

**California Air Resources Board  
Panel Discussion  
on the  
Reformulated Gasoline Regulations**

**Sacramento California  
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## **Issues Related to Permeation Emissions**

**Information Submission by  
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on behalf of  
The Renewable Fuels Association**

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## **Introduction**

This written submission and my comments today are on behalf of the Renewable Fuels Association (RFA). The RFA is the national trade association for the U.S. fuel ethanol industry. RFA member companies produce approximately 90% of all the domestic fuel grade ethanol made.

Today I want to comment on the recent Coordinating Research Council (CRC) report “Fuel Permeation From Automotive Systems (CRC Project E65)”. First, we commend the Air Resource Board for initiating this first step to begin to quantify the permeation rates of different fuels in different model year vehicles.

For years, the technical literature has shown that fuel permeation through fuel system plastics and elastomers can be impacted by fuel composition including oxygenate content and aromatics content. Similarly previous programs have demonstrated that certain elastomers are more susceptible to permeation than others. Of course, one problem with previous tests is they have typically used one component employing test procedures that have changed over the years. Moreover, these test results were difficult to apply in the real world due to various lengths and diameters (or surface area) of these materials as used in the in-use fleet.

The idea behind the rig design approach employed in the CRC E65 project was to isolate the fuel system components subject to permeation, from all other sources of evaporative hydrocarbon emissions. It was thought this design would best capture/isolate the permeation emissions without interference from other hydrocarbon sources. We believe the approach of using test rigs incorporating the entire fuel system, as was done in this study, to be a sound approach. There is little doubt that this work represents the most extensive assessment of permeation emissions by fuel/vehicle type to date.

As ARB is aware, I represented the RFA on the E65 project steering committee and the report review committee. The RFA appreciates being included in this important work. While we agree with the procedures employed and measurement techniques, like all studies or programs that have budgets, this study has limitations. Likewise, this is the first time this approach and procedure was used so there may be opportunities to improve upon procedures and the precision of the technique in future work. While we discuss such issues in these comments, they are not meant to be critical of the process, but rather issues that, in the ease of hindsight, leave questions. It is also important that these limitations be

recognized in considering any regulatory steps or modifications to the Predictive Model. Finally, we believe any regulatory changes or modifications should also incorporate other assessments such as Phase II of the CRC permeation study and the CRC E67 project results (ethanol/exhaust emissions) which should be completed in the near future. Our specific observations are as follows.

### **Observations and Comments on CRC E65 Permeation Study**

1. The sample size (i.e. 10 vehicles) was a pragmatic choice reflecting budget limitations and program manageability while still trying to represent a cross section of the in-use fleet. In addition, the vehicles selected, due to the program start date, included no model year beyond 2001. California's light duty vehicle fleet is ~ 18.45 million vehicles. A ten vehicle sampling represents 0.0000542% of the in-use fleet. Each vehicle was selected from an age grouping that represented 10% of the total vehicle population. In some cases, this approach results in one model year representing all makes and model years for a three year period and in the case of the 1978 Cutlass (Rig 10) all makes and model years prior to 1983. Also, four of the ten vehicles (40%) had plastic fuel tanks which likely overrepresents their application in the fleet. This is important because plastic tanks have large permeable surface areas whereas metal tanks do not. Obviously, the above considerations call for caution when applying results across the entire vehicle population.
2. Since the tests were initiated, the vehicle population has aged 3 years resulting in more in-use cars meeting enhanced evaporative emissions standards and fewer older vehicles which had higher emissions overall and a greater increase from the ethanol fuel on a grams per day basis. Even excluding these newer vehicles just properly weighting the vehicles tested, to represent three years of fleet turnover, reduces the emissions increase of the ethanol blends compared to the non-oxygenated fuel (see additional comments at Item 3 on why we focus on comparisons to non-oxy fuel as opposed to the MTBE blend).

The following weighting of the fleet as it exists now and reweighting of emissions provides an example.

Rigs 1-5 (2001, 2000, 1999, 1997, 1995)	represents 1995 and newer	- 55% of fleet
Rigs 6-8 (1993, 1991, 1989)	represents 1987-1994	- 35% of fleet
Rigs 9-10 (1985, 1978)	represents 1986 and older	- 10% of fleet

Thus the weighting for the VOC increase would be as follows:

1995 and newer	= 0.680 Avg VOC grams/day x 55%	= 0.374
1987-1994	= 1.107 Avg VOC grams/day x 35%	= 0.387
1986 and older	= 2.165 Avg VOC grams/day x 10%	= 0.217
Weighted average	grams/day	= 0.978

In the above exercise, the properly weighted grams/day permeation emissions increase of Fuel B (ethanol blend) over Fuel C (non-oxygenated) is 0.978 grams day as opposed to the 1.1 grams/day increase reflected in the CRC report. Obviously if 2002 through 2005 model years were added, the weighted average would drop even more due to their lower emissions levels

CRC is currently preparing a Phase II permeation test that will include additional testing on rigs 1, 2, and 3 from the existing program and add a 2004 LEV II model and a PZEV. Note that in its report, the CRC recommends that the study “be expanded to assess the newer California LEV II compliant vehicles”. This study will also examine 10v% ethanol blends and the effect of varying aromatic levels.

These results will likely be available in a matter of months and any changes in regulatory procedures or the Predictive Model should correctly reweight the fleet and include these new test results as well as correct for the aforementioned over-representation of plastic tanks in the test program.

3. The ARB is required by legislation to insure that California Phase III Cleaner Burning Gasoline, i.e., CaRFG III be at least as clean burning (i.e., no back sliding) as California's Phase II Cleaner Burning Gasoline (CaRFG II). CaRFG II contained 2 wt% oxygen. With ARB as a major sponsor of the CRC work, the report focuses to some degree on Fuel B (ethanol blend) compared to Fuel A (MTBE blend). While RFA recognizes the need to use Fuel A to represent CaRFG II, it must also be realized that MTBE use is no longer an option in California. A more meaningful comparison for Fuel B is the non-oxygenated fuel (Fuel C) which would be the only other option to an ethanol blend. The permeation emissions increase of Fuel B over Fuel C is 1.1 grams/day (but of much less reactivity) while Fuel C is 0.29 grams higher than Fuel A (and of higher reactivity). So some mitigation strategy would be needed even for Fuel A.

We encourage ARB to focus on the comparison between the fuel options it has available while recognizing its need to comply with certain legislative requirements.

4. It is important to point out that the stabilization technique was to keep the tank full (at listed capacity) and the rigs at 105°F until they were determined stable. This is a sound and valid approach to achieve stabilization. However, once designated stable, the vehicle then had the 85°F steady state test followed by reducing the tank fill to 40% of capacity. Rigs then underwent the two-day diurnal. This means that when the rig underwent its diurnal test, the tank walls on the plastic tanks (4 rigs) were likely saturated and may have contributed to the SHED measurement. Note that in the report section on "Effect of Preconditioning Fill Level on Non-Metallic Tank Systems (100% vs, 20%)" (page 59 of the report) that rig 2 (2000 Honda Odyssey) and rig 4 (1997 Chrysler Town & Country) showed much lower diurnal test emissions on a 20% preconditioning fill, 27% and 35% lower respectively. The reverse was found on the older (1995 and 1993 rigs) for the diurnal tests although they did show decreases on the 105°F steady state test. The important point here is that vehicles do not drive around full. Much of the

time they are at less than 50% full. In the real world, many consumers usually drive vehicles down to 1/4 tank and refill. Lower income consumers may simply purchase a set dollar amount periodically (e.g., \$10.00) in which case the vehicle seldom has a full tank. The stabilization technique may result in an overstatement of permeation emissions compared to what happens in the real world.

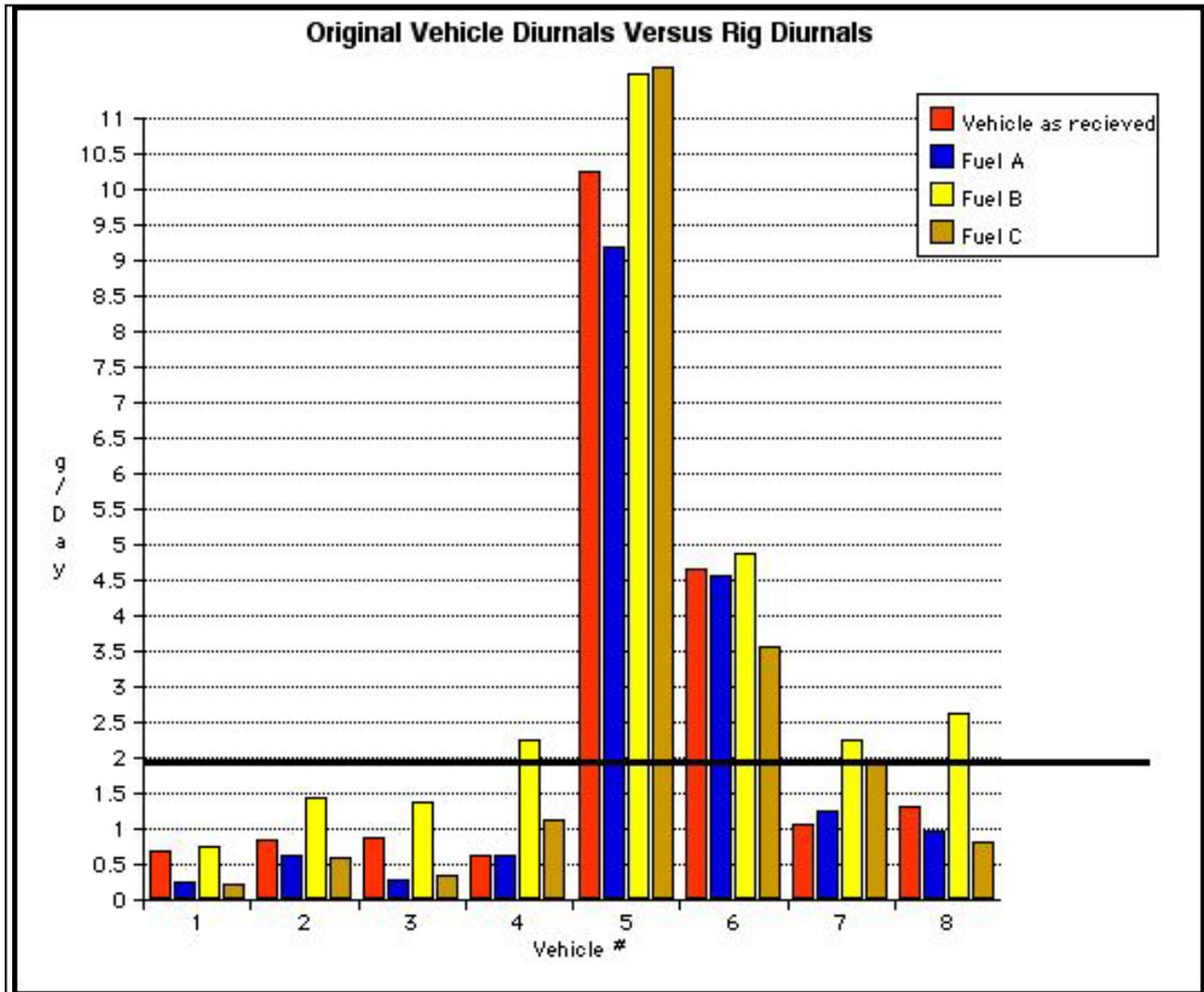
5. There are also some unique observations in comparing rig diurnal results to original vehicle diurnal results. When the vehicles were received, an engineering diurnal was run to measure evaporative emissions in as-received condition. These measurements are listed in the following table. The as-received diurnals were run on in-use California gasoline (MTBE blend).

<b><u>Vehicle #</u></b>	<b><u>Date</u></b>	<b><u>1st 24</u></b>	<b><u>2nd 24</u></b>	<b><u>Average</u></b>
1	4/2/02	0.51	0.86	0.685
2	4/8/03	0.87	0.80	0.835
3	4/17/02	0.83	0.90	0.865
4	11/28/02	0.63	0.62	0.625
5	12/18/02	11.19	9.34	10.265
6	10/8/02	4.66	-	4.660
7	10/23/02	0.90	1.20	1.050
8	10/23/02	0.76	1.86	1.310
9*	3/30/03	4.44	4.60	4.520
10	1/8/03	38.93	—	38.930

\*The results here are not a full vehicle diurnal. There were numerous leaks and the incoming vehicle tests were high, 77.3-113.1 grams/day. The rig was assembled and leaks repaired. The numbers listed for vehicle #9 are its rig measurements immediately before entering the program on fuel A.

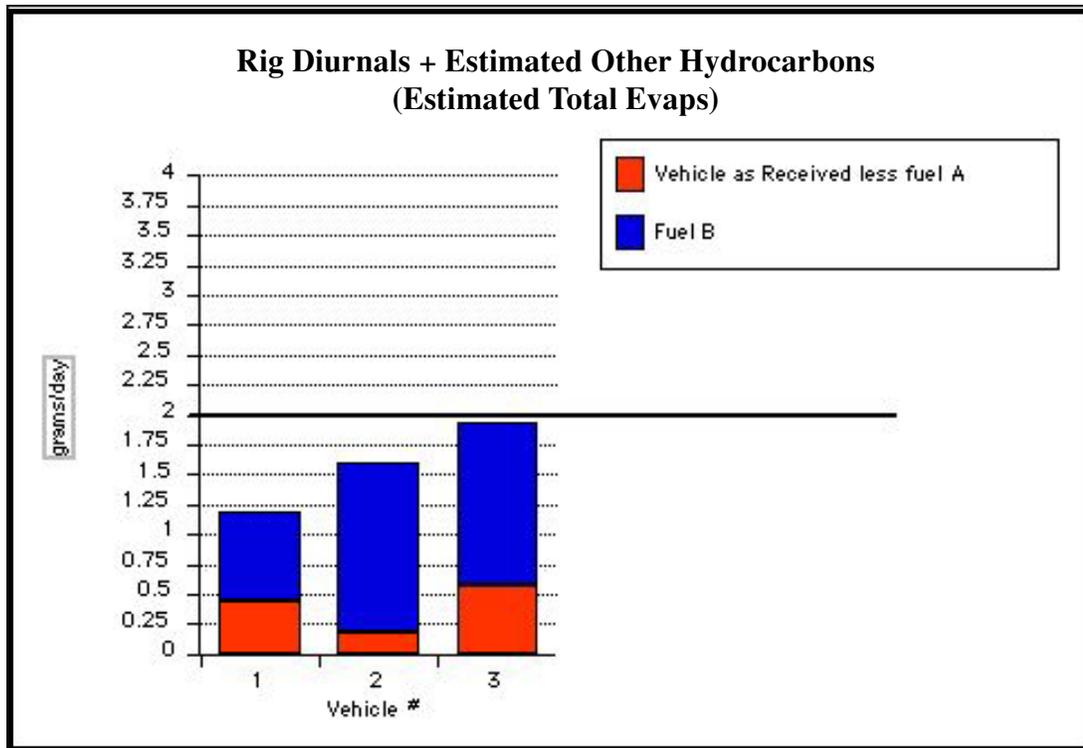
These original vehicle measurements would, of course, include not only the permeation emissions for the MTBE blend in the vehicle but all other sources of evaporative emissions as well. However, if you plot the vehicle diurnal emissions against the rig diurnal emissions on Fuel A,

also a MTBE blend, you will note that rig 4 had permeation emissions as high as the entire vehicle and rig 6 actually showed greater permeation emissions than total evaporative emissions. The following bar graph compares the original vehicle diurnals to the rig diurnals.



6. As noted earlier, with fleet aging, newer vehicles make up a greater portion of the fleet than when the test program was initiated. The auto manufacturers have often stated that for newer vehicles they are over-complying, i.e., evaporative emissions are well below the required level. This work seems to support that position. The three newest vehicle rigs, even on the highest permeating fuel, would be below the 2 gram evaporative emissions standard. This can be

demonstrated by taking the original vehicle diurnal measurement and subtracting the Fuel A (MTBE) permeation emissions, thereby rendering a reasonably accurate estimate of all other evaporative emissions. If you add Fuel B permeation emissions to that baseline of other emissions, all three of the newer vehicles were below the 2 grams/day evaporative emissions standard. This is demonstrated in the figure below.



7. It should also be noted that, as is normally done with these types of studies, modifications were made to the fuels to hold certain parameters close to the same on all fuels. In this case certain modifications were made to match volatility parameters and fuel composition as closely as possible. In the case of Fuel B (ethanol), the olefin content was found to be much lower than the other fuels and FCC Naphtha was added to increase olefin content. Additional ethanol was then added to bring the oxygen content back to the desired level.

While this approach obtained the desired target, it should be noted that the compliant Fuel B that was received had an olefin content of only 0.5v% which was raised to 5.8v%. This could

affect permeation emissions in two ways. First, to the extent the increased olefin levels are present in the permeate, at a greater level than in the fuel, this may increase total mass of permeate emissions. In addition, the reactivity of the permeate would increase. In short, had the compliant fuel, as received, been tested it may have had lower permeation emissions than the modified fuel. Secondly, the combination of olefins and ethanol stored over long periods, and at elevated temperatures, could lead to increased peroxide levels in the fuel which in turn could have a deleterious effect on the fuel system elastomers (see discussion next item). The combination of fuel modification and the 105°F stabilization cycle may have created permeation levels higher than that which would be experienced in real world use.

8. No tests were performed on the fuels immediately after they were used for the stabilization cycle. The concern here (as noted above) is the potential for peroxide formation.

The following table shows the number of days the fuels were in storage plus the 105°F stabilization cycle before the diurnal tests.

<b>Fuel Aging Comparison</b>						
<b>Diurnal Test Date Days From 01/01/03</b>						
<b>Rig #</b>	<b>Fuel A Date</b>	<b>Number of Days</b>	<b>Fuel B Date</b>	<b>Number of Days</b>	<b>Fuel C Date</b>	<b>Number of Days</b>
1	03/14/03	73	05/29/03	149	09/08/03	251
2	08/08/03	230	10/17/03	290	new fuel	
3	04/02/03	92	08/22/03	234	11/07/03	311
4	06/03/03	154	08/26/03	238	new fuel	
5	05/08/03	128	07/03/03	184	09/24/03	263
6	05/21/03	141	08/22/03	234	11/20/03	324
7	04/23/03	113	07/16/03	197	09/23/03	266
8	03/24/03	83	06/25/03	176	08/26/03	238
9	06/04/03	155	09/16/03	259	new fuel	
10	05/21/03	141	09/29/03	272	new fuel	

The MTBE blends were tested first so fuels were (measuring from January 1, 2003) typically around 150 days old or less (except rig 2 at 230 days) by the time the diurnals were run. Fuel B was the second fuel tested with fuels from 149 days (~ 5 months) to 290 days (~ 9.5 months) old before the diurnal tests were completed.

Compared to Fuel A, Fuel B was much older (aged) when the diurnals were performed. The additional number of days in storage combined with the stabilization cycle for Fuel B, compared to Fuel A, are listed in the following table.

<b>Fuel B Storage &amp; Stability Cycle Days</b>										
<b>Rig #</b>	1	2	3	4	5	6	7	8	9	10
<b>Days</b>	76	60	142	84	56	93	84	93	104	131

The concern here is that the olefin content and ethanol content of Fuel B could lead to increased peroxide levels. It is widely understood the peroxides (sour gas) can be very challenging to the durability of elastomers.<sup>(1,2,3)</sup>

Peroxide formation is not normally a real world issue with ethanol blends because the ethanol blending occurs just before delivery to retail facilities. As such the residence time for any peroxide formation is ~ 10-20 days. Here, however we are talking time periods greatly in excess of that.

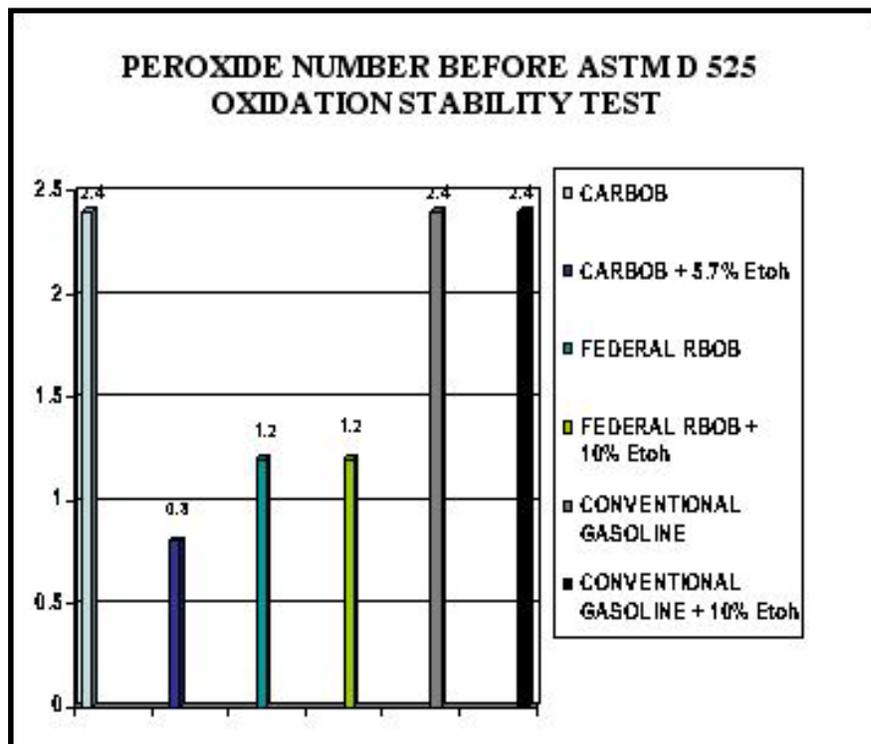
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- (1) SAE #840408 A Survey of Performance Elastomers Meeting Automotive Requirements of the '80s; S. Foster, et.al.; DuPont; 1984
  - (2) Fluorelastomers and the Automobile-Automotive Engineering, Volume 100, Number 7; Dennis Hull; 3M Industrial Chemical Products Division, June 1992
  - (3) SAE #880709 Effects of Alcohol Expended Fuels on the Rate of Fuel Hose Permeation; G. Baltz; Outboard Marine Corporation; February 1988

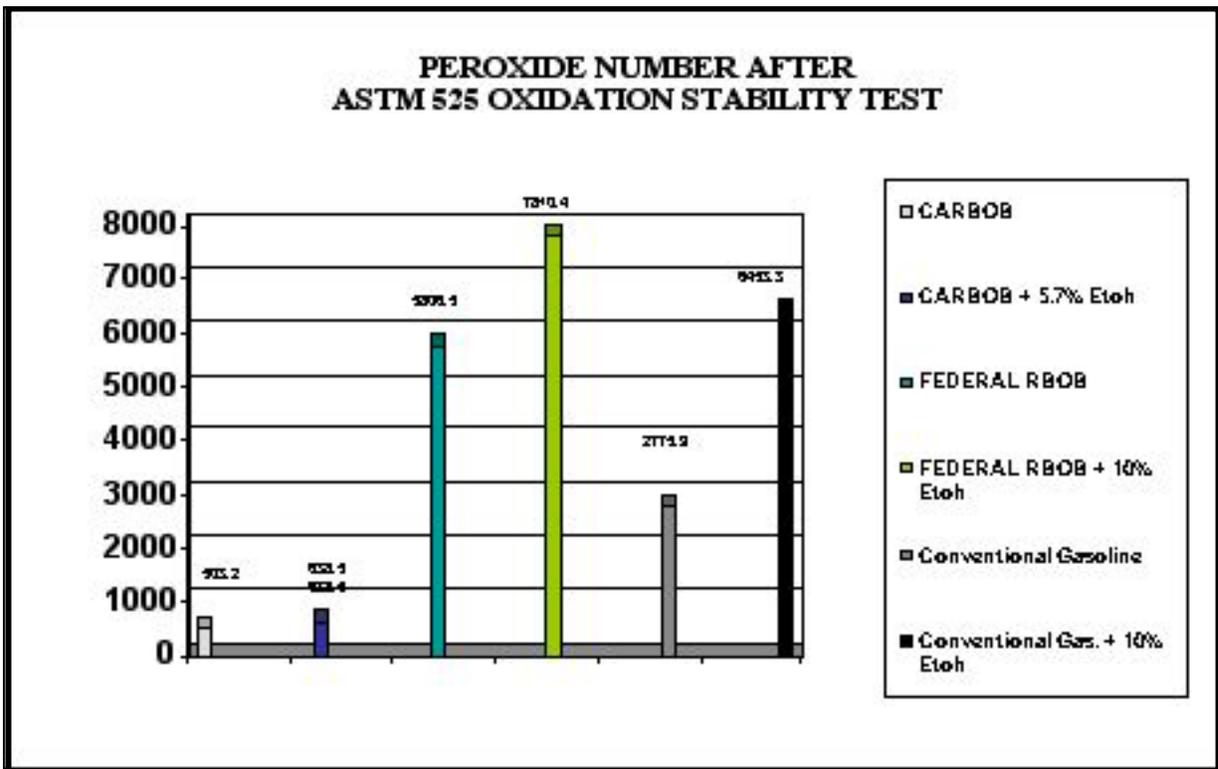
If peroxides were formed resulting in elastomer deterioration, this could result not only in non-real world permeation increases for Fuel B but may have carried over to diurnal tests on Fuel C. This may explain why Fuel C had, on average, higher permeation emissions than Fuel A, which is not what would be expected based on the literature and past testing.

Since no tests were conducted on the fuels immediately after the diurnals to determine any peroxide levels, or other properties, this remains an unanswered question at present.

The Renewable Fuels Association recently had some oxidation stability tests conducted at a widely recognized independent test facility. These tests also measured peroxide levels before and after the oxidation stability tests. While the report on this work is only now being written, I would like to share some of the results with you. While the oxidation stability of the gasoline ethanol blends performed similarly to the base gasolines, there was an increase in peroxide number after the oxidation stability test. The following figure shows the peroxide numbers of the fuels before an ASTM D 525 Oxidation Stability Test.

The next figure shows the peroxide numbers after the ASTM D 525 Oxidation Stability Test.





The above graphs demonstrate that the ethanol blended CaRBOB had a 27% increase in peroxide number compared to the base CaRBOB. The federal RBOB with ethanol showed a 35% increase in peroxide number versus its all hydrocarbon counterpart. The olefin content of the fuel was 6.246v% for the base CaRBOB, 7.128v% for the federal RBOB, and 14.728v% for the base conventional gasoline. While ethanol was blended at the 5.7v% level for the CaRBOB, it was blended at 10v% for the federal RBOB and conventional gasoline.

As noted earlier, this is not typically an issue in the real world because from the time the ethanol is added to the gasoline, to the time it is dispensed at retail and used by the consumer, is very short. However in the CRC E65 project the ethanol blends were much older and were exposed to a constant 105°F temperature for extended periods. Any potential for impact of peroxides on permeation emissions in these tests needs to be explored.

9. We would also draw attention to the test results for rig 5. The tank on this rig was the only single layer non-treated High Density Polyethylene (HDPE) tank in the test. This tank is of material similar to that used for portable gasoline containers. It has been assumed by many that ethanol blend permeation rates from HDPE gasoline containers would be higher than for a non-oxygenated fuel. In the case of test rig 5, the permeation results for the ethanol containing fuel were actually slightly lower. If the test results are representative of what would be expected from HDPE, then there may be no permeation increase (over non-oxygenated fuel) from storing gasoline ethanol blends in HDPE portable gasoline containers.

### **Other Important Issues**

Even after taking all of the above items into consideration (such as correcting fleet weighting), there is still some level of permeation increase that results from the addition of ethanol, at least for the fuels used in this test program. However, these results must be viewed in the context of the total emissions impact of adding ethanol to CaRBOB versus a non-oxygenated CaRBOB III (California's only other reasonable option since MTBE has been banned),

### **Impact on Carbon Monoxide Emissions**

It has been well established that oxygenates reduce tailpipe emissions of carbon monoxide (CO). However both USEPA and CARB originally believed that post 1994 cars would not realize CO reductions from fuel oxygen.

However, the most recent data on this issue provided to ARB by the Auto Alliance<sup>(1)</sup> indicates that for each 1.0wt% oxygen in the fuel, there is a corresponding CO emissions reduction of 7.5%. If ethanol were blended at the 10v% level (3.5wt% oxygen), this equates to a 26.25% CO reduction on these later technology vehicles.

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(1) Alliance, AIAM, Honda, 2001, "Industry Low Sulfur Test Program", presented at ARB Workshop, 2/2001. Available at <http://www.arb.ca.gov/fuels/gasoline/meetings/2001/071201AAPrstn.pdf>

The fact that these CO reductions occur with oxygenated fuels provides a valuable tool in reducing ozone formation. There are two significant studies addressing this issue, the first of which was released in 2001.<sup>(1)</sup> This study used grid modeling for three major metropolitan areas (South Coast Air Quality Management District, Chicago and New York). It concluded that the appropriate maximum incremental reactivity for CO should be 0.12 tons of ozone per ton of CO emitted. In 2003, another study,<sup>(2)</sup> based on analysis of the southern seaboard of the United States, showed even higher reactivity for CO to form ozone, on the order of 0.17 to 0.25. This means that for every four tons of CO emitted up to one ton of ozone can be formed.

### **Impact on NOx Emissions**

The Federal RFG Complex Model, which relates emissions of 1990-technology vehicles to several fuel parameters, shows very little impact on NOx emissions from fuel oxygen. This results from a dual model approach used by the U.S. EPA that gives a combination of a NOx increase from normal-emitting 1990-technology vehicles and a NOx decrease from higher-emitting 1990-technology vehicles. The California RFG Predictive Model uses newer statistical software that purports to eliminate the need for a dual model. The California Predictive Model also incorporates both older and newer technologies than the EPA Complex Model. California, during its construction of the Predictive Model, also assumed (due to lack of data) that post-'94 vehicles had essentially the same NOx increases with fuel oxygen seen from the earlier normal-emitting vehicles. The data from the Auto Alliance now show that this assumption was incorrect. California's Predictive Model shows a NOx increase with fuel oxygen similar to the normal-emitter part of the Federal Complex Model. Given the unproven elimination of the dual model approach (that would presumably include the negative NOx relationship to fuel oxygen for high emitters), and the incorrect assumption for newer vehicles, the California Predictive Model is, at best, uncertain in its relationship between NOx and fuel oxygen.

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- (1) U.S. Environmental Protection Agency, Office of Transportation and Air Quality, "Technical Support Document: Analysis of California's Request for a Waiver of the Reformulated Gasoline Content Requirement for California Covered Areas," EPA420-R-01-016 (June 2001) at 114-27.
  - (2) W.P.L. Carter, G. Tonnessen, and G. Yarwood (2003) "Investigation of Reactivity Effects Using Existing Regional Air Quality Models" Report to the American Chemistry Council. Available at <http://pah.cert.ucr.edu/~carter/RRWG/index.htm>. It is worth noting that Dr. Carter was the scientist who originally developed the 0.07 MIR for CO that has been used in earlier analyses regarding the impact of CO reductions on ozone formation.

The recent data by the Auto Alliance indicate that vehicles produced since 1994 appear to show emissions from non-oxy fuels than similar fuels blended with either MTBE or ethanol. California has estimated that in 2005 that 53 percent of the total gasoline-related on-road NO<sub>x</sub> emissions will come from '94 plus model year vehicles. Hence, as the fleet turns over with the passing of time, these post '94 vehicles will replace the earlier technology vehicles that have been the source of this uncertain oxygen-NO<sub>x</sub> controversy.

The CO and NO<sub>x</sub> emissions in post 1994 model year vehicles is of critical importance. This is why the RFA believes it is very important to consider the results of the CRC E67/University of California program. If this work confirms the earlier results of the Auto Alliance, and especially if the Predictive Model is modified to eliminate the NO<sub>x</sub> penalty for higher oxygen levels (i.e., above 2.0wt% O<sub>2</sub>), these benefits may largely, or entirely, offset the permeation emissions increase.

Equally as important, the permeation increase (if any) for California LEV II and PZEV vehicles ,must be quantified and considered. The second phase of CRC's permeation studies will include such vehicles and this data should be incorporated into permeation emissions estimates.

## **Summary**

The CRC findings, while significant, are a first step in quantifying the permeation emissions increases of CaRFG III containing ethanol. More data on newer vehicles is needed. We encourage waiting on the test results from CRC's second phase of permeation testing. There are some questions about the test results such as any impact of peroxide formation that need to be explored more thoroughly. Likewise more study is needed to determine if the preconditioning cycle could have resulted in higher permeation emissions than would be experienced in real world conditions.

Permeation increases from ethanol must be assessed in the context of total air quality impact, including the benefits of CO reduction, not only in older vehicles but in post 1994 vehicles which is currently not recognized in the EPA and California models. Likewise post 1994 vehicles may actually show a reduction in NO<sub>x</sub> emissions from oxygenates. We encourage a thorough review of the CRC E67 project to assess these factors.

The fleet age and resulting average emissions need to be reweighted to more accurately represent the permeation emissions profiles of the in-use fleet. Obviously it is necessary to exercise a great deal of caution when applying the test results from ten vehicles to try and estimate the permeation effect on 18.45 million vehicles.

The Renewable Fuels Association appreciates the opportunity to submit these comments and stands ready to work with ARB on this very important issue.

If there are any questions that arise from our comments, or if we can provide additional information, feel free to contact RFA president Bob Dinneen or RFA's technical consultant Bob Reynolds at the contact information on the cover page of this submission.