

Oxygenated Fuel Considerations for In-Shop Fuel System Leak Testing Hazards

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ABSTRACT

Because of domestic production from renewable sources and their clean burning nature, alcohols, especially ethanol, have seen growing use as a blending agent and replacement for basic hydrocarbons in gasoline. The increasing use of alcohol in fuels raises questions on the safety of these fuels under certain non-operational situations. Modern vehicles use evaporative emission control systems to minimize environmental emissions of fuel. These systems must be relatively leak-free to function properly and are self-diagnosed by the vehicle On-Board Diagnostic system. When service is required, the service leak testing procedures may involve forcing test gases into the "evap" system and also exposure of the fuel vapors normally contained in the system to atmosphere. Previous work has discussed the hazards involved when performing shop leak testing activities for vehicles fuelled with conventional hydrocarbon gasoline [1, 2]. Oxygenate-blended fuels have significantly different vapor behaviors than conventional gasoline, and these changes affect the flammable mixture hazards associated with leak testing procedures.

This paper discusses the relevant vapor/liquid equilibrium and vapor properties of various oxygenate fuels and examines how these affect the flammable mixture hazards associated with shop leak testing procedures for fuel systems containing high oxygenate blends. The emphasis is on E85 as the most common currently used alternative fuel. A simple binary hexane-ethanol model was used to predict the equilibrium fuel vapors that are present in the fuel tank vapor space during shop leak testing with E85 present. The model was compared to experimental results that included the effects of weathering. The hazard associated with other oxygenated fuels could be predicted using previous literature. The results show that the vapor flammability hazards of oxygenate-blended gasoline fuels during leak

testing activities are initially similar to those from conventional gasoline. However, the potential effects of fuel weathering during shop testing and of anomalous temperatures are significantly more severe for some oxygenated fuel blends, particularly the high alcohol blends including E85.

INTRODUCTION

Alcohols, particularly methanol and ethanol, are seeing increased use as automotive fuels. The ability to produce alcohol domestically in North America from renewable sources and the clean burning nature of oxygenate-blended fuels have led to their use as a blending agent and a replacement for basic hydrocarbons in gasoline. The growing use of alcohols and other oxygenates in fuel raises some questions on the safe handling of such fuels across the production, transportation and usage phases.

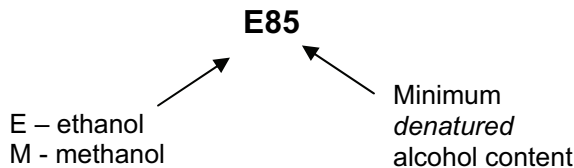
Modern vehicles are equipped with evaporative emission control systems to minimize fuel vapor loss to the environment through evaporation. These systems must be relatively leak-free to function properly and, if leaks are present, on-board diagnostic systems should detect them. The repair procedure generally involves some exposure of the potentially flammable fuel vapors in the fuel system. Previous work has illustrated the potential for flammable mixtures to be formed when performing shop-based leak testing activities on fuel systems containing conventional hydrocarbon gasoline [1, 2]. Alcohol-based fuel properties vary from those of conventional gasoline, raising the question of whether the flammability hazard associated with leak testing procedures will increase or decrease.

This paper examines the potential for flammable mixtures to be present in the fuel system vapor space when performing leak testing procedures on automotive fuel systems containing alcohol-based

fuels. Several alcohol fuels are considered, including E85, E100, M85, and M100, with emphasis on E85 as the most common alternative gasoline currently in use. A short discussion on flammability effects of other oxygenates such as MTBE is also included. Note that igniting a fire or explosion requires an ignition source in contact with any flammable mixture. The ignition source is not considered here although others have reported on potential ignition sources, (e.g. [3-5]).

COMPOSITION OF ALCOHOL-BASED ALTERNATIVE FUELS

Alcohol is used as a blend rather than in pure form to solve various concerns including preventing human consumption, controlling volatility, producing a visible flame in the event of a fire and controlling corrosive behavior. Several different alcohol-based fuel blends are in common use: E85, E100, M85, and M100. The naming convention for alcohol based fuels is as follows:



Note that the alcohol portion of fuels typically includes a significant amount of denaturing hydrocarbon (about 5%) used to prevent human consumption and provide flame color. Hence E100 is typically about 92% ethanol, 5% hydrocarbons, 2% other alcohols and 1% water. Composition specifications for the alcohol-based fuels considered in this study are given in Tables 1 through 4.

Species	Class 1 Spec	Class 2 Spec	Class 3 Spec
Ethanol + higher alcohols	min. 79% vol.	min. 74% vol.	min. 70% vol.
Other alcohols/ethers	max. 2% vol.	max. 2% vol.	max. 2% vol.
Hydrocarbons	17-21% vol.	17-26% vol.	17-31% vol.
Water	max. 1.0% mass	max. 1.0% mass	max. 1.0% mass
Vapor Pressure (psi)	5.5-8.5	7.0-9.5	9.5-12

Table 1. E75-E85 Specification (Source: ASTM D5798 [6]).

Species	Specification
Ethanol	min. 92% vol.
Other alcohols/ethers	max. 2% mass
Hydrocarbons	max. 5% mass
Water	max. 1.25% mass

Table 2. E100 composition (Source: ASTM D4806 [7]).

Species	Specification
Methanol	min. 84% vol.
Other alcohols/ethers	max. 2% mass
Hydrocarbons	13-16% mass
Water	max. 0.5% mass

Table 3. M85 composition (Source: California Code of Regulations s 2292.2 [8]).

Species	Specification
Methanol	min. 96% vol.
Other alcohols/ethers	max. 2% mass
Hydrocarbons	max. 2% mass
Water	max. 0.3% mass

Table 4. M100 composition (Source: California Code of Regulations s 2292.1[9]).

VOLATILITY

Alcohol-based fuels, comprised of a mixture of alcohol and hydrocarbons, deviate significantly from ideal vapor-liquid equilibrium theory because of the polar nature of alcohol molecules. Neat (pure) alcohols have low vapor pressures relative to hydrocarbons of comparable molecular weight due to hydrogen bonding between the alcohol molecules [10]. When hydrocarbons are mixed with alcohols some of the hydrogen bonds between alcohol molecules are released and the alcohol vapor-liquid equilibrium shifts, creating more alcohol vapor than would be expected based on the component vapor pressures. The non-ideal volatility effect of mixing ethanol with gasoline is illustrated by the curve in figure 1 [10].

The volatility of alcohol fuels can be controlled by adjusting both the volatility and the quantity of hydrocarbons blended with the alcohol. Low molecular weight hydrocarbons such as butane can be blended to increase volatility. The volatility adjustment range is limited by the fraction of hydrocarbon present in the liquid fuel. The volatility of E100 and M100, containing a minimum of 92% liquid ethanol (5% hydrocarbon) and 96% liquid methanol (2% hydrocarbon) respectively, can only be adjusted in a very limited range. In contrast, the 17% to 30% hydrocarbon content of E85 allows a wide range of volatility variation, with RVP varying from 5.5 psi (38 kPa) to 12 psi (83 kPa) [6].

Modeling the non-ideal vapor-liquid equilibrium of a gasoline (containing multiple hydrocarbon components) – ethanol mixture is quite complex. A simple binary mixture of one hydrocarbon and ethanol is suitable for the purpose of explaining the non-ideal equilibrium behavior of hydrocarbon-ethanol mixtures. For this purpose, hexane in ethanol blends provide a useful approximation of typical ethanol-blended gasoline vapor pressure and molecular properties. As shown in figure 2, a

mixture of 80% ethanol and 20% hexane gives the approximate alcohol content and volatility of a low-volatility E85 gasoline with about 5.8 psi (40 kPa) RVP.

VAPOR COMPOSITION

Calculating the vapor composition above an alcohol-hydrocarbon mixture is not straightforward because of the non-ideal nature of the mixture vapor-liquid equilibrium. In general, the liquid / vapor phase equilibrium of a component in a mixture can be given as:

$$y_i P = \gamma_i x_i P_{vp}$$

where y_i is the vapor phase mole fraction of the component i , P is the vapor pressure above the mixture, x_i is the liquid volume fraction of component i , P_{vp} is the vapor pressure of the pure component i , and γ_i is an activity coefficient that corrects for the non-ideal nature of the mixture. In the ideal case, the activity coefficients, γ_i would be 1 but with alcohol/hydrocarbon mixtures they are variables obtained by experiment. Reid [11] gives a calculation procedure for the activity coefficients for binary ethanol and hydrocarbon mixtures as:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)$$

where species 1 and 2 are the ethanol and hydrocarbon respectively. Values for Λ_{12} and Λ_{21} are available for a binary ethanol-hexane mixture, which results in a vapor pressure of 5.8 psi (40 kPa) for an 80% ethanol mixture at 100°F, similar to low volatility E85 [12].

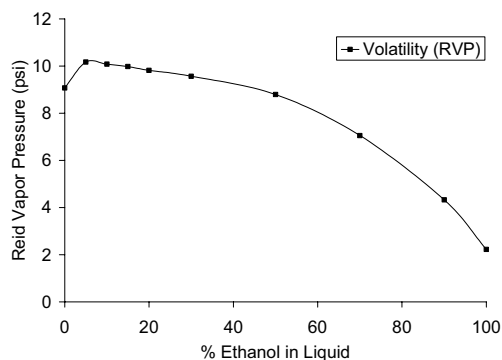


Figure 1. Volatility of gasoline-ethanol mixtures, with a base gasoline RVP of 9 psi. [11] The non-linear nature of the volatility curve suggests the non-ideal behavior of gasoline-ethanol blends. Note that the volatility of the blend is actually higher than the base hydrocarbon fuel for all blends up to 50% ethanol.

The alcohol vapor fraction above E85 will vary substantially, depending on the volatility of the blended hydrocarbon and the temperature of the mixture. For example, consider the low-RVP E85 formed by an 80% ethanol-20% hexane blend. As shown by the relationship in figure 3, the vapor fraction at 20°C (68°F) will be approximately 29% ethanol and 71% hydrocarbon which is almost the

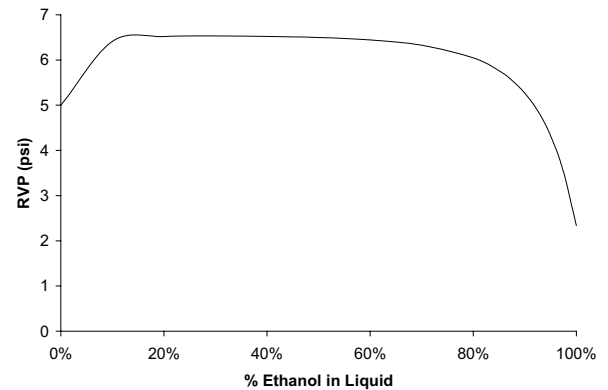


Figure 2. Calculated RVP of hexane-ethanol mixtures. RVP is approximately 5.8 psi (40 kPa) for a 80% ethanol-20% hexane blend.

reverse of the liquid composition. A higher volatility E85 would have even less ethanol, (and more hydrocarbon) in the vapor since the extra fuel volatility comes from substantially raising the volatility of the 20% hydrocarbon portion in the liquid.

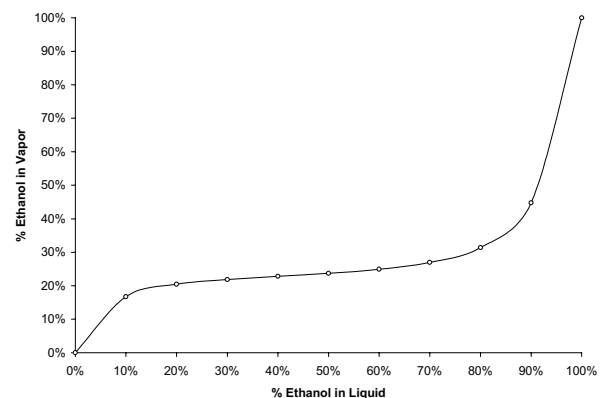


Figure 3. Ethanol concentration in vapor above a liquid ethanol-hexane mixture at 20°C (68°F).

The high hydrocarbon concentration in the vapor phase gives E85 fuel vapor similar transport properties (such as diffusivity) to gasoline vapor. Vapor density is somewhat affected by the alcohol content with its low molecular weight. For example undiluted fuel vapor which is 29% ethanol

and 71% hexane is 15% lighter than pure hexane vapor. However, the ethanol-containing vapor is still substantially heavier than air (the specific gravity of pure ethanol vapor is 1.6) so it will still behave like a heavy vapor relative to air. As fuel vapors are mixed with air, the density difference between E85 vapor/air mixtures and hydrocarbon gasoline vapor/air mixtures diminishes to become negligible for near-flammable mixtures. In summary, the hydrocarbon dominance in the vapor makes fuel vapor physical properties for high-alcohol fuels very similar to those for conventional gasoline fuels.

WEATHERING EFFECT ON VAPOR COMPOSITION

As discussed above, E85 mixtures have a much higher hydrocarbon fraction in the vapor phase than in the liquid phase. When fuel vapor escapes from the fuel tank vapor space and more liquid evaporates to replace it, high-alcohol fuels experience accelerated weathering compared with conventional gasoline because they are preferentially losing the light hydrocarbons added to provide volatility. The actual rate of weathering is determined by the relative rate of alcohol and hydrocarbon evaporation, generally under conditions that depart from equilibrium.

To measure the weathering effect under conditions typical of shop leak detection activities, a low vapor pressure E85 fuel, (unweathered RVP = 7.0 psi, 48 kPa), was blended using 80% neat ethanol and 20% 10.5 psi (72 kPa) RVP gasoline. Four litres, (1.1 US gallon) of this fuel was placed in a 60 L (16 US gallon) automotive fuel tank to simulate a low fuel level condition most susceptible to weathering. A series of repeated 20 minute leak test cycles was run on the tank, with the vapor allowed to return to equilibrium in the tank between these tests. The testing procedure consisted of flowing 11 L/min (0.4 cfm) of air through the tank with typical leak detection connections as described in greater detail elsewhere [2].

Figure 4 shows the Reid Vapor Pressure of the E85 mixture after each test cycle. Figure 5 shows the ethanol fraction of the fuel vapor, as measured by gas chromatography. The fuel weathering effect is shown by the drop in fuel volatility and the increasing ethanol fraction in the fuel vapor. Figure 4 shows that the fuel volatility (RVP) dropped substantially with the first twenty minute cycle, from 7 psi (48 kPa) to 5.5 psi (38 kPa) and continued to drop with each subsequent test, reaching 4 psi (28 kPa) after four tests. At the same time, the ethanol fraction of the remaining fuel vapor progressively increased with weathering, reaching 14% after the first 20 minute test and 33% after four, 20 minute tests. These

results show the effects of weathering in an extreme case, (low fuel level and prolonged leak testing period), while using a normal leak testing configuration and a flow rate near the maximum typically seen during leak testing. Weathering is important because it affects the fuel vapor flammable range as discussed in the next section.

FLAMMABLE RANGE

The presence of oxygen in alcohol molecules gives alcohols a much higher flammable concentration range than hydrocarbons. Typically, the flammable range of hydrocarbon gasoline vapor in air is given as 1.4 to 7.6% volume fraction.

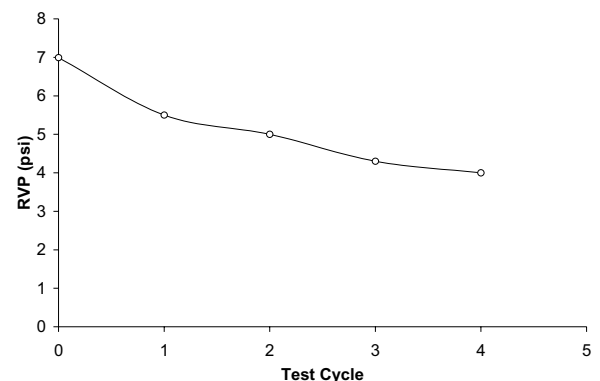


Figure 4. Reid vapor pressure reduction of E85 over 4 weathering test cycles. 4 L of E85 fuel. Each test cycle is 20 min of air flow at 11 L/min (0.4 cfm)

Pure ethanol vapor is flammable between 3.3% and 19% concentration in air while pure methanol vapor is flammable between 6.7% and 36% in air [13]. The combination of low vapor pressure and high flammable range allow alcohol vapors to form flammable mixtures with air while at equilibrium at normal ambient conditions. Figures 6 and 7 demonstrate the temperature ranges over which equilibrium methanol and ethanol vapors produce flammable mixtures with atmospheric air. Methanol at equilibrium forms flammable mixtures between 5 and 37°C (40 to 100°F), while ethanol forms flammable mixtures between 12 and 40°C (55 to 105°F). Basically, the vapor space over pure alcohol fuels is likely to be at equilibrium and therefore will normally be flammable at typical ambient temperatures.