

Literature Search Summary

Emission Effects (Permeation) of Ethanol in Gasoline

Overview

The substitution of ethanol for MTBE (in 2003) in California's gasoline will increase the evaporative emissions (HC) of the current fleet of California vehicles, mainly due to the effects of co-mingling and permeation. The magnitude of the increase is in question. How significant is the permeation impact? While current and future vehicle systems certified to the enhanced evap standards (e.g., 1995 model year and later vehicles) have very low levels of permeation, there is a concern for the older vehicles (pre 1995) present in the population in 2003, many of which have carburetors, and sensitive elastomeric components.

A literature search was made to see if there were existing data or insight into the effect(s) on permeation emissions of ethanol in gasoline. Twenty eight (28) reports were reviewed. Summaries of the individual reports are contained on the following pages.

Findings

During the development of California's portable fuel container regulation (Report 1), test measurements indicated that adding 5.3V% ethanol to gasoline increased the permeation for HDPE plastic containers by 45%, which calculates to 3.6 tons per day statewide in 2007.

Vehicle tests resulted in increased hot soak emissions with ethanol fuels, even when adjusted to equivalent volatility. SAE 800261 reported a 71% (1.25 grams per hour) increase in hot soak emissions on a 1978 production vehicle. SAE 810438 reported evap increases of 253% to 315% for two late 70's production vehicles. The Auto-Oil Program reported (SAE 920326) a 50.1% increase in hot soak emissions for a 10V% ethanol RVP adjusted fuel. The one hour diurnal emission results reported were generally higher, but understate the real increase due to two reasons: 1) the one hour period misses the real 24 hour contribution of the permeation losses, and 2) the components were not allowed to stabilize with the ethanol containing fuels.

Fuel hose deterioration and swell with ethanol was mentioned (page 5) in SAE 800261, as a contributor to increased permeation with the rubber (nitrile) hose from the bowl vent to the canister.

Reports on component effects were found concluding that adding ethanol to gasoline increased permeation on elastomers that have been used in automotive applications. (See reports 4, 17, 18) The increase in permeation for NBR (rubber) was 54%. Unpublished data on plastic fuel tanks was provided to the reviewer indicating that component permeation increased 300% or more with 10% ethanol fuels compared to non-oxygenated fuel tests.

Many of the reviewed reports point out that permeation takes time to stabilize. SAE 970307 focused on the “recovery time” required for permeation to return to “normal” after exposure to alcohol fuels. None of the reports involving vehicle tests allowed sufficient time for permeation effects to stabilize, and as such, probably understated the true emissions values.

Recommendations

A focused test program is needed to quantify the permeation emission impact(s) of ethanol. The program to quantify the permeation effects must comprehend the changing nature of future fuel compositions, the fraction of the fleet that is sensitive to ethanol, and the summer temperature variations. Once this is established, the positive impacts (CO credits, aromatic reduction, others) can be factored in, and a net balance made.

Individual Paper Review Summary

(1) California ARB - Monitoring and Laboratory Division May 19, 1999

“Test Protocol and Results for the Determination of Permeation Rates from High Density Polyethylene Containers and Barrier Surface Treatment Feasibility Study” (Preliminary Draft)

The average permeation rate from untreated HDPE portable containers was found to be 1.57 grams/gallon/day. Permeation with a similar fuel containing 5.3% ethanol was 2.28 grams/gallon/day, a 45% increase. It was concluded that alcohol based oxygenated fuel increases permeation, and that permeation from HDPE containers contributes significantly to the overall hydrocarbon emissions associated with the use of these products.

(2) California ARB – Staff Report August 6, 1999

“Initial Statement of Reasons for Proposed Rule Making Public Hearing to Consider the Adoption of Portable Fuel Container Spillage Control Regulations”

(At page 10) The report states that approximately 75% of the residential population of portable fuel containers in California are made from HDPE, and that permeation emissions have been determined to be approximately 8 tons per day statewide in 2007. If the increase identified in the report above is used, the effect of adding ethanol to California’s in-use fuel would add 3.6 tons/day statewide due to the portable containers alone.

(3) National Research Council ISBN 0-309-06445-7 1999

“Ozone Forming Potential of Reformulated Gasoline”

The report directly addresses the subject of the emission effects of oxygenates in gasoline, but has little data or insight on evaporative emissions, save the increased emissions of splash blended, higher RVP fuel. There is no mention of the ethanol permeation issues in the text.

(4) SAE 981376 May 1998

“Speciation of Evaporative Emissions from Plastic Fuel Tanks”

This paper presents the results of a study conducted to determine the composition of the emissions from a number of multilayer coextruded plastic fuel tanks soaked in 10% ethanol and 15% methanol fuels. Data presented showed that the methanol fuel permeation continued to increase after 22 weeks of soak time. Ethanol soaked tanks are expected to have the ethanol account for only 10% of the total permeation emissions.

(5) CA Air Resources Board November 1998

“Comparison of the Effects of a Fully-Complying Gasoline Blend and a High RVP Ethanol Gasoline Blend on Exhaust and Evaporative Emissions”

Six 1990-1995 model year vehicles were evaluated for real-time diurnal and hot soak emissions using the California 2 day procedure with regular, and splash blended 10% ethanol fuels. Duplicate back-to-back tests were performed on both fuels. Evaporative emissions increased on the order of 50% with the higher RVP ethanol containing fuels.

Permeation emissions were not addressed in the program, as fuels were changed without allowing permeation emissions to stabilize.

(6) SAE 970307 February 1997

“Fuel Permeation Rates of Elastomers After Changing Fuel”

This study investigated the condition where fuel system elastomers are exposed to various fuel-oxygenate blends and tested for permeation. The elevated permeation rates experienced by many materials returned to lower levels after 336 hours of exposure. Certain advanced materials had very low permeation rates and were insensitive to the presence of ethanol.

(7) SAE 961092 May 1992

“Federal Test Procedure Emission Test Results from Ethanol Variable-Fuel Vehicle Chevrolet Lumina”

One hour compressed-time evaporative emissions tests were run on the low mileage variable fuel Lumina using RFG, E50, and E85 fuels. One of the conclusions was that: “Evaporative emissions were not sensitive to the three test fuels (RFG, E50, E85), which were all blended to the same nominal Reid vapor pressure.”

(8) SAE 952751 December 1995

“Powertrain Development of the 1996 Ford Flexible Fuel Taurus”

A discussion is offered of the challenge required to manage the high levels of vapor generated by low percentage alcohol fuels.

(9) SAE 952748 December 1995

“Gasoline Evaporative Emissions – Ethanol Effects on Vapor Control Canister Sorbent Performance”

The University of North Dakota conducted a study of the evaporation rate and properties of gasoline splash blended with 10% ethanol. They also designed a test system to investigate how the presence of ethanol in the vapors affects the vehicle’s canister performance. They basically conclude that ethanol adsorbs well on activated carbon.

(10) SAE 941965 October 1994

“Sources of Vehicle Emissions in Three Day Diurnal SHED Tests – Auto/Oil Air Quality Improvement Research Program”

Mini-SHED permeation tests were conducted on vapor and liquid fuel lines from four in-use vehicles. Permeation levels were found to be low on 3 of the 4. The vehicle with significant permeation was a small sedan with a carburetor fuel system, a 1989 Honda Accord. “Seepage”, or liquid fuel leaks, was distinguished as different from permeation. All tests were conducted on a single non-oxygenated fuel.

(11) SAE 940765 February-March 1994

“In-Use Volatility Impact of Commingling Ethanol and Non-Ethanol Fuels”

The paper focuses entirely on the RVP effects of mixing ethanol and non-ethanol fuels.

(12) SAE 940164 February – March 1994

“Understanding How Molecules Permeate Through Solid Substances”

This paper describes how molecules in a fluid move (permeate) through a solid material. It provides a general understanding of the terms and theory of permeation, and mentions that methanol permeates more than ethanol because of it’s smaller molecule. No data is included.

(13) SAE 940166 February – March 1994

“ETFE-Nylon 12 Multi-Layer Fuel Lines and the Requirements of a Changing Fuel Line Environment”

Permeation results are presented for ETFE/nylon 12 samples on several fuels, including one containing 15% methanol and 4.23% ethanol. Gasohol was not evaluated.

(14) SAE 940165 February – March 1994

“Development of Multilayer Thermoplastic Fuel Lines with Improved Barrier Properties”

Multilayer tubing is evaluated for a variety of properties using different fuels, including a mixture of methanol and ethanol. Gasohol was not evaluated.

(15) SAE 930992 March 1993

“Fuel Hose Permeation of Fluoropolymers”

This study compares the fuel permeabilities of several fluoropolymers and nylon in various fuels, and was based on the SAE J-30.6.12 test for hose material. Ethanol was not included in the test matrix.

(16) SAE 931841 August 1993

“Emission Control Cost-Effectiveness of Alternative-Fuel Vehicles”

This paper did not address any change in evaporative emissions resulting from low percentage ethanol fuels.

(17) SAE 920164 January 1992

“Permeation of Gasoline-Alcohol Fuel Blends Through High-Density Polyethylene Fuel Tanks with Different Barrier Technologies”

A scholarly and well-done paper addressing theory and data concerning permeation in fuel tanks, although it is almost 100% focused on methanol as the appropriate alcohol. Empirical correlation parameters are provided in Table 2 for gasoline-ethanol-HDPE systems. Figure 8 suggests that permeation requires approximately 100 days to stabilize with a 85% methanol fuel at room temperature.

(18) SAE 920163 February 1992

“Fuel-Alcohol Permeation Rates of Fluoroelastomers Fluoroplastics, and Other Fuel Resistant Materials”

This paper presents permeation data for various material and fuels using the ASTM E96-66 “Thwing Albert” cup method, a process for screening various polymer materials. The base fuel is a “Fuel C”, a 50% iso-octane/50% toluene mixture. The analysis contained is a comparison of the various materials permeation rates, but the charts can be reanalyzed to compare the base fuel and a mixture of the base fuel and 10% ethanol. Substantial increases in permeation rates are shown for the 10% ethanol fuel for all of the materials. Excerpts from Table 1 on page 27 are presented below with a calculation of the percent increase in permeation reported for the 10% ethanol fuel compared to the base fuel. The increase ranged from -40% to 838%

Table 1 - Part B
Average Permeation Rate (g x mm)/(m² x day)

Material	Fuel C	10% Ethanol	% Increase
NBR (33% ACN)	669	1028	54
FVMQ (Fluorosilicone)	455	584	28
HNBR (44% ACN)	230	553	140
Nylon 12	5.5	24.0	336
FKM GLT (65% F)	2.6	14.0	438
FKM GFLT (67% F)	1.8	6.5	261
FKM A200 (66% F)	0.8	7.5	838
FKM B70 (66% F)	0.8	6.7	738
FKM B200 (68% F)	0.7	4.1	486
FKM GF (70% F)	0.7	1.1	57
PFA 1000LP	0.1	0.03	-40
FEP 1000L	0.03	0.03	0
ETFE 1000LZ	0.03	0.1	67

(19) Auto/Oil AQIRP Technical Bulletin No. 6 September 1991

“Emissions Results of Oxygenated Gasolines and Changes in RVP”

One hour compressed-time evaporative emissions tests were run on twenty 1989 model year vehicles with a variety of fuel blends. Fuels A and W compared base and 10% ethanol fuels at 9 psi RVP. Diurnal emissions were lower with the ethanol fuel (W), but the hot soak emissions were higher. Permeation emissions were not addressed in the program, as fuels were changed without allowing permeation emissions to stabilize.

And

(20) SAE 920326 February 1992

“Effects of Oxygenated Fuels and RVP on Automotive Emissions – Auto/Oil Air Quality Improvement Program”

This SAE paper examines the same data set as Tech Bulletin No. 6 mentioned above, but offers additional analysis. Included in the conclusions are “Ethanol was found to increase both diurnal and hot soak emissions by 30.3 and 50.1%, respectively, probably due to the RVP increase associated with splash blended ethanol fuels.” Caveats are offered concerning fuel scheduling and possible permeation and/or leakage effects that may have had an appreciable influence on the data. Again, the time required for permeation to stabilize was not addressed.

(21) SAE 912429 October 1991

“Composition and Reactivity of Fuel Vapor Emissions from Gasoline-Oxygenate Blends”

The reactivity of the oxygenated fuel vapor emissions is addressed in excellent detail. Permeation effects are not mentioned.

(22) SAE 912373 October 1991

“Real-Time Non-Fuel Background Emissions”

Fuel hose permeation and crank/case intake system breathing losses are studied, and data is shown indicating that hydrocarbon emissions continue from elastomers long after the gasoline is removed. Ethanol permeation is not addressed.

(23) SAE 902131 October 1990

“Assessment of Unregulated Emissions from Gasoline Oxygenated Blends”

One hour compressed time evaporative emission tests were performed on five vehicles with various fuels. Diurnal emissions were lower on 2 of the 5 with a 10% ethanol fuel compared to a base fuel. Hot soak emissions were higher on all 5 fuels with ethanol. Permeation was not addressed in the planning of the program.

(24) SAE 901114 May 1990

“Volatility Characteristics of Blends of Gasoline with Ethyl Tertiary-Butyl Ether (ETBE)”

This paper makes the case for the lower vapor generation of ETBE compared to an ethanol blended fuel, when made to the same oxygenate level. It mentions (without documentation) that ethanol has adverse effects on certain fuel system materials, mostly in older cars.

(25) SAE 810438 February 1981

“Impact of Gasohol on Automotive Evaporative and Tailpipe Emissions”

One hour compressed time evaporative emission tests were performed on two 1970’s vehicles with five fuels, including a 10% ethanol blend. The use of gasohol substantially increased evaporative emissions. Permeation increases were not mentioned or addressed.

(26) SAE 800858 June 1980

“Exhaust and Evaporative Emissions from Alcohol and Ether Fuel Blends”

Eight 1978 model year vehicles were evaluated for evaporative emissions using the one hour compressed time procedures of the day. Total evaporative emissions increased from 2.8 grams to 4.0 grams (diurnal + hot soak) when using splash blended 10% ethanol in Indolene test fuel. Highly purged canisters were part of the test procedure. Permeation emissions were probably not addressed in the program, as there is no mention in the report that time was allowed for stabilization between fuel changes.

(27) SAE 800891 August 1980

“Gasohol: Technical, Economic, or Political Panacea ?”

This report is a 1980 timeframe review of the technical and political environment concerning the use of ethanol splash blended into gasoline, authored by two employees of the California Air Resources Board. The authors concluded on page 30, “Gasohol increases evaporative emissions and refueling emissions from all vehicles...”

(28) SAE 800261 February 1980

“Evaporative and Exhaust Emissions from Cars Fueled with Gasoline Containing Ethanol or Methyl tert-Butyl Ether”

Vehicle tests showed that evaporative emissions were increased significantly by adding 10% ethanol to gasoline, even when the volatility was adjusted for the ethanol increase, using the one hour compressed-time procedures of the day. Page 5 suggests that the progressive deterioration of the rubber (nitrile) hose which vents the carburetor bowl to the canister may have been caused by the ethanol, and cites to other publications which have reported fuel hose deterioration and swell.

The report commented (page 9); “These studies support the earlier conclusion that activated carbon adsorbs ethanol and MTBE more strongly than some hydrocarbons. However, ethanol and MTBE can be purged, and therefore it does not appear that they will accumulate on the activated carbon to such an extent that the working capacity of the carbon will be severely degraded.”