect emissions in advanced technology vehicles. Some of the more recent studies also include some contradictory data, including a recent study in which slightly higher NO_x emissions were found for a fuel with no oxygenates in comparison with the oxygenated fuels [1].

The goal of this project is to expand the database of information available on the impacts of gasoline volatility parameters and ethanol content on exhaust emissions. This program includes a comprehensive set of test fuels with varying ethanol content and mid- and back-end volatility, and a test fleet with the newest technology vehicles. Measurements include detailed non-methane organic gas (NMOG) speciation for a subset of fuels. The information obtained from this study is valuable in better understanding and predicting the implications of changes in fuel properties for regulatory or other reasons.

2. Experimental Procedures

2.1 Test Vehicles

Twelve vehicles were recruited for testing. The vehicles included present day technologies with California low-emission vehicle (LEV), ultra-low emission vehicle (ULEV), and super-ultra-low-emission vehicle (SULEV) certification. The test fleet was evenly split between passenger cars and light-duty trucks. Within each general certification category, e.g., LEV, the passenger cars and trucks are certified to different standards, and as such represent different emissions categories. Vehicles were obtained from a combination of sources including rental agencies, private parties, and corporate sponsors. All vehicles had accumulated at least 10,000 miles. Prior to entering the program, all vehicles were inspected using a standard checklist to ensure that they were in sound mechanical and operational condition. The vehicles were fitted with catalysts that had been bench-aged to the equivalent of 100,000 miles for testing. The specific details of the vehicles used in this project are listed in Table 1.

Table 1. Description of Test Vehicles

#	MY	OEM	Model	California Certification	Type	Engine Size	Mileage	Engine Family
1	2002	Ford	Taurus	LEV	PC	3.0 L	19,414	1FMXV03.0VF4
2	2003	Chevrolet	Cavalier	LEV	PC	2.2 L	28,728	1GMXV02.2025
3	2003	Ford	F-150	LEV	LDT	4.6 L	13,856	3FMXT05.4PFB
4	2003	Dodge	Caravan	LEV	LDT	3.3 L	18,342	3CRXT03.32DR
5	2003	Ford	Explorer	LEV	LDT	4.0 L	16,445	3FMXT04.02FB
6	2003	Chevrolet	Trailblazer	LEV	LDT	4.2 L	13,141	3GMXT04.2185
7	2002	Toyota	Camry	ULEV	PC	2.4 L	14,731	1TYXV02.4JJA
8	2003	Buick	LeSabre	ULEV	PC	3.8 L	10,364	3GMXV03.8044
9	2001	VW	Jetta	ULEV	PC	2.0 L	28,761	1VWXV02.0223
10	2003	Ford	Windstar	ULEV	LDT	3.8 L	20,523	3FMXT03.82HA
11	2003	Chevrolet	Silverado	ULEV	LDT	5.3 L	10,298	3GMXT05.3176
12	2003	Honda	Accord	SULEV	PC	2.4 L	12,432	3HNXV02.4KCP

PC = passenger car; LDT = light-duty truck; vehicles equipped with catalysts aged to 100,000 miles for testing

2.2 Fuels

Twelve fuels were prepared and provided for testing for this project. These 12 fuels were designed to encompass three levels of ethanol content (0%, 5.7% and 10%), three levels of T_{50} (195°F, 215°F and 235°F), and three levels of T_{90} (295°F, 330°F, and 355°F). The values for ethanol represent typical ethanol concentrations found in California (5.7%) and the rest of the US (10%). The ranges for both T_{50} and T_{90} span the 10th and 90th percentile values based on summer fuel surveys during/through calendar year 2002. Previous studies had shown that in addition to the main effects of ethanol, T_{50}, and T_{90}, curvature effects for each of these factors and interactions between ethanol and each of T_{50} and T_{90} might be important. From a full factorial design matrix of 27 fuels obtained from the three fuel factors each at three levels, statistical optimality criteria combined with practical concerns about what fuels could be blended

from refinery streams led to the selection of 12 fuels as best for estimating the possible fuel effects. The fuel design matrix is shown graphically in Figure 1. A summary of the design and actual values of the fuel properties is provided in Table 2. The actual fuel property values shown in Table 2 represent averages of measurements from four or five laboratories, depending on the specific property. Driveability Index (DI) was calculated for each fuel using the equation recently balloted by ASTM. A more detailed listing of the fuel properties is provided in Appendix A.

The fuels were blended from refinery streams with the general properties targeted to be constant for all fuels in order to reduce or eliminate any potential confounding effect of these properties with the design parameters. The target values for the general fuel properties are provided in Table 3. The general fuel properties are intended to be representative of fuels that are available in the commercial marketplace, but are not necessarily representative of all commercial fuels. The fuels were blended by Haltermann Products, Channelview, TX.

The lubricant used for this study was a zero-sulfur, synthetic base lubricant containing ashless, zero-sulfur antiwear and anti-oxidant additives. This is the same lubricant that was used in two other recent vehicle emissions test programs [13, 14].

Figure 1. CRC E-67 Fuel Cube Design

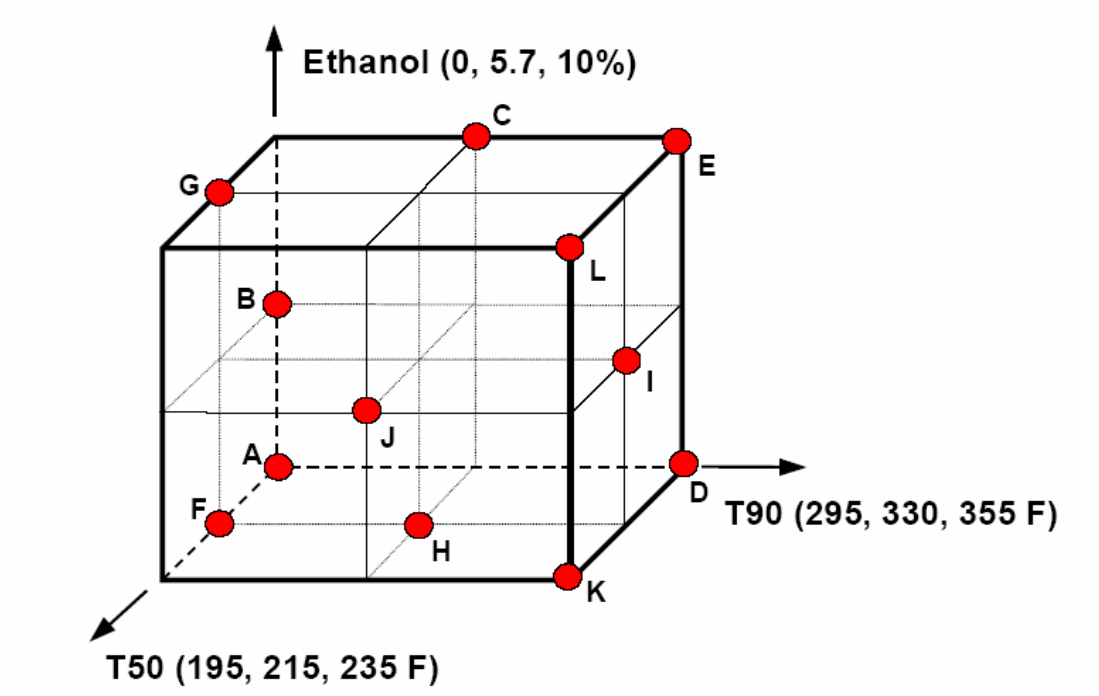


Table 2. Summary of Target and Actual Fuel Properties.

	Target Properties for Design Variables				Actual Values					
Fuel	T_{50},°F	T_{90},°F	Ethanol, %		T_{50},°F	T_{90},°F	Ethanol, %	E200, %	E300, %	Driveability Index (DI)*
A	195	295	0		195	294	0.0	54	91	1082
B	195	295	5.7		191	290	5.6	58	92	1076
C	195	330	10		193	329	10.4	52	84	1128
D	195	355	0		199	355	0.0	51	84	1153
E	195	355	10		198	352	10.3	51	80	1165
F	215	295	0		217	295	0.0	40	91	1148
G	215	295	10		212	291	10.1	47	80	1151
H	215	330	0		216	327	0.1	42	85	1177
I	215	355	5.7		216	354	5.9	43	78	1211
J	235	330	5.7		237	329	5.9	35	78	1255
K	235	355	0		236	355	0.0	38	75	1258
L	235	355	10		233	349	10.5	39	78	1282

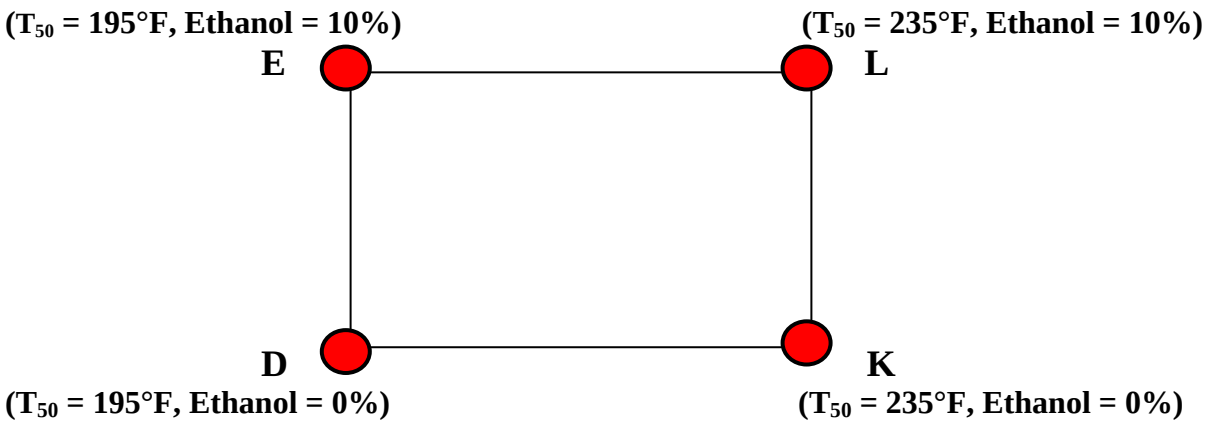
***** DI = $1.5*T_{10} + 3.0*T_{50} + 1.0*T_{90}$ + 2.4*vol% Ethanol **(**Equation recently balloted by ASTM**)**

Table 3. Description of General Fuel Properties.

Property	Limits	Test Method
RVP	7.5-7.8 psi	ASTM 5191
FBP	<437 °F	ASTM D 86
RON	91-95	ASTM D 2699
MON	83-87	ASTM D 2700
(R+M)/2	87-91	
Aromatics	23-27%	ASTM D1319 (Vol. %), or D5580 (Wt. %)
Benzene	0.9-1.0 wt. %	ASTM D 5580 or D3606
Olefins	8-12%	ASTM D 1319 (Vol. %) or D6550 (Wt.%)
Sulfur	15-20 ppm	ASTM D2622
Note: All fuels met the quality levels in ASTM D4814 and contained a detergent additive.		

In addition to the regulated emissions, full NMOG speciation measurements were made on the subset of fuels D, E, K, and L. These fuels represent the four corners of the right face of the fuel cube presented in Figure 1. These fuels all had the same T_{90} target value of 355°F, but differed in ethanol content and T_{50}. The characteristics of these fuels are presented in the fuel square in Figure 2.

Figure 2. Fuel Square for Fuels D, E, K, and L (all Target T_{90} = 355°F)



In conducting more detailed analyses of the hydrocarbon species, it was determined that some fuels had become contaminated with low levels of vinyl acetate during the blending process. The vinyl acetate was introduced through one of the blend stocks and as such was more or less prevalent in the particular fuels that either used or did not use that blend stock. In total, 9 of the 12 fuels were contaminated with the vinyl acetate at levels ranging from 100-600 ppm.

Although it was not believed that vinyl acetate at these levels would influence the emissions results being measured in this study, a series of tests were performed to confirm this belief. Both bench and vehicle tests were performed to evaluate the potential effects of vinyl acetate. The bench tests included unwashed and solvent-washed gum (D 381), peroxides (D 3703/D 6447), and bench PFI deposits (D 6421). Vehicle emissions tests were performed on a subset of vehicles comparing an undoped, in-use, unoxygenated California gasoline with the same fuel doped with vinyl acetate. For each of the tests conducted, no effects were observed from the vinyl acetate contamination/doping. A summary of the test results for the vinyl acetate testing is provided in Appendix B.

2.3 Catalyst and Oxygen Sensor Aging

For this program, each vehicle was tested using a bench-aged catalyst system. All catalyst aging was conducted at Johnson Matthey Testing in Taylor, MI. New catalyst systems were obtained from local dealerships for each of the vehicles. This included the underfloor catalyst(s), any close-coupled catalyst(s), and pre- and post-catalyst oxygen sensors. The catalyst systems were aged for 75 hours (100,000 mile equivalent) using the Rapid Aging Test-A (RAT-A) protocol [15]. All catalysts were aged using a single engine with the RAT-A temperature profile maintained for each catalyst. The aging protocol is discussed in detail in Appendix C. A site visit to Johnson Matthey Testing was performed by CRC to verify the aging setups and protocols utilized.

2.4 Test Sequence Randomization

A key feature of this research was the randomized fuel test order within each vehicle. All fuels were tested once before starting the second test of each fuel. This resulted in the fuels being tested in two blocks. This randomized approach allows the use of more robust statistical methods during the data analysis phase. Although such randomization can result in higher test-to-test variability for a given fuel on an individual vehicle, this reflects the true variability in emissions testing. The randomization matrix is provided in Table 4. It should be noted that analyses of the data showed very little confounding of test sequence with the variables under study and indicated that the randomization has no substantial problems.

Table 4. Fuel Randomization Matrix.

Block	Vehicle 1	Vehicle 2	Vehicle 3	Vehicle 4	Vehicle 5	Vehicle 6	Vehicle 7	Vehicle 8	Vehicle 9	Vehicle 10	Vehicle 11	Vehicle 12
1	Fuel K	Fuel A	Fuel G	Fuel A	Fuel B	Fuel G	Fuel D	Fuel L	Fuel H	Fuel B	Fuel C	Fuel E
1	Fuel I	Fuel H	Fuel J	Fuel K	Fuel I	Fuel D	Fuel E	Fuel D	Fuel J	Fuel K	Fuel F	Fuel K
1	Fuel H	Fuel J	Fuel B	Fuel L	Fuel F	Fuel L	Fuel A	Fuel C	Fuel L	Fuel L	Fuel I	Fuel G
1	Fuel E	Fuel E	Fuel D	Fuel H	Fuel J	Fuel C	Fuel F	Fuel A	Fuel I	Fuel F	Fuel D	Fuel B
1	Fuel G	Fuel F	Fuel E	Fuel E	Fuel G	Fuel J	Fuel L	Fuel F	Fuel C	Fuel E	Fuel H	Fuel J
1	Fuel D	Fuel C	Fuel H	Fuel J	Fuel A	Fuel I	Fuel H	Fuel K	Fuel G	Fuel J	Fuel J	Fuel I
1	Fuel C	Fuel G	Fuel L	Fuel G	Fuel D	Fuel E	Fuel C	Fuel I	Fuel F	Fuel H	Fuel K	Fuel L
1	Fuel A	Fuel B	Fuel C	Fuel B	Fuel H	Fuel K	Fuel J	Fuel B	Fuel K	Fuel A	Fuel A	Fuel C
1	Fuel J	Fuel K	Fuel A	Fuel I	Fuel C	Fuel F	Fuel B	Fuel E	Fuel A	Fuel I	Fuel L	Fuel H
1	Fuel L	Fuel I	Fuel K	Fuel D	Fuel E	Fuel H	Fuel K	Fuel J	Fuel B	Fuel G	Fuel G	Fuel D
1	Fuel B	Fuel L	Fuel F	Fuel C	Fuel L	Fuel A	Fuel G	Fuel H	Fuel E	Fuel D	Fuel E	Fuel F
1	Fuel F	Fuel D	Fuel I	Fuel F	Fuel K	Fuel B	Fuel I	Fuel G	Fuel D	Fuel C	Fuel B	Fuel A
2	Fuel I	Fuel C	Fuel B	Fuel G	Fuel D	Fuel F	Fuel H	Fuel L	Fuel A	Fuel F	Fuel L	Fuel K
2	Fuel F	Fuel K	Fuel H	Fuel C	Fuel G	Fuel B	Fuel D	Fuel G	Fuel J	Fuel I	Fuel G	Fuel I
2	Fuel B	Fuel G	Fuel E	Fuel H	Fuel B	Fuel C	Fuel C	Fuel B	Fuel B	Fuel K	Fuel I	Fuel H
2	Fuel K	Fuel H	Fuel K	Fuel J	Fuel C	Fuel I	Fuel G	Fuel C	Fuel K	Fuel D	Fuel E	Fuel J
2	Fuel G	Fuel L	Fuel A	Fuel B	Fuel H	Fuel G	Fuel B	Fuel J	Fuel I	Fuel L	Fuel A	Fuel A
2	Fuel H	Fuel A	Fuel G	Fuel F	Fuel E	Fuel E	Fuel A	Fuel A	Fuel E	Fuel J	Fuel D	Fuel G
2	Fuel A	Fuel D	Fuel C	Fuel L	Fuel J	Fuel H	Fuel L	Fuel H	Fuel H	Fuel E	Fuel B	Fuel D
2	Fuel J	Fuel J	Fuel L	Fuel I	Fuel K	Fuel J	Fuel F	Fuel K	Fuel C	Fuel A	Fuel C	Fuel F
2	Fuel C	Fuel E	Fuel D	Fuel A	Fuel L	Fuel L	Fuel I	Fuel E	Fuel F	Fuel B	Fuel J	Fuel E
2	Fuel E	Fuel F	Fuel I	Fuel K	Fuel I	Fuel K	Fuel E	Fuel F	Fuel G	Fuel G	Fuel K	Fuel L
2	Fuel D	Fuel B	Fuel F	Fuel D	Fuel A	Fuel A	Fuel J	Fuel I	Fuel L	Fuel H	Fuel H	Fuel B
2	Fuel L	Fuel I	Fuel J	Fuel E	Fuel F	Fuel D	Fuel K	Fuel D	Fuel D	Fuel C	Fuel F	Fuel C

2.5 Test Protocol

The test sequence for the E-67 test program is provided in the flowchart in Figure 3 and summarized briefly below.

Prior to beginning the test sequence on any particular vehicle, a sequence of three oil changes including a 15 minute warm-up period and a change of the oil filter was performed. After the three oil changes, the in-use vehicle catalyst was replaced by a catalyst that was bench-aged as described above. The vehicle was then driven for 100 miles at a steady state speed of 55 mph.

The vehicle fuel preconditioning procedure incorporated multiple drains and fills to ensure complete changeover of the fuel and to minimize or eliminate carryover effects between test fuels. This drain and fill sequence included one additional drain and 4 gallon fill and one drain and 40% fill. After each of these drains and fills, the vehicle was idled for two minutes with the vehicle being rocked back and forth. The vehicle was then conditioned on the road over a course designed to simulate the LA4 portion of the FTP in terms of typical speeds as well as number of stops. Following the road LA4, a sequence of engine off and idles was performed. Based on the results of a recent CRC tank flush effectiveness study, a flush procedure utilizing two 4 gallon

drain and fills resulted in a 96.9% flush effectiveness when the vehicle was subsequently filled for the test sequence [16].

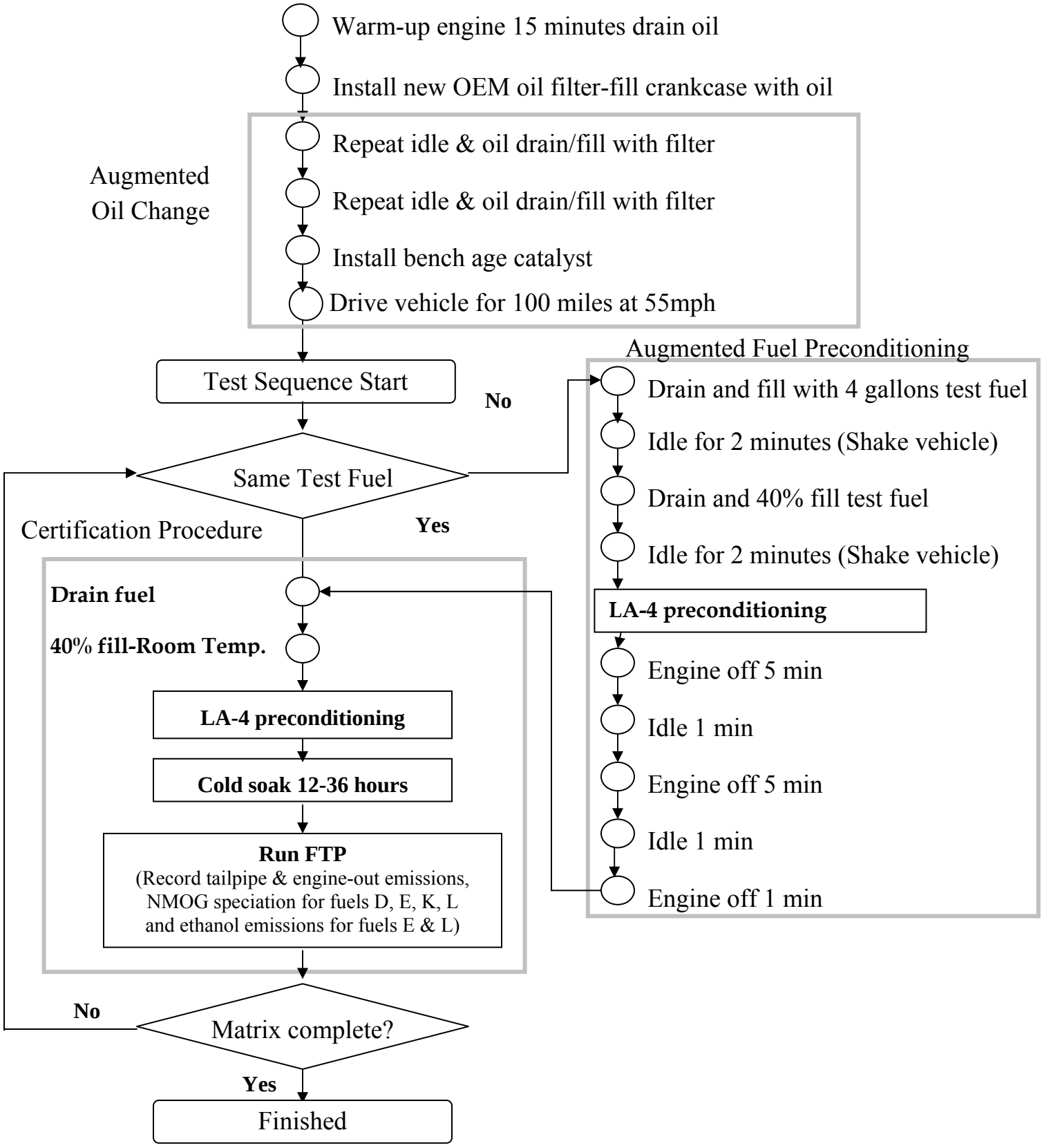
After this sequence, the vehicle entered the certification procedure portion of the preconditioning. For this preconditioning, the vehicle was drained and filled again to the 40% level and then operated over the LA4 on the dynamometer. The vehicle was then placed into cold soak overnight prior to performing the FTP test.

The integrity of the fuel was preserved throughout the multiple drain and fill sequence by maintaining it at or slightly below room temperature (~70°F) in a temperature-controlled facility up until the time the fuel was actually used to fill the vehicle. Each barrel of fuel was equilibrated for a period of at least 24 hours prior to use in the test program. A temperature-controlled storage facility was also secured off-site for longer-term storage of the fuels prior to use in the program. A Reid Vapor Pressure test was conducted prior to test to ensure no change in the integrity of the fuel properties between the time the fuel drum was opened and following a full preconditioning procedure. Separate fuel pumps were also used for each of the test fuels to avoid any possibility of cross-contamination of different fuels.

After both blocks of the randomized testing sequence were completed, the data were evaluated to determine whether additional testing was required. A third test was performed if the difference in the composite FTP emissions exceeded the following: HC 33%, NO_x 29%, CO 70% (provided the absolute difference in the measurements was greater than 5 mg/mi). A total of 43 third tests were performed out of 331 total tests, or approximately one extra test for every 6.7 tests. The majority of third tests were required because the NO_x criterion was exceeded. When a third test was required using fuels D, E, K, and L, this test also included NMOG speciation measurements.

The third FTP test was conducted after the completion of the full randomization schedule for the duplicate tests on all fuels on a particular vehicle. Triplicate tests were performed in the same fuel order as used for the first block of randomized testing for that vehicle.

Figure 3. Flow Chart for CRC Project E-67 Vehicle Testing



2.6 Vehicle Emissions Measurements

2.6.1 Regulated Pollutants and Carbon Dioxide

All tests were conducted in CE-CERT's Vehicle Emissions Research Laboratory (VERL) equipped with a Burke E. Porter 48-inch single-roll electric dynamometer. For these tests, standard bag measurements were obtained for total hydrocarbons (THC), non-methane hydrocarbons (NMHC), carbon monoxide (CO), nitrogen oxides (NO_x), and carbon dioxide (CO_2). Modal tailpipe and engine-out measurements were also taken for THC, NMHC, NO_x, CO, and CO_2. Bag measurements were conducted with a Pierburg AMA-4000 bench while the pre- and post-catalyst emissions measurements were made with a Pierburg AMA-2000 emissions bench. Both the AMA-4000 and the AMA-2000 emission benches incorporate a separate methane (CH_4) analyzer for the determination of NMHC.

2.6.2 Detailed Organic Gas Speciation Sampling and Analysis

The California Air Resources Board definition of non-methane organic gases (NMOG) was used in this study:

$$\text{NMOG} = \text{NMHC (FID)} + \sum\text{Alcohols} + \sum\text{Carbonyls}$$

Full NMOG speciation measurements were made on fuels D, E, K, and L for all vehicles. CE-CERT has a fully operational in-house analytical laboratory for the measurement of C_1-C_{12} NMOG species for gasoline vehicles. The NMOG speciation measurements were performed in accordance with protocols developed previously as part of the Auto/Oil Air Quality Improvement Research Program, including the validation criteria [17]. Given the low levels of emissions for the individual species that were expected for some of the most advanced vehicles being tested, some additional procedures were incorporated to enhance the detection levels for the NMOG species. These improvements were based on procedures utilized in the CARB Haagen-Smit Laboratory and included doubling the size of the sample loop from 5 to 10 ml, changing the flame ionization detector (FID) make-up gas from helium to nitrogen, which roughly doubles the FID sensitivity, and adding a liquid nitrogen cold trap to improve the signal to noise level. The combined enhancements provided approximately a factor of four improvement on the detection limits compared to the earlier Auto/Oil methods.

Samples for the C_1-C_{12} HC speciation were collected in 8L black Tedlar GC bags. Light hydrocarbons (C_1 through C_4) were measured using a Hewlett-Packard (HP) 5890 Series II gas chromatograph with a flame ionization detector (GC/FID) maintained at 250°C. A 15 m x 0.53 mm polyethylene glycol pre-column and a 50 m x 0.53 mm aluminum oxide "S" deactivation porous layer open tubular (PLOT) column were used. A second HP 5890 Series II GC with a FID maintained at 300°C was used to measure the C_4 to C_{12} hydrocarbons. A 2 m x 0.32 mm deactivated fused silica pre-column and a 60 m x 0.32 mm HP-1 column were used. The C_4-C_{12} GC/FID is also set up with a dual column and dual detector to allow simultaneous analysis of two GC bag samples. Separate 10-ml stainless steel sample loops were used for the C_1-C_4 and C_4-C_{12} analyses.

Dilute exhaust gas carbonyls were collected through a heated line onto silica gel cartridges coated with dinitrophenyl-hydrazine (DNPH). The DNPH cartridges were subsequently eluted using acetonitrile to provide samples for analysis. The resulting extract was analyzed using a Shimadzu high performance liquid chromatograph (HPLC) equipped with an SPD-10AV UV-VIS detector. The HPLC sample injection, column, and operating conditions were set up according to the specifications of the HPLC method as described in ref. [17].

2.6.3 Ethanol Exhaust Measurements

To fully characterize the NMOG species in the exhaust, it is important to incorporate the relevant fuel species. In the case of fuels with ethanol, it is useful to include ethanol exhaust measurements as part of the NMOG speciation. Ethanol was measured using the procedures developed for the Auto/Oil Air Quality Improvement Research Program [17]. These procedures incorporate collection of ethanol and other exhaust alcohols in HPLC grade water impingers. The impinger solution was subsequently analyzed using a HP 5890 Series II GC/FID with automatic injection for liquid samples. The exhaust ethanol measurements were made in conjunction with all of the NMOG measurements conducted on fuels E and L (both with 10% ethanol content). Since fuels D and K do not contain ethanol, no ethanol measurements were made on these fuels.

2.7 Statistical Analysis

The statistical analysis procedures are summarized in this section and discussed in greater detail in Appendix D. Emissions analyses for each pollutant were run using the Proc Mixed procedure in PC/SAS from SAS Institute, Inc.

The primary analysis was to estimate the regression parameters for the fuel effects, with the levels of EtOH, T_{50}, and T_{90} used as continuous variables within the model. This model was run on the fuel factors after centering the data by subtracting the average for each fuel factor over the data set. The use of a mixed model was required since the Vehicle effect is a random effect. This model included T_{50}, T_{50}^2, T_{90}, T_{90}^2, EtOH, $EtOH^2$, and the EtOH by T_{50} and EtOH by T_{90} interactions. Terms where variables are squared (i.e., T_{50}^2) are non-linear or second order effects.

The analyses were run using the natural logarithms of the data for the regulated emissions, toxics, and NMOG. Analyses using the logarithmic transform of the data have been conducted in similar previous studies that have shown that emissions standard deviation is relatively constant as a percentage of the emission level [18]. For example, vehicles with higher emission levels will tend to have a higher variability on an absolute basis than those with lower emissions levels. Examination of the current data revealed that this relationship between the emissions level and variability holds true even for the very low emitting vehicles.

In the Results section that follows, effects are referred to as statistically significant if $p<0.05$. Other effects that come close to, but do not meet this criterion are referred to as marginally significant; these variables have $0.05<p<0.10$. The p values are rounded to two decimal places in the tables which follow, but all digits are considered in determining significance. In the case of marginally significant effects, p values are noted in the text to help convey how close they were to being statistically significant. It should also be noted that the results from the ln models

were used to derive the percentage changes and the "balanced averages" shown on the following charts, as described in Appendix D. Finally, statistically significant effects that do not involve interactions are discussed in terms of their quantitative (i.e., %) impact on emissions, while statistically significant effects involving interactions are discussed in qualitative terms.

3. Results

3.1 FTP Regulated Emissions Results

The results of the statistical analyses for the regulated emissions and fuel consumption (inverse of fuel economy) are discussed in this section. It should be noted that for all emissions a statistically significant interaction was typically found both between the vehicles and the intercept and between the fuel design variables (T_{50}, T_{90}, and ethanol) and vehicles. This indicates that both the emission levels and the emission response to the design variables differed between vehicles, as would be expected.

In modern vehicles such as those tested in this program, it is well established that the bulk of the emissions measured over the course of an FTP test are generated in the first seconds of operation following a cold start before the catalyst systems have warmed up to their normal operating temperatures. As such, statistical analyses were performed on both the FTP composite emissions and the Bag 1 emissions to determine whether different effects were evident.

3.1.1 FTP NMHC Emissions

The statistical analysis results for NMHC are presented in Table 5.

Table 5. Mixed Model Summary for NMHC

	FTP Composite		Bag 1	
Random Factor	P value		P value	
Vehicle	0.01		0.01	
T_{50} x Vehicle	0.05		0.05	
T_{90} x Vehicle	0.02		0.02	
EtOH x Vehicle	0.04		0.04	
Fuel Factor	Coefficient	P value	Coefficient	P value
Intercept	-3.2942		-1.8333	
T_{50}	0.006300	0.00	0.006247	0.00
T_{90}	0.001685	0.06	0.001581	0.13
EtOH	0.005679	0.11	0.006024	0.09
T_{50}^2	0.000176	0.00	0.000194	0.00
T_{90}^2	0.000058	0.00	0.000052	0.01
$EtOH^2$	0.000722	0.28	0.000197	0.77
T_{50} x EtOH	0.000195	0.08	0.000223	0.05
T_{90} x EtOH	0.000244	0.00	0.000273	0.00

3.1.1.1 Composite NMHC Emissions

Neither the first nor second order effects were even marginally significant for ethanol. Ethanol was included in a significant interaction with T_{90} (described below) and a marginally significant interaction with T_{50}.

Both the first order and second order effects were significant for T_{50}. Figure 4 shows increasing NMHC emissions as a function of increasing T_{50}. The fleet-averaged percentage increases in NMHC emissions were 36% and 25%, respectively, in going from the low and mid-point for T_{50} to the high T_{50} point. The interaction between T_{50} and ethanol was found to be marginally significant (p=0.08).

T_{90} had a significant second order effect and a marginally significant first order effect (p=0.06). A significant interaction was found between T_{90} and ethanol. In cases where a significant interaction is present, the interaction is plotted instead of the main effect to illustrate how the effects change for different values of the interacting variable. This interaction is illustrated in Figures 5a and 5b. Figure 5a shows that the magnitude of the effect of higher levels of ethanol content on NMHC emissions increased as T_{90} increased. Figure 5b shows that NMHC emissions increased with increasing T_{90} for the 5.7% and 10% ethanol levels, but not for the 0% ethanol level.

Figure 4. Composite NMHC Balanced Average by T_{50}
Fleet Average and Individual Vehicles

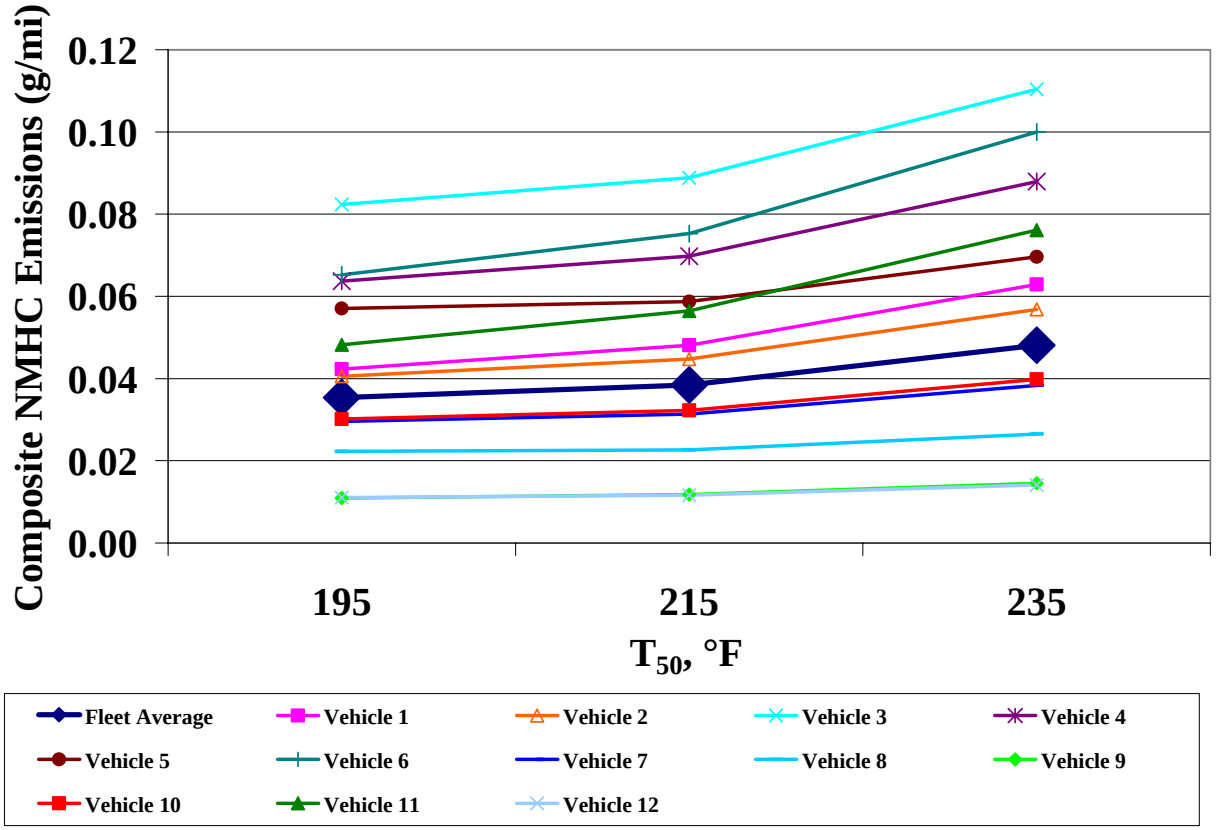


Figure 5a. Composite NMHC Balanced Average by EtOH x T_{90} Fleet Average

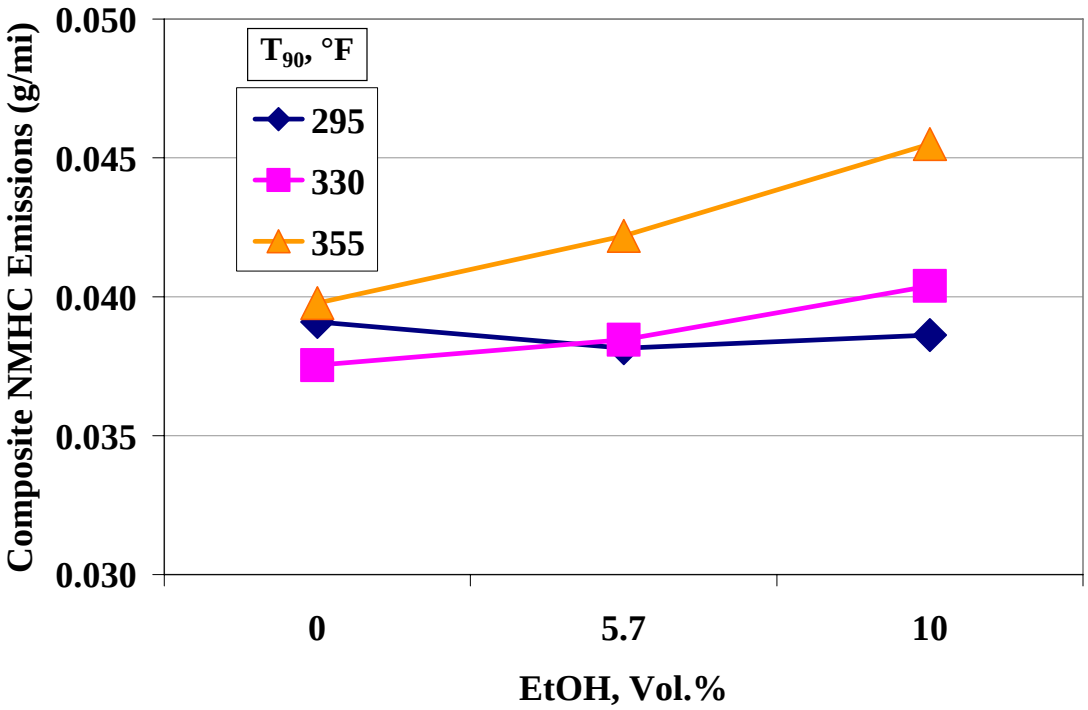
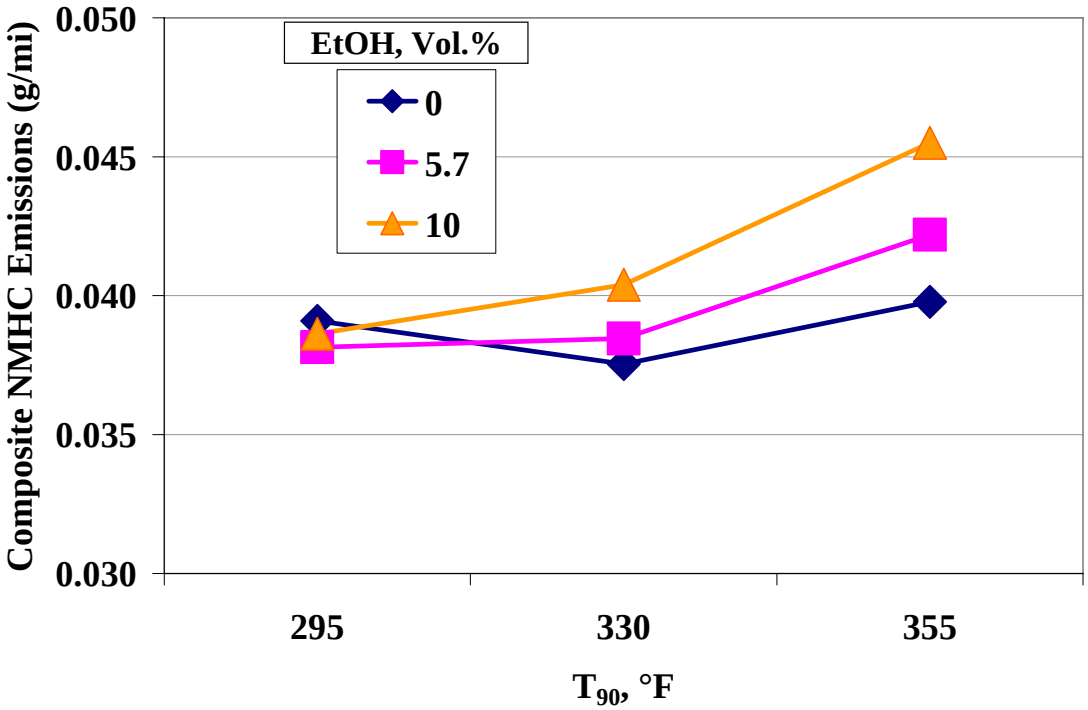


Figure 5b. Composite NMHC Balanced Average by T_{90} x EtOH Fleet Average



3.1.1.2 Bag 1 NMHC Emissions

Neither the first nor second order effects were significant for ethanol for Bag 1, but the first order effect was marginally significant (p=0.09). Ethanol was included in a significant interaction with both T_{50} and T_{90}, as described below.

Both the first order and second order effects were significant for T_{50}. The interaction between T_{50} and ethanol was also found to be significant. This interaction is illustrated in Figures 6a and 6b. Figure 6a shows that the magnitude of the increase in NMHC emissions as ethanol content increased became larger as T_{50} increased. Figure 6b shows that the magnitude of the increase in NMHC emissions as T_{50} increased became larger as ethanol content increased.

T_{90} had a significant second order effect, but not a significant first order effect. A significant interaction was also found between T_{90} and ethanol. This interaction is illustrated in Figures 7a and 7b. Figure 7a shows that increasing ethanol content produced a modest decrease in NMHC at the lowest level of T_{90}, but produced substantial increases in NMHC at the mid and high levels of T_{90}. Figure 7b shows that NMHC emissions increased with increasing T_{90} for the 5.7% and 10% ethanol levels, but not for the 0% ethanol level.

Figure 6a. Bag 1 NMHC Balanced Average by EtOH x T_{50}
Fleet Average

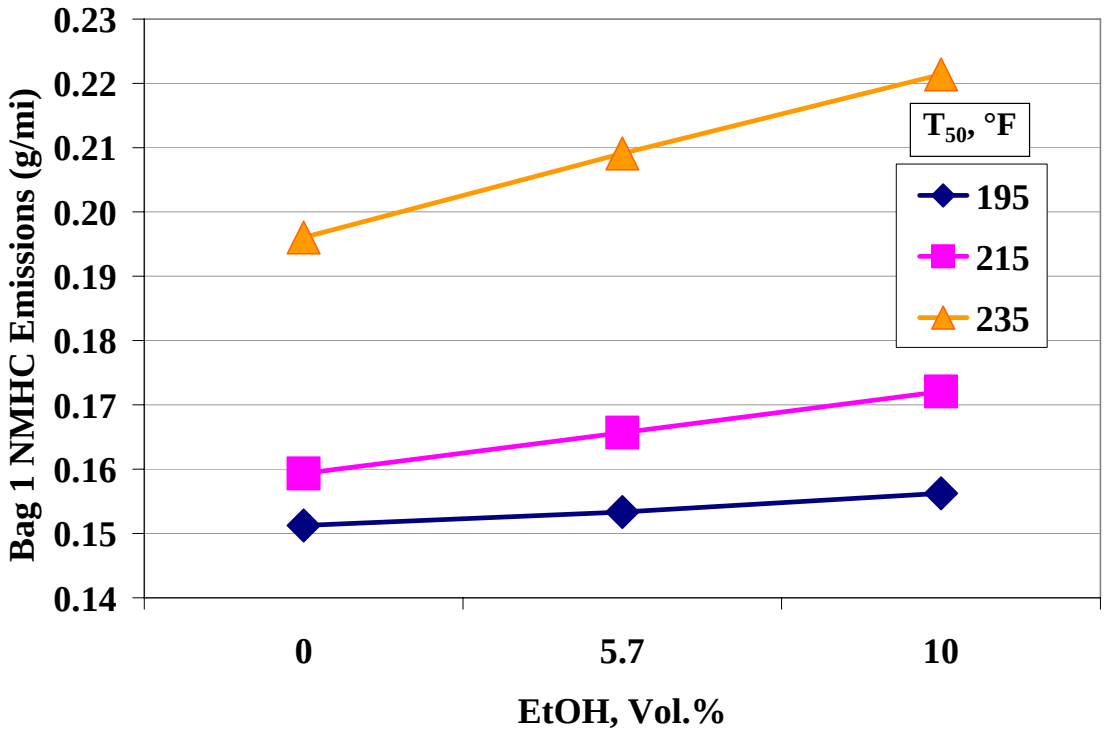


Figure 6b. Bag 1 NMHC Balanced Average by T_{50} x EtOH
Fleet Average

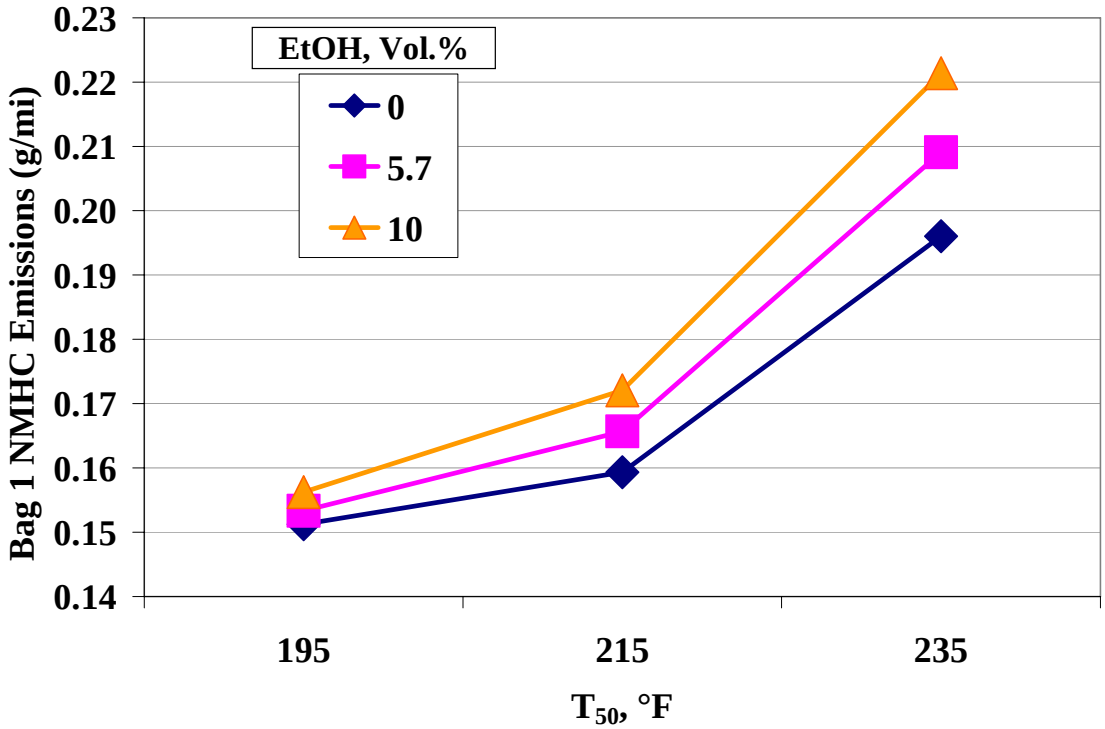


Figure 7a. Bag 1 NMHC Balanced Average by EtOH x T_{90}
Fleet Average

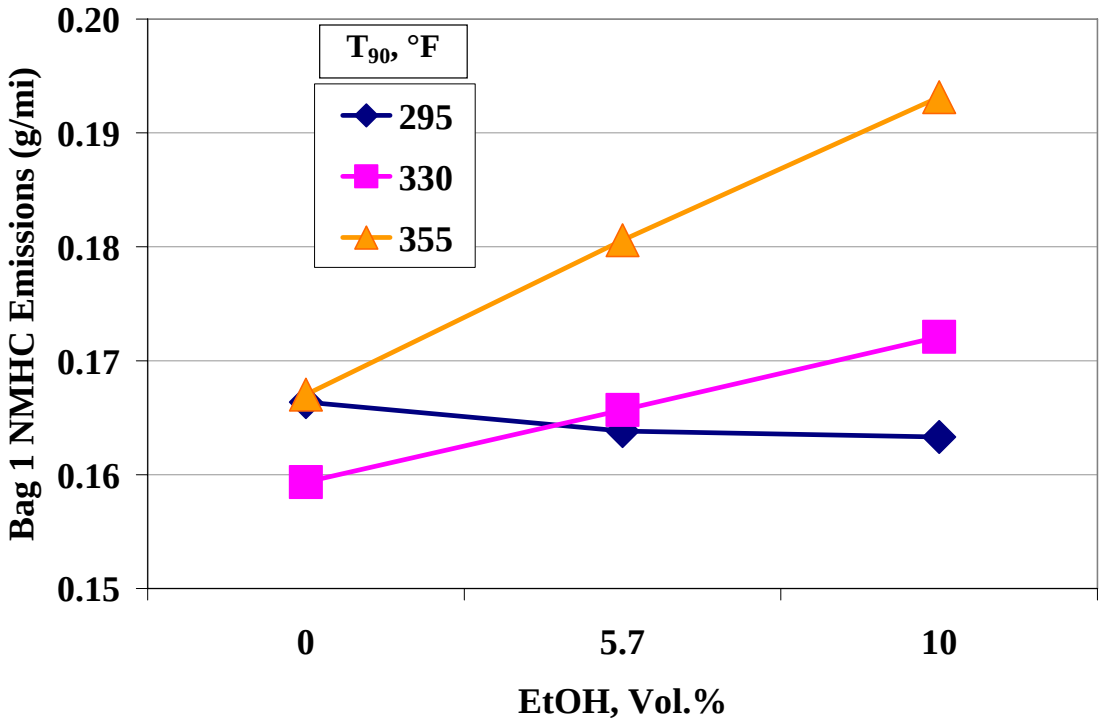
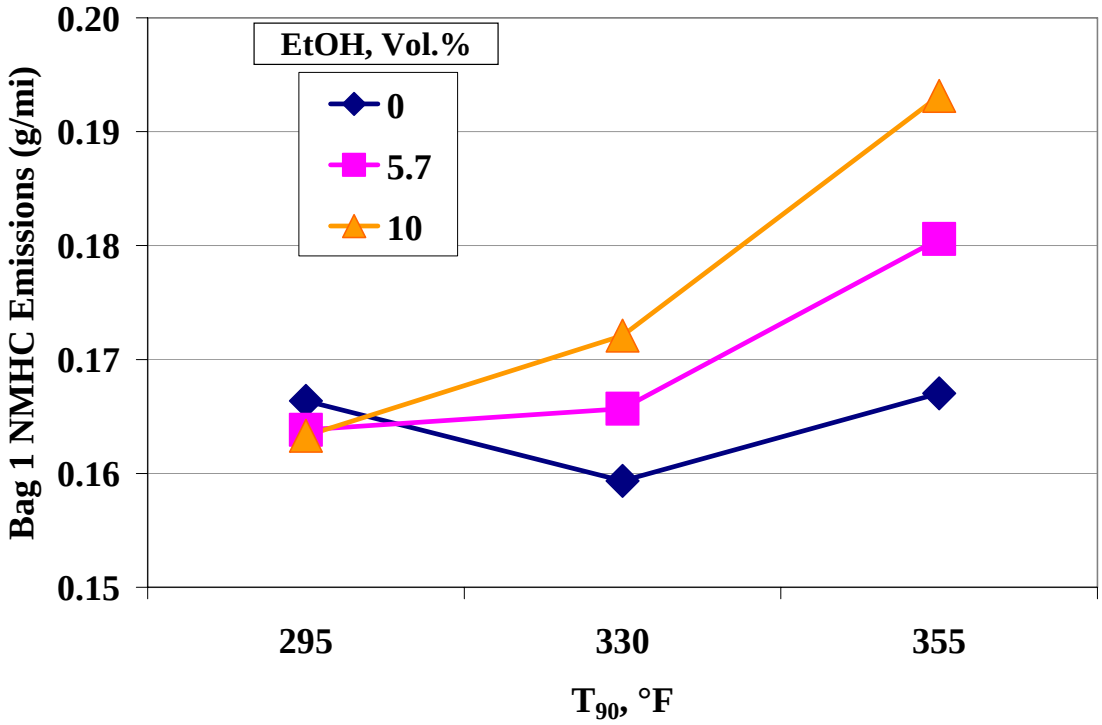


Figure 7b. Bag 1 NMHC Balanced Average by T_{90} x EtOH
Fleet Average



3.1.2 FTP CO Emissions

The statistical analysis results for CO are presented in Table 6.

Table 6. Mixed Model Summary for CO

	FTP Composite		Bag 1	
Random Factor	P value		P value	
Vehicle	0.01		0.01	
T_{50} x Vehicle	0.06		0.03	
T_{90} x Vehicle	0.02		0.01	
EtOH x Vehicle	0.02		0.02	
Fuel Factor	Coefficient	P value	Coefficient	P value
Intercept	-0.7966		0.3652	
T_{50}	0.001227	0.31	-0.000640	0.69
T_{90}	-0.004500	0.01	-0.006600	0.00
EtOH	-0.015810	0.02	-0.018350	0.02
T_{50}^2	0.000099	0.04	0.000104	0.05
T_{90}^2	0.000045	0.08	0.000044	0.12
$EtOH^2$	0.003118	0.00	0.002981	0.00
T_{50} x EtOH	0.000355	0.02	0.000458	0.00
T_{90} x EtOH	0.000174	0.05	0.000179	0.07

3.1.2.1 Composite CO Emissions

Significant first and second order effects were found for ethanol. Ethanol was included in a significant interaction with T_{50} (described below) and a marginally significant interaction with T_{90}.

The second order T_{50} effect was significant, but the first order effect was not. T_{50} was also included in a significant interaction with ethanol, which is shown in Figures 8a and 8b. Figure 8a shows that increasing ethanol from the zero to the mid level decreases CO at all levels of T_{50}; however, increasing ethanol from the mid level to the high level produced little or no change in CO at the low and mid levels of T_{50} and an increase in CO emissions at the high level of T_{50}. Figure 8b shows that CO did not change as T_{50} changed at the zero level of ethanol, but CO tended to increase with T_{50} at the mid and high levels of ethanol.

A significant first order effect was found for T_{90}, while the second order effect was marginally significant (p=0.08). CO emissions as a function of T_{90} are shown in Figure 9. Fleet average FTP composite CO emissions showed a 7% decrease in going from the mid T_{90} value to the high T_{90} value and a 24% decrease in going from the low T_{90} value to the high T_{90} value. The T_{90} by ethanol interaction was marginally significant (p=0.053).

Figure 8a. Composite CO Balanced Average by EtOH x T_{50} Fleet Average

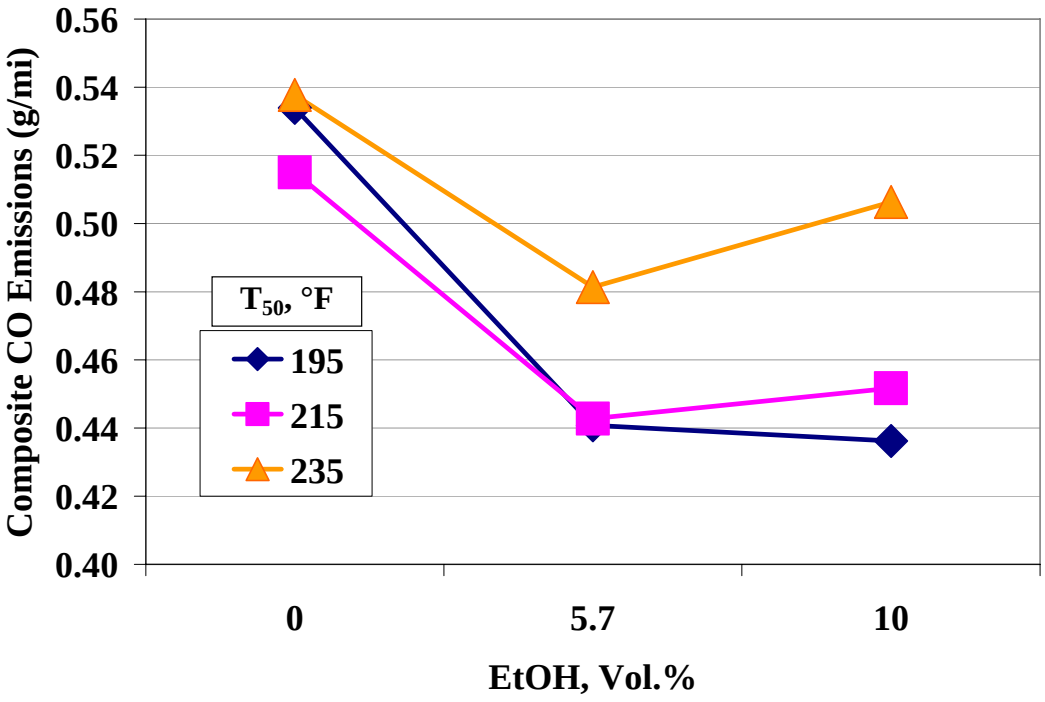


Figure 8b. Composite CO Balanced Average by T_{50} x EtOH Fleet Average

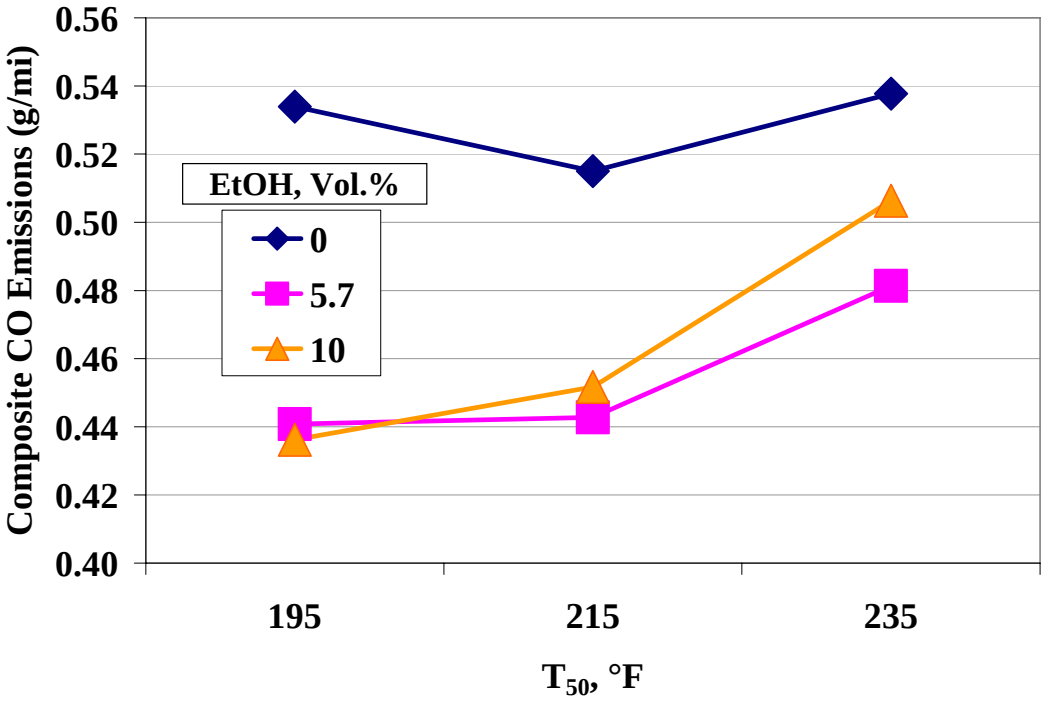
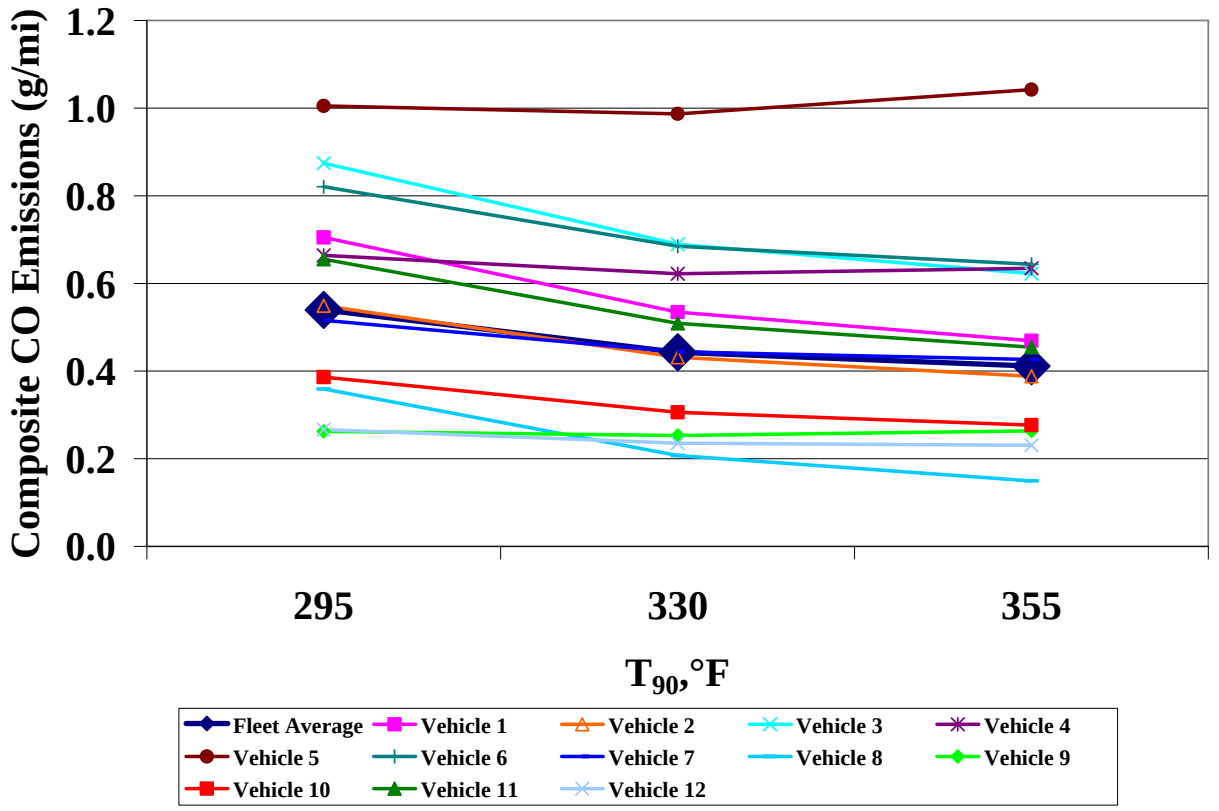


Figure 9. Composite CO Balanced Average by T_{90}
Fleet Average and Individual Vehicles



3.1.2.1 Bag 1 CO Emissions

The Bag 1 CO results were generally consistent with the FTP composite CO emissions. Both the first and second order ethanol effects were significant. Ethanol was also included in a significant interaction with T_{50} (described below), as well as a marginally significant interaction with T_{90}.

The second order effect for T_{50} was significant, but not the first order effect. T_{50} was also included in a significant interaction with ethanol, which is shown in Figures 10a and 10b. Figure 10a shows that the mid and high levels of ethanol behaved similarly in response to increasing levels of T_{50} and differently than the zero level of ethanol. Figure 10b shows that increasing ethanol from the zero to the mid level decreases CO at all levels of T_{50}; however, increasing ethanol from the mid level to the high level produced little or no change in CO at the low and mid levels of T_{50} and an increase in CO emissions at the high level of T_{50}.

The first order effect of T_{90} was significant, but the second order effect was not. Figure 11 shows the T_{90} effect on CO for the fleet average Bag 1 data. A marginally statistically significant interaction ($p=0.07$) was found between T_{90} and ethanol.

Figure 10a. Bag 1 CO Balanced Average by EtOH x T_{50}
Fleet Average

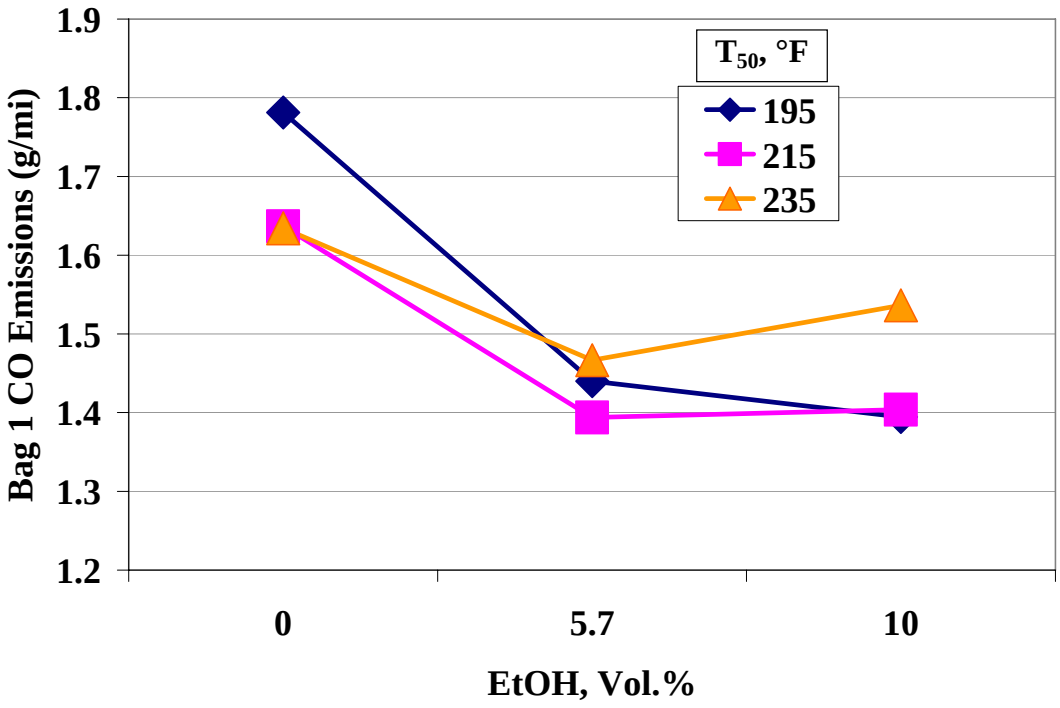


Figure 10b. Bag 1 CO Balanced Average by T_{50} x EtOH
Fleet Average

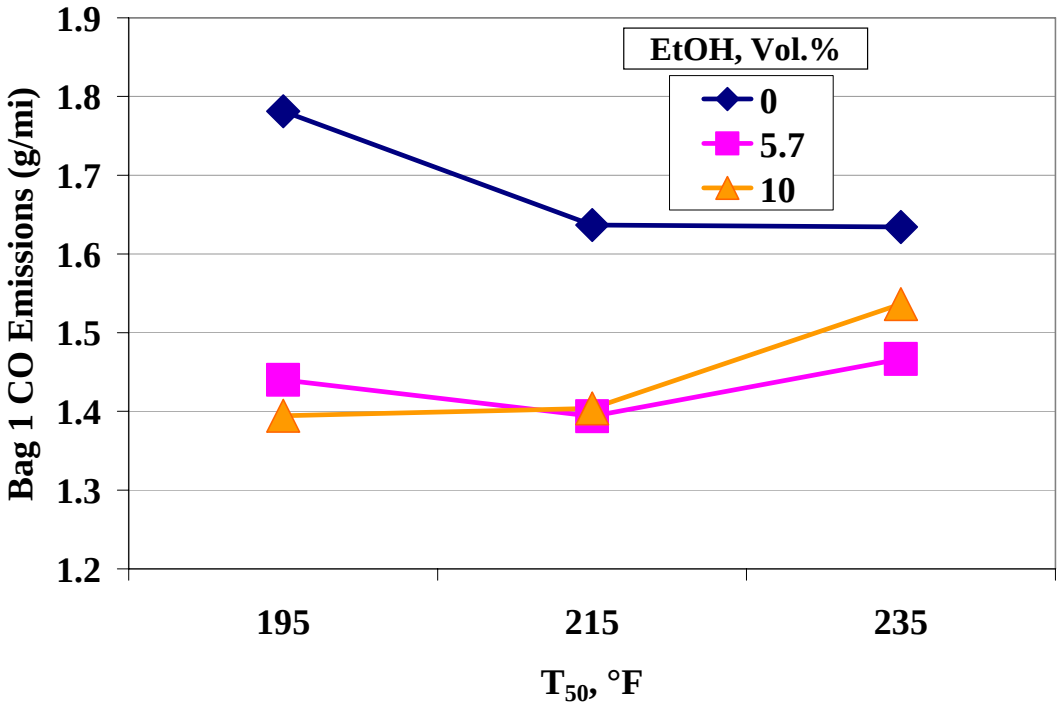
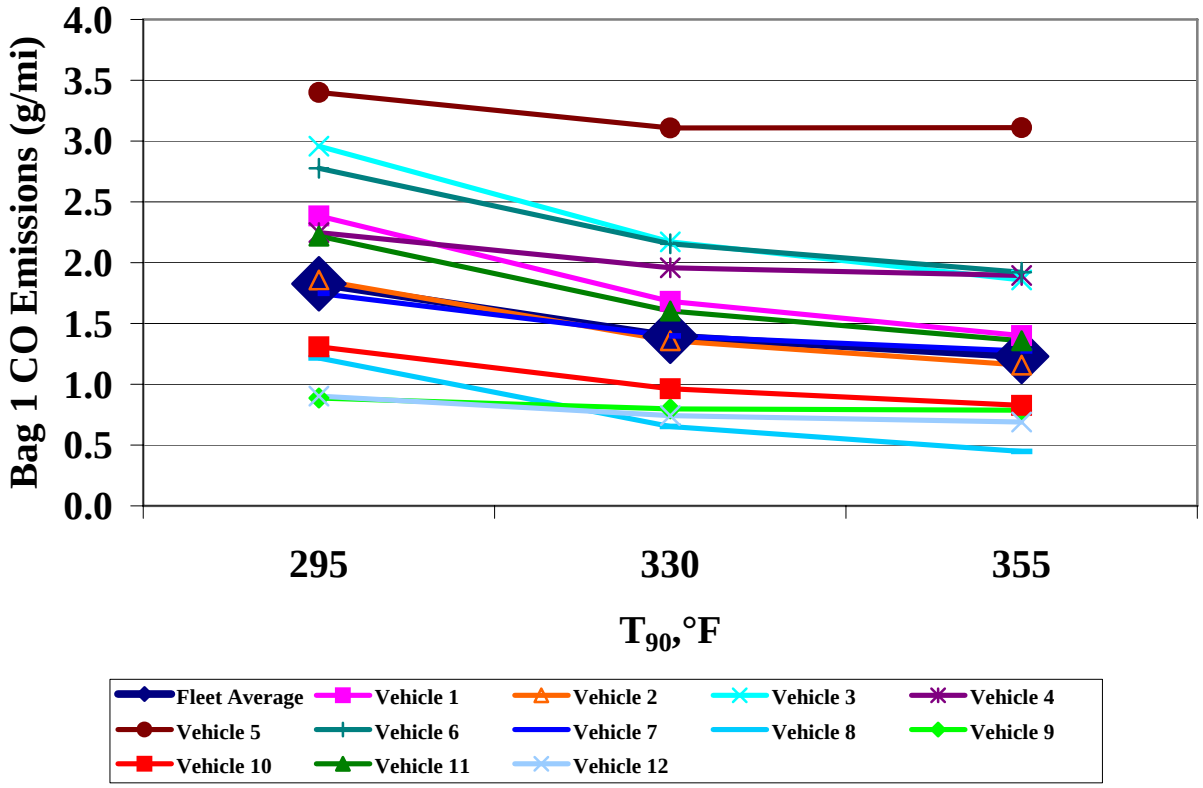


Figure 11. Bag 1 CO Balanced Average by T_{90}
Fleet Average and Individual Vehicles



3.1.3 FTP NO_x Emissions

The statistical analysis results for NO_x are presented in Table 7.

Table 7. Mixed Model Summary for NO_x

	FTP Composite		Bag 1	
Random Factor	P value		P value	
Vehicle	0.01		0.01	
T_{50} x Vehicle	0.17		0.09	
T_{90} x Vehicle	0.05		0.02	
EtOH x Vehicle	0.31		-	
Fuel Factor	Coefficient	P value	Coefficient	P value
Intercept	-2.6183		-1.5043	
T_{50}	-0.000130	0.89	0.000416	0.66
T_{90}	0.000240	0.76	-0.000090	0.92
EtOH	0.005710	0.05	0.005022	0.03
T_{50}^2	-0.000060	0.22	-0.000090	0.05
T_{90}^2	0.000043	0.12	0.000009	0.69
$EtOH^2$	0.001622	0.09	0.000988	0.23
T_{50} x EtOH	-0.000320	0.04	-0.000140	0.29
T_{90} x EtOH	-0.000001	0.99	-0.000003	0.97

3.1.3.1 Composite NO_x Emissions

Neither the first nor second order effects were significant for ethanol, but both were marginally significant (p=0.05 and 0.09, respectively). Ethanol was included in a significant interaction with T_{50}, as described below.

Neither the first nor second order effects were even marginally significant for T_{50}. The interaction between T_{50} and ethanol was found to be significant, which is shown in Figures 12a and 12b. Figure 12a shows higher NO_x emissions for 10% ethanol at the low and mid T_{50} levels, but no differences at the high T_{50} level. Figure 12b shows that NO_x emissions tended to decrease as T_{50} increased at the high level of ethanol, but not at the other two levels.

Neither the first nor second order effects were even marginally significant for T_{90}.

Figure 12a. Composite NO_x Balanced Average by EtOH x T_{50} Fleet Average

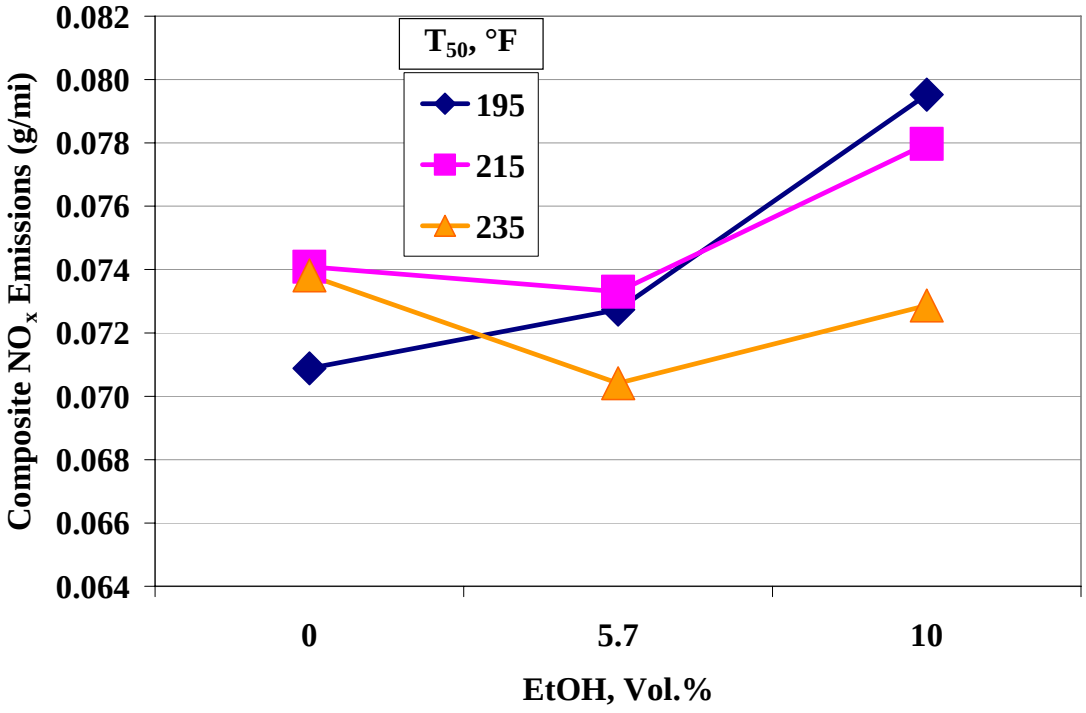
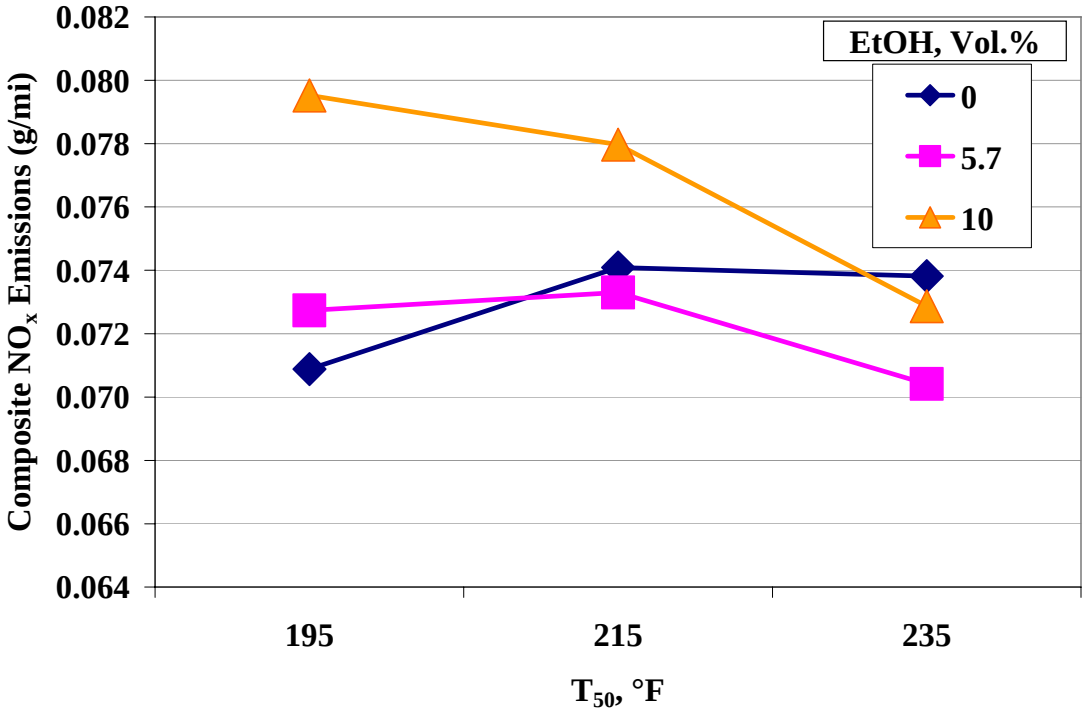


Figure 12b. Composite NO_x Balanced Average by T_{50} x EtOH Fleet Average



3.1.3.2 Bag 1 NO_x Emissions

The first order effect for ethanol was significant, but the second order effect was not even marginally significant. Figure 13 shows that the fleet average Bag 1 NO_x emissions increased slightly as ethanol increased.

The second order effect for T_{50} was significant, but the first order effect was not. Figure 14 shows that the fleet average Bag 1 NO_x levels look to be generally flat as T_{50} increased.

Figure 13. Bag 1 NO_x Balanced Average by EtOH
Fleet Average and Individual Vehicles

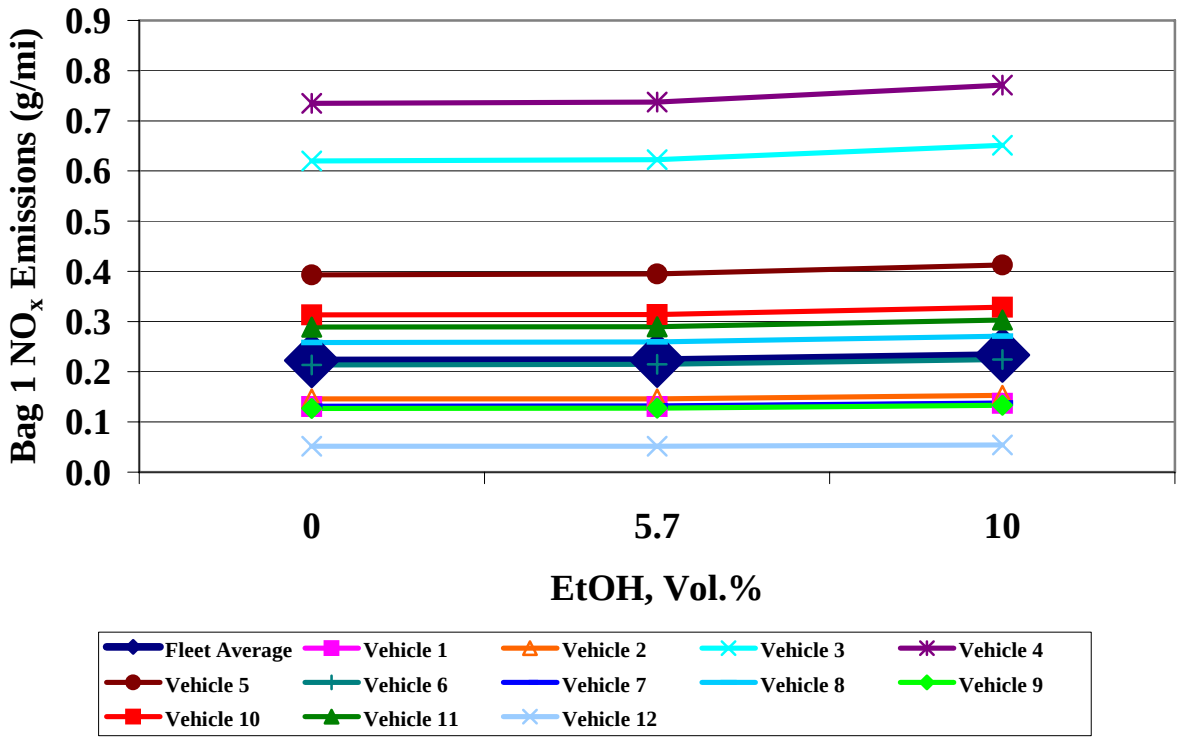
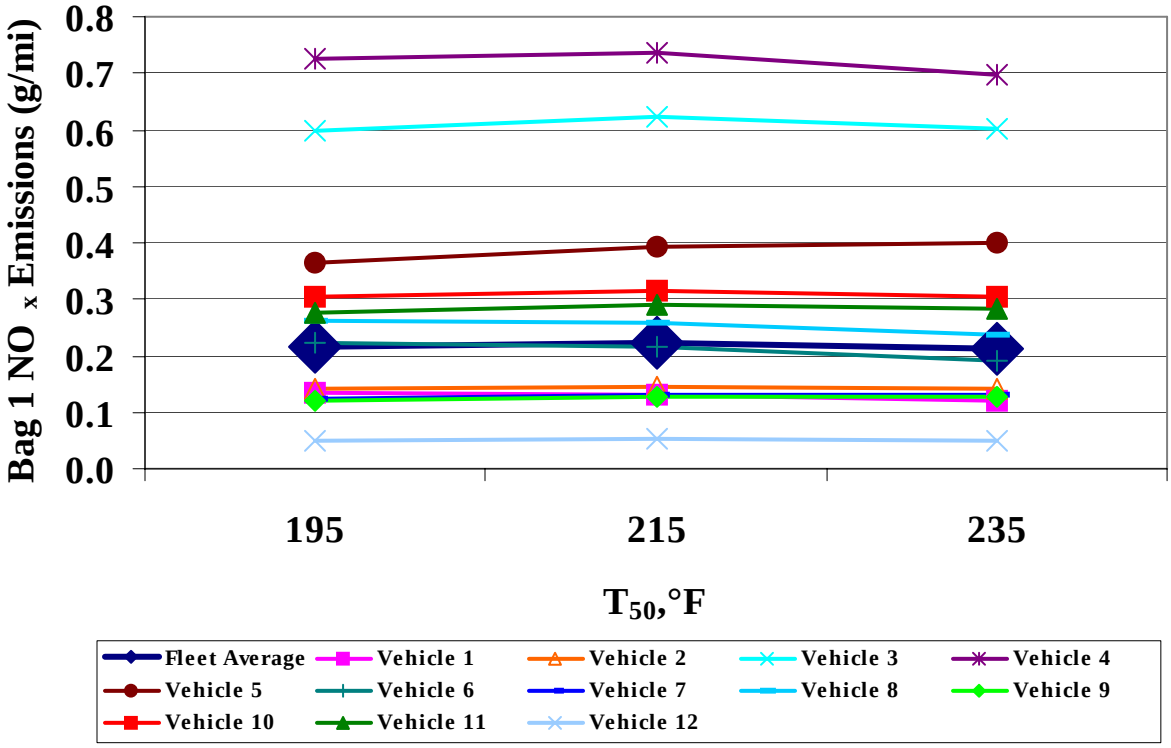


Figure 14. Bag 1 NO_x Balanced Average by T_{50}
Fleet Average and Individual Vehicles



3.1.4 FTP Fuel Consumption

It has become standard practice to analyze fuel consumption rather than fuel economy partly because the chassis dynamometer tests are run with constant mileage, and it is the amount of fuel consumed during the test that varies. This puts the variable in the numerator rather than the denominator and thereby produces residuals that more closely match the assumptions implied by standard statistical modeling.

The statistical analysis results for fuel consumption are presented in Table 8.

Table 8. Mixed Model Summary for Fuel Consumption*1000

	FTP Composite		Bag 1	
Random Factor	P value		P value	
Vehicle	0.01		0.01	
T_{50} x Vehicle	-		-	
T_{90} x Vehicle	-		-	
EtOH x Vehicle	-		-	
Fuel Factor	Coefficient	P value	Coefficient	P value
Intercept	49.8527		52.7471	0.00
T_{50}	-0.015380	0.00	-0.014230	0.00
T_{90}	-0.0042	0.03	-0.007080	0.00
EtOH	0.07376	0.00	0.092850	0.00
T_{50}^2	0.000175	0.41	0.000174	0.48
T_{90}^2	0.000098	0.39	0.000103	0.43
$EtOH^2$	0.004197	0.28	0.001995	0.65
T_{50} x EtOH	-0.000650	0.32	-0.001060	0.16
T_{90} x EtOH	-0.000680	0.08	-0.000740	0.10

3.1.4.1 Composite Fuel Consumption

The first order effect for ethanol was significant, but the second order effect was not even marginally significant. Neither interaction was significant, but the interaction between ethanol and T_{90} was marginally significant (p=0.08). Figure 15 shows that the fleet average fuel consumption increased with increasing ethanol content; the magnitude of the increase when ethanol increased from 0% to 10% was 1.4%. Given that the addition of 10% ethanol to a hydrocarbon blend typically decreases the volumetric heat content of the blend by about 3.5%, the observed increase in fuel consumption appears to be low. However, it should be remembered that this experiment relied on a fuel set designed to provide independent variation in the ethanol content, T_{50} and T_{90} while maintaining other fuel parameters at constant values. As a result, the addition of ethanol was accompanied by the addition of heavier hydrocarbon components that mitigated the impact of ethanol on the volumetric heat content of the blends. In the fuel set used in this work, 10% ethanol tended to decrease volumetric heat content by 2.2%.

The first order effect for T_{50} was significant, but the second order effect was not even marginally significant. Figure 16 shows that the fleet average fuel consumption decreased with increasing T_{50}; the magnitude of the decrease when T_{50} increased from 195°F to 235°F was 1.2%.

The first order effect for T_{90} was significant, but the second order effect was not even marginally significant. Figure 17 shows that the fleet average fuel consumption decreased with increasing T_{90}; the magnitude of the decrease when T_{90} increased from 295°F to 355°F was 0.6%.

Figure 15. Fuel Consumption Balanced Average by EtOH
Fleet Average and Individual Vehicles

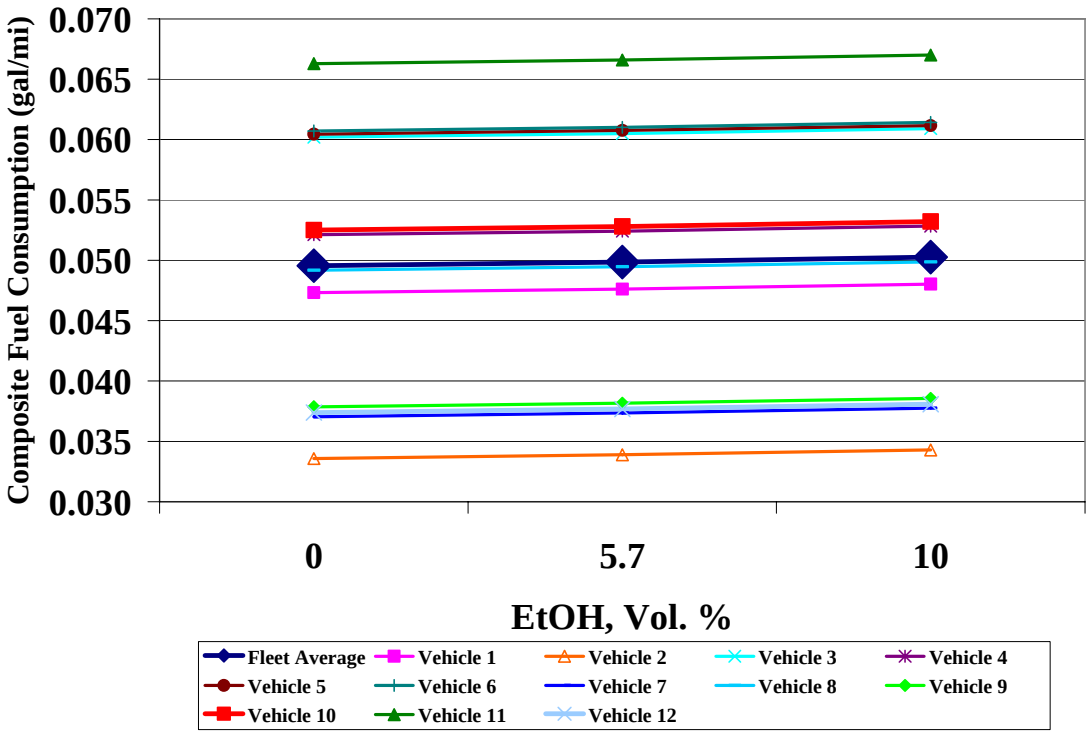


Figure 16. Fuel Consumption Balanced Average by T_{50}
Fleet Average and Individual Vehicles

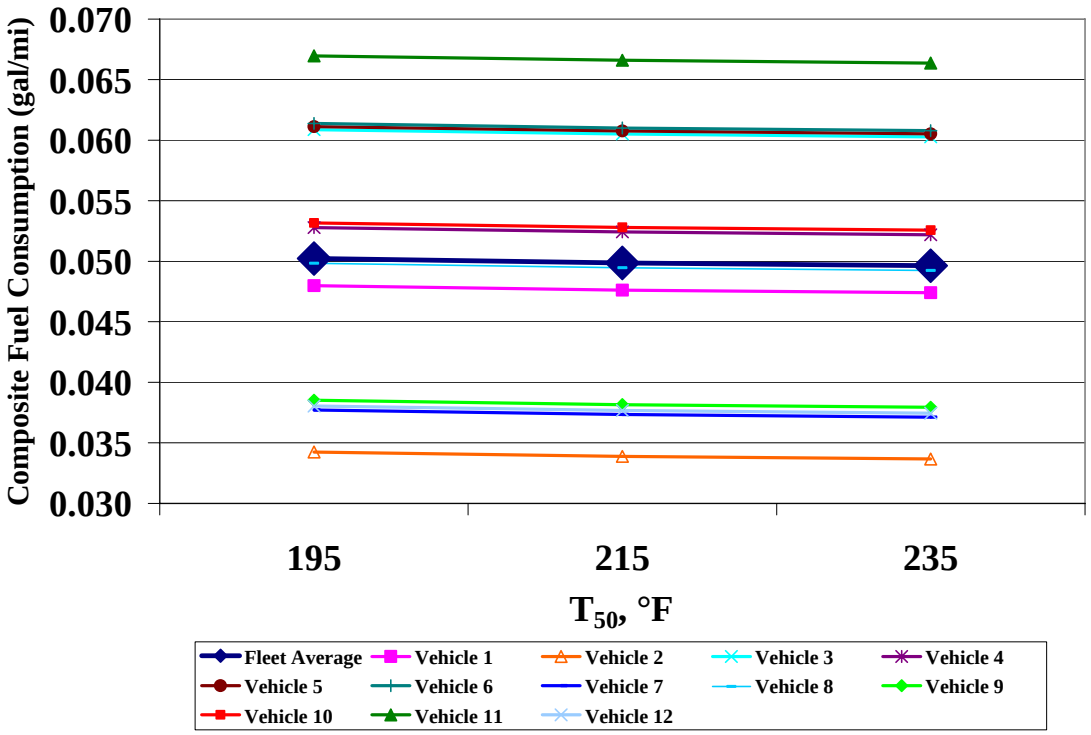
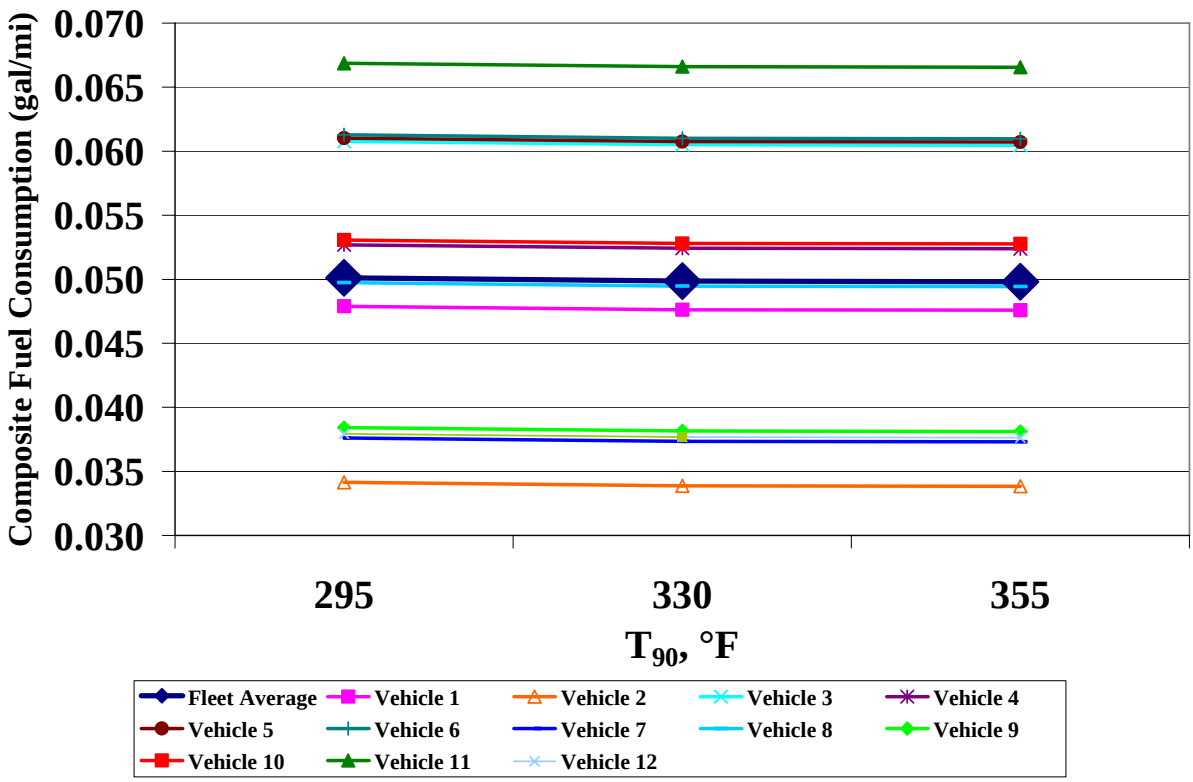


Figure 17. Fuel Consumption Balanced Average by T_{90} Fleet Average and Individual Vehicles



3.1.4.2 Bag 1 Fuel Consumption

The first order effect for ethanol was significant, but the second order effect was not even marginally significant. Neither interaction was significant, but the interaction between ethanol and T_{90} was marginally significant (p=0.10). Figure 18 shows that the fleet average fuel consumption increased with increasing ethanol content; the magnitude of the increase when ethanol increased from 0% to 10% was 1.7%.

The first order effect for T_{50} was significant, but the second order effect was not even marginally significant. Figure 19 shows that the fleet average fuel consumption decreased with increasing T_{50}; the magnitude of the decrease when T_{50} increased from 195°F to 235°F was 1.1%.

The first order effect for T_{90} was significant, but the second order effect was not even marginally significant. Figure 20 shows that the fleet average fuel consumption decreased with increasing T_{90}; the magnitude of the decrease when T_{90} increased from 295°F to 355°F was 0.9%.

Figure 18. Bag 1 Fuel Consumption Balanced Average by EtOH Fleet Average and Individual Vehicles

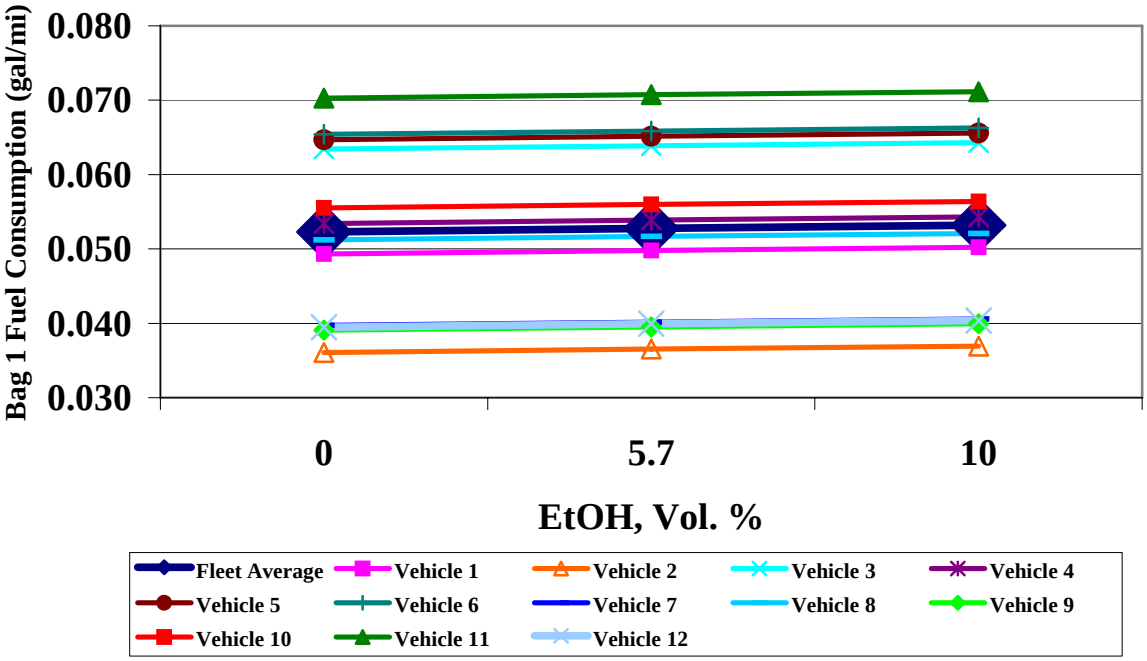


Figure 19. Bag 1 Fuel Consumption Balanced Average by T_{50} Fleet Average and Individual Vehicles

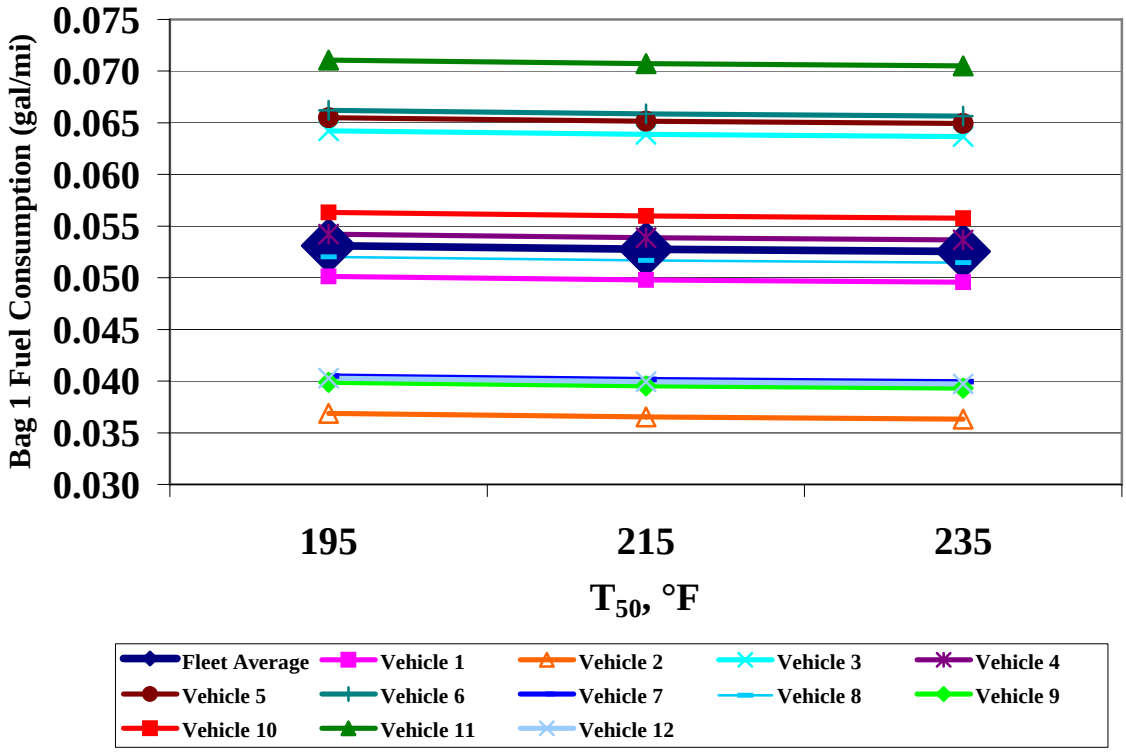
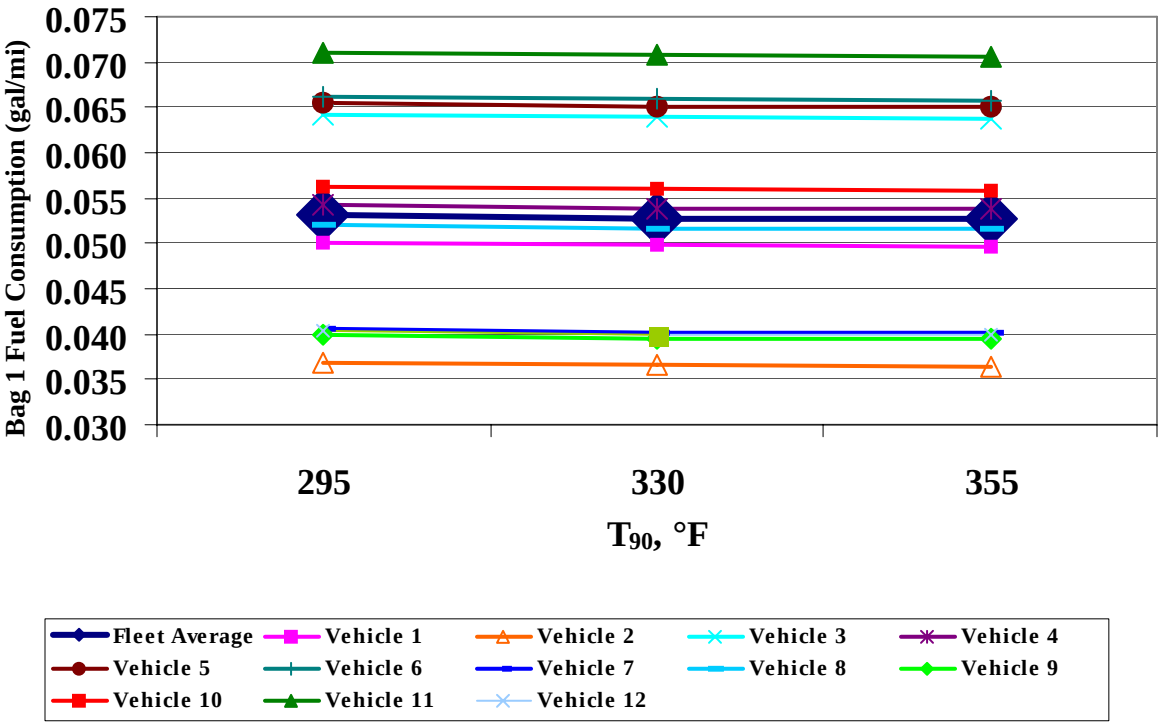


Figure 20. Bag 1 Fuel Consumption Balanced Average by T_{90} Fleet Average and Individual Vehicles



3.2 NMOG and Toxics Emissions Results

The results of the statistical analyses for NMOG and four mobile source air toxics (formaldehyde, acetaldehyde, benzene, and 1-3 butadiene) are discussed in this section. These analyses were performed on the subset of fuels D, E, K and L which had a constant target T_{90} value of 355°F. The regression model was run with a reduced parameter set that included only first order effects for ethanol and T_{50} and an ethanol by T_{50} interaction. Terms that involved T_{90} were not included because T_{90} did not vary for the four fuels included. Likewise, second order effects for ethanol and T_{50} could not be evaluated because only two levels of those variables were tested.

3.2.1 FTP NMOG Emissions

The statistical analysis results for NMOG emissions are presented in Table 9. Note that NMOG was only calculated for FTP composite emissions, so no Bag 1 analysis was possible.

Table 9. Mixed Model Summary for NMOG

Random Factor	P value	
Vehicle	0.01	
T_{50} x Vehicle	0.08	
EtOH x Vehicle	0.21	
Fuel Factor	**Coefficient**	**P value**
Intercept	-3.0679	
T_{50}	0.007531	0.00
EtOH	0.013010	0.00
T_{50} x EtOH	-0.000010	0.90

At first glance, the NMOG results appear different from the NMHC results summarized in Section 3.1.1. However, this is due to the fact that NMOG was only analyzed on a four fuel subset of the data, while NMHC was analyzed on the full 12 fuel set. Analysis of NMHC of the four fuel subset produces very similar results to the NMOG analysis, as shown in Table 10.

Table 10. Four Fuel Mixed Model Summary for NMHC

Random Factor	P value	
Vehicle	0.01	
T_{50} x Vehicle	0.13	
EtOH x Vehicle	0.31	
Fuel Factor	**Coefficient**	**P value**
Intercept	-3.1442	
T_{50}	0.0081	0.00
EtOH	0.0116	0.00
T_{50} x EtOH	0.0000	0.95

3.2.1.1 Composite NMOG Emissions

The results for NMOG showed a significant effect for ethanol. Figure 21 shows that NMOG increased as ethanol increased; the magnitude of this increase was 14% when ethanol increased from 0% to 10%. The interaction between ethanol and T_{50} was not even marginally significant.

A significant effect was found for T_{50}. Figure 22 shows that NMOG increased with increasing $T_{50;}$ the magnitude of this increase was 35% when T_{50} increased from 195°F to 235°F.

Figure 21. NMOG Balanced Average by EtOH
Fleet Average and Individual Vehicles

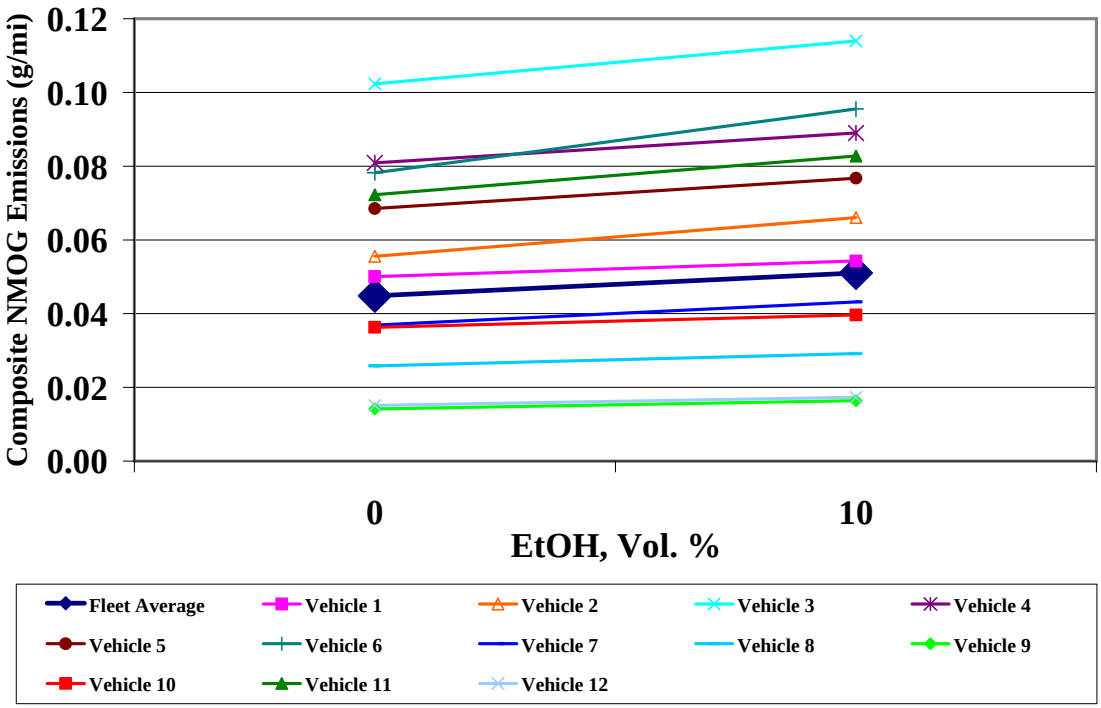
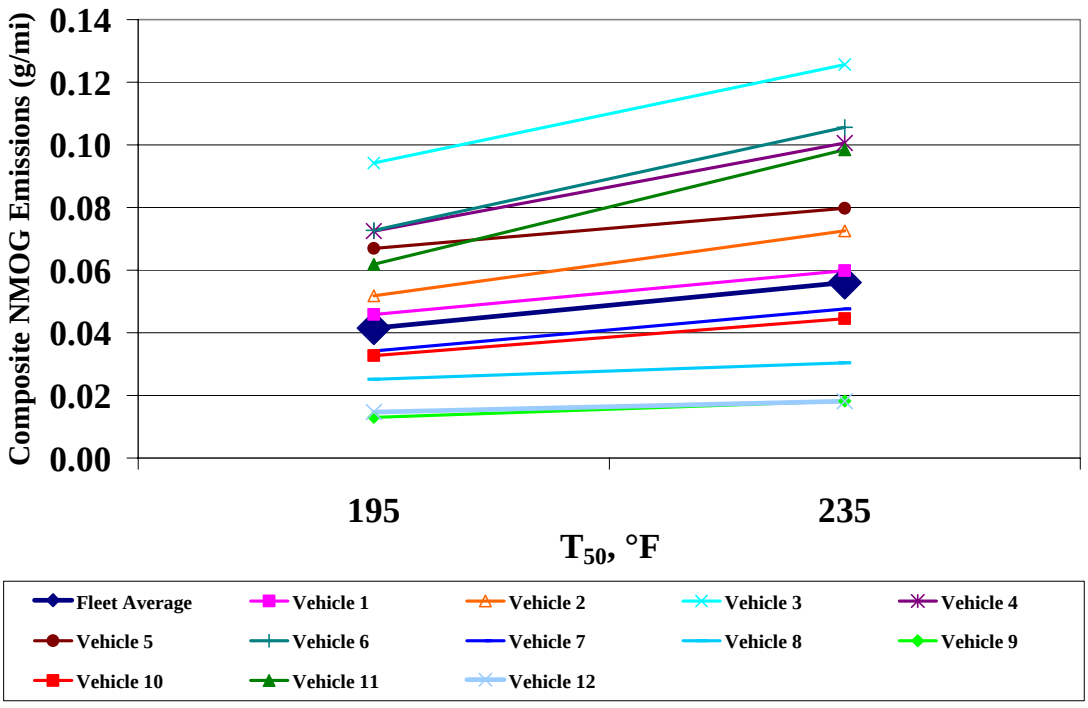


Figure 22. NMOG Balanced Average by T_{50}
Fleet Average and Individual Vehicles



3.2.2 FTP Formaldehyde Emissions

The statistical analysis results for formaldehyde emissions are presented in Table 11.

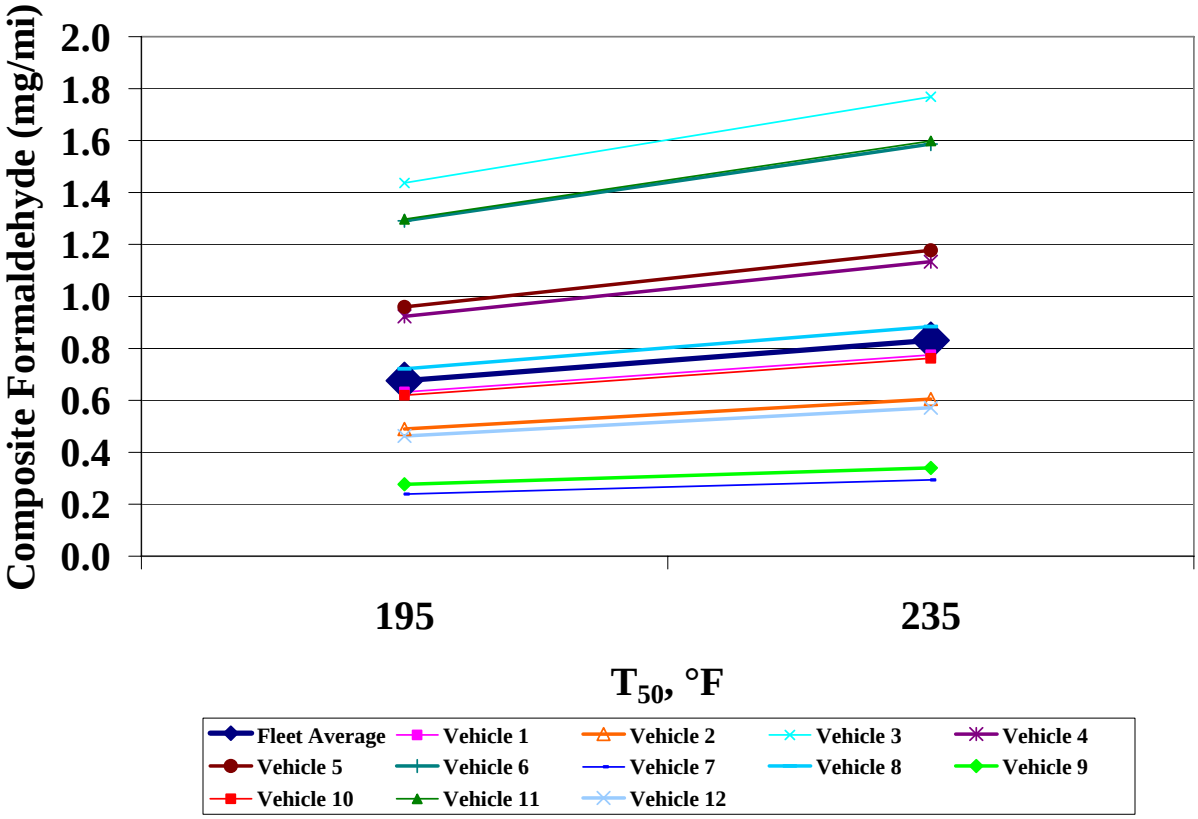
Table 11. Mixed Model Summary for Formaldehyde

	FTP Composite		Bag 1	
Random Factor	P value		P value	
Vehicle	0.01		0.01	
T_{50} x Vehicle	0.49		-	
EtOH x Vehicle	0.29		-	
Fuel Factor	Coefficient	P value	Coefficient	P value
Intercept	-0.3148		0.8741	
T_{50}	0.005152	0.01	0.006327	0.00
EtOH	0.009851	0.15	0.012790	0.04
T_{50} x EtOH	0.000020	0.94	-0.000030	0.94

3.2.2.1 Composite Formaldehyde Emissions

For formaldehyde, the only significant effect was T_{50}, as shown in Figure 23. The results show that fleet average FTP composite formaldehyde emissions increased by 23% going from the low level to the high level of T_{50}. Neither ethanol nor the interaction between T_{50} and ethanol were even marginally significant.

Figure 23. Composite Formaldehyde Balanced Average by T_{50} Fleet Average and Individual Vehicles



3.2.2.2 Bag 1 Formaldehyde Emissions

For Bag 1, a significant effect was found for both ethanol and T_{50}, but the interaction was not even marginally significant. The Bag 1 formaldehyde emissions as a function of ethanol content are shown in Figure 24; fleet average formaldehyde increased 14% when going from the zero level to the high level of ethanol. The Bag 1 formaldehyde emissions as a function of T_{50} are shown in Figure 25; fleet average formaldehyde increased 29% when going from the low level to the high level of T_{50}.

Figure 24. Bag 1 Formaldehyde Balanced Average by EtOH
Fleet Average and Individual Vehicles

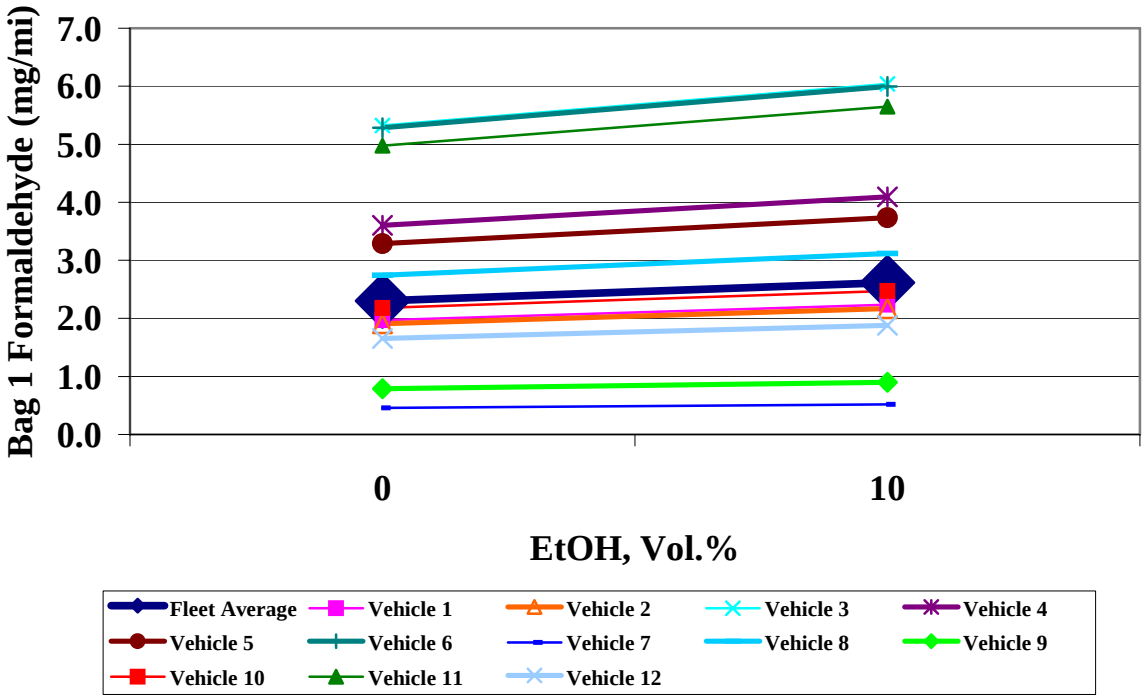
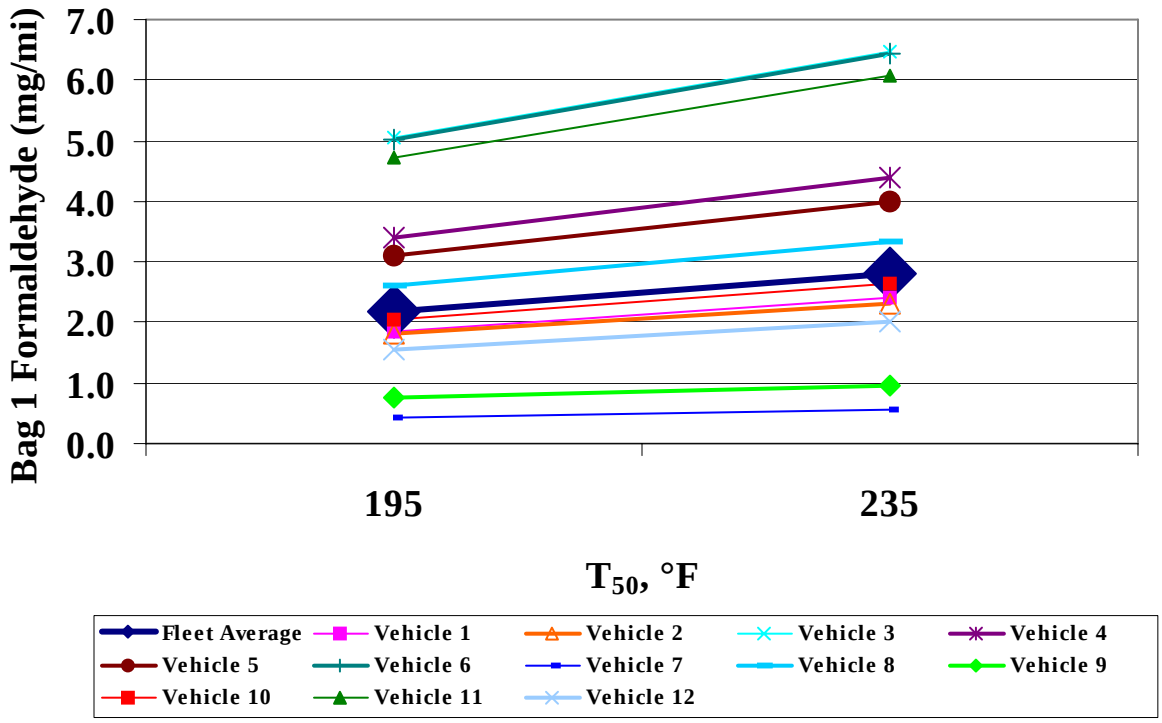


Figure 25. Bag 1 Formaldehyde Balanced Average by T_{50}
Fleet Average and Individual Vehicles



3.2.3 FTP Acetaldehyde Emissions

The statistical analysis results for acetaldehyde emissions are presented in Table 12.

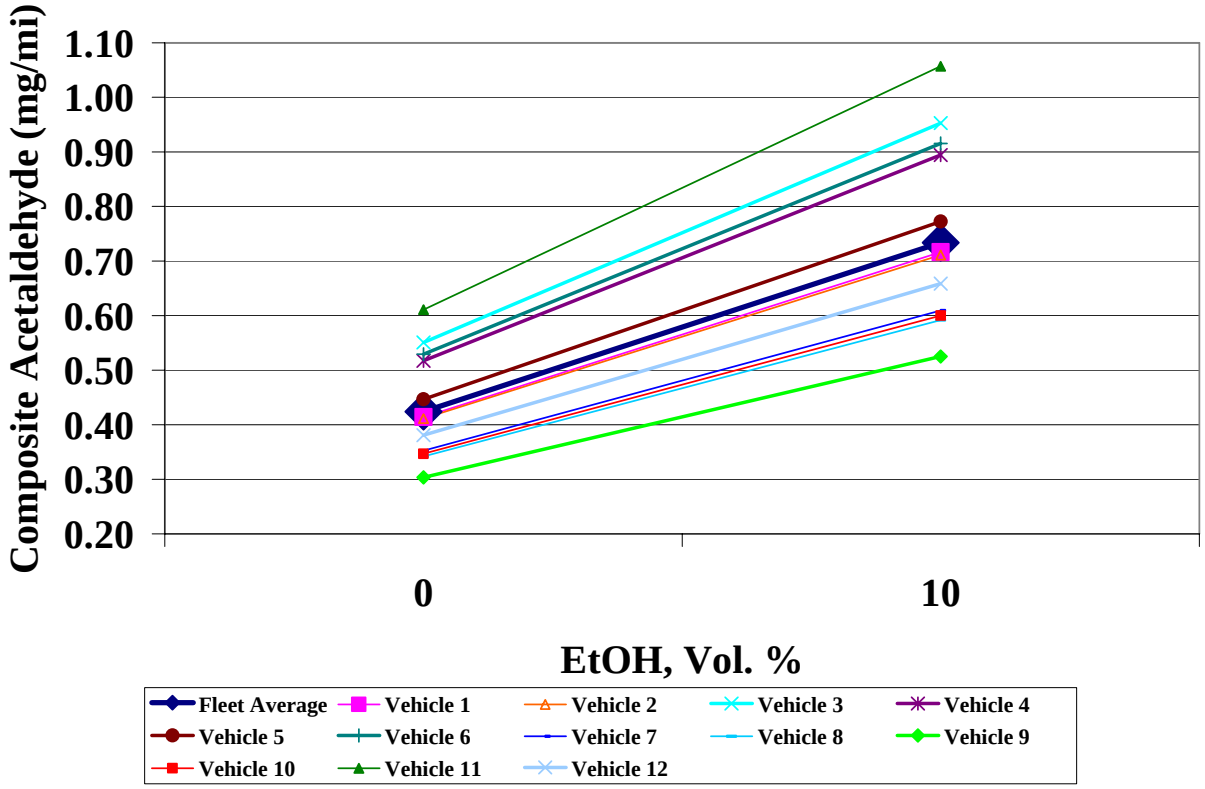
Table 12. Mixed Model Summary for Acetaldehyde

	FTP Composite		Bag 1	
Random Factor	P value		P value	
Vehicle	0.0343		0.0133	
T_{50} x Vehicle	-		-	
EtOH x Vehicle	-		0.4206	
Fuel Factor	Coefficient	P value	Coefficient	P value
Intercept	-0.5976		0.5625	
T_{50}	0.001629	0.47	0.002437	0.19
EtOH	0.054480	0.00	0.074890	0.00
T_{50} x EtOH	0.000097	0.82	-0.000003	0.99

3.2.3.1 Composite Acetaldehyde Emissions

For acetaldehyde, a significant effect was found for ethanol. Figure 26 shows that fleet average acetaldehyde increased as ethanol increased; the magnitude of this increase was 73% when ethanol increased from 0% to 10%. Neither the T_{50} effect nor the interaction between ethanol and T_{50} were even marginally significant.

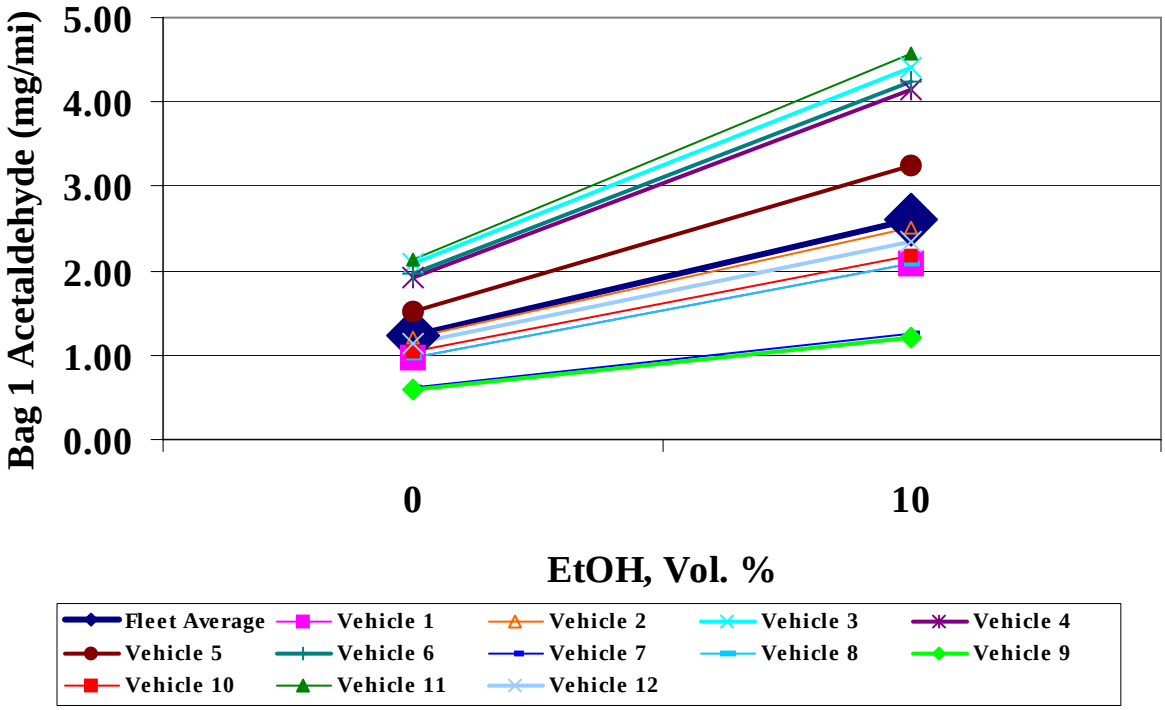
Figure 26. Composite Acetaldehyde Balanced Average by EtOH Fleet Average and Individual Vehicles



3.2.3.2 Bag 1 Acetaldehyde Emissions

The Bag 1 acetaldehyde results were similar to those for the composite emissions. A significant effect was found for ethanol. Figure 27 shows that fleet average acetaldehyde increased as ethanol increased; the magnitude of this increase was 111% when ethanol increased from 0% to 10%. Neither the T_{50} effect nor the interaction between ethanol and T_{50} were even marginally significant.

Figure 27. Bag 1 Acetaldehyde Balanced Average by EtOH Fleet Average and Individual Vehicles



3.2.4 FTP Benzene Emissions

The statistical analysis results for benzene emissions are presented in Table 13.

Table 13. Mixed Model Summary for Benzene

	FTP Composite		Bag 1	
Random Factor	P value		P value	
Vehicle	0.01		0.01	
T_{50} x Vehicle	0.29		0.26	
EtOH x Vehicle	0.32		0.40	
Fuel Factor	Coefficient	P value	Coefficient	P value
Intercept	0.3967		1.8362	
T_{50}	0.008186	0.00	0.008386	0.00
EtOH	0.016890	0.00	0.017780	0.00
T_{50} x EtOH	-0.000120	0.52	-0.000110	0.57

3.2.4.1 Composite Benzene Emissions

A significant effect was found for ethanol. Figure 28 shows that fleet average benzene emissions increased as ethanol increased; the magnitude of this increase was 18% when ethanol increased from 0% to 10%. The interaction between ethanol and T_{50} was not even marginally significant.

A significant effect was found for T_{50}. Figure 29 shows that fleet average benzene emissions increased as T_{50} increased; the magnitude of this increase was 38% when T_{50} increased from 195°F to 235°F.

Figure 28. Composite Benzene Balanced Average by EtOH Fleet Average and Individual Vehicles

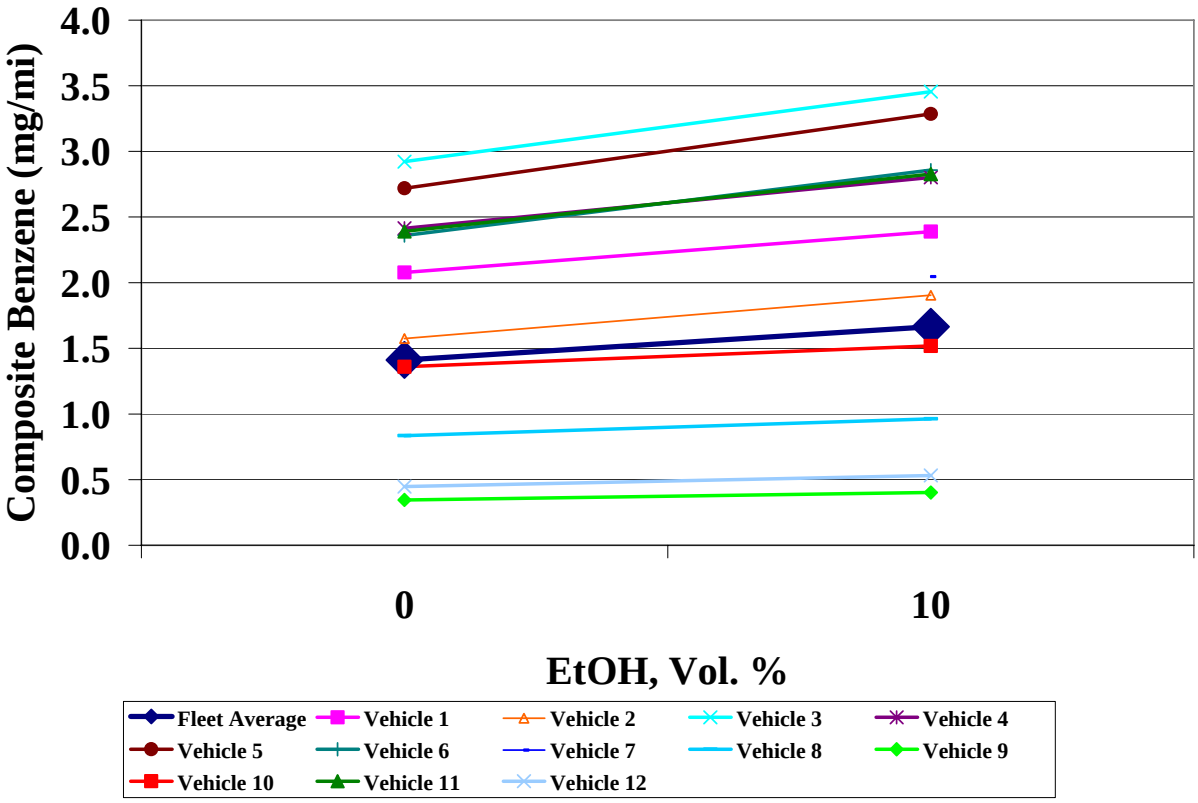
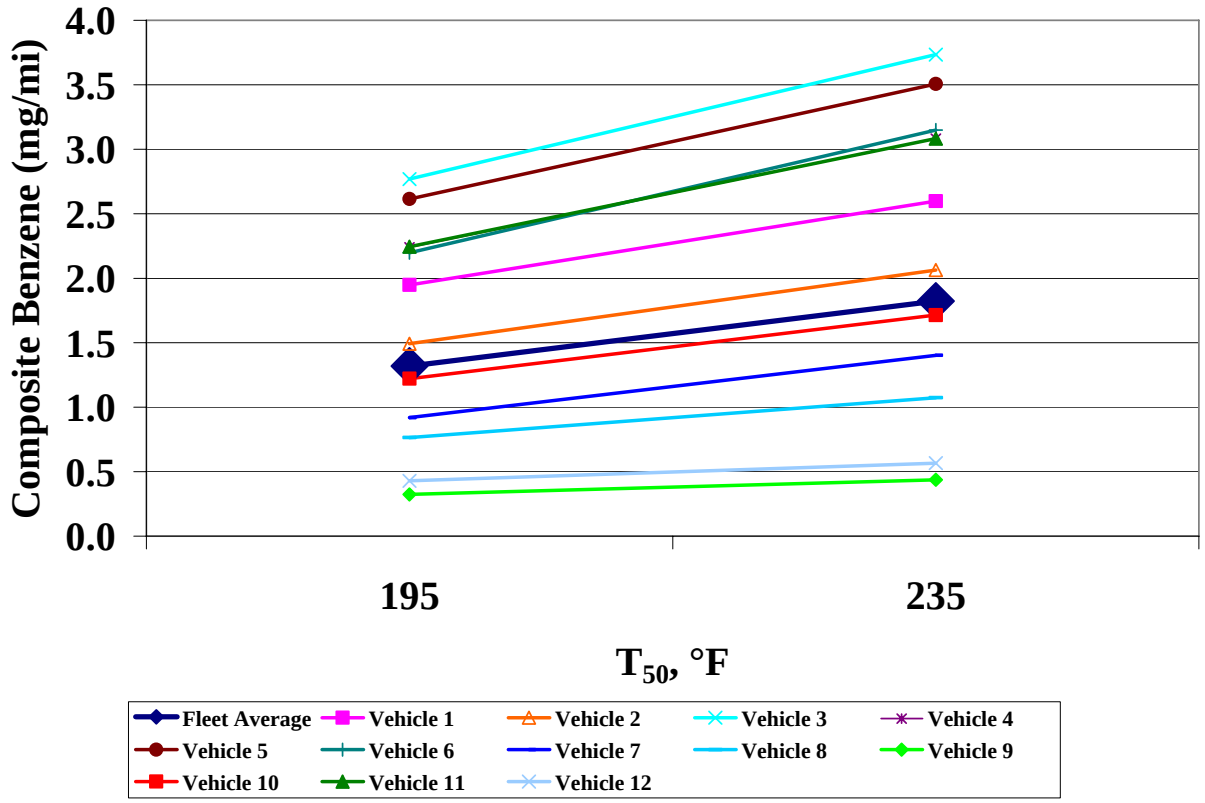


Figure 29. Composite Benzene Balanced Average by T_{50} Fleet Average and Individual Vehicles



3.2.4.2 Bag 1 Benzene Emissions

Bag 1 benzene results were similar to those for the composite emissions. A significant effect was found for ethanol. Figure 30 shows that fleet average benzene emissions increased as ethanol increased; the magnitude of this increase was 19% when ethanol increased from 0% to 10%. The interaction between ethanol and T_{50} was not even marginally significant.

A significant effect was found for T_{50}. Figure 31 shows that fleet average benzene emissions increased as T_{50} increased; the magnitude of this increase was 39% when T_{50} increased from 195°F to 235°F.

Figure 30. Bag 1 Benzene Balanced Average by EtOH
Fleet Average and Individual Vehicles

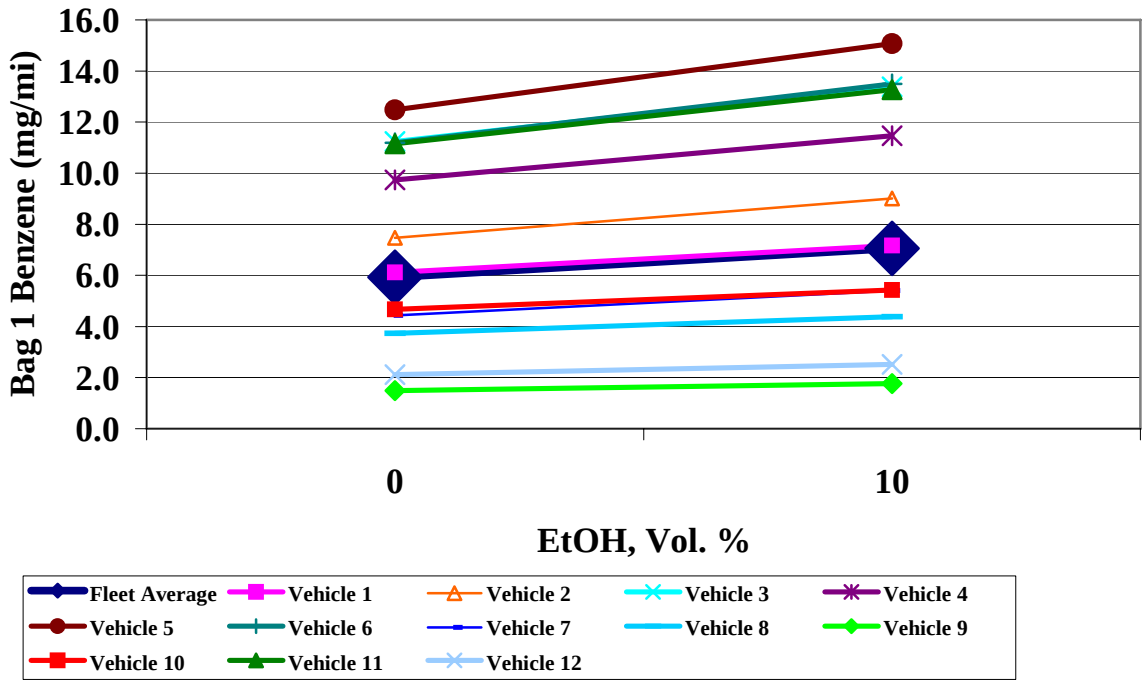
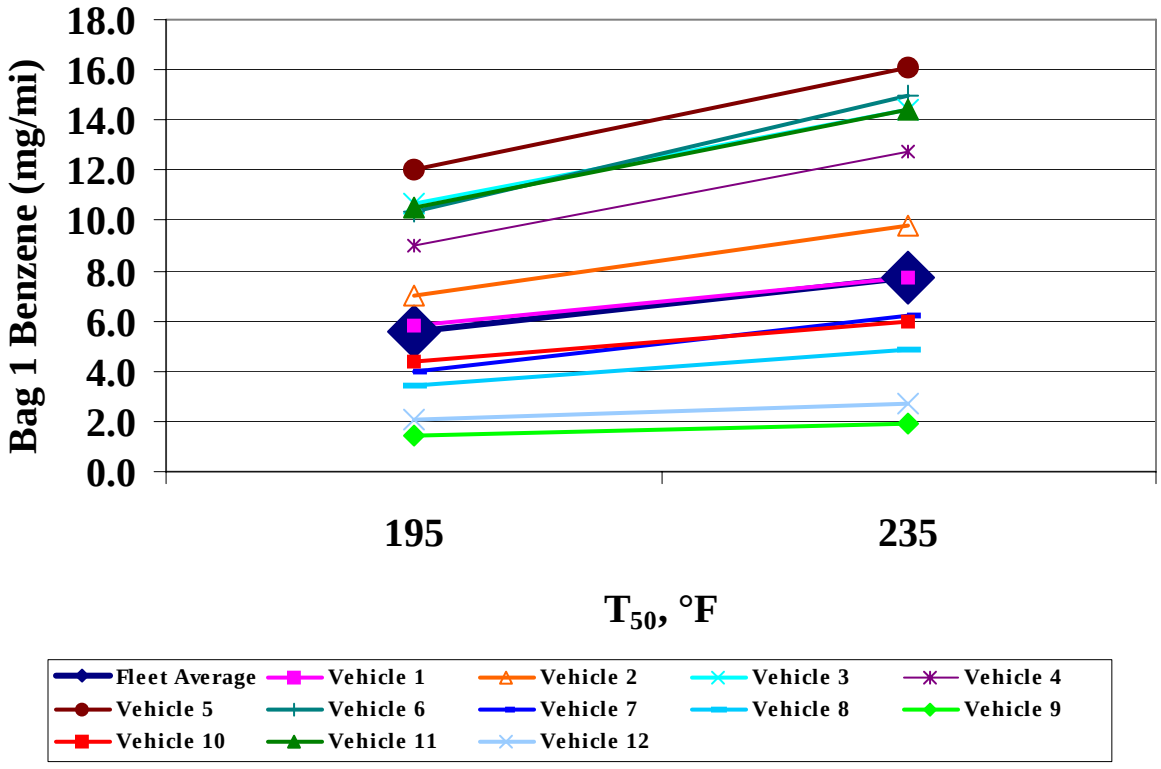


Figure 31. Bag 1 Benzene Balanced Average by T_{50}
Fleet Average and Individual Vehicles



3.2.5 FTP 1,3-Butadiene Emissions

The statistical analysis results for 1,3-butadiene emissions are presented in Table 14.

Table 14. Mixed Model Summary for 1,3-Butadiene

	FTP Composite		Bag 1	
Random Factor	P value		P value	
Vehicle	0.01		0.01	
T_{50} x Vehicle	-		0.45	
EtOH x Vehicle	-		-	
Fuel Factor	Coefficient	P value	Coefficient	P value
Intercept	-1.0109		0.5366	
T_{50}	0.011320	0.00	0.011060	0.00
EtOH	0.020270	0.00	0.019610	0.00
T_{50} x EtOH	-0.000220	0.44	-0.000160	0.57

3.2.5.1 Composite 1,3-Butadiene Emissions

A significant effect was found for ethanol. Figure 32 shows that fleet average 1,3-butadiene emissions increased as ethanol increased; the magnitude of this increase was 22% when ethanol increased from 0% to 10%. The interaction between ethanol and T_{50} was not even marginally significant.

A significant effect was found for T_{50}. Figure 33 shows that fleet average 1,3-butadiene emissions increased as T_{50} increased; the magnitude of this increase was 56% when T_{50} increased from 195°F to 235°F.

Figure 32. Composite 1,3-Butadiene Balanced Average by EtOH Fleet Average and Individual Vehicles

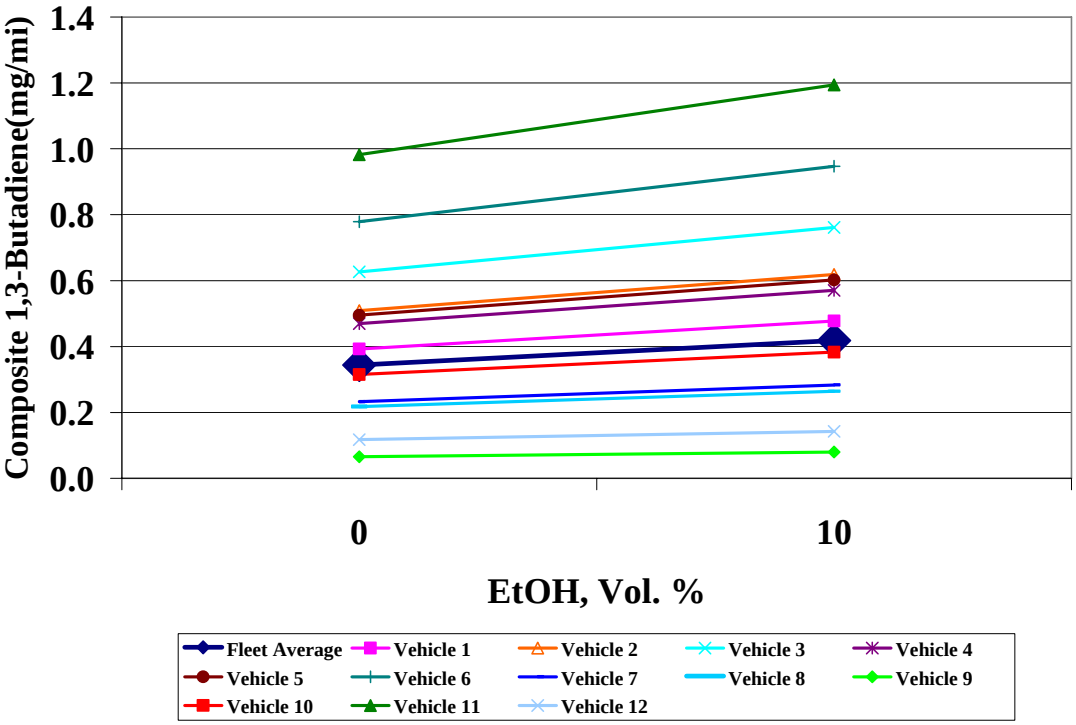
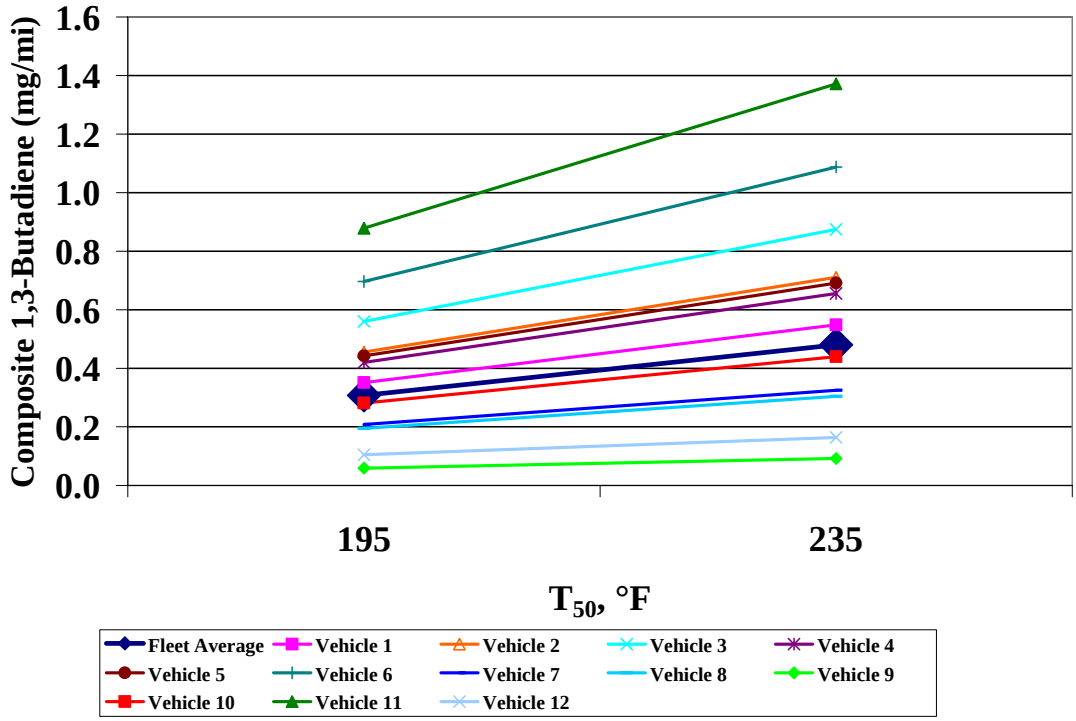


Figure 33. Composite 1,3-Butadiene Balanced Average by T_{50} Fleet Average and Individual Vehicles



3.2.5.2 Bag 1 1,3-Butadiene Emissions

Bag 1 1,3-butadiene results were similar to those for the composite emissions. A significant effect was found for ethanol. Figure 34 shows that fleet average 1,3-butadiene emissions increased as ethanol increased; the magnitude of this increase was 21% when ethanol increased from 0% to 10%. The interaction between ethanol and T_{50} was not even marginally significant.

A significant effect was found for T_{50}. Figure 35 shows that fleet average 1,3-butadiene emissions increased as T_{50} increased; the magnitude of this increase was 55% when T_{50} increased from 195°F to 235°F.

Figure 34. Bag 1 1,3-Butadiene Balanced Average by EtOH
Fleet Average and Individual Vehicles

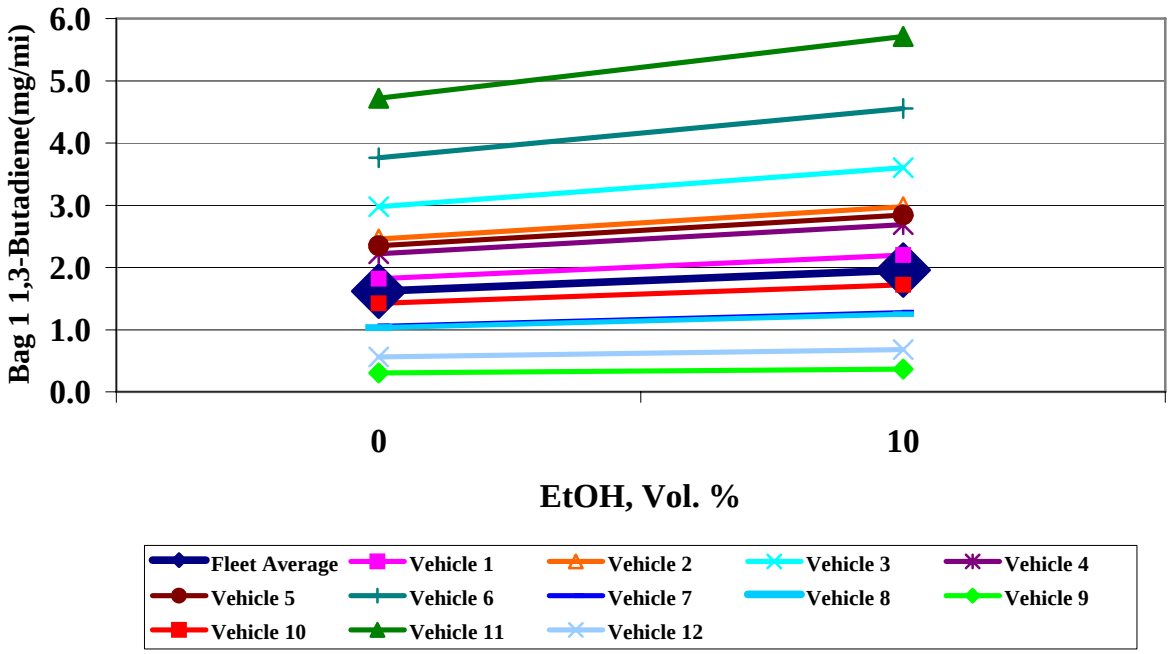
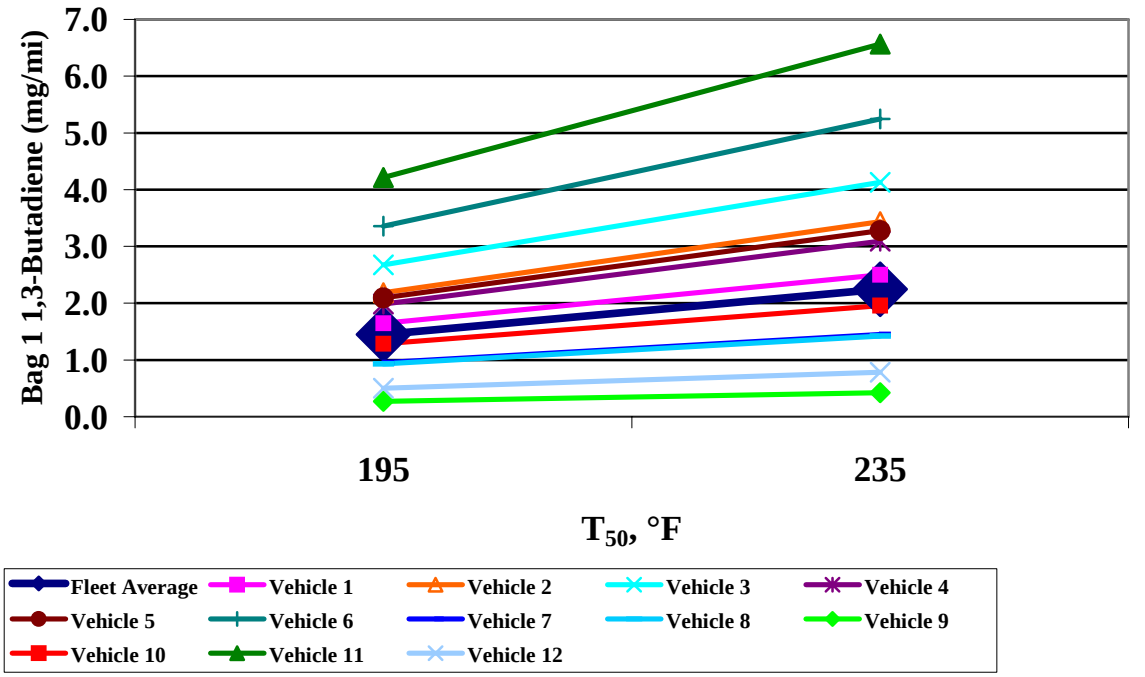


Figure 35. Bag 1 1,3-Butadiene Balanced Average by T_{50}
Fleet Average and Individual Vehicles



4. Comparisons with Previous Studies

The results from this study did not show significant changes in NMHC emissions with ethanol content. However, as described below, a significant interaction between ethanol and T_{90} was observed. Larger studies of older vehicles have generally shown decreases in HCs with increasing ethanol content [6,7,8]. More limited data are available on newer technology vehicles [1,19,20]. For newer vehicles, studies by the Colorado Department of Health at cold temperatures [19] and by the automotive industry [1] showed decreases in HCs with increasing ethanol content, comparable with the results for the older vehicles. A study by Environment Canada of 1999-2001 vehicles, however, did not find any significant effects of ethanol on NMHC [20].

The trend of increasing NMHC emissions with increasing T_{50} observed in this study is consistent with results reported by the Auto/Oil Air Quality Improvement Research Program and other studies [4,5]. Rutherford et al. found increases in NMHC of 4-12% for T_{50} going from 185°F to 215°F, with slightly higher increases observed for the studies that focused on more advanced vehicles [4]. The NMHC increase of approximately 36% seen in this study in response to a T_{50} increase from 195°F to 235°F is greater than those of the previous studies, although a larger range of T_{50} was examined.

Previous studies of older technology vehicles have generally indicated that HC emissions also increase with increasing T_{90} [4,5,8,9]. In the present study, a statistically significant interaction between T_{90} and ethanol was found for NMHC, with NMHC emissions increasing with T_{90} only for fuels containing ethanol.

In this study, CO emissions were shown to be significantly affected by both ethanol content and an interaction between ethanol and T_{50}. The 6 to 18% decrease in CO emissions in going from 0 to 10% ethanol levels, depending on T_{50} level, is comparable to the 13.4% reduction found by Reuter et al. in a previous Auto/Oil study with 1989 vehicles [7]. However, this study shows that the majority of the CO benefit was achieved between 0 and 5.7% ethanol; increasing ethanol above 5.7% produced little change in CO emissions at the low and mid levels of T_{50}, and actually increased CO at the high level of T_{50}. A recent study by the automotive industry for ULEV/LEV vehicles showed a negative 9% slope in the CO linear regression for oxygen going from 0 to 4% [1]. Environment Canada found CO reductions ranging from 12 to 49% for four of five 1999-2001 vehicles on a 20% ethanol blend [20]. Only one of these five vehicles showed a statistically significant reduction on 10% and 15% ethanol blends. Overall, these results seem to suggest that some CO reductions with ethanol can be expected for LEV/ULEV technologies, consistent with trends for older vehicles.

The effect of T_{90} on CO emissions that was observed in this study wherein CO emissions decreased as T_{90} increased has also been observed in previous studies [4], while other studies have shown the opposite effect [8, 9]. Rutherford et al. [4] found decreases in CO of 6-15% as T_{90} was increased from 280 to 325°F, compared to the 24% decrease observed in this study for increasing T_{90} from 295 to 355°F.

The results in the literature show some tendency for NO_x emissions to increase with greater ethanol levels, but this trend is not consistent or statistically significant over a wide range of studies. For this study, a statistically significant ethanol by T_{50} interaction was found, where higher NO_x emissions were observed for the 10% ethanol fuels at the low and mid-T_{50} values. For the low T_{50} value, NO_x emissions were 12% higher with 10% ethanol than with 0% ethanol; for the mid T_{50} value, they were 5-6% higher, while for the high T_{50} value they were unchanged. Reuter et al. found NO_x emissions to increase by 5.1% for fuels with 10% ethanol content in comparison with a base hydrocarbon fuel. Mayotte et al. in Phase 1 studies for the EPA found a 5.7% increase in NO_x for a fleet of 20 1987 to 1990 normal emitters using a fuel containing 3.7% oxygen in the form of ethanol [8]. In Phase 2 studies of 28 1986 to 1991 normal emitters, however, Mayotte, et al. did not find any significant differences between a base fuel and a fuel designed to have an oxygen content of 2.0% using ethanol (although this fuel also contained some amount of MTBE) [9]. The Colorado Department of Health did find an increase in NO_x of 19.8% with an ethanol based fuel for 12 Tier 1 vehicles at 35°F, but no changes in NO_x for 12 Tier 0 vehicles tested at the same temperature [19]. Interestingly, a recent study by the automotive industry found NO_x emissions for a non-oxygenated fuel were higher than those containing higher levels of oxygen (2 to 4%), somewhat in contrast with previous studies [1].

Fuel consumption was found to increase with increasing ethanol concentration, decreasing T_{50}, and decreasing T_{90}. In each case, the increase/decrease in fuel consumption between the lowest and highest values of a particular fuel parameter was 0.6 to 1.4%. Previous Auto/Oil studies have also found that ethanol and T_{90} can both affect fuel consumption [21]. For T_{90}, in that study, it was found that increasing T_{90} from 280°F to 360°F lowered fuel consumption by 1.5%, slightly greater than the value found in this study of 0.6%. Fuel consumption was also found to increase by 1.6% in the previous Auto/Oil study by adding 2.7 wt% oxygen to the fuel for a fleet of older (1983-1985 model year) vehicles. The "current" (1989 model year) vehicles from the previous Auto/Oil study showed greater changes in fuel consumption, with a 2.3% increase in fuel consumption for an addition of 2.7 wt% oxygen. Both of these results are comparable with the results from the present study of a 1.4% increase in fuel consumption for the addition of 10% ethanol (i.e., 3.5 wt% oxygen).

The effects of ethanol on toxic emissions have been studied in a number of previous studies. Ethanol studies have consistently shown that higher levels of fuel ethanol lead to increases in acetaldehyde emissions [7-9,20,22]. Reuter et al. [7] reported increases of over 150% in acetaldehyde for a fleet of 20 1989 model year vehicles using a fuel with 10% ethanol. Mayotte et al. found increases ranging from approximately 50 to 140% for studies with 1986 to 1991 vehicles including normal and high emitters [8,9]. The increase of 73% in acetaldehyde for a 0 to 10% increase in ethanol in the present study is similar in magnitude to that observed previously.

Interestingly, benzene emissions were found to increase with higher concentrations of ethanol in this study. This is in contrast to results from a number of studies that have shown decreasing benzene emissions with increasing ethanol or oxygen content [7-9]. It is important to note, however, that in some of these previous studies, the fuels with higher ethanol concentrations also typically had lower levels of benzene in the fuel. In the present study, the fuel benzene levels were relatively constant, and the exhaust benzene levels appear to track NMHC. This study also showed a 22% increase in 1,3-butadiene for the 10% ethanol fuel and a 14% increase in Bag 1

formaldehyde for the 10% ethanol fuel. Previous studies have not shown any consistent effects for ethanol on formaldehyde or 1,3-butadiene [7-9].

The effects of T_{50} on toxic emissions appear to be strong in the present study compared to previous Auto/Oil studies. In this study, formaldehyde increased by 23%, benzene increased by 38%, and 1,3-butadiene increased by 56% when T_{50} was increased from 195 to 235°F. Rutherford et al. previously examined the effects of T_{50} on toxics [4]. This study showed statistically significant increases in benzene and 1,3-butadiene in changing T_{50} from 185 to 215°F for the advanced (1995 and later) technology vehicles. This increase was on the order of 11% for both benzene and 1,3-butadiene. Similar effects were not found in the current fleet (1989 vehicles) or a fleet of Federal Tier 1 vehicles. Mayotte et al. made some comparisons between an industry average fuel, a high T_{50} fuel and a series of other fuels [9]. The industry average fuel and the high T_{50} fuel had essentially the same T_{50} values (~240°F), however, so any differences between these fuels would probably be related to fuel properties other than T_{50}.

5. Driveability Index

Driveability Index (DI) was originally developed to correlate vehicle driveability performance to fuel volatility. Due to the connection between driveability performance and NMHC emissions, DI has also been proposed as a simpler predictor of emissions than the individual fuel volatility parameters. Given this history, it is useful to examine the ability of DI to correlate emissions as compared to the study design variables.

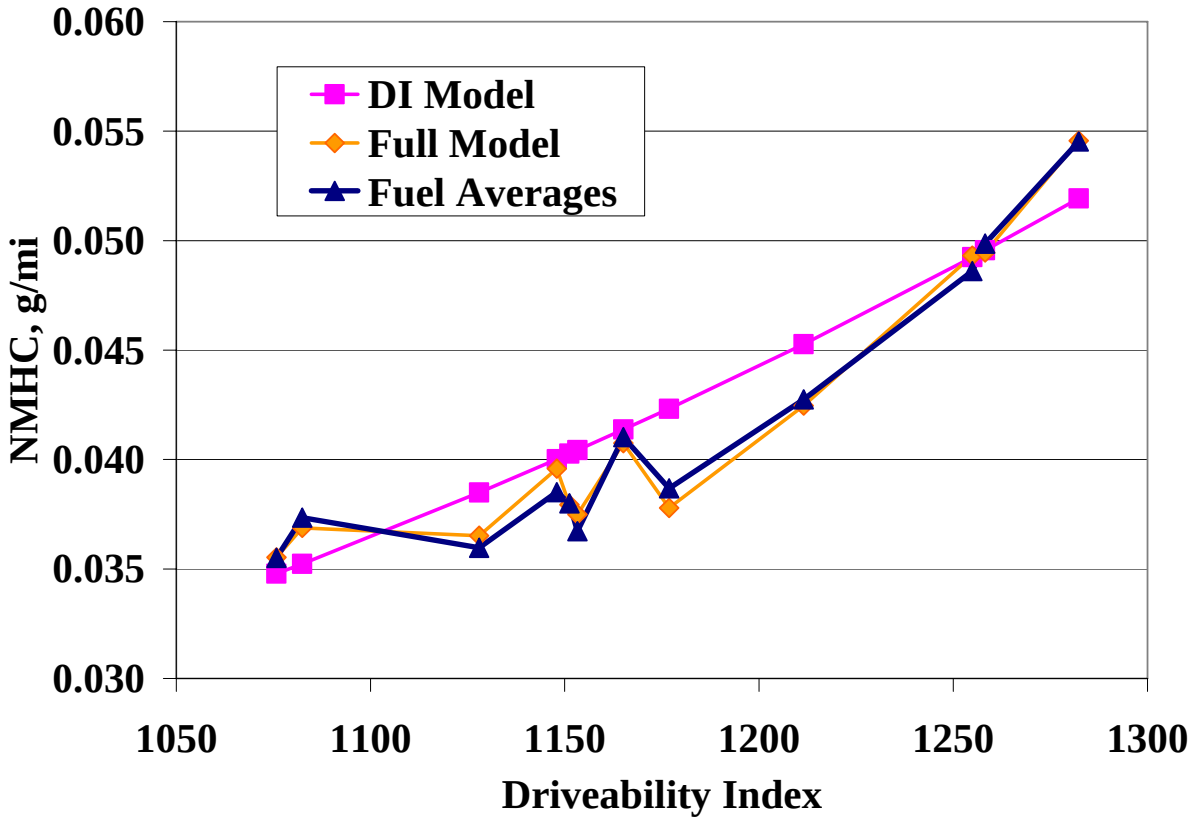
For this analysis, the definition of DI that is currently being balloted by ASTM was used:

$$DI = 1.5*T_{10} + 3.0*T_{50} + 1.0*T_{90} + 2.4*\text{vol\% Ethanol}$$

This equation is based on the most recent CRC analysis of vehicle driveability performance [23]. A model for NMHC emissions as a function of DI was developed similarly to the other models in this study, using DI as a fixed effect and Vehicle as a random effect.

Figure 36 is a comparison of the predictions made using the DI model with the predictions made using the full model developed using the design variables (Table 5) and the observed average NMHC emissions for the twelve fuels in the study. While the DI model does provide an approximation of the overall trend in NMHC emissions, it does not track detailed differences in the observed emissions that are captured in the full model (the full model accounts for 99.1% of the variation in the twelve fuel means, while the DI model accounts for 88.5%). It should be noted that DI is highly correlated (r=0.91) with T_{50} in this fuel set, despite the inclusion of T_{90} and ethanol terms in the DI equation.

Figure 36. DI Model Results



6. Summary and Conclusions

For this study, the emissions impacts of 12 fuels were evaluated in 12 vehicles. The 12 vehicles included California-certified LEV to SULEV vehicles split between passenger cars and light-duty trucks. The 12 fuels had independently varying levels of ethanol concentration (0%, 5.7%, and 10%), T_{50} (195°F, 215°F, and 235°F), and T_{90} (295°F, 330°F, and 355°F) in a partial factorial design intended to represent both non-oxygenated and oxygenated fuels available in California and the rest of the US. Vehicles were tested with catalysts that were bench-aged to an equivalent of 100,000 miles.

The final analysis of project data estimated regression coefficients for the fuel effects, with the levels of ethanol, T_{50}, and T_{90} used as continuous variables. Models predicting emissions and fuel consumption from first order effects, second order effects, and interactions of the fuel parameters were derived.

Key findings are as follows:

Regulated Emissions and Fuel Consumption

- NMHC:
    - There was a statistically significant interaction between ethanol and T_{90}. The interaction showed that NMHC emissions increased with increasing ethanol content at the mid-point and high level of T_{90}, but were unaffected at the low T_{90} level. Looked at another way, NMHC emissions increased with increasing T_{90} at the mid-point and high level of ethanol, but were unaffected by T_{90} at the zero level of ethanol.
    - NMHC emissions increased with increasing T_{50}. The percentage increases in NMHC emissions in going from the low and mid-point level for T_{50} to the high T_{50} level were 36 and 25%, respectively.

- CO:
    - There was a statistically significant interaction between ethanol and T_{50}. The interaction showed that CO emissions decreased as ethanol content was increased from the low to the mid-point level for all levels of T_{50}. However, increasing ethanol content from the mid-point to the high level produced little to no change in CO for the low and mid-point levels of T_{50}, and increased CO at the high level of T_{50}. Looked at another way, CO emissions increased with increasing T_{50} at the mid-point and high levels of ethanol, but were unaffected by T_{50} at the zero level of ethanol.
    - CO emissions decreased with increasing T_{90}. The percentage decreases in CO emissions in going from the low and mid-point level for T_{90} to the high T_{90} level were 24% and 7%, respectively.

- NO_x:
    - There was a statistically significant interaction between ethanol and T_{50}. The interaction showed that NO_x emissions increase with increasing ethanol content at the low level of T_{50}. At the mid-point level of T_{50}, NO_x emissions are largely

unaffected as ethanol content is increased from the zero to the mid-point level, but increase as ethanol is increased to the high level. At the high level of T_{50}, NO_x emissions are largely unaffected by ethanol content. Looked at another way, NO_x emissions decreased with increasing T_{50} at the high level of ethanol, but were largely unaffected by T_{50} at the zero and mid-point levels of ethanol.

- Fuel Consumption:
  - Fleet average fuel consumption increased by 1.4% when ethanol content was increased from the zero to the high level.
  - Fleet average fuel consumption decreased by 1.2% when T_{50} was increased from the low to the high level.
  - Fleet average fuel consumption decreased by 0.6% when T_{90} was increased from the low to the high level.

In the fuel set used in this work, 10% ethanol tended to decrease volumetric heat content by 2.2%.

NMOG and Unregulated Emissions

Detailed speciation measurements were performed for a subset of four fuels with target T_{90} = 355°F in order to evaluate the fuel effects of ethanol and T_{50} on NMOG and the four mobile source air toxics: benzene, 1,3-butadiene, formaldehyde and acetaldehyde. Key findings are as follows:

- NMOG:
  - NMOG emissions increased by 14% when ethanol content was increased from the zero to the high level.
  - NMOG emissions increased by 35% when T_{50} was increased from the low to the high level.

- Formaldehyde:
  - Formaldehyde emissions increased by 23% when T_{50} was increased from the low to the high level.

- Acetaldehyde:
  - Acetaldehyde emissions increased by 73% when ethanol content was increased from the zero level to the high level.

- Benzene:
  - Benzene emissions increased by 18% when ethanol content was increased from the zero to the high level.
  - Benzene emissions increased by 38% when T_{50} was increased from the low to the high level.

- 1,3-butadiene:
    - 1,3-butadiene emissions increased by 22% when ethanol content was increased from the zero to the high level.
    - 1,3-butadiene emissions increased by 56% when T_{50} was increased from the low to the high level.

The effects of ethanol and T_{50} on NMOG and mobile source toxics described above were only observed for the subset of fuels having the high level of T_{90}. The results of this study do not permit any conclusions as to what effects ethanol or T_{50} might have had on NMOG or toxics emissions for fuels having low or mid-point T_{90} levels.

The following table presents in summary form the fuel effects (i.e., first order, second order, or interactions) which were determined to be either statistically significant, marginally significant, or not significant in predicting composite FTP emissions, fuel economy, and toxics in this study.

		12 fuel set Regulated Emissions				4 fuel set (D, E, K, L) NMOG & Toxic Emissions				
		NMHC	CO	NOx	FC*1000	Formaldehyde	Acetaldehyde	Benzene	1,3-Butadiene	NMOG
Composite FTP	T_{50}	S	N	N	S	S	N	S	S	S
	T_{90}	M	S	N	S	--	--	--	--	--
	EtOH	N	S	M	S	N	S	S	S	S
	T_{50}^2	S	S	N	N	--	--	--	--	--
	T_{90}^2	S	M	N	N	--	--	--	--	--
	$EtOH^2$	N	S	M	N	--	--	--	--	--
	T_{50} x EtOH	M	S	S	N	N	N	N	N	N
	T_{90} x EtOH	S	M	N	M	--	--	--	--	--

S = significant, M = marginally significant, N = not significant "--" = not analyzed

Driveability Index

The recently-balloted ASTM Driveability Index (DI) equation was compared with the full model as a predictor of NMHC results from this study. While the DI model does provide an approximation of the overall trend in NMHC emissions, it does not track detailed differences in the observed emissions that are captured in the full model (the full model accounts for 99.1% of the variation in the twelve fuel means, while the DI model accounts for 88.5%). It should be noted that DI is highly correlated (r=0.91) with T_{50} in this fuel set, despite the inclusion of T_{90} and ethanol terms in the DI equation.

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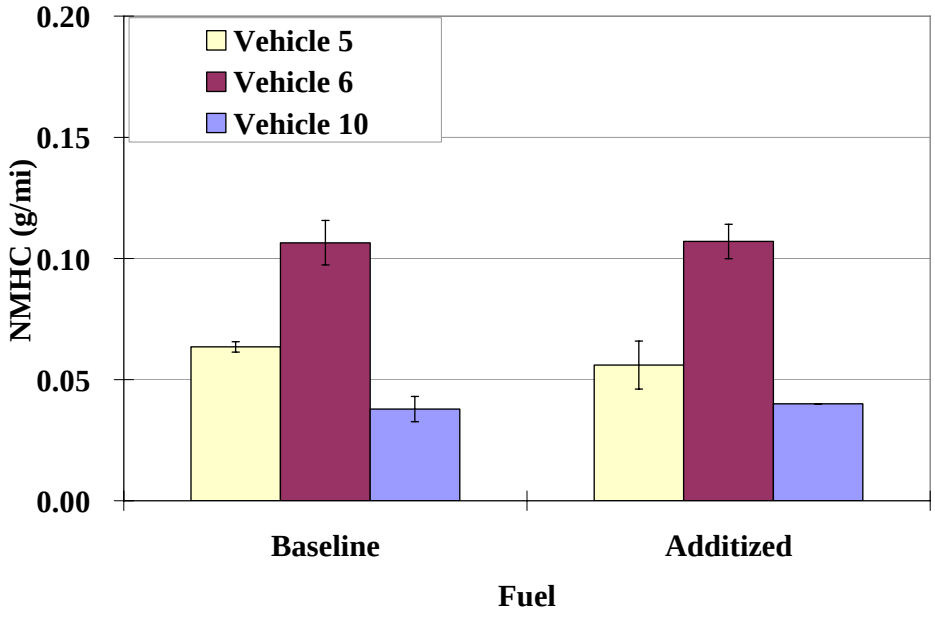
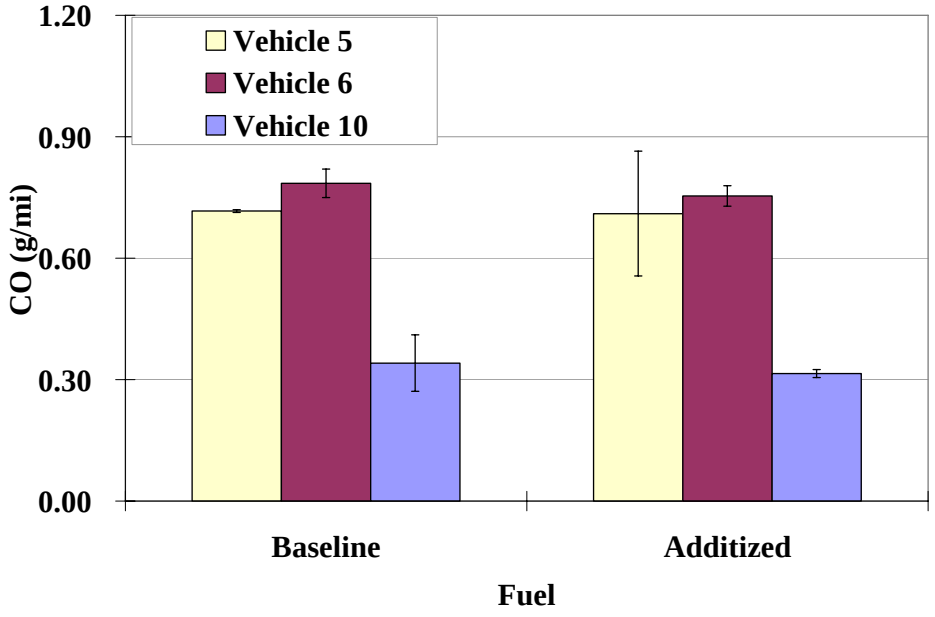
Appendix A. Properties of the Test Fuels.

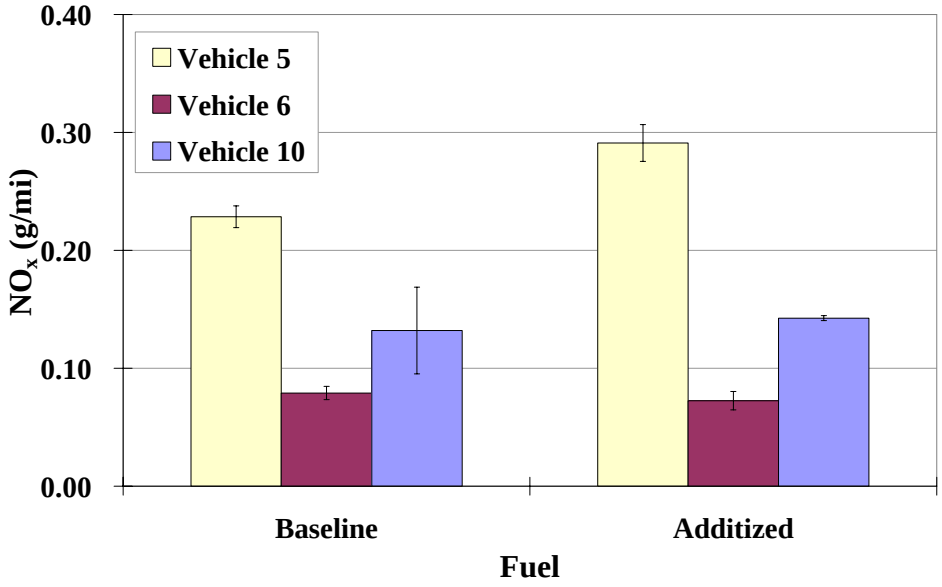
Inspection		Units	Fuel A	Fuel B	Fuel C	Fuel D	Fuel E	Fuel F	Fuel G	Fuel H	Fuel I	Fuel J	Fuel K	Fuel L
API Gravity		°API	62.1	59.9	57.6	61.4	56.7	60.1	57.1	60.6	57.2	56.6	59.3	54.4
Relative Density		60/60°F	0.7310	0.7393	0.7482	0.7337	0.7519	0.7387	0.7502	0.7366	0.7498	0.7525	0.7416	0.7611
DVPE		psi	7.74	7.84	7.70	7.65	7.80	7.62	7.78	7.85	7.68	7.57	7.71	7.69
Oxygenates--D 4815	MTBE	vol %	0.03	0.03	0.13	0.03	0.11	0.08	0.13	0.09	0.16	0.13	0.16	0.16
	ETBE	vol %	0.02	0.02	0.01	0.01	0.01	0.08	0.04	0.01	0.01	0.01	0.02	0.01
	EtOH	vol %	0.02	5.62	10.37	0.00	10.26	0.00	10.15	0.05	5.94	5.90	0.00	10.49
	O2	wt %	0.02	2.10	3.84	0.01	3.78	0.03	3.76	0.04	2.22	2.19	0.03	3.83
Sulfur Content		ppm	18.8	16.7	19.0	18.2	17.2	18.1	17.5	18.6	16.8	19.1	21.9	20.6
D86 Distillation	IBP	°F	94.2	107.6	104.3	88.8	106.3	94.2	103.7	94.2	100.7	102.6	93.9	106.1
	5% Evaporated	°F	126.3	127.2	124.6	123.2	124.3	121.6	125.3	122.7	124.0	126.0	117.9	129.4
	10% Evaporated	°F	136.0	133.2	130.5	133.3	130.5	135.0	133.2	134.0	130.2	134.4	129.7	140.0
	20% Evaporated	°F	148.6	140.8	138.8	147.6	139.5	154.7	143.7	151.6	139.0	146.6	148.4	152.4
	30% Evaporated	°F	163.6	154.1	146.6	164.1	147.2	177.0	152.9	173.3	150.8	175.5	174.4	158.8
	40% Evaporated	°F	179.8	176.1	153.7	182.3	153.8	200.2	163.4	197.0	191.0	220.5	208.5	202.1
	50% Evaporated	°F	194.7	190.9	192.7	199.5	197.7	216.8	212.2	216.3	215.9	236.6	236.1	232.7
	60% Evaporated	°F	209.0	203.2	223.5	216.9	226.2	227.6	226.7	230.4	235.9	251.5	255.2	248.7
	70% Evaporated	°F	224.2	219.3	245.7	237.9	259.2	238.2	237.0	245.9	260.9	271.9	279.6	273.5
	80% Evaporated	°F	243.4	240.9	281.5	274.3	299.7	254.7	251.7	273.7	311.3	305.2	319.1	307.7
	90% Evaporated	°F	294.3	289.8	329.2	355.0	351.7	295.0	290.7	326.9	354.2	329.2	355.5	349.1
	95% Evaporated	°F	327.4	325.9	343.4	367.3	364.9	324.0	327.8	343.7	366.6	338.7	368.6	367.4
	EP	°F	351.2	352.0	374.0	392.0	385.4	361.2	365.4	374.4	391.8	365.8	390.3	389.6
	Recovery	vol %	97.0	97.9	97.7	97.9	97.4	97.2	96.7	98.0	97.9	97.6	98.1	97.3
	Residue	vol %	1.8	1.1	1.2	0.8	1.4	1.7	1.5	1.0	1.1	1.2	1.0	1.0
	Loss	vol %	1.2	1.0	1.1	1.3	1.2	1.1	1.8	1.0	1.0	1.3	0.9	1.7
Driveability Index			1082.4	1075.8	1128.0	1153.3	1165.1	1148.0	1151.2	1176.8	1211.5	1254.9	1258.2	1282.3
E200		vol %	53.6	57.6	52.1	50.6	50.6	40.0	47.4	41.7	43.1	35.2	37.6	39.4
E300		vol %	90.9	91.5	84	83.6	80.0	90.9	79.5	85.2	77.8	78.4	75.2	78.0
Aromatics		vol %	25.9	25.9	25.4	25.1	26.7	26.7	25.2	25.6	26.8	26.4	26.0	26.4
Olefins		vol %	5.3	5.5	5.3	5.4	5.3	5.5	5.2	5.1	5.2	5.4	5.5	5.5
Saturates		vol %	68.8	68.6	69.3	69.5	68.0	67.8	69.6	69.3	67.7	68.2	68.5	68.1
Benzene		vol %	0.9	0.9	1.0	1.0	0.9	1.0	1.0	1.0	0.9	0.9	1.0	0.9
Heating Value		BTU/gal	113,037	111,424	110,737	113,714	111,052	114,068	110,937	113,978	112,884	113,286	114,795	112,365
Research Octane Number			92.0	91.5	93.2	93.2	93.9	94.5	94.0	92.2	93.6	94.7	92.5	94.5
Motor Octane Number			84.0	83.2	84.0	84.6	84.4	84.8	85.1	84.8	85.5	85.8	84.2	85.2
(R+M)/2			88.0	87.4	88.6	88.9	89.2	89.7	89.6	88.5	89.6	90.3	88.4	89.9

Appendix B. Results for Testing of Vinyl Acetate Fuel Effects.

Vehicle emissions tests were conducted on 3 of the 12 test vehicles with an in-use, non-oxygenated California gasoline. Each vehicle was tested over the FTP twice on the undoped fuel and twice on the doped fuel. Some additional tests were performed on Vehicle 10 due to greater variability that was observed in the NO_x measurements. The results for NMHC, CO, and NO_x are plotted below, with the error bars representing one standard deviation of the measurement averages. The results show no statistically significant differences in the undoped and the doped fuels for these emissions.






0.40
0.30
0.20
0.10
0.00
NOx (g/mi)
Vehicle 5
Vehicle 6
Vehicle 10
Baseline
Additized
Fuel

Appendix C. Description of Catalyst Aging.

Catalyst aging was performed for 12 individual catalyst assemblies. Catalyst aging was performed over the RAT-A cycle for a period of 75 hours. This cycle is described below. Catalyst systems included all closed-coupled and underbody catalysts and oxygen sensors. The catalysts were provided in the original configuration and returned in the original configuration.

RAT-A Aging Protocol.

Step	Description
1	Duration=40 seconds. Stoichiometric, closed loop exhaust conditions (A/F=14.3). Catalyst inlet temperature ~ 800°C.
2	Duration= 6 seconds. Open loop, fuel injector pulse width same as used in Step 3.
3	Duration=10 seconds. Open loop, fuel injection pulse width increased from Step 1 to achieve 2.9 percent CO at catalyst inlet with secondary air source supplying additional air to achieve an oxygen concentration of 3.0 percent at the catalyst inlet. Typical catalyst bed temperature= 940±10°C (catalyst bed temperature measured one inch downstream of catalyst front face).
4	Duration=4 seconds. Fuel control returned to closed-loop (stoichiometric conditions). Air injection from Step 3 continues for duration (air injection point is located downstream of oxygen sensor used to control the engine).

General Steps of Catalyst Aging Procedure Including Configuration for Testing

Step	Description
1	CE-CERT provided 12 new catalyst systems (including close coupled and underfloor catalyst, and oxygen sensors) in their as purchased configuration.
2	The catalysts were configured for the aging cell, including addition of thermocouples. Temperature was monitored continuously throughout the actual aging of the catalyst.
3	The engine oil was drained and replaced with standard oil.
4	The RAT-A aging cycle was set up and cycle specifications verified. If more than one converter was in a system, then setup was performed on the first catalyst only. Flows were adjusted to provide equal flows through each of the two catalyst systems being simultaneously aged. Aging was conducted with a 15 ppm sulfur fuel. Raw exhaust concentrations were monitored at the start of the aging (zero hours).
5	After 25 hours of aging, the exhaust conditions were verified to insure correct and stable operating conditions.
6	After 50 hours of aging, the exhaust conditions were verified and the test parts were

rotated between the banks of the engine.

7 After 75 hours of aging, final emissions verification was made and the parts were removed from the test stand.

8 Catalysts were configured into original as-received configuration and returned to CE-CERT.

Appendix D. Detailed Description of Statistical Analysis

D.1 Statistical Analysis Methodology

All analyses were run using the Proc Mixed procedure in PC/SAS from SAS Institute, Inc. The use of a mixed model was required because the Vehicle effect is a random effect. Vehicle effects, as distinguished from vehicle type or certification effects, are random because the specific vehicles selected from each certification class and vehicle type are only representative of all possible vehicles that could be selected from the classes and types.

The main analysis was used to estimate the coefficients for the fuel effects, with the levels of EtOH, T_{50}, and T_{90} used as continuous variables within the model. This model estimates regression coefficients for the fuel effects as opposed to testing for differences between levels of the factors. This model tests the quantitative effects (linear, quadratic, and interactions) of the fuels. This model included T_{50}, T_{50}^2, T_{90}, T_{90}^2, EtOH, $EtOH^2$, and the EtOH by T_{50} and EtOH by T_{90} interactions, but did not include the T_{50} by T_{90} or EtOH by T_{50} by T_{90} interactions. The study was not designed to include these latter interactions because previous studies had not found them significant. This model was run on the fuel factors after centering the data by subtracting the average for each fuel factor over the data set.

The analyses used the natural logarithms of the data for the regulated emissions, toxics, and NMOG. The data were log transformed partially to correct for skewness and unequal variances in the residuals. Analyses using the logarithmic transform of the data have been conducted in similar previous studies that have shown that emissions variance is relatively constant as a percentage of the emission level [18]. For example, vehicles with higher emission levels will tend to have a higher variability than those with lower emissions levels. Taking the logarithm of the data helps to provide a more constant variability across the range of the data set, produce residuals that are more normally distributed thus better satisfying assumptions for the standard analyses, and might reduce non-inherent complexity in models through multiplicative rather than additive fuel parameter effects.

Analyses for fuel economy were run using the inverse of fuel economy multiplied by 1000. The multiplication factor was used because of numerical instabilities in estimating variance components using SAS Proc Mixed without the scaling factor. It has become standard practice to analyze fuel consumption rather than fuel economy partly because the chassis dynamometer tests are run with constant mileage and it is the amount of fuel consumed during the test that varies. This puts the variable in the numerator rather than the denominator and thereby produces residuals that more closely match the assumptions implied by standard statistical modeling. The reader should note that this transformation, unlike the logarithmic transformation, reverses the scale; i.e., with fuel consumption lower is better. The fuel consumption values presented here are also based on the inverse of the fuel economy calculation and the inherent weighting factors used in making this calculation and, as such, might differ slightly from those obtained in making a straight FTP weighted calculation of fuel consumption.

The model equations developed for each dependent variable are listed in Table D-1. These equations represent the emissions responses of the twelve vehicle test fleet to changes in the design fuel properties. Responses for an individual vehicle are the sum of the fleet response and the random effects that represent the interaction between that vehicle and the intercept, T_{50}, T_{90}, and ethanol. As a measure of how well the fleet responses match the data, the percentage of the total squared variation about the mean for the twelve fuels that is explained by the fleet model equations is also presented in Table D-1.

The "balanced averages" used these main analysis model results to calculate emissions values for specific combinations of the design variables. For each calculation, the desired level(s) of the design parameter(s) of interest were used in the full model for that emission; all other design parameters were assumed to be at their mid-level design value. This includes the random effects for vehicle x intercept and vehicle x design parameters, with the modification that the vehicle effect is given a value of 1 if the calculation of interest is for that specific vehicle and 0 if not (i.e., all vehicles get a value of 0 for fleet effects. The resulting model predictions using the analysis model were then transformed back to the arithmetic scale to create the balanced averages. The percentage changes presented are based on the appropriate combinations of these balanced averages.

In another model, an ANOVA using the fuel factors (EtOH, T_{50}, and T_{90}) at their three target values was used to characterize the twelve fuels. This model broke the 12 fuels down into the three factors that characterize each fuel. The actual values were compared against the target values prior to running the ANOVA. It was determined that the actual values and target values were sufficiently close that the target values could be used throughout the course of this analysis. The statistical significance of the fuel factors was also examined using pairwise difference comparisons. This provides information on differences between specific fuel combinations to supplement the ANOVA results that merely indicate the existence of statistically significant differences between some fuels within the test matrix. The pairwise comparisons were conducted using least squares means with a Tukey-Kramer multiple comparisons test adjustment.

An ANOVA was also run to test the simple hypothesis that there were no significant differences in emissions among the individual test fuels. This model treated the individual fuels without regard to fuel characteristics.

D.2 Outliers

Outlier test results were identified simultaneously on an individual emission basis, as well as on a multivariate basis across NMHC, CO, and NO_x. Potential individual outlier test results were identified with the studentized residuals from the individual fuels means model. The analyses were re-run without the potential outliers to determine the influence of the identified data points. Because the analysis of these data is focused on one variable at a time, this check of the effects of the influential test results is an essential step prior to final analysis. A total of 17 tests were found to have one or more emissions with studentized residuals greater than 3 in absolute value. The second analyses run without these flagged data points showed only minor differences in results, indicating that the potential outliers were not having a large influence on the results.

A multivariate outlier test was also conducted to identify test runs that were potential outliers. Multivariate outlier analysis should be more sensitive than univariate analyses to tests where the entire run may have been affected by unusual test conditions or unusual operating behavior of the vehicle. The SAS macro program "outlier.sas" developed by Michael Friendly was used to screen the data for multivariate outliers using Mahalanobis distance for each observation. Using Mahalanobis distance has the advantage of considering if a case is an outlier relative to a particular set of group data where individual measurements are not unusual, but the particular combination of measurements is unusual. This procedure was found to be somewhat sensitive to the specific variables included in the analysis. In the final versions the analysis focused on the tailpipe emissions of CO, THC, and NO_x after logarithmic transformation and a second run focusing on the difference of each observation from its replicate average after logarithmic transformation.

No significant outliers were found in the lnTHCw, lnCOw, and lnNO_xw measurements at α=0.01. Twenty-one tests were flagged by the procedure for the difference of each observation from its corresponding replicate average (n=2 or n=3). The majority of the tests identified by the multivariate approach did not match up with the cases identified by the univariate approach. Identified tests' logbooks were re-checked for problems in the test and no significant deviations from test procedures were found. The effect of these tests on the analysis of individual emissions would be less than the cases found using the studentized residual outlier analysis. After conducting the two outlier tests, it was concluded that the analysis should be conducted using the entire data set.

Studentized residuals were examined for lack of fit using the SAS GLM procedure with random effects. While GLM uses an approximation for random effects, ANOVA's and Proc Mixed are preferred. GLM does provide estimates of the model and allows for checking of residuals. Individual large (>3) studentized residuals were indicative of individual data points with problems. The models were checked for lack of fit for groups of observations such as would be observed if the model did not fit for a particular vehicle and fuel combination. For lnCO_2 Vehicle 10 had large studentized residuals for both observations for Fuel C, indicating a potential lack of fit for the model for that vehicle/fuel combination. Other emissions only had individual observations with studentized residuals greater than 3.

Additional comparisons were made between the bag measurements and the raw exhaust tailpipe and engine out modal emissions. Since these measurements were taken with separate sets of analyzers, similar trends in the data between the bag and modal emissions provide an additional check of the data consistency. For tests identified as outliers, comparisons were made for specific bags where outliers were observed to identify emissions events, higher engine-out emissions or other characteristics that might have contributed to the outlier observation. Tests in which a poor comparison between the bag measurements and the modal tailpipe emissions was found were also more closely scrutinized to ensure there were no measurement errors in the bag emissions results.

Table D-1 Model Equations

ln(NMHC) = -3.2942

$$+0.005679*(EtOH-4.8502)+0.006300*(T_{50}-211.60)+0.001685*(T_{90}-326.84)$$
$$+0.000722*(EtOH-4.8502)^2+0.000176*(T_{50}-211.60)^2+0.000058*(T_{90}-326.84)^2$$
$$+0.000195*(EtOH-4.8502)*(T_{50}-211.60)+0.000244*(EtOH-4.8502)*(T_{90}-326.84)$$

Explained Variation = 99.1%

ln(CO) = -0.7966

$$-0.015810*(EtOH-4.8502)+0.001227*(T_{50}-211.60)-0.004500*(T_{90}-326.84)$$
$$+0.003118*(EtOH-4.8502)^2+0.000099*(T_{50}-211.60)^2+0.000045*(T_{90}-326.84)^2$$
$$+0.000355*(EtOH-4.8502)*(T_{50}-211.60)+0.000174*(EtOH-4.8502)*(T_{90}-326.84)$$

Explained Variation = 95.5%

ln(NO_X) = -2.6183

$$+0.005710*(EtOH-4.8502)-0.000130*(T_{50}-211.60)+0.000240*(T_{90}-326.84)$$
$$+0.001622*(EtOH-4.8502)^2-0.000060*(T_{50}-211.60)^2+0.000043*(T_{90}-326.84)^2$$
$$-0.000320*(EtOH-4.8502)*(T_{50}-211.60)-0.0000012*(EtOH-4.8502)*(T_{90}-326.84)$$

Explained Variation = 98.8%

1000/mpg = 49.8527

$$+0.073760*(EtOH-4.8502)-0.015380*(T_{50}-211.60)-0.004200*(T_{90}-326.84)$$
$$+0.004197*(EtOH-4.8502)^2+0.000175*(T_{50}-211.60)^2+0.000098*(T_{90}-326.84)^2$$
$$-0.000650*(EtOH-4.8502)*(T_{50}-211.60)-0.000680*(EtOH-4.8502)*(T_{90}-326.84)$$

Explained Variation = 97.9%

ln(Formaldehyde) = -0.3148

$$+0.009851*(EtOH-4.8502)+0.005152*(T_{50}-211.60)$$
$$+0.000020*(EtOH-4.8502)*(T_{50}-211.60)$$

Explained Variation = 99.5%

ln(Acetaldehyde) = -0.5976

$$+0.054480*(EtOH-4.8502)+0.001629*(T_{50}-211.60)$$
$$+0.000097*(EtOH-4.8502)*(T_{50}-211.60)$$

Explained Variation = 99.7%

ln(Benzene) = 0.3967

$$+0.016890*(EtOH-4.8502)+0.008186*(T_{50}-211.60)$$
$$-0.000120*(EtOH-4.8502)*(T_{50}-211.60)$$

Explained Variation = 99.7%

ln(1,3 Butadiene) = -1.0109
$$+0.020270*(EtOH-4.8502)+0.011320*(T_{50}-211.60)$$
$$-0.000220*(EtOH-4.8502)*(T_{50}-211.60)$$
Explained Variation = 99.9%

ln(NMOG) = -3.0679
$$+0.013010*(EtOH-4.8502)+0.007531*(T_{50}-211.60)$$
$$-0.000010*(EtOH-4.8502)*(T_{50}-211.60)$$
Explained Variation = 100.0%