CRC Report No. E-65-3

FUEL PERMEATION FROM AUTOMOTIVE SYSTEMS: E0, E6, E10, E20 AND E85

Final Report

December, 2006

COORDINATING RESEARCH COUNCIL, INC.
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E0, E6, E10, E20 and E85

A. Background and Introduction

CRC Project E-65 investigated the effects of three different fuels on the permeation rates of the fuel systems from 10 different California vehicles, covering model years from 1978 to 2001. Results from this study were published in the report "Fuel Permeation from Automotive Systems" in September 2004, and are available on the websites of the Coordinating Research Council (CRC) and California Air Resources Board (CARB). Permeation is one of the three mechanisms identified as responsible for "evaporative emissions." The other two are leaks (liquid and vapor) and fuel tank venting (canister losses).

The original study vehicles were selected to represent a cross-section of the California in-use fleet as it existed in calendar year 2001, where pre-1983 model year (MY) vehicles were 10% of the registered fleet. The fuels tested in the original study included two oxygenated fuels: one with 11% MTBE and the other with 5.7% ethanol, and a non-oxygenated fuel for comparison. All the fuels had properties typical of California summer gasoline. The two oxygenated fuels contained 2.0 weight percent oxygen, the minimum oxygen content required by then-existing regulations for federal reformulated gasoline. Permeation increased in all vehicles when evaluated with the ethanol fuel.

Based on the previous work, four issues were identified for further study in CRC Project E-65-3:

1. Investigate the permeation characteristics of "near zero" evaporative emission control systems scheduled for California in MY 2004 and later.
2. Determine if changes in ethanol content affect permeation levels.
3. Establish the permeation effects of E85 (85 Volume% ethanol fuel) in a flexible fuel vehicle.
4. Determine if permeation rates are sensitive to changes in aromatics content of the fuel.

Harold Haskew & Associates, Inc. was selected as the prime contractor, with Automotive Testing Laboratories, Inc, in Mesa, AZ serving as the testing laboratory. It was agreed to re-commission Rigs 1 and 2, the 2000 and 2001 MY systems from the E-65 project, and build three new test rigs, one representing a MY 2004 California "Near Zero" evap control vehicle, another representing the California "Zero Evap" control technology, and finally, a "Flexible-Fuel" vehicle, capable of operating on E85 or gasoline.

Six test fuels were blended for this project:

1. E0 – Non-oxygenated base fuel
2. E6 – 5.7 Volume% ethanol fuel (2 Weight% oxygen)
3. E6Hi – 5.7 Volume % ethanol fuel with increased aromatics content
4. E10 – 10 Volume% ethanol fuel
5. E20 – 20 Volume% ethanol fuel, and
6. E85 – 85 Volume% ethanol fuel

The testing for this project commenced in January of 2005, and continued through early August 2006. An Interim Report was made available in August of 2006 with the results from the E0, E6, E6Hi, E10, and E85 fuel testing results. This final report adds the results from the tests with the E20, or 20 volume percentage, ethanol fuel, as well as additional test results on the E0 fuel.

These data represent a limited number of samples; care should be taken in extending these results to the fleet.

B. Conclusions and Findings

Conclusions:

1. The low-level ethanol blends (E6, E6Hi, E10 and E20) increased permeation in all the vehicle systems and technologies tested, compared to the non-ethanol fuel (E0). These increases were statistically significant.
2. The advanced technology LEV II and PZEV[1] systems (2004 MY) had much lower permeation emissions than the MY 2000-2001 enhanced evaporative systems. The zero evaporative emissions system (PZEV) had the smallest increase due to ethanol of all the vehicles tested.
3. The high-level ethanol blend (E85) tested in the flexible fuel vehicle system had lower permeation emissions than the non-ethanol (E0) fuel.
4. Diurnal permeation rates do not appear to increase between E6 and E10, but do appear to increase between E6 and E20; however, this increase is not statistically significant.
5. The highest diurnal permeation rate for three of the five rigs (1, 2, and 12) tested was measured when these rigs were tested on the E20 fuel. The highest diurnal permeation rate for Rig 11 was recorded on the E6 fuel, while the highest diurnal permeation rate for Rig 14 was measured on the E10 fuel.
6. Diurnal permeation emissions were lower on all four rigs tested with the higher-level aromatics fuel (E6Hi) versus the lower aromatics fuel (E6); however, this decrease was not statistically significant.
7. Permeation rates with the E0 fuel at the start and the end of the test program were not significantly different on all five rigs, indicating that there was no shift in the permeation performance during the program.
8. The average specific reactivities of the permeates from the low-level ethanol blends were significantly lower than those measured with the non-ethanol fuel (E0). There was no significant difference in the average specific reactivities within the low-level ethanol blends.

Findings:

1. The average diurnal permeation rate increased 347 mg/day (from 177 to 524 mg/day) when the E6 fuel was substituted for the base non-ethanol E0 fuel.
2. The average diurnal permeation rate increased 253 mg/day (from 177 to 430 mg/day) when the E6Hi fuel was substituted for the base non-ethanol E0 fuel.
3. The average diurnal permeation rate increased 307 mg/day (from 177 to 484 mg/day) when the E10 fuel was substituted for the base non-ethanol E0 fuel.
4. The average diurnal permeation rate increased 385 mg/day (from 177 to 562 mg/day) when the E20 fuel was substituted for the base non-ethanol E0 fuel.

[1] Partial Zero Emission Vehicle – a vehicle with Super Ultra Low Exhaust Emission Levels (SULEV), and Zero Fuel Evaporative Emissions, certified to 150,000 mile and 15 year performance levels for the state of California

5. On the “Flexible Fuel” Rig 14, the diurnal permeation rate increased 205 mg/day (from 261 to 466 mg/day) from the base non-ethanol fuel (E0) rate when the E10 fuel was evaluated, increased 99 mg/day (from 261 to 360 mg/day) from the base fuel rate when the E20 fuel was evaluated, but decreased 133 mg/day (from 261 to 128 mg/day) from the base fuel rate when the E85 fuel was evaluated.
6. Relative to Rigs 1, 2 and 11, the “Zero Fuel Evaporative Emission” system (Rig 12) had a lower increase in permeation rate when the ethanol-containing fuels were evaluated. A 14 mg/day (from 36 to 50) increase was measured with fuel E6, a 9 mg/day (from 36 to 45 mg/day) increase with fuel E6Hi, a 28 mg/day (from 36 to 64 mg/day) increase with fuel E10, and a 39 mg/day (from 36 to 75 mg/day) increase with fuel E20.
7. The average specific reactivity of the base E0 fuel permeate was 3.99, the highest of the five fuels evaluated.
8. Average specific reactivity of the E6 fuel permeate was 3.00.
9. Average specific reactivity of the E6Hi fuel permeate was 3.17.
10. Average specific reactivity of the E10 fuel permeate was 2.94.
11. Average specific reactivity of the E20 fuel permeate was 3.04.
12. Average specific reactivity of the E85 fuel permeate was 2.73.
13. Rig 11 permeate had the lowest specific reactivity of all the rigs on all the fuels tested.

C. General Discussion

I. Test Program Overview

The objective of this test program was to measure the permeation emissions of the newer (MY 2000 to 2005) California vehicles with gasolines containing ethanol at various volume percent concentrations: 0, 6[2], 10, 20 and, on one system, 85. At the 6% ethanol level, two fuels were blended to meet different targets of total aromatics (designated as “E6” and “E6Hi”) in order to evaluate the effect of this latter parameter on permeation.

Five vehicle fuel systems were included in this project. Two California Enhanced Evap vehicles were carried over from the previous CRC E-65 project (the newest, Rigs 1 and 2). Three new rigs were constructed for this evaluation: a California LEV-II “near-zero” passenger car, a California PZEV Zero Evaporative Emission car, and a “Flexible-Fuel” vehicle capable of operation on gasoline, 85% ethanol, or any mixture in between.

Stabilization - Once qualified as ready for test, each test rig was filled (100% of rated capacity) with the appropriate test fuel and stored in a room (“soak room”) at 105°F and periodically tested in a SHED[3] until the results indicated that stabilization of the permeation emissions was achieved. During this stabilization period, the fuel in each rig was circulated twice a week. Every seventh week all of the fuel in each rig was drained and replaced with fresh fuel. Once a week, each rig was removed from the soak room and

[2] The federal minimum requirement for “reformulated” fuel was 2.0 weight percent oxygen. That correlates to 5.7 volume percent ethanol. For purposes of this report, we will refer to the 5.7 Volume% specification in its rounded off value of 6, as in E6.

[3] SHED – Sealed Housing for Evaporative Determination

placed in a hot soak SHED at a temperature of 105°F for three to five hours to estimate the current permeation rate.

The constant-temperature tests to determine stabilization were performed in a 105°F hot-soak SHED for a three-hour test period, with the emissions measured during the last two hours (later tests on the lower permeation rigs were increased to a five hour period). All fixed-temperature (105°F) testing was performed in ATL's SHED 14. Variable-temperature diurnal (65° to 105° to 65°F) testing was performed in ATL SHEDs 13 and 15. These three SHEDs are variable volume/variable temperature (VV/VT) equipment that can be operated in fixed or variable-temperature modes, and are referred to as VT-SHEDs. All the SHED's and equipment used for this program were the same as were utilized for the original E-65 program.

Diurnal Evaluation - After the steady-state permeation rate of a rig was stabilized at 105°F, and approved by the CRC E-65-3 Steering Committee, it was evaluated for diurnal permeation performance using the California "Real-Time" 24-hour diurnal (65 to 105 to 65°F) emission test procedures. The fuel was drained from the rig, and a 40% fresh fill of the appropriate test fuel added. The rig was then placed in a VT-SHED, and the California diurnal procedure was performed over a period of 24 hours. Samples of the ambient air in the VT-SHED were taken at the start of the diurnal and at the end of the 24-hour test period for later hydrocarbon speciation analysis. The fuel tanks and the canisters were vented to the outside of the SHED to eliminate the possibility of the tank venting emissions being counted as permeation. Emission rates were calculated using the 2001 California certification test procedure, with the appropriate corrections for the ethanol in the permeate.

Testing Chronology - Figure 1 on the following page shows the testing chronology to illustrate when the various rigs were being tested with the different fuels. Testing started on January 11, 2005, and the last diurnal test on Rig 2 was finished on August 10, 2006. The solid bar indicates the time interval for the steady-state and the diurnal evaluations. The interval between the solid bars indicates the decision period where the Steering Committee was considering approval of the data and authorizing the move to the next test fuel.

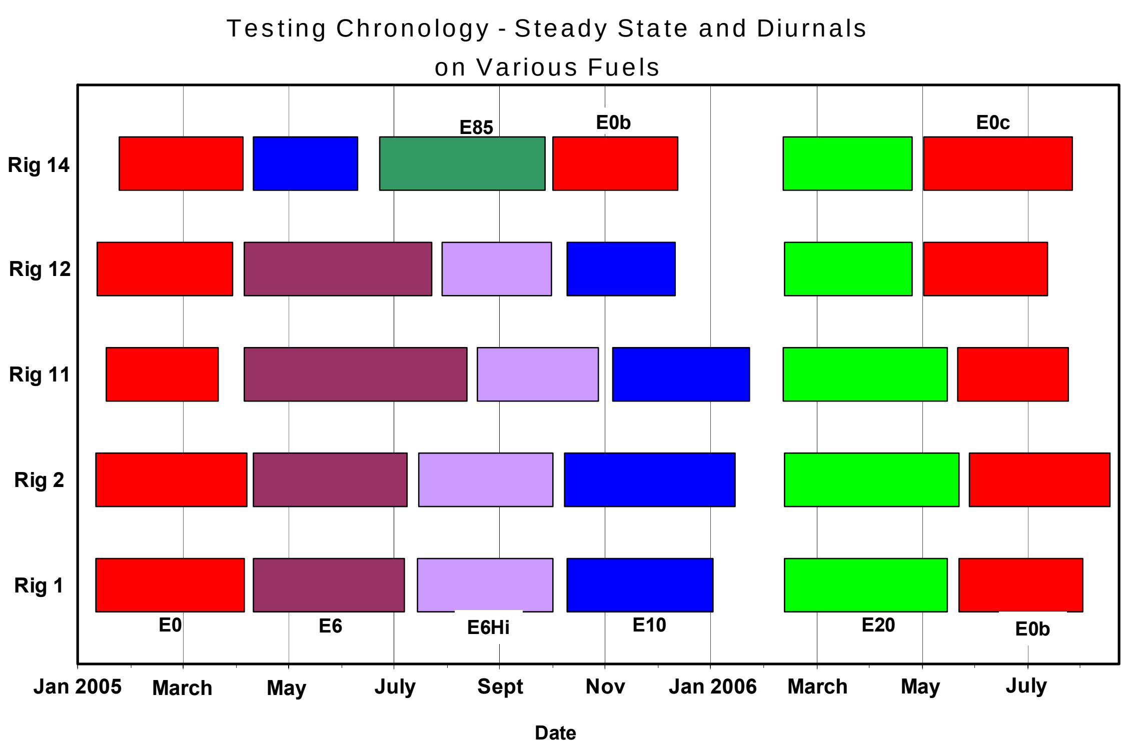

Figure 1

II. Project Scope – Fuel System Technology and Rig Construction

Fuel System Technology

Two enhanced evap rigs were carried over from the original E-65 project (Rigs 1 and 2), and three new rigs were added. The technologies are described in Tables 1 and 2.

Table 1

Technology Groups and Corresponding Rig	
Enhanced Evaporative Emissions	Rigs 1 & 2
California Near-Zero (LEV II)	Rig 11
California PZEV (Zero Fuel Evaporative Emission)	Rig 12
Flexible Fuel Vehicle (FFV)	Rig 14

Table 2
Vehicle Information for the Test Rigs

Rig No.	MY	Make	Model	Odo (miles)	Evap Family	Tank Size (Gal)	Tank Material	VIN
1	2001	Toyota	Tacoma	15,460	1TYXE0095AE0	15.8	Metal	5TENL42N01Z718176
2	2000	Honda	Odyssey	119,495	YHNXE0130AAE	20	Plastic	2HKRL1852YH518467
11	2004	Ford	Taurus	29,973	4FMXR015GAK	18	Metal	1FAFP55S54G142635
12	2004	Chrysler	Sebring	6434	4CRXR0130GZA	16	Metal	1C3EL46J74N363042
14	2005	Chevrolet	Tahoe	4054	5GMXR0176820	26	Plastic	1GCEK13U85X7313EX

The California Enhanced Evaporative Emission Control regulations were the first to require "real-time" diurnal emission measurements (three 24-hour day diurnals) and were phased in during the 1995 – 1998 model year period. The pre-enhanced evap emission standard was 2.0 g/test, but the test consisted of a one hour simulated diurnal day, with the fuel tank locally heated from 60° to 84°F. Only one hour's worth of vehicle evaporative emissions was measured during the diurnal, and that was with the vehicle at room temperature in a SHED, typically 72°F. The hot soak was measured in a SHED following an 11 mile drive at room temperature. The enhanced evap procedure measured the emissions from the vehicle in a variable-temperature SHED (VT-SHED), and the SHED ambient temperature was varied from 65° to 105°F, exposing the entire vehicle and the fuel system component to the ambient temperature. The one hour hot soak was performed as before but after the running loss test, a one hour drive at 105°F.

These regulations incorporated significant changes to the emissions certification test requirements, and produced corresponding changes in the vehicle materials and hardware used by the automobile manufacturers. The emission control system useful life and warranty period were extended to 10 years or 100,000 miles. Two-day and three-day diurnal tests were required, as was the measurement of "running-loss" emissions. The allowable limits for the highest one day of diurnal emissions for the three-day test, plus the one hour of hot soak following the drive are 2.0 g/test, or 2.5 g/test for vehicles with fuel tanks rated at 30 or more gallons. Light-duty trucks are allowed slightly higher limits.

California's Near Zero (LEV II) requirements dropped the allowable limits for passenger cars by 75% to 0.5 g/test for the three-day diurnal, and to 0.65 g/test for the two-day test. Phase-in started with 40% of production in model year 2004, 80% in 2005, and 100% in 2006. Significant improvements in permeation performance and tank vapor control (carbon canister design) were required.

California's PZEV vehicles are developed and certified to have "Zero" fuel evaporative emissions where zero is defined as less than 0.0 grams per test when measured on California's evaporative emission test procedures. This is agreed to be less than 54 milligrams per test (highest of the 3 diurnal days + one hour high temperature hot soak). This standard requires the highest level of emission control in every aspect of the vehicle's fuel and vapor control system, both in performance and durability.

Flexible Fuel Vehicle is a vehicle capable of performing on gasoline or a high percentage of ethanol (85%), or any mixture of the two. The evaporative emission standards are the enhanced emission standards with certain test procedure modifications. Sensors (or in later versions, software) are used to detect the mixture in the fuel system and make the appropriate adjustments for the engine and emission control system. This is performed automatically, and no action is required by the vehicle operator. Flexible fuel vehicles are certified to meet the evaporative emission performance limits on gasoline, or the worst combination of the ethanol/gasoline mixture (currently thought to be 10% ethanol).

Test Rig Construction

Fuel system test "rigs" are used in the automotive development process to isolate the fuel system's contribution to the emissions. Since tires, adhesives, paint and vinyl trim can also emit hydrocarbons, they need to be removed to provide a better chance of properly identifying the fuel-related emissions. Isolating the fuel system components on a "rig" is the appropriate choice.

Refueling vapor controls are commonly developed in the automotive industry using rigs, or "test bucks", but they feature only the tank and canister system, with the carbon canister located close to the tank. This project included the fuel and vapor lines, and their chassis-to-engine connection hoses at the front of the vehicle. All the fuel system components (with the exception of the engine mounted injectors and hoses[4]) that could contribute to permeation losses were kept in the original spatial relationship. This meant that the rigs were almost as long as the vehicles. For system integrity, all components were removed and remounted on the rigs without any fuel or vapor line disconnections.

In the original E-65 project, the vehicle was sacrificed to remove the fuel system components, and the remaining body parts and pieces sold as scrap. Our previous experience indicated that the fuel system on the newer vehicles (mid-90s and later) could be removed from the vehicle without catastrophic surgery.

The test rig frame was constructed of 1.5" square aluminum tube, with metal caster wheels at the four corners. A photo of Rig 12 appears in Figure 2 to show a typical configuration. There is a lot of empty space required to keep all of the fuel system components in their x, y, and z orientation as present in the vehicle.

[4] It was decided in the original E-65 project to eliminate the engine-mounted fuel system components (including carburetors and injectors) to avoid the compromising contributions of leaks and vapor losses. The investigators wanted to identify the contribution of permeation, not leaks. The fuel supply lines and hoses, and the return components, if fitted, are present on the rigs, with terminations where the engine connections are made. This practice was continued for the current project.

Figure 2 - Overall View - Rig 12

Enhanced Evaporative Emissions Technology – Rigs 1 & 2

Rigs 1 and 2 were carry-over systems from the previous CRC fuel permeation project reported in September of 2004, and photos of the fuel tank end of the rigs are shown here

Figure 3 - Rig 1 Fuel Tank

Figure 4 - Rig 2 Fuel Tank

Rig 1 was fabricated to evaluate the permeation performance of the metal fuel tank system from a 2001 MY Toyota Tacoma pick-up truck, and is shown in Figure 3 above. The metal tank was coated with a black anti-rust paint with a short metal fill-pipe that ran to the side of the truck body. The carbon canister and purge control solenoid for this pre-ORVR[5] system was located in the left front side of the engine compartment.

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[5] ORVR – On-board Refueling Vapor Recovery, an emission control configuration with components and function to capture the refueling vapors and store them for later combustion. The Toyota pick-up was not required by the California regulatory roll-out requirements to have such a system until MY 2003.

Rig 2's (2002 MY Honda Odyssey, a light-duty passenger van) fuel system features a large (20 gallon capacity) plastic fuel tank of multi-layer blow-molded construction for a high degree of permeation control (Figure 4). The carbon canister for this pre-ORVR system is located in the vehicle's under-body close to the position of the driver's seat.

Both of these rigs were certified to the California enhanced evaporative emission standard of 2.0 grams per test for the three-day diurnal + hot soak, and 2.5 grams per test for the two-day diurnal + hot soak.

Rig 11 (Figure 5) was created from the fuel system components of a 2004 MY Ford Taurus sedan. The vehicle was purchased from a California dealer and driven to the laboratory in Mesa AZ, where after inspection and approval, the fuel system was removed and mounted in the aluminum frame to become a "rig." The fuel tank was of steel construction and had a rated capacity of 18 gallons. The fuel tank was located near the rear seat position on the vehicle, and the on-board refueling vapor recovery (ORVR) canister was positioned further aft, as shown in Figure 5.

Figure 5 - Rig 11 Fuel Tank and Canister

Rig 12 (Figures 6 & 7) was fabricated using the fuel system components from a 2005 MY Chrysler Sebring sedan. It also featured a steel fuel tank and a carbon canister mounted adjacent to the tank. It was certified as an on-board refueling vapor recovery system (ORVR).

Figure 6 - Rig 12 Fuel Tank

Figure 7 - Rig 12 Fuel Tank and Canister

Rig 14 (Figure 8) featured the fuel system components from a 2005 MY Chevrolet Tahoe SUV. It was certified to be a "Flexible-Fuel" system, which means it can operate on gasoline or E85, or any mixture of the two. The Tahoe has a 26 gallon multi-layer "plastic" fuel tank, and a close-mounted carbon canister for tank vapor control. It is also an ORVR design system.

Figure 8 - Rig 14 Fuel Tank and Canister

III. The Project and Procedures

Fuels

Six test fuels were blended for the CRC E-65-3 follow-up project. All of the low-level ethanol blends (i.e., E0-E20) were made from California blending components and were targeted at California summer fuel characteristics with vapor pressures targeted at 7.0 psi. The gasoline used to blend the E85 fuel was a high vapor pressure conventional gasoline, but butane still had to be added to the blend to approach the target 7.0 psi vapor pressure. These fuels were:

Tag	Description
E0	Non-oxygenated base fuel
E6	5.7 Volume% ethanol fuel (2 Weight% oxygen)
E6Hi	5.7 Volume% ethanol fuel with increased aromatics content
E10	10 Volume% ethanol fuel
E20	20 Volume% ethanol fuel
E85	85 Volume% ethanol fuel

The basic inspections of the six test fuels are shown in Table 3.

Table 3
Test Fuel Inspections

Inspection	Units	E0	E6	E6Hi	E10	E20	E85
API Gravity	°API	61.4	58.8	52.3	58.3	55.4	48.6
Relative Density	60/60°F	0.7334	0.7434	0.7699	0.7455	0.7572	0.7855
DVPE	psi	7.00	7.25	7.19	7.17	7.06	6.80
Oxygenates--D 4815							
MTBE	vol %	0.01	0.00	0.00	0.00	0.00	0.00
ETBE	vol %	0.00	0.00	0.00	0.00	0.12	0.00
EtOH	vol %	0.00	6.02	6.28	10.29	19.82	84.69
MeOH	vol %	0.00	0.00	0.00	0.00	0.00	0.83
O2	wt %	0.00	2.23	2.25	3.81	7.23	29.73
FIAM Corrected--D 1319							
Aromatics	vol%	22.57	26.79	41.47	26.03	26.18	3.86
Olefins	vol%	10.70	4.91	3.32	4.77	4.85	1.57
Saturates	vol%	66.73	62.24	50.45	58.83	49.23	9.82
Oxygenates	vol%	0.00	6.02	6.28	10.31	19.94	85.21
Aromatics--D 5580							
Benzene	vol%	0.41	0.55	0.43	0.51	0.70	0.17
Toluene	vol%	5.26	6.84	5.25	6.50	8.31	0.67
Ethylbenzene	vol%	1.08	1.46	1.13	1.39	1.71	0.15
p/m-Xylene	vol%	4.67	5.38	4.21	5.13	6.01	0.59
o-Xylene	vol%	1.67	1.98	1.81	1.89	2.14	0.22
C9+	vol%	8.86	10.01	25.71	9.52	7.55	2.02
Total	vol%	21.96	26.22	38.55	24.93	26.42	3.82

Table 3 (Continued)

Test Fuel Inspections

Inspection	Units	E0	E6	E6Hi	E10	E20	E85
D 86 Distillation							
IBP	°F	101.1	108.9	98.0	107.7	112.1	116.8
5% Evaporated	°F	123.2	125.8	124.8	127.2	130.6	153.5
10% Evaporated	°F	134.5	130.7	132.1	132.1	135.8	164.0
20% Evaporated	°F	148.5	136.8	142.4	138.2	143.4	168.7
30% Evaporated	°F	165.0	144.8	159.0	144.7	149.7	170.4
40% Evaporated	°F	186.2	175.8	206.3	150.8	155.1	171.2
50% Evaporated	°F	209.5	202.0	241.9	182.6	159.6	171.5
60% Evaporated	°F	231.1	225.6	274.0	221.8	165.9	171.8
70% Evaporated	°F	251.2	249.3	302.8	246.0	234.6	172.0
80% Evaporated	°F	273.4	275.7	324.5	273.3	257.9	172.4
90% Evaporated	°F	305.6	309.9	345.3	309.4	291.1	173.1
95% Evaporated	°F	330.6	335.9	363.2	335.7	312.4	174.1
EP	°F	389.9	380.4	411.4	378.3	352.0	297.4
Recovery	vol %	97.7	97.6	97.2	98.0	97.3	97.1
Residue	vol %	1.0	1.0	1.2	1.1	1.0	1.9
Loss	vol %	1.3	1.4	1.5	0.8	1.7	1.0
Karl Fischer Water	wt %	-	-	-	-	-	0.42

Additional Inspections

Fuel	Units	E0	E6	E6Hi	E10	E20	E85
Gum							
Unwashed	mg/100ml	20	16	18	17	19	9
Washed	mg/100ml	1	1	0	0	0	0
Peroxide Number	ppm	<1	<1	<1	1.0	<1	4.4
Induction Period	Hr	24	24	24	24	24	24
Potential Gum							
Unwashed	mg/100ml	22	22	24	20	19	7
Washed	mg/100ml	0	0	0	0	0	2
Research ON		90.5	92.1	96.2	94.5	98.7	105.8
Motor ON		83.2	84.2	86.2	86.4	86.6	89.2
(R+M)/2		86.9	88.2	91.2	90.5	92.7	97.5

Complete speciation analyses of the fuels were also furnished, and the files are available with the following names:

Tag	File Name
E0	E0-FR41677-LDR
E6	E6-FR41678-LDR
E6Hi	E6High-FR41785-LDR
E10	E10-FR41681-LDR
E20	E20-FR43560-LD
E85	E85-FR42011-LDR

Compositions of the E0 and low level ethanol blends are presented by hydrocarbon type and carbon number in Tables 4, 5 and 6 below.

Table 4
Test Fuel Composition Comparison - Paraffins

	Paraffins by Volume %									
Fuel	C3-	C4	C5	C6	C7	C8	C9	C10	C11	C12+
E0		0.419	18.789	10.322	6.783	14.017	4.341	1.618	0.502	0.068
E6		0.163	14.938	17.492	8.016	9.732	3.613	0.919	0.442	0.031
E6Hi		1.609	10.58	13.061	6.091	7.394	2.808	1.343	0.424	0.126
E10		0.150	14.22	16.649	7.753	9.15	3.412	0.865	0.417	0.027
E20		0.876	9.202	12.752	8.295	9.066	1.585	0.446	0.049	0.007

Table 5
Test Fuel Composition Comparison - Olefins

	Olefins by Volume %									
Fuel	C3-	C4	C5	C6	C7	C8	C9	C10	C11	C12+
E0	0.029	0.101	2.025	5.126	0.579	0.514	0.013			
E6		0.013	0.914	1.613	0.771	0.347	0.007			
E6Hi		0.008	0.66	1.197	0.595	0.273	0.007			
E10		0.011	0.876	1.509	0.727	0.324	0.007			
E20	0.016	0.004	0.669	2.040	0.873	0.448				

Table 6

Test Fuel Composition Comparison – Aromatics

	Aromatics by Volume %									
Fuel	**C3-**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**C10**	**C11**	**C12+**
E0				0.448	5.286	7.971	6.443	2.696	0.594	0.087
E6				0.6	6.875	9.249	7.055	2.928	0.568	0.048
E6Hi				0.454	5.25	7.603	16.538	9.101	1.724	0.216
E10				0.569	6.502	8.715	6.650	2.753	0.523	0.045
E20				0.693	8.250	9.878	5.978	1.505	0.146	0.042

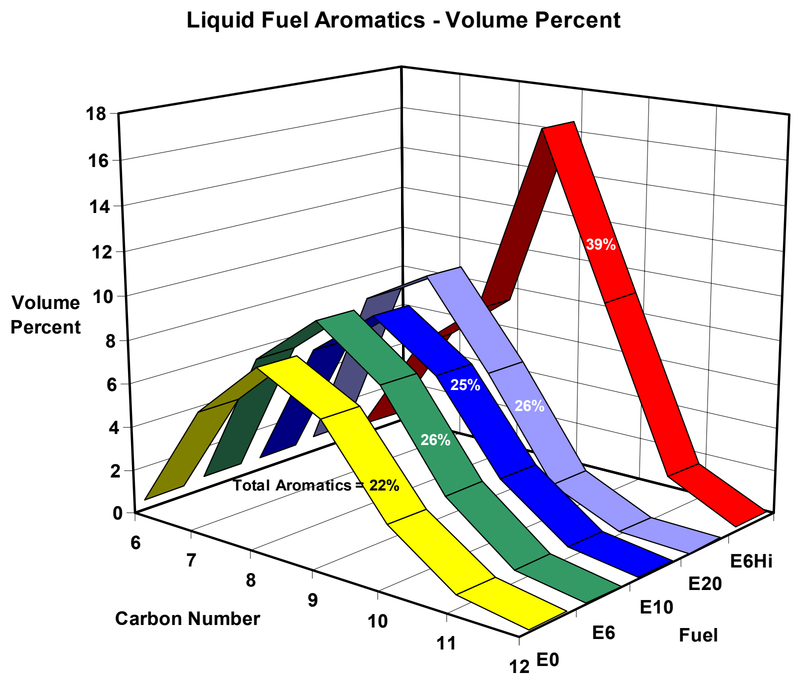


Figure 9

Figure 9 illustrates the distribution of the aromatics content in the base non-ethanol fuel and the four low-ethanol concentration fuels. The aromatics total and the distribution of the aromatics by carbon number are similar for fuels E0, E6, E10 and E20. The high aromatics fuel (E6Hi) has 39% aromatics compared to the 22-26% for the other three, and the concentration of the higher carbon number molecules (C9-C11) is much higher.

Procedures for Measuring Steady-State Permeation and Determining Stabilization

Permeation is a molecular migration of the fuel through the elastomeric materials of the vehicle fuel system. The test plan anticipated that time would be required for stabilization to occur after a new fuel composition was introduced. This would be possibly six to twelve weeks at the 105°F stabilization temperature. The vehicle fuel tank was filled to 100% of its rated capacity for stabilization, and the contents circulated through the liquid and vapor system twice a week for a 20 minute period to keep the liquid and vapor in the hoses "fresh." The canister was purged by drawing ambient air through the canister bed for a period of 20 minutes, twice a week, using a vacuum pump.

The rigs were kept in a constant-temperature test cell at 105°F during the stabilization period. A photo of the cell occupied by various rigs is shown in Figure 10.

Figure 10 - Constant-Temperature Test Cell

Once each week the rig was moved from the "soak room" to the SHED for the permeation determination. The steady-state test involved placing the rig in the pre-heated 105°F SHED, connecting the tank and canister vent hoses to a bulk-head fitting in the SHED wall so that any tank or canister venting losses would not be measured as permeation, closing the door and allowing the SHED to come back to a to a stabilized temperature.

Either a three- or five-hour test was conducted to measure permeation. The three-hour test was used for the three higher permeation level rigs, 1, 2 and 14. The five-hour test was used for rigs 11 and 12 for tests starting in June 2005 on fuels E6 and later.

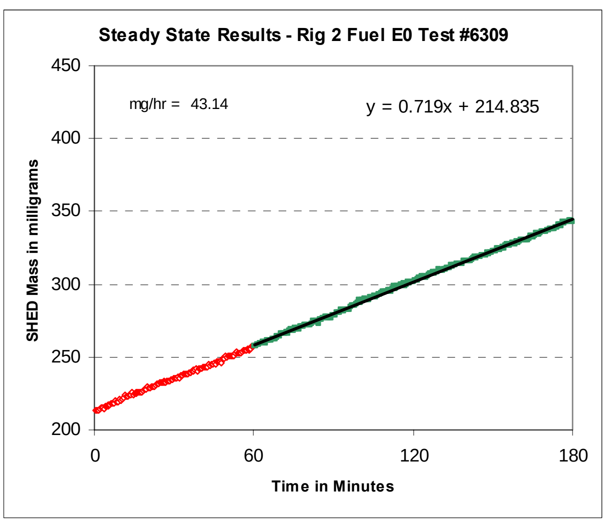


Figure 11

A sample plot of the steady-state test results is shown in Figure 11. The horizontal axis is time, in minutes, and the vertical axis is the mass (in milligrams) as measured in the SHED using the conventional SHED test procedure and equipment. The mass was calculated every 30 seconds and the results are plotted in Figure 11. The first hour of the test is shown in the red dots, and the last two hours in green. The trendline function in Microsoft EXCEL® was used to calculate the rate of change in the SHED mass over the second and third hours (the green data). This slope became the estimate of the steady-state permeation rate in mg/hour.

The five-hour test adopted for the E6 stabilization tests during June of 2005 was an attempt to improve the precision of the measurement on these really low permeation rigs (e.g., 3 mg per hour). The five-hour test used the last four hours of the five-hour test for the permeation measurement. An example of the five-hour test results is shown in Figure 12.

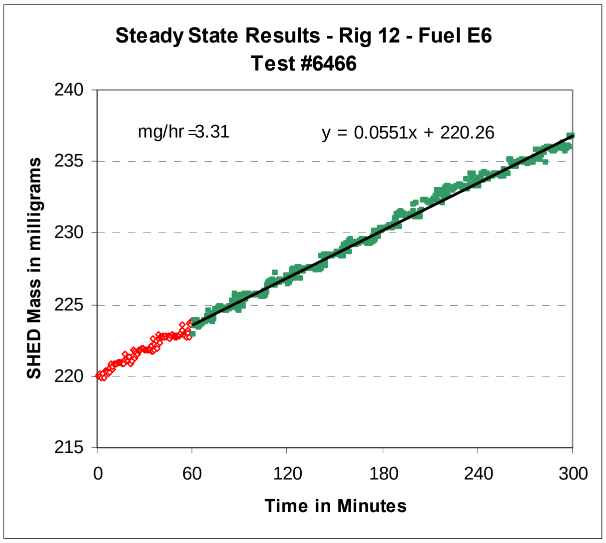


Figure 12

This plot illustrates the conditions that are created when one tries to measure 3 mg/hour in a 2100 ft3 enclosure. The SHED concentration, as determined by the FID went from 7.105 ppm at 60 minutes to 7.551 ppm at the 300 minute mark, an increase of one half of a part per million (ppm) carbon in the enclosure over the four hour period. The mass in the SHED rose from 223 mg to 237 mg during the four hour period. That the SHED can measure these differences, and identify them with the precision and resolution shown in Figure 12, would have been thought impossible just a few years ago. A smaller SHED volume (a mini-SHED) would increase the concentration change, and help with the precision, but these rigs were almost the same length as the vehicles they represented – a significantly smaller SHED was not possible.

The plot format used here was also an excellent quality check on the data, and could point out leaks and test irregularities. The mass as measured by the FID had to be corrected for the misidentification of the ethanol (if ethanol was present).

Stabilization was established when the four-week average of the permeation rate reversed in trend, i.e., when the average rate either increased or decreased over the previous trend's rate. A recommendation was made by the program administrator in a weekly status report, and the Steering Committee approved (or disapproved) the recommendation. The time required for stabilization ranged from five weeks (Rig 14, Fuel E0) to 13 weeks for Rig 12, Fuel E6. Once declared stable, the rig was drained and prepped for the diurnal measurement.

IV. Results

This section of the report begins with the details of the diurnal and steady-state test results. Following that, the hydrocarbon speciation of the diurnal measurements is addressed and the average specific reactivities of the permeates are calculated for the various technologies on the various fuels.

Diurnal[6] performance measurements are emphasized in this permeation study because the ultimate use of this information is to improve the ability of emissions inventory models to estimate the contribution of motor vehicles to air pollution. A portion of this report is also devoted to the steady-state results, as it is hoped that the steady-state (constant temperature) results can one day be used to predict the diurnal emission performance.

[6] "Diurnal", occurring daily, or having a daily cycle

Diurnal Performance – Technology

The diurnal permeation performance of the different emission technologies tested in this study is summarized in Figure 13. These results were obtained when the rigs were tested with the base fuel, E0. On the left are the two vertical bars representing the diurnal permeation performance for the two enhanced evap Rigs 1 and 2.

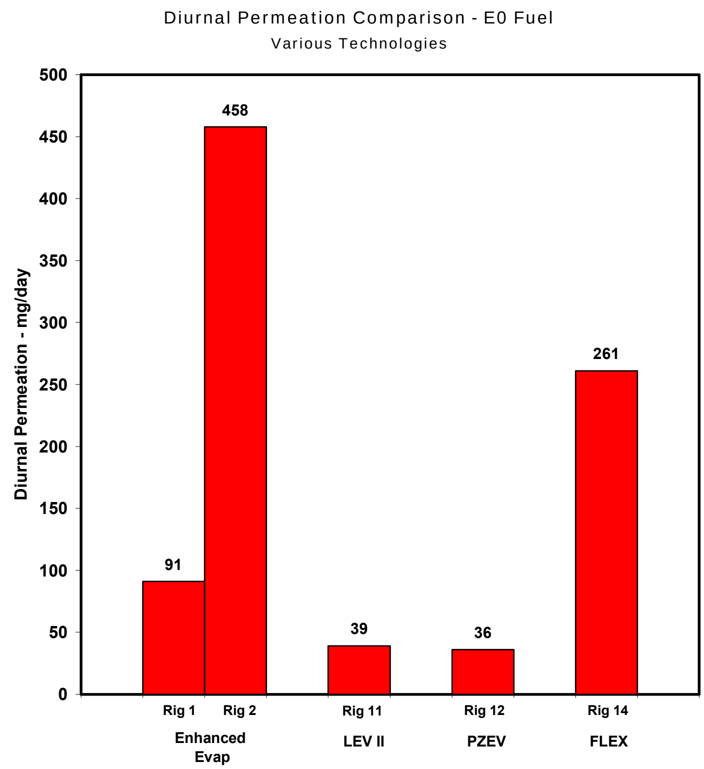


Figure 13

The third bar from the left shows the 39 mg/day level of Rig 11, the LEV II, or California Near-Zero vehicle fuel system. The fourth bar is the 36 mg/day performance of the California "Zero Fuel Emission" vehicle. To qualify as a Zero Fuel Evaporative Emission system, this vehicle is certified to have less than 54 mg/day evaporative emissions, including the canister loss and a one hour hot soak. Finally, the last bar is the permeation performance of the "flexible fuel" Chevrolet Tahoe.

While the 458 mg/day permeation result on fuel E0 on Rig 2 seems high compared to the 91 mg/day from Rig 1, it is lower than previously measured with the plastic tank systems on the non-ethanol fuel in the E-65 project, one of which measured over 11,000 mg/day. The expanded plot shown in Figure 14 includes some of the technologies from the previous CRC E-65 report[7] "Fuel Permeation from Automotive Systems." The blue bars on the left (Rigs 1-6) are the permeation results on the non-oxygenated fuel, "Fuel C" measured in the previous program. The red oval highlights the performance level of Rigs 1 and 2 on Fuel C and the current program's Fuel E0.

[7] Coordinating Research Council (CRC) web site, http://www.crcao.org

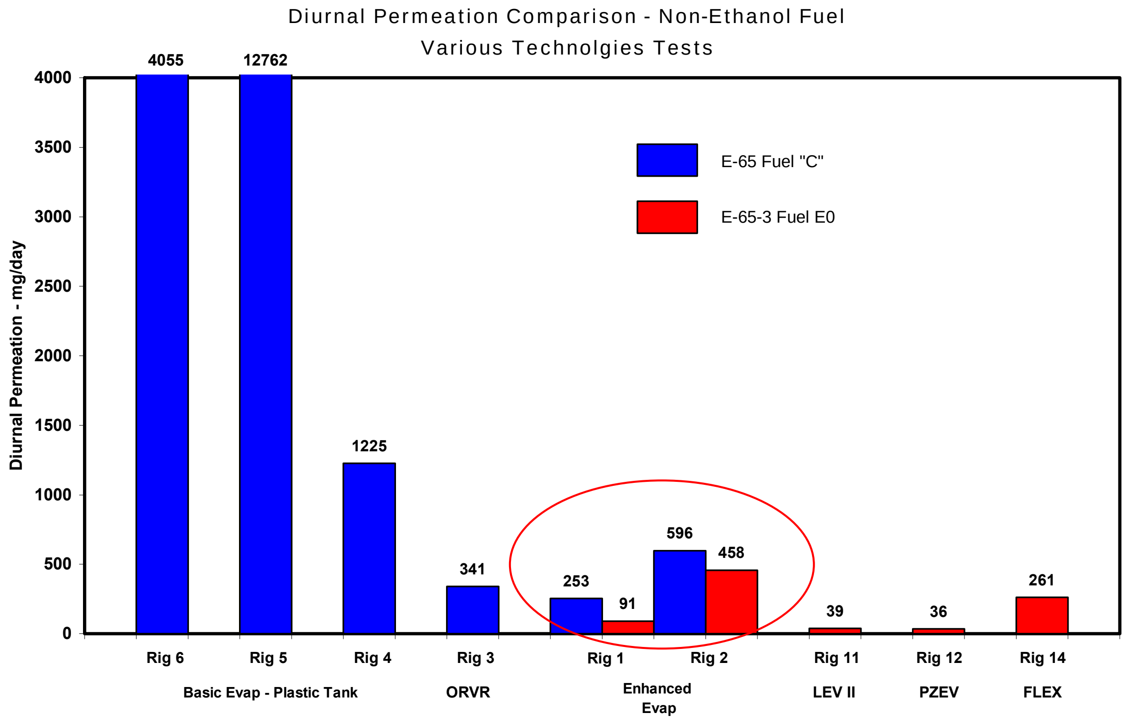


Figure 14

A plot showing the diurnal results for the five test rigs on the fuels tested in this program is shown in Figure 15**.**

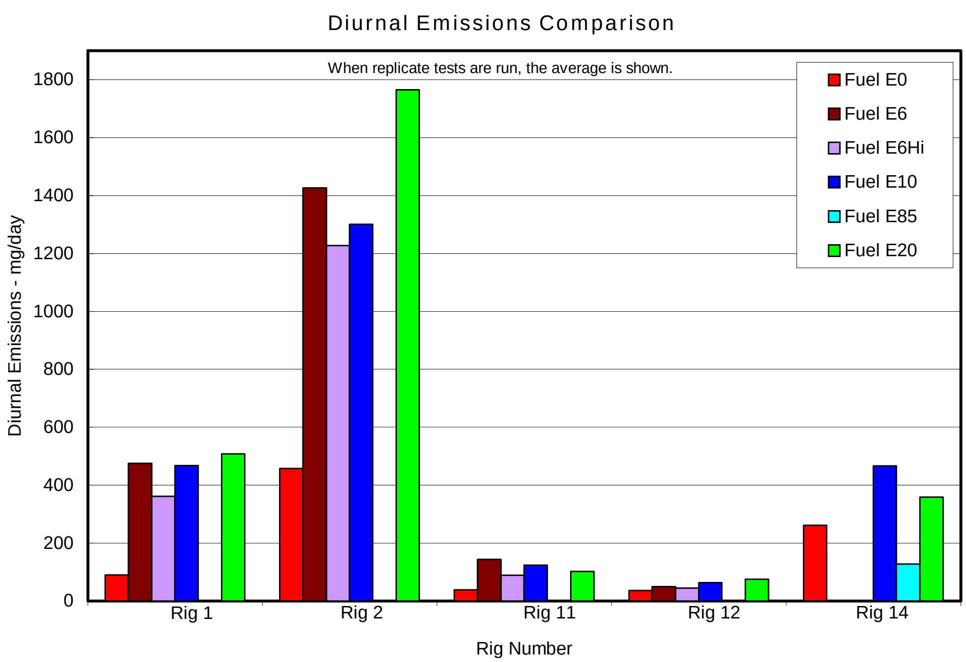


Figure 15

Diurnal Performance - Fuels

Rig 1 - The diurnal emissions measured for Rig 1, the MY 2001 enhanced evap system, ranged from 91 mg/day on the base fuel (E0) to 508 mg/day on the E20 fuel. Figure 16 compares the results for the five fuels tested. Where multiple tests were run, such as those for the E0 and E6 fuels, the average results are presented. (Table 7 at the end of this section details the actual tests used.) The component on the top of each bar illustrates the ethanol fraction of the total emissions. For example, the E6 test total of 475 mg/day had 149 mg/day of ethanol. A very small amount of the E0 test (1 mg/day) was ethanol, even though there was no ethanol in the fuel, apparently a "hang-up" from the rig's previous experience on ethanol fuel. The issue of the "hang-up" and the concerns thereof is discussed in the appendix of this report.

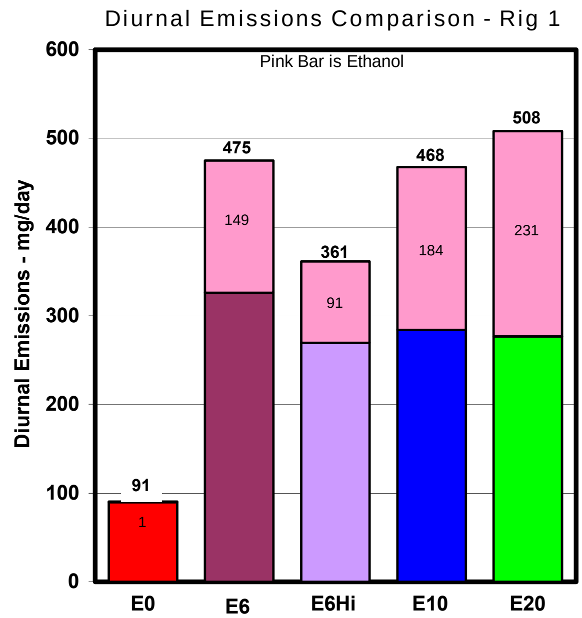


Figure 16

The diurnal permeation emissions with the E6 fuel increased by 384 mg/day compared to E0. The diurnal results with the E6Hi (high aromatics) fuel were 114 mg/day lower than the E6 fuel, with lower (91 mg/day compared to 149 mg/day) ethanol in the permeate. The permeation with the E10 fuel was almost identical compared to the E6 fuel (7 mg/day lower), but with higher ethanol in the results. The E20 permeation was the highest measured on this rig.

Rig 2 - Rig 2, another enhanced evap system (2000 MY), also had substantial increases in permeation when tested with the ethanol-containing fuels, as shown in Figure 17. The permeation increased from 458 mg/day with the base (E0) fuel to 1765 mg/day with the E20 fuel. The ethanol fraction was about 400 to 600 mg/day for the four ethanol blends evaluated. The permeation for the E10 fuel was 125 mg/day lower than for the E6 fuel. The higher aromatics fuel, E6Hi, showed a 199 mg/day lower permeation than the E6 fuel. The E20 permeation was also the highest measured on this rig.

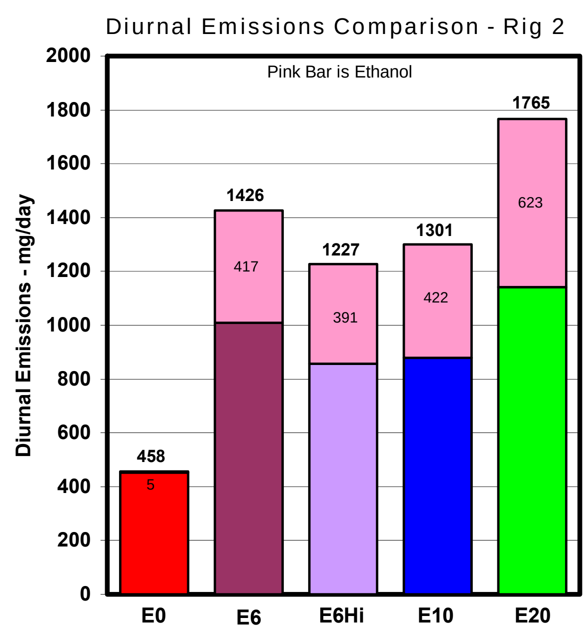


Figure 17

Rig 11 - The results for Rig 11, shown in Figure 18, indicate that all the ethanol blends increased the permeation rate compared to the base (E0) fuel. The permeation rate for the E6 fuel was 105 mg/day higher than for the E0 fuel. The higher aromatics fuel, E6Hi, had 55 mg/day lower permeation than the E6 fuel. The E10 fuel had 21 mg/day lower permeation than the E6 fuel, and the E20 fuel was 42 mg/day lower than the E6 fuel.

This rig and Rig 14 were different in their ethanol response than Rigs 1, 2 and 12, in that they had lower permeation on the E20 fuel than the E6 or E10 fuels. Rig 11 also had the lowest specific reactivity over all the fuels tested, as is described in a later section of this report on speciation and reactivity.

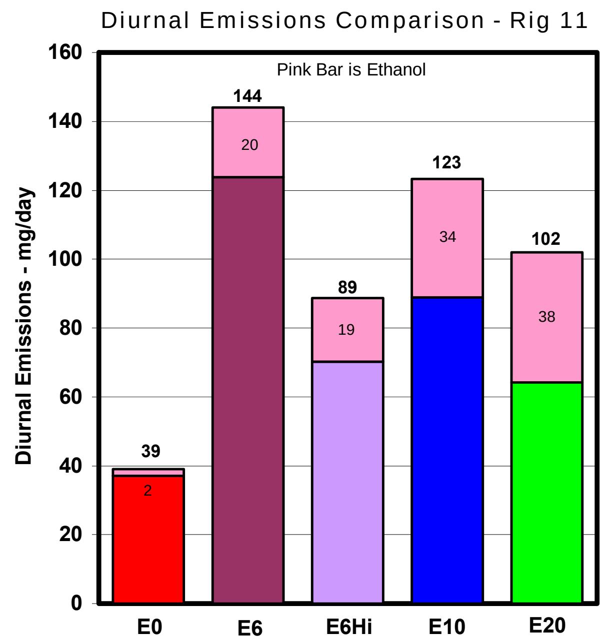


Figure 18

Rig 12 - When tested on the base (E0) non-ethanol fuel, this rig was measured at 36 mg/day. Rig 12 was found to have less than 4 mg/day ethanol "hang-up" when tested with the E0 fuel. The diurnal permeation increased when this rig was tested on any of the ethanol-containing fuels, as shown in Figure 19. The permeation for the E6 fuel was 14 mg/day greater than the E0 fuel. The permeation for the E6Hi fuel was 5 mg/day lower than the E6 fuel. This was the only rig that demonstrated a greater diurnal permeation for the E10 fuel vs. the E6 fuel, 14 mg/day higher. The highest permeation measured was on the E20 fuel, at 75 mg/day.

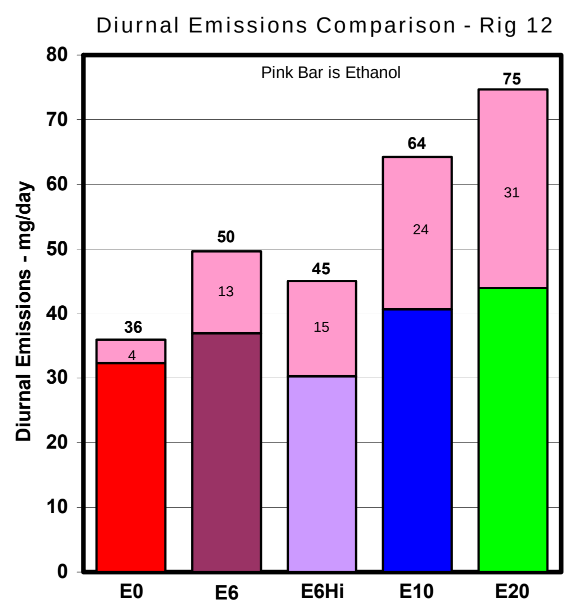


Figure 19

Rig 14 - A "FlexFuel" system evaluation was included in this project. Flexible fuel vehicles are designed and developed to perform on fuels containing just gasoline, or up to 85% ethanol fuel**,** and any combination in between.

Diurnal emissions were measured on four fuels, with the average results shown in Figure 20. The permeation emissions were nearly doubled (466 vs. 261 mg/day) with the E10 fuel, compared to the E0 fuel, but were approximately halved (128 vs. 261 mg/day) when the E85 fuel was tested. Like Rig 11, the permeation was lower on the E20 fuel compared to the E10 results. The ethanol was 139 mg/day when tested with the E10 fuel, similar in its fraction of the permeation total to the results from the other rigs evaluated. The ethanol of the E85 test results was 76 mg/day, almost 2/3rd of the total permeation. It seems reasonable that if the fuel is almost all ethanol, the permeate ought to be mostly ethanol.

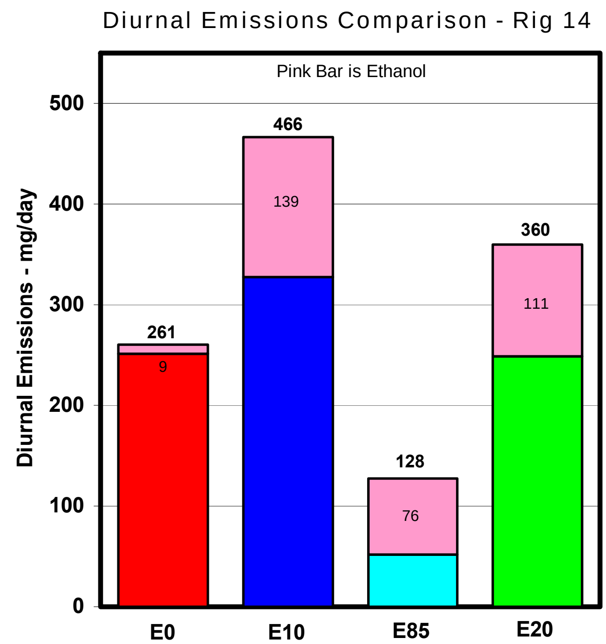


Figure 20

Data Summary

A comprehensive table, Table 7, follows with the diurnal permeation results for each vehicle and fuel, as well as the steady-state permeation results, the ratio of the diurnal result to the steady-state result, and the specific reactivity of the permeate calculated for the individual diurnal tests.

Table 7
Detailed Permeation Emission Results

Rig #1 - 2001 Toyota Tacoma					
Fuel	**4-week Avg. mg/hour**	**Diurnal Test ID**	**mg/day**	**Ratio**	**Specific Reactivity g O_3/g VOC**
E0	7.04	6389	83.9	11.9	4.31
E0b	8.57	6886	97.2	11.4	4.15
Avg. =	**7.80**		**90.6**	**11.7**	**4.23**
E6	25.6	6471	417.1	16.3	3.05
		6479	533.3	20.8	3.08
		Avg. =	**475.2**	**18.6**	**3.07**
E6Hi	29.2	6571	360.9	12.4	3.30
E10	35.2	6665	467.8	13.3	3.03
E20	43.4	6806	508.1	11.7	3.20

Rig #2 - 2000 Honda Odyssey					
Fuel	**4-week Avg. mg/hour**	**Diurnal Test ID**	**mg/day**	**Ratio**	**Specific Reactivity g O_3/g VOC**
E0	42.5	6390	463.3	10.9	4.26
E0b	33.7	6913	451.6	13.3	4.16
Avg. =	**38.1**		**457.5**	**12.1**	**4.21**
E6	97.7	6481	1426.0	14.6	3.54
E6Hi	88.9	6570	1227.0	13.8	3.66
E10	101.5	6673	1300.6	12.8	3.45
E20	148.8	6816	1765.1	11.9	3.32

Table 7 (cont)

Detailed Permeation Emission Results

Rig #11 - 2004 Ford Taurus					
Fuel	**4-week Avg. mg/hour**	**Diurnal Test ID**	**mg/day**	**Ratio**	**Specific Reactivity g O_3/g VOC**
E0	3.59	6370	48.0	13.4	2.91
E0b	2.53	6889	29.7	11.7	3.51
Avg. =	**3.06**		**38.9**	**12.6**	**3.21**
E6	11.2	6507	144.1	12.9	2.09
E6Hi	4.02	6598	88.7	20.3	2.58
E10	6.36	6675	149.3	24.1	2.23
		6676	97.3	15.7	2.43
		Avg. =	**123.3**	**19.9**	**2.33**
E20	5.42	6805	102.0	18.8	2.40

Rig #12 - 2004 Chrysler Sebring					
Fuel	**4-week Avg. mg/hour**	**Diurnal Test ID**	**mg/day**	**Ratio**	**Specific Reactivity g O_3/g VOC**
E0	3.22	6372	38.7	12.0	5.48
		6383	31.0	9.64	4.10
E0b	2.68	6874	38.3	14.3	3.73
Avg. =	**2.95**		**36.0**	**12.0**	**4.44**
E6	3.45	6492	49.6	14.4	3.30
E6Hi	3.86	6569	45.0	11.7	3.14
E10	4.65	6642	64.3	13.8	2.85
E20	5.38	6778	74.7	13.9	2.92

Table 7 (cont)

Detailed Permeation Emission Results

Rig #14 - 2005 Chevrolet Tahoe					
Fuel	**4-week Avg. mg/hour**	**Diurnal Test ID**	**mg/day**	**Ratio**	**Specific Reactivity g O_3/g VOC**
E0	18.8	6360	250.5	13.3	3.80
		6388	248.1	13.2	3.85
E0b	18.4	6645	282.7	15.4	3.89
E0c	20.5	6892	262.8	12.8	3.91
Avg. =	**19.2**		**261.0**	**13.7**	**3.9**
E10	29.8	6454	466.3	15.6	3.05
E85	16.3	6555	142.3	8.68	2.63
		6566	112.8	6.88	2.82
		Avg. =	**127.6**	**7.78**	**2.73**
E20	27.6	6779	359.5	13.0	3.36

Rig and Fuel Type Diurnal Result Comparisons

A table was made of the diurnal emission rates for the various rigs and fuels to look for trends or relationships. Table 8 below shows the diurnal results for all of the test fuels. Rig 1 showed a large increase in permeation when any of the ethanol-containing fuels was evaluated. Rig 2 was higher in basic permeation level, and showed proportionately less of an increase from the ethanol fuels. Rig 11 had very low permeation emissions but still increased when evaluated on the ethanol fuels. Rig 12, the "Zero Fuel Evaporative Emission" system, had a different result when tested on the ethanol-containing fuels in that the increase due to the ethanol was only 9 to 39 mg/day more than the base permeation rate, a much smaller increase than seen in the other rigs.

Table 8

Diurnal Emissions Test Results
Total (Ethanol) – mg/day

	Test Fuel						**Difference from E0, mg/day**			
	E0	E6	E6Hi	E10	E20	E85	E6	E6Hi	E10	E20
Rig 1	91 (1)	475 (149)	361 (91)	468 (184)	508 (231)		384	270	377	417
Rig 2	458 (5)	1426 (417)	1227 (391)	1301 (422)	1765 (623)		968	769	843	1307
Rig 11	39 (2)	144 (20)	89 (19)	123 (34)	102 (38)		105	50	84	63
Rig 12	36 (4)	50 (13)	45 (15)	64 (24)	75 (31)		14	9	28	39
Rig 14	261 (9)	-	-	466 (139)	360 (111)	128 (76)				
Average*	177 (4)	524 (150)	430 (129)	484 (161)	562 (207)		347	253	307	385

* Averages for E0, E10 and E20 are five-rig; those for E6 and E6Hi are four-rig.

Steady-State Permeation Measurements

The plot format shown in Figures 21-25 was developed to compare the steady-state permeation rate results for each rig on the various fuels. The horizontal axis is a chronological sequence (not necessarily a linear time-scale) of the tests as they were accumulated. The red filled-box data points represent the ethanol permeation rate. The laboratory established that 1 mg/hour was the detection limit of the analytical procedure used to establish the ethanol content, and if the test level was less than 1.0 mg/hour it was reported as "below detection limit," or BDL, and counted as zero in the calculation of the total. The black diamonds are the (non-ethanol) hydrocarbon, and the blue triangles are the total of the two, or the total permeation rate in mg/hour. A horizontal blue line is drawn at the average level of the last four data points.

Rig 1 started the stabilization on fuel E0 with an initial fill on January 11, 2005 and was tested on the following day to measure the permeation rate. Permeation measurements were made each week, not necessarily on the same day of the week, although that was the normal case. The actual test dates are contained in the data record file known as "rigsum.xls," and are available on the CRC web-site.

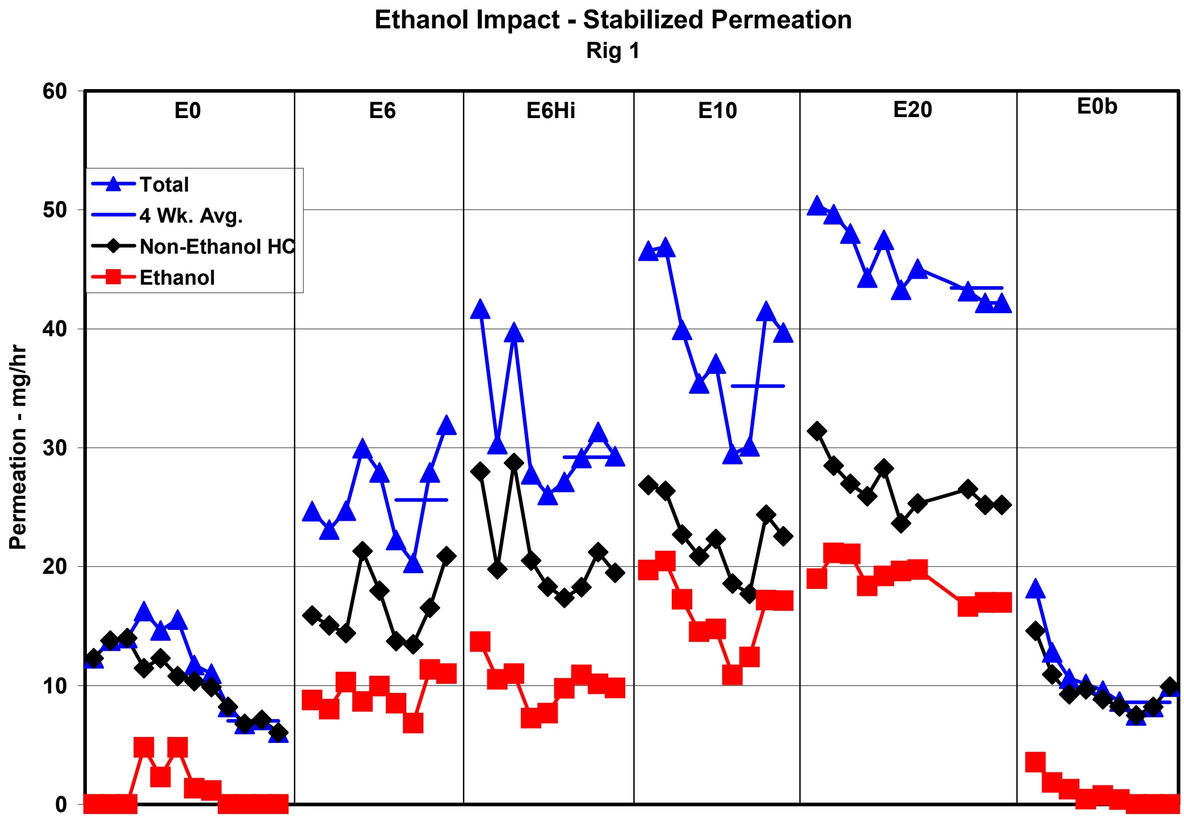


Figure 21

A concern arose when ethanol was detected in the steady-state permeation results on the E0 fuel, even though there was no ethanol in the test fuel. The first three tests on the E0 fuel reported no ethanol, but the fourth test (#6306 on February 2, 2005) reported 4.8 mg/hour as the ethanol component. A discussion arose concerning the source and authenticity of the measurement. The following week's measurement was 2.3, and then 4.8, 1.2 and 1.2 mg/hour in succeeding weeks. The test on March 9 returned to BDL for ethanol. A similar pattern arose, at the same time period, on Rig 2, as will be discussed later. Ethanol was not detected in Rigs 11, 12 or 14 during the initial steady-state permeation E0 testing. A separate discussion concerning the "ethanol hang-up" is provided in the appendix at the end of this report.

The steady-state permeation rate increased when the 5.7 Volume% ethanol fuel (E6) was introduced, as shown in Figure 21. The four-week final average permeation rate was 7.04 mg/hour on Fuel E0 and increased to 25.6 mg/hour on the 5.7 Volume% ethanol fuel. The steady-state permeation rate increased slightly on the higher aromatics E6Hi fuel, with an average of 29.2 mg/hour, and was higher yet (35.2 mg/hour) on the 10 Volume% ethanol fuel. The E20 steady-state average value was 43.4 mg/hour. The average of the original and the final steady-state permeation rate measurements on the E0 fuel (7.04 and 8.57) was 7.8 mg/hour

Rig 2 also received its initial fill of the E0 test fuel on January 11, 2005, with its first test on the following day. (The practice was later changed to not test on the day following the fuel change, but test after a week or more exposure.) It showed ethanol in the permeate on the fourth week, on February 4, of 8.8 mg/hour, and 7.9 mg/hour the following week, during the same time period as was seen on Rig 1. A check was made for any sort of a laboratory or soak room contamination problem, without finding any source of contamination or error. An expanded discussion on the ethanol "hang-up" appears in the appendix to this report.

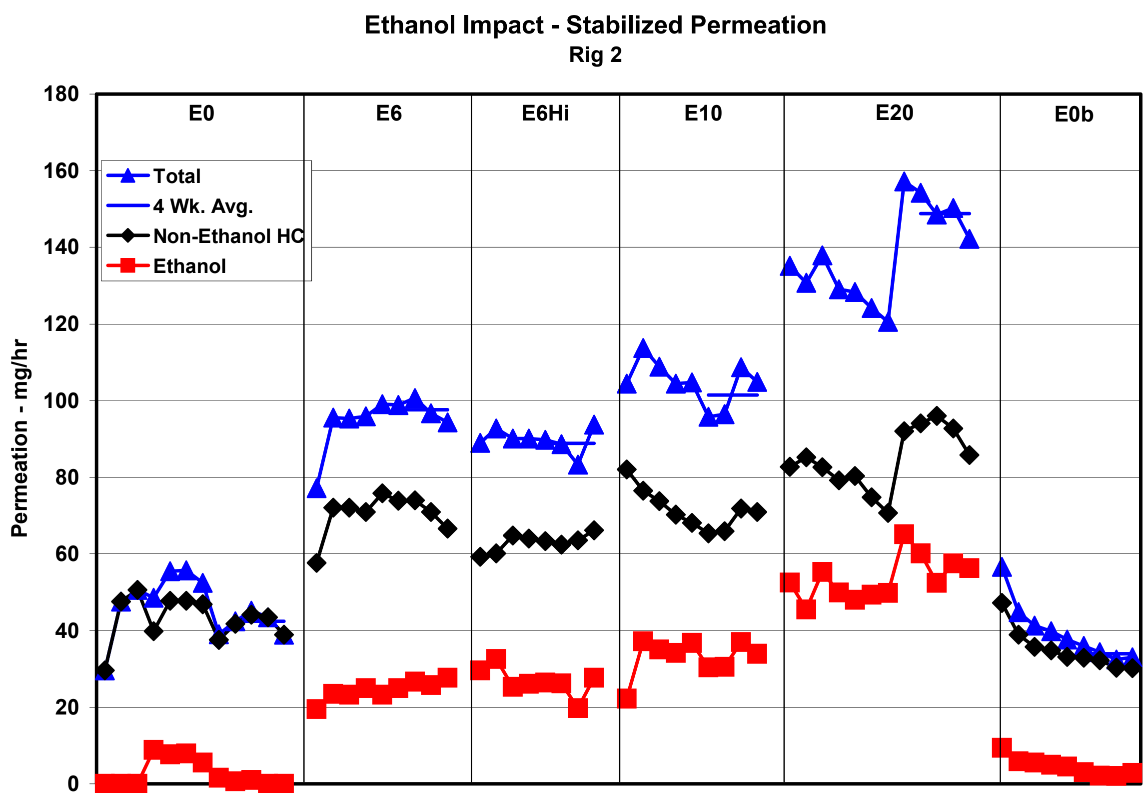


Figure 22

The following observations were made regarding the second test band in Figure 22. The first test on the E6 fuel was made after nine days of exposure. The second week's test after 17 days shows that the total permeation trend had approached the eventual stabilized level. The ethanol content, shown in the red solid squares as the lower of the three trends in the plot, appeared to be increasing slightly over the nine weeks of exposure. The permeation was declared to be stabilized after the 10th week of stabilization, and the rig was then submitted for the diurnal test.

The permeation rate decreased slightly when the higher aromatics E6Hi fuel was introduced, and then increased with the introduction of the 10 Volume% ethanol fuel (E10). The 4-week average for the tests on the E10 fuel was 101.5 mg/hour, and 148.8 mg/hour on the E20 fuel. The average of the two steady-state averages on the E0 fuel (42.5 and 33.7) was 38.1 mg/hour

The permeation rate for **Rig 11** was very low, ~ 3 mg/hour on the E0 fuel, as shown in Figure 23, which created measurement challenges. The measurement period was increased from three to five hours during the E6 fuel measurement period as was discussed earlier in this section.

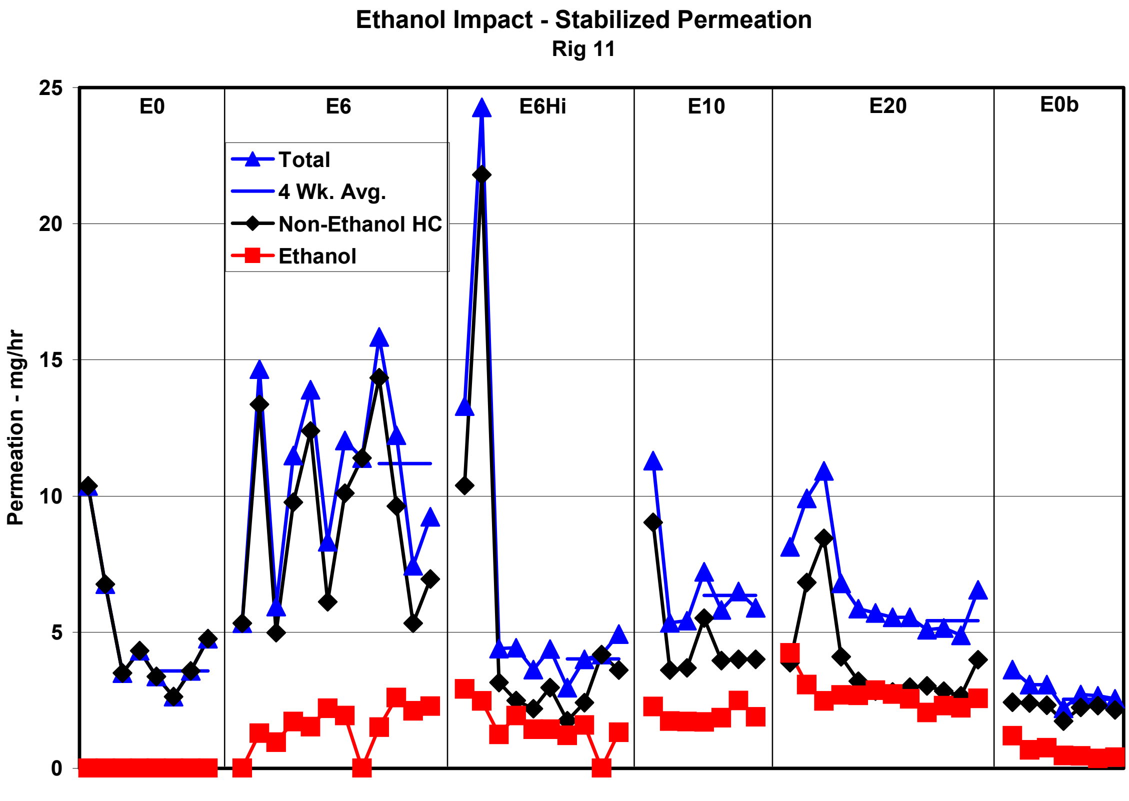


Figure 23

The permeation performance of Rig 11 was erratic on the E6 fuel. The erratic performance continued for the first two tests on the E6Hi fuel, when the permeation suddenly dropped from 24 mg/hour to ~4 mg/hour for no identified reason. This erratic condition may have also been present during the diurnal evaluation on the E6 fuel, but there is at present no basis to invalidate the data.

Rig 12 was expected to have low permeation as it was produced and certified to be a "zero fuel evaporative emission" vehicle. As anticipated, the steady-state permeation results were very low (Note the vertical scale on Figure 24). The 4-week average permeation rate on the E0 fuel was 3.2 mg/hour for the original test sequence, with any ethanol content below the detectable limit and 2.7 mg/hour on the final series, with about a 0.5 g/hour ethanol fraction. The E6 fuel increased the permeation rate slightly, mainly because the ethanol component triggered into the detectable limit of 1 mg/hour.

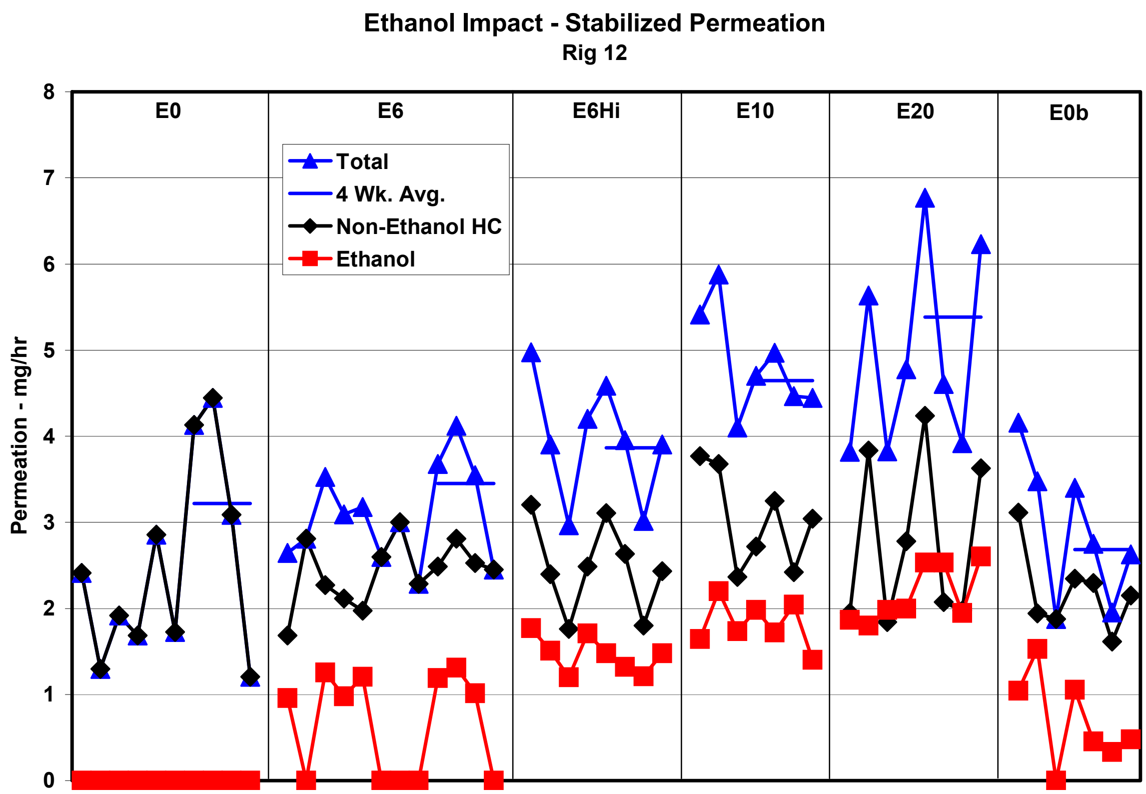


Figure 24

Unlike the other rigs, the high aromatics fuel, E6Hi, increased the permeation rate of Rig 12 over the value established for the lower aromatics E6 fuel. The 4-week average level was 3.4 mg/hour on the E6 fuel, and 3.9 mg/hour on the E6Hi fuel. The data suggests that although the non-ethanol measurement stayed about the same, there was an increase in the mass rate of the ethanol in the permeate with the higher aromatics fuel compared to the E6 fuel. The E10 steady-state average was 4.6 mg/hour, and the E20 value was 5.4 mg/hour

The final test sequence on the E0 fuel shows an ethanol content at the 0.5 mg/hour level, where the initial E0 tests were declared as below the detectable limit. This is attributed to the fact that the laboratory became more confident in declaring ethanol measurements below the level of 1 mg/hour as the program progressed.

The permeation results with the E20 fuel were the highest measured of the four test fuels, but the magnitude of the increase, when compared to the base fuel (E0), was low, less than 3 mg/hour.

Rig 14 was tested on the E0, E10, E20 and E85 fuels. The committee authorized a final test on the E0 fuel after the E85 evaluation to see if it would return to the previously measured E0 level. The results of the steady-state evaluation are shown in Figure 25. The ethanol in the permeate jumped to the 8 mg/hour level on the second test with the E10 fuel. The E10 steady-state permeation (29.8 mg/hr) was 1.6 times the E0 steady-state rate of 18.8 mg/hr, more like the results from Rigs 11 and 12, than Rigs 1 and 2. The 4-week steady-state average on the E20 test fuel was 27.6 mg/hour, close, but slightly less, than the E10 4-week average of 29.8 mg/hour.

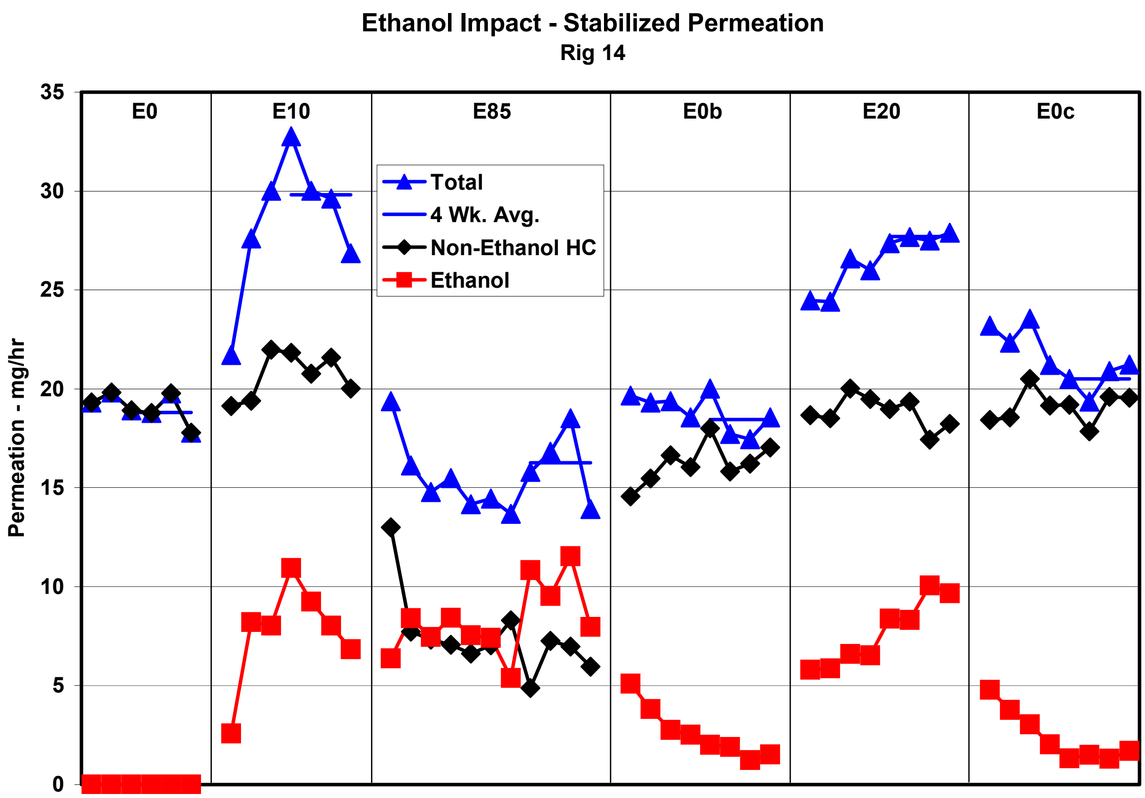


Figure 25

Steady-State Permeation Results by Rig

The steady-state tests were used to determine fuel system stability following the introduction of a new fuel and to indicate that the rig was ready for the diurnal evaluation. A three or five hour steady-state test was performed in a SHED to determine the 105°F hourly permeation rate. The 4-week average steady-state permeation rates provide another measure of the permeation performance of the various fuels on the different fuel systems, and are presented below.

Rig 1 - The bar chart in Figure 26 is used to illustrate the steady-state performance of the five test fuels on Rig 1. The hourly permeation rate is the lowest on the base fuel (E0) and increases to 43 mg/hour on fuel E20. The higher aromatic E6Hi fuel had slightly higher permeation than the E6 fuel on the steady-state measurement, a different finding than was indicated on the diurnal test.

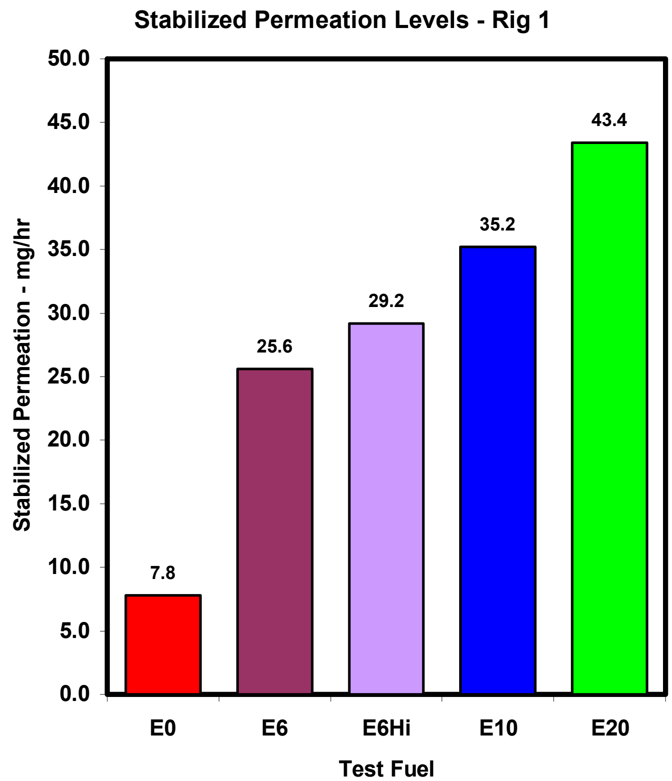


Figure 26

Rig 2 – Figure 27 shows the steady-state permeation estimate on the E6Hi fuel to be lower than the E6 fuel, more in line with the diurnal test results, while the E10 permeation is slightly higher than the E6 result, and the E20 permeation is substantially higher.

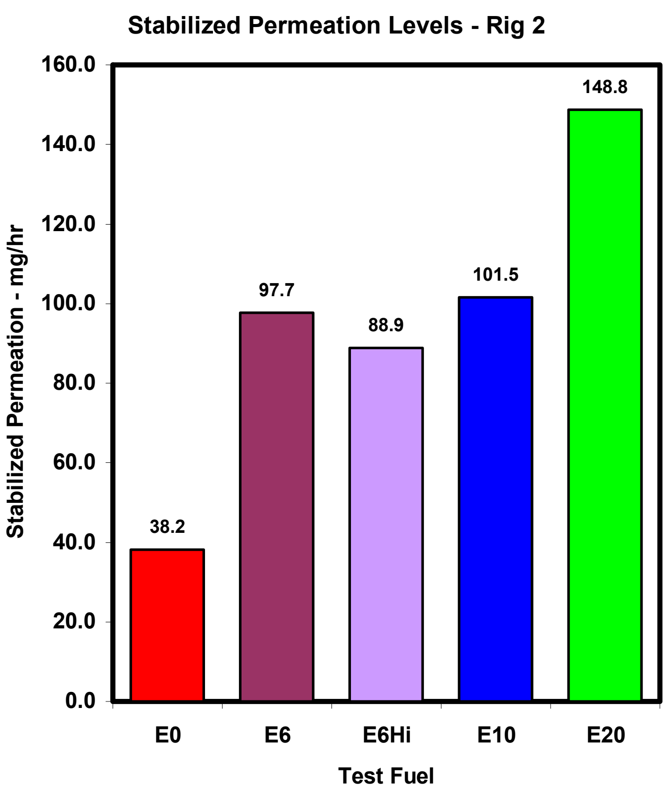


Figure 27

Rig 11 steady-state test results, shown in Figure 28, are distorted by the highly variable results experienced during the tests on the E6 fuel (see the earlier steady-state discussion on Rig 11). The E20 permeation was lower than the results measured with the E10 fuel, a different result than was seen on Rigs 1, 2 and 12.

Rig 12 steady-state permeation results, shown in Figure 29 are more like the relationship seen with Rigs 1 and 2.

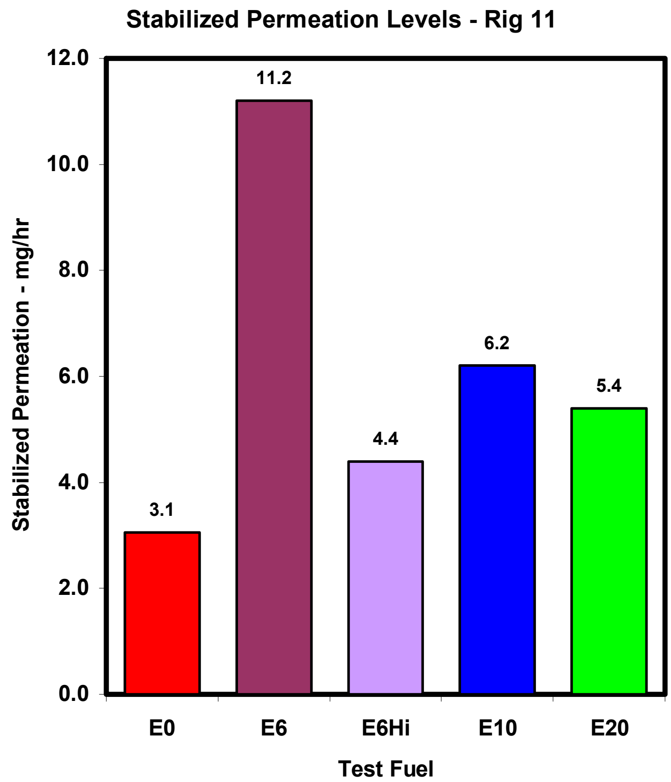


Figure 28

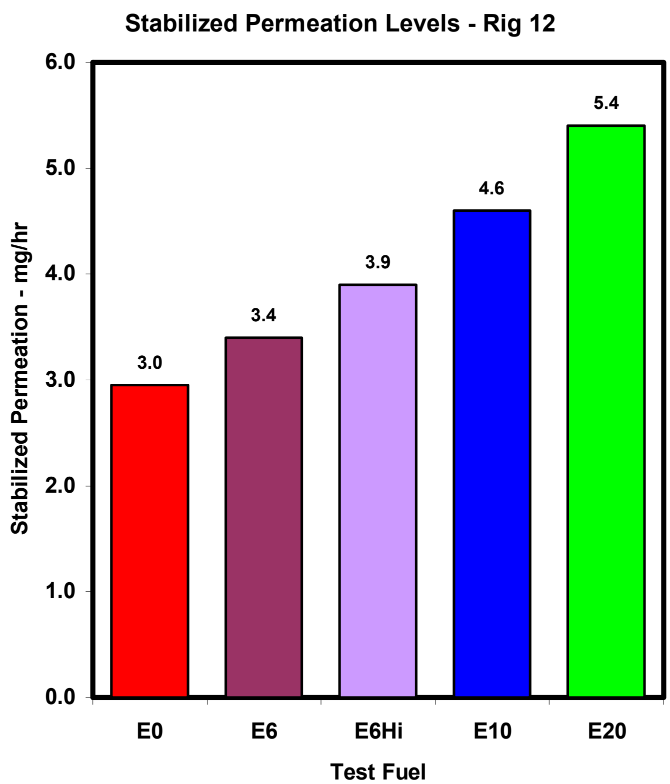


Figure 29

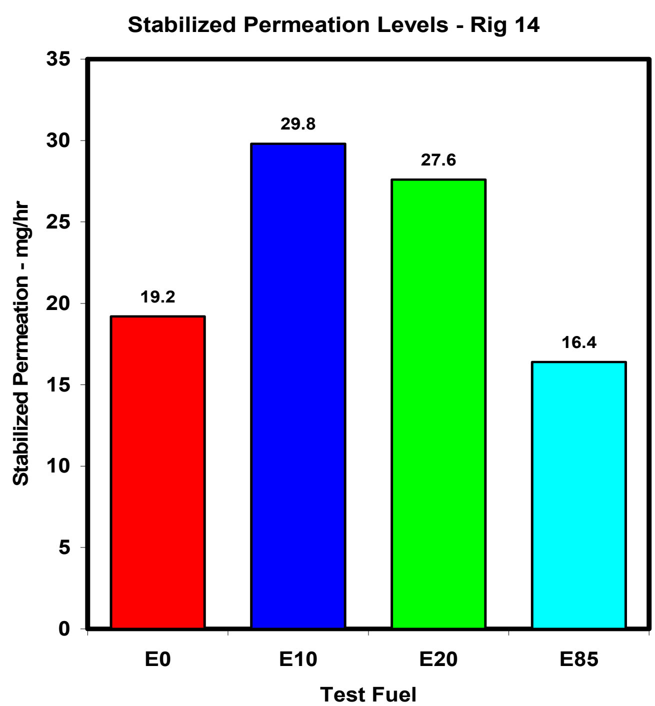


Figure 30

Rig 14 steady-state results, shown in Figure 30, indicate lower emission on the E20 fuel than was measured on E10, similar to the behavior of Rig 11. The steady-state 105°F permeation result on the E85 fuel was lower (-2.8 mg/hour) than the E0 base fuel, but not at half the value, as the diurnal results indicated.

In summary, the steady-state results may offer a slightly different picture of the permeation behavior of the different fuels on the different rigs, relative to the diurnal results. The small sample size, and the limited testing conducted, suggest some caution in evaluating these observed differences.

Speciation and Reactivity

Diurnal Speciation Results – A sample of the ambient HC concentration in the VT-SHED was collected in a Tedlar™ bag at the start and the end of the 24-hour diurnal period and later analyzed for HC species using a Varian™ chromatograph. The results of this "speciation" allowed the calculation of the average reactivity of the permeate for each of the rigs and fuels.

An example of the speciation results and the reactivity calculations for Rig 1 – Fuel E0, Test 6389, is shown in Table 9. Table 9 is one file in a Microsoft EXCEL® workbook titled "SHED Speciation and Reactivity Calculations for the Final Report.xls," available on the CRC web-site in the files for the E-65-3 report. This workbook contains all of the SHED speciations for the test fuels evaluated in this program.

Each file has been reordered into three vertical groups. The top group is those molecules with identified mass that have an assigned Carter Maximum Incremental Reactivity (MIR) value. The second vertical group is those measured mass components that do not have an assigned MIR value, and the last group is the molecules that had zero measured mass, but would have been identified if they were present, using the "Auto-Oil" chromatographic test technique. The first and second vertical groups were sorted in descending order of mass in each group. The lengthy listing of the third group, of those molecules with no detected mass, is offered to indicate to the reader what would have been measured, if present, using the chromatographic techniques available at the laboratory.

This table, and the others in the workbook, are organized from left to right as follows. The first column is the elution order number, or the order that the molecules would appear at the end of the chromatographic column. The second column is the specific molecule's name. The third column is the CAS number[8] for the molecule. The fourth column is the MIR value for the molecule, or the specific grams of ozone formed for each gram of HC identified under certain conditions. The fifth column is the net mass of each species identified in the SHED sample by the chromatograph. The sixth column is the percentage of the total mass identified as this species. The final column is the prediction of the mass of ozone that would be produced by that mass of that molecule using the Carter methodology.

[8] The CAS number is the Chemical Abstract Service registry number assigned to each specific molecule. CAS registry numbers are copyrighted by the American Chemical Society. Redistribution rights for CAS registry numbers are reserved by the American Chemical Society. "CAS registry" is a registered trademark of the American Chemical Society. The CAS REGISTRY mostly covers substances identified from the scientific literature from 1957 to the present with some classes (fluorine- and silicon-containing compounds) going back to the early 1900s. Each substance in REGISTRY is identified by a unique numeric identifier called a CAS Registry Number.

Table 9

Rig:	01E0					
Test#:	**6389**					
Detailed Hydrocarbon Speciation Results				24-Hour		
Elution No.	Species Name	CAS #	MIR g O_3/g HC	Net mass (mg)	% total mass	Predicted Ozone mg
81	Toluene	00108-88-3	3.97	14.321	17%	56.85
18	2-Methylbutane (Isopentane)	00078-78-4	1.67	10.787	13%	18.01
111.1	m-Xylene	00108-38-3	10.61	8.835	10%	93.74
21	n-Pentane	00109-66-0	1.53	3.666	4%	5.61
117	ortho-Xylene	00095-47-6	7.48	2.951	3%	22.08
111.2	p-Xylene	00106-42-3	4.24	2.591	3%	10.99
36.1	2-MePentane	00107-83-5	1.78	2.289	3%	4.08
135.1	1,2,4-TriMeBenz	00095-63-6	7.18	2.131	2%	15.30
109	Ethylbenzene	00100-41-4	2.79	2.066	2%	5.77
53	Benzene	00071-43-2	0.81	1.952	2%	1.58
34	2,3-Dimethylbutane	00079-29-8	1.13	1.514	2%	1.71
128	1-Methyl-3-Ethylbenzene	00620-14-4	9.37	1.501	2%	14.06
40	n-Hexane	00110-54-3	1.43	1.475	2%	2.11
63	2,2,4-TriMePentane (IsoOctane)	00540-84-1	1.43	1.437	2%	2.05
26	2-Methyl-2-butene	00513-35-9	14.44	1.298	2%	18.75
	Ethanol	00064-17-5	1.69	1.260	1%	2.13
49	Methylcyclopentane	00096-37-7	2.40	1.244	1%	2.99
56	Cyclohexane	00110-82-7	1.44	1.130	1%	1.63
79	2,3,4-Trimethylpentane	00565-75-3	1.22	0.986	1%	1.20
74	Methylcyclohexane	00108-87-2	1.97	0.955	1%	1.88
130	1,3,5-Trimethylbenzene	00108-67-8	11.22	0.953	1%	10.69
23	t-2-Pentene	00646-04-8	10.23	0.910	1%	9.31
38	3-Methylpentane	00096-14-0	2.06	0.905	1%	1.87
9	2-Methylpropane	00075-28-5	1.34	0.892	1%	1.20
12	n-Butane	00106-97-8	1.32	0.874	1%	1.15
86	3-Methylheptane	00589-81-1	1.33	0.832	1%	1.11
57	2-Methylhexane	00591-76-4	1.36	0.809	1%	1.10
42	t-2-Hexene	04050-45-7	8.35	0.754	1%	6.30
59.2	3-Methylhexane	00589-34-4	1.84	0.722	1%	1.33
129	1-Methyl-4-Ethylbenzene	00622-96-8	3.75	0.705	1%	2.64
127	n-Propylbenzene	00103-65-1	2.20	0.661	1%	1.45
136	n-Decane	00124-18-5	0.81	0.608	1%	0.49
90	2,2,5-Trimethylhexane	03522-94-9	1.31	0.541	1%	0.71
96	n-Octane	00111-65-9	1.09	0.532	1%	0.58
45.1	c-2-Hexene	07688-21-3	8.35	0.520	1%	4.34
83	2-Methylheptane	00592-27-8	1.18	0.500	1%	0.59
66	n-Heptane	00142-82-5	1.26	0.495	1%	0.62
77	2,4-Dimethylhexane	00589-43-5	1.79	0.476	1%	0.85
29	2,2-Dimethylbutane	00075-83-2	1.33	0.465	1%	0.62
50	2,4-Dimethylpentane	00108-08-7	1.63	0.447	1%	0.73
58	2,3-Dimethylpentane	00565-59-3	1.53	0.376	0%	0.58

Table 9 (continued)

Detailed Hydrocarbon Speciation Results			24-Hour			
Elution No.	Species Name	CAS #	MIR g O_3/g HC	Net mass (mg)	% total mass	Predicted Ozone mg
133	1-Ethyl-2-Methylbenzene	00611-14-3	6.61	0.365	0%	2.41
25	c-2-Pentene	00627-20-3	10.23	0.361	0%	3.69
115	Styrene	00100-42-5	1.94	0.346	0%	0.67
14	t-2-Butene	00624-64-6	13.90	0.331	0%	4.60
84.2	4-MeHeptane	00589-53-7	1.46	0.321	0%	0.47
113	3-Methyloctane	02216-33-3	1.42	0.257	0%	0.36
140	1,2,3-Trimethylbenzene	00526-73-8	11.25	0.239	0%	2.69
39.1	2-Methyl-1-pentene	00763-29-1	5.15	0.235	0%	1.21
48	2,2-Dimethylpentane	00590-35-2	1.21	0.199	0%	0.24
16	c-2-Butene	00590-18-1	13.22	0.184	0%	2.44
20	2-Methyl-1-butene	00563-46-2	6.47	0.179	0%	1.16
1	Methane	00074-82-8	0.01	0.124	0%	0.00
76.1	2,5-DiMeHexane	00592-13-2	1.66	0.121	0%	0.20
30	Cyclopentene	00142-29-0	7.32	0.099	0%	0.72
19.1	1-Pentene	00109-67-1	7.73	0.096	0%	0.74
76.2	EtCyPentane	01640-89-7	2.25	0.062	0%	0.14
39.2	1-Hexene	00592-41-6	6.12	0.033	0%	0.20
			Mass w/MIR Values	81.9	95.7%	352.7
				Specific Reactivity		4.31
43	3-Methyl-t-2-pentene	00616-12-6		1.196	1%	
47	Unknown #16			0.686	1%	
61	3-Methyl-c-2-pentene	00922-62-3		0.534	1%	
82.2	c-1,3-Dimethylcyclopentane	02532-58-3		0.330	0%	
88	2-Me-3-Et-pentane	00609-26-7		0.316	0%	
36.2	c-1,3-Dimethylcyclohexane	00638-04-0		0.288	0%	
62	4-Me-c-2-Pentene	00691-38-3		0.140	0%	
45.2	t-1,2-Dimethylcyclopentane	00822-50-4		0.130	0%	
123	3-MeCyclopentene	01120-62-3		0.069	0%	
			Mass w/o MIR Values	3.69	4.3%	
4	Ethane	00074-84-0		0.000	0%	
2	Ethylene	00074-85-1		0.000	0%	
3	Acetylene (Ethyne)	00074-86-2		0.000	0%	

Table 9 (continued)

Detailed Hydrocarbon Speciation Results			24-Hour			
Elution No.	Species Name	CAS #	MIR g O_3/g HC	Net mass (mg)	% total mass	Predicted Ozone mg
6	Propane	00074-98-6		0.000	0%	
8	Propyne	00074-99-7		0.000	0%	
22	2-Methyl-1,3-butadiene	00078-79-5		0.000	0%	
168	Naphthalene	00091-20-3		0.000	0%	
135.2	1,2,4,5-Tetramethylbenzene	00095-93-2		0.000	0%	
122	t-Butylbenzene	00098-06-6		0.000	0%	
162	Isopropylbenzene (Cumene)	00098-82-8		0.000	0%	
141	1,3-Diisopropylbenzene	00099-62-7		0.000	0%	
166	4-Isopropyltoluene (p-Cymene)	00099-87-6		0.000	0%	
70.1	1,4-Diisopropylbenzene	00100-18-5		0.000	0%	
147	n-Butylbenzene	00104-51-8		0.000	0%	
145	1,4-Diethylbenzene	00105-05-5		0.000	0%	
10.2	1-Butene	00106-98-9		0.000	0%	
11	1,3-Butadiene	00106-99-0		0.000	0%	
15	1-Butyne	00107-00-6		0.000	0%	
125.2	244Trimethyl1pentene	00107-39-1		0.000	0%	
75	2,4,4-Trimethyl-2-Pentene	00107-40-4		0.000	0%	
59.1	Cyclohexene	00110-83-8		0.000	0%	
91	1-Octene	00111-66-0		0.000	0%	
120	n-Nonane	00111-84-2		0.000	0%	
172	n-Dodecane	00112-40-3		0.000	0%	
169	1-Dodecene	00112-41-4		0.000	0%	
5	Propene	00115-07-1		0.000	0%	
10.1	2-Methylpropene	00115-11-7		0.000	0%	
118	1-Nonene	00124-11-8		0.000	0%	
146	1,2-Diethylbenzene	00135-01-3		0.000	0%	
138	sec-Butylbenzene	00135-98-8		0.000	0%	
143	1,3-Diethylbenzene	00141-93-5		0.000	0%	
32	Cyclopentane	00287-92-3		0.000	0%	
7	AlBenz	00300-57-2		0.000	0%	
163.1	Allene (Propadiene)	00463-49-0		0.000	0%	
13	2,2-Dimethylpropane	00463-82-1		0.000	0%	
51	2,2,3-Trimethylbutane	00464-06-2		0.000	0%	
163.2	1,2,3,4-TetMeBenzene	00488-23-3		0.000	0%	
142	Indan	00496-11-7		0.000	0%	
19.2	2-Butyne	00503-17-3		0.000	0%	
158	1,2,3,5-Tetramethylbenzene	00527-53-7		0.000	0%	
137	Amylbenz	00538-68-1		0.000	0%	
80	Isobutylbenzene	00538-93-2		0.000	0%	
28	Cyclopentadiene	00542-92-7		0.000	0%	
24	3,3-Dimethyl-1-butene	00558-37-2		0.000	0%	
78	2,3,3-Trimethylpentane	00560-21-4		0.000	0%	

Table 9 (continued)

Detailed Hydrocarbon Speciation Results				24-Hour		
Elution No.	Species Name	CAS #	MIR g O_3/g HC	Net mass (mg)	% total mass	Predicted Ozone mg
54	3,3-Dimethylpentane	00562-49-2		0.000	0%	
92	3,3-Dimethylhexane	00563-16-6		0.000	0%	
17	3-Methyl-1-butene	00563-45-1		0.000	0%	
82.1	2,3-dimethylhexane	00584-94-1		0.000	0%	
98.2	1,1-Dimethylcyclohexane	00590-66-9		0.000	0%	
73	2,2-DiMeHexane	00590-73-8		0.000	0%	
84.1	1-MeCyHexene	00591-49-1		0.000	0%	
64	1-Heptene	00592-76-7		0.000	0%	
37	c-1,4-DiMeCyHexane	00624-29-3		0.000	0%	
44	2-Methyl-2-pentene	00625-27-4		0.000	0%	
46	ETBE	00637-92-3		0.000	0%	
69	4-Methyl-t-2-pentene	00674-76-0		0.000	0%	
31.1	4-methyl-1-pentene	00691-37-2		0.000	0%	
52	1-Methylcyclopentene	00693-89-0		0.000	0%	
31.2	3-methyl-1-pentene	00760-20-3		0.000	0%	
150	3-Ethyl-c-2-Pentene	00816-79-5		0.000	0%	
153	1-Undecene	00821-95-4		0.000	0%	
151	1,3-Dimethyl-4-Ethylbenzene	00874-41-9		0.000	0%	
105	3,5-Dimethylheptane	00926-82-9		0.000	0%	
148	1,2-Dimethyl-4-Ethylbenzene	00934-80-5		0.000	0%	
100	2,3,5-Trimethylhexane	01069-53-0		0.000	0%	
144	1-Methyl-2-Propylbenzene	01074-17-5		0.000	0%	
149	1-Methyl-3-Propylbenzene	01074-43-7		0.000	0%	
154	n-Undecane	01120-21-4		0.000	0%	
33	MTBE	01634-04-4		0.000	0%	
104	Ethylcyclohexane	01678-91-7		0.000	0%	
125.3	PrCyHexane	01678-92-8		0.000	0%	
119	1,4-Dimethyl-2-Ethylbenzene	01758-88-9		0.000	0%	
103	c- & t-4-Nonene	02198-23-4		0.000	0%	
98.1	c-1,2-Dimethylcyclohexane	02207-01-4		0.000	0%	
89	t-1,3	02207-03-6		0.000	0%	
67.1	t-1,4-Dimethylcyclohexane	02207-04-7		0.000	0%	
101	2,4-Dimethylheptane	02213-23-2		0.000	0%	
112	4-Methyloctane	02216-34-4		0.000	0%	
152	2-Methyl-2-Hexene	02738-19-4		0.000	0%	
110.1	1,3-Dimethyl-2-Ethylbenzene	02870-04-4		0.000	0%	
55	2,3-DiMeHeptane	03074-71-3		0.000	0%	
110.2	2-MeOctane	03221-61-2		0.000	0%	
68.1	3-Me-1-Hexene	03404-61-3		0.000	0%	
139	3-Me-t-3-Hexene	03899-36-3		0.000	0%	
125.1	2,4-DiMeOctane	04032-94-4		0.000	0%	
121	1-Methyl-4-Isobutylbenzene	05161-04-6		0.000	0%	

Table 9 (continued)

Detailed Hydrocarbon Speciation Results				24-Hour		
Elution No.	Species Name	CAS #	MIR g O_3/g HC	Net mass (mg)	% total mass	Predicted Ozone mg
71	t-2-Nonene	06434-78-2		0.000	0%	
97.2	c-2-Heptene	06443-92-1		0.000	0%	
99	t-1,2-DiMeCyHexane	06876-23-9		0.000	0%	
70.2	c-2-Octene	07642-04-8		0.000	0%	
41.2	c-3-Hexene	07642-09-3		0.000	0%	
67.2	c-3-Heptene	07642-10-6		0.000	0%	
97.1	23-diMe-2-pentene	10574-37-5		0.000	0%	
41.1	t-3-Hexene	13269-52-8		0.000	0%	
27	t-2-Octene	13389-42-9		0.000	0%	
68.2	t-2-Heptene	14686-13-6		0.000	0%	
65	t-3-Heptene	14686-14-7		0.000	0%	
94	t-4-Octene	14850-23-8		0.000	0%	
87	2,2-Dimethyloctane	15869-87-1		0.000	0%	
161	1c-2t-3-TriMeCyPentane	15890-40-1		0.000	0%	
157	Methylindan	27133-93-3		0.000	0%	
35	Unknown #1			0.000	0%	
60	Unknown #2			0.000	0%	
72	Unknown #3			0.000	0%	
85	Unknown #4			0.000	0%	
95	Unknown #5			0.000	0%	
102	Unknown #7			0.000	0%	
106	Unknown #8			0.000	0%	
107	Unknown #9			0.000	0%	
108	Unknown #10			0.000	0%	
114	Unknown #11			0.000	0%	
116	Unknown #12			0.000	0%	
124	Unknown #13			0.000	0%	
126	Unknown #14			0.000	0%	
131	Unknown #15			0.000	0%	
132	Unknown #17			0.000	0%	
134	3-Methylnonane			0.000	0%	
155	Unknown #18			0.000	0%	
156	Unknown #19			0.000	0%	
159	Unknown #20			0.000	0%	
160	Unknown #21			0.000	0%	
165	Unknown #23			0.000	0%	
167	Unknown #24			0.000	0%	
170	Unknown #25			0.000	0%	
	Total			85.6	100.0 %	
				83.9	SHED FID (mg)	
				102.0	% GC of SHED FID	

Specific Reactivity Calculations - The Carter Maximum Incremental Reactivity (MIR) scale for the various VOC molecules was adopted by the CARB. It estimates that for each gram of the various VOC molecules, X grams of ozone would be produced under ideal conditions for ozone formation. The reference (approved by the CARB Staff for this purpose) to the values and the documentation is "THE SAPRC-99 CHEMICAL MECHANISM AND UPDATED VOC REACTIVITY SCALES" which can be found at

http://helium.ucr.edu/~carter/reactdat.htm

The link to the actual data is found down two thirds of the page, under the heading VOC Reactivity Data (Excel format) as of February 5, 2003 (r02tab.xls). It contains CAS number, MIR value and species name for 543 different species.

The average specific reactivity of the permeate was calculated for each of the 25 diurnal tests conducted on the five rigs and five fuels.

VOC reactivity varies with atmospheric conditions, in particular the VOC/NOx ratio. The MIR scale is based on low VOC/NOx ratios. The reactivity measure reported in this study, average VOC specific reactivity, has units of potential grams of ozone per gram of VOC and is a function of the composition of the VOC permeate. Specific reactivity provides an estimate of the ozone-forming potential per unit mass of the VOC permeate under conditions favorable for ozone formation, but it is not meant to predict actual levels of ozone and should be interpreted on a relative basis. Further, there are uncertainties in these reactivity estimates, e.g., the MIR scale represents a limited range of atmospheric conditions, does not include carryover of emissions from one day to the next, and does not include three-dimensional spatial variation in emissions.

The mass emissions times the MIR gives the theoretical potential ozone that would be formed by that mass under ideal conditions. This calculation was performed on all the identified molecules that had MIR factors. Not all the molecules measured had MIR factors. The unidentified compounds were assumed to have the same reactivity as the average of the identified compounds with MIR factors. The mass of the compounds for which no MIR factors existed was determined to be insignificant.

The specific reactivity for a speciated SHED diurnal sample was calculated by summing the mass of the individual species, and the predicted potential ozone using the MIR factor. The specific reactivity is the mass of ozone predicted divided by the mass of the hydrocarbons measured, in our example, 352.7 mg/81.9 mg, or 4.31 g of potential O_3/g VOC permeate emissions.

The next part of this report discusses the specific reactivities calculated for the six fuels tested in this project. When the permeate specific reactivities of the five rigs were compared across test fuels, it was observed that Rig 11 consistently produced the lowest result.

Thirteen diurnal tests on the E0 fuel were speciated (Table10). The average specific reactivity of the permeate of all the E0 diurnals was 3.99 (grams of ozone per gram of HC mixture), with two "eyeball" outliers, (test 6370 – Rig 11 = 2.91), and (test 6372 – Rig 12 = 5.48). The other six tests ranged from 3.80 to 4.26. The third and fourth columns in Table 9 allow a comparison of the SHED calculation of mass and the gas chromatograph's value. In general, reasonable agreement was found between the two estimates. The fifth and sixth columns report the identified mass (in mg and % of total) that had MIR factors for the individual species. Usually 90% or more had MIR values

Table 10

Fuel E0 Diurnal Permeate Reactivity Results

Rig (test #)	Test ID	Reported SHED mg	**Total GC** Mass - mg	**Mass w/MIR Values** mg	%	Specific Reactivity	Rig Wtd. Average
1	6389	83.9	85.6	81.9	95.7%	4.31	
1b	6900	97.2	101.6	96.1	94.7%	4.15	
2	6390	463.3	391.4	369.8	94.5%	4.26	
2b	6913	451.6	435.6	412.6	94.7%	4.16	
11	6370	48.0	36.6	32.5	88.8%	2.91	
11b	6889	29.7	32.4	30.9	95.4%	3.51	
12(1)	6372	38.7	29.3	26.0	88.8%	5.48	3.99
12(2)	6383	31.0	34.1	33.4	97.9%	4.10	
12b	6874	38.3	41.0	39.8	97.3%	3.73	
14(1)	6360	250.5	250.4	239.2	95.5%	3.80	
14(2)	6388	248.1	241.3	236.9	98.2%	3.85	
14b	6645	282.7	274.7	259.7	94.6%	3.89	
14c	6892	262.8	265.8	247.9	93.3%	3.91	

The average specific reactivity of the permeates for the five diurnal tests on the E6 fuel was 3.00 (Table 11), but this included one relatively low result (test 6507 – Rig 11 = 2.09). The average specific reactivity with that test omitted was 3.24. The 3.24 number compares well with the Fuel B permeate average of 3.27 from the original E-65 test program.

Table 11
Fuel E6 Diurnal Permeate Reactivity Results

Rig (test #)	Test ID	Reported SHED mg	Total GC Mass - mg	Mass w/MIR Values mg	%	Specific Reactivity	Rig Wtd. Average
1(1)	6471	417.1	264.1	264.1	100.0%	3.05	
1(2)	6479	533.3	461.3	447.3	97.0%	3.08	
2	6481	1426.0	1357.6	1326.8	97.7%	3.54	3.00
11	6507	144.1	127.7	127.7	100.0%	2.09	
12	6492	49.6	36.8	36.0	97.8%	3.30	

Four tests on the E6Hi fuel were speciated, with an average permeate specific reactivity of 3.17 (Table 12). Rig 11 had the lowest reactivity value for the four tests.

Table 12
Fuel E6Hi Diurnal Permeate Reactivity Results

Rig (test #)	Test ID	Reported SHED mg	Total GC Mass - mg	Mass w/MIR Values mg	%	Specific Reactivity	Rig Wtd. Average
1	6571	360.9	270.9	270.9	100.0%	3.30	
2	6570	1227.0	1400.7	1290.1	92.1%	3.66	3.17
11	6598	88.7	82.0	82.0	100.0%	2.58	
12	6569	45.0	39.2	38.7	98.6%	3.14	

The six diurnal tests on the E10 fuel had an average permeate specific reactivity of 2.94 (Table 13), with Rig 11 again yielding the lowest values. There is no current explanation why the fuel system components used in Rig 11 might produce a lower, or less reactive permeate.

Table 13
Fuel E10 Diurnal Permeate Reactivity Results

Rig (test #)	Test ID	Reported SHED mg	**Total GC** Mass - mg	**Mass w/MIR Values** mg	%	Specific Reactivity	Rig Wtd. Average
1	6665	467.8	443.2	438.2	98.9%	3.03	
2	6673	1300.6	1289.2	1262.3	97.9%	3.45	
11(1)	6675	149.3	163.2	160.8	98.6%	2.23	2.94
11(2)	6676	97.3	118.5	116.3	98.2%	2.43	
12	6642	64.3	54.9	53.8	98.0%	2.85	
14	6454	466.3	436.6	426.4	97.7%	3.05	

The five diurnal tests on the E20 fuel had an average specific reactivity of 3.04 (Table 14), with a range of values from 2.40 to 3.36. Again, the lowest specific reactivity of the rigs evaluated was Rig 11.

Table 14
Fuel E20 Diurnal Permeate Reactivity Results

Rig (test #)	Test ID	Reported SHED mg	Total GC Mass - mg	Mass w/MIR Values mg	%	Specific Reactivity	Rig Wtd. Average
1	6806	508.1	568.4	558.3	98.2%	3.20	
2	6816	1765.1	1687.5	1650.8	97.8%	3.32	
11	6805	102.0	94.5	93.1	98.6%	2.40	
12	6678	74.7	63.6	63.5	100.0%	2.92	3.04
14	6779	359.5	399.0	388.7	97.4%	3.36	

Two speciated diurnals were conducted on Rig 14 with the E85 fuel, and the results are shown in Table 15. The two permeate specific reactivities measured were 2.63 and 2.82 with an arithmetic average value of 2.73. The specific reactivity of the E85 permeate is expected to be low compared to other fuels since the ethanol fraction of the diurnal permeate was approximately two-thirds of the total mass (59 to 65 mass %).

Table 15
Fuel E85 Diurnal Permeate Reactivity Results

Rig (test #)	ID	Reported SHED mg	Total GC Mass -mg	Mass w/MIR Values mg	Mass w/MIR Values %	Specific Reactivity	Rig Wtd. Average
14(1)	6555	142.3	137.6	137.4	99.9%	2.63	
14(2)	6566	112.8	105.6	102.5	97.0%	2.82	2.73

Statistical Analysis

Statistical analyses were performed on the diurnal and steady-state emissions results, as well as on the specific reactivity results. Analysis of the residuals from preliminary regressions indicated that the variability in the diurnal data tended to be proportional to the magnitude of the measurement; therefore, a natural log transformation was used on the diurnal data, which yielded a constant standard deviation over the range of the data. However, the steady-state and reactivity data exhibited constant standard deviations without the log transformation, so no transformation was used for those variables.

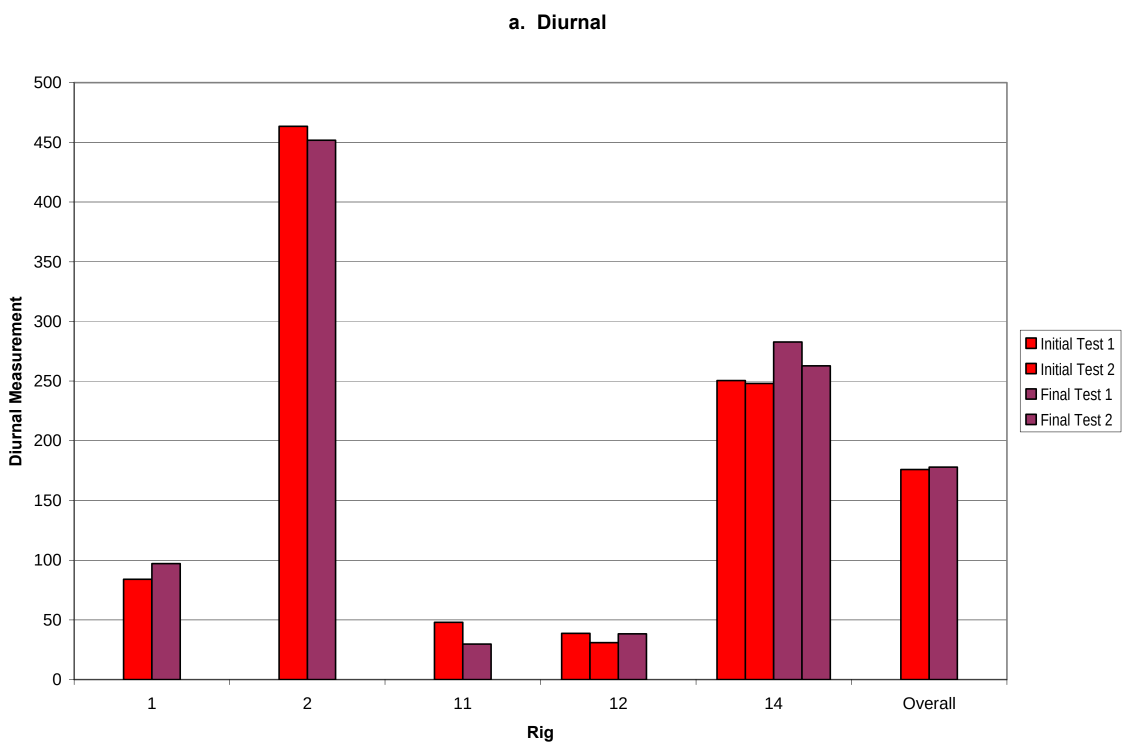
For each of the three dependent variables evaluated, tests were performed to determine the significance of three possible independent variables: 1) test timing; 2) fuel aromatics level; and 3) fuel ethanol content. Because E85 was only tested in one of the five vehicles (rigs), data for that fuel were not included in any of the analyses. All five vehicles (rigs) were included in the analyses for test timing and fuel ethanol content, but Rig 14 was not included in the analysis of the effect of fuel aromatics content because it was not tested on fuels E6 and E6Hi.

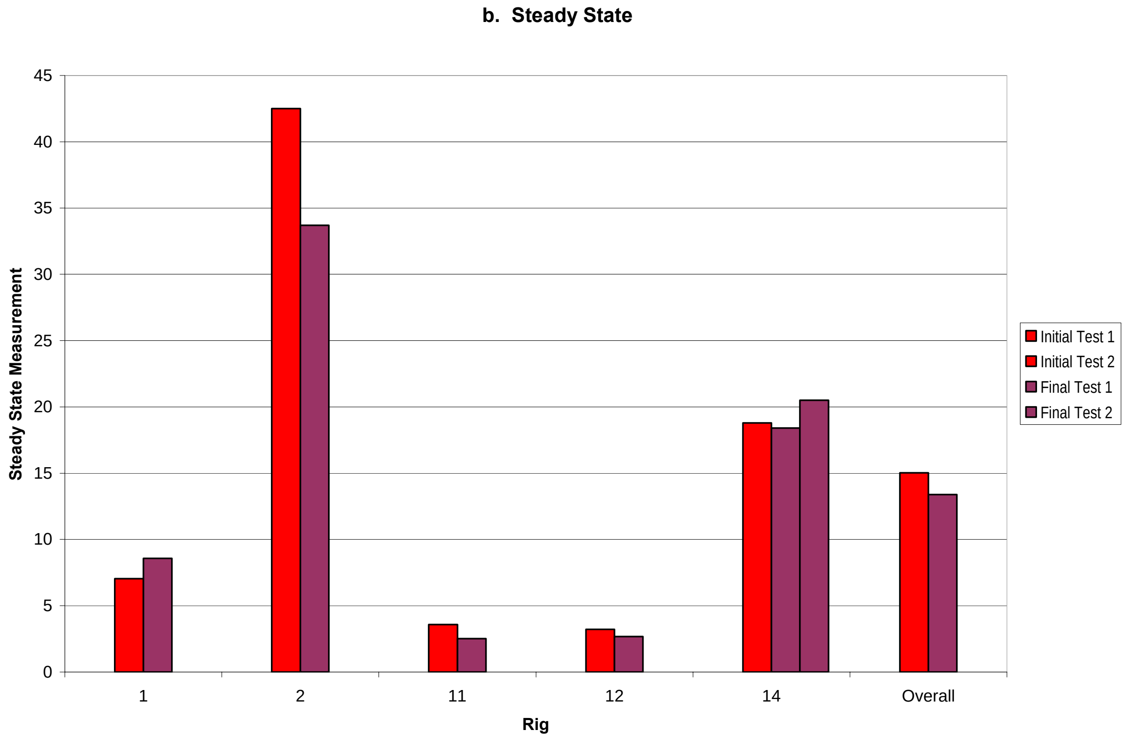
In recent years, CRC has employed mixed models that include both fixed and random effects in the analysis of emissions data. In these analyses, the random effects are the vehicle intercepts and vehicle-by-fixed effect interactions. The advantage of these mixed models is that the random effects are treated as being samples drawn from a normal population, and the resulting statistical tests include the observed variation in the random sample of vehicles. As a result, the tests of significance are applicable to the population of vehicles from which the sample was drawn. On the other hand, statistical tests using fixed-effect models are applicable only to the specific vehicles tested.

While mixed models permit more powerful conclusions to be drawn, they also depend on having a large enough random vehicle sample to be able to draw conclusions on fuel effects in the face of vehicle-to-vehicle variation. In this study, the small sample size (five vehicles) was not judged to be large enough to permit the use of mixed models, so fixed effects models were used. As a result, the statistical significance determinations made in this report apply only to the specific vehicles tested.

Test Timing

The E0 fuel was evaluated first and last on all the rigs. In addition, Rig 14 tested E0 after E85 and before E20. Examination of these tests on E0 allows determination of whether there was any change in rig performance over the course of the testing. These E0 results are shown graphically in Figure 31. The multiple initial E0 tests on Rigs 12 and 14 are the result of repeat diurnal tests and were thus very close together in time. The multiple final E0 results for Rig 14 are due to the testing of E0 before and after E20 and are thus further apart in time, but not as far apart as they are from the initial E0 tests.





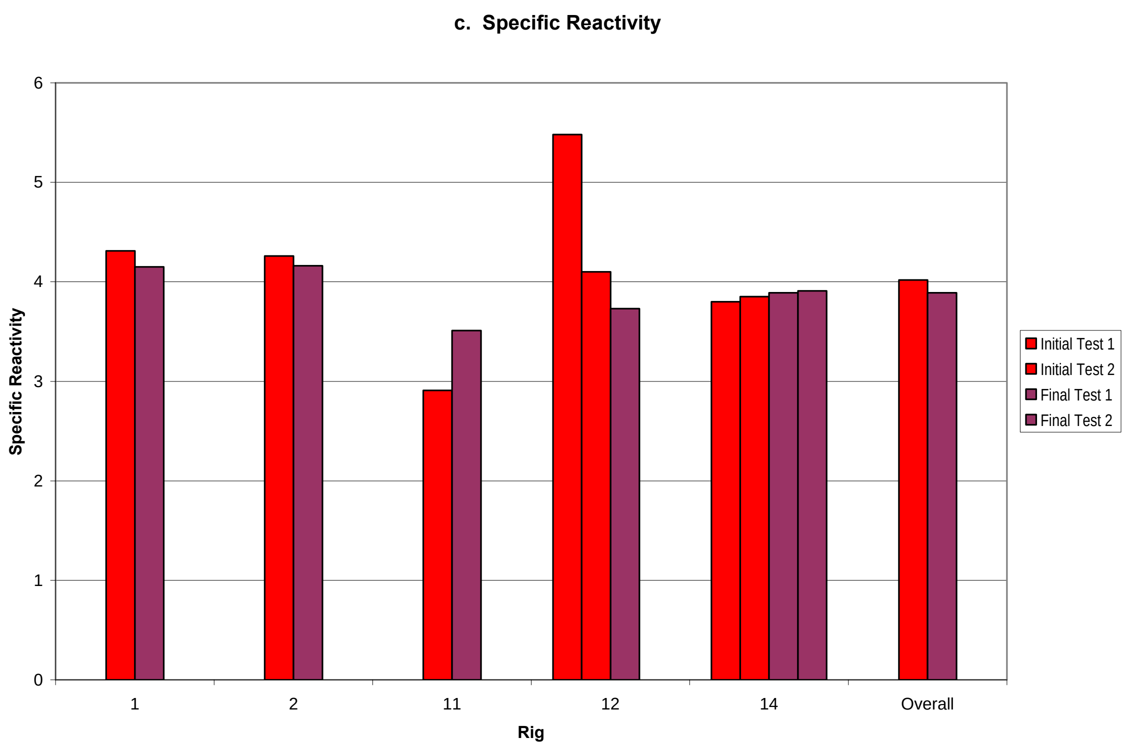


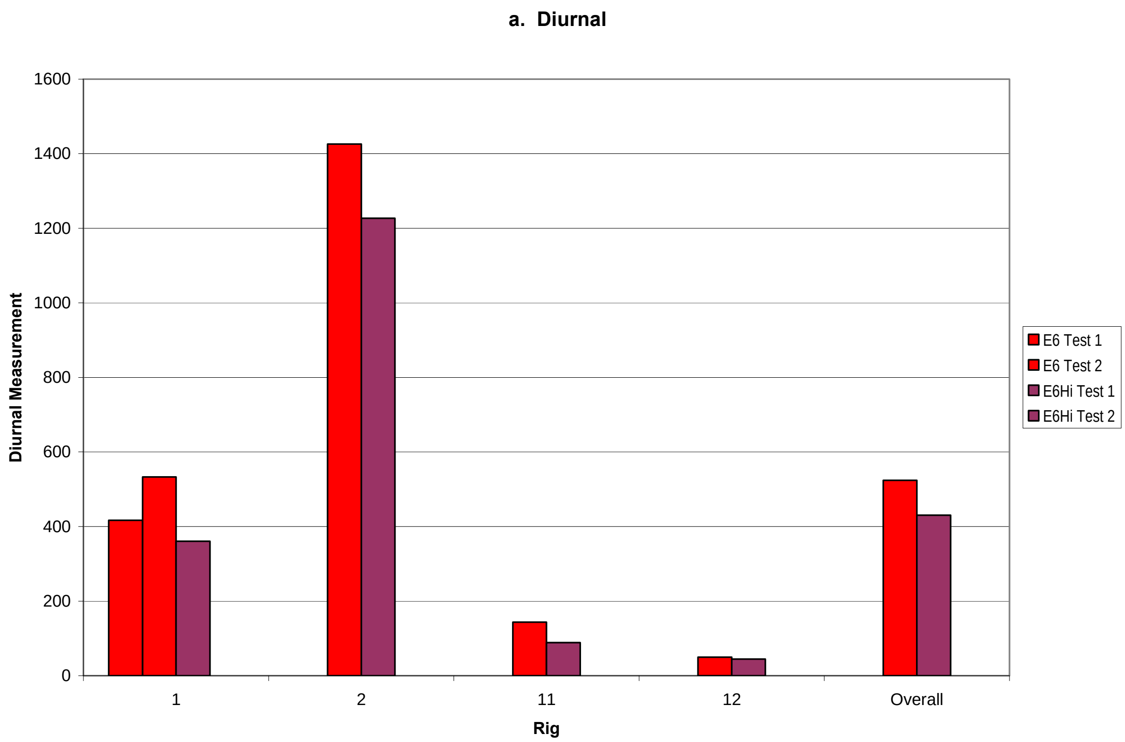
Figure 31

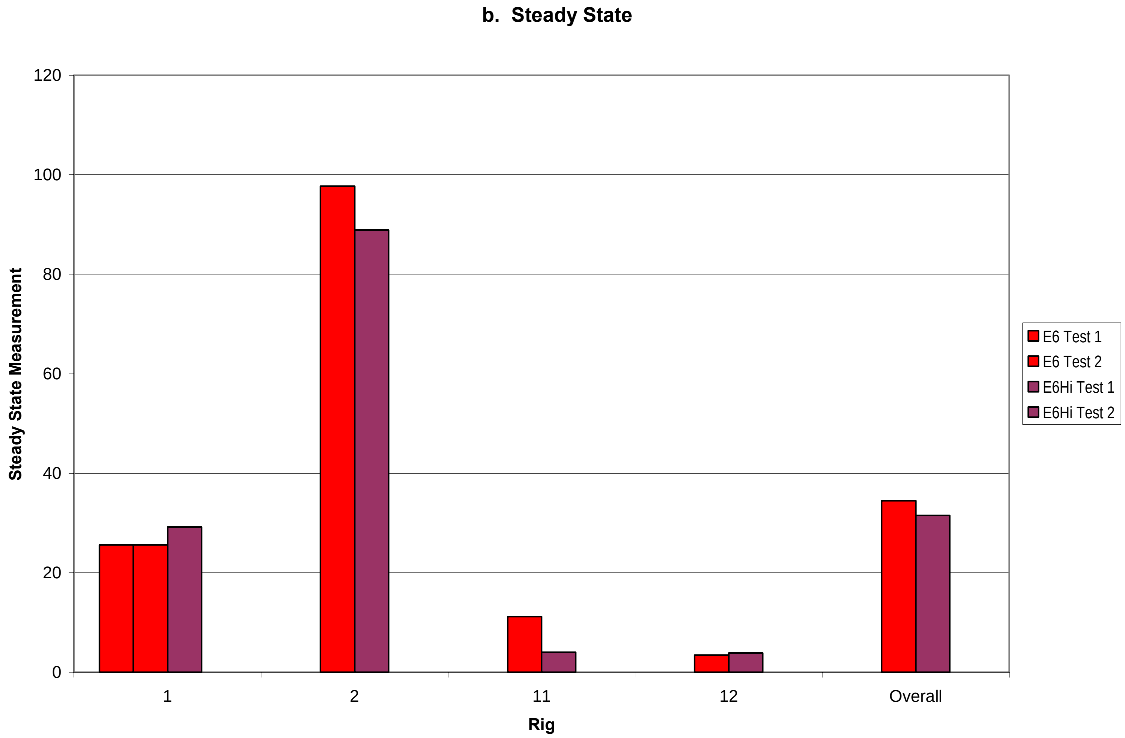
An ANOVA that treated the individual fuels without regard to fuel characteristics was run for each of the dependent variables. The model included fixed effects for fuel, rig and fuel by rig interaction. Within the

ANOVA, a contrast was set up to test the hypothesis that there were no significant differences between the E0 results at the beginning of the testing and the E0 results at the end of the testing (the extra E0 test on Rig 14 was treated as if it were made at the end of the test). No significant effect of test timing was observed for any of the three dependent variables ($p \geq 0.32$). Given that no significant effect was observed, all E0 measurements were treated the same, regardless of when they were obtained, in subsequent analyses.

Aromatics

Fuels E6 and E6Hi differed from one another primarily in their aromatics level. Comparison of these two fuels can thus determine the significance of any effect of aromatics content that was observed. These results are shown graphically in Figure 32.





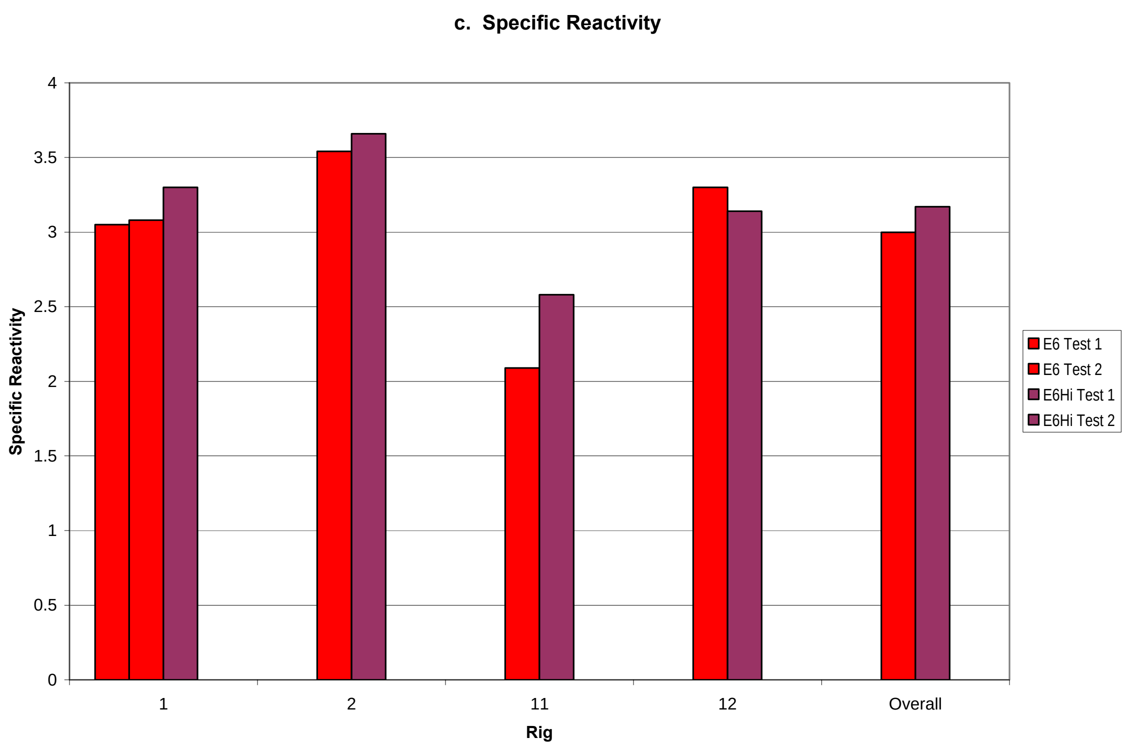


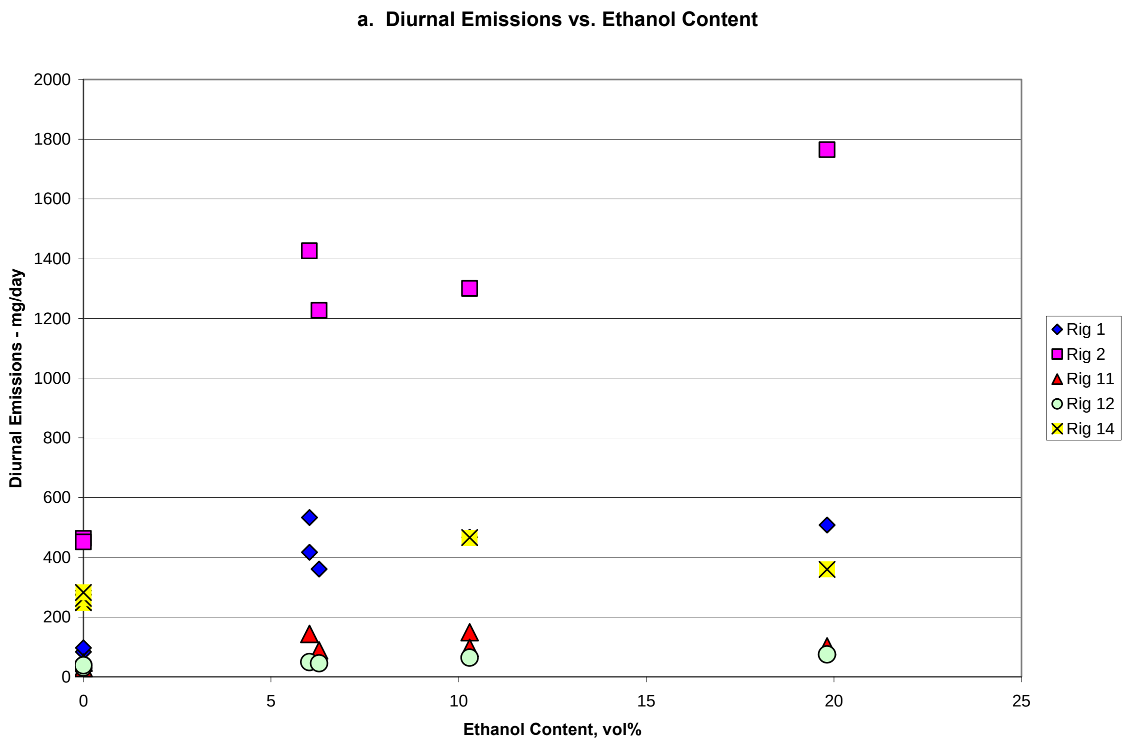
Figure 32

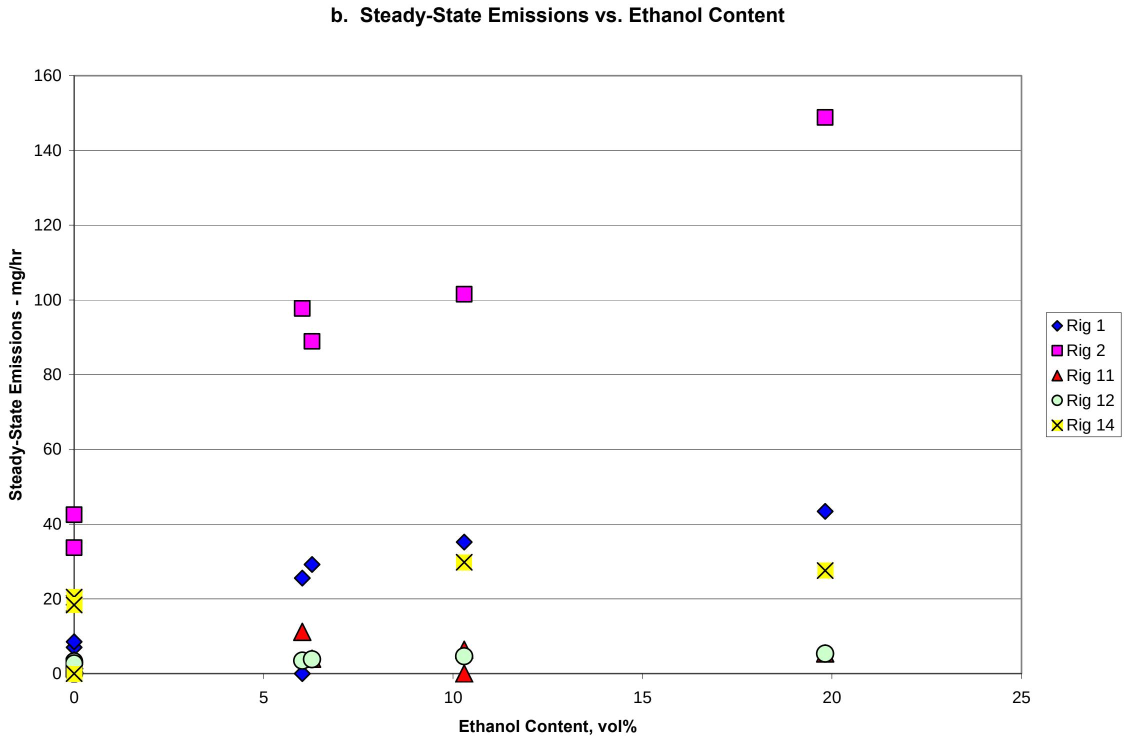
An ANOVA that treated the individual fuels without regard to fuel characteristics was run for each of the dependent variables. The model included fixed effects for fuel, rig and fuel by rig interaction. Within the

ANOVA, a contrast was set up to test the hypothesis that there were no significant differences between the E6 results and the E6Hi results. No significant effect of aromatics level was observed for any of the three dependent variables ($p \geq 0.11$). Given that no significant effect was observed, aromatics level was not considered in subsequent analyses.

Ethanol Content

In contrast to the other evaluations, the design of this experiment allows the evaluation of ethanol content as a continuous variable. Figure 33 shows the results for the three dependent variables vs. ethanol content for each rig.




b. Steady-State Emissions vs. Ethanol Content
Steady-State Emissions - mg/hr
Ethanol Content, vol%
0
20
40
60
80
100
120
140
160
0
5
10
15
20
25
Rig 1
Rig 2
Rig 11
Rig 12
Rig 14

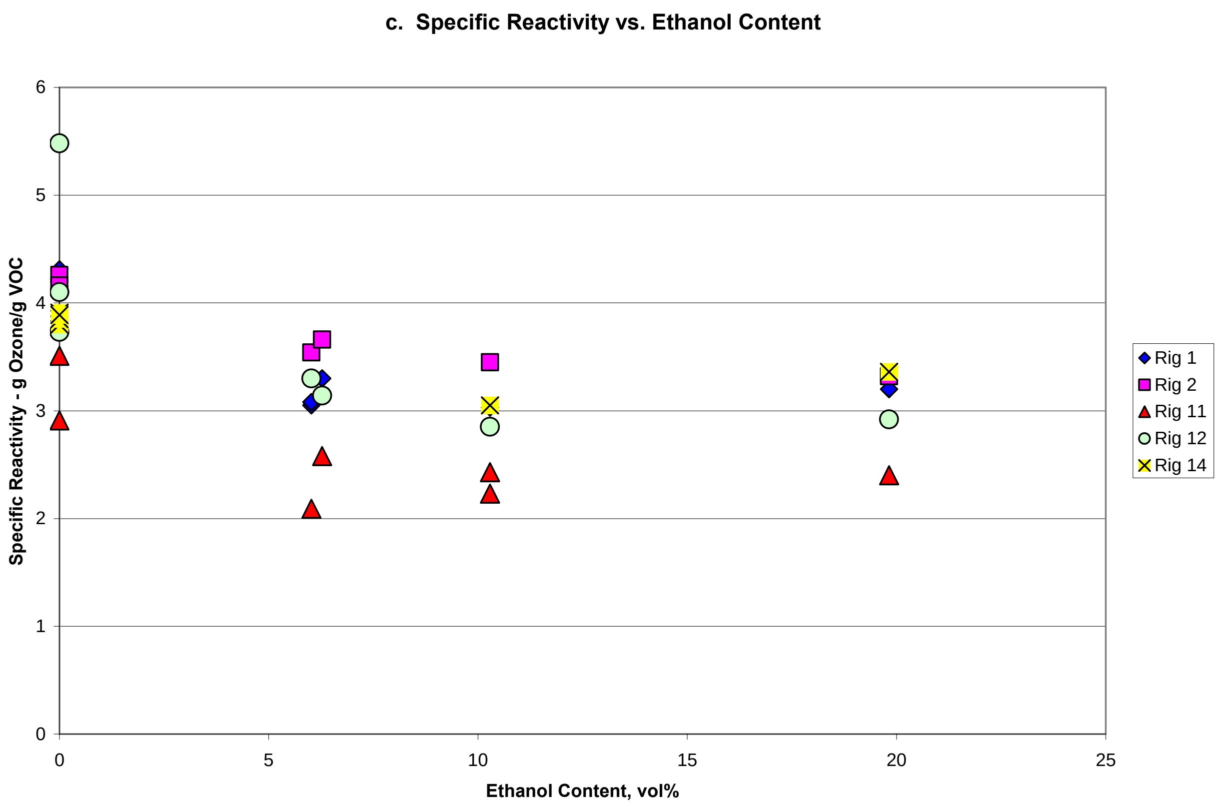

c. Specific Reactivity vs. Ethanol Content
Specific Reactivity - g Ozone/g VOC
Ethanol Content, vol%
0
1
2
3
4
5
6
0
5
10
15
20
25
Rig 1
Rig 2
Rig 11
Rig 12
Rig 14

Figure 33

The plots indicate a general nonlinear relationship between the dependent variables and ethanol content. Closer inspection of the data reveals that, while the overall relationship is nonlinear, the data at nonzero ethanol contents is actually fairly linear: the nonlinearity exists between the E0 and ethanol-containing fuels. An example of this is shown in Figure 34 for Rig 1 diurnal emission results.

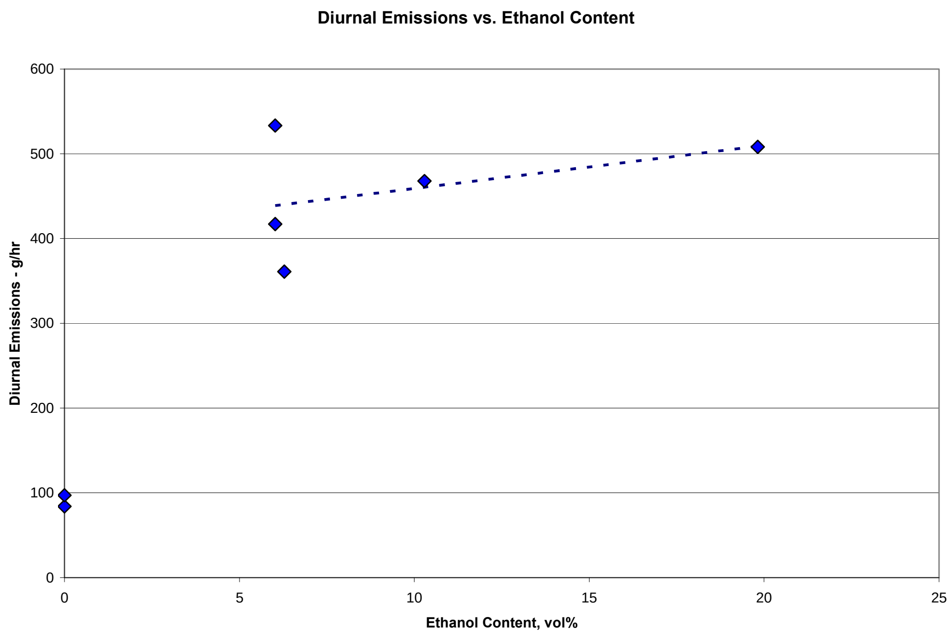


Figure 34

The dashed line is a linear fit vs. ethanol content for the five observations at nonzero ethanol contents. The reasonably good fit for these points contrasts with the E0 data. As a result of patterns like this in the data, a model was fit to the data that provides for a discontinuous function that includes a single point (intercept) based on the E0 data and a linear fit based on the fuels with nonzero ethanol content. This allows two tests to be performed to determine the effect of ethanol: one test that evaluates the effect of the presence or absence of ethanol, and another that evaluates the effect of changes in ethanol content for ethanol-containing fuels.

The regression model is thus:

$$y = a * Rig + b * Present + c * Ethanol + Rig * Present + Rig * Ethanol + \varepsilon$$

Where:

Rig	=	Test rig identifier
Present	=	Presence or absence of ethanol
Ethanol	=	Ethanol content, vol%
ε	=	Error term

The presence or absence of ethanol was statistically significant ($p \leq 0.05$) for all three independent variables. Both ln(diurnal) and steady-state emissions increased when ethanol was present, while Specific Reactivity decreased. Varying the ethanol content was significant for the steady-state data (emissions increased as ethanol content increased), but was not significant ($p \geq 0.44$) for the ln(diurnal) and reactivity data.

D. The CRC E-65-3 Steering Committee Members

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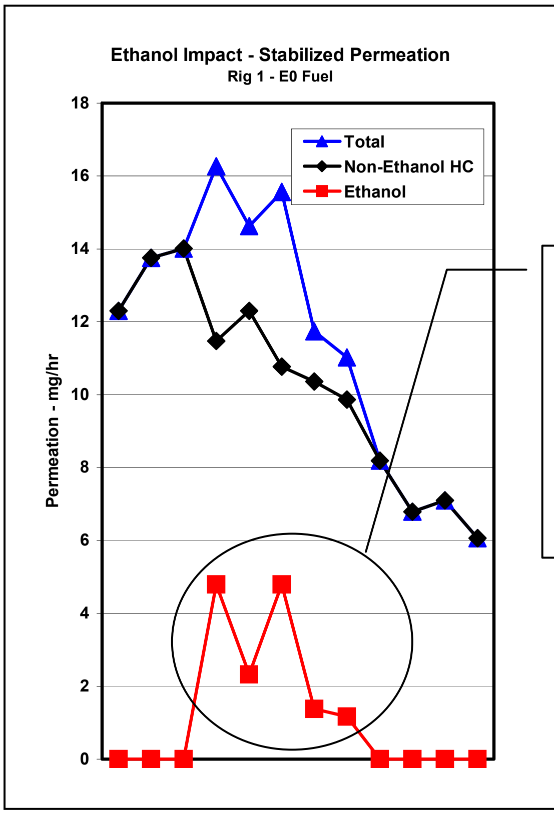
E. Appendix

The Ethanol Hang-up

During our initial stabilization with the E0 fuel, Rigs 1 and 2 unexpectedly exhibited ethanol content in the permeate, which created considerable concern and discussion. It was surprising when Rigs 1 and 2 indicated an ethanol component in the permeate long after the use of any ethanol-containing fuel. This led to the hypothesis that ethanol can lie dormant in the vehicle's fuel system, or be stored and reappear at a much later time.



The first three tests on Rig 1 detected no ethanol in the permeate, but the fourth test on 2-02-05, resulted in an ethanol rate estimate of 4.8 mg/hour. Rig 2 had a similar result during the same time period, as indicated later. The tests after 3-9-05 did not indicate ethanol in the permeate sample.

Figure 35

Table 16 - 2001 Toyota Tacoma Stabilization – Fuel E0

Rig	Fuel	Week	Date	Test#	NonEtOH mg/hour	EtOH mg/hour	NonEtOH + EtOH mg/hour	Running Average mg/hour
01	E0		01/11/05	Drain and 100% fill Fuel E0				
		0	01/12/05	6286	12.3	BDL	12.3	
		1	01/19/05	6293	13.8	BDL	13.8	
		2	01/26/05	6301	14.0	BDL	14.0	
		3	02/02/05	6306	11.5	4.8	16.3	14.1
		4	02/09/05	6313	12.3	2.3	14.6	14.7
		5	02/16/05	6324	10.8	4.8	15.6	15.1
			02/18/05	Drain and 100% fill Fuel E0				

NonEtOH Running

Rig	Fuel	Week	Date	Test#	NonEtOH mg/hour	EtOH Mg/hour	+ EtOH mg/hour	Average mg/hour
		6	02/23/05	6331	10.4	1.4	11.7	14.6
		7	03/02/05	6341	9.9	1.2	11.0	13.2
		8	03/09/05	6352	8.2	BDL	8.2	11.6
		9	03/16/05	6364	6.8	BDL	6.8	9.4
		10	03/23/05	6373	7.1	BDL	7.1	8.3
		11	03/29/05	6381	6.1	BDL	6.1	7.0

The stabilization data for Rig 1 on fuel E0 are listed in Table 15 and shown in Figure 35, and a similar presentation for Rig 2 follows in Table 16 and Figure 36. These rigs had been tested in the previous program with an E6 fuel (Fuel B), but had finished the program on the non-ethanol "Fuel C", and were stored for the down time (roughly six months) with the non-ethanol fuel in their tanks. Rigs 11, 12 and 14 did not show any ethanol in their measurements during the same time period. The measured levels were low, 5 mg/hour or less, but the source of the ethanol was not identified.

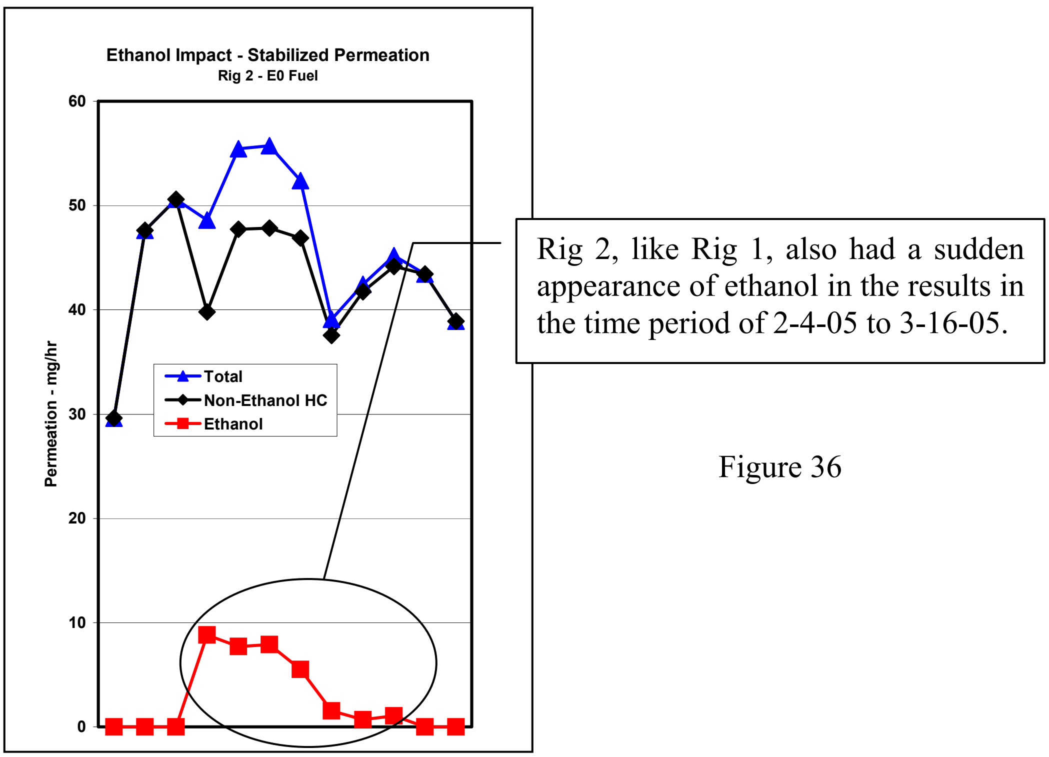


Figure 36

Table 17 - 2000 Honda Odyssey Stabilization – Fuel E0

Rig	Fuel	Week	Date	Test#	NonEtOH	EtOH	NonEtOH + EtOH	Running Average
2	E0		01/11/05	Drain and 100% fill Fuel E0				
		0	01/12/05	6284	29.6	BDL	29.6	
		1	01/19/05	6294	47.6	BDL	47.6	
		1	01/20/05	6296	50.6	BDL	50.6	
		3	02/04/05	6309	39.8	8.8	48.6	44.1
		4	02/09/05	6314	47.7	7.7	55.5	45.3
		5	02/16/05	6326	47.8	7.9	55.7	51.9
			02/18/05	Drain and 100% fill Fuel E0				
		6	02/22/05	6330	46.9	5.5	52.4	53.1
		7	03/02/05	6343	37.6	1.5	39.1	50.7
		8	03/09/05	6354	41.7	0.7	42.4	47.4
		9	03/16/05	6365	44.2	1.0	45.2	44.8
		10	03/24/05	6375	43.4	BDL	43.4	42.5
		11	03/30/05	6385	38.9	BDL	38.9	42.5

That Rigs 1 and 2 had ethanol in their measured results at the same time, that later disappeared, can not be explained at this time.

Ethanol can persist as an element of the permeation emissions of a fuel system long after use of the ethanol fuel has been discontinued. The results from the previous E-65 test program indicated the presence of ethanol in the permeate at a measurable level for a period of up to 7 weeks after the fuel had been changed to the non-ethanol fuel (Fuel C). It is thought that this "hang-up" is due to the time it takes for the permeation components to make their way through the various elastomers in the vehicle's fuel system. Figure 37, representing the 10 rigs tested in the E-65 test program, is used to illustrate this effect. There appears to be a lingering presence of ethanol at levels of up to 5 mg/hour for a considerable period of time.

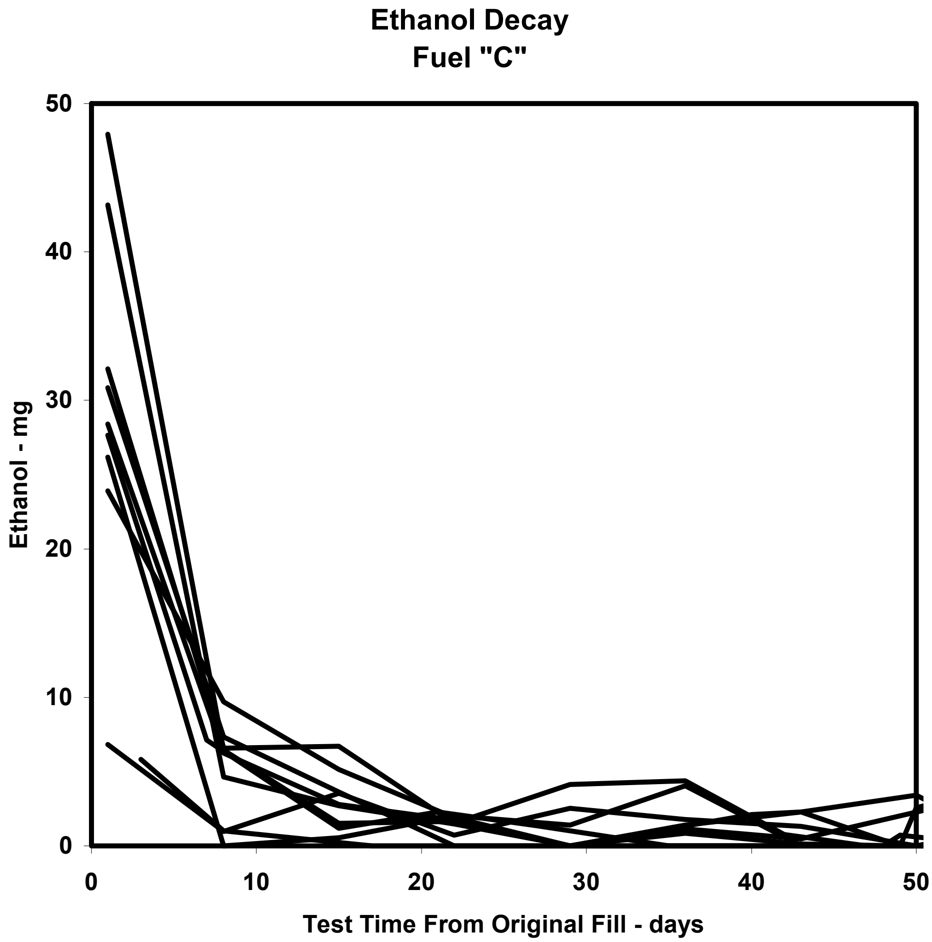


Figure 37

The data used for this plot came from the original E-65 permeation test program, and represents the ethanol permeation measured after the switch from the 5.7% ethanol fuel evaluation (Fuel B) to the non-ethanol fuel (Fuel C). The ten systems included in this analysis came from vehicle systems ranging from model year 1978 to 2001. All of the rigs exhibited “hang-up”, or carry-over of the ethanol component from the previous fuel, during the new stabilization period with the non-ethanol fuel.