

California Environmental Protection Agency



**Gasoline Dispensing Facility (GDF)
Balance Hose Permeation Study**

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June 19, 2008

Revised October 6, 2010

Introduction

During April and May of 2008, the California Air Resources Board (CARB) conducted testing to determine saturated vapor permeation rates of gasoline dispensing facility (GDF) balance style hoses used in California. Staff was also interested in characterizing the effects of test fuel degradation on observed permeation rates.

Staff selected three identical samples of balance style vapor recovery hoses to undergo testing. Hoses were filled with California summer blend commercial pump fuel and placed in a testing chamber where temperature was recorded continuously throughout the testing. Hoses were weighed daily over the course of the testing and permeation results were calculated from the observed mass losses.

CARB staff observed that a balance style GDF hose, when subjected to an average temperature of 71.0°F (21.7°C), and filled in both the vapor and liquid paths with California summer blend commercial pump fuel, permeates at a rate of approximately 104.5 g/m²/day. By applying the theory that a saturated fuel vapor permeates at approximately the same rate as it would in liquid form under the same conditions^{1,2,3,4}, CARB staff determined that a balance style GDF hose would permeate at a rate of 104.5 g/m²/day when exposed to a saturated vapor of California summer blend commercial pump fuel at 71.0°F (21.7°C). Note that this vapor permeation rate is only valid for a saturated vapor. CARB staff is currently conducting a separate analysis to characterize typical vapor quality within balance style GDF hose.

CARB staff observed that test fuel degradation, beyond a mass loss of 5%, leads to a reduction of permeation rates. If not corrected for during testing, this will lead to an underestimation of actual emissions. It is possible that this effect may be present for test fuel degradations corresponding to fuel mass loss slightly lower than 5%, but temperature fluctuations in this area of the data set made this impossible determine.

Note that permeation results are highly dependent upon temperature, permeate type (fuel type) and permeation barrier material (hose material type). Because CARB staff only tested one type of fuel and used an uncontrolled temperature profile, CARB staff realizes that the results from this study only provide the basis for a rough estimate of emissions from GDF hoses. CARB staff intends to conduct further GDF hose permeation tests in the near future under highly controlled conditions to establish definitive statewide emissions for this source.

Background

It is part of CARB's mission to promote and protect the public health and welfare through the effective and efficient reduction of air pollutants. In carrying out this mission, CARB has sought to control hydrocarbon emissions at GDFs in California since 1975. Hydrocarbon emissions are reactive organic gases which can react in the atmosphere to form photochemical smog. Recently, CARB staff has identified GDF hoses as a sources of uncontrolled reactive organic gas emissions due to gasoline's ability to permeate through common GDF hose materials.

California GDFs, which are permitted by the local air pollution control districts, in most cases must use vapor recovery style hose. Vapor recovery hose is different from conventional fuel delivery hose in that it has two paths: one for fuel delivery and the other for vapor return. There are two different styles of vapor recovery hose: balance and vacuum assist. For permeation purposes, vacuum assist hoses are similar to conventional fuel delivery hoses in that the liquid fuel is carried against the inside of the outer hose wall. Balance hoses are different, carrying vapor against the outer hose wall (Figure 1). Thus special consideration should be taken when designing a permeation test for balance style GDF hoses.



Figure 1 Balance style vapor recovery GDF hose showing vapor and liquid paths.

In 2004, ARB staff conducted a GDF hose permeation test as an initial attempt to try to estimate the amount of reactive organic gasses which were being emitted in California from GDF hoses.⁵ However, that testing failed to address test fuel degradation throughout the testing period and it did not characterize vapor concentrations in the balance hose vapor path. The GDF balance hose

permeation test discussed in this paper is an attempt to more accurately estimate permeation emissions from balance hoses when exposed to a saturated fuel vapor.

Test Protocol

For Approximately 28 days, from April 11th to May 9th of 2008, CARB staff conducted in-house gravimetric testing of 3 balance style vapor recovery GDF hoses under non-controlled ambient conditions. The hoses were placed on racks within a fuel storage cabinet in a fuel storage room throughout the testing (Figure 2). Hoses were removed from this environment daily only for the purpose of recording weight and refreshing fuel (dumping old test fuel in the hose and replacing with fresh test fuel). Time was recorded for all weighings during the test.



Figure 2 (a) Hoses in testing room. (b) Hose being weighed.

Testing room temperature was continuously recorded via data logger over the course of the testing. Temperature was only controlled to the extent that building temperature controls limited the temperatures to small diurnal swings of an average of 5.2 °F (2.9°C) at an average temperature of 71.0°F (21.7°C) throughout the testing (Attachment 2). Although it would have been preferable to control testing temperature more precisely, staff was able to observe clear trends in the data and draw robust conclusions.

Staff purchased 3 balance hoses from a local distributor. These hoses were each measured to be approximately 48 1/2 inches in length as measure from o-ring flange to o-ring flange. The average internal diameters were measured to be approximately 1 3/8 inches. Because the inner path of the balance hose was not of any importance in this permeation test, the inner hose was removed from all samples. For the purpose of identification, the hoses were labeled B1, B2, and B3. The hoses had been used in a previous test conducted by CARB staff in the summer of 2006 to observe fuel temperature profiles in GDF hoses. The hoses had been filled with summertime pump fuel and hung outdoors in various degrees of shade for approximately 3 months. Staff believes that this exposure was beneficial in that helped to precondition the hoses to behave more closely to hoses taken from service. All hoses were within the normal life expectancy age of approximately 2 years and in serviceable condition. However, during the previous testing hose B1 was kept in full shade throughout that experiment whereas hoses B2 and B3 were exposed to partial and full sun throughout that testing. Staff believes that this difference in UV exposure between the hoses may have played a role in differences in permeation rates measured throughout the testing.

Approximately 7.5 gallons of California summer blend commercial pump fuel was purchased from a local station of a major brand name retailer to use as test fuel on April 11, 2004. The fuel was dispensed into two 5 gallon low permeation CARB certified portable fuel containers. The test fuel was weighed throughout the testing to control for any fuel degradation not related to the hose permeation testing.

On Friday, April 11th, the first day of testing, each of the hoses was weighed empty, then filled with 1.0 liters of test fuel (75% of each hose's capped volume). The hoses were immediately capped after filling, then weighed. The hoses were placed in the testing room and allowed to precondition for approximately 3 days, at which point they were pulled from the testing room and their weights recorded. At this point, the hoses were each emptied and refilled with 1.25 liters of fresh fuel (90% of each hose's capped volume), reweighed, then placed back in the testing room. This process was repeated at approximately 24 hour intervals through the 7th day of testing. From this point, fuel refreshing was discontinued. Daily weighings were continued throughout the testing.

Note, that fuel refreshing for of all three hoses generally took about 1 hour. In order to correct for this time discrepancy, time that elapsed between taking the weight of all of the hoses before fuel refreshing and taking the weight of all of the hoses after fuel refreshing was omitted from the calculations so as not to underestimate emissions. This omitted time is also corrected for in all graphs that have been included in this paper.

Throughout the testing, the hose caps were inspected daily both visually and by smell for fuel leaks. On April 23rd (day 12), a small amount of wetness was detected at the threads for hose sample B1, that is best characterized as dampness consisting of 1 to 2 drops total. The damp area around the threads was wiped clean and the threads further tightened. No further episodes of leakage were detected throughout the testing. The effect of this minor amount of leakage is hardly noticeable in the data, as the permeation rate of hose sample B1 lagged the other samples significantly during this period of the testing. Because the high permeation rates observed greatly eclipsed the minor amount of fuel lost from this one episode of leakage in one sample, CARB staff believes that this minor leakage created no significant problems in the analysis of the overall study.

Test Results

It was staff's intent to determine a balance hose's steady state permeation rate when using California summer blend commercial pump fuel for a given temperature. For the purposes of this paper, steady state permeation is loosely defined as a permeation rate which appears to change very little when testing conditions (temperature and test fuel composition) are held constant. Because temperature was not able to be controlled precisely, staff needed to monitor the data closely to make this determination and only an approximate determination could be made. Technical papers published by the Society of Automotive Engineers (SAE) suggest that a change in temperature of 1°C typically results in a permeation change of approximately 10%.^{6,7} Test fuel composition was controlled early in the procedure by refreshing the fuel within the hoses daily so that test fuel composition would be maintained. From testing days 3 through 7, fuel mass loss did not exceed 1.7% (Figure 3). Note that this amount of fuel loss does not exceed the 2% limit given in SAE's most rigorous test procedure for low permeation fuel hoses, SAE J1737.⁸

CARB staff calculated daily permeation rates for each hose by dividing the daily weight loss by the hose's internal surface area. Staff calculated the internal hose surface areas to be 209.5 in² (0.135 m²). Staff believes that the data demonstrates that steady state permeation was approximately achieved on the 7th day of testing, noting that the average permeation rate of the 3 hoses increased at 0.5% while temperature decreased only 1.1°F (0.62°C) as fuel degradation was controlled below 2% loss. The average steady state permeation rate of the 3 hose samples was determined to be 104.5 g/m²/day. Staff believes this number to be slightly conservative, as the slight temperature decrease likely would have had a small lowering effect on the permeation rate.

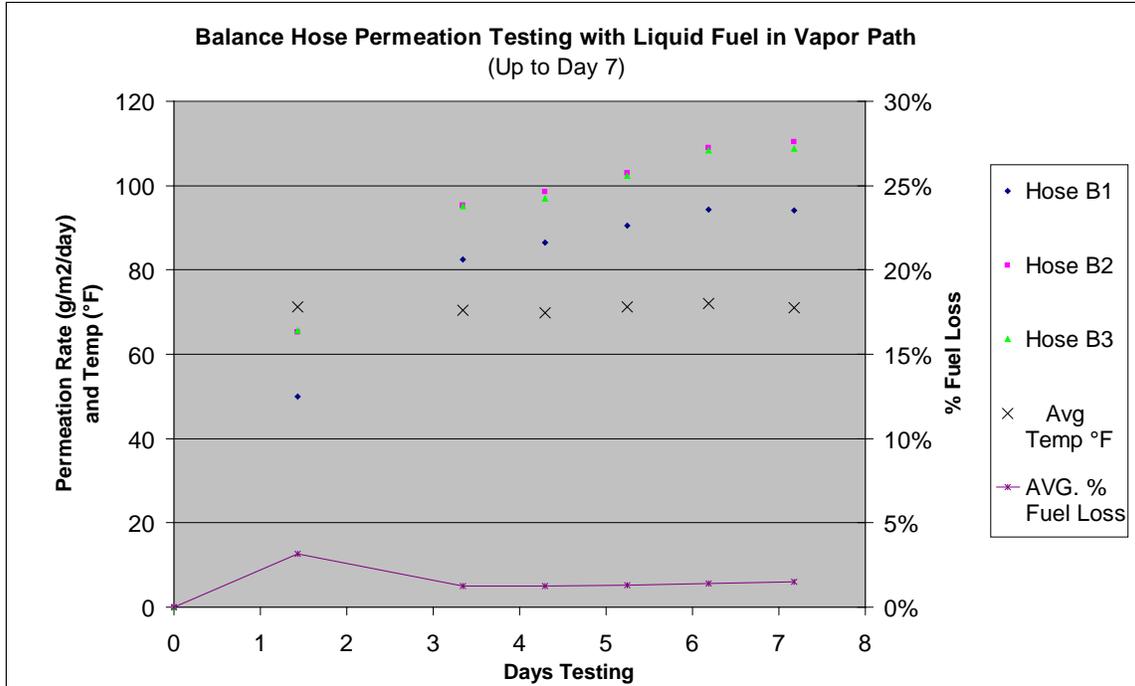


Figure 3 Steady state hose permeation rates achieved in 7 days.

After the 7th day of testing, fuel composition began changing beyond 2% fuel loss as fuel refreshing was not continued after the 7th day of testing due to limited testing resources. Also, the average daily temperature dropped significantly after the 7th day, by 3.4°F (1.9°C). Because of these factors, permeation rates dropped. Because the permeation rate change through day 9 fell 21.6%, and is roughly within the predictability of a temperature drop of 3.4 °F (1.9°C), it is hard to tell if fuel degradation had an effect. However, after the 9th day of testing, it is clear that fuel degradation did have an effect on the permeation rate, as temperature increased while permeation rates decreased. Thus, at approximately 5% fuel loss by weight, fuel degradation of this test fuel has become significant enough to bias permeation rates downward. Therefore, all data taken after day 9 should not be used to determine the steady state permeation rate for California summer blend commercial pump fuel and this type of hose.

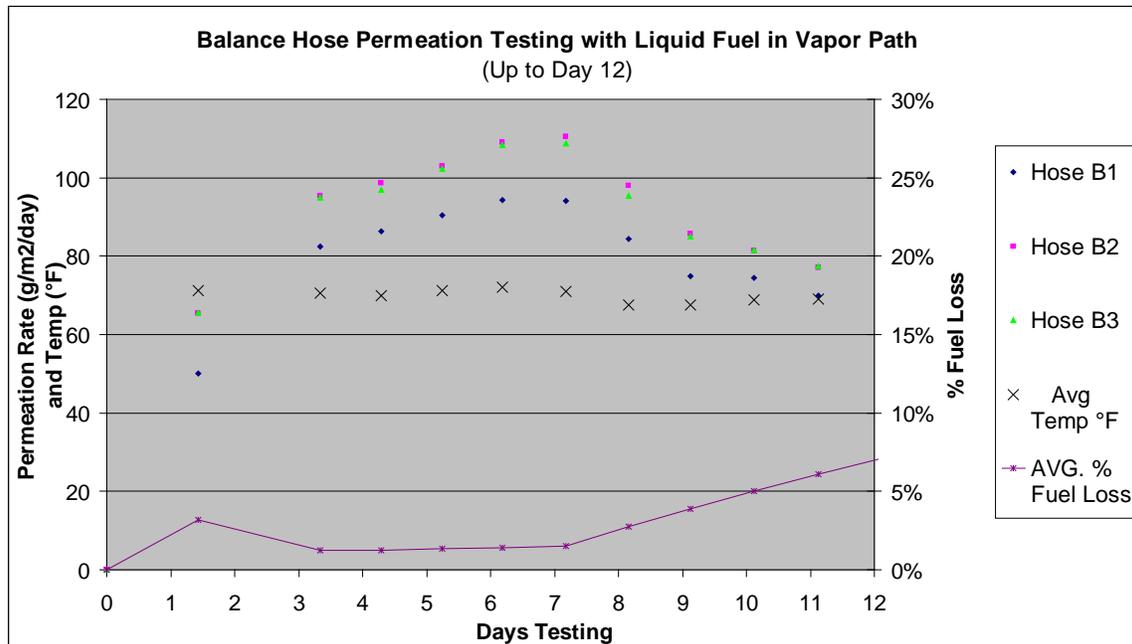


Figure 4 Fuel degradation effects become apparent at day 10 for 5% fuel loss.

Fuel Analysis

Samples of both the original test fuel and spent test fuel (from hose B3) were taken and subjected to laboratory analysis. The purpose of this testing was to observe any constituents that may permeate at higher rates than the average constituent, as this information may prove valuable for future permeation analysis. Due to a lack of testing resources, the fuel was only examined for criteria upon which CARB performs active enforcement. The results of the analysis are given in Table 1.

The most striking observation is that all of the ethanol completely permeated out during the test period while only 14.4% of the overall test fuel was lost through permeation. This observation is consistent with other studies that have shown ethanol tends to permeate at a higher rate than other fuel constituents.^{9,10} However, it is noteworthy in this study that ethanol appears to have permeated out at a rate extremely fast relative to the other fuel constituents. It is not known at exactly what point all of the ethanol permeated out as analysis was only performed on the original test fuel and the spent test fuel that was remaining at the end of the test.

Another noteworthy observation was that benzene, as a percent of the total volume of the fuel had decreased by over 36%. Since Benzene is listed by the EPA as a Toxic Air Pollutant, and is a known carcinogen, it is important to note that not only can this substance be emitted into the atmosphere via permeation,

but that is appears to permeate at a higher rate than many other fuel constituents.

Table 1: Test Fuel Analysis

Test criteria	Original Test Fuel	Spent Test Fuel	Units	Test Method
Ethanol	6.1	0.0	%V	ASTM D4815-99
Toluene	6.29	4.85	%W	ASTM D5580-00
Benzene	0.55	0.35	%V	ASTM D5580-00
E-Benzene	1.50	1.34	%W	ASTM D5580-00
m,p - Xylene	5.98	5.38	%W	ASTM D5580-00
o - Xylene	2.20	1.99	%W	ASTM D5580-00
Olefins	3.1	2.9	%V	ASTM D6550-00 (modified)
Total Aromatics	23.9	19.4	%V	ASTM D5580-00
C9+ (carbon chains of 9 or greater)	11.5	9.05	%W	ASTM D5580-00
Sulfur	7	7	ppm	ASTM D5453-93
Specific Gravity	0.742	0.737		ASTM D4052-96
RVP (Reid Vapor Pressure)	6.8	5.35	PSI	13 CCR Section 2297
T50 (Temp at which 50% boils off)	211	216	°F	ASTM D86-99
T90 (Temp at which 90% boils off)	307	313	°F	ASTM D86-99

Other Observations

Staff believes that the average steady state permeation rate of 104.5 g/m²/day derived from this study is conservative due to the permeation rate of hose B1 clearly lagging the permeation rates of the other two samples (Attachment 2). As described in the testing protocol section, hose B1 had not had direct sun exposure, whereas the other two hose samples had had significant sun exposure. Staff believes hoses B2's and B3's exposure to UV had led to a degrading, or aging, effect on the hoses which may have caused higher permeation rates more reflective of in-service hoses which are generally exposed to some degree of sunlight throughout the course of a normal day. If the permeation rate of hose B1 is eliminated from the average steady state permeation rate, that permeation rate would rise to 109.6 g/m²/day, or by approximately 5%. However, due to the limited number of samples involved in this testing, additional testing should be done before drawing conclusions on the effects of UV light exposure and hose permeation.

Another observation that staff drew from this permeation study is the overall importance of controlling for fuel degradation, or test fuel composition. The final mass loss measurement taken for each hose in this study shows an average permeation rate of 16.3 g/m²/day at 72.5°F (22.5°C). This average rate also

corresponds to a total average fuel loss from the 3 hoses of 14.4% by mass. With a fuel loss of only 14.4%, the permeation rate has fallen from its steady state permeation rate by more than 84% (Attachment 2). Such a large change in permeation rate corresponding to a relatively modest loss in fuel mass greatly highlights the importance of controlling for fuel degradation when reporting steady state permeation rates.

Conclusion

Based upon the testing data discussed in this paper, CARB staff estimates that the liquid, and saturated vapor, steady state permeation rate for balance style GDF hoses is 104.5 g/m²/day when using California summer blend commercial pump fuel at an average temperature of 71.0°F (21.7°C). CARB staff also observed that to avoid under reporting of steady state permeation rates during testing, test fuel degradation should be minimized to the greatest extent possible. Staff observed that fuel loss within the sample of over 5% of the total fuel mass led to lower permeation rates due to fuel degradation. CARB staff further observed that ethanol permeates at a much greater rate than many of the other fuel constituents which make up California summer blend commercial pump fuel. This may be an especially important consideration in light of many proposals to increase ethanol content in fuels nationwide. Although these observations offer valuable insight into the understanding of emissions from GDF hoses, CARB staff believes that these numbers are conservative. CARB staff intends to do a larger and more rigorously controlled GDF hose permeation test in the near future to better estimate actual statewide emissions from this source.

Works Cited

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Attachment 1

GDF Balance Hose Testing Data

Date	Mass Loss (grams)			Initial Fuel Mass (grams)			Time of Permeation Period (days)	Average Temp (°C)	Maximum Temp (°C)	Minimum Temp (°C)
	Hose B1	Hose B2	Hose B3	Hose B1	Hose B2	Hose B3				
11-Apr	N/A	N/A	N/A	732.07	735.66	732.98	N/A	N/A	N/A	N/A
<u>12-Apr</u>	19.35	25.29	25.39	N/A	N/A	N/A	2.86	21.75	24.50	20.38
<u>13-Apr</u>				N/A	N/A	N/A		21.75	24.50	20.38
<u>14-Apr</u>				953.57	943.65	946.1		21.75	24.50	20.38
15-Apr	10.64	12.3	12.27	962.89	950.98	953.54	0.95	21.37	22.81	19.75
16-Apr	11.11	12.68	12.46	955.66	950.92	952.55	0.95	21.06	22.56	19.75
17-Apr	11.59	13.18	13.11	956.27	956.67	949.05	0.95	21.76	23.19	20.38
18-Apr	12.03	13.91	13.84	963.47	955.12	949.99	0.94	22.28	23.88	20.38
19-Apr	13.03	15.29	15.07	N/A	N/A	N/A	1.02	21.67	22.56	19.75
20-Apr	10.81	12.55	12.22	N/A	N/A	N/A	0.95	19.79	23.19	20.38
21-Apr	10.03	11.45	11.37	N/A	N/A	N/A	0.99	19.76	23.88	20.38
22-Apr	10.02	10.96	10.99	N/A	N/A	N/A	1.00	20.41	21.44	19.00
23-Apr	9.62	10.6	10.64	N/A	N/A	N/A	1.02	20.56	21.44	19.38
24-Apr	9.06	9.86	9.97	N/A	N/A	N/A	0.99	20.04	21.19	18.63
25-Apr	8.47	9.3	9.49	N/A	N/A	N/A	1.03	20.76	21.81	19.38
26-Apr	8.02	8.59	8.91	N/A	N/A	N/A	1.02	21.94	23.13	20.38
27-Apr	7.68	7.88	8.02	N/A	N/A	N/A	0.98	23.19	24.50	21.81
28-Apr	7.12	7.44	7.63	N/A	N/A	N/A	0.98	24.09	25.69	22.50
29-Apr	6.1	6.76	6.28	N/A	N/A	N/A	1.02	22.92	24.56	21.38
30-Apr	4.9	4.81	4.78	N/A	N/A	N/A	0.97	21.57	23.19	20.00
1-May	4.1	4.44	4.19	N/A	N/A	N/A	1.06	20.99	22.13	19.75
2-May	3.19	3.27	3.23	N/A	N/A	N/A	0.92	21.60	22.81	20.38
3-May	2.96	3.22	3.01	N/A	N/A	N/A	0.98	21.29	22.81	20.00
4-May	2.99	3.32	3.24	N/A	N/A	N/A	1.10	22.00	23.19	20.75
5-May	2.47	2.75	2.56	N/A	N/A	N/A	0.94	21.98	23.50	20.38
6-May	2.49	2.6	2.59	N/A	N/A	N/A	1.01	22.14	23.94	20.75
7-May	2.28	2.83	2.65	N/A	N/A	N/A	1.03	22.82	24.13	21.38
8-May	2.37	2.4	2.46	N/A	N/A	N/A	1.02	22.69	24.13	21.38
9-May	1.88	2.22	2.08	N/A	N/A	N/A	0.94	22.50	24.13	21.13
Note: All positive mass numbers indicate mass loss.										
Note: Initial fuel masses refer to initial fuel fill and fuel refreshing episodes.										
<u> </u> Underlined dates indicate dates for which mass loss was taken over multiple dates.										

Attachment 2

