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# MATHEMATICAL PREDICTION OF FLAMMABILITY OF ETHANOL-CONTAINING FUELS

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## **Mathematical Prediction of Flammability of Ethanol-Containing Fuels**

Submitted by

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## Mathematical Prediction of Flammability of Ethanol-Containing Fuels

## Abstract

One of the concerns with denatured ethanol and ethanol-containing fuels for use in spark-ignition engines is their higher flammability temperatures. However, the flammability temperatures of these fuels were not known as a function of vapor pressure DVPE (Dry Vapor Pressure Equivalent) and ethanol concentration. A UNIFAC group contribution theory based mathematical model was used for estimating the upper and lower flammability temperatures of various fuels with a commercial range of vapor pressures and ethanol concentrations. The agreement between the predicted and measured flammability temperatures was excellent. Key findings include the following:

- For a given vapor pressure ethanol-containing fuel, the flammability temperature was nearly constant for various concentrations of ethanol above 10 vol%.
- Flammability temperatures of most common ethanol-containing fuels were 5 to 10°F higher (5°F for winter fuels and 10°F for summer fuels) than those of gasolines with comparable DVPE. For example, 7 psi gasoline (7DVPE / E0) had an upper flammability temperature of 3°F compared to 13°F for the flammability temperature of 7 psi DVPE ethanol-containing fuels (E10-E85); and 15 psi DVPE gasoline upper flammability temperature was -28°F compared to 23°F for 15 psi DVPE ethanol-containing fuels (E10-E25). Note that it is not possible to blend a 15 psi DVPE fuel containing more than 25 vol% ethanol.
- Upper flammability temperatures of denatured ethanol range from 97°F (2 vol% 5.7 psi DVPE denaturant) to 60°F (5 vol% 15 psi DVPE denaturant); and lower flammability temperatures range from 38°F (2 vol% 5.7 psi DVPE denaturant) to -8°F (5 vol% 15 psi DVPE denaturant).
- Fuel weathering can result in 4 to 6°F increase in flammability temperatures of E85 fuels.

### Introduction

The vapor space (headspace) in a gasoline fuel tank is occupied by equilibrium fuel vapor, which is a mixture of air and hydrocarbons; the hydrocarbons are mostly butanes and pentanes. The concentration of hydrocarbons in the fuel vapor depends on the fuel vapor pressure and temperature. In the forthcoming discussion, the fuel vapor pressure refers to DVPE (Dry Vapor Pressure Equivalent) or vapor pressure at 100°F. Note that DVPE replaced RVP (Reid Vapor Pressure) because of ethanol presence in most fuels and they are about the same for fuels containing 0% ethanol. The following table shows a few examples of gasoline vapor compositions estimated by using a mathematical model described later in the report.

| <u>Gasoline DVPE, psi</u> | <u>Temperature, °F</u> | Vol% HC in Vapor |  |  |
|---------------------------|------------------------|------------------|--|--|
| 15                        | 0                      | 12               |  |  |
| 15                        | 32                     | 27               |  |  |
| 9                         | 75                     | 38               |  |  |
| 9                         | 100                    | 61               |  |  |
| 7                         | 75                     | 29               |  |  |
| 7                         | 100                    | 48               |  |  |
| 7                         | 16                     | 8                |  |  |

#### Table 1

Hydrocarbon Concentration in Gasoline Headspace Vapors

As seen in Table 1, the headspace vapor at normal ambient temperatures is too rich to be flammable. However, under some unusual conditions (e.g., 7 psi DVPE fuel at 16°F, or summer fuels in cold winter temperatures), the vapor can become flammable [1-8]. As discussed below, gasoline vapor becomes flammable when the HC concentration drops to about 8 vol%. It is believed that the ethanol-containing fuels become flammable at higher temperatures than the gasolines of comparable vapor pressure [1-5, 7]. Therefore, the objective of this study was to predict and compare flammability

limits of gasoline and ethanol-containing fuels (including denatured ethanol) for use in spark-ignition engines by using proven mathematical models. For the upcoming discussion, the flammability of a fuel refers to flammability of its vapor, vapor refers to headspace vapor, and fuel vapor refers to fuel vapor in equilibrium with liquid fuel.

## **Mathematical Model**

A previously developed vapor/liquid equilibrium thermodynamic model [9-11] was used for this study. As described in reference [9] and also in Appendix A, ethanol-gasoline blends form non-ideal solutions and the non-ideality of ethanol-gasoline blends is modeled using the UNIFAC (Universal Quasi-chemical Functional Group Activity Coefficients) method. The basic idea is that a physical property of an organic molecule is the sum of the contributions made by each molecule's functional groups. The functional groups are structural units, which combine to form the parent molecule. For example, n-butane is made of two CH<sub>3</sub> and two CH<sub>2</sub> groups. The usefulness of this approach lies in the fact that the number of functional groups that constitute various fuel compounds is a small number compared to the number of compounds, which are made of these groups. Therefore, by using the properties or parameters of only a small number of functional groups, it is possible to estimate the thermodynamic properties of multi-component mixtures such as ethanol-gasoline blends.

Gasoline consists of hundreds of different hydrocarbons; for the purpose of fuel tank headspace vapor modeling, it was adequate to treat it as a mixture of forty different hydrocarbons [9]. Higher vapor pressure fuels contain higher concentrations of butanes and pentanes. The model [9-11] has proven to be capable of predicting the vapor pressures and vapor compositions of any oxygenated fuel. The model predicted fuel vapor pressures, vapor compositions, and vapor emissions have been verified with experimental data [9-11]. Unlike various other semi-empirical models, the UNIFAC based model contains no adjustable parameters or constants; therefore, it is reliable and useful in predicting fuel vapor properties. For this study, the model was used for estimating the headspace vapor compositions of various ethanol-containing fuels; the estimated vapor compositions were then used for computing the flammability limits as described in the following sections.

# **Fuel Vapor Flammability**

A fuel tank headspace vapor is considered to be flammable if an ignition source produces a flame that can propagate throughout the headspace (1-7). A flammable vapor might fail to ignite if the ignition source (e.g., electrical spark) is not strong enough to start an ignition. A successful ignition does not guarantee successful flame propagation into the headspace. In some cases, the ignition source is strong enough to start ignition or initiate a small flame, but the flame is extinguished as it moves away from the ignition source. In such cases, only a small portion of the headspace vapor is burned and such vapor may be considered not flammable. For sustained flame propagation to occur, heat production via the enthalpy of combustion must be greater than heat loss from the incipient flame kernel.

Hydrocarbon and air mixtures are flammable over a wide range of hydrocarbon concentrations in air. Therefore, lower and upper limits are defined as follows. Lower Flammability Limit (LFL) is the lowest concentration (vol%) of a HC in air capable of producing a propagating flame by an ignition source. At concentrations below the LFL there is not enough HC in the fuel-air mixture to start a propagating flame. Upper Flammability Limit (UFL) or rich limit, is the highest concentration (vol%) of a HC in air capable of producing a propagating flame by an ignition source. Concentrations higher than UFL are "too rich" to ignite and produce a propagating flame. The flammability limits of the most predominant gasoline vapor components are shown in Table 2 [7]. Note that the UFL of ethanol is much higher than those of hydrocarbons, which makes the ethanol-containing fuel vapor ignitable at higher concentrations and higher temperatures as shown later in this report.

# **Flammability of Mixtures**

As mentioned earlier, fuel vapor is a mixture of different hydrocarbons (butanes, pentanes, etc.). The upper flammability limit (UFL) of a fuel vapor is calculated using a well known <u>Le Chatelier</u>'s mixing rule [4-7].

$$UFL = \frac{1}{\frac{x_1}{UFL_1} + \frac{x_2}{UFL_2} + \frac{x_3}{UFL_3} + \cdots}$$
(1)

Where:

 $x_1$ ,  $x_2$ ,  $x_3$  ..... are the volume fractions of various hydrocarbons in the vapor; and UFL<sub>1</sub>, UFL<sub>2</sub>, UFL<sub>3</sub>.... are corresponding upper flammability limits of hydrocarbons in air (vol%). The lower flammability limit (LFL) of a mixture is calculated using a similar equation.

#### Table 2

Flammability Limits (vol% in air) of Predominant Fuel Vapor Components

|            | <u>LFL</u> | <u>UFL</u> |
|------------|------------|------------|
| N-butane   | 1.6        | 8.4        |
| Isobutane  | 1.8        | 9.6        |
| N-pentane  | 1.4        | 7.8        |
| Isopentane | 1.3        | 9.2        |
| Ethanol    | 3.3        | 19.0       |

Fuel vapor UFL and LFL can be estimated using Equation (1). The following (Table 3) are some of the estimated flammability limits.

#### Table 3

Estimated Flammability Limits (vol% Organic Compounds) of Fuel Vapors

|                  | <u>LFL</u> | <u>UFL</u> |
|------------------|------------|------------|
| 9 psi DVPE / E0  | 1.5        | 8.3        |
| 9 psi DVPE / E10 | 1.6        | 8.7        |

The higher upper flammability limit of 9DVPE / E10 fuel (9 psi DVPE fuel containing 10 vol% denatured ethanol) is due to the presence of some ethanol in the vapor (the UFL and LFL of ethanol are nearly twice those of the hydrocarbons in fuel vapor). Figure 1 shows the model predicted concentration of ethanol in fuel vapor for two different vapor pressure fuels at two different temperatures (9 psi DVPE fuel curves do not extend to 85 vol% denatured ethanol because it is not possible to blend 9DVPE / E85 fuel using any base gasoline as seen in Appendix A). For example, 9DVPE / E10 fuel vapor at 0°F contains 5 vol% ethanol. Note that 5 vol% ethanol in the vapor means 5 vol% of total organic compounds (HCs plus ethanol excluding air) in the headspace (the total concentration of organic compounds in the headspace will be about 6 vol%). In Figure 1, it is assumed that the denatured ethanol contains 2 vol% denaturant. Note that the denaturant concentration can vary from 2 - 5 vol% and the vapor pressure of denaturant can be anywhere from 5.7 psi to 15 psi. The effects of denaturant concentration and vapor pressure on denatured ethanol flammability limits are discussed in a separate section of this report.



At room temperature (75°F), the total concentration of HC in headspace vapors of 9DVPE / E0 fuel will be 38 vol% (Table 1), which is too rich for ignition. However, if the temperature is slowly decreased, the concentration of HC in the headspace vapor decreases and reaches an upper flammability limit of 8.3 vol% at 6°F, which will be called the Upper Flammability Temperature (UFT) of 9DVPE / E0 fuel. As the fuel temperature decreases further, the headspace vapor remains flammable until the concentration drops to a LFL of 1.6 vol% HC at -49°F, which will be called Lower Flammability Temperature (LFT) of 9DVPE / E0 fuel. The following table shows the UFT and LFT values of both the fuels.

#### Table 4

Predicted Flammability Limit Temperatures of 9 psi DVPE (9DVPE) Fuels

|             | <u>LFT (°F)</u> | <u>UFT (°F)</u> |
|-------------|-----------------|-----------------|
| 9DVPE / E0  | -49             | 6               |
| 9DVPE / E10 | -46             | 12              |

Note that the E10 fuel vapor is flammable at a higher temperature (6°F higher) than E0 fuel.

### Flammability Temperatures of Ethanol-Containing Fuels

Several independent studies of fuel vapor flammability [1-8] found that a sustainable ignition and flame propagation does not occur at the estimated (based on the mixing rule) fuel vapor concentrations shown in Table 3, nor does it occur at the temperatures shown in Table 4. In fact, measured UFL and UFT were much lower than those estimated using the mixing rule equation. The discrepancy can be explained using the following reasoning provided in references [4] and [7]: there is not an absolute upper flammability limit below which ignition occurs and above which it does not; rather, there is a band of temperatures in which the probability of ignition goes from 0 to 100%. Therefore, it appears that the estimated UFL and UFT values indicate that the ignition may be possible but the flame may not sustain and propagate at those concentrations

and temperatures. For sustainable flame propagation, the fuel vapor concentration has to be much lower than the estimated upper rich limit or much lower flammability temperatures than those estimated. A similar vapor ignition probability scale is proposed for the ethanol-containing fuel vapor flammability as shown in Figure 2. The upper curve (0% probability of ignition UFT0) corresponds to rich limits estimated using the mixing rule equation; the lower curve (100% probability UFT1) was obtained by comparing the predicted flammability temperatures with the experimental data [1-3] as described below. Note that, in Figure 2, UFT0 and UFT1 lines do not extend to 85 vol% denatured ethanol because it is not possible to blend 9DVPE / E85 fuel using any base gasoline as seen in the nomograph for blending ethanol-containing fuels (Appendix A).



For estimating 100% probability flammable temperature (UFT1), estimated rich limit (UFL) based on the mixing rule was decreased by multiplying by a factor F (F <1); the new value of UFL was used for estimating the upper flammability temperature (UFT1). For example, the estimated rich limit (UFL) of 9DVPE / E0 fuel is 8.3 vol% HC, which corresponds to UFT0 of 6°F; for estimating UFT1, the rich limit was decreased to 5.8% (by multiplying by F=0.7), thus the computed value of UFT1 was -7.5°F. The calculations were repeated for 9 psi DVPE fuels containing various concentrations of ethanol and the results are shown in Figure 2. Calculations were repeated using various values of F and predicted flammability temperatures (UFT1) were compared with the measured values (UFT). The best agreement between the measured upper flammability temperatures and predicted UFT1 values was observed when the value of F was 0.7, and those results are shown in Figure 3) were obtained from references [1-3].



Marshall and Schoonveld [6] also estimated upper flammability limits and temperatures of gasoline vapors using the mixing rule and compared them with the measured flammability temperatures. The estimated UFL was about 8.2 vol% HC in air; however, they did not observe any ignition at these vapor concentrations. Based on a value of UFL quoted in the literature, they proposed a lower UFL (7.1 vol% HC); however, they did not notice consistently repeatable ignition and flame propagation at 7.1 vol% HC in air. It appears that a consistently reliable ignition and propagating flame occurs if the fuel vapor HC concentration is about 6 vol% HC in air, which is about 70% of mixing rule predicted UFL. API sponsored Southwest Research Institute study [8] also concluded that the fuel vapor mixture seldom ignites when the HC concentration exceeds 8 vol% and almost always ignites when the HC concentration is less than 6 vol%.

The results in Figure 2 show that the upper flammability (UFT0) increases with increases in ethanol concentration from 0 to 10 vol%, then decreases slightly or remains constant depending on the denaturant vapor pressure. Note that the effect of denaturant concentration is negligible at lower ethanol concentrations. In further discussion, it will be assumed that, for a given vapor pressure ethanol-containing fuel, the flammability temperatures (UFT0 and UFT1) remain constant for various concentrations of ethanol in the fuel.

Figures 4 and 5 show predicted flammability limit temperatures of gasoline (E0 fuels) and ethanol-containing fuels (>10 vol% ethanol). For experimental verification, the measured upper flammability temperatures [1-3] are also shown in Figure 4 and 5. The agreement between the measured and predicted flammability temperatures is excellent. Note that the shaded areas in Figures 4 and 5 (flammability temperature ranges bounded by UFT0 and UFT1 curves) appear similar except that the shaded area of ethanol-containing fuels (Figure 5) is shifted upwards by a few degrees (°F).

For comparing the flammability temperatures that are of practical significance, the upper flammability temperatures (UFT1) from Figure 4 and 5 are shown in Figure 6. The flammability temperatures of most common ethanol-containing fuels (15 to 7 psi DVPE) are 5 to 10°F higher than those of E0 fuels with comparable DVPE as indicated in

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Figure 6. Please note the following when comparing the flammability temperatures of gasolines and ethanol-containing fuels:

- 5 to 10°F higher flammability temperatures of ethanol-containing fuels refers to the comparison of matched DVPE fuels only; it does not mean that a gasoline flammability temperature increases by 5 to 10°F when blended with any concentration of ethanol.
- Splash blending with high concentrations of ethanol to a gasoline can increase the flammability temperature of the gasoline significantly (>10°F) by decreasing the vapor pressure. For example, the flammability temperature of 9 psi DVPE gasoline is -8°F (Figure 6); when blended with 85 vol% ethanol, the DVPE of the blend drops to 5.3 psi (Figure A-1) and flammability temperature increases to 27°F (Figure 6). However, the fuel blend (5.3 psi DVPE / E85) is not a commercially viable fuel and it does meet ASTM D 5798 specifications.



# Flammability of Denatured Ethanol

The flammability of denatured ethanol is a major concern, because it is flammable at most ambient temperatures. The model was used for estimating the upper and lower flammability temperatures of denatured ethanol as a function of denaturant concentration (0 to 5 vol%) and vapor pressure (5.7, 11, and 15 psi DVPE). The denaturant can be 5.7 psi CARBOB (California Reformulated Gasoline Blendstock for Oxygenate Blending) fuel or 15 psi DVPE natural gasoline.

Figure 7 shows the predicted flammability temperatures of denatured ethanol. Depending on the denaturant vapor pressure and concentration, the upper flammability temperatures range from 60 to 97°F and the lower flammability temperatures range from -5 to 50°F; therefore, denatured ethanol is flammable from -5 to 100°F. The very high flammability temperatures of denatured ethanol are due to its low vapor pressure



(about 3 psi DVPE) and high concentration of ethanol in the vapor (about 47 vol% ethanol in vapor with 5 vol% 15 psi DVPE denaturant; about 86 vol% ethanol in vapor with 2 vol% 5.7DVPE denaturant). The flammability temperatures (Figure 7) decreased with denaturant concentration because of the increase in vapor pressure with denaturant concentration. Note that the experimentally measured [1-5] upper and lower flammability temperatures (shown in Figure 7) are within the range of predicted flammability temperatures. The limited available data show that estimated flammability limits based on the mixing rule agree with those measured; therefore, there was no need for using the probability scale to show flammability temperature ranges of denatured ethanol.

## Effect of Fuel Weathering on Flammability

One of the concerns with ethanol-containing fuels is excessive fuel weathering in a vehicle fuel tank and its effect on flammability temperatures. Excessive fuel weathering will result in lower vapor pressure fuel and also increased the ethanol concentration, both of which can increase flammability temperature. Fuel weathering occurs due to vapor loss from the vehicle fuel tank; the vapor loss is due to diurnal and running vapor generation. The model [9] is capable of estimating diurnal and running vapor generation and resultant fuel weathering. Figure 8 shows predicted fuel weathering with various ethanol-containing fuels under two different scenarios: a) 9 psi DVPE fuels (E0, E10, and E76), daily EPA diurnal (72-96°F), and two trips per day (at 72°F and 96°F) and each trip results in 10°F tank temperature increase; b) 7 psi DVPE fuels (E0, E10, and E85), daily CARB diurnal (65-105°F), and two trips per day (at 65°F and 105°F) and each trip results in 10°F tank temperature increase. It is assumed that the initial tank fuel level is 100% and it decreases by 10% every day. As seen in Figure 8, weathering of E10 fuels was about the same as that of E0 fuels. By the time 90% of the fuel is consumed, the tank fuel vapor pressure decreases by about 1 psi. The E85 and E76 fuels weather slightly more than E0 and E10 fuels because of the reduced amounts of base gasoline in E85 and E76 and higher concentrations of light hydrocarbons compounds in the vapor. For example, 7DVPE / E85 contains nearly 83 vol% ethanol in the liquid phase, but only 24 vol% ethanol in the vapor phase (Figure 1); therefore, fuel

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weathers rapidly and the liquid phase ethanol concentration increases with fuel weathering. The results shown in Figure 8, indicate that excessive weathering of (E76-E85) fuels results in vapor pressure loss of about 0.5 psi more than E0 or E10 fuels, which increases the upper flammability by 4-6°F (Figure 5 or 6).

## Summary

The following summarizes predicted fuel flammability temperatures:

- 1. Upper flammability temperature ranges of:
  - o gasoline: -28°F (15 psi DVPE) to 3°F (7 psi DVPE).
  - ethanol-containing fuels: -23°F (15 psi DVPE E10-E25) to 13°F (7 psi DVPE E10-E85); 5 to 10°F higher than those of gasoline with comparable

DVPE. Note that it is not possible to blend a 15 psi DVPE fuel containing more than 25 vol% ethanol as seen in Figure A-1.

- denatured ethanol: 60°F (5 vol% natural gasoline) to 97°F (2 vol%
  CARBOB) flammable even at high ambient temperatures.
- 2. Lower flammability temperature ranges of:
  - o gasoline and ethanol-containing fuels: extremely low.
  - denatured ethanol: -5°F (5 vol% natural gasoline) to 38°F (2 vol%
    CARBOB) making them flammable at many ambient temperatures.
- 3. Weathering of ethanol-containing fuels in a vehicle fuel tank can result in 4 to 6°F increase in upper flammability limit temperature.

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#### Appendix A

#### Nomograph for Blending of Ethanol-Containing Fuels

If two hydrocarbon fuels (Fuel 1 and Fuel 2) are mixed, the vapor pressure of the blend can be easily estimated from the vapor pressures of Fuel 1 and Fuel 2 because they form an ideal solution. The vapor pressure (DVPE) of the hydrocarbon fuel blend is nearly equal to the volume-weighted average of vapor pressures of Fuel 1 and Fuel 2. For example, 10 gal 7 psi (DVPE) fuel is blended with 10 gal 11 psi fuel. The vapor pressure of the blend is estimated to be 9 psi (7\*0.5+11\*0.5). However, the vapor pressures of ethanol/gasoline blends cannot be estimated by using the volumeweighted average vapor pressures of ethanol and gasoline because ethanol and gasoline form non-ideal solutions. For example, if 10 gal 7 psi gasoline is blended with 10 gal ethanol (2.4 psi DVPE), the vapor pressure of the ethanol blend will not be the estimated 4.7 psi (7\*0.5+2.4\*0.5); instead, the blend vapor pressure will be 7.25 psi, which is much higher than the volume-weighted average. As described in references [9, 10], the vapor pressures of non-ideal ethanol/gasoline blends can be estimated using the UNIFAC (Universal Quasi-chemical Functional Group Activity Coefficients) method. A nomograph (Figure A-1) is prepared by computing and plotting the vapor pressures of various base gasolines (6-15 psi DVPE) containing various concentrations of denatured ethanol (0-100 vol%). Note that it was assumed that the concentration of denaturant in the ethanol is 2 vol% and the vapor pressure of denaturant is assumed to be the same as that of the corresponding base gasoline. For example, if 7 psi base gasoline is blended with 50 vol% denatured ethanol; it is assumed that the denaturant in the ethanol is also 7 psi fuel. As indicated earlier, the denaturant concentration can be up to 5 vol% and its vapor pressure can vary from 5.7 psi to 15 psi. It is beyond the scope of this study to prepare nomographs to cover all possible denaturant concentrations and vapor pressures. Figure A-1 shows an example of the way in which the nomograph can be used in blending ethanol-containing fuels. To blend 9DVPE/E15 fuel, draw a vertical line at 15 vol% ethanol from x-axis and a horizontal line at 9 psi on y-axis; the intersection of both lines shows the base fuel RVP needed for blending 9DVPE/E15.

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For estimating the flammability limit of an ethanol-containing fuel, it is necessary to know the vapor pressure of the blend. The nomograph can be used for estimating the fuel blend vapor pressure. For example, at a fuel-blending terminal, 10 vol% denatured ethanol is blended with 7 psi base gasoline. From the nomograph, the vapor pressure of the blend is 8.3 psi; from the flammability chart in Figure 5, the upper flammability temperature (UFT1) of the blend is 3°F.

