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Hydrocarbon Permeation in Gasoline Vehicle Fuel Systems Using Isobutanol Blends

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ABSTRACT

In the past decade, a significant market has emerged for automotive fuels produced from renewable sources. Blends containing low concentrations of ethanol have been the readily-available choice for providing renewable content in gasoline fuels.

The simple addition of ethanol to gasoline significantly increases the mixture's vapor pressure, which can promote higher vehicle evaporative emissions. Gasoline specifications and blending practices have been updated to help offset the increase to vapor pressure and evaporative emissions. However, recent studies have shown that even at reduced vapor pressure, ethanol can increase gasoline evaporative emissions by enhancing the permeation of hydrocarbons through the elastomeric materials found in vehicle fuel systems.

Technology is currently in development that will allow for the production of isobutanol from renewable sources. In addition to high energy density, high octane, and good material compatibility, isobutanol has low vapor pressure impact when blended with gasoline and hence, low potential to drive evaporative emissions. However, until recently the impact of isobutanol to permeation emissions had not been determined.

A test program was initiated in 2007 to explore the permeation effects of using isobutanol in gasoline in place of ethanol. The study compared seven isobutanol and ethanol blends at varying concentrations while matching fuel properties such as vapor pressure, aromatics, distillation and oxygen content. Testing was conducted using fuel systems removed from seven vehicles representing three technology groups across model years 1981 through 2006. The program duplicated the Coordinated Research Council (CRC) E-65-3 study protocols which quantified the permeation impacts of MTBE (Methyl Tertiary Butyl Ether) and ethanol. The fuel systems were removed from the vehicles and mounted on custom aluminum frames in positions closely approximating the vehicle layout. The fuel system rigs were then exposed to each fuel until the permeation emissions were stable over a three week average. Permeation emissions were measured in an emissions test SHED (Sealed Housing for Evaporative Determination) at 105°F (40.6°C). After stabilization has been determined, the rigs were placed in a variable temperature SHED (VT-SHED) and tested on the California two-day diurnal (65°F - 105°F, 18.3°C - 40.6°C) to determine the permeation impact of each fuel. The results confirm that isobutanol can be used in gasoline with reduced impact on fuel permeation emissions.

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INTRODUCTION

A significant market has developed for automotive fuels produced from renewable sources. Ethanol has emerged as a leading candidate to fill this demand. When compared to petroleum-based gasoline, ethanol has lower energy density (which affects miles driven per tank of fuel) and increases the absorption of water, which can create fuel distribution difficulties. It has also been found to increase vehicle evaporative emissions when compared to a non-oxygenated blend, or one using MTBE. There are two reasons for the

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increase in emissions. The first one results from a vapor pressure increase, unless the base fuel is modified. The second and more important reason, is the increase in permeation emissions created when ethanol is added at low concentrations. As vehicle emission standards get tighter, evaporative emissions become a bigger issue. The California Air Resources Board (CARB) and the Environmental Protection Agency (EPA) have modified their predictive models to account for fuel permeation in vehicle evaporative systems.

Butanol, or butyl alcohol, is a primary alcohol with a 4 carbon structure and the molecular formula of $C_4H_{10}O$. There are four isomeric structures for Butanol: 1-butanol (or n-butanol), isobutanol, 2-butanol (or sec-butanol) and tert-butanol. With the exception of tert-butanol, the isomers occur naturally as a product of fermentation of carbohydrates, thus providing a renewable pathway required for the Renewable Fuels Standard [1] and the California Low Carbon Fuels Standard [2].

Biobutanol (Butanol produced from renewable sources) has the potential to be a good renewable component for gasoline. It offers higher energy density, lower Reid Vapor Pressure (RVP) and a lower oxygen content, which should allow for higher blend levels than ethanol, given the RVP constraints in Reformulated Gasoline (RFG). What was unknown is the potential permeation impact biobutanol will have on automotive fuel systems. This will be one of the questions that will need to be answered before its use will be allowed in California and other RFG regions.

In recent years, there has been an increasing interest in the potential use of butanol as an advanced biofuel component. This interest has been driven by the following:

• A higher energy density than ethanol, offering improved fuel consumption

• Greater water stability than ethanol, facilitating the introduction of butanol into the supply chain and providing the option of transporting gasoline/butanol blends by pipeline

• A lower vapor pressure than ethanol, facilitating the blending of light hydrocarbons into gasoline.

• Higher blend volume allowed due to oxygen content limitation. 10% ethanol = 16 % butanol on an oxygen content basis.

• Equivalence value of 1.3 RINs (Renewable Identification Number) relative to conventional ethanol for the Renewable Fuels Standard.

This report describes an extensive test program designed to evaluate the evaporative emission impacts and potential for using isobutanol instead of ethanol as a renewable component in North American gasoline.

Four questions were posed in the program in regards to permeation emissions.

1. Does isobutanol decrease permeation emissions when compared to ethanol at equivalent oxygen content levels?

2. Is there a positive synergistic impact of commingling ethanol and isobutanol blended fuels?

3. What impact does isobutanol have on ozone reactivity of the permeation emissions?

4. What impact does isobutanol have on potential ozone formation?

APPROACH

The test program objective was to compare the permeation levels of a variety of California summer type fuels using fuel systems from a range of vehicles. The approach was to emulate the practices and test procedures used in the CRC test studies conducted for the California Air Resources Board [3, 4]. The program was performed in two phases. Phase 1 testing involved alcohol blends with a target of 2% oxygen content and phase 2 testing utilized fuels with a target of 3.7% oxygen content. Fuels were tested in the following order: E0 - 2008, Bu9, E6, E6:Bu9 blend, E0 - 2009, E10, Bu16 and E10:Bu16 blend with the ethanol and butanol blends interchanged to account for any possible alcohol conditioning effects.

Seven vehicle fuel systems and a total of seven gasoline blends were included in this program. The vehicles were chosen to represent much of the current in-use California fleet, and the oxygenate levels tested spanned those proposed for California and Federal fleets. The testing laboratory (Automotive Testing Laboratory or ATL) procured the vehicles for testing from California retail sources, brought the vehicles to the laboratory in Arizona, and carefully inspected the vehicles to insure that the original fuel system was present and in good working order. After passing this initial inspection, the lab personnel removed the entire fuel system intact (without making any disconnections to the liquid or vapor system), and fabricated an aluminum rack or "rig" that held the components in their approximate x, y and z positions for the evaluation.



Figure 1. Typical test rig

All the fuel system components (with the exception of the engine mounted carburetor/injectors and hoses) 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, and required a "full-size" vehicle test SHED be used for the evaluation. For system integrity, all

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components were removed and remounted on the rigs without any fuel or vapor line disconnections. The test rig frame was constructed of 1.5″ (3.81 cm) square aluminum tube, with metal caster wheels at the four corners. Figure 1 shows a typical test rig used in the program.

Vehicle Selection

Seven vehicles (MY 1981 - 2006) were selected for this program. Each vehicle was inspected at time of purchase for any indication of non-representative operation, major repair, or for any modifications to the body or fuel systems. The vehicles were to be representative of in-use samples covering three major technology groups as shown in Table 1. The selected test vehicles are listed in Table 2. In Phase 1 of the study, only the three newest vehicles were tested, whereas all seven vehicles were tested in Phase 2.

Table 1. Vehicle Categories

Technology Class	Model Year	Emission Controls
Tech 3	1981-1985	older closed-loop three-way catalyst
Tech 4	1986-1995	closed-loop three-way catalyst
Tech 5	1996-2015	three-way catalyst, adaptive learning, LEVs

Table 2. Test Vehicles.

Rig ID	Make/Model	Cyl	Disp	Tank	Cert	Tech Group
1	2003 Toyota Camry	4	2.4L	Metal	ULEV	5
2	2006 Chevrolet Impala	6	3.5L	Plastic	Tier 2 Bin 8	5
3	2005 Dodge Caravan	6	3.3L	Plastic	LEV II	5
4	1991 Honda Accord	4	2.2L	Metal	Tier 0	4
5	1985 Nissan Sentra	4	1.6L	Metal		3
6	1981 Buick Riviera	8	5.0L	Metal		3
7	1994 Ford Taurus	6	3.0L	Metal	Tier I	4

Each vehicle was drained and filled with non-oxygenated fuel when they arrived at the laboratory. The vehicles were operated on the dynamometer for a minimum of 45 minutes (2 X LA-4 preconditioning) at least once per week until dismantled. The incoming vehicle inspection documented the vehicle condition and all identification data including odometer reading, vehicle identification number (VIN), engine size, emission identification data, and a description of emission control systems. Digital photographs were included in the vehicle log. An evaporative system evaluation test was performed and reported before the vehicle was dismantled. The test consisted of an LA-4 preconditioning, drain and 40% fill with non-oxygenated 7.0 psi (48.3 kPa) fuel, 12 to 36 hour soak, a bag-only Federal Test Procedure (FTP) exhaust emission cycle, a one-hour hot soak evaporative test, and one 24-hour 65-105°F (18.3- 40.6°C) California diurnal test. This was done to verify that the vehicles were performing consistent with their certification. After each vehicle was evaluated and determined to be a suitable candidate, the fuel system was carefully removed from the vehicle and mounted on a custom constructed aluminum frame for testing.

As was done for the CRC E-65 [3, 4] program, the fuel tank, fuel inlet and cap, vapor control canister, vapor and purge lines, and fuel lines to the inlet at the manifold were tested. The intake manifold, fuel injectors, and other engine parts were not included in the permeation test. This same protocol was followed during this study. Fuel caps were fitted with a stainless steel Swagelok® adapter to permit venting of the fuel tank vapor space. The outlet of the fuel vapor evaporative control canister was sealed and fitted with a similar adaptor. During testing, fuel vapors were directed from the two rig outlets to matching bulkhead fittings in the SHED wall, using non-permeable Teflon® hoses. Provisions were made to activate the fuel pump, permitting weekly circulation of fuel in the rig through all OEM lines and hoses. Similar adaptors to operate the purge control valves were installed for weekly system purge simulation. All openings, other than the two vent outlets, were fitted with caps and/or valves to positively seal the rigs during testing.

The expressed purpose and intent of this operation was to insure that only the low-level fuel system permeation emissions existing on the whole vehicle are measured during the test program. No repairs or additional parts were added, and no joints or connections on the vehicle's fuel system were broken during transfer from vehicle to fuel test rig. The resulting rig represented the fuel system as it previously existed on the production vehicle.

Test Fuels

Seven fuels were involved in this program:

1. Non-Oxygenated CARB Phase 3 Gasoline - E0
2. 6 V% Ethanol Blend - E6
3. 9 V% Isobutanol blend - Bu9
4. A 50:50 blend of E6 and Bu9
5. 10 V% Ethanol Blend - E10
6. 16 V% Isobutanol Blend - Bu16
7. A 50:50 blend of E10 and Bu16

The seven finished fuels are intended to mirror California Phase 3 specifications for 87 Octane gasoline. However, due to the match blending of the fuels, they do not comply with the California predictive model and the octane levels varied. There were also two batches of E0 fuel blended using identical blend recipes to cover the needs of the program from the 2007 to 2010 timeframe. Detailed properties are available for all test fuels in Appendix A, Table 8.

Two sets of fuels would target 2.0 wt% and 3.7 wt% oxygen content along with the non-oxygenate gasoline as shown in Figure 2. The blend RVP was matched at 7.0 psi (48.3 kPa) and an effort was made to minimize the differences in total aromatic content, olefin, benzene, toluene and distillation. This was done to minimize the impact those

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properties may have on fuel permeation. Figure 3 illustrates how closely the distillation characteristics (ASTM D86) of the test fuels were matched.

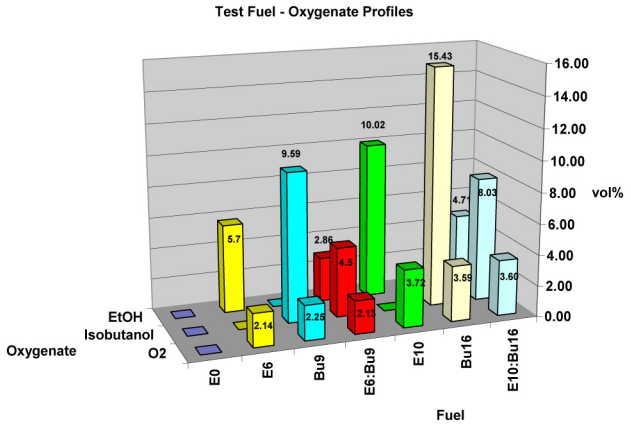


Figure 2. The oxygen content in weight %.

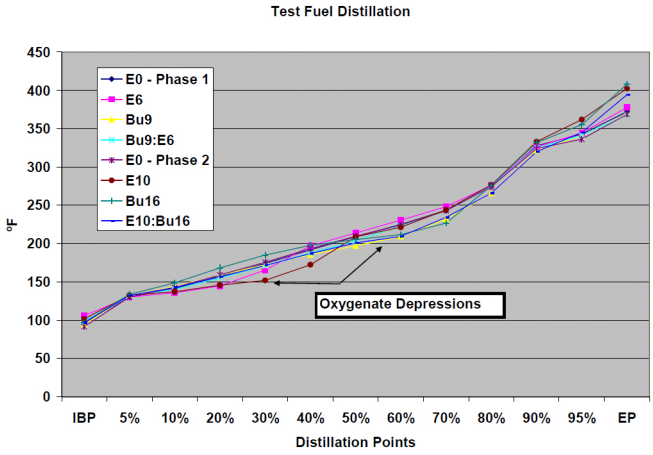


Figure 3. Consistent Distillation profile for all fuels

Test Procedures

Permeation is molecular migration of fuel through the elastomeric materials of the vehicle fuel system. The fuel systems had been carefully removed from the donor vehicles to isolate the fuel permeation emissions from the other vehicle sources, and there was concern about maintaining the integrity of the system during the conduct of the program. Fuel changes were made by using the vehicle's fuel pump to deliver the fuel to the fuel line connector (normally plugged) at the carburetor/fuel injector termination, and collecting the fuel in a catch can for disposal. Fuel fills were made through the vehicle's normal fuel cap/fill pocket component. Care was used to avoid any splash or spills that could contaminate the emission measurement. The test plan acknowledged that time would be required for permeation emission stabilization to occur after a new fuel composition was introduced, and could possibly require six to twelve weeks at the 105°F (40.6°C). Once stabilized on the candidate fuel, a California 2-day diurnal test was used to establish the permeation level

Stabilization

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 test rigs were kept in a constant-temperature test cell at 105°F (40.6°C) during the stabilization period as shown in Figure 4:



Figure 4. Test rigs in soak room

Table 3. Permeation Stabilization

Week	Date	Test#	HC mg/hr	r^2	Running Average
	04/23/08	Drain and 100% fill Fuel Bu9 (105°F soak)			
1	04/30/08	7222	15.3	1.00	
2	05/07/08	7227	20.0	1.00	
3	05/14/08	7231	21.3	1.00	18.9
4	05/21/08	7235	22.4	1.00	21.2
5	05/28/08	7242	24.5	1.00	22.7
6	06/04/08	7248	22.1	1.00	23.0
7	06/11/08	7253	23.1	1.00	23.2
8	06/18/08	7257	23.8	1.00	23.0
	06/23/08	Drain and 40% fill Fuel Bu9			
D1	07/08/08	7266	258.5		DHB
D2	07/09/08	7266	233.3		DHB

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 (40.6°C) 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 stabilized temperature. A five hour steady state test, using the average hourly permeation rate for the last three hours was used to quantify the weekly permeation level. An example of

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the data and reporting is shown in Table 3 for rig 1, the Toyota Camry system, tested on the Bu9 fuel.

A plot of the weekly stabilization measurements is provided in Figure 5. The weekly status report recommended that this rig be considered "stable" and advanced to the two-day diurnal evaluation.

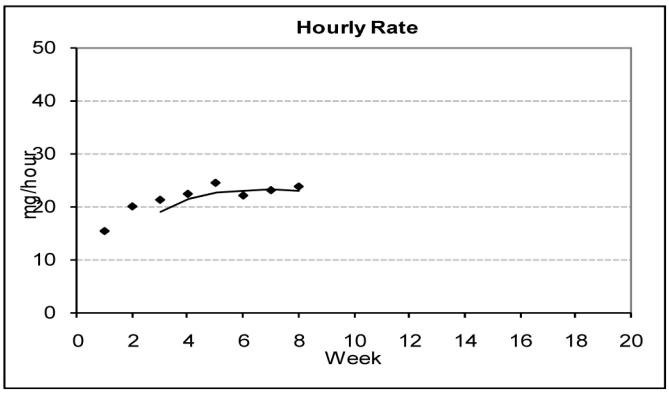


Figure 5. Permeation Stabilization

Diurnal Evaluation

After the rig's permeation rate was stabilized at 105°F (40.6°C), it was evaluated for diurnal permeation performance using the California "Real-Time" 24-hour diurnal (65 to 105 to 65°F, 18.3 to 40.6 to 18.3°C) 2-day 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, the canister vented to the outside, and the California 2-day diurnal procedure performed. 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 alcohols in the permeate.

The SHED atmosphere was sampled at the start of the test (T_0), at the end of the first day (T_{24}), and at the end of the second day (T_{48}) to allow a detailed speciation analysis for each diurnal day using Gas Chromatography (GC). The process was repeated for all fuel/vehicle combination. A synopsis of the detailed test procedures are listed in Appendix B.

Test Equipment

The SHEDs used in this test program comply with the requirements described at 40 CFR §86.107-96, Sampling and Analytical Systems; Evaporative Emissions, and use the calculations described at 40 CFR §86.143-96, Calculations; Evaporative Emissions with modifications to accommodate the various alcohols.

ATL developed a hydrocarbon speciation method that is functionally equivalent to the dual-GC AQIRP (Auto/Oil Air Quality Improvement Research Program) method that was first documented in two SAE publications [5,6] and later updated in a third publication [7].

Instrumentation demands are simplified, and overall analysis time is shortened with the new procedure; yet high resolution and sensitivity are still achieved. In this single-GC/ dual column method, all components are separated using on-column type and temperature program. Analysis time for a cycle is 65 minutes. Each exhaust or evaporative gas sample is simultaneously injected (using a single sampling from the bag) into two identical columns present in the GC. A Varian Model 3400 GC is used for hydrocarbon (HC) analysis. The GC is equipped with a dual temperature-controlled Valco 6-port valve injector; dual flame ionization detectors (FID), and dual 60 meter × 0.32-mm ID fused silica capillary columns with a 1.0 µ polydimethylsiloxane stationary phase (J&W DB-1). One of the injectors uses an 85 µl sampling loop for low sensitivity analysis of C_1-C_{12} while the other injector either uses a 1000 µl loop for high sensitivity analysis of C_4-C_{12} (for simultaneous low/high sensitivity analysis of a single bag sample). Column A contains an 85µl sample loop (split-less injection) that provides an injection volume that is small enough to allow resolution of the C_1 through C_4 hydrocarbons while large enough to retain the highest sensitivity possible. Column B receives a 1000 µl split-less injection, providing higher sensitivity for components eluting after isobutane. Quantitative comparison of two overlap components (butane and isopentane) provides a quality control measure. Data from Column A is used to detect and quantitate the 12 earliest eluting hydrocarbons with detection limits of 15-25 ppb_vC, corresponding to 0.2-0.3 mg/mi (0.12-0.19 mg/km) hydrocarbon for FTP stages 1 and 3, and 0.3-0.5 mg/mi (0.19-0.31 mg/km) for FTP stage 2. Data from Column B gives detection limits 0.017-0.04 mg/mi (0.011-.025 mg/km) HC for components eluting after isopentane (18^{th} in elution order). The components eluting between the 9^{th} and 18^{th} in elution order have detection limits ranging between the levels listed above for each column.

The advantage of this approach is that, even for relatively clean vehicles, essentially all of the first 12 species are typically present at levels exceeding the Column A detection limit. Those speciated components that are below the first column detection limit tend to be in the molecular weight range best suited for the 1000 µl injection analysis, which provides the limits 0.017-0.04 mg/mi (0.011-.025 mg/km) HC for components eluting after isopentane (18^{th} in elution order), where additional sensitivity is needed. In previous work that applied this analysis approach, detection limits were determined to be between 0.02-0.06 mg/mi (0.12-0.037 mg/km) for the toxics 1, 3-butadiene and benzene.

ATL's hydrocarbon method uses Varian 3600 GCs with dual injectors, columns, and flame ionization detectors, allowing two similar analyses to be run simultaneously, as

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Table 4. As-received Vehicle Data.

Rig ID	As Received Vehicle Evaluation NMHC g/mile	CH4 g/mile	HC g/mile	CO g/mile	NOX g/mile	CO2 g/mile	FC mpg	As received Evap Test grams
1	0.023	0.005	0.028	0.361	0.070	337.7	26.3	2.546
2	0.042	0.026	0.068	1.247	0.030	429.9	20.6	0.188
3	0.024	0.012	0.036	0.410	0.031	457.7	19.4	0.398
4	0.242	0.047	0.289	2.336	1.307	334.2	26.2	0.41
5	6.482	0.237	6.722	48.27	0.283	217.5	28.3	13.53
6	0.192	0.143	0.336	5.642	0.694	556.4	15.7	22.45
7	0.342	0.040	0.383	4.132	2.009	394.6	22.1	16.21

Note: As received Evaporative Test is a one day diurnal + hot soak [9].

mentioned above. A Varian Star PC-based (using Microsoft Windows) data system is used for data acquisition. Custom-made software is used for peak identification and converting data into a Microsoft Excel spreadsheet format. A comparison of the total hydrocarbon determined using the GC versus the Continuous Volume Sampler (CVS) ("speciation recovery") is used as a quality control measure, and ATL routinely achieves hydrocarbon speciation recoveries ranging from 93% to 105% for lower emitting vehicles. A 23-hydrocarbon component standard mixture is analyzed at the start of each day on each GC to provide quantifying coefficients and a quality control check on daily reproducibility of instrument performance.

The GC used to speciate the permeation is not very good at measuring ethanol. To compensate for this deficiency a special procedure was utilized to improve the accuracy of the ethanol measurements in the permeate. The test rigs were isolated in a SHED. During each SHED test, periodic samples were withdrawn from the enclosure and analyzed with a GC to determine alcohol ppm concentrations by volume. New vehicle certification procedures were used to separate the concentration of each alcohol from the total hydrocarbon concentration. This requires the determination of a response factor for the SHED flame ionization detector for each alcohol, subtraction of the corrected alcohol ppm from the FID total, calculation of the remaining mass of the HC using the average density for each SHED measurement, and an independent computation of the mass of the alcohol. The two masses (alcohol and HC) are then summed to provide the total SHED mass.

The Rosemont FIDs at ATL have an r factor (identification factor) of 0.66 for ethanol. This means that it undercounts the ethanol by about 1/3rd. The INNOVA analyzer was used to estimate the "real "concentration of ethanol, as allowed and approved by CARB [8]. The apparent ethanol was subtracted from the FID concentration, and the "non-ethanol" fuel mass in the sample was calculated. The real ethanol mass was added to the total to get the final mass number for total ethanol content.

The isobutanol was not "corrected" in the report. The ATL analyzers have an r factor of 1.04 for the isobutanol molecule, so they over-count the isobutanol by 4%. Since the isobutanol is less than 20% of any of the measurements (as identified by the GC), the isobutanol "correction was considered as a de minimus correction (.2 × .04 or less than 1% of the total) and was not applied to the calculations.

Vehicle Evaluations

Each vehicle was tested on a non-oxygenated fuel to evaluate the vehicle emissions performance to insure that the vehicle was operating properly, as shown in Table 4. A diurnal test was also conducted to evaluate the performance of the evaporative system on the vehicle. The diurnal testing did not show anything unusual. As expected, because of its age and the low technology level of the system, rig 6 (1981 Buick) produced the highest diurnal emissions, as shown in Figure 6. Test rigs 1 through 3 were previously tested in phase 1 of this study and were exposed to lower levels of ethanol and isobutanol content. The remaining fleet was only exposed to the higher blends.

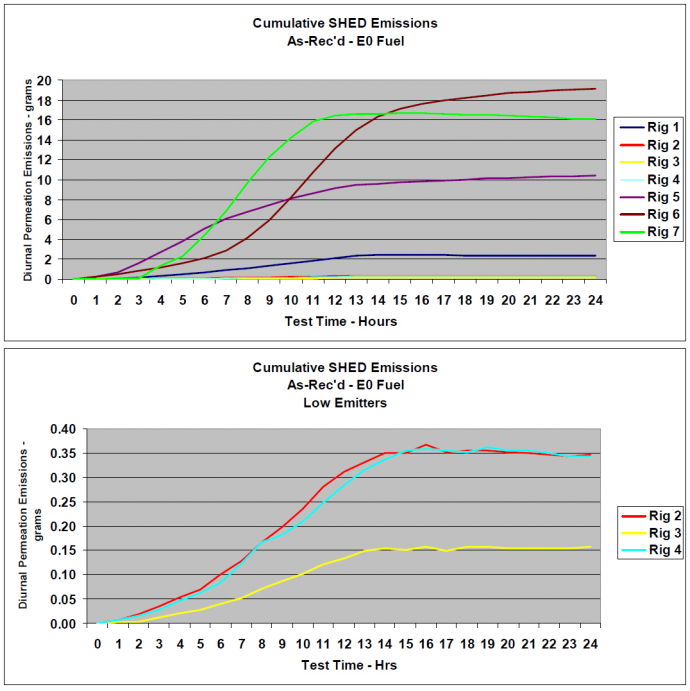


Figure 6. As-received diurnal evaporative emissions testing.

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The vehicle selection was intended to cover three technology classes and roughly represent the California fleet in 2007 as shown in Figure 7.

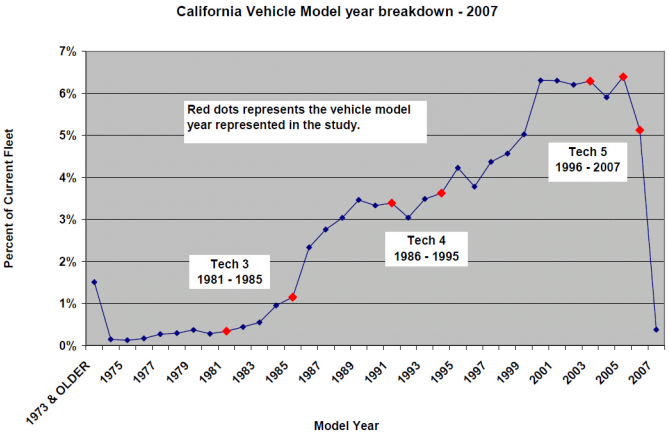


Figure 7. Vehicle selection profile based on the 2007 California fleet data from R.L. Polk.

MEASUREMENTS AND RESULTS

This section presents the test results for the steady state permeation measurements, the diurnal permeations, and the Ozone Forming Potential.

Steady State Permeation Emissions

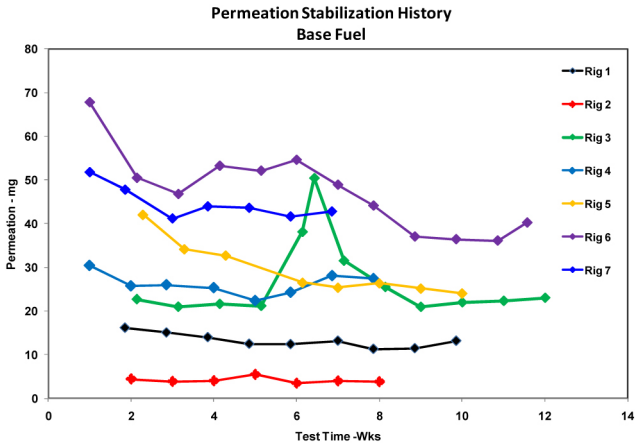


Figure 8. 105°F Steady State Stabilization Permeation Results - Baseline.

Figure 8 shows the steady state stabilization history of each test rig with E0 fuel. As expected, rig 6 had the highest permeation rate and rig 2 had the lowest permeation rate. Rig 2 is the most recent model year vehicle, and was the low emitter in all cases. Compared to the CRC E-65-3 [3] study, the permeation rates of the seven vehicles in this study compared favorably to the range seen in E-65 as shown in Figure 9.

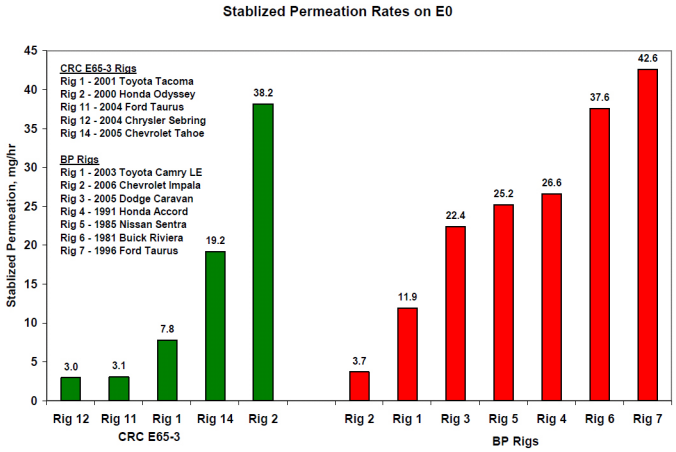


Figure 9. Steady State Permeation Comparison to CRC E-65-3 study on E0.

The steady state stabilization at 105°F (40.6°C) for each vehicle displayed a trend showing isobutanol to permeate less than ethanol, which is shown in Figure 10. Five of the seven rigs produced the anticipated results with the E0 producing the lowest permeation rate and E10 producing the highest. However, on Rig 3, the E0 in 2007 was measured to have the highest permeation rate of all the fuels, which is in contrast with the rest of the fleet. Generally, the mixed 50:50 blended fuels produced permeation rates between the respective ethanol and isobutanol blends. Rig 3 was the lone exception again, displaying higher permeation in the mixed fuel in Phase 2 (2009), but E10 was lower than E0. Rig 7 produced the highest average permeation rate across the fuel slate. The general trend in the test fleet was increasing steady state permeation in the following order E0 < Bu16 < E10:Bu16 < E10 for the higher blends. For the lower blends, the trends were not quite clear except that Bu9 < E6:Bu9 <E6.

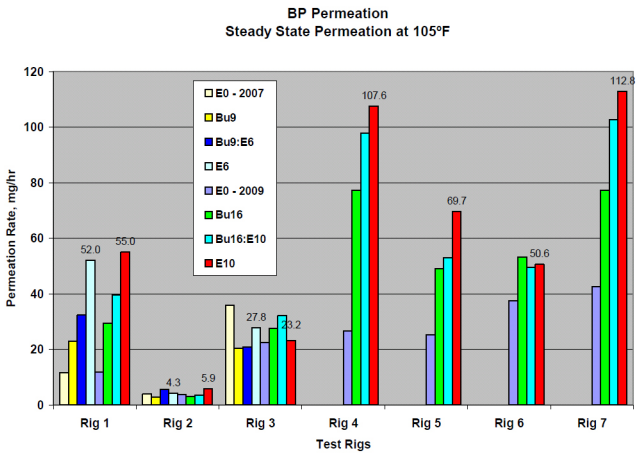


Figure 10. Steady State Stabilization Permeation Results

Diurnal Permeation Emissions

The diurnal permeation rates varied from a low of 95 milligrams/48 hours when tested with Bu9 on rig 2, to 3,129

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mg/48 hours when the E10 was tested on rig 7. As shown in Figure 11, rig 7 was shown to have the highest diurnal permeation rate out of the seven vehicles which is consistent with the steady state testing. However, the diurnal permeation behavior between fuels was not consistently comparable to the steady state permeation rates. This is not unexpected as the diurnal test was temperature cycling below and up to the steady state test temperature and was conducted with a different fuel level in the tank. Rig 6 had shown the highest permeation rate with Bu16. However, the general trend across the fleet, with the exception of rig 6, was higher permeation rate for ethanol blends vs. isobutanol blends. The synergistic effect of the 50:50 blends of the higher blends of ethanol and isobutanol was mixed with rigs 3 and 5 showing a negative effect, meaning higher permeation rates than the ethanol or isobutanol blends alone and rig 6 showing a positive effect which was also lower than the corresponding E0 fuel. The effect occurred on one rig from each technology group. All other rigs fell between the ethanol and isobutanol blends. For lower blends, the 50:50 blends produced the highest diurnal permeations compared to E0 and the lower alcohol blends. The diurnal permeation pattern was consistent from Day 1 to Day 2 as can be seen in figures 11 and 12.

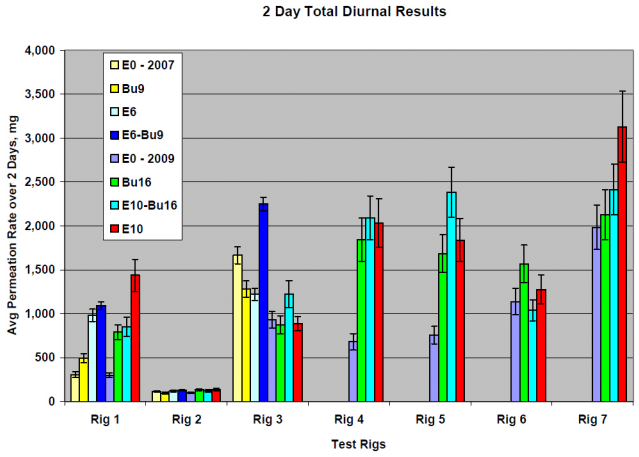


Figure 11. Two Day Total Emissions of the 24-hour California Diurnal Cycle (65°F to 105°F to 65°F, 18.3°C to 40.6°C to 18.3°C).

Eight rig/fuel combinations produced higher permeation rates on the second day of the 2-day diurnal test. This behavior was not seen previously in E-65. Statistical analysis of phase 2 data indicated that Day 1 emissions were on average higher than Day 2 by about 8%. Including a day*rig interaction in the statistical analysis gave statistically significant coefficients for rigs 2, 3 and 4. (rigs 2 and 4 were about 20% higher on Day 1 while Rig 3 was 10% lower. Other rigs were between 3% and 8% higher on Day 1.) The rig*day effect may not have been detected in the CRC E-65 program simply because its magnitude is small or the experimental rigs all showed the same trend. In any case, this effect is not related to fuel type. So, it is not a concern of this report. Rig 2 has consistently demonstrated very low permeation rates across all fuels.

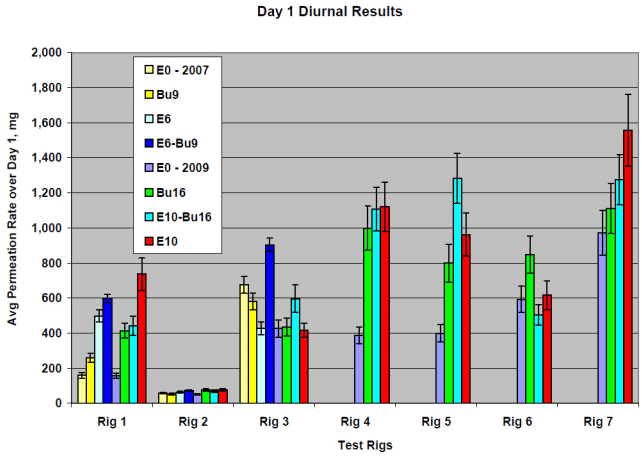


Figure 12. Day 1 Diurnal Permeation Rates

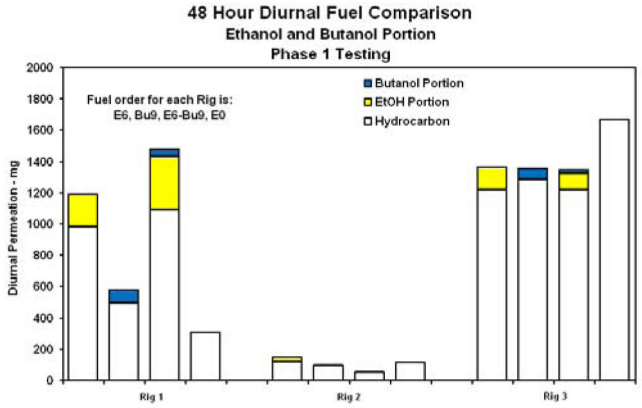


Figure 13. Phase 1 General Permeate comparison, 48 hr total

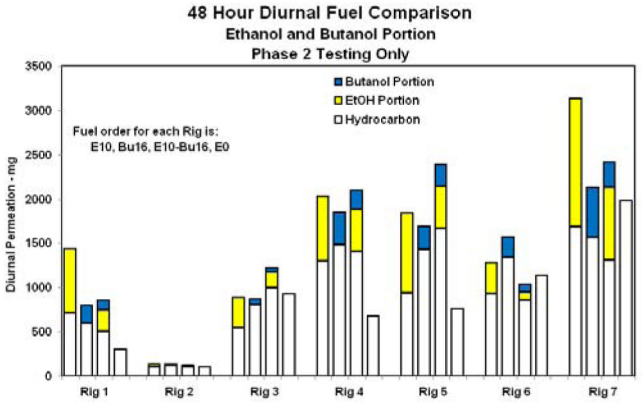


Figure 14. Phase 2 General Permeate comparison, 48 hr total.

During the diurnal testing, the permeate was speciated to determine the alcohol and hydrocarbon content that was

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being emitted. Figures 13 and 14 show a general profile for each vehicle on each oxygenated fuel. They show that the ethanol blend permeations have a higher concentration of oxygenate in the permeate than the isobutanol blend permeations in both phase 1 and phase 2 testing. The concentration of isobutanol is significantly lower than that of ethanol in the permeate of the 50:50 blends despite the higher isobutanol content in the fuel relative to the ethanol content. Rig 6 was the lone exception. Rig 2 has consistently produced ultra low levels of permeation emissions across all fuels with the highest total diurnal permeation rate of 136 mg.

Hydrocarbon Species Comparison

In this study, the permeate was speciated to determine what kind of hydrocarbons were permeating out of the fuel systems. This discussion will focus on the phase 2 blends. Past studies have indicated that aromatics are a significant component in the permeate. The hydrocarbons from the permeate were compared with the hydrocarbon makeup of the fuels. In examining the top 20 hydrocarbon species in the permeate for each fuel, they account for more than 75% of the total permeation emissions across all test rigs with the lone exception of Rig 2 on Bu16 where the top 20 species accounted for 64% of the total. Tables showing the comparison of the top 20 species in the diurnal permeation emissions and the component composition in the test fuels are located in Appendix C, Table 9, 10, 11, 12, 13, 14, 15, 16.

From a compositional standpoint, benzene, toluene, butane, pentane and isopentane are disproportionately higher in the permeate relative to the concentration in the fuel regardless of fuel type on each rig. Ethanol dominated the permeate at more than 3 - 5 times the level seen in the fuel. The average isobutanol concentrations across the fleet in the permeate on the other hand tend to be closer to the concentration seen in the fuel. The same behaviour can also be seen in the 50:50 blends (E10:Bu16, E6:Bu9) where ethanol dominates the permeate and the isobutanol content in the permeate mirrors the concentrations seen in the liquid fuel.

Although the concentration of the two main aromatic compounds (benzene and toluene) in the permeate are similar across all fuels and rigs, the mass contribution as shown in Table 5 indicates on average a significant increase due to the presence of alcohol. Unlike in phase 1, where only Tech 5 vehicles were tested, the isobutanol blend did not outperform the ethanol blend in regards to the dominant aromatic compounds in the permeation emissions. Benzene and Toluene were lower in the isobutanol blend when compared to the ethanol blend in phase 1 testing. In phase 2, E10 produced the highest average permeation rate for benzene across the test fleet. For toluene, the highest average permeation rate across the test fleet was produced by the Bu16 and the 50:50 blends. Four out of seven rigs recorded their highest toluene permeation rate by mass on Bu16 when compared to the other fuels. Those four test rigs were taken from the older vehicle group.

Table 5. Impact on Aromatic Emissions

Benzene	mg/48 hrs							
	Phase 1				Phase 2			
	E0 - 2008	E6	Bu9	E6:Bu9	E0 - 2009	E10	Bu16	E10:Bu16
Rig 1	13.4	35.6	23.8	45.2	14.5	66.4	27.2	34.8
Rig 2	4.5	3.3	3.0	3.3	4.2	3.9	3.4	3.4
Rig 3	56.1	41.0	27.7	72.1	31.2	25.7	25.9	31.0
Rig 4					41.9	94.7	106.2	89.2
Rig 5					32.9	80.4	58.7	85.3
Rig 6					46.9	35.2	30.1	27.1
Rig 7					53.1	104.0	88.8	87.9
Toluene	**mg/48 hrs**							
	Phase 1				**Phase 2**			
	E0 - 2008	**E6**	**Bu9**	**E6:Bu9**	**E0**	**E10**	**Bu16**	**E10:Bu16**
Rig 1	34.0	108.4	56.8	125.4	35.5	189.8	128.2	124.9
Rig 2	13.5	9.4	7.7	9.3	11.3	11.9	16.2	14.8
Rig 3	158.8	124.1	72.6	202.9	84.6	67.2	109.2	111.5
Rig 4					123.2	288.4	393.8	345.3
Rig 5					101.0	246.1	244.4	351.9
Rig 6					146.4	114.0	152.2	128.1
Rig 7					182.2	281.6	323.5	311.8

Ozone Forming Potential

The Ozone reactivity for each fuel was calculated using the Carter Maximum Incremental Reactivity (MIR) methodology [10]. The Carter MIR scale for various Volatile Organic Compound (VOC) molecules has been adopted by CARB to estimate the ozone forming potential. Utilizing the Carter MIR methodology, the ozone forming potential of the permeation emissions can be estimated. As shown in Appendix D, the ozone reactivity of the fuels are similar. Ethanol is estimated to be lower on average than the other fuels due to the dilution effect of ethanol even though the fuel produces much higher mass emissions. On average across the seven systems, the isobutanol impact is no worse than the base fuel in regards to ozone reactivity. In phase 1 testing, which covered the three newest vehicles only, the data suggests that at lower oxygenate concentrations in the fuel, the ethanol dilution effect was not sufficient enough to overcome the mass emission impact. In this case, the ethanol produced the highest ozone reactivity.

DISCUSSION OF RESULTS

In the data analysis, there was an attempt to discern a trend in the data set. Four questions were posed in the program in regards to permeation emissions. 1) Does isobutanol decrease permeation emissions when compared to ethanol at equivalent oxygen content levels, 2) is there a positive synergistic impact of commingling ethanol and isobutanol blended fuels, 3) what impact does isobutanol have on ozone reactivity of the permeation emissions and 4) what impact does isobutanol have on potential ozone formation? These questions were addressed in the following section.

Statistical analyses of the levels of diurnal emissions, hydrocarbons (VOC), ozone and permeate reactivity were conducted using general linear models. Alcohol concentration, rig, testing phase, diurnal time and various interactions were independent variables. Appendix E, Table

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