LEAK TESTING FLAMMABILITY HAZARDS
WITH HIGH ALCOHOL CONTENT FUEL

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1.0 PREAMBLE

Alcohols, including 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 alcohol-blended fuels have seen alcohol implemented as a blending agent and replacement for basic hydrocarbons in gasoline. The growing use of alcohol in fuels raises questions on the safety of these fuels.

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, repairs are required. The repair procedure requires exposure of the potentially flammable fuel vapors in the fuel system, raising questions of the hazards involved with the repair process. Previous work has shown a measure of hazard when performing leak testing activities on fuel systems containing conventional hydrocarbon gasoline [1]. Alcohol-based fuels have different properties than conventional gasoline, raising the question of whether alcohol fuel will increase or decrease the hazard associated with leak testing procedures.

This report examines the potential hazards associated with performing leak testing procedures on automotive fuel systems containing alcohol-based fuels. Several alcohol fuels are examined, including E85, E100, M85, and M100, with emphasis on E85 as the most common currently used alternative gasoline. A short discussion on flammability effects of other oxygenates such as MTBE is also included.

2.0 INTRODUCTION

Evaporative emissions system leak testing procedures have been shown to produce a significant amount of flammable fuel-air mixtures under certain conditions [1]. The introduction of oxygenate or alcohol blends has various effects on gasoline vapor properties and may alter the potential to create flammable mixtures.

The most common oxygenate-blended gasoline in use today is reformulated gasoline, (RFG), which contains a small percentage of either MTBE or ethanol. Ethanol-blended RFG with 10% ethanol, (E10), is very common, in part because nearly every gasoline-fueled vehicle currently produced is approved to use up to 10% ethanol. Beyond E10, the use of more radical alternative fuels is forecast to rise sharply. Alternative fuels are defined by the Energy Policy Act of 1992 as "methanol, denatured ethanol, and other alcohols; mixtures containing 85 percent or more (or some other percentage, but not less than 70 percent". Currently, high ratio blends of ethanol and methanol, (E85, E100, M85 and M100), are used in relatively small numbers of vehicles. However, ethanol can be produced domestically from renewable sources and has clean burning characteristics so its use as an automotive fuel, particularly as E85, has a strong growth potential.

This report examines the relative leak testing flammability hazards of oxygenated fuels when compared with conventional, non-oxygenated gasoline. Comparable reports have covered the leak detection hazards for conventional gasoline [1] and low alcohol content fuel, up to E10 [2]. The focus of this report is to consider leak detection hazards with high alcohol content fuels, particularly represented by E85 as it is likely to be a widely used alternative fuel in the future.

3.0 IGNITION SOURCES AND PROPAGATION

Creating an explosion or flash fire requires the combination of a flammable fuel/air mixture and an ignition source. The research work leading to this report is mainly concerned with flammable mixture formation rather than control of ignition sources. Hence, this section simply lists ignition sources that are likely to be present in or around a vehicle fuel system during leak testing activities. The assumption is that it is difficult to positively limit all ignition sources in the vehicle service environment and hence servicing equipment and procedures should be designed to minimize the formation and discharge of flammable mixtures.

Potential ignition sources include those inside the fuel system itself, on the vehicle outside the fuel system, and in the service shop environment beyond the vehicle. Ignition sources inside the fuel system include electrical wiring, (especially fuel pump wiring and connectors but also fuel sensor wiring), sparks from fuel pump brushes, heat and grinding sparks from malfunctioning fuel pumps and static electrical discharges from spraying or splashing fuel. Conventional gasoline fuel systems have generally been designed with the assumption that the fuel tank vapor space is too fuel-rich to burn so there is no incentive to eliminate ignition sources within the fuel system or flame propagation into the fuel tank. Electrical fuel pumps have been shown to create sufficient energy to ignite flammable vapors [3]. Likewise, electrical connection problems in the high-power wiring to the fuel pumps been shown to produce both arcing and sufficient heat to melt surrounding materials [4]. In contrast, for flex-fuel vehicles, designed for the use of high alcohol-content fuels, specific fuel tank safety measures are common [5]. The electrical equipment inside the fuel system is specified with totally enclosed or brush-less motors and a flame arrestor is

typically installed on the filler neck to prevent outside flames from propagating into the fuel tank vapor space.

External ignition sources on the vehicle include direct heat sources such as exhaust lines and friction-heated components, direct sparks from electrical equipment (especially alternators and relays), and also static electrical sparks from various sources including belts. External ignition sources in the service shop around the vehicle include electrical equipment such as battery chargers and fans, other operating vehicles, static electrical discharges from vehicles or clothing, as well as the actual test equipment or temporary lighting being used under the vehicle.

For a vehicle with openings in the fuel system larger than the flame quench diameter, (such as an open fuel cap to a broken evap system hose), a flash fire ignited in fuel/air mixtures outside the fuel system can propagate back to the fuel system and hence external flash fires can be another ignition source for any flammable mixtures formed *inside* the fuel system.

Vehicles in normal operation with proper maintenance would almost never have flammable mixtures inside the fuel system nor are they likely to leak enough fuel vapor to produce flammable mixtures outside the system. However, the wide range of possible faults in vehicles presented for servicing significantly raises the likelihood of abnormal fuel system operation and lack of fuel vapor containment. Likewise, the purge flows and subsequent pressurizations used in the leak testing procedures can force significant quantities of fuel vapor out of the tank vapor space and significant quantities of air into the fuel system [15]. Since it is impossible to positively eliminate all ignition points, we are forced to consider the degree to which leak detection activities produce flammable mixtures and the effects of alternative fuels on the resultant hazards.

4.0 COMPOSITION OF ALCOHOL-BASED ALTERNATIVE FUELS

Alcohol is used as a blend rather than in pure form to solve various concerns including safety issues, preventing human consumption, 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:

E85

E – ethanol   Minimum *denatured*
M - methanol   alcohol content
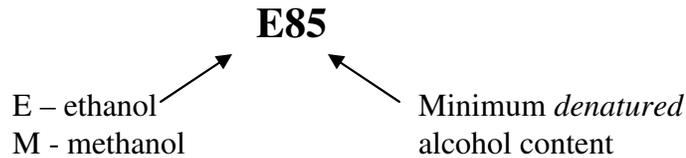
Note that the alcohol portion of fuels typically includes a significant amount of *denaturing* hydrocarbon (about 5%) used to prevent human consumption and provide flame color. Hence E100 is typically about 92% ethanol, 5% hydrocarbons, 2% other alcohols and 1% water. Composition specifications for the 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]).

One issue that arises with the use of flex-fuel vehicles is the co-mingling of various types of fuel. A consumer could fuel up a flex-fuel vehicle with regular gasoline, drive it until the fuel tank is half full, and refuel with E85, creating a 40% ethanol blend fuel. For the purposes of this report, the fuel in the vehicle will be considered to meet alternative fuel specifications.

5.0 PROPERTIES OF ALCOHOL-BASED ALTERNATIVE FUELS

5.1 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 shown in figure 1 [10].

The volatility of alternative fuels can be controlled by adjusting the hydrocarbon blended with the alcohol. Low molecular weight hydrocarbons such as butane can be blended to increase volatility. The ability to change the volatility of the fuel is limited by the fraction of hydrocarbon present in the liquid fuel. The volatility of E100 and M100, containing 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[a] varying 5.5 psi (38 kPa) to 12 psi (83 kPa).

A simple binary mixture that approximates a high-alcohol fuel would be a hexane-ethanol blend. 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.

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[a] Gasoline volatility is rated by the Reid Vapor Pressure (RVP) which is the gasoline vapor pressure in a sealed container over liquid gasoline at 100°F (38°C).
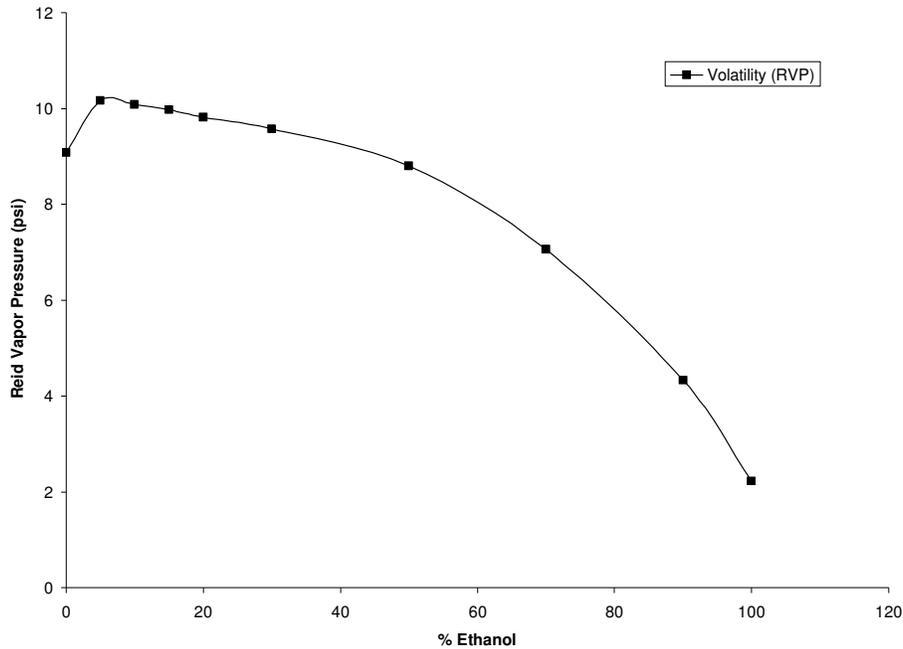
Figure 1. Volatility of gasoline-ethanol mixtures, with a base gasoline RVP of 9 psi. (REFA) The non-linear nature of the volatility curve suggests the non-ideal behavior of gasoline-ethanol blends. Note that the volatility of the blend is actually higher than the base hydrocarbon fuel for all blends up to 50% ethanol.
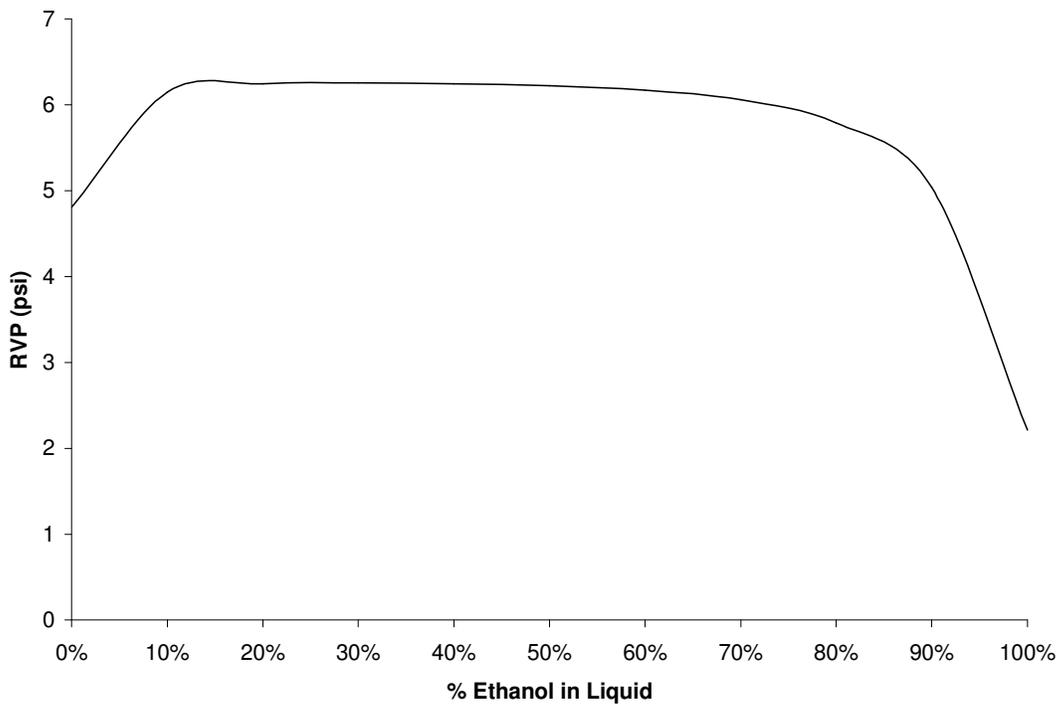

Figure 2. Calculated RVP of hexane-ethanol mixtures.

RVP is approximately 5.8 psi (50 kPa) for a 80% ethanol-20% hexane blend.

5.2 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. Wilson [11] gives a calculation procedure for the activity coefficients for 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].
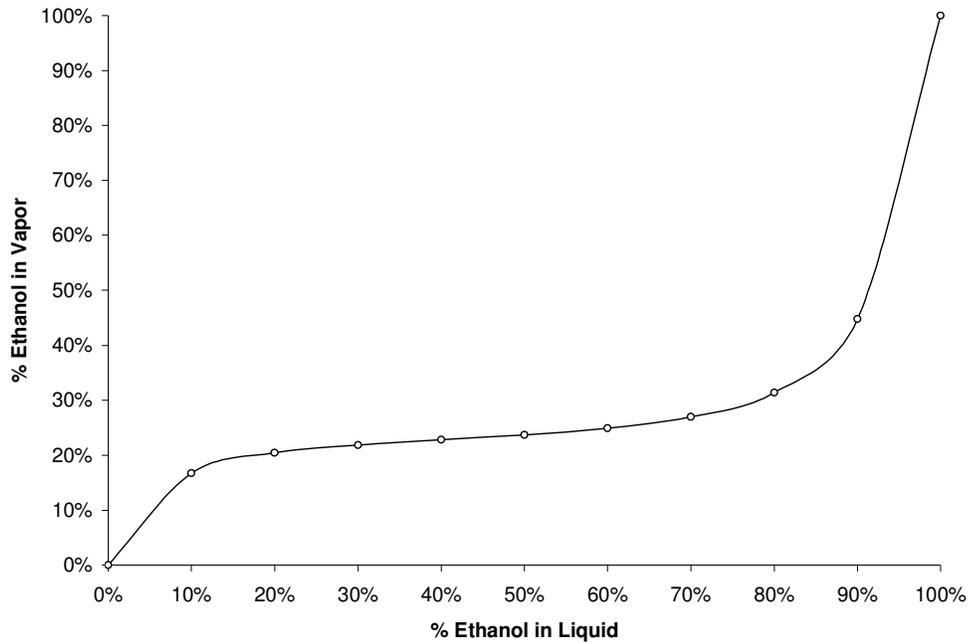
Figure 3. Ethanol concentration in vapor above a liquid ethanol-hexane mixture at 20°C (68°F).

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 a low-RVP E85 formed by an 80% ethanol-20% hexane blend, (which gives 5.8 psi or 40 kPa RVP). 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 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.

The high hydrocarbon concentration in the vapor phase gives E85 fuel vapor transport properties, (such as diffusivity and conductivity), which are similar to gasoline vapor. Vapor density is somewhat affected by the alcohol content with its low molecular weight. For example a pure fuel vapor which is 29% ethanol and 71% hexane is 15% lighter than pure hexane vapor. However, this is still substantially heavier than air so the

fuel vapor will behave like a heavy vapor. Likewise, as it mixes with air, the density difference between E85 vapor/air mixtures and hydrocarbon gasoline vapor/air mixtures diminishes to become negligible for near-flammable mixtures. Hence, fuel vapor behavior of high-alcohol fuels is very similar to that of conventional gasoline fuels.

5.3 Weathering Effect on Vapor Composition

As discussed above, E85 mixtures have a much higher hydrocarbon composition in the vapor phase than in the liquid phase. If fuel vapor escapes from the fuel tank vapor space and more liquid evaporates, high-alcohol fuels experience accelerated weathering compared with conventional gasoline because they are preferentially losing the hydrocarbons that control 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 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 flow cycles were run on the tank, with the vapor allowed to return to equilibrium in the tank between these tests. Oxygen sensors present in the tank were used to determine when equilibrium had been achieved. The oxygen sensors would show a measurable increase in output when air was flowing into the tank from the increased oxygen concentration. Once the flow was stopped, the fuel vapor displaced the oxygen as it returned to equilibrium, reducing the output. Once the output stabilized, the fuel was

considered to be at equilibrium. This generally took approximately 2 hours. The testing

procedure is described in greater detail elsewhere [1].

Figure 4 shows the Reid Vapor Pressure of the E85 mixture after each test cycle. It

should be noted that this is a measure of the vapor pressure in the tank once the fuel vapor

reached equilibrium. The air flowing into the tank reduces the concentration such that

evaporation occurs. While the fuel concentration was not measured real-time while the air

was flowing into the tank, it likely dipped into the flammable region during the air flow

cycles, as seen in previous testing with conventional gasoline [1].   Figure 5 shows the

ethanol fraction of the fuel vapor, as measured by gas chromatography, (Appendix A). 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.
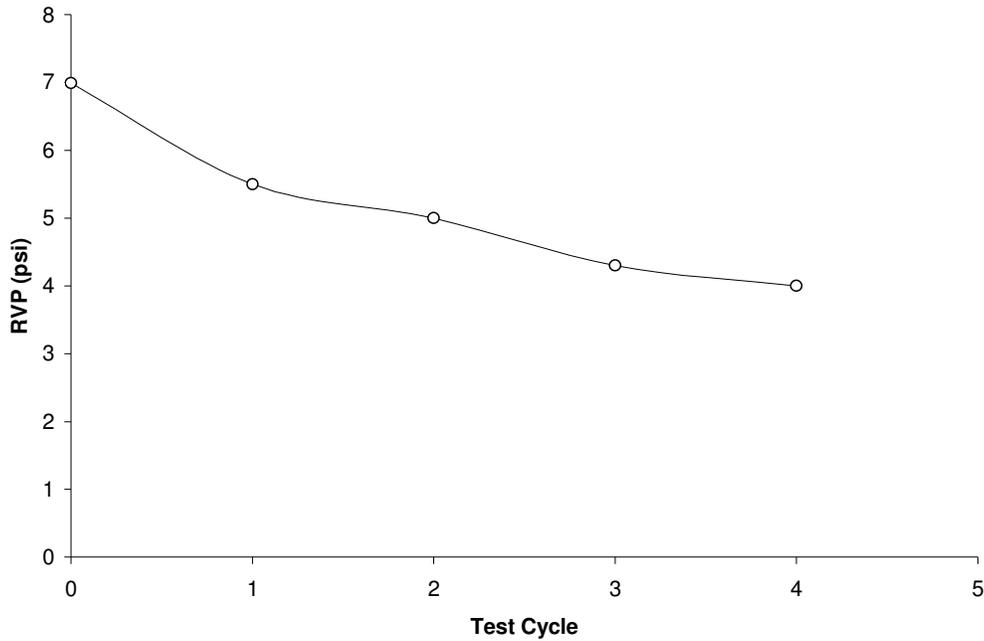
Figure 4. Reid vapor pressure reduction of E85 over 4 weathering test cycles with 4 L of E85 fuel. Test cycle is 20 min of air flow at 11 L/min (0.4 cfm) (See Figure 15 for the vapor concentration during the test cycle).
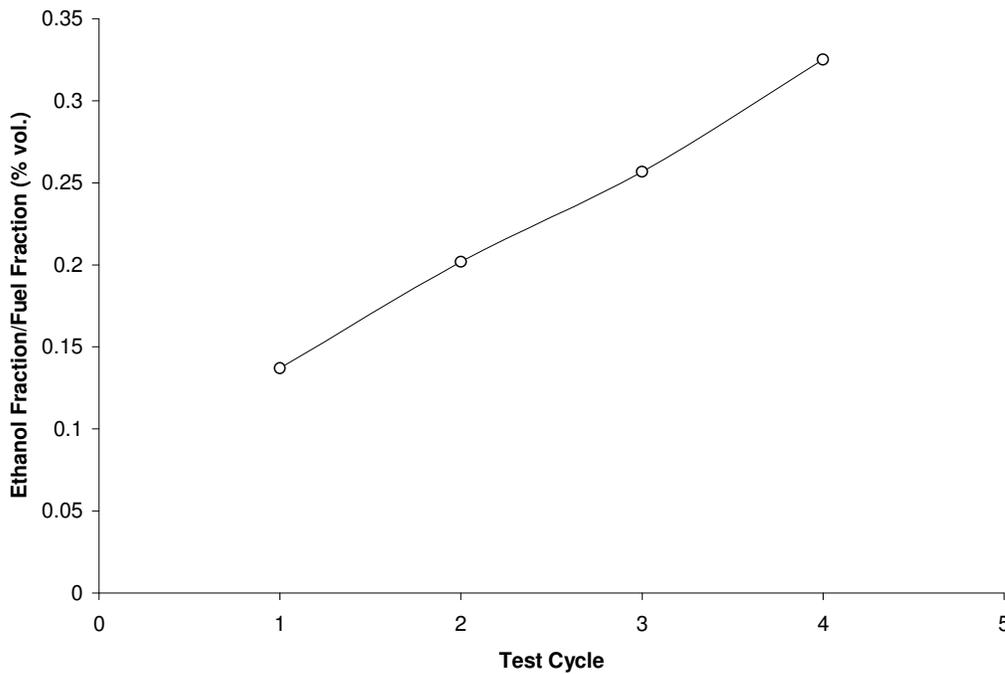

Figure 5. Vapor ethanol fraction rise over E85 liquid fuel for 4 weathering test cycles. 23°C, 4 L of E85 fuel in 60 L (16 US gal) tank, gas chromatograph measurements.

Test cycle is 20 min of air flow at 11 L/min (0.4 cfm).

5.3 Flammable Range

The presence of oxygen in alcohol molecules gives alcohols have 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 concentration. 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 low vapor pressures of alcohols combined with the high flammable range cause equilibrium alcohol vapors to form flammable mixtures with air at normal ambient conditions. Figures 6 and 7 demonstrate the temperature range over which equilibrium methanol and ethanol vapors produce flammable mixtures with atmospheric air, showing that flammable vapor/air mixtures are likely to occur at normal ambient temperature.
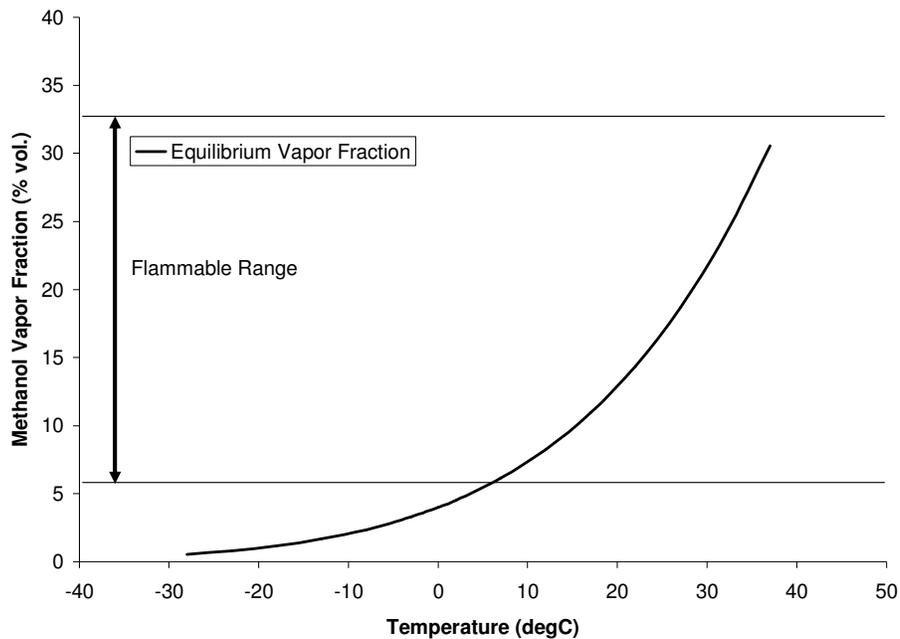
Figure 6. Methanol equilibrium vapor fraction formed above neat methanol in air at standard atmospheric pressure. At standard atmospheric pressure, pure methanol vapor is flammable between approximately 5°C and 37°C (40°F and 100°F).
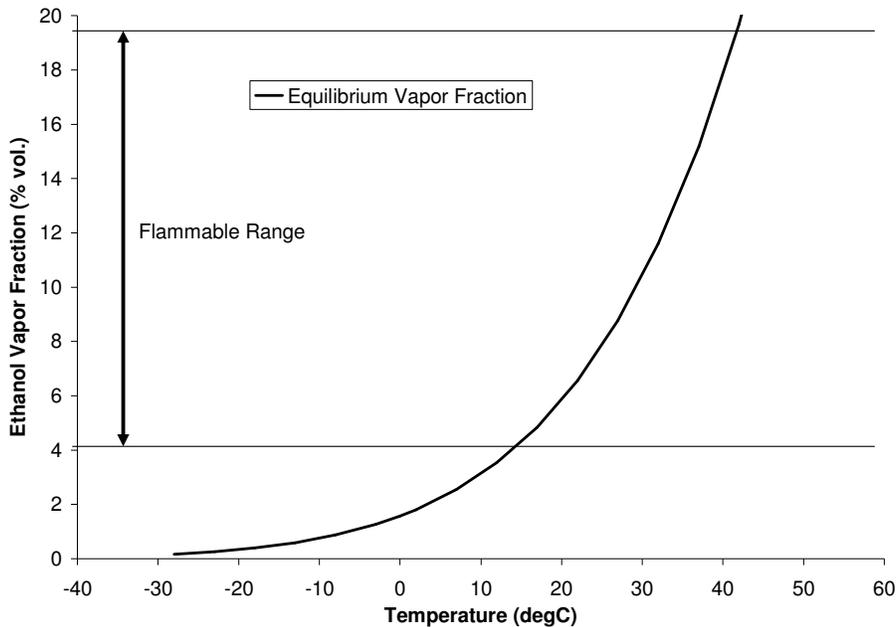

Figure 7. Ethanol equilibrium vapor fraction formed above neat ethanol in air at standard atmospheric pressure. At standard atmospheric pressure, pure ethanol vapor is flammable between approximately 12°C and 40°C (55°F and 105°F).

Depending on the hydrocarbon denaturant used, E100 and M100 will approach the properties of neat ethanol and methanol, respectively. Properly functioning evaporative emissions systems contain fuel vapor at near-equilibrium conditions so fuel vapor concentrations can be assumed to be close to those shown in Figures 6 and 7 for neat alcohol fuels. Hence, the vapor space in fuel systems containing E100 and M100 should be considered to be potentially flammable during any testing. Note that vapor space contents leaking out of the fuel and evap system will diffuse into the air and the fuel concentration will diminish towards the lower flammability limit and ultimately towards zero. This

means that there will be a flammable plume of vapor space contents exiting from the vapor space during testing.

The flammable range of alcohol fuels such as E85 or M85 depends on the alcohol fraction in the hydrocarbon-alcohol mixture which affects both the fuel volatility, (vapor fraction in air), and the flammable range of the resultant vapor. The flammable range for alcohol-hydrocarbon-air mixtures can be estimated using Le' Chatelier's law [14]:

$$LFL(\%vol) = \frac{100}{C_{alcohol}/LFL_{alcohol} + C_{gasoline}/LFL_{gasoline}}$$

$$UFL(\%vol) = \frac{100}{C_{alcohol}/UFL_{alcohol} + C_{gasoline}/UFL_{gasoline}}$$

where $C_{alcohol}$ and $C_{gasoline}$ are the volumetric concentrations of ethanol and gasoline, respectively, and LFL, $LFL_{alcohol}$, $LFL_{gasoline}$ are the lower flammable limits for the mixture, the alcohol, and gasoline, respectively. The UFL follows a similar naming convention.

Figures 8 and 9 show the LFL, UFL, and equilibrium vapor concentration in air for ethanol - hexane mixtures at 20°C (68°F) and 10°C (50°F) respectively. Considering Figure 8, the equilibrium vapor concentration is close to 20% while the vapor UFL remains close to 9% for alcohol contents up to the maximum 80% ethanol typical of E85. The flammability characteristics of a fresh E85 mixture remain similar to a gasoline mixture of equivalent volatility because the vapor fraction is dominated by hydrocarbon, (as shown in section 5.2). For higher alcohol content fuels (beyond 90% ethanol), the equilibrium fuel vapor fraction falls sharply and the upper flammable limit rises sharply. As shown in Figure 8, the equilibrium vapor mixture at 20°C (68°F) is likely to be flammable for ethanol fuels above about 95% ethanol concentration.

As the temperature decreases, the fuel vapor fraction drops, in this case to about 11% which is much closer to the vapor upper flammable limit. In consequence, the alcohol content at which the equilibrium vapor mixture becomes flammable drops to something closer to 90% ethanol. At lower ambient temperatures, the ethanol/hexane mixture would be flammable for any range of alcohol content. The hydrocarbon content would need to be replaced with a compound more volatile than hexane to keep E85 vapors from becoming flammable at lower temperatures.
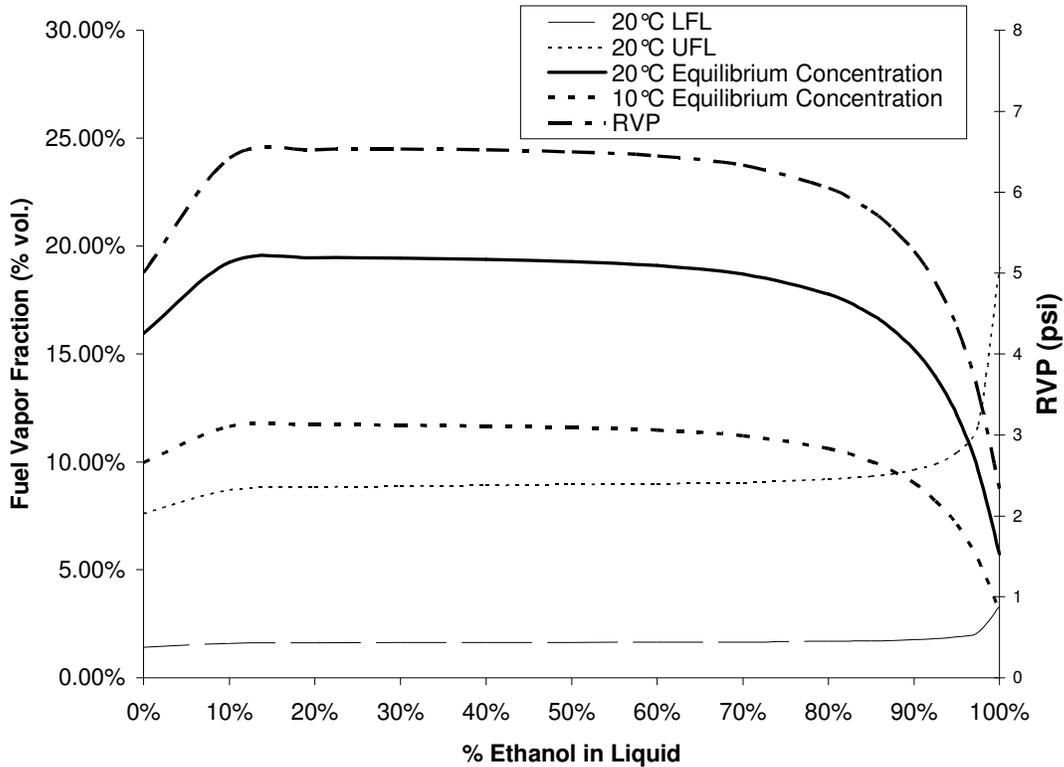
Figure 8. Flammable range and equilibrium ethanol concentration of vapor fraction for theoretical ethanol-hexane mixtures at 20°C (68°F) and 10°C (50°F). The RVP scale is on the right, the vapor fraction scale for all other curves is on the left.

Figure 9 shows the effect of weathering on gasoline flammability for a high-alcohol gasoline (E85). As the gasoline weathers and loses hydrocarbon content, (due to exposure to air flow as described in Section 5.2 above), the equilibrium fuel vapor concentration in air falls and the upper flammable limit rises, reducing the safety margin between tank vapor space concentration and flammable conditions.

The vapor pressure of the weathered E85 mixtures was measured between ambient temperature and 38°C. The data was curve fitted with an Antoine equation of the following form:
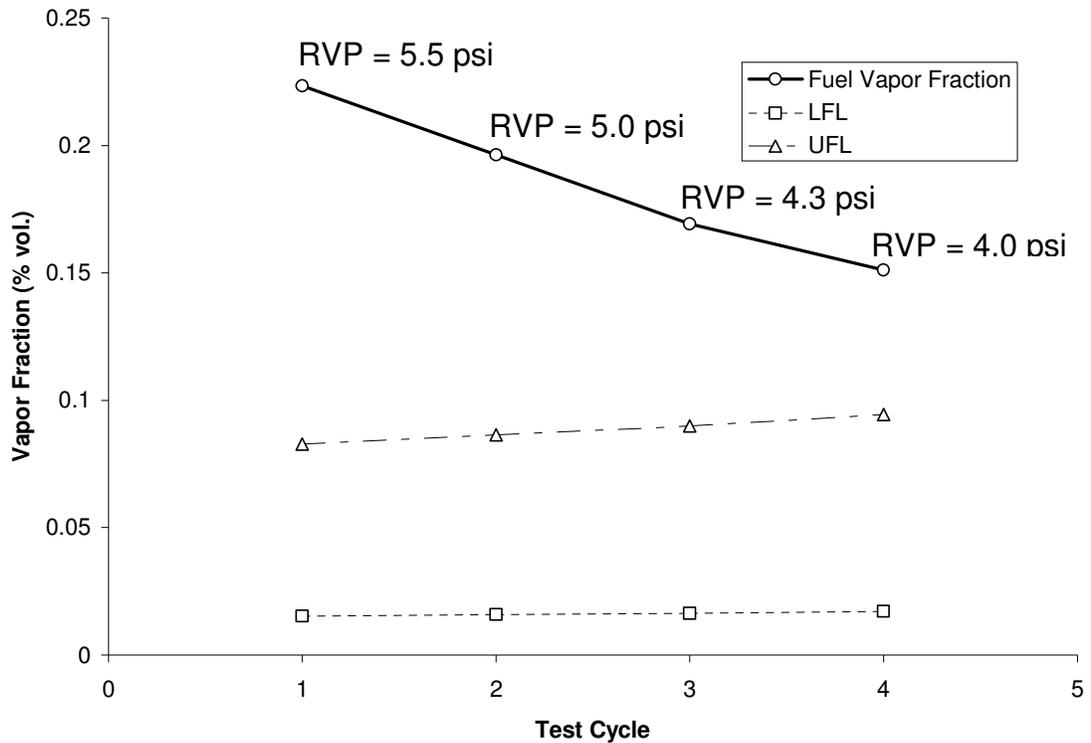
Figure 9. Flammable range and equilibrium fuel vapor concentrations for extreme weathered E85 at T = 23°C (73°F). During test cycles the vapor concentration in the tank is diluted away from equilibrium with the incoming air into the flammable range. See figure 15 for the concentration measured in the tank for the first cycle. Subsequent cycles experienced similar reductions in vapor concentration.

$$\log_{10} vP = C + \frac{B}{T + A}$$

Where T was the temperature in degrees Celsius and vP was the vapor pressure in kPa. This data was extrapolated to predict the temperature where the equilibrium fuel vapor formed above the fuel would reach the upper flammable limit. It should be noted that this method is likely not very accurate for an ethanol-gasoline mixture, and also extrapolated outside the data set. It is unlikely to be accurate to more than ±5°C (9°F). However, it is adequate to show the effect of weathering on the temperature where the equilibrium mixture will become flammable. Figures 10, 11, 12, and 13 show the predicted equilibrium vapor fraction curve for the fresh 7.0 psi, weathered 5.5 psi, weathered 5 psi, and weathered 4.3 psi RVP E85 respectively. 7.0 psi E85 was predicted to become flammable at -2°C (28°F). By weathering the fuel to 5.5 psi RVP, the temperature to reach UFL

increased by 5°C (9°F). Subsequent weathering to 5.0 psi RVP and 4.3 psi RVP increased the temperature to reach UFL by 6°C (11°F) and 4°C (8°F), respectively.
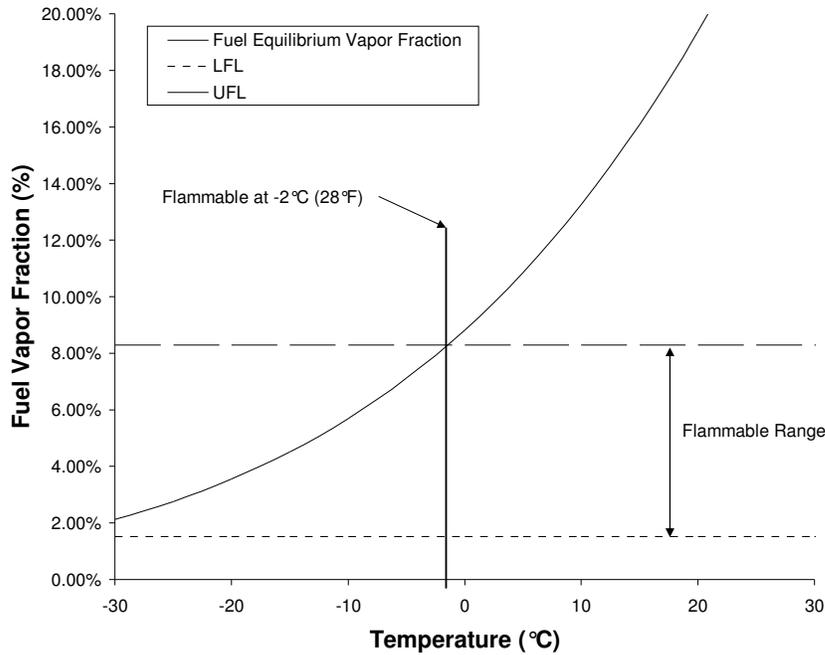

Figure 10. Predicted equilibrium fuel vapor fraction formed above 7.0psi RVP E85 in air at standard atmospheric pressure. Concentration is below the UFL at -2°C (28°F).
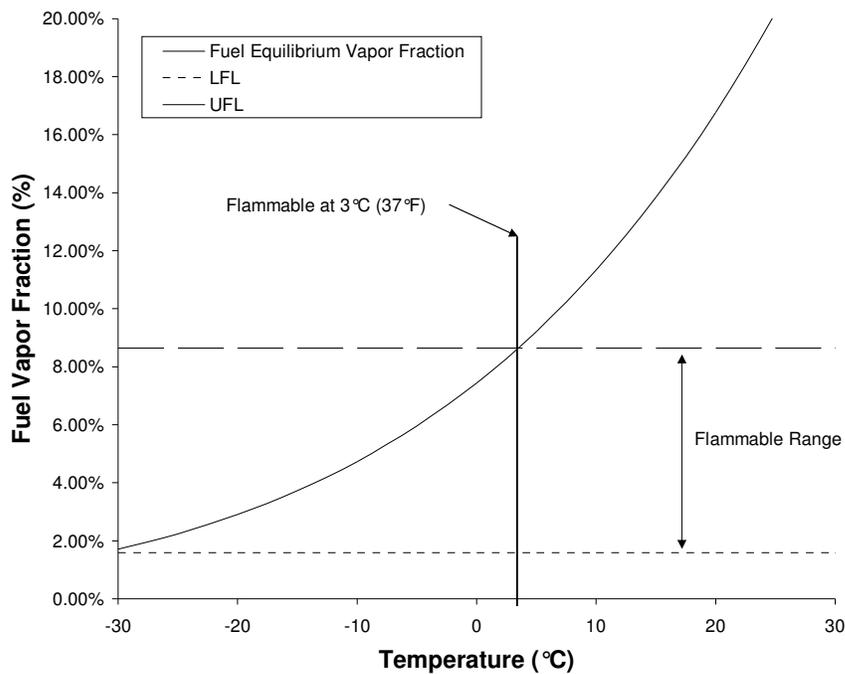

Figure 11. Predicted equilibrium fuel vapor fraction formed above weathered 5.5 psi E85 in air at standard atmospheric pressure. Concentration is below the UFL at 3°C (37°F).
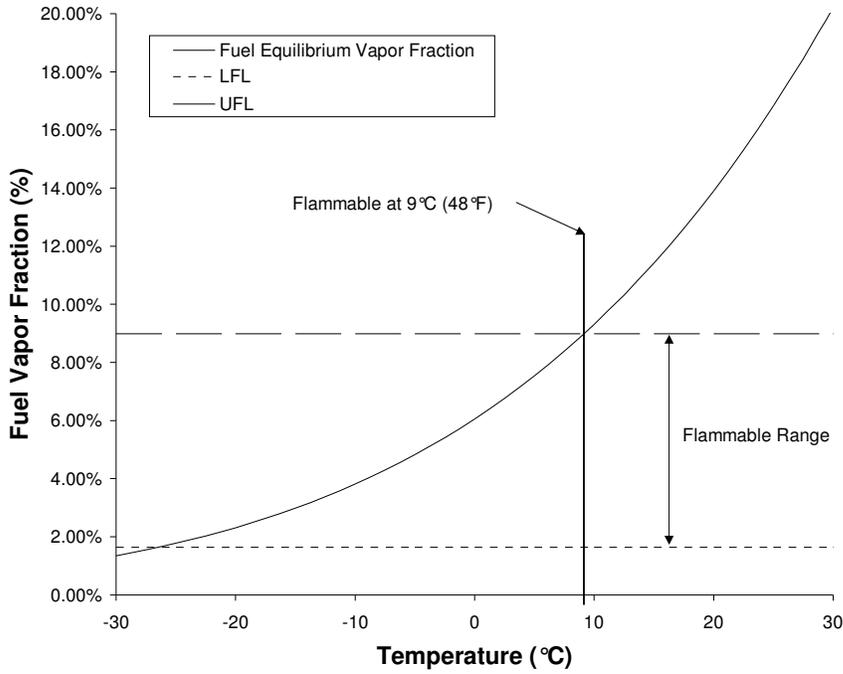
Figure 12. Predicted equilibrium fuel vapor fraction formed above weathered 5.0psi E85

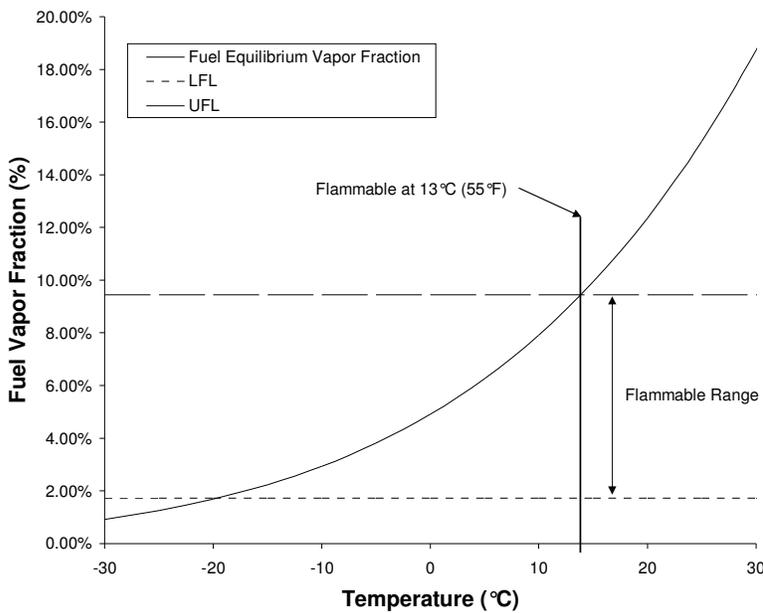in air at standard atmospheric pressure. Concentration is below the UFL at 9°C (48°F).

Figure 13. Predicted equilibrium fuel vapor fraction formed above weathered 4.3psi RVP

E85 in air at standard atmospheric pressure. Concentration is below the UFL at 13°C

(55°F).

6.0 OTHER OXYGENATES

Various oxygenates, particularly ethers, have been used as blending agents in reformulated gasoline. The most common ether used for reformulated gasoline is MTBE (methyl tertiary butyl ether), but TAME (tertiary amyl methyl ether) and ETBE (ethyl tertiary butyl ether) have also been used [15]. Ethers exhibit less polarity than alcohols and as such have liquid-vapor equilibrium behavior closer to ideal.

	Gasoline	MTBE	TAME	ETBE
LFL, % vol.	1.4	1.6	1.0	1.0
UFL, % vol.	7.6	8.4	7.1	6.8
Vapor Pressure, psi	7.0-15.0	7.8	1.5	4.0
Vapor Density (Relative to air)	3.4-5.0	3.0	NA	3.5

Table 5. Properties of common ether blending components compared with gasoline. Low vapor pressure ethers are usually compensated by blending higher volatility hydrocarbon components (ie more pentane and butane) with the gasoline [15].

Table 5 compares key properties of typical ether blending components with those of hydrocarbon gasoline. The flammable ranges and vapor density relative to air are very similar. High concentrations of some ethers such as TAME or ETBE could significantly reduce the vapor pressure, however, for most blends the volatility effect of the ether can be counteracted with high volatility hydrocarbon components. Therefore, reformulated gasoline containing ethers as the oxygenate component will have similar flammability characteristics to gasoline under leak testing conditions, both inside the fuel system and externally.

7.0 FUEL VAPOR RELEASE HAZARD FOR ALCOHOL FUELS (THE HAZARD OUTSIDE OF THE FUEL SYSTEM)

Leak testing procedures where the fuel system vapor space is purged or evacuated will release some volume of fuel vapor to the environment. Typically, leak detection equipment is connected to the fuel system and the system is filled with indicating "smoke" fluid while purging through an open vent. Once the system is filled with "smoke", as identified by smoke issuing from the open vent, the vent is sealed and the evaporative emissions system monitored for smoke exiting at any leaks. Purge flow rates can vary from 1 to 15 Litres/min (0.04 to 0.5 cfm) [1,15] and the time for purging and leak testing can vary from 1 to 15 minutes, depending on the system under test. Fuel vapor is displaced into the environment by the "smoke" entering the evaporative emissions system, and the displaced volume is proportional to the time and flow rate of the purging flow. The quantity of flammable mixture formed as these vapor space contents mix with air in the shop environment depends on the volume displaced, its fuel vapor content and the fuel vapor flammable limits. The assumption is that the volume displaced depends on fuel system volume and test time independent of fuel type. However, the way the fuel vapor mixes with air, the fuel content and the flammable limits are all a function of the fuel properties discussed in Section 5 of this report. When discussing the differences between conventional gasolines and high-alcohol-content fuels, it is worth emphasizing that flex-fuels like E85 and M85 produce fuel vapor very similar to conventional gasoline while "pure" denatured alcohol fuels like E100 and M100 have significantly different properties.

Alcohols have a much lower density than hydrocarbons (see table 6), so pure alcohol vapor will tend to mix more readily with air rather than fall to the floor and pool like gasoline vapor. This effect is particularly significant for significant for neat alcohol

fuels, (M100 has vapor density 1.1 times as heavy as air while gasoline has vapor density around 3 times as heavy as air). However, the difference is much less significant for fuels like M85 or E85 where the fuel vapor is dominated by the hydrocarbon content, (see Section 5.2).

Species	Vapor SG
Methanol	1.1
Ethanol	1.6
Butane	2.0
Pentane	2.5
Hexane	3.0

Table 6.   Vapor specific gravity (SG) for methanol, ethanol, and common gasoline hydrocarbon components found in gasoline vapor. SG measures the density of a substance relative to air. (Eg. pure methanol vapor is 10% more dense than air at equivalent temperature and pressure while hexane is 3 times as dense as air.)

For a given leak detection purge flow rate, the fuel fraction of the vapor space contents purged into the shop environment depends on fuel volatility and temperature. For an extreme winter gasoline with 15 psi (103 kPa) RVP in a warm fuel tank at 100°F (38°C), the tank vapor space will be close to 100% fuel vapor. The maximum allowable vapor pressure for E85 is RVP = 12 psi (83 kPa) so the tank vapor space would be approximately 80% fuel vapor with warm fuel. For a low volatility summer gasoline with 7 psi (48 kPa) RVP, the vapor space would be about 50% fuel by volume when warm. At lower ambient temperature, the fuel content in the vapor space drops correspondingly for both conventional and alcohol-based gasolines and a common assumption is 26% fuel vapor by volume. In general, high-alcohol-content fuels are specified with lower volatility compared to gasoline and this will result in a lower quantity of fuel vapor purged out into the shop environment for a given purge volume at given test conditions. Likewise, the vapor from high-alcohol-content fuels is of lower density and will dissipate in air faster

than conventional gasoline vapor. At the same time, neat alcohols have a wider flammable range than gasoline with fuel percentages at both the lower and upper flammable limits being much higher. The result of combining these three factors, (lower volatility, faster mixing and higher flammable range) is that the maximum flammable volume that can be formed from an equivalent volume purged from a tank vapor space is much lower for neat alcohols compared with conventional gasoline. For example, a mixture of 26% gasoline vapor (balance air), being blended homogenously with additional air, requires a 19 times dilution to reach the lower flammable limit. In contrast, pure ethanol vapor in air at 20°C (68°F) requires only a 2 times dilution to reach the lower flammable limit.

Although neat ethanol and methanol fuels produce significantly less flammable mixture than hydrocarbon gasolines, the difference is much less for E85, M85, flex-fuels. As discussed in Section 5.2, the fuel vapor over E85 and M85 fuels is dominated by the hydrocarbon content and behaves in a manner very similar to conventional hydrocarbon gasolines. This is in agreement with API 1642, which states in Section 6.2.3 Vapor Releases, "Vapors from oxygenated gasolines and M85 represent the same fire-safety hazard as the vapors from base gasoline." [16]

8.0 FUEL IN-TANK HAZARD FOR ALCOHOL FUELS

The fuel vapor over neat methanol and ethanol fuels, coming to equilibrium at normal temperatures, will generally be flammable in the fuel tank vapor space as discussed in Section 5.3. This makes it imperative to avoid any ignition sources within the confines of the fuel system and vapor space and to avoid openings into the tank vapor space and evap system which might transmit an external flash fire into this confined space.

E85 fuel vapor has a slightly wider flammable range and similar transport properties compared with gasoline, because hydrocarbon vapors make up the greatest fraction of the fuel vapor in the tank vapor space. However, ASTM standards allow E85 to have substantially lower volatility than conventional gasoline. For example, Class 1 E85 can have a RVP as low as 5.5 psi (38 kPa) while gasoline is typically limited to 7.0 psi (48 kPa) [17]. This lowers the safety margin between the equilibrium vapor concentration and the upper flammable limit for summer E85 as compared with summer conventional gasoline, as shown Figure 14, particularly at low ambient temperatures. Whereas the low-RVP gasoline has an equilibrium vapor concentration well above UFL down to around -10°C (14°F), the E85 fuel, is approaching flammability around +10°C (50°F). (This result, based on an ethanol-hexane mixture, is in close agreement with other work using real E85 [3]).

The vapor space of a fuel system containing low volatility (5.5 psi RVP) "summer" E85 can become entirely flammable at equilibrium if the fuel temperature is below +10°C (50°F).   Further, if the tank vapor space is marginally above the flammable region, it can rapidly be made flammable with the air flow rates typical of a leak testing procedure, which push the tank vapor space into a non-equilibrium condition. Figure 15 demonstrates the decrease in fuel vapor concentration during a flow cycle in a fuel tank with 4 litres of

7.0 psi RVP E85. Portions of the fuel tank vapor space volume were flammable after 6 minutes of 11 LPM air flow. The flammability remained through the remaining flow cycle and for 10 minutes after the flow was stopped, for a total of 24 minutes where a flammable mixture was detected. This behavior has been seen previously with conventional gasoline [1]. And, if the fuel level is low and the test flows continue for an extended period, E85 and M85 fuels will weather rapidly which lowers the equilibrium vapor content towards the flammable zone.
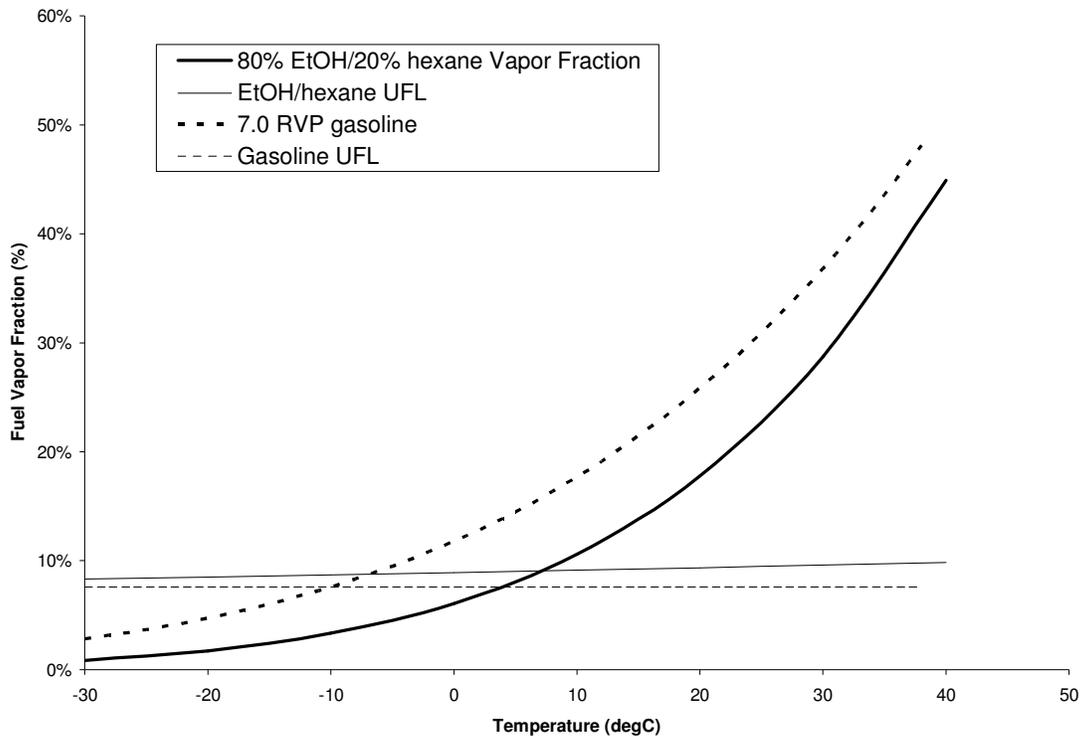

Figure 14. Vapor pressure and upper flammable limit for summer conventional gasoline compared with summer E85, approximated as an 80% ethanol/20% hexane mixture.
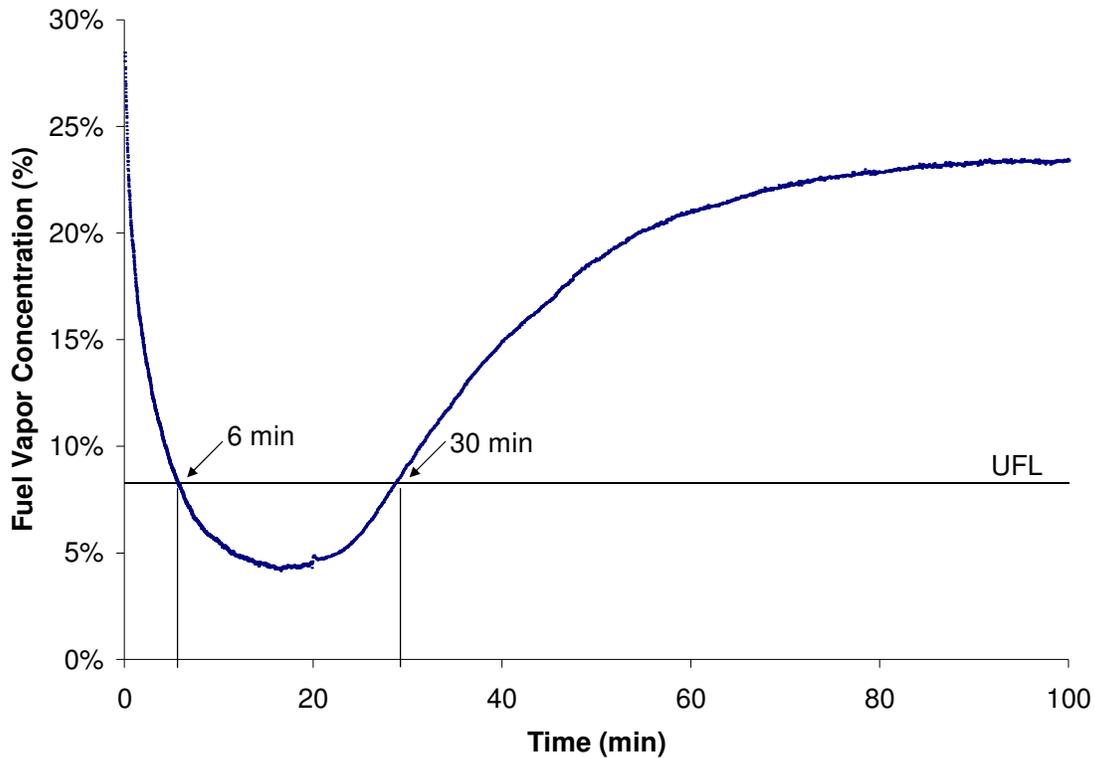
Figure 15. Fuel vapor concentration as calculated from the output of an oxygen sensor placed near the top of the fuel tank. The concentration in the tank is flammable after 6 minutes and continues to be flammable 30 minutes after the flow was initiated or 10 minutes after the flow was shut off. The equilibrium concentration in the tank has dropped off from 29% to 23% due to the weathering of the fuel. The flow cycle consisted of 20 minutes of 11 LPM air flow into the evap service port of a Chevrolet Cavalier fuel tank containing 4 litres of 7.0 psi RVP E85.

As discussed in Section 3, flex fuel vehicles are generally designed to prevent ignition sources inside the fuel system vapor spaces. However, vehicles brought in for leak testing are more likely to have substantial leaks that represent potential flame propagation paths into the fuel system vapor space and the leak testing procedures, (such as opening fuel tank caps), may provide such flame propagation paths.   The existence of a flammable vapor/air mixture inside the fuel system and a flame propagation path to the outside allows an outside ignition source, (on the vehicle or in the service shop), to ignite the mixture

exiting from the leak path and possibly explode the mixture inside the tank with unpleasant consequences.

An inert gas such as nitrogen can be used as the leak detection carrier gas to prevent fuel system vapor contents from becoming flammable. Figure 15 demonstrates the mixing process characteristics for fuel vapor-air mixtures when nitrogen is added [13].   The triangular graphs in Figure 15 are a 3-component mixing diagram with pure air at the lower left corner, pure fuel at the top corner and pure nitrogen at the lower right corner. In a normal fuel tank situation, the tank vapor space contains a mixture of fuel and air, represented by a point somewhere along the left edge of the mixing diagram. Adding nitrogen to the fuel-air mixture would change composition along a line towards the pure nitrogen point at the lower right corner of the diagram. Under normal conditions, both E85 and gasoline tend to form fuel-rich equilibrium mixtures because fuel volatility is controlled so that fuel vapor concentrations are around 25 to 50% at 20°C (68°F). The flammable ranges for these fuels in pure air are 1.4 to 7.6% for typical gasoline and 3.3 to 19% for pure ethanol. If nitrogen is added to a fuel/air mixture, the flammable range narrows and eventually disappears as the oxygen content diminishes. This is shown by the diminishing width of the flammable regions in Figure 15, (colored zones), as they move away from the left edge of mixing diagrams.

The typical fuel tank situation is represented by a point along the left edge of the fuel/air/nitrogen mixing diagram that is usually somewhere above the flammable zone. Figure 15a compares the flammable regions for gasoline, neat ethanol and E85. Figures 15b and 15c show the effect of nitrogen purging, starting with typical equilibrium fuel/air mixtures somewhere above the flammable region along the left hand side (fuel/air line) of

the mixing triangle. Adding nitrogen moves the mixture along a line towards the pure

nitrogen point, (lower right corner) on the triangle and this keeps the mixture outside the

flammable zone. In contrast, adding air would move the mixture towards the lower left

corner, thus tending to pass into the flammable zone. A fuel/air mixture that is initially

flammable in the tank vapor space, (such as neat ethanol or methanol), is represented by

Figure 15d.   Adding nitrogen to the mixture will eventually inert the mixture once

sufficient nitrogen has been added to reach a flammable oxygen concentration limit.
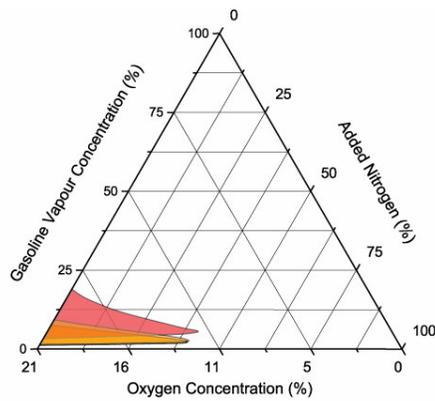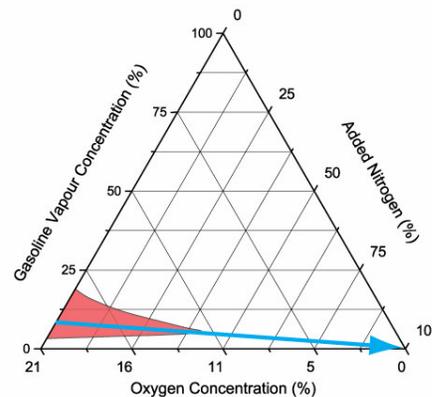

a.) Gasoline, E85, and neat ethanol
flammable range
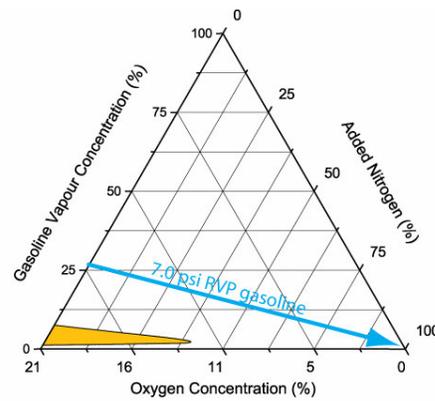
b.) Mixing 7.0 psi RVP gasoline equilibrium vapor/air
mixture with nitrogen at standard ambient conditions
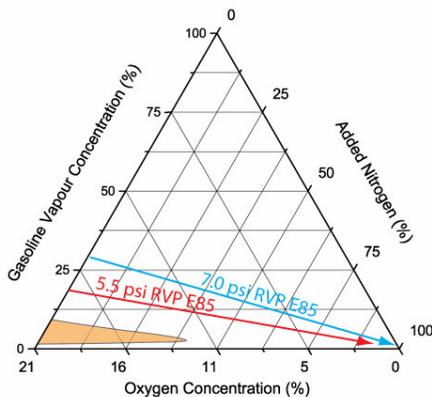
c.) Mixing summer E85 equilibrium vapor/air mixtures
with nitrogen at standard ambient conditions

d.) Mixing neat ethanol equilibrium vapor/air mixtures
with nitrogen at standard ambient conditions

Figure 15. Nitrogen mixing characteristics for summer gasoline, summer E85, and neat

ethanol equilibrium fuel vapor-air mixtures. Mixtures that start out flammable (such as

neat ethanol at normal ambient conditions) will remain flammable for some time until the oxygen content of the mixture has been depleted below a flammable limit.

9.0 SUMMARY AND CONCLUSIONS

This report examines the relative flammability hazards of leak testing a fuel system with high alcohol content fuels, compared to the hazards previously reported for conventional gasoline [1,18,19]. Neat or near-neat alcohols (E100, M100) have substantially different properties than conventional gasoline. While these fuels have a much wider flammable range than hydrocarbon gasoline, they will not produce as great of a hazard outside the tank as gasoline because they are less volatile. However, the vapor space inside fuel systems containing such alcohols is likely to be flammable at normal ambient temperatures.

E85 has vapor characteristics close to gasoline because the vapor produced from E85 is dominated by the fuel hydrocarbon fraction. The flammable range is slightly larger. However, since E85 RVP can be specified to lower values than gasoline, the initial fuel vapor concentration in the fuel tank can be much lower. The hazards of high alcohol content fuels during leak testing can be summarized as follows:

Fuel Vapor Release (Outside the Fuel System) – The hazard outside the tank is (generally, depending on the specific fuel blend) less than that of gasoline, because less fuel vapor will leave the tank for a given purge flow (lower volatility). Alcohol will disperse faster than gasoline and become non-flammable faster, because the LFL is higher.

Flammable Mixtures Within the Fuel System - It is easier to get flammable mixtures inside the tank for alcohol-based fuels compared with conventional gasoline. Neat alcohol fuels are likely to form flammable mixtures within the fuel system at normal ambient shop conditions, and must be treated with extreme care. Vapor spaces containing E85 can become **entirely** flammable at equilibrium with ambient temperatures slightly below

normal, around +10°C (50°F). If the vapor space concentration is slightly above the upper flammable limit, a partial volume can also easily be made flammable by air addition during leak testing activities.   Introducing air flow to the tank locally dilutes the fuel vapor concentration below equilibrium into the flammable range.

The shop personnel are not likely to know the condition of the fuel in a vehicle that has been brought in, particularly in flex-fuel vehicles that can contain different types of fuel. The composition and volatility are unknown so each vehicle must be treated as containing the worst case fuel. For the hazard outside the fuel system, this means a high volatility fuel producing lots of vapor with a low LFL. For the hazard inside the fuel system, this means a low volatility, high alcohol content fuel with a high UFL.

Manufacturers have recognized the more extreme vapor space hazards of high-alcohol-content fuels and have attempted to eliminate ignition sources inside the fuel system of flex-fuel and neat alcohol vehicles. They have also added filler neck flame arrestors in some cases. However, a vehicle brought into the shop environment with a leak has a potential path for flame to propagate into the tank. Therefore, ignition sources and vapor accumulation outside the tank must be avoided. Good shop practice (eg. proper ventilation) and normal safety procedures as used with conventional gasoline will reduce the possibility of igniting any flammable fuel vapor mixture outside the fuel system.

As with conventional gasoline, flammability hazards inside the fuel system can be eliminated by using an inert gas such as nitrogen to purge the vapor space during leak testing activities. E85 vapors in particular can be maintained above the flammable limits at all times if nitrogen is used to purge the system. However, systems containing neat alcohols may be flammable at equilibrium and can remain flammable for some time while nitrogen is added to the system.

Other oxygenates, including ethers, have very similar properties to gasoline and do not significantly affect the flammability hazards experienced during leak testing relative to conventional gasoline.

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<u>11.0 APPENDIX A – GC MEASUREMENT</u>

7.1 GC Measurement Calculations

A gas chromatograph with a flame ionization detector (FID) was used to measure the relative ethanol-hydrocarbon composition in the vapor samples pulled from the fuel tank during the weathering test. An initial sample of pure ethanol was run to determine the location of the ethanol peak. A FID detector produces a signal proportional to the active carbon present in a substance. Since ethanol contains oxygen, the FID produces a substantially different voltage output relative to the weight of ethanol measured, when compared with hydrocarbons. A relative sensitivity factor (F) for ethanol of 0.46 was obtained from literature. (1) The gasoline portion of the mixture was assumed to be composed of saturated hydrocarbons, which all have a sensitivity of approximately 1.

The weight percentage of ethanol was calculated by applying the relative sensitivities to the areas obtained from the chromatographs as follows.

$$\%Weight_{Ethanol} = \frac{Area_{Ethanol} F_{ethanol}}{\sum Area * F}$$

From the weight percentage, the volume percent was determined by accounting for the molar weights of ethanol and the hydrocarbon mixture. The hydrocarbon vapor content was assumed to have a molar weight equivalent to hexane (MW = 86 g/mol).

7.2 References

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