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

Interim Report
CRC Project No. E-65-3

August, 2006

Prepared for:

Coordinating Research Council, Inc.
3650 Mansell Road, Suite 140 - Alpharetta, Georgia 30022

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Fuel Permeation from Automotive Systems: E0, E6, E10 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.

Five 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, and
5. E85 – 85 Volume% ethanol fuel

The testing for this project commenced in January of 2005.

During the project, a fuel with 20 Volume% ethanol (E20) was added to the program. These tests are being finished as this report is written. This is an interim report, and a final report will be written after all the data are collected. The final report is expected to be available in the late fall, 2006.

The results of this program have not been statistically analyzed, so differences noted in this report among and between the permeation rates and specific reactivities for the various test fuels and test rigs should not be assumed to be statistically significant. 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 and E10) increased permeation in all the vehicle systems and technologies tested, compared to the non-ethanol fuel (E0).
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.
5. Diurnal permeation emissions were lower on all four rigs tested with the higher-level aromatics fuel (E6Hi) versus the lower aromatics fuel (E6).
6. The average specific reactivities of the permeates from the low-level ethanol blends were similar to one another and lower than those measured with the non-ethanol fuel (E0).

Findings:

1. The average diurnal permeation rate increased 366 mg/day (from 158 to 524 mg/day) when the E6 fuel was substituted for the base non-ethanol E0 fuel on the four rigs evaluated.
2. The average diurnal permeation rate increased 272 mg/day (from 158 to 430 mg/day) when the E6Hi fuel was substituted for the base non-ethanol E0 fuel on the four rigs evaluated.
3. The average diurnal permeation rate increased 326 mg/day (from 158 to 484 mg/day) when the E10 fuel was substituted for the base non-ethanol E0 fuel on the five rigs evaluated.

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[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

4. On the “Flexible Fuel” Rig 14, the diurnal permeation rate increased 206 mg/day (from 260 to 466 mg/day) from the base non-ethanol fuel (E0) rate when the E10 fuel was evaluated, but then decreased 132 mg/day (from 260 to 128 mg/day) of the base fuel value when the E85 fuel was evaluated.
5. 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 15 mg/day (from 35 to 50) increase was measured with fuel E6, a 10 mg/day (from 35 to 45mg/day) increase with fuel E6Hi, and a 29 mg/day (from 35 to 64 mg/day) increase with fuel E10.
6. The average specific reactivity of the base E0 fuel permeate was 4.02, the highest of the five fuels evaluated.
7. Average specific reactivity of the E6 fuel permeate was 3.00.
8. Average specific reactivity of the E6Hi fuel permeate was 3.17.
9. Average specific reactivity of the E10 fuel permeate was 2.94.
10. Average specific reactivity of the E85 fuel permeate was 2.73.
11. 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 levels, 0, 6[2], 10 and, on one system, 85 volume percentage. 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 and five gasoline blends 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

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[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

week, each rig was removed from the soak room and 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. 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 rig's permeation rate 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 11 was finished on January 18, 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.

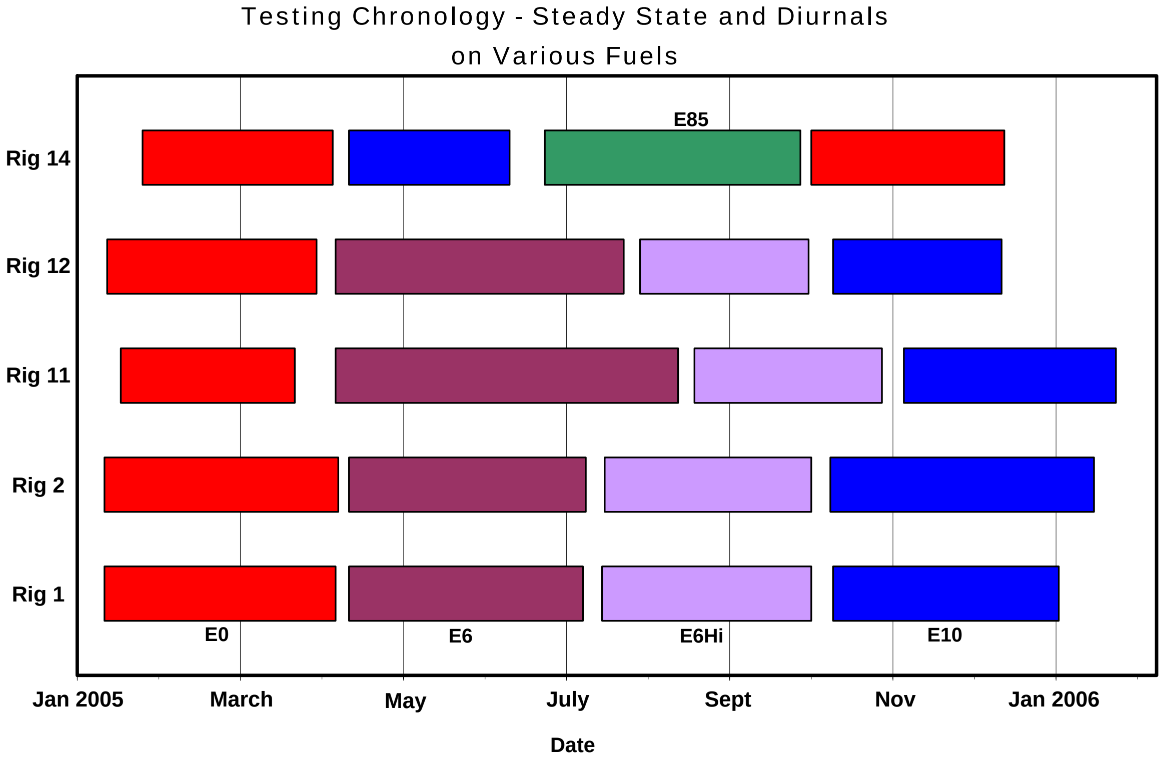
Testing Chronology - Steady State and Diurnals on Various Fuels
Rig 14
Rig 12
Rig 11
Rig 2
Rig 1
E85
E0
E6
E6Hi
E10
Jan 2005
March
May
July
Sept
Nov
Jan 2006
Date

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 (24-hour) and were phased in during the 1995 – 1998 model year period. 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/day for the three-day diurnal, and to 0.65 g/day 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 day when measured on California’s evaporative emission test procedures. This is agreed to be less than 54 milligrams per day. 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.

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[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.

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

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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 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

Five test fuels were blended for the CRC E-65-3 follow-up project. All were made from California blending components and were targeted at California summer fuel characteristics with vapor pressures targeted at 7.0 psi. 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
E85	85 Volume% ethanol fuel

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

Table 3

Test Fuel Inspections

Inspection	Units	E0	E6	E6Hi	E10	E85
API Gravity	°API	61.4	58.8	52.3	58.3	48.6
Relative Density	60/60°F	0.7334	0.7434	0.7699	0.7455	0.7855
DVPE	psi	7.00	7.25	7.19	7.17	6.80
Oxygenates--D 4815						
MTBE	vol %	0.01	0.00	0.00	0.00	0.00
ETBE	vol %	0.00	0.00	0.00	0.00	0.00
EtOH	vol %	0.00	6.02	6.28	10.29	84.69
MeOH	vol %	0.00	0.00	0.00	0.00	0.83
O2	wt %	0.00	2.23	2.25	3.81	29.73
FIAM Corrected--D 1319						
Aromatics	vol%	22.57	26.79	41.47	26.03	3.86
Olefins	vol%	10.70	4.91	3.32	4.77	1.57
Saturates	vol%	66.73	62.24	50.45	58.83	9.82
Oxygenates	vol%	0.00	6.02	6.28	10.31	85.21
Aromatics--D 5580						
Benzene	vol%	0.41	0.55	0.43	0.51	0.17
Toluene	vol%	5.26	6.84	5.25	6.50	0.67
Ethylbenzene	vol%	1.08	1.46	1.13	1.39	0.15
p/m-Xylene	vol%	4.67	5.38	4.21	5.13	0.59
o-Xylene	vol%	1.67	1.98	1.81	1.89	0.22
C9+	vol%	8.86	10.01	25.71	9.52	2.02
Total	vol%	21.96	26.22	38.55	24.93	3.82
D 86 Distillation						
IBP	°F	101.1	108.9	98.0	107.7	116.8
5% Evaporated	°F	123.2	125.8	124.8	127.2	153.5
10% Evaporated	°F	134.5	130.7	132.1	132.1	164.0
20% Evaporated	°F	148.5	136.8	142.4	138.2	168.7
30% Evaporated	°F	165.0	144.8	159.0	144.7	170.4
40% Evaporated	°F	186.2	175.8	206.3	150.8	171.2
50% Evaporated	°F	209.5	202.0	241.9	182.6	171.5
60% Evaporated	°F	231.1	225.6	274.0	221.8	171.8
70% Evaporated	°F	251.2	249.3	302.8	246.0	172.0
80% Evaporated	°F	273.4	275.7	324.5	273.3	172.4
90% Evaporated	°F	305.6	309.9	345.3	309.4	173.1
95% Evaporated	°F	330.6	335.9	363.2	335.7	174.1
EP	°F	389.9	380.4	411.4	378.3	297.4
Recovery	vol %	97.7	97.6	97.2	98.0	97.1
Residue	vol %	1.0	1.0	1.2	1.1	1.9
Loss	vol %	1.3	1.4	1.5	0.8	1.0
Karl Fischer Water	wt %	-	-	-	-	0.42

Table 3, cont.

Additional Inspections

Fuel		Units	E0	E6	E6Hi	E10	E85
Gum							
	Unwashed	mg/100ml	20	16	18	17	9
	Washed	mg/100ml	1	1	0	0	0
Peroxide Number		ppm	<1	<1	<1	1.0	4.4
Induction Period		Hr	24	24	24	24	24
Potential Gum							
	Unwashed	mg/100ml	22	22	24	20	7
	Washed	mg/100ml	0	0	0	0	2
Research ON			90.5	92.1	96.2	94.5	105.8
Motor ON			83.2	84.2	86.2	86.4	89.2
(R+M)/2			86.9	88.2	91.2	90.5	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
E85	E85-FR42011-LDR

Compositions by hydrocarbon type and carbon number are shown in Tables 4, 5 and 6.

Table 4

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	6.65	2.753	0.523	0.045

Table 5
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		0.15	14.22	16.649	7.753	9.15	3.412	0.865	0.417	0.027

Table 6
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	0.013	0.914	1.613	0.771	0.347	0.007			
E6Hi	0	0.008	0.66	1.197	0.595	0.273	0.007			
E10	0	0.011	0.876	1.509	0.727	0.324	0.007			

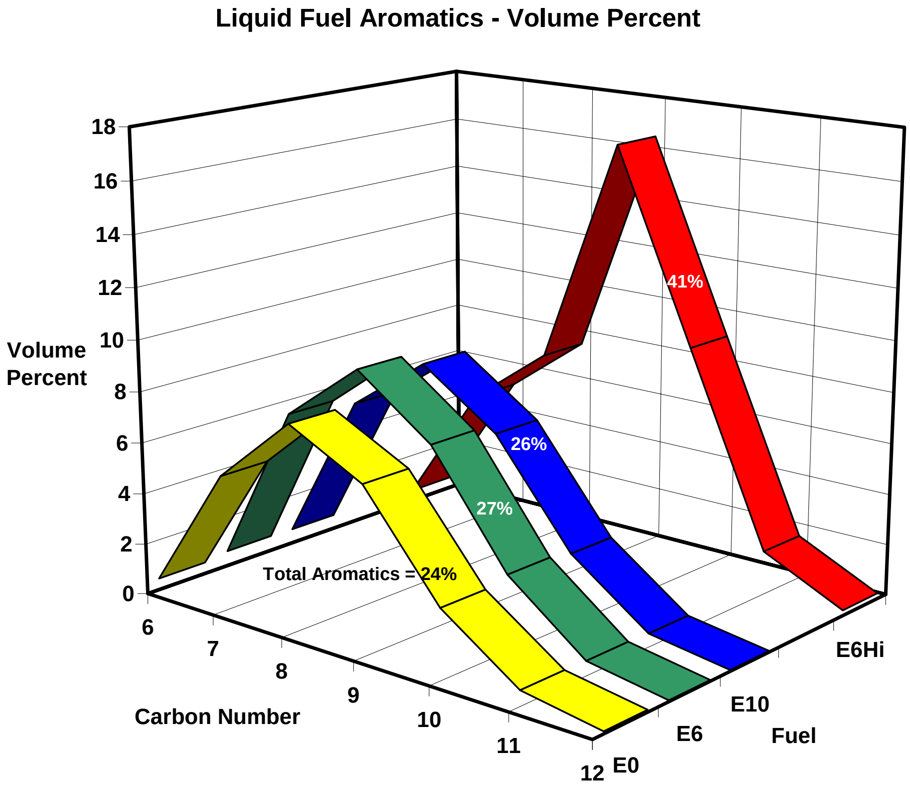

Figure 9

Figure 9 illustrates the distribution of the aromatics content in the four low-ethanol concentration fuels. The aromatics total and the distribution of the aromatics by carbon number are similar for fuels E0, E6, and E10. The high aromatics fuel (E6Hi) has 41% aromatics compared to the 24-27% 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's 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 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 with various rigs in it is shown in Figure 10.

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.

Figure 10 - Constant-Temperature Test Cell

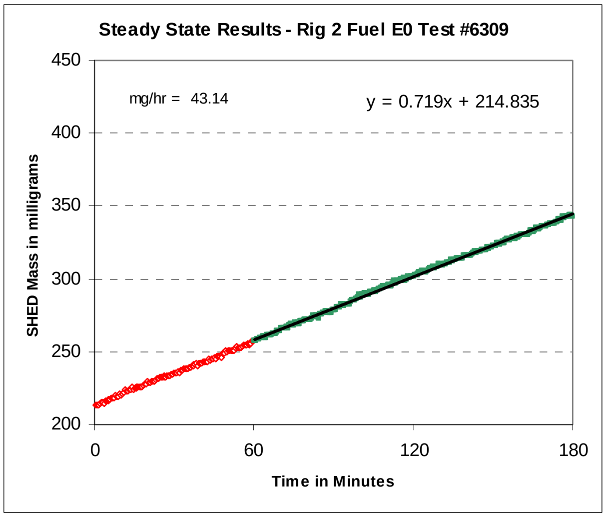

Figure 11

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.

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. EXCEL's trendline function was used to return the permeation rate for the second and third hour results (the green data). This slope became the estimate of the 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.

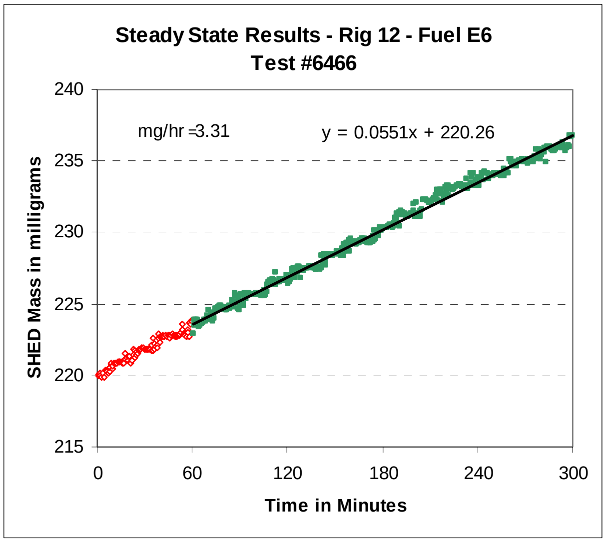

Figure 12

This plot illustrates the conditions that are created when one tries to measure 3 mg/hour in a 2000 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 speciation of the diurnals 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.

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[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.

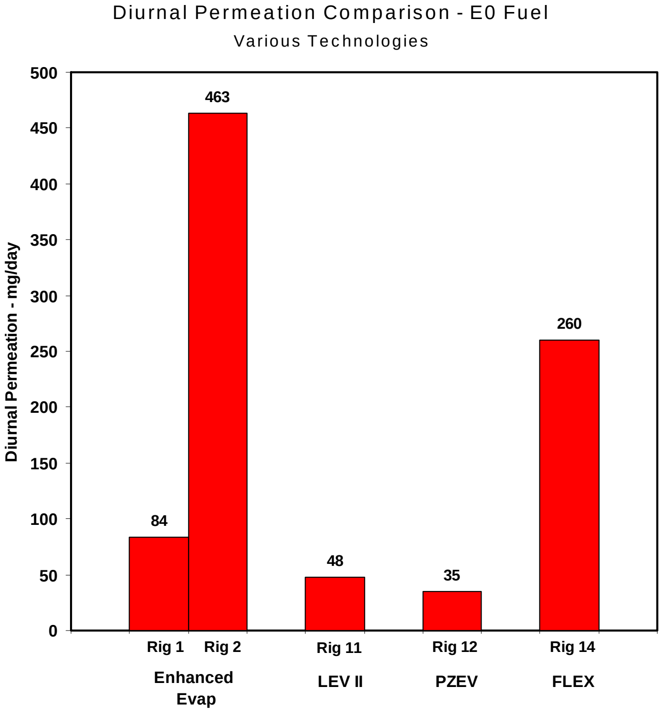

Figure 13

The third bar from the left shows the 48 mg/day level of Rig 11, the LEV II, or California Near-Zero vehicle fuel system. The fourth bar is the 35 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 463 mg/day permeation result on fuel E0 on Rig 2 seems high compared to the 84 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.

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

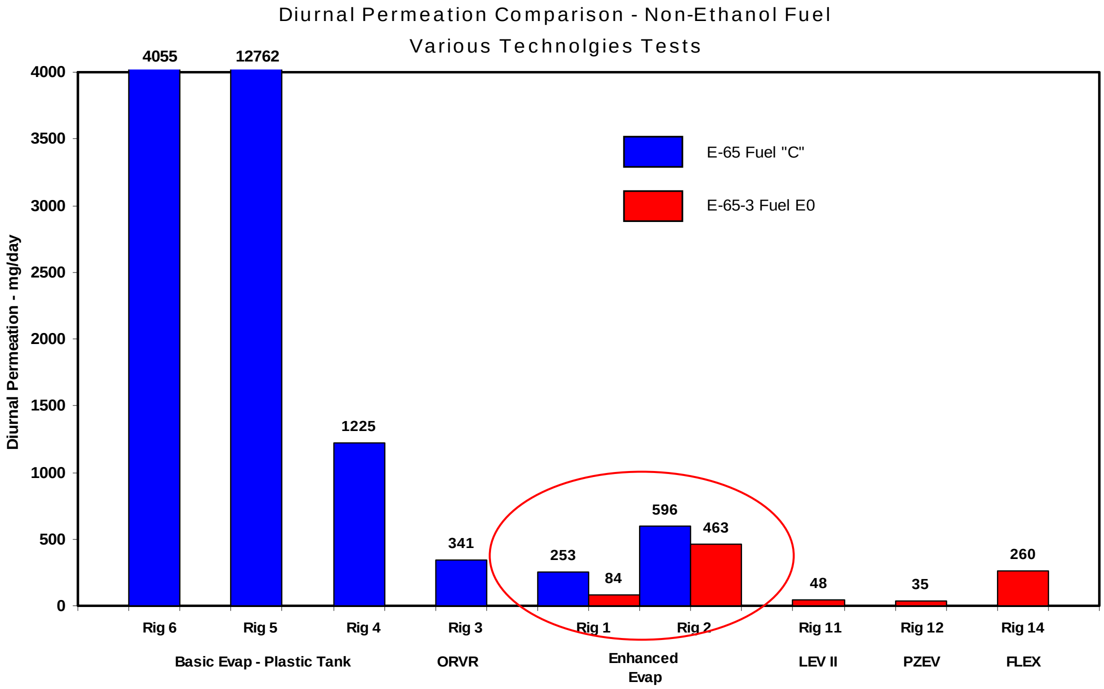

Figure 14

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

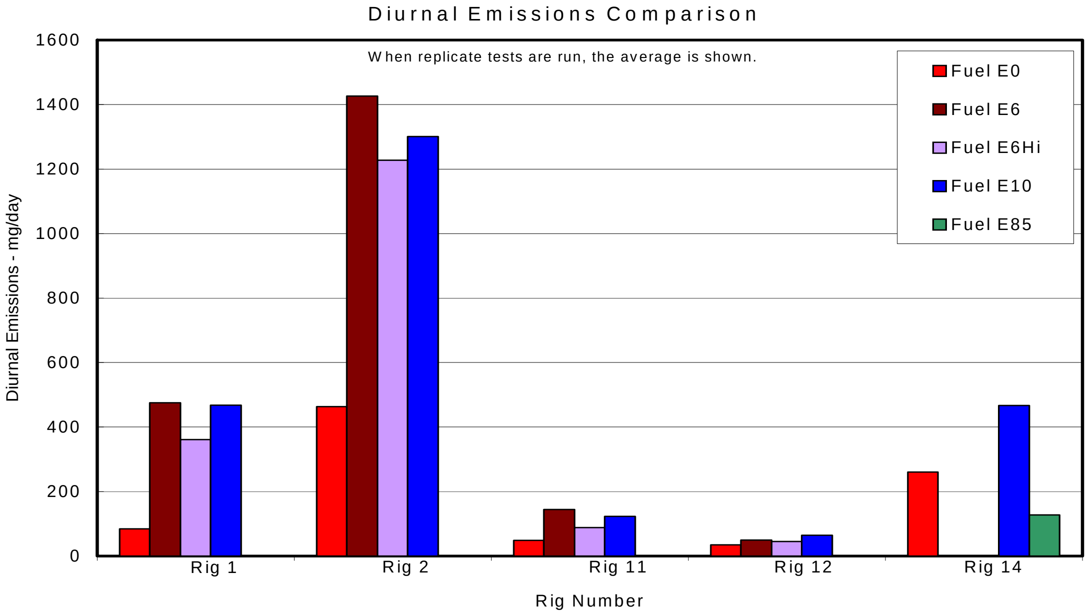

Figure 15

Diurnal Performance - Fuels

Rig 1 - The diurnal emissions measured for Rig 1, the MY 2001 enhanced evap system, ranged from 84 mg/day on the base fuel (E0) to 475 mg/day on the E6 fuel. Figure 16 compares the results for the four fuels tested. Where multiple tests were run, such as those for the E6 fuel, 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.

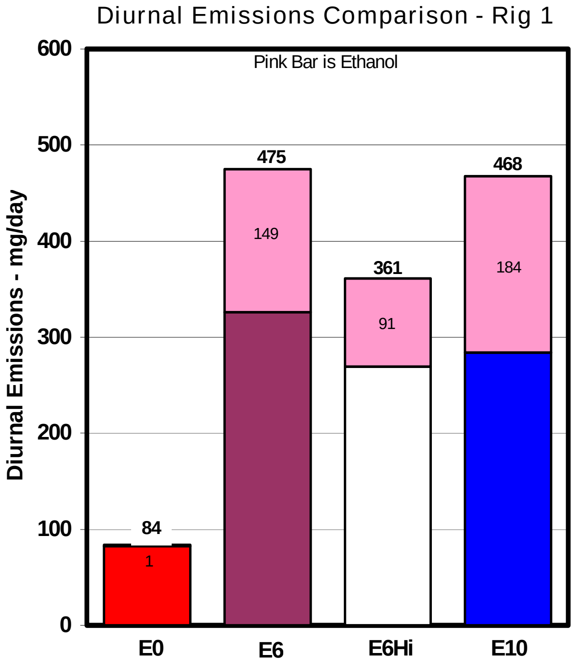

Figure 16

The diurnal permeation emissions with the E6 fuel increased by 391 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.

Rig 2 - Rig 2, another enhanced evap system (2000 MY), also had significant increases in permeation when tested with the ethanol-containing fuels, as shown in Figure 17. The permeation increased from 463 mg/day with the base (E0) fuel to 1426 mg/day with the E6 fuel. The ethanol was about 400 mg/day for the three 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.

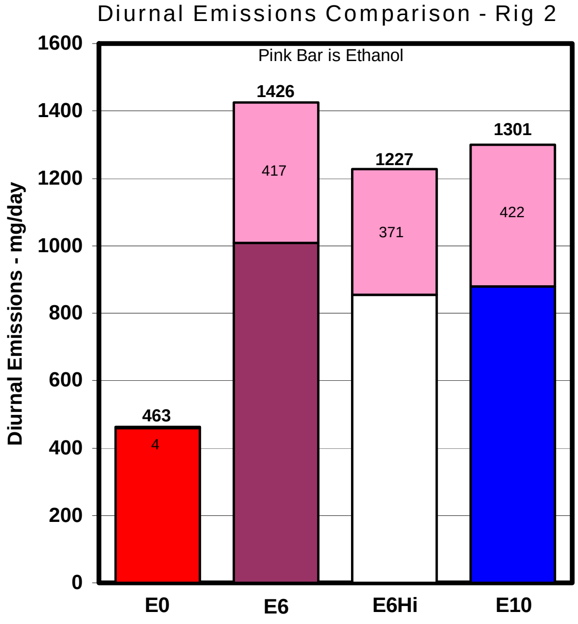

Figure 17

Rig 11 - The results for Rig 11, shown in Figure 18, show a trend in permeation results similar to what was observed on the other rigs. The permeation rate for the E6 fuel was 96 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.

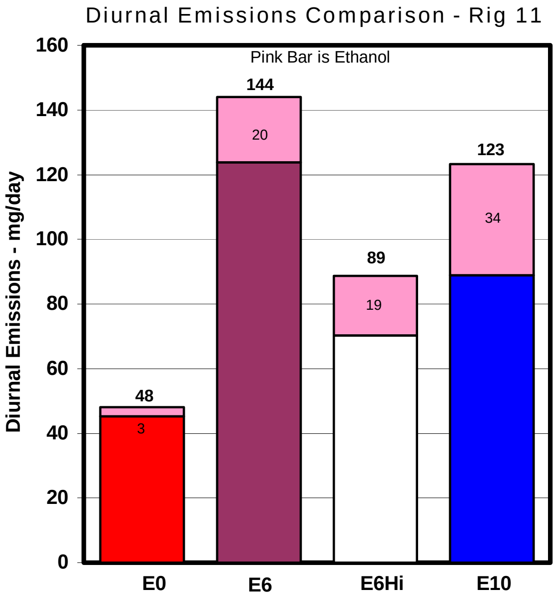

Figure 18

Rig 12 - When tested on the base (E0) non-ethanol fuel, this rig was measured at 35 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 15 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.

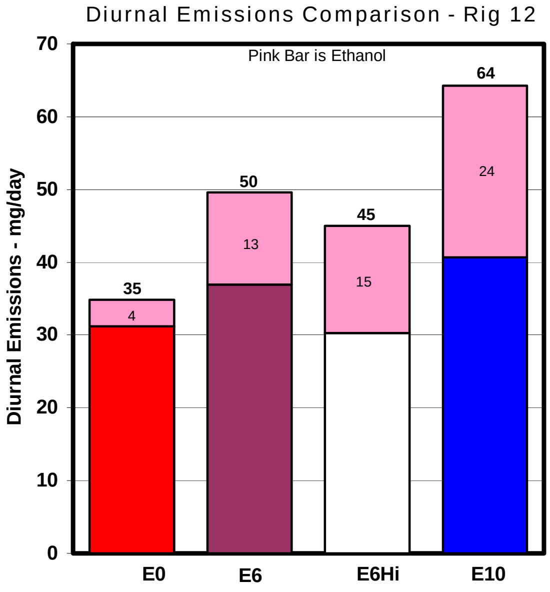

Figure 19

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 three fuels, with the average results shown in Figure 20. The permeation emissions were nearly doubled (466 vs. 260 mg/day) with the E10 fuel, compared to the E0 fuel, but were approximately halved (128 vs. 260 mg/day) when the E85 fuel was tested. The ethanol was 139 mg/day when tested with the E10 fuel, similar 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.

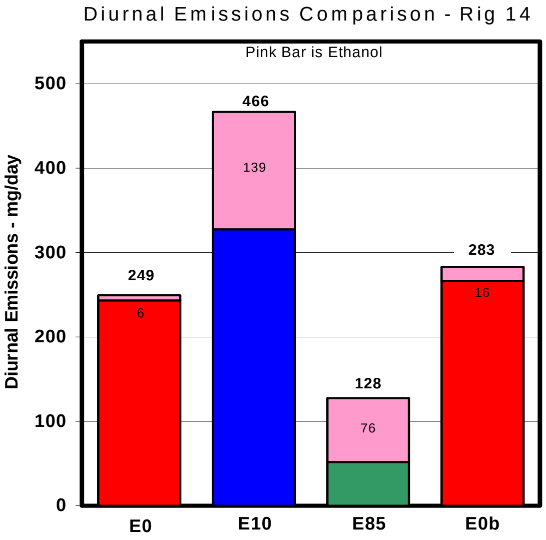

Figure 20

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	Steady-State 4-Week Avg. mg/hour	Diurnal Test ID	Diurnal mg/day	Ratio*	Permeate Specific Reactivity
E0	7.04	6389	83.9	11.9	4.31
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

Rig #2 - 2000 Honda Odyssey

Fuel	Steady-State 4 Week Avg. mg/hour	Diurnal Test ID	Diurnal mg/day	Ratio*	Permeate Specific Reactivity
E0	42.5	6390	463.3	10.9	4.26
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

Rig #11 - 2004 Ford Taurus

Fuel	Steady-State 4 Week Avg. mg/hour	Diurnal Test ID	Diurnal mg/day	Ratio*	Permeate Specific Reactivity
E0	3.59	6370	48.0	13.4	2.91
E6	11.2	6507	144.1	12.9	2.09
E6Hi	4.37	6598	88.7	20.3	2.58
E10	6.19	6675	149.3	24.1	no data
		6676	97.3	15.7	2.43
		Avg. =	**123.3**	**19.9**	**2.43**

*This is the ratio of the diurnal to the steady-state permeation.

Table 7 (cont)

Detailed Permeation Emission Results

Rig #12 - 2004 Chrysler Sebring

Fuel	Steady-State 4 Week Avg. mg/hour	Diurnal Test ID	Diurnal mg/day	Ratio*	Permeate Specific Reactivity
E0	3.22	6372	38.7	12.0	5.48
		6383	31.0	9.64	4.10
		Avg. =	**34.8**	**10.8**	**4.79**
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	3.03

Rig #14 - 2005 Chevrolet Tahoe

Fuel	Steady-State 4 Week Avg. mg/hour	Diurnal Test ID	Diurnal mg/day	Ratio*	Permeate Specific Reactivity
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
		Avg. =	**260.4**	**14.0**	**3.85**
E10	29.8	6454	466.3	15.6	3.05
E85	16.4	6555	142.3	8.68	2.63
		6566	112.8	6.88	2.82
		Avg. =	**127.6**	**7.78**	**2.73**

*This is the ratio of the diurnal to the steady-state permeation.

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 significantly when evaluated on the ethanol fuels. Rig 12, the “Zero Fuel Evaporative Emission” system, had a significantly different result when tested on the ethanol containing fuels in that the increase due to the ethanol was only 10 to 29 mg/day more than the base permeation rate, a much smaller increase than seen in the other rigs.

Table 8

Diurnal Emissions
Test Result (Average) – mg/day

	Test Fuel					Difference from E0, mg/day		
	E0	E6	E6Hi	E10	E85	E6	E6Hi	E10
Rig 1	84	475	361	468		391	277	385
Rig 2	463	1426	1227	1301		963	764	838
Rig 11	48	144	89	123		96	41	75
Rig 12	35	50	45	64		15	10	29
Average	158	524	430	484		366	272	326
Rig 14	260	-	-	466	128			

Steady-State Permeation Measurements

The plot format shown in Figure 21 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 from the author or CRC upon request.

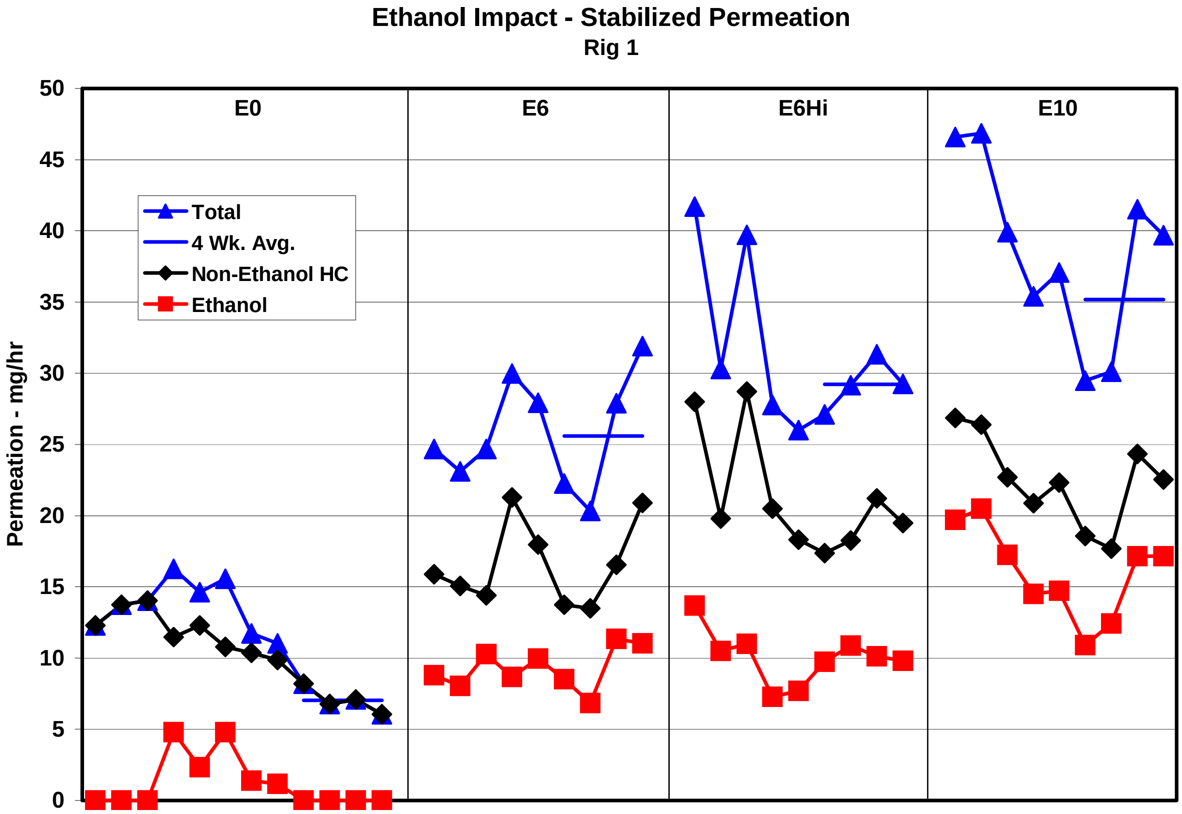

Figure 21

A concern arose when ethanol was detected in the steady-state permeation results, 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.

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.

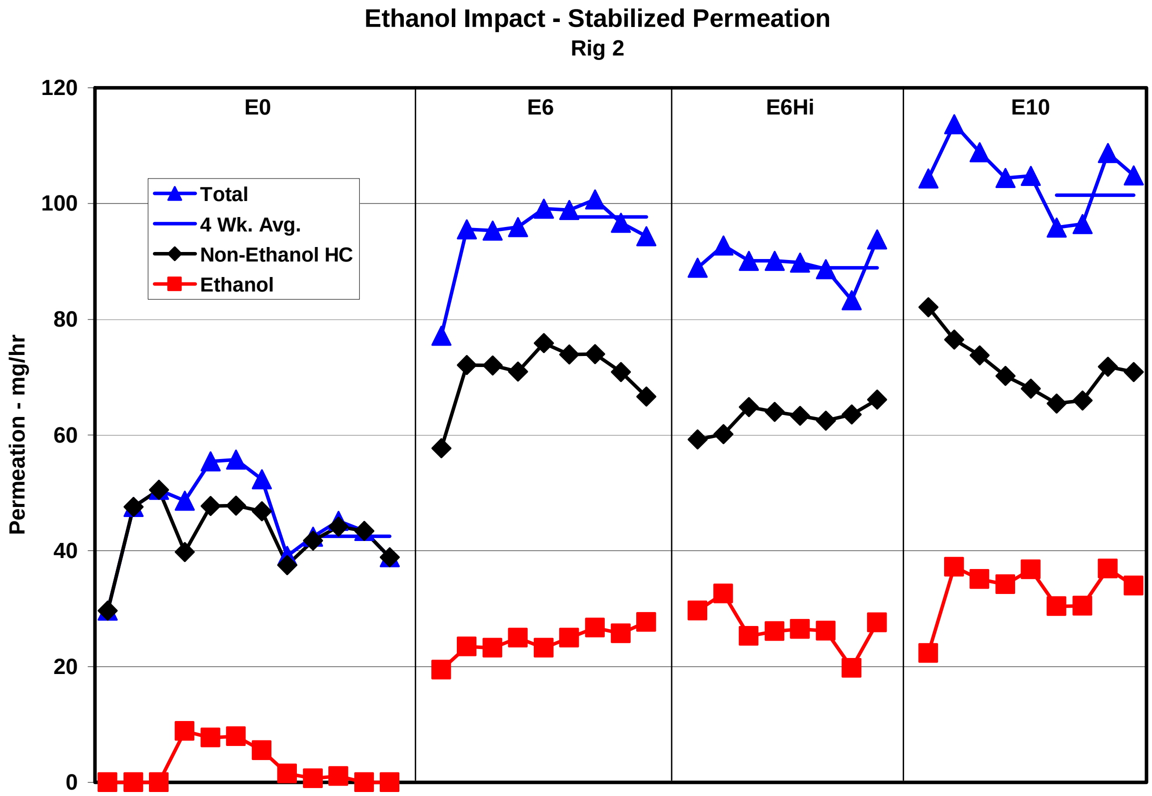

Figure 22

Rigs 1 and 2 showed similar trends in the permeation rate effect of the various fuels. Referring to Figure 21, the permeation rate increased sharply when the ethanol-containing E6 fuel was introduced. 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.

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).

Rig 11's permeation rate 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.

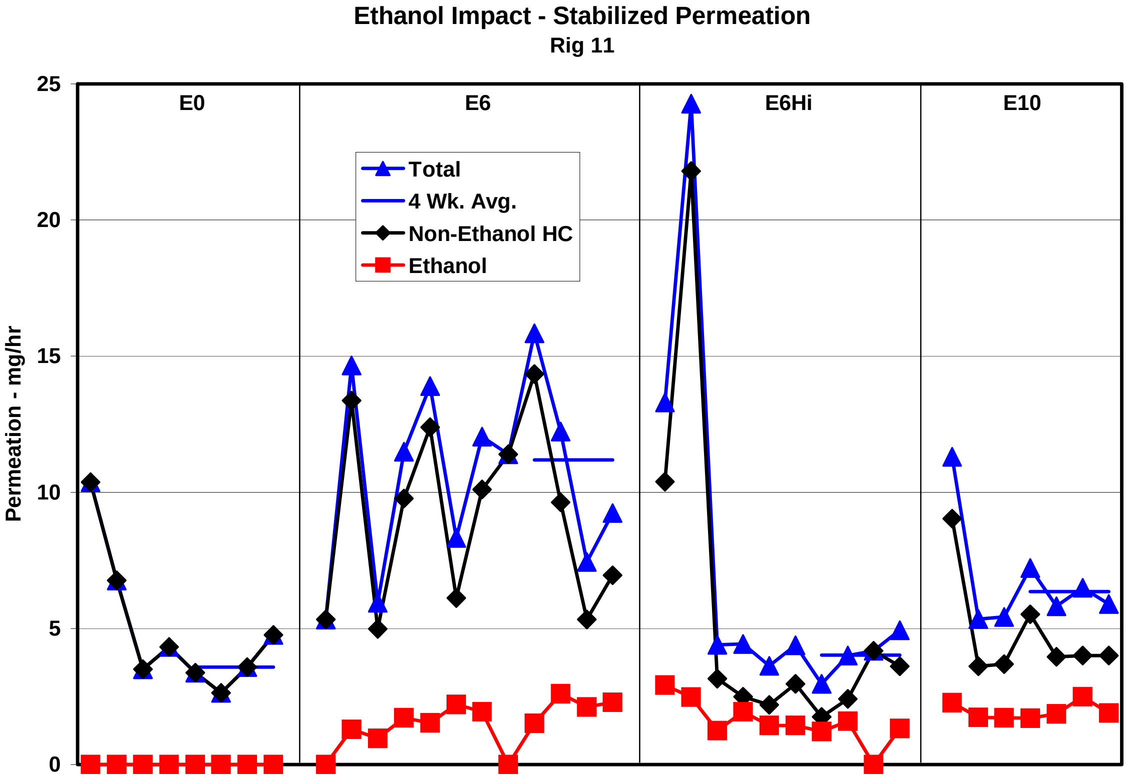

Figure 23

Rig 11's permeation performance 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, with any ethanol content below the detectable limit. The E6 fuel increased the permeation rate slightly, mainly because the ethanol component triggered into the detectable limit of 1 mg/hour.

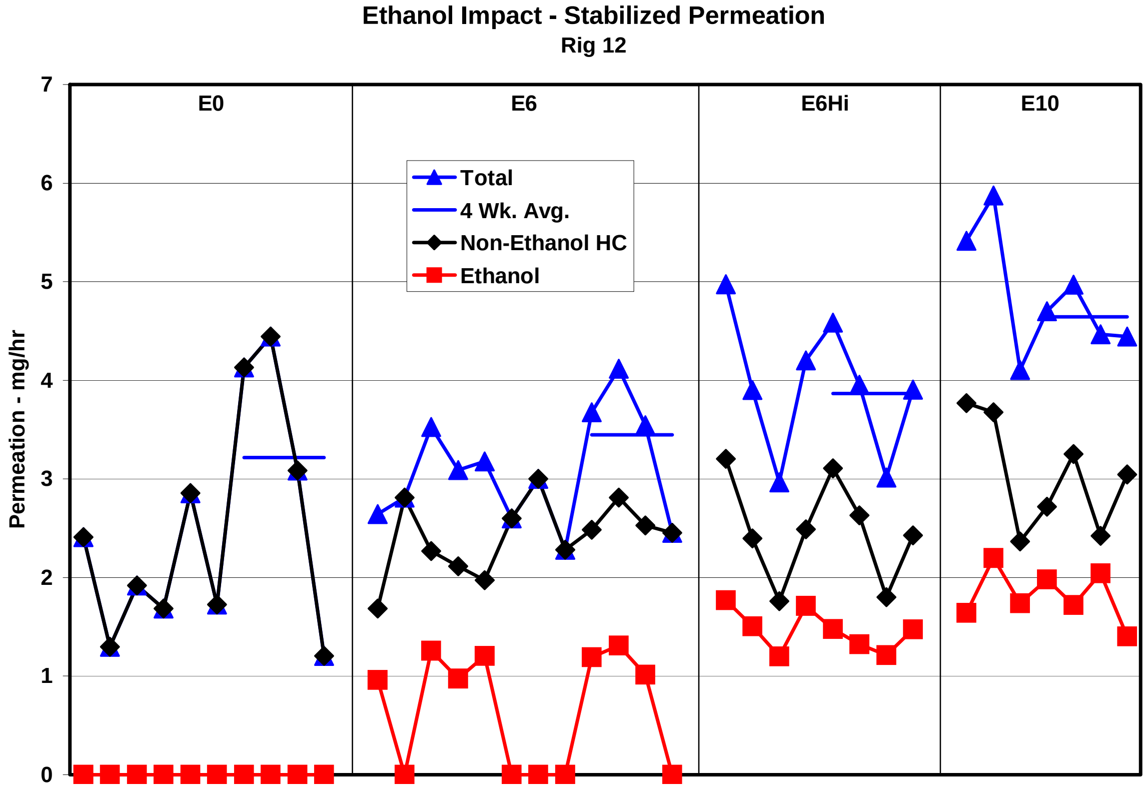

Figure 24

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 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 permeation results with the E10 fuel were the highest measured of the four test fuels, but the increase, when compared to the base fuel (E0), was low. This suggests that the better permeation performance systems may not be as sensitive to the increase with an ethanol blended fuel.

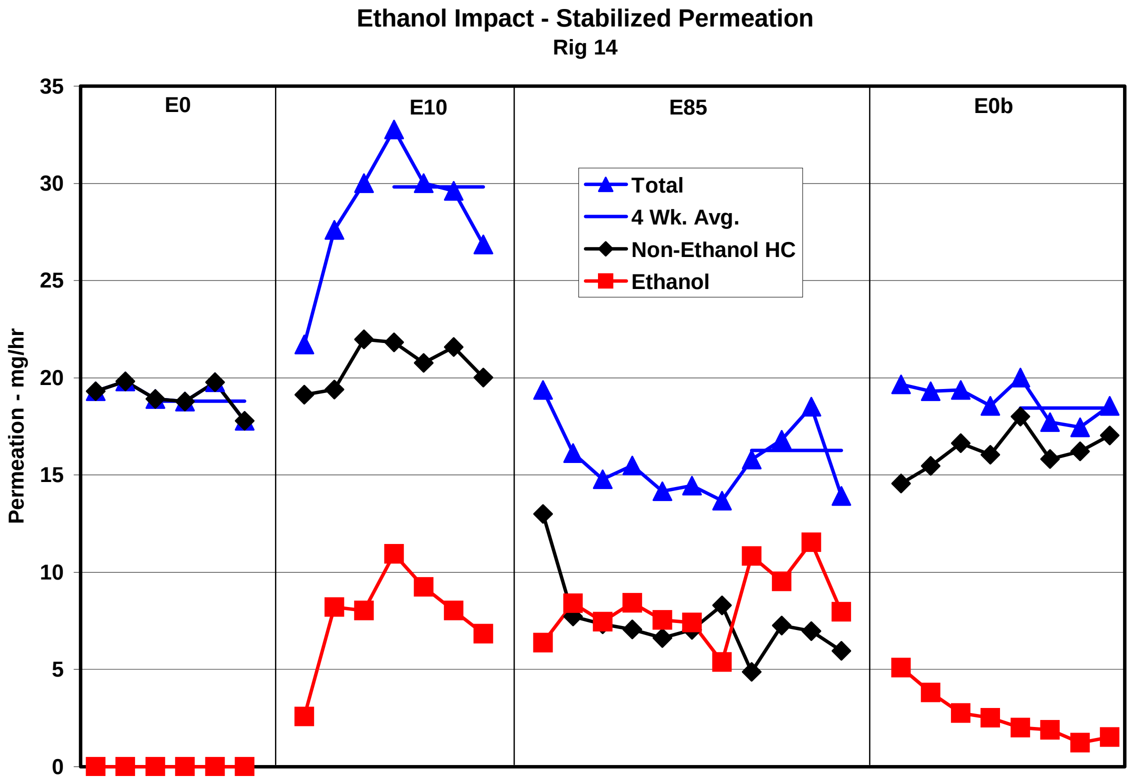

Figure 25

Rig 14 was tested on the E0, E10, and E85 fuels. The committee authorized a return to 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 1 and 2.

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 for Rig 1 – Fuel E0 Test 6389 is shown in Table 9. The complete speciation results are available from CRC. The listing has been reordered to match the speciation of the liquid E0 fuel, which was reordered to show the largest mass at the top of the list, then in decreasing order down to the lowest detected levels.

Table 9

Sample Speciation Results			24 Hour			
			Net mass	**Net conc.**	**%total**	
	Species Name	**CAS #**	**(mg)**	**(ppmC)**	**(mg)**	**(ppmC)**
18	2-Methylbutane (Isopentane)	00078-78-4	10.787	0.345	13%	12%
81	Toluene	00108-88-3	14.321	0.495	17%	18%
111.1	m-Xylene	00108-38-3	8.835	0.302	10%	11%
63	2,2,4-TriMePentane (IsoOctane)	00540-84-1	1.437	0.046	2%	2%
21	n-Pentane	00109-66-0	3.666	0.117	4%	4%
36.1	2-MePentane	00107-83-5	2.289	0.073	3%	3%
135.1	1,2,4-TriMeBenz	00095-63-6	2.131	0.073	2%	3%
49	Methylcyclopentane	00096-37-7	1.244	0.041	1%	1%
117	ortho-Xylene	00095-47-6	2.951	0.101	3%	4%
80	2,3,3-Trimethylpentane	00560-21-4	0.000	0.000	0%	0%
79	2,3,4-Trimethylpentane	00565-75-3	0.986	0.031	1%	1%
38	3-Methylpentane	00096-14-0	0.905	0.029	1%	1%
128	1-Methyl-3-Ethylbenzene	00620-14-4	1.501	0.051	2%	2%
59.2	3-Methylhexane	00589-34-4	0.722	0.023	1%	1%
40	n-Hexane	00110-54-3	1.475	0.047	2%	2%
34	2,3-Dimethylbutane	00079-29-8	1.514	0.048	2%	2%
109	Ethylbenzene	00100-41-4	2.066	0.071	2%	3%
111.2	p-Xylene	00106-42-3	2.591	0.089	3%	3%
57	2-Methylhexane	00591-76-4	0.809	0.026	1%	1%
74	Methylcyclohexane	00108-87-2	0.955	0.031	1%	1%
44	2-Methyl-2-pentene	00625-27-4	0.000	0.000	0%	0%
58	2,3-Dimethylpentane	00565-59-3	0.376	0.012	0%	0%
66	n-Heptane	00142-82-5	0.495	0.016	1%	1%
29	2,2-Dimethylbutane	00075-83-2	0.465	0.015	1%	1%
37	4-Methyl-t-2-pentene	00674-76-0	0.000	0.000	0%	0%
83	2-Methylheptane	00592-27-8	0.500	0.016	1%	1%
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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 five 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.

Table 10

Fuel E0 Diurnal Permeate Reactivity Results

Rig (test #)	Test ID	Reported SHED mg	Total GC Mass - mg	Mass w/MIR Values mg	Mass w/MIR Values %	Specific Reactivity	Rig Wtd. Average
1	6389	83.9	85.6	81.9	95.7%	4.31	
2	6390	463.3	391.4	369.8	94.5%	4.26	
11	6370	48.0	36.6	32.5	88.8%	2.91	
12(1)	6372	38.7	29.3	26.0	88.8%	5.48	4.02
12(2)	6383	31.0	34.1	33.4	97.9%	4.10	
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	

Eight diurnal tests on the E0 fuel were speciated (Table10). The average specific reactivity of the permeate of all the E0 diurnals was 4.02 (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 11

Fuel E6 Diurnal Permeate Reactivity Results

Rig (test #)	Test ID	Reported SHED mg	Total GC Mass - mg	Mass w/MIR Values		Specific Reactivity	Rig Wtd. Average
				mg	%		
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	

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 12

Fuel E6Hi Diurnal Permeate Reactivity Results

Rig (test #)	Test ID	Reported SHED mg	Total GC Mass - mg	Mass w/MIR Values		Specific Reactivity	Rig Wtd. Average
				mg	%		
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	

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

Table 13
Fuel E10 Diurnal Permeate Reactivity Results

Rig (test #)	Test ID	Reported SHED mg	Total GC Mass - mg	Mass w/MIR Values mg	Mass w/MIR Values %	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 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 14
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

Two speciated diurnals were conducted on Rig 14 with the E85 fuel, and the results are shown in Table 14. 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 2/3rds of the total mass (59 to 65 mass %).

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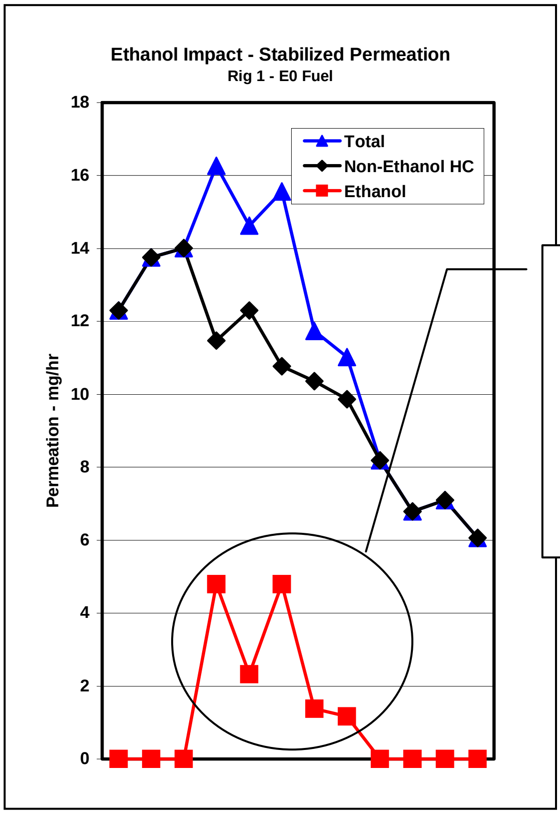
E. Appendix

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.

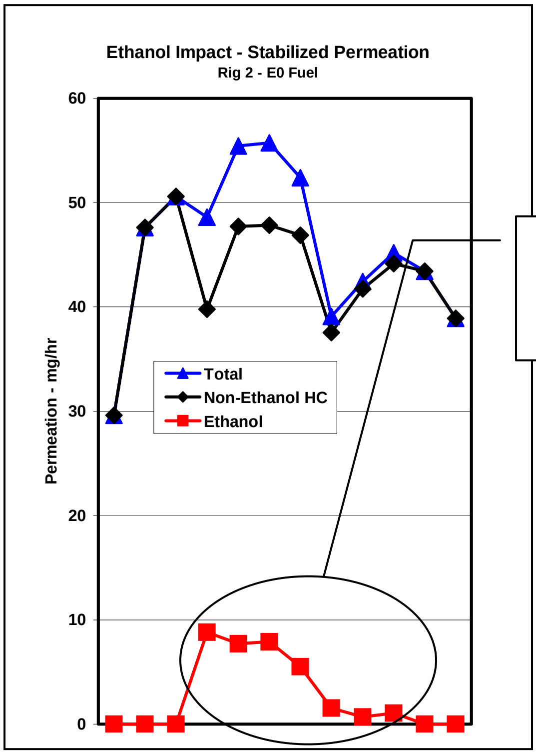
Figure 26

Table 15 - 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				

Rig	fuel	Week	Date	Test#	NonEtOH mg/hour	EtOH Mg/hour	NonEtOH + EtOH mg/hour	Running 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 26, and a similar presentation for Rig 2 follows in Table 16 and Figure 27. 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.



Rig 2, like Rig 1, also had a sudden appearance of ethanol in the results in the time period of 2-4-05 to 3-16-05.

Figure 27

Table 16 - 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 28, 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.

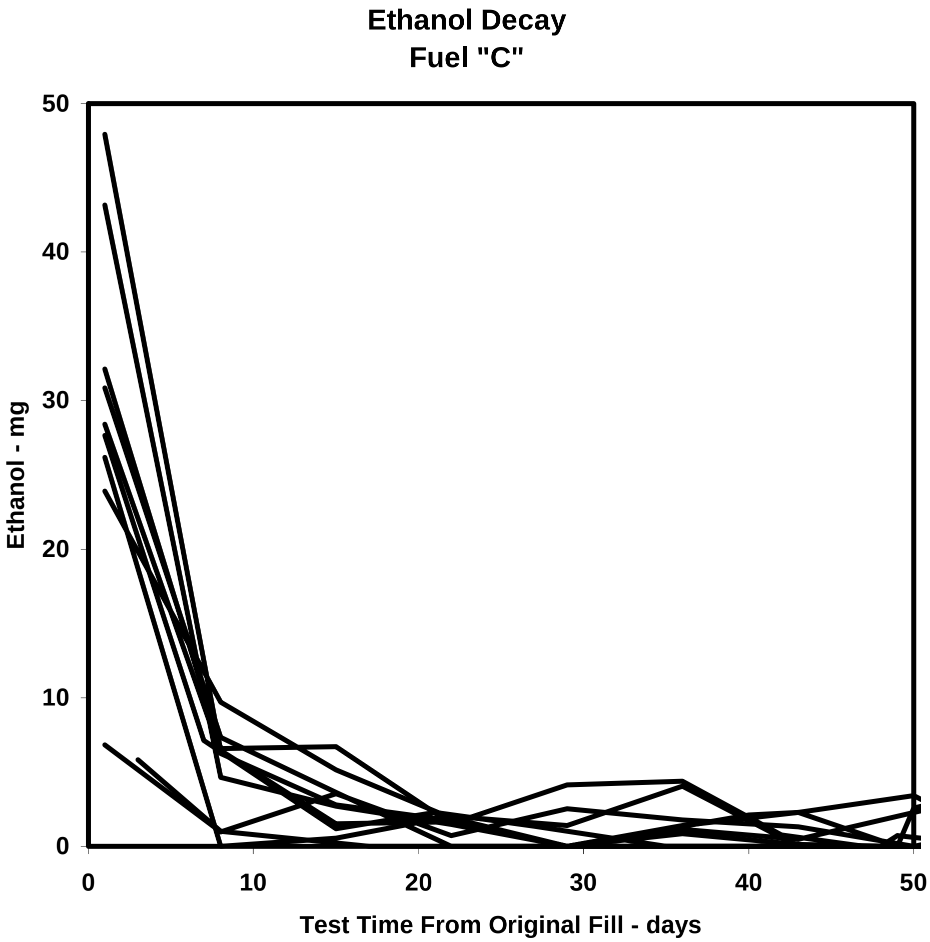


Figure 28

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.