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D.P. Gardiner and M.F. Bardon
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**Technical Report**
NREL/TP-5400-52043
July 2011

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National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401
303-275-3000 • www.nrel.gov

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## Foreword

The U.S. Department of Energy (DOE) supports efforts to increase the use of ethanol-rich transportation fuels such as "E85" (51 to 83 percent ethanol). Furthermore, the mission of the DOE's Clean Cities program is to advance the energy, economic, and environmental security of the United States by supporting local decisions to adopt practices that reduce the use of petroleum in the transportation sector. However, infrastructure compatibility and safety have historically been among the most difficult deployment hurdles to address when introducing a new transportation fuel. The proximity in the fuel supply chain of self-serve fuel dispensers and underground storage tanks to the consumer elevates concerns regarding potential unintended consequences. The physical and chemical properties of ethanol-rich fuels are different from those of conventional transportation fuels; therefore, it is critical to evaluate the situation to ensure safety. In addition to testing that led to Underwriters Laboratories listing of dispensers (http://www.nrel.gov/docs/fy11osti/49187.pdf), the National Renewable Energy Laboratory undertook the testing described in this report and two previous reports (http://www.nrel.gov/vehiclesandfuels/npbf/pubs_ethanol.html) to assess the difference in headspace flammability between typical summertime gasolines, which have accepted levels of safety, and these new high-ethanol content fuel blends. The results apply to vehicle fuel tanks as well as to underground storage tanks.

This project evaluated the effects of ambient temperature and fuel formulation on the headspace vapor flammability of ethanol/gasoline blends. When a fuel tank is partially filled with liquid fuel, the remaining space (i.e., the headspace) is filled with fuel vapors and air. Depending on the degree of tank filling, fuel type, and ambient temperature, the fuel vapors can be flammable or non-flammable. Vapors in fuel tanks containing pure gasoline generally are too rich (i.e., the ratio of fuel vapor to air is too high) to be flammable except when ambient temperatures are extremely low. However, fuels containing high percentages of ethanol blended with gasoline can be less volatile than pure gasoline and thus can produce flammable headspace vapors at common ambient temperatures. The study is also intended to provide knowledge to support the refinement of fuel ethanol volatility specifications and to show the potential consequences of using fuels that do not comply with such specifications. A risk analysis/hazard assessment will be required to fully judge the safety implications, if any, of the introduction of these new fuel blends into the hands of the public.

The results show that in general "E85" is flammable at low temperatures whereas denatured ethanol is flammable at warmer temperatures. If both fuel types are stored in separate tanks at the same location, one or both of the tanks' headspace vapors will be flammable over a wide range of ambient temperatures. This is relevant to the issue of splash-blending ethanol and gasoline at fueling stations and allowing consumers to blend ethanol and gasoline themselves. Fuels that are compliant with volatility specifications in ASTM D5798 are relatively safe, but the field samples of "E85" tested in this work indicate that at least some of the ethanol fuels currently available when ASTM D5798 Class 3 conditions (-5°C and below) exist are likely to produce flammable vapors within the ambient temperature range where they are used. Whether or not flammable headspace vapors represent a significant hazard to the public is unknown at this time.

### Acknowledgments

This project was funded by the Department of Energy Office of Vehicle Technologies (Dennis Smith, Clean Cities Program Manager, and Kevin Stork, Fuels Technologies Team Lead) through the National Renewable Energy Laboratory.

## Executive Summary

### Background

The flammability of a fuel blend in the head space of a storage tank is controlled by the vapor pressure of the blend. Conventional gasolines are so volatile that the headspace vapors are normally too rich to sustain combustion at most ambient temperatures. Only under very cold conditions does the vapor-air mixture in the tank become flammable.

Because of its different vapor pressure and stoïchiometry, pure ethanol produces vapor-air mixtures in the tank that are flammable over a wide range of ambient temperatures. Blends of ethanol and gasoline form non-ideal mixtures in which the gasoline components render the vapor-air mixture in a tank too rich for combustion at warm temperatures. Like gasoline, as temperature drops, the vapor-air mixture becomes leaner and eventually falls into the flammable region. However, the mixture becomes flammable at higher temperatures than conventional gasoline, and so presents a hazard over a greater range of conditions if a suitable ignition source is present.

### Objectives of the Work Reported

The mission of the US Department of Energy's Clean Cities program is to advance the energy, economic, and environmental security of the United States by supporting local decisions to adopt practices that reduce the use of petroleum in the transportation sector. Part of this program includes the replacement of petroleum by alternative and renewable fuels.

Introduction of fuels that have chemical and physical properties different from petroleum must be done with the safety of the public foremost in mind. Since even perceived safety issues can be barriers to deployment, analytical testing is needed to ensure that decisions are based upon scientific knowledge rather than assumptions about potential issues. This flammability study is part of the research into the properties of ethanol blends to address, understand, and quantify the issues involved in the deployment of a new fuel.

This project was comprised of an experimental study to measure the flammability of fuel vapors at low ambient temperatures, and further development of a mathematical model to predict the temperatures at which flammable vapors were likely to form.

The fuels investigated in the current project were provided by Marathon Petroleum Company. The fuel samples were produced in a laboratory to systematically investigate the effects of varying ethanol content on the volatility and flammability of the resulting blends. There were three sets of ethanol/gasoline blends (including the partial set originally evaluated during the

Phase 2 study [2]), which were all provided and characterized by Marathon Petroleum Company, and are referred to throughout this report as "laboratory samples". The blend matrix was comprised of three gasoline vapor pressure levels (83.0 kPa (12.04 psi) DVPE, 89.2 kPa (12.94 psi) DVPE, and 101.2 kPa (14.68 psi) DVPE) and seven different blend levels (E0, E15, E55, E60, E68, E75, and E83). The three gasoline vapor pressure levels were intended to represent low, typical, and high levels for available winter gasoline.

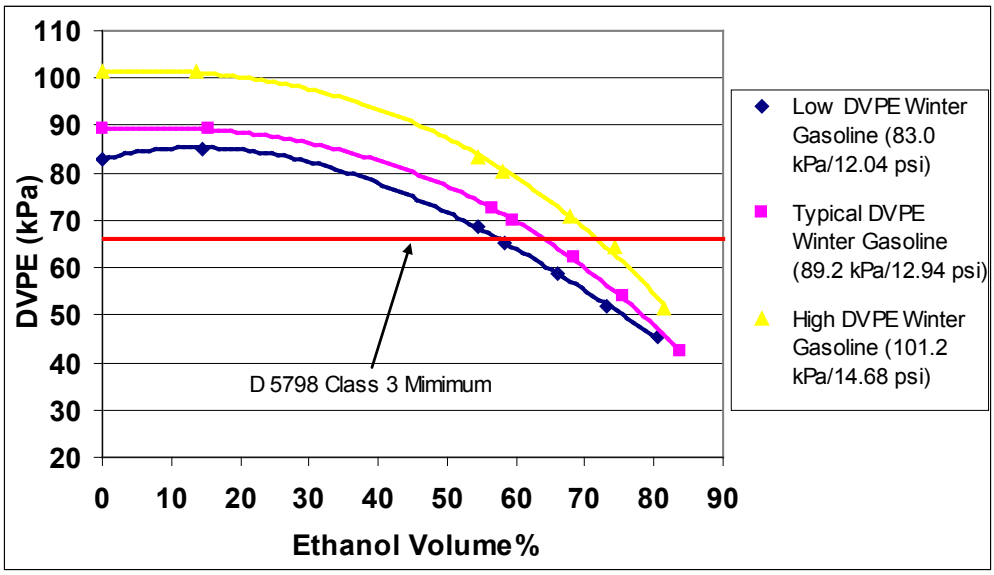
Investigations involving these fuels were intended to provide information to guide future fuel specifications. Such specifications could be developed based upon knowledge of the compromise between avoiding flammable mixtures at low ambient temperatures and maximizing the ethanol content of the fuel.

## Principal Results

### Experimental Study

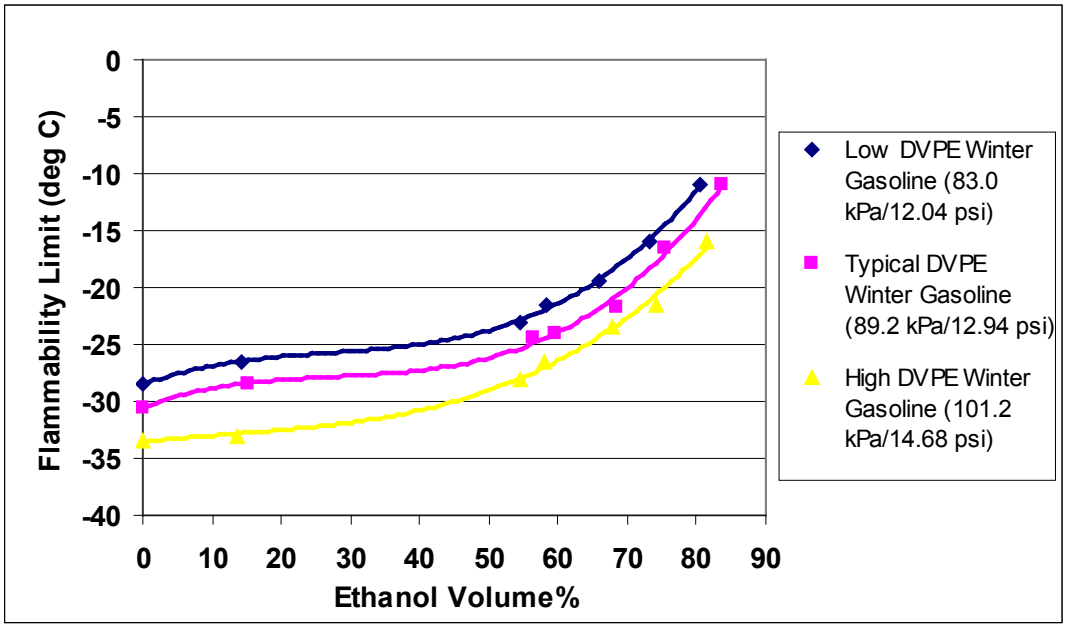
1. The experimental results presented in this report are, to some extent, unique to the apparatus and test conditions that were used for the experiments. Important factors that would have affected the observed behavior included the use of a fill level of 5%, the use of a strong spark for ignition, and the use of test chambers with a relatively small internal volume. Thus, the combustion pressures and flammability limit temperatures presented in this report would be expected to differ from those that might be encountered in other situations. For example, a higher fill level or a weaker ignition source would lower the upper flammability limit temperature (the headspace vapors would have to be colder to be flammable), while a larger headspace volume would likely lead to higher maximum pressures and higher rates of pressure rise. Therefore, the results presented in this report should be interpreted primarily as a relative indication of the headspace vapor flammability of the test fuels. It should also be noted that results were obtained with blends made from specific gasoline samples. The quantitative results at a given vapor pressure level might not be exactly the same if different gasoline samples with different hydrocarbon compositions were used.

2. The figure below summarizes the results of the study with respect to the vapor pressure of the blends.




The matrix of the laboratory fuel blends tested in the study was comprised of three gasoline vapor pressure levels (83.0 kPa (12.04 psi) DVPE, 89.2 kPa (12.94 psi) DVPE, and 101.2 kPa (14.68) DVPE) and seven different blend levels (E0, E15, E55, E60, E68, E75, and E83). The three gasoline vapor pressure levels were intended to represent low, typical, and high levels for available winter gasoline. Of these fuel samples, only blends made with the high DVPE (101.2 kPa (14.68 psi)) winter gasoline could achieve the minimum vapor pressure value for Class 3 fuels (specified in ASTM D5798-09) of 66 kPa (9.5 psi) at the former and revised D5798 minimum ethanol content (volume %) levels of 70% and 68%, respectively. *In order to be compliant with the D5798 minimum vapor pressure specification, blends made with the typical DVPE (89.2 kPa (12.94 psi)) winter gasoline would have to have an ethanol content of less than 65%, while blends made with the low DVPE (83.0 kPa (12.04 psi)) winter gasoline would have to have an ethanol content of about 58% or less.*

3. The figure below summarizes the results of the study with respect to the headspace vapor flammability of the blends.




Headspace vapors from E0 and E15 blends of the low DVPE (83.0 kPa (12.04 psi)) winter gasoline were not flammable until the temperature was below -25° C (-13° F). *In order to maintain the flammability limit temperature at or below -25°C (-13°F) (i.e., comparable to that of a low vapor pressure winter gasoline), blends made with the high DVPE (101.2 kPa (14.68 psi)) winter gasoline would have to have an ethanol content of less than 65%. Blends made with the typical DVPE (89.2 kPa (12.94 psi)) winter gasoline would have to have an ethanol content of about 55% or less, and blends made with the low DVPE (83.0 kPa (12.04 psi)) winter gasoline would have to have an ethanol content of less than 40%.*

4. For the laboratory fuel blends evaluated in this study, the ranking of upper flammability limits correlated well with the vapor pressure values of the blends. The most notable exceptions involved the differences between the E0 and E15 blends with a given base gasoline. This was because the addition of 15% ethanol resulted in little change in the vapor pressure, but resulted in a significant increase in the limit temperature. When all of the laboratory fuels, field samples, and experimental "E85" fuels evaluated throughout the three phases of the study (the present study and the two previous studies) are considered, the correlation between vapor pressure and flammability was markedly inferior to that with only the laboratory blends. This suggests that the details of the hydrocarbon portions of the blends may be responsible for differences in flammability at a given vapor pressure level.

5. Two different samples of denatured ethanol were evaluated to determine both the upper and lower flammability limits of the headspace vapors. Both of these samples contained 97% ethanol and 3% denaturant (E97). One sample (97% ethanol, 1% water, and 2% denaturant) produced flammable headspace vapors at temperatures above -5°C (23°F) and below 19.5°C (67°F). The other sample (97% ethanol, 0.74% water, and 2.26% denaturant) produced flammable headspace vapors at temperatures above -3.5°C (25.5°F) and below 22.5°C (72.5°F). The differences in headspace vapor flammability were most likely due to differences in the volatility of the denaturant used in the two samples.

6. The denatured ethanol samples exhibited the highest pressure rise values and rates of pressure rise at temperatures in the vicinity of 10°C (50°F). High rates of pressure rise for a burning mixture are indicative of a fuel/air mixture that burns rapidly and destructively and is relatively easy to ignite. *The fact that these high rates of pressure rise for E97 were measured at temperatures that are typical of those in many storage tanks should raise serious concern about any proposal to store denatured ethanol at retail fuel outlets.*

7. It is recommended that further experimental work be carried out to examine the headspace vapor flammability of ethanol/gasoline blends made with base gasolines which have vapor pressure values lower than those tested thus far, as surveys of available fuels indicate that such fuels are currently in use. The rationale for this recommendation is detailed in Appendix B.

8. It is recommended that further experimental work be carried out to examine the effects of denaturant properties on the flammability of denatured ethanol. This data would facilitate the consideration of flammability issues as a factor in the selection of preferred denaturants for fuel ethanol.

## Modeling Study:

1. For the fuels tested in this third phase of the work, the experimental data can be rank ordered successfully using either the model or DVPE for high alcohol blends (E55 and higher); i.e., both the DVPE and the model correctly predicted the order of the rich flammability limits of the various fuels, from coldest to warmest.

2. When the entire data set provided by all three phases of this work so far is considered, DVPE did not successfully rank order the high ethanol blends. The model had insufficient data on the gasoline base stock for the fuels tested in phase 1 and part of phase 2 to be used to make a ranking on the entire data set.

3. Comparing an ethanol-free gasoline with its E15 blend, the DVPE did not correctly rank order any of the three blends tested in this phase. The model correctly rank ordered all three when comparing E0 and E15.

4. The exaggerated inflexion in the predicted upper limit curve (Figures 16-18 shown later in the report) produces some incorrectly predicted rankings between E15, E55 and E60 blends.

5. It would be useful to carry out experiments on some selected pure components in the present test rig, in order to determine upper limits that are more realistic for the scenarios of interest involving fuel tanks at low temperatures. This would allow the model to predict the upper limit temperatures more accurately.

6. The model already predicts the upper limit trends well for higher ethanol blends, and successfully captures the inflexion occurring in the measured data for low ethanol blends, albeit in a slightly exaggerated form. However, it needs refinement to more accurately portray that inflexion and make correct flammability rankings. In order to permit this, two or three additional

low ethanol blends are needed along with the other blends used here. This could be accomplished by adding 5% and 10% blends, or preferably 4%, 8% and 12% blends with their full data sets as supplied for the fuels in this phase of the work. Additional blends in the 30-40% range could also be useful to bridge between the low ethanol (E0-E15) and the high ethanol (E55-E83) blend ranges.

7. Since most gasolines now contain some oxygenates, the D86 data for the base gasoline often is not available. In order to permit the model to be used when only routine field data are known, namely D86, ethanol content and specific gravity, it would be desirable to attempt to devise a technique for extracting the necessary gasoline data from the D86 data of a low alcohol blend. That is not trivial, but the detailed data already provided for the fuels studied so far in this work may allow such a technique to be developed, thereby making the use of the model much more practical and broadly accessible.

8. Despite the success of the current model, using the actual light hydrocarbon composition in a model rather than deriving an approximation for volatility from only the D86 data is likely to provide greater insight into flammability behaviour at low temperatures. A new mathematical model incorporating the detailed composition of the light components has been created and some initial runs conducted to better predict the impact of light ends on cold flammability. These preliminary results showed considerable promise. Further work on the new model is recommended for future work.

## Table of Contents

## LIST OF FIGURES

# I. EXPERIMENTAL STUDY

## 1 Introduction

The project described in this report was carried out to examine the potential for flammable fuel/air mixtures to form in fuel tanks containing blends of ethanol and gasoline. The current project followed two earlier projects [1,2] in which an experimental technique and a mathematical model were developed to investigate the flammability issue. The ethanol/gasoline blends evaluated in the first project were experimental fuels originally produced for vehicle driveability studies. These blends (referred to as"E85" fuels) contained about 70-80% ethanol, and a variety of hydrocarbon components.

In the second project, two sets of fuels were investigated. The first set consisted of 'real world' fuel samples obtained from refuelling stations, which are referred to as 'field samples' throughout this report. These samples included "E85" blends, as well as low and mid-level blends containing approximately 10-30% ethanol. Investigations involving these fuels were intended to provide information about the possibility of flammable mixtures forming with the fuels that are currently available.

The second set of fuels (provided by Marathon Petroleum Company) was produced in a laboratory to systematically investigate the effects of varying ethanol content on the volatility and flammability of the resulting blends. These fuels were produced by blending denatured ethanol with varying percentages of a single type of gasoline. The gasoline used for the blends had properties that were representative of a typical winter grade fuel, had a vapor pressure (DVPE) value of 89.2 kPa (12.94 psi).

In the current project, two additional sets of laboratory blends were prepared by Marathon Petroleum Company to further investigate the effects of base gasoline volatility on the flammability of ethanol/gasoline blends. These sets of blends were prepared using two different base gasolines. These gasolines had vapor pressure (DVPE) values of 83.0 kPa (12.04 psi) and 101.2 kPa (14.68 psi), which were representative of the lower and higher vapor pressure ranges for winter grade fuel.

The new fuel blends were evaluated at nominal ethanol/gasoline blend levels of E0 (base gasoline), E15, E55, E60, E68, E75 and E83. Furthermore, the 89.2 kPa (12.94 psi) DVPE gasoline (typical winter volatility) used previously in the Phase 2 study [2] was evaluated as E0 and E15 blends, as these blend levels had not been evaluated in the earlier study.

The current report presents the results for all three sets of blends (using low, typical, and high vapor pressure base gasolines), and as such, includes some of the data originally published in the Phase 2 report [2]. Investigations involving these fuels were intended to provide information to guide future fuel specifications. Such specifications could be developed based upon knowledge of the compromise between avoiding flammable mixtures at low ambient temperatures and maximizing the ethanol content of the fuel.

The current report also presents results for the flammability limits of two different denatured ethanol (E97) samples. The lower (lean) flammability limit for vapors from blends of E85 or less normally occurs at temperatures that are too low to be of practical interest, so these fuels are considered to be flammable at temperatures below their respective upper (rich) flammability limits. This is not the case with denatured ethanol, where fuel tank vapors enter the flammable range at temperatures below the upper flammability limit, but reach the lower flammability limit at winter ambient temperatures. For this reason, both the upper and lower flammability limits were determined for the denatured ethanol samples.

# 2 Background

The following background information was presented earlier in reference [2]. It has been included in the present report for the convenience of the reader.

## 2.1 The Flammability Problem

Gasoline is so volatile at most ambient temperatures that the headspace vapors (the gaseous fuel/air mixture above the liquid in the fuel tank) are actually too rich to burn, as long as some liquid fuel remains. However, as temperature drops, or as the liquid fuel level goes down, the volatility of the fuel decreases. As liquid level drops, there is less fuel vapor mixed with the air in the tank.

If the ambient temperature is cold enough and the tank is nearly empty, then the fuel-air mixture in the tank becomes flammable and can pose an explosion hazard if ignited. This has always been the case with gasoline, but the temperatures and fill levels needed to produce a hazard are rarely encountered, so fires and tank explosions are very unlikely, although not impossible.

Ethanol by itself in a fuel tank produces headspace vapors that are flammable at room temperature and over a broad range of commonly encountered ambient temperatures. Ethanol/gasoline blends generally have volatility characteristics between those of the two major constituents. Any given high-alcohol blend tends to produce flammable fuel tank vapors at higher (i.e., less cold) temperatures than pure gasoline. The extent of the difference, and hence of any increased risk, depends on composition of the gasoline part of the blend and how much gasoline is present in the fuel mixture [3-6]. It is therefore prudent to assess the extent of any differences in the fire hazards of fuel tank headspace vapors between gasoline and ethanol fuel blends.

The standard specifications for fuel ethanol are described in ASTM D5798 [7], which provides three different vapor pressure classes for fuel ethanol, depending upon the seasonal and climatic conditions that apply. The coldest of these is referred to as Class 3, which encompasses geographic areas with 6-h tenth percentile minimum ambient temperature less than or equal to -5º C (41° F). Since low ambient temperatures present the greatest risk of the formation of flammable headspace vapors, Class 3 fuels and climatic conditions are the focus of the current study.

## 2.2 Flammability versus Ignitability

A fuel-air mixture is considered to be flammable if, when ignited, it produces a flame that can propagate throughout the available mixture. A flammable mixture might fail to ignite if the ignition source is too weak. However, successful ignition does not guarantee successful flame propagation. In some cases, the ignition source is strong enough to initiate a small flame, but the flame is extinguished as it moves away from the ignition source. In such cases, only a portion of the available mixture is burned, and the mixture is not, therefore, considered flammable.

In the studies referred to in this report, the objective has been to determine the flammability of the headspace vapors rather than address the potential for flammable headspace vapors to be ignited by weak ignition sources. As such, the strategy was to employ an ignition source strong enough to ensure that any flammable mixture could be ignited reliably. With this achieved, flammability experiments should show evidence of partial combustion when the limits are reached.

The use of closed combustion chambers and pressure measurements in the experiments provided a means of differentiating between ignition failures, successful ignition followed by partial flame propagation, and substantially complete flame propagation. Tests in which the mixture fails to ignite show no increase in chamber pressure. Partial flame propagation produces a small but detectable pressure rise.

Tests in which most of the mixture in the chamber is burned should exhibit similar peak pressure levels. Assuming nearly complete flame propagation, differences in peak pressure levels would mainly be due to differing amounts of heat lost to the chamber walls. As the flammability limits are approached, greater heat losses (therefore, lower peak pressure levels) are expected due to slower combustion. However, even these reduced pressure levels are well above those that occur when only a small portion of the mixture is burned (i.e., the partial propagation case).

Another diagnostic tool for examining flame propagation in the chamber is the rate of pressure rise. The rate of pressure rise (obtained through differentiation of the pressure signal) reflects the overall heat release rate within the chamber. This rate is influenced by the laminar burning velocity of the mixture and the surface area of the flame front. For example, a weak flame that extinguishes near the ignition source will reach a relatively small maximum surface area and will have a relatively low burning velocity prior to extinction. These factors will result in a very low rate of pressure rise compared with a case in which combustion is nearly complete. The rate of pressure rise also provides a sensitive means of comparing cases with similar peak pressure levels but different combustion rates. The peak rate of pressure rise falls as the flammability limit is approached.

## 3 Apparatus and Test Procedures

Eight identical test chambers were constructed so that a number of fuel samples could be chilled simultaneously. Photographs of one of the test chambers are shown in Figure 1. The interior volume of each chamber was 295 ml (18 cubic inches).

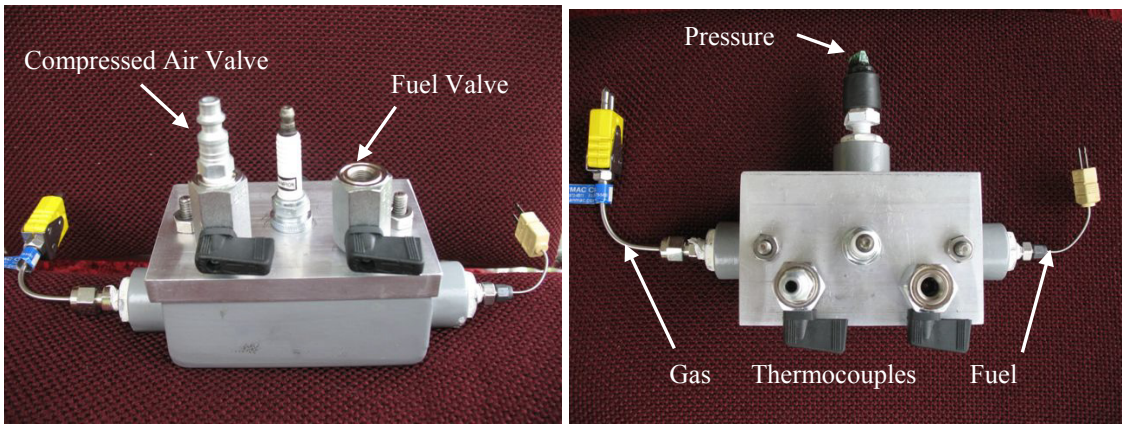



**Figure 1: Flammability test chamber**

The pressure sensor was a Honeywell model 19CP300PA4K absolute pressure sensor with a full-scale range of 0–2,070 kPa (0–300 psia). The sensor had a response time of 0.1 ms, which was found to be fast enough to capture the transient features of the pressure rise events during combustion. The gas temperature inside the chamber was measured using a Nanmac "right angle" K-type thermocouple. This thermocouple was a fast-response design with a low-inertia ribbon junction. The thermocouple was not fast enough to detect the actual transient gas temperature during combustion, but it could track the dynamic temperature behaviour well enough to provide relative comparisons between tests.

The temperature of the liquid fuel at the bottom of the chamber was measured using a conventional 1.6-mm (1/16 in) sheathed K-type thermocouple with a grounded junction. This thermocouple was positioned so that it would be immersed in the liquid layer (about 5 mm deep).

The ignition source for the experiments was composed of an automotive spark plug and a laboratory programmable ignition system. The ignition system discharged 1 J of stored energy during each spark, producing a saw-tooth spark current waveform (50-100 mA) with a duration of 1 ms. The spark plug was a Champion model 7034, which had platinum pins in the center and ground electrodes. This type of spark plug was selected because the pins ensure that the spark location is consistent from spark to spark. The electrode gap was set at 2 mm (0.079 in). This particular spark plug model also had a projected tip, which placed the spark gap closer to the vertical center of the chamber.

The experiments were carried out in an Espec model PUA-3AP temperature chamber. During most of the experiments, all eight fuel chambers were chilled together. The fuel chambers were placed on racks within the "assured test volume" of the temperature chamber, where (according to the manufacturer) the rated temperature uniformity (+/- 0.5ºC (0.9°F)) should exist. During

some tests, the same type of fuel was used in each chamber. In other cases, two or three different fuels were tested. The choice of fuel for the chambers depended on the test temperature and the results of previous tests.

All the experiments were conducted using a 1/20$^{th}$ (5%) fill level. As shown by Vaivads *et al.* [4], the fuel tank headspace vapors of gasoline and alcohol/gasoline blends are flammable at higher temperatures if there is less liquid fuel in the tanks. The 5% fill level was selected, in consultation with the project sponsor, to represent a worst-case scenario in terms of how low an automobile operator might allow the fuel level to become.

The fuel storage containers and the syringes used to transfer the fuel were stored at -12ºC. Before each test, fuel was extracted with a syringe from one of the fuel storage containers and transferred to the appropriate test chamber. The storage container was opened just long enough to extract the fuel (to limit vapor losses from the samples), and the test chamber was sealed immediately after the fuel was injected through the fuel valve.

The sealed chambers were placed in the cold chamber, connected to the instrumentation cables, and chilled until the gas temperature inside the chamber reached the desired test temperature. This initially caused the gas pressure in the chambers to fall below atmospheric pressure. The chamber pressure levels were then equalized to atmospheric pressure by quickly opening and closing each fuel valve. Following equalization, the chambers were cold soaked until the gas and fuel temperatures were within 0.5°C of each other and then maintained at the test temperature (+/- 0.5°C) for at least 1 hour before ignition was attempted.

During each ignition attempt, the data acquisition system was activated and the ignition system was triggered. The ignition system sparked at a frequency of 2 Hz once triggered. Flammable mixtures usually ignited with the first spark.

## 3.1 Test Fuels

The properties of the test fuels are listed in Appendix A. There were three sets of ethanol/gasoline blends (including the partial set originally evaluated during the Phase 2 study [2]), which were all provided and characterized by Marathon Petroleum Company, and are referred to throughout this report as “laboratory samples”. The blend matrix was comprised of three gasoline vapor pressure levels (83.0 kPa (12.04 psi)DVPE, 89.2 kPa (12.94 psi)DVPE, and 101.2 kPa (14.68 psi) DVPE) and seven different blend levels (E0, E15, E55, E60, E68, E75, and E83). The three gasoline vapor pressure levels were intended to represent low, typical, and high levels for available winter gasoline.

## 3.2 Experimental Results and Discussion

### *3.2.1 Pressure Measurements of Laboratory Blends*

Measurements of the maximum pressure rise in the chambers and the rate of pressure rise in the chamber are shown in Figures 2-7. As shown in Figures 2, 4, and 6, the pressure rise values were

either below 100 kPa (14.5 psi) or above 300 kPa (43.5 psi). Similar behavior was also seen in the previous studies [1,2]. The tests where only a low pressure rise was produced are believed to indicate cases where the mixture could be ignited by the apparatus, but only a small portion of the mixture in the chamber was burned. Test results in the higher pressure range indicate that a substantial portion of the mixture in the chamber was burned, so the mixture was, by definition, flammable.

Since each fuel tested produced some low pressure results, it is proposed that the spark ignition source was strong enough to ensure that the apparatus was capable of identifying true flammability limits rather than ignition limits imposed by the ignition source. In other words, the spark energy of this apparatus was great enough to ensure that it could ignite any mixture that was capable of sustained burning once it was ignited. For all of the fuels tested, only upper flammability limits were encountered. That is, the vapor/air mixture in the chamber headspace was flammable below a critical temperature, and was too rich to burn above that temperature.

The results for the maximum rate of pressure rise shown in Figures 3, 5, and 7 provide a relative indication of how fast the mixture burned following ignition. This is related to the flame speed of the mixture, and affects both the potential destructiveness of combustion within a fuel tank, and the potential for igniting the mixture with relatively weak sparks. A well known example of this relationship is hydrogen, which is easily ignited and potentially destructive because it has a high flame speed.

The ranking of the fuel blends by the pressure measurements was as expected, but it can be seen that with a given base gasoline, there were only small differences between E60 and E55 in terms of the pressure rise and rate of pressure rise results. Similarly, the differences between E0 and E15, although significant, were relatively small.

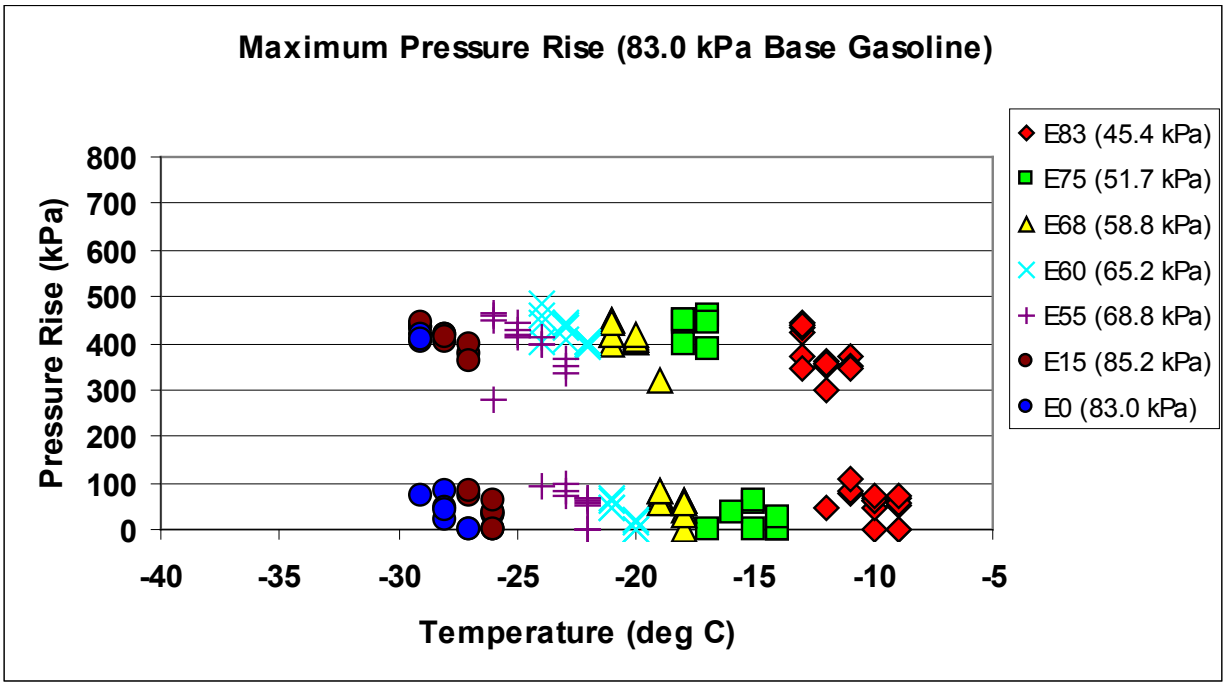



**Figure 2: Maximum Pressure Rise of Samples Blended with Low DVPE (83.0 kPa (12.04 psi)) Winter Gasoline**

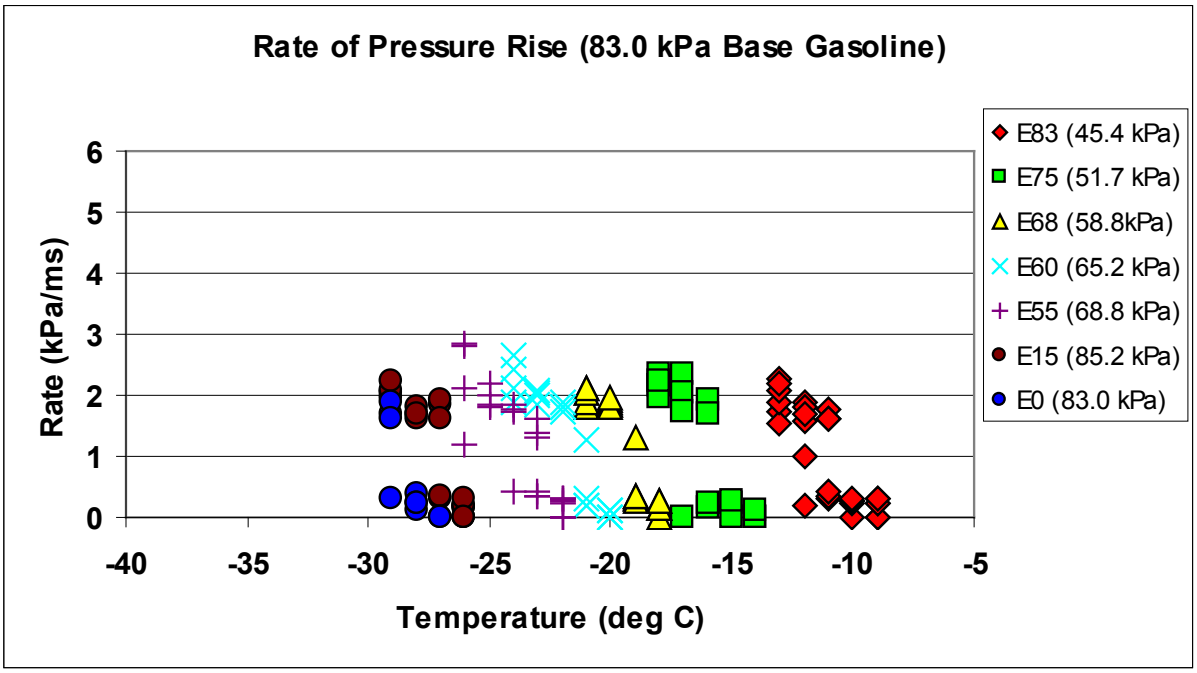



**Figure 3: Maximum Rate of Pressure Rise of Samples Blended with Low DVPE (83.0 kPa (12.04 psi)) Winter Gasoline**

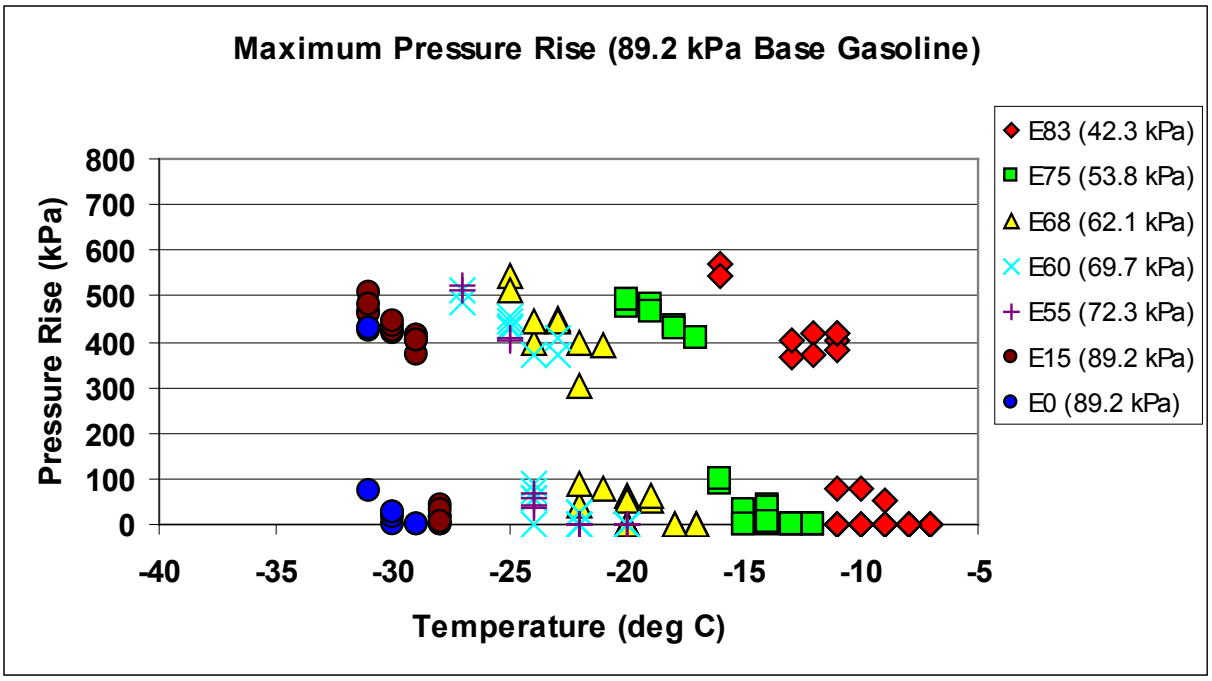



**Figure 4: Maximum Pressure Rise of Samples Blended with Typical DVPE (89.2 kPa (12.94 psi)) Winter Gasoline**

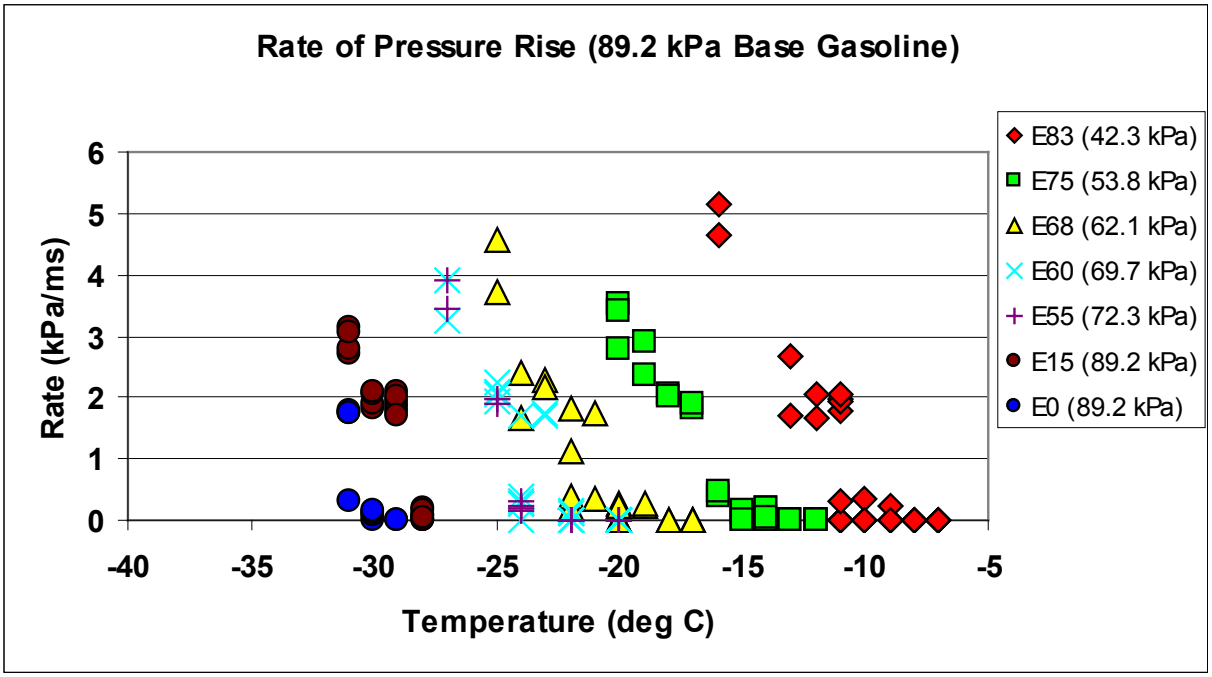



**Figure 5: Maximum Rate of Pressure Rise of Samples Blended with Typical DVPE (89.2 kPa (12.94 psi)) Winter Gasoline**

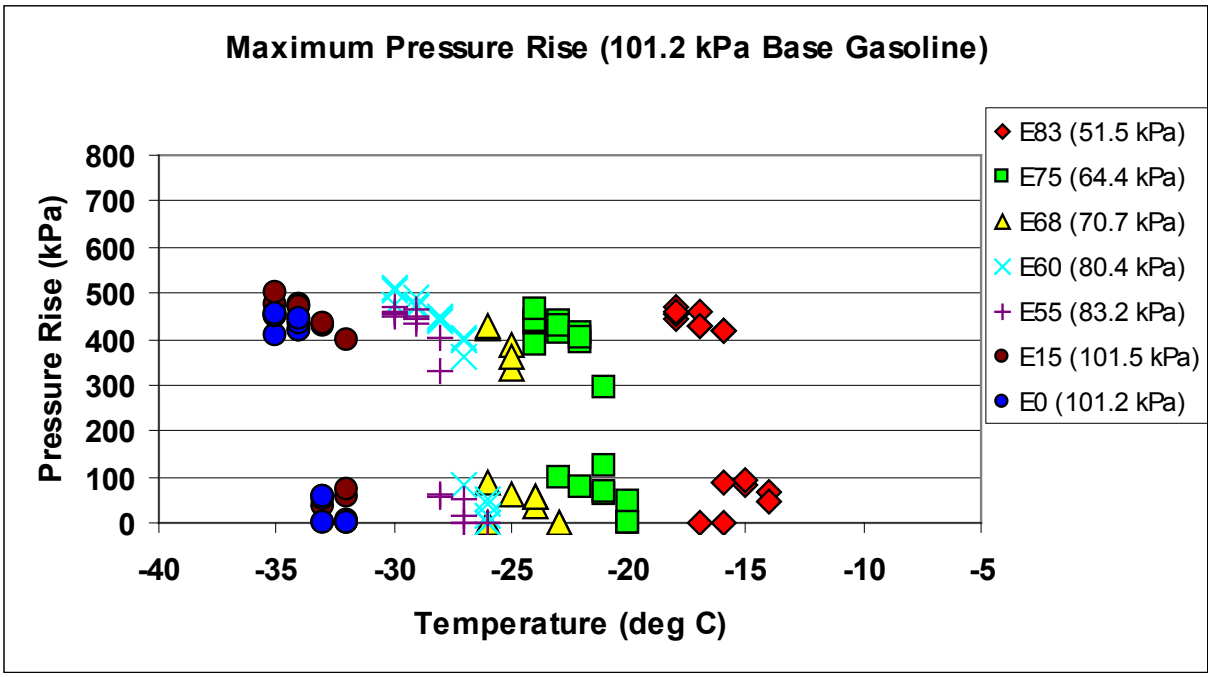



**Figure 6: Maximum Pressure Rise of Samples Blended with High DVPE (101.2 kPa (14.68 psi)) Winter Gasoline**

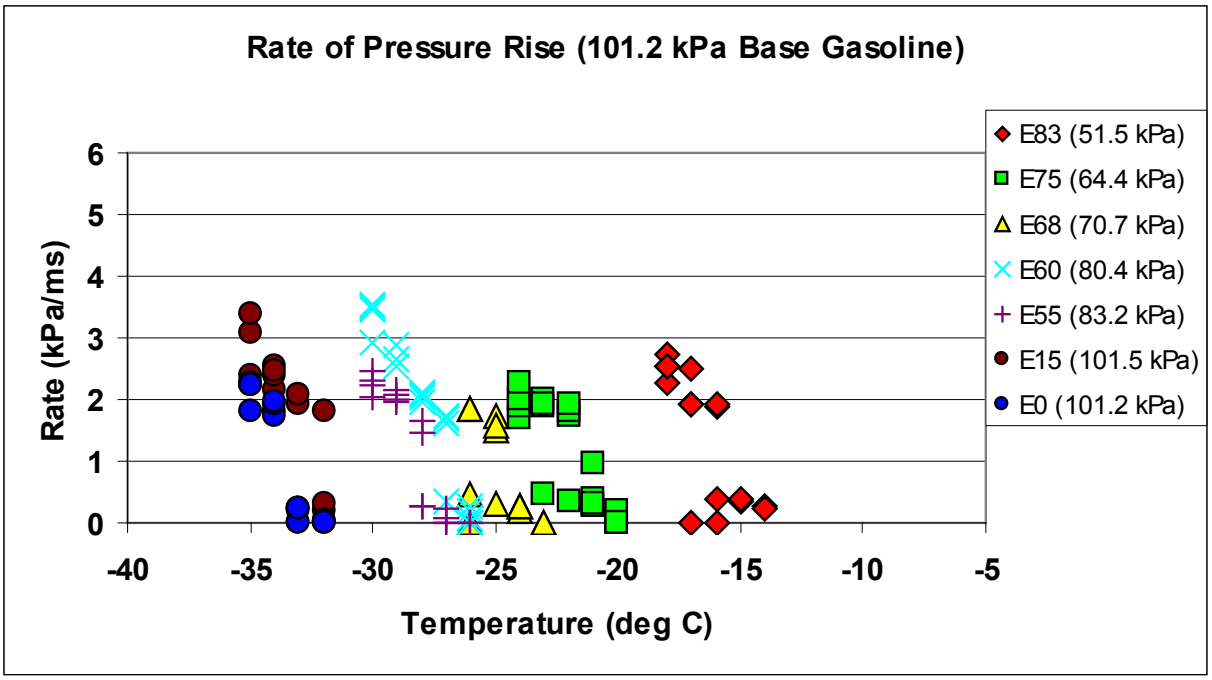



**Figure 7: Maximum Rate of Pressure Rise of Samples Blended with High DVPE (101.2 kPa (14.68 psi)) Winter Gasoline**

### 3.3 Upper Flammability Limits of Laboratory Blends

Based upon the pressure rise data shown in Figures 2, 4 and 6, a statistical analysis was carried out to arrive at values for the upper flammability limits of each fuel and their associated uncertainties. Statistical analysis of the peak pressure rise data was implemented using a PROBIT technique [8]. The use of this digital technique was justified by the binomial nature of the data. A threshold pressure of 200 kPa (29 psi) was used to differentiate between flammable mixtures that were ignitable but not flammable.

In the analysis, pressure rise values in the high-pressure range (representing flammable mixtures) were assigned a high logic value (1), while pressure rise values in the low-pressure range (ignitable but not flammable) and zero pressure rise values (ignition failure) were assigned a low logic value (0). The technique generated a most likely curve fit for the temperature region where both high-pressure and low-pressure results were recorded in the experiments. From this curve fit, the mean temperature value and the upper bound temperature value were determined. The criterion chosen for the upper bound temperature was a 50% probability (at 95% confidence) of a high-pressure event occurring. In the following flammability limit graphs, the mean values from the analysis have been plotted.

In Figure 8, the upper flammability limits of the laboratory fuels are plotted versus their respective ethanol content (volume % as determined by analysis). Note that since these are upper (rich) flammability limits, the fuel/air vapors are flammable at or below the temperatures shown. The results for these laboratory fuel blends show a non-linear relationship between the ethanol content of the fuel and its upper flammability limit. It can be seen that the limit temperature was lowered substantially as the ethanol content was reduced from about 80% to about 60%. However, further reductions in ethanol content had less relative effect on the limit temperature.

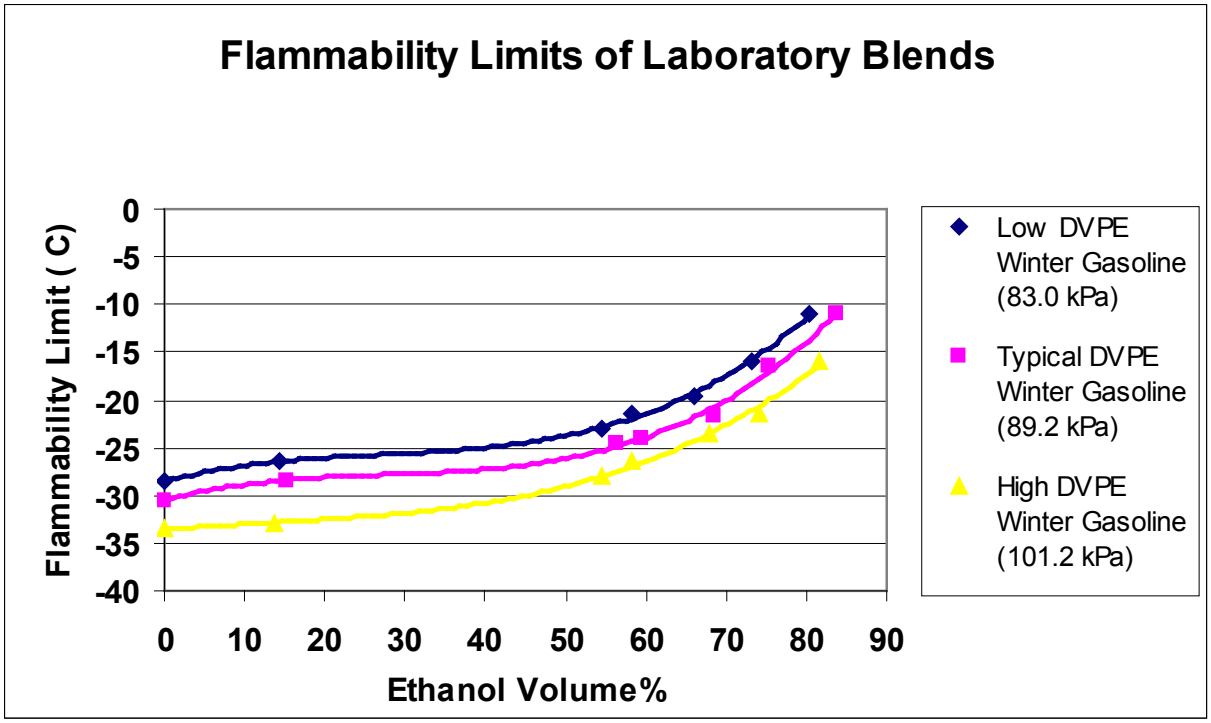



**Figure 8: Effect of Ethanol Content on Upper flammability Limit**

Figure 8 shows that even with the least volatile base gasoline, the headspace vapors with E0 and E15 were not flammable until the temperature was below -25° C (-13° F). Since the 83.0 kPa (12.04 psi) base gasoline was intended to represent the low end of the vapor pressure range for Class 3 fuels, it is arguable that the flammability of these fuels could be considered as representative of the current "worst case scenario" for headspace vapor flammability. Figure 9 identifies the maximum ethanol content that would be allowable with each base gasoline while maintaining the flammability limit temperature at or below -25° C (-13° F).

As shown in Figure 9, the maximum ethanol content in this scenario was highly dependent on the vapor pressure of the base gasoline. Due to the relatively low slope of the curve below about 60% ethanol, blends made with the low vapor pressure winter gasoline would have to have an ethanol content of less than 40% to meet the aforementioned flammability criterion. A typical winter gasoline would have to have an ethanol content of about 55% or less, and even a high vapor pressure winter gasoline would have to have an ethanol content of less than 65%.

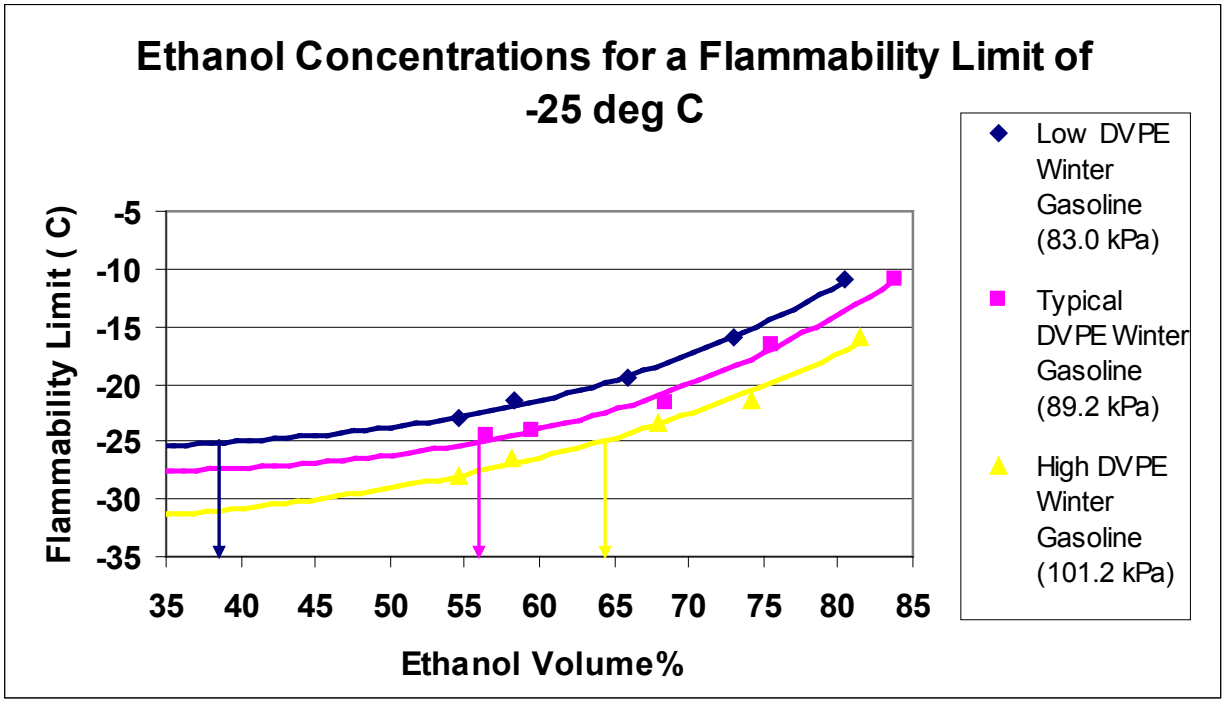



**Figure 9: Effect of Ethanol Content on Upper flammability Limit**
**(Comparison with -25°C (-13°F) Limit Temperature)**

Figure 10 shows the measured DVPE values of the test fuels as a function of ethanol content. The minimum vapor pressure value for Class 3 fuels (specified in ASTM D5798) is depicted for comparison. Figure 11 highlights the maximum ethanol content that could be used with each base gasoline while maintaining a vapor pressure level compliant with the ASTM standard. As shown in Figure 11, only blends made with the high DVPE (101.2 kPa (14.68 psi)) base gasoline could achieve the minimum vapor pressure specification of 66 kPa (9.5 psi) at the former and revised D5798 minimum ethanol content levels of 70% and 68% respectively.

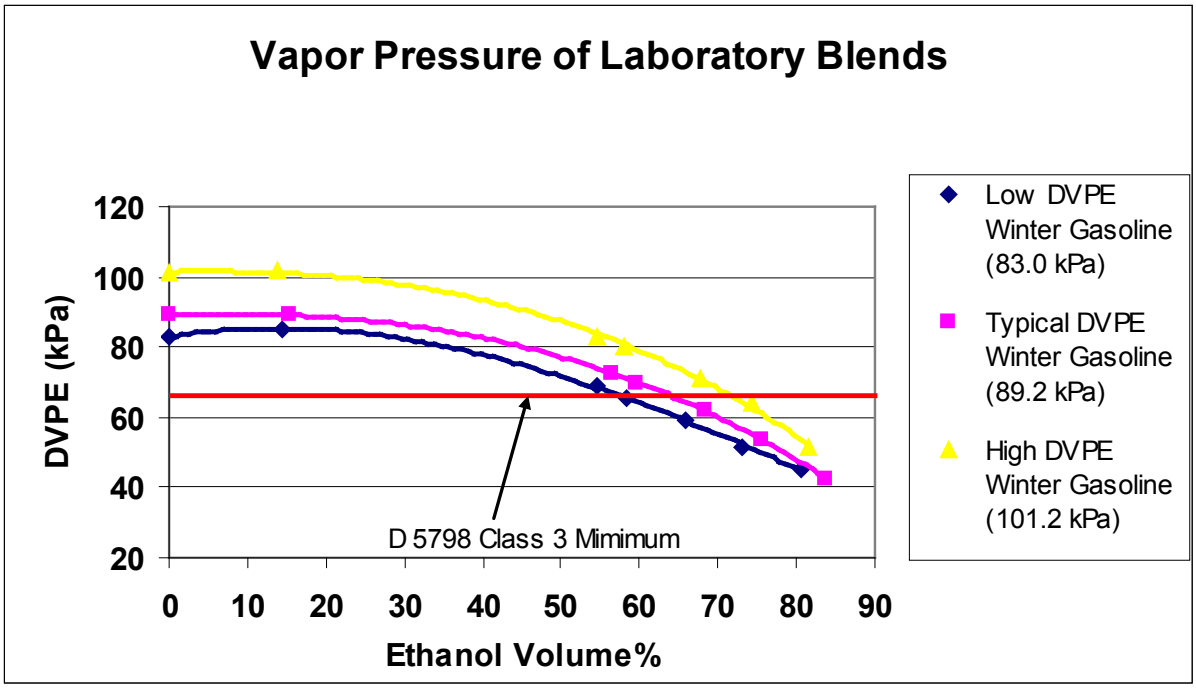



**Figure 10: Effect of Ethanol Content on Vapor Pressure (DVPE) of Test Fuels**

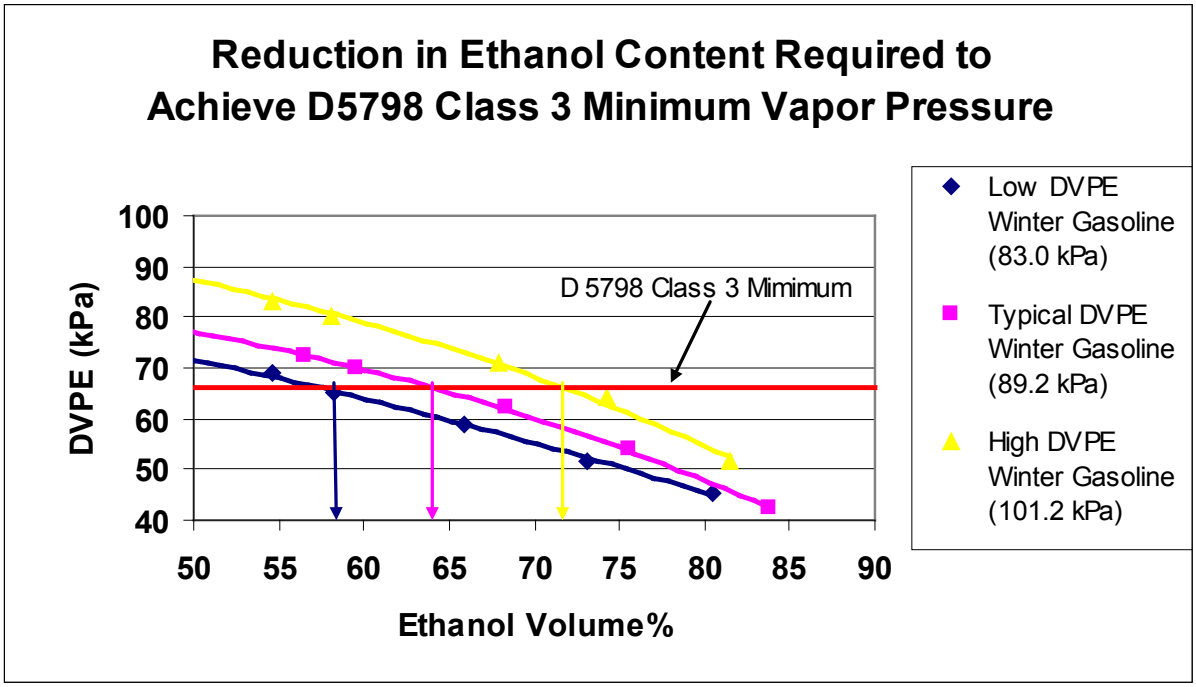



**Figure 11: Comparison of Blend Vapor Pressure and Class 3 Minimum Vapor Pressure**

Based upon the curve fits for the other two sets of blends, it appears that the ethanol content of fuels blended with "typical" 89.2 kPa (12.94 psi) base gasoline would have to be reduced to below 65% to achieve the Class 3 minimum DVPE value of 66 kPa (9.5 psi), while the low vapor pressure (83.0 kPa (12.04 psi) DVPE) base gasoline would only allow a maximum ethanol content of about 58%. It should be noted, however, that just meeting the D5798 vapor pressure standard would result in fuel tank vapors that would be flammable at significantly higher temperatures than those from even a low vapor pressure winter gasoline. Comparison with Figure 9 reveals that achieving an upper flammability limit temperature of -25°C (-13°F) would require reductions in ethanol content to below the levels that would provide D5798 compliant vapor pressure values.

Furthermore, it is likely that some winter fuels are being used that have vapor pressure values below that of the low DVPE base gasoline used in the current study. For example, vapor pressure data from a national survey of "E85" quality suggest that the base gasolines used to make some of these blends had vapor pressure values of well below 83.0 kPa (12.04 psi).

Figure 12 shows the upper flammability limits of the laboratory fuels as a function of their respective vapor pressure values. In these cases, there was reasonably good agreement between the flammability limit temperatures and the vapor pressure of the blends. The most notable exceptions involve the differences between the E0 and E15 blends with a given base gasoline. This was because the addition of 15% ethanol resulted in little change in the vapor pressure, but resulted in a significant increase in the limit temperature.

Figure 13 shows the relationship between vapor pressure and flammability for all of the gasoline and ethanol/gasoline blends tests evaluated during the current study and the previous two studies [1,2]. The fuels from the first study have been identified as "Experimental E85 Fuels". Some of the blends evaluated in that study contained hydrocarbons other than commercial gasoline (such as natural gasoline and isopentane). In Figure 13, the overall agreement is not as good as that when only the laboratory blends were considered. This suggests the details of the hydrocarbon portions of the blends may be responsible for differences in flammability at a given vapor pressure level.

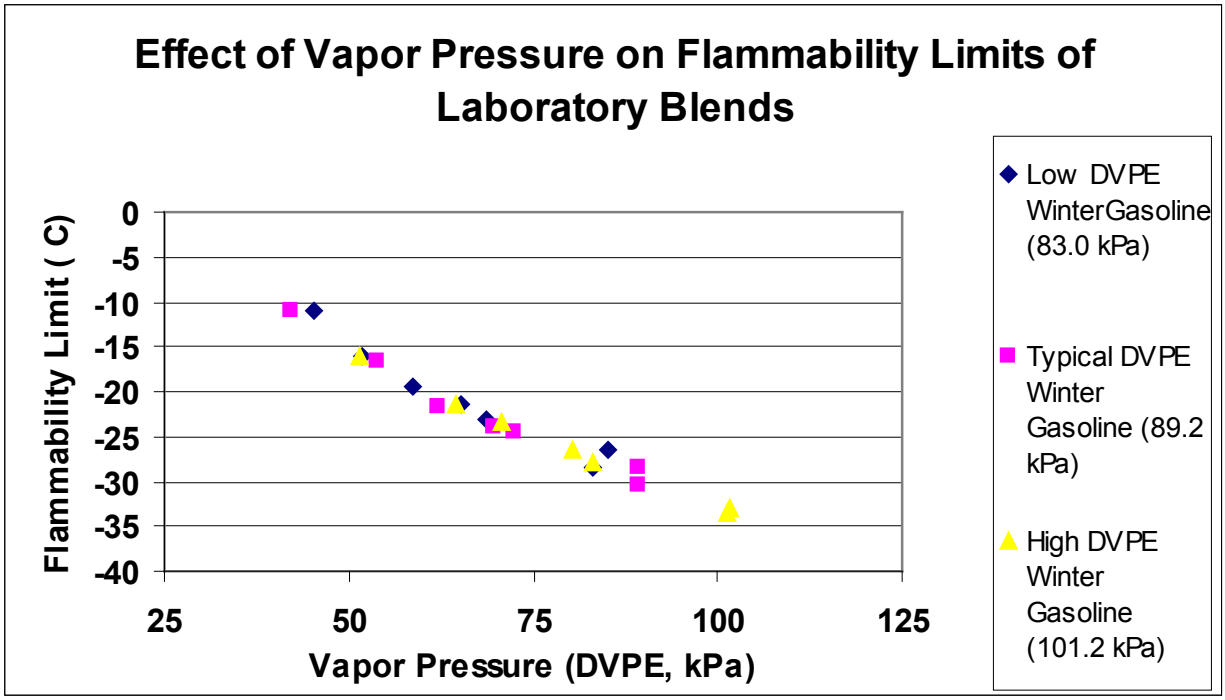



**Figure 12: Effect of Vapor pressure (DVPE) on Flammability of Laboratory Blends**

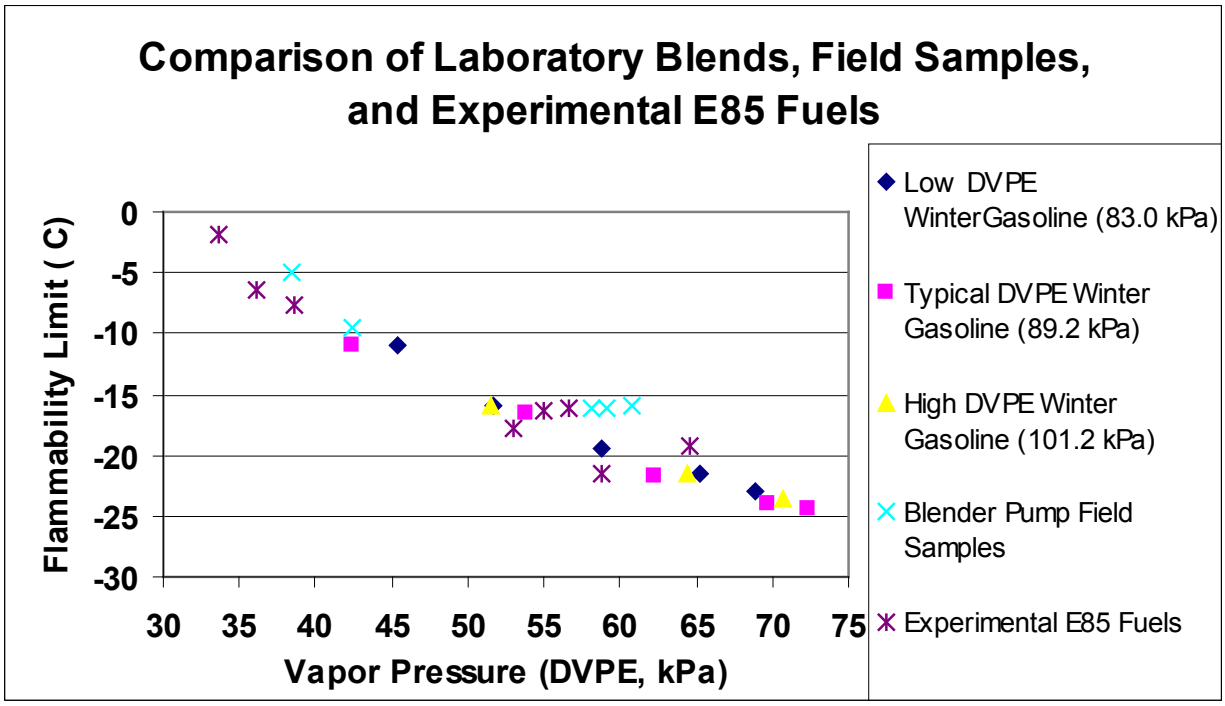



**Figure 13: Effect of Vapor pressure (DVPE) on Flammability of all Test Fuels**

## 3.4 Results with Denatured Ethanol Samples

Figures 14 and 15 show the results for maximum pressure and rate of pressure rise for the two denatured ethanol samples that were tested during the project. Sample 1 was a sample of the denatured ethanol used to make the laboratory blends with 89.2 kPa (12.94 psi) gasoline in the previous study. Sample 2 was a sample of the denatured ethanol used to make the laboratory blends with 83.0 kPa (12.04 psi) and 101.2 kPa (14.68 psi) gasoline that were evaluated in the current study. Both of these denatured ethanol samples had a hydrocarbon content of 3%, as so are referred to as E97.

The E97 samples were evaluated for flammability at temperatures warm enough to encounter the upper (rich) flammability limit, and at temperatures cold enough to encounter the lower (lean) flammability limit. As the temperature approached the upper flammability limit, test results showed relatively low values of maximum pressure rise and rate of pressure rise. This was similar to the behavior observed with the laboratory ethanol/gasoline blends.

In contrast, near the lower flammability limit, there was an abrupt change in pressure behavior as the temperature was reduced. In these cases, there was a transition from tests yielding relatively high maximum pressures and rates for pressure rise to tests where there was no detectable ignition of the fuel/air mixture. This suggests that the headspace vapors were more difficult to ignite near the lower flammability limit, whereas at the upper flammability limit ignition often occurred but only part of the mixture was burned.

Based upon the results shown in Figure 14, it was calculated that E97 Sample 1 had flammable headspace vapors between -5°C (23°F) and 19.5°C (67°F), while E97 Sample 2 had flammable headspace vapors between -3.5°C (25.5°F) and 22.5°C (72.5°F). The slightly lower flammable temperature range for E97 Sample 1 is consistent with greater fuel vaporization, and suggests that the denaturant in this sample was more volatile than the denaturant in E97 Sample 2.

Figure 15 shows that the denatured ethanol samples resulted in very high rates of pressure rise at temperatures in the region of 10°C. Compared with the rates of pressure rise measured (at very low temperatures) with the laboratory ethanol/gasoline blends (see Figures 3, 5, and 7), the rates of pressure rise with E97 results were about five times greater. The rate of pressure rise is an important indication of the real-world hazard posed by flammable mixtures, as it impacts both the destructive force of an explosive event, and the likelihood that relatively weak sparks (such as static discharges) could ignite such a mixture. The fact that these high rates of pressure rise for E97 were measured at temperatures that are typical of those in many storage tanks should raise serious concern about any proposal to store denatured ethanol at retail fuel outlets.

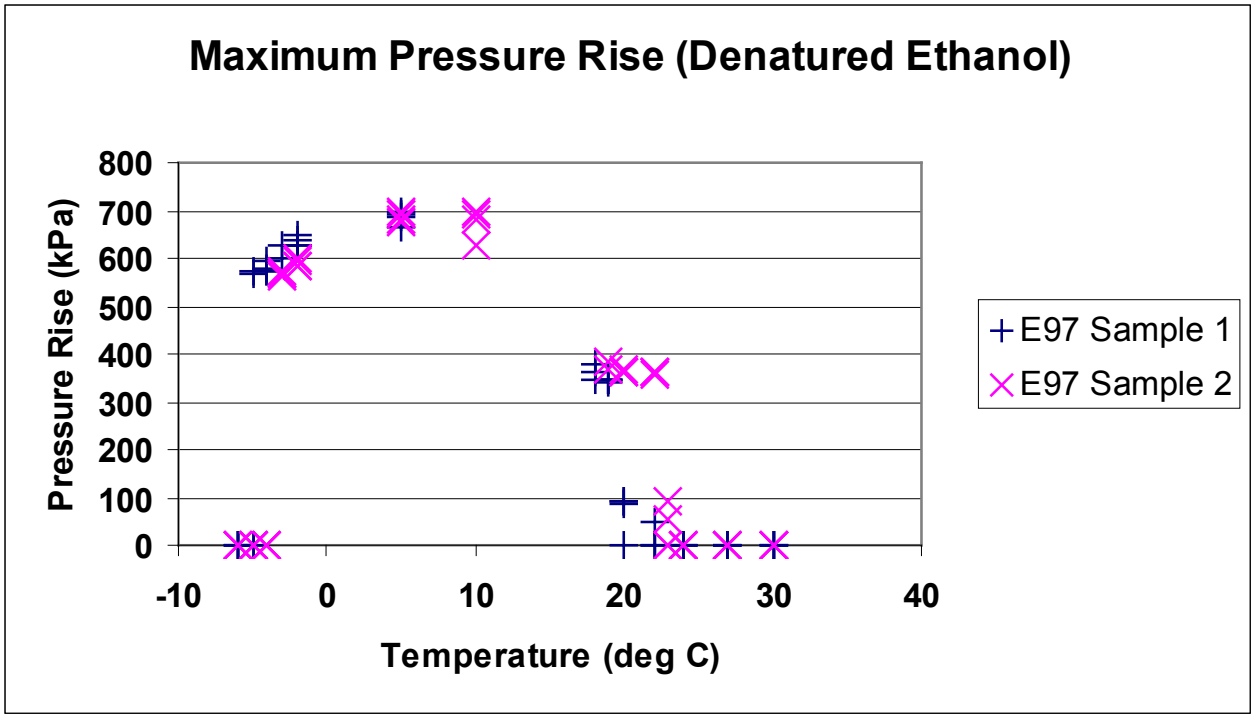



**Figure 14: Maximum Pressure Rise of Denatured Ethanol (E97) Samples**

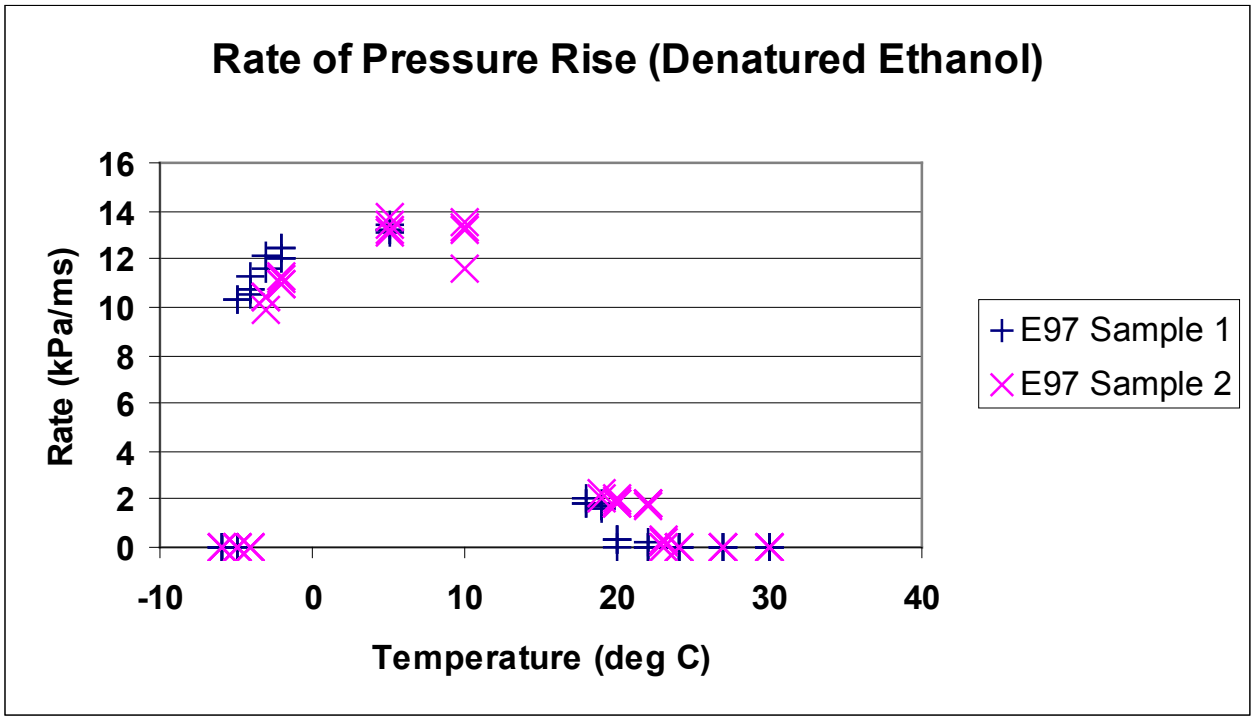



**Figure 15: Maximum Rate of Pressure Rise of Denatured Ethanol (E97) Samples**

# 4 Conclusions from Experimental Study

1. The experimental results presented in this report are, to some extent, unique to the apparatus and test conditions that were used for the experiments. Important factors that would have affected the observed behavior included the use of a fill level of 5%, the use of a strong spark for ignition, and the use of test chambers with a relatively small internal volume. Thus, the combustion pressures and flammability limit temperatures presented in this report would be expected to differ from those that might be encountered in other situations. For example, a higher fill level or a weaker ignition source would lower the upper flammability limit temperature (the headspace vapors would have to be colder to be flammable), while a larger headspace volume would likely lead to higher maximum pressures and higher rates of pressure rise. Therefore, the results presented in this report should be interpreted primarily as a relative indication of the headspace vapor flammability of the test fuels. It should also be noted that results were obtained with blends made from specific gasoline samples. The quantitative results at a given vapor pressure level might not be exactly the same if different gasoline samples with different hydrocarbon compositions were used.

2. The matrix of the laboratory fuel blends tested in the study was comprised of three gasoline vapor pressure levels (83.0 kPa (12.04 psi) DVPE, 89.2 kPa (12.94 psi) DVPE, and 101.2 kPa (14.68) DVPE) and seven different blend levels (E0, E15, E55, E60, E68, E75, and E83). The three gasoline vapor pressure levels were intended to represent low, typical, and high levels for available winter gasoline. Of these fuel samples, only blends made with the high DVPE (101.2 kPa (14.68 psi)) winter gasoline could achieve the minimum vapor pressure value for Class 3 fuels (specified in ASTM D5798-09) of 66 kPa (9.5 psi) at the former and revised D5798 minimum ethanol content (volume %) levels of 70% and 68%, respectively. *In order to be compliant with the D5798 minimum vapor pressure specification, blends made with the typical DVPE (89.2 kPa (12.94 psi)) winter gasoline would have to have an ethanol content of less than 65%, while blends made with the low DVPE (83.0 kPa (12.04 psi)) winter gasoline would have to have an ethanol content of about 58% or less.*

3. Headspace vapors from E0 and E15 blends of the low DVPE (83.0 kPa (12.04 psi)) winter gasoline were not flammable until the temperature was below -25° C (-13° F). *In order to maintain the flammability limit temperature at or below -25°C (-13°F) (i.e., comparable to that of a low vapor pressure winter gasoline), blends made with the high DVPE (101.2 kPa (14.68 psi)) winter gasoline would have to have an ethanol content of less than 65%. Blends made with the typical DVPE (89.2 kPa (12.94 psi)) winter gasoline would have to have an ethanol content of about 55% or less, and blends made with the low DVPE (83.0 kPa (12.04 psi)) winter gasoline would have to have an ethanol content of less than 40%.*

4. For the laboratory fuel blends evaluated in this study, the ranking of upper flammability limits correlated well with the vapor pressure values of the blends. The most notable exceptions involved the differences between the E0 and E15 blends with a given base gasoline. This was because the addition of 15% ethanol resulted in little change in the

vapor pressure, but resulted in a significant increase in the limit temperature. When all of the laboratory fuels, field samples, and experimental "E85" fuels evaluated throughout the three phases of the study (the present study and the two previous studies) are considered, the correlation between vapor pressure and flammability was markedly inferior to that with only the laboratory blends. This suggests that the details of the hydrocarbon portions of the blends may be responsible for differences in flammability at a given vapor pressure level.

5. Two different samples of denatured ethanol were evaluated to determine both the upper and lower flammability limits of the headspace vapors. Both of these samples contained 97% ethanol and 3% denaturant (E97). One sample (97% ethanol, 1% water, and 2% denaturant) produced flammable headspace vapors at temperatures above -5°C (23°F) and below 19.5°C (67°F). The other sample (97% ethanol, 0.74% water, and 2.26% denaturant) produced flammable headspace vapors at temperatures above -3.5°C (25.5°F) and below 22.5°C (72.5°F). The differences in headspace vapor flammability were most likely due to differences in the volatility of the denaturant used in the two samples.

6. The denatured ethanol samples exhibited the highest pressure rise values and rates of pressure rise at temperatures in the vicinity of 10°C (50°F). High rates of pressure rise for a burning mixture are indicative of a fuel/air mixture that burns rapidly and destructively and is relatively easy to ignite. *The fact that these high rates of pressure rise for E97 were measured at temperatures that are typical of those in many storage tanks should raise serious concern about any proposal to store denatured ethanol at retail fuel outlets.*

7. It is recommended that further experimental work be carried out to examine the headspace vapor flammability of ethanol/gasoline blends made with base gasolines which have vapor pressure values lower than those tested thus far, as surveys of available fuels indicate that such fuels are currently in use. The rationale for this recommendation is detailed in Appendix B.

8. It is recommended that further experimental work be carried out to examine the effects of denaturant properties on the flammability of denatured ethanol. This data would facilitate the consideration of flammability issues as a factor in the selection of preferred denaturants for fuel ethanol.

# II. MATHEMATICAL MODELLING STUDY

## 5 Introduction

It is desirable to have a manageable mathematical model to characterize the volatility and flammability of ethanol gasoline blends. Such a model would permit the assessment of fuels with regard to flammability without resorting to costly and time consuming combustion tests for every candidate fuel.

In Phases One and Two of this work, it was shown that the volatility of ethanol-gasoline blends could be represented as a pseudo-binary mixture, treating the ethanol as one component, and gasoline as the other. Ethanol vapor pressure is calculated using the Antoine Equation, a well-established correlation for pure compounds. Its molecular mass, $M$, is constant at 46 in both phases at all times. Its vapor pressure is a function of temperature only, and does not depend upon how much of the alcohol is evaporated. Gasoline, on other hand, is a multi-component mixture, whose vapor pressure and vapor phase molecular mass depend on both the temperature and the extent of evaporation. When most of the fuel is liquid, the vapor pressure is high, and the vapor phase molecular mass is low. However, as evaporation proceeds, the vapor pressure drops by an order of magnitude, and the average molecular weight of the vapor phase increases by a factor of about two.

Details of the gasoline model and the pseudo binary treatment of ethanol-gasoline blends as used in this part of the work are summarized in Appendix C.

In Phase 1, due to the limited data available on the hydrocarbon portions of the blends tested at that time, it was not possible to create models of the hydrocarbon components in each blend in accordance with the full modelling technique. Instead, a number of existing models for representative gasoline hydrocarbons were used.

In Phase 2, detailed information on the gasoline hydrocarbons was available and the originally published model (14,15) was used to make predictions of the rich flammability limit. This was compared to measured data found in the tests carried out in the experimental portion of the work.

### 5.1 Conclusions from the Modelling in Phases One and Two

Two important conclusions drawn from the modelling results shown in Phase 1 were:

1) Volatility at high temperatures, such as that used in determining DVPE did not necessarily reflect the behaviour of the different ethanol blends at low temperatures. A simple comparison of DVPE to rank low temperature flammability was insufficient and led to erroneous ranking of the fuels.
2) Simply using generic gasoline models did not reliably assess low temperature flammability of a particular fuel blend.

The principal conclusions drawn from the modelling results shown in Phase 2 were:

1. When properties of the base oxygenate-free gasoline are known, then the model can rank the flammability characteristics of the gasoline-ethanol blends tested quite well.
2. The use of conventional flammability data in the model leads to the prediction of higher rich limit temperatures than those actually measured in this apparatus.
3. In Phase 2 the required base gasoline data were available only for a single set of blends tested. Therefore, further work was needed to compare ethanol blends produced from different gasoline base stock, so as to determine the reliability of the model in comparing the relative hazards of different fuel sources.

## 5.2 Scope of the Present Modelling Study

Like the previous two phases of the work, the experimental data from this study determine the upper temperature limits of flammability (i.e. the rich limit) of the fuel blend under test, in the particular apparatus used.

In order to predict flammability, one requirement of the model implementation is that the final distribution between liquid and vapor phases must be determined for the conditions of the test. As in the previous work, the model for the fuel volatility and its resulting flammability must be incorporated into a larger computer program that will iteratively find the quantity of liquid and vapor pressure in the test volume that meets the phase equilibrium requirements. As in the previous study, a commercial equation-solving software package (TK Solver™) was used for these determinations in this part of the work. The work in Phase 2 used the original modeling approach described in References [14] and [15]. A later version [9] followed the same basic approach but used an iterative method to better estimate the liquid and vapor phase properties during the distillation. In the present work, the full FORTRAN version of that more advanced form of the gasoline volatility model was used to derive the required modelling coefficients for each gasoline, as described in reference [9].

In addition, curves were fitted to the fuel specific gravity data provided for the various fuels tested that had been blended from each base gasoline. This allowed the blend densities to be determined for other proportions of ethanol and that base gasoline stock that were examined using the model.

Unlike the case in previous phases of this work, a full set of data was available for each blend across a broad range of ethanol content. This allowed the non-ideality of the blends to be treated differently than in the two previous phases. The measured DVPE of each blend made using a given base gasoline was used to derive the Margules coefficient A, used in the model for that blend. By fitting a curve to those experimentally-determined values of the coefficient A, the values of A for other blends to be studied in the model could be calculated. This was the approach used to produce the predicted results shown below.

The model was then used to make predictions of the flammability for comparison to the experimental results. It was also used to examine the discrepancies between predicted and measured data, and to draw some conclusions regarding the modelling of the non-ideal mixtures formed when the polar molecules of alcohols and the non- polar molecules of gasoline are blended together.

# 6 Modelling Results

Figures 16 to 18 show the results for the three sets of fuel blends studied. As noted earlier in this report, the three sets were blended from three different gasoline base stocks. Those base gasolines had measured DVPE values of 83.0 kPa (12.04 psi), 89.2 kPa (12.94 psi) and 101.2 kPa (14.68 psi).

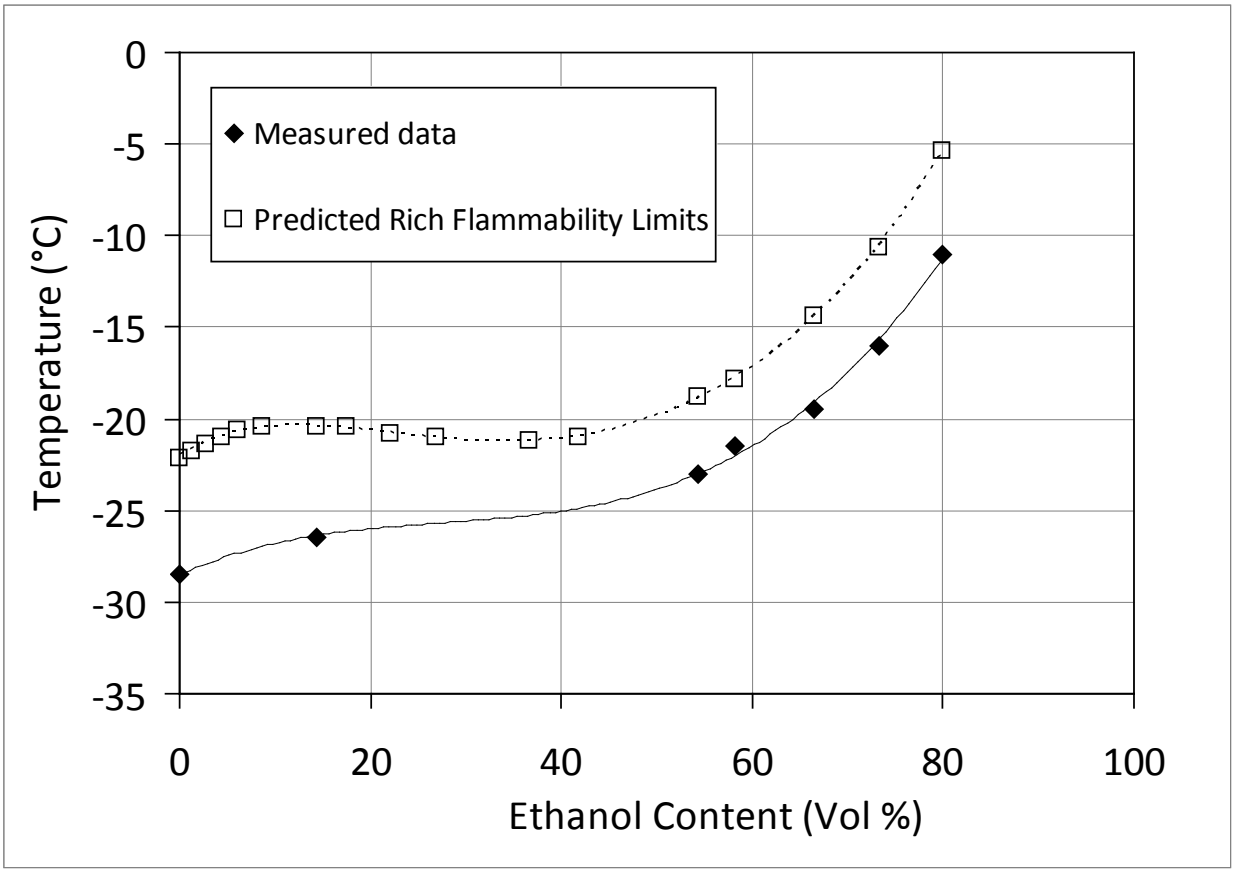



**Figure 16: Flammability of Blends Using 83.0 kPa (12.04 psi) Base Gasoline**

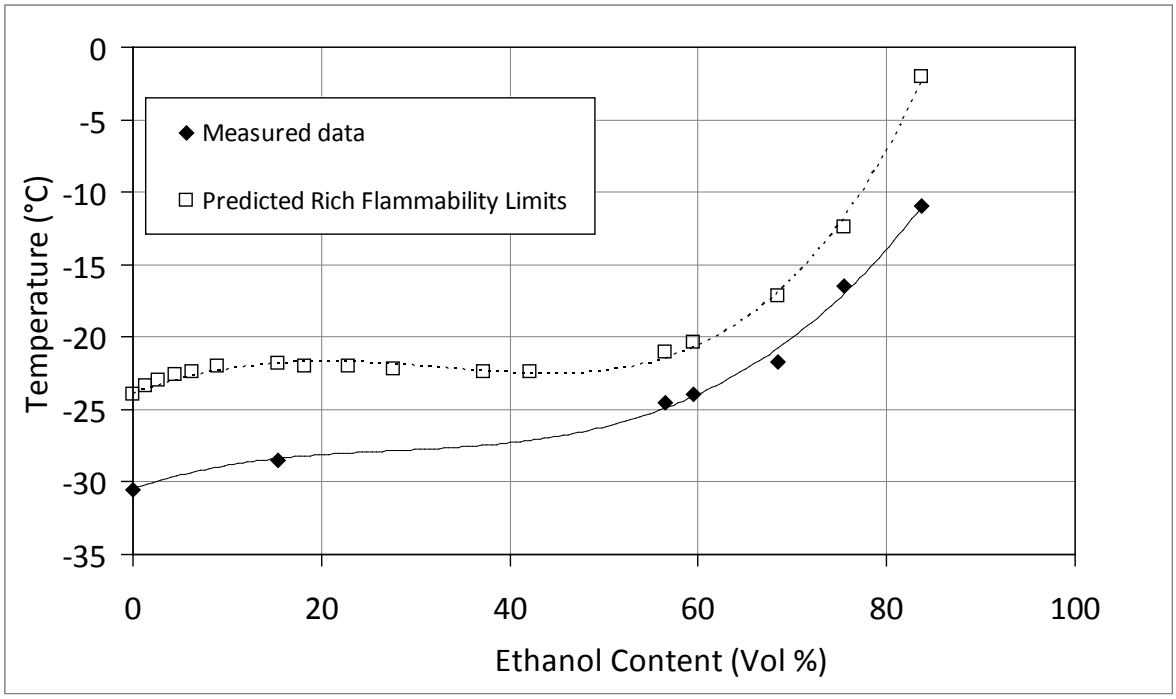



**Figure 17: Flammability of Blends Using 89.2 kPa (12.94 psi) Base Gasoline**

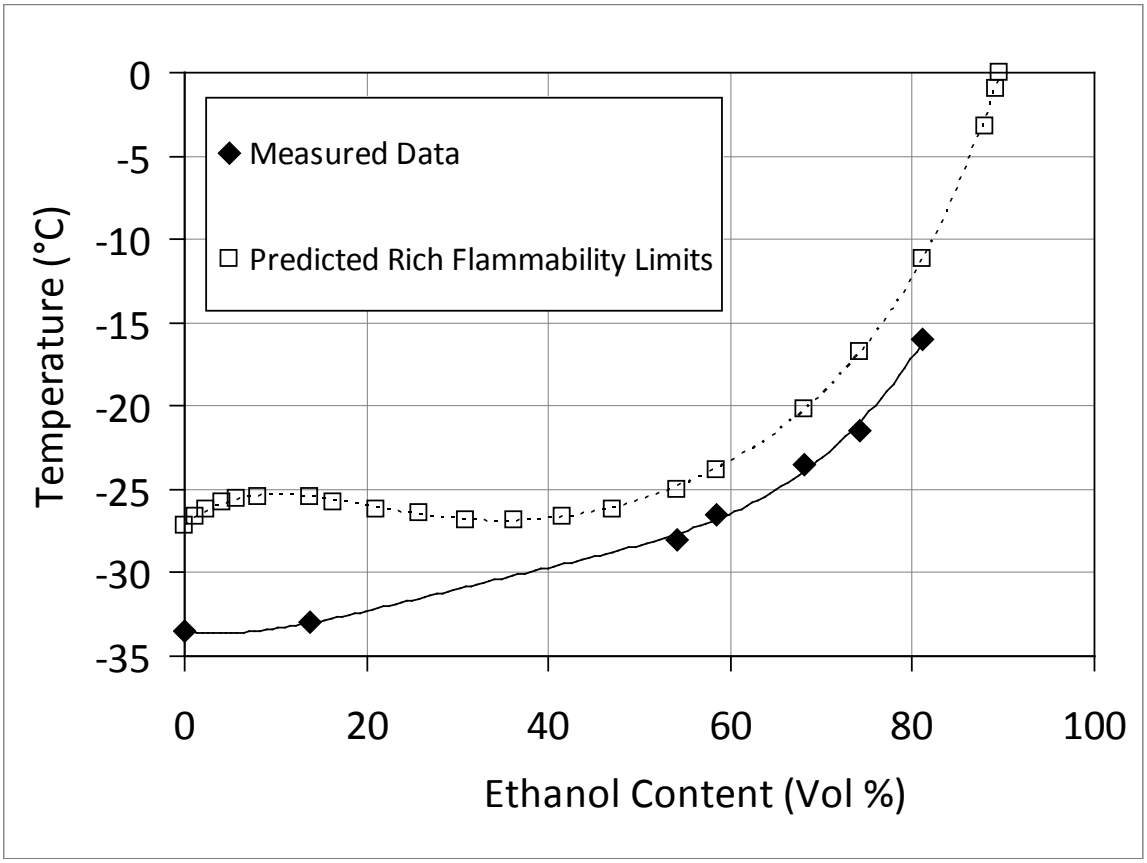



**Figure 18: Flammability of Blends Using 101.2 kPa (14.68 psi) Base Gasoline**

These three figures display several points of interest:

1. As observed previously, the model consistently predicts upper limits of flammability that are higher than the experimentally determined values.
    a. In part, this is simply due to the use in the model of standard flammability data for hydrocarbons and ethanol, found in the usual references [10,11]. These standard values have been found using upward flame propagation in large diameter flame tubes with no wall effects, and consequently represent the scenario in which flame propagation is most likely to succeed. The present test conditions, using a different geometry and direction of flame propagation would give rich limits lower than the ideal ones that provided the standard published data used in the model at present.
    b. It would be useful to carry out experiments on some selected pure components in the present test rig, in order to determine upper limits that are more realistic for the scenarios of interest involving fuel tanks at low temperatures.
2. The shape of the predicted curve follows the data well for blends containing more than about 50% ethanol.
3. For blends containing less than about 50% ethanol, the model predicts a rise in rich limits initially, as ethanol is progressively added to the gasoline, followed by a drop at higher levels before again beginning to rise for the high alcohol content blends to the right. The experimental data do indeed show such an effect, but to a smaller extent – a point of inflexion in the data rather than the actual decrease in the rich limit that is predicted by the model. This issue will be discussed at greater length below, since it is a direct consequence of how the non-ideality of these blends is treated in the model and how it behaves in reality.

## 6.1 Discussion of the Non-Ideality Effects Observed

Raoult's Law for ideal mixtures can be written:

$$P_{fuel\ sat} = \sum_{i=1}^{i=N} X_i P_{i\ sat} \qquad (1)$$

where
$P_{fuel\ sat}$ = total vapor pressure of the blend
$X_i$ = mole fraction of component $i$ in the liquid phase of the blend at equilibrium
$P_{i\ sat}$ = equilibrium saturation pressure of component $i$ alone

Mixtures of hydrocarbons, such as gasoline, are made up of non-polar molecules and conform to Raoult's Law quite well. However, alcohols consist of strongly polar molecules. This leads to large deviations from the behaviour predicted by Raoult's Law when alcohols are mixed with hydrocarbons. Thus Raoult's Law (Equation 1) does not apply as written and a modification to account for the non-ideality of the resulting alcohol/hydrocarbon mixture must be used. By convention, this has the following form for a blend such as ethanol and gasoline (designated below in the form EX where X is the volume% of ethanol in the blend):

$$P_{EX} = \gamma_g X_g P_{gsat} + \gamma_{EtOH} X_{EtOH} P_{EtOHsat} \quad (2)$$

where

| | |
|---|---|
| $P_{EX}$ | = equilibrium saturation pressure of the EX mixture |
| $\gamma_g$ | = activity coefficient for gasoline in the blend |
| $\gamma_{EtOH}$ | = activity coefficient for ethanol in the blend |
| $X_g$ | = mole fraction of gasoline in the liquid phase |
| $X_{EtOH}$ | = mole fraction of ethanol in the liquid phase |
| $P_{gsat}$ | = saturated vapor pressure of the gasoline |
| $P_{EtOHsat}$ | = saturated vapor pressure of the ethanol |
| $X$ | = percent ethanol in the blend e.g. E55 contains 55% ethanol |

Note that $X_g$ and $X_{EtOH}$ as well as $P_{gsat}$ vary continuously as the fuel evaporates. Furthermore, at any point in the evaporation process, when the overall mass fraction vaporized is some given value between 0 and 1, say 0.4, the mass fraction of gasoline vaporized is different from the mass fraction of ethanol vaporized, and neither is equal to the overall value of 0.4 in this example. Since the mole fractions of each of the two components in the liquid phase are not known *a priori* for any given overall value of mass fraction vaporized, iteration is required to determine the vapor pressure and other volatility characteristics needed, such as the molecular weight of the vapor phase. This latter is needed, as well as the partial pressures of the two components, as part of the determination of vapor phase flammability.

In order to model the vaporization behaviour of such a blend and the resulting flammability of the vapor phase above the liquid in a fuel tank, representative values for the two activity coefficients must be determined for use in this binary model. As in the previous work, the Margules two-suffix equation was used [4].

This has the form:

$$\gamma_{gasoline} = e^{\frac{AX_{ethanol}^2}{T}} \quad (3)$$

$$\gamma_{ethanol} = e^{\frac{AX_{gasoline}^2}{T}} \quad (4)$$

where

$\gamma_{gasoline}$ = activity coefficient of the gasoline
$\gamma_{ethanol}$ = activity coefficient of the ethanol
$A$ = the Margules 'constant'
$X_{gasoline}$ = mole fraction of gasoline remaining in the liquid at equilibrium
$X_{ethanol}$ = mole fraction of ethanol remaining in the liquid at equilibrium

One aspect of this equation that is pertinent to this study is the effect of temperature on the non-ideality of a blend. Because of the Arrhenius-type expression in Equation 4, the activity coefficients increase as temperature drops, giving a greater vapor pressure than would otherwise be the case. As an example, for an E80 blend, the increase in vapor pressure of the gasoline

component compared to an ideal mixture is more than 30% greater at a temperature of -20°C than at the standard DVPE temperature of 37.8°C (100°F).

If A were indeed a constant, as used in the original Margules technique, then the activity coefficients would be symmetrical; that is, the magnification of ethanol vapor pressure provided by the high value of $\gamma_{ethanol}$ in low ethanol blends would be exactly mirrored by the same magnification given to the gasoline vapor pressure by $\gamma_{gasoline}$ in high ethanol blends.

However, in the work reported earlier in this project [2], the following expression was used for the value of A, as presented in Reference (4):

$$A = C_1 + C_2 \times \left( \frac{X_{ethanol}}{1 - X_{ethanol}} \right) \qquad (5)$$

This skews the non-ideality effects so they are no longer symmetrical between the two fuels, but rather have a stronger impact on gasoline vapor pressure in the high ethanol blends than in the lower ethanol blends. This had previously given better results in modelling the data available on various methanol and ethanol blends. In that original work [4], the measured vapor pressures of various blends of methanol and ethanol were used to derive values of $C_1$ and $C_2$ of 600 and 5.25, respectively. These were values that gave reasonable results for a broad range of methanol and ethanol blends with gasoline, but were skewed towards the high alcohol, rather than low alcohol blends, due to the particular data set available at the time.

In Phase 2 of the present study, only high alcohol blends had sufficient data on the base gasoline to allow use of the model. Since measured DVPE was available for those high ethanol blends, those values were used to estimate a value of A so as to make the predicted DVPE match the measured values better than occurred when the earlier published values were used in the model. It was found that a good fit to the DVPE values of the high ethanol blends studied in Phase 2 could be obtained using values for $C_1$ and $C_2$ of 600 and -2.27, respectively. These values of the two constants were then used in the model to predict the low temperature flammability of the blends under study in Phase 2, with reasonable success.

Since DVPE for all the blends used in the present phase of the work was provided, the values of A for each blend could be determined for DVPE conditions (100 °F). Using these values of A essentially matched the model prediction to the measured DVPE of each individual ethanol/gasoline blend. A curve was fitted to these discrete values of A so that any other blend could be studied. All predictions presented in this report used those values of A, derived at DVPE conditions but used for low temperature predictions.

One unresolved issue from the earlier phases of the work was whether the characteristic humps seen in the predictions for low ethanol blends were real or merely some sort of artefact of the modelling techniques.

It is now possible to resolve this, because there are measured as well as predicted values of both DVPE and upper flammability limit temperature for both low and high ethanol blends with full fuel blend property data sets. Although the bumps in the predicted curves are more pronounced than in the experimental measurements, the inflexion points are indeed present in the actual

measured data, albeit smaller than predicted. The anomaly is indeed the result of the actual fuel behaviour, although the model in its current form exaggerates the effect somewhat.

To understand why this feature is present at all, it is helpful to consider the impact of the non-ideality. The following Figure 19 is the same as Figure 18 except that the flammability has been calculated for the case of an imaginary ideal mixture of ethanol and this same gasoline. In the absence of non-ideality effects, the curve shown would be the predicted rich flammability limit. The rich temperature limit would rise almost linearly between that of neat gasoline and that of neat alcohol, which would occur (for pure rather than denatured ethanol) at a temperature in excess of 40°C.

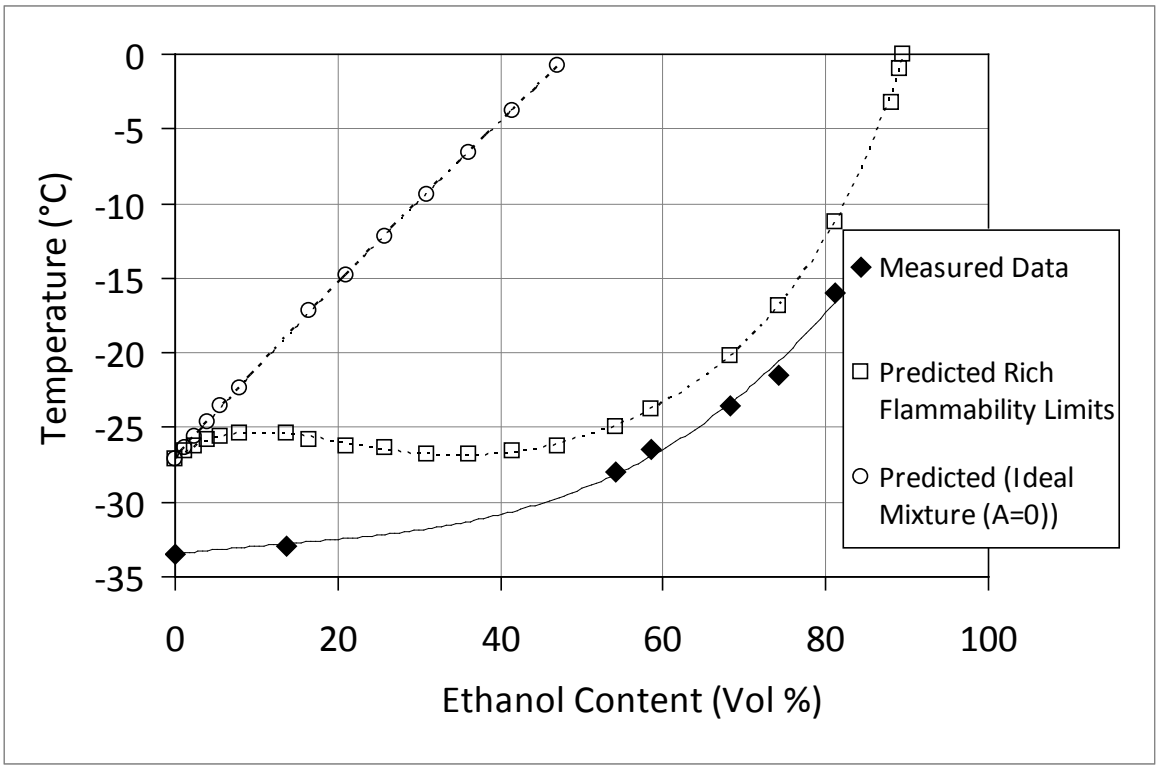



**Figure 19: Flammability of Real and Ideal mixtures Using 101.2 kPa (14.68 psi) Base Gasoline**

As an aside, it can be noted that the denaturant found in commercial ethanol results in a significant decrease in the upper temperature flammable limit compared to the pure compound, due again to the non-ideality of the blend. As has been seen in the limited experimental data found in this project for two samples of commercial ethanol provided, the differences in the denaturant composition can have a significant impact on that limit temperature. However, those differences in denaturant impact are likely to be overwhelmed by the gasoline effect in any ethanol gasoline blends that contain more than trivial amounts of gasoline.

The impact of the non-ideality is felt most strongly when the concentration of one component is much smaller than that of the other; i.e. towards the left and towards the right side of the graph as

drawn. Since the effect of the non-ideality is essentially to boost the vapor pressure of the ingredients, it might plausibly be expected that the rise in ethanol partial pressure, hence total vapor pressure for low ethanol blends might lower the rich temperature flammable limit compared to that of the neat gasoline. It does not do so because of the much higher flammable limit for ethanol. The blend vapor pressure close to the left axis is indeed higher than that of gasoline (as it was in the corresponding DVPE), tending to push the flammability curve downwards. However, the vapor mixture has a higher concentration of ethanol, whose upper flammable limit is about 19 vol% compared to gasoline at less than 8%. This tends to raise the upper limit, pushing the curve in the opposite direction; i.e. upwards. The increase in the mixture rich limit temperature due to the ethanol is more than enough to offset the effect of the higher vapor pressure for the low ethanol blends, resulting in the inflexion seen in both experimental and predicted curves.

An analogous point of inflexion does not appear at the right of the graph because the additional vapor is now gasoline, having a lower upper limit temperature. Thus both the extra vapor produced as well as the resulting decrease in the upper limit flammability of the vapor mixture both push the curve in the same downwards direction, leaving no reversal or inflexion of the kind seen at the left of the curve.

# 7 Conclusions and Recommendations from the Modeling Study

Ranking the comparative flammability hazard of different fuel blends is the ultimate aim of this work. The experimental data provide the answer unambiguously. However, a means to predict the comparative flammability with reasonable accuracy without costly and time consuming testing is highly desirable.
In comparing the ranking of fuels based either on DVPE and or on the model, the following overall conclusions can be drawn:

1. For the fuels tested in this third phase of the work, the experimental data can be rank ordered successfully using either the model or DVPE for high alcohol blends (E55 and higher); i.e., both the DVPE and the model correctly predicted the order of the rich flammability limits of the various fuels, from coldest to warmest.

2. When the entire data set provided by all three phases of this work so far is considered, DVPE did not successfully rank order the high ethanol blends. The model had insufficient data on the gasoline base stock for the fuels tested in phase 1 and part of phase 2 to be used to make a ranking on the entire data set.

3. Comparing an ethanol-free gasoline with its E15 blend, the DVPE did not correctly rank order any of the three blends tested in this phase. The model correctly rank ordered all three when comparing E0 and E15.

4. The exaggerated inflexion in the predicted upper limit curve (Figures 16-18 shown later in the report) produces some incorrectly predicted rankings between E15 E55 and E60 blends.

5. It would be useful to carry out experiments on some selected pure components in the present test rig, in order to determine upper limits that are more realistic for the scenarios of interest involving fuel tanks at low temperatures. This would allow the model to predict the upper limit temperatures more accurately.

6. The model already predicts the upper limit trends well for higher ethanol blends, and successfully captures the inflexion occurring in the measured data for low ethanol blends, albeit in a slightly exaggerated form. However, it needs refinement to more accurately portray that inflexion and make correct flammability rankings. In order to permit this, two or three additional low ethanol blends are needed along with the other blends used here. This could be accomplished by adding 5% and 10% blends, or preferably 4%, 8% and 12% blends with their full data sets as supplied for the fuels in this phase of the work. Additional blends in the 30-40% range could also be useful to bridge between the low ethanol (E0-E15) and the high ethanol (E55-E83) blend ranges.

7. Since most gasolines now contain some oxygenates, the D86 data for the base gasoline often is not available. In order to permit the model to be used when only routine field data are known, namely D86, ethanol content and specific gravity, it would be desirable to attempt to devise a technique for extracting the necessary gasoline data from the D86 data of a low alcohol blend. That is not trivial, but the detailed data already provided for the fuels studied so far in this work may allow such a technique to be developed, thereby making the use of the model much more practical and broadly accessible.

8. Despite the success of the current model, using the actual light hydrocarbon composition in a model rather than deriving an approximation for volatility from only the D86 data is likely to provide greater insight into flammability behaviour at low temperatures. A new mathematical model incorporating the detailed composition of the light components has been created and some initial runs conducted to better predict the impact of light ends on cold flammability. These preliminary results showed considerable promise. Further work on the new model is recommended for future work.

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# Appendix A: Analytical Results for Flammability Study Blends and Base Fuels

**Table 1**: Properties of Test Fuels Containing Typical Vapor Pressure Winter Gasoline (12.94 psi/89.2 kPa DVPE)

| Product | E83 | E75 | E68 | E60 | E55 | E15 | E0 | EtOH |
|---|---|---|---|---|---|---|---|---|
| Sample ID | 3057180 | 3057179 | 3057178 | 3057177 | 3057168 | 3195923 | 3055540 | 3055538 |
| D4052 Specific Gravity at 60°F | 0.7821 | 0.7748 | 0.7680 | 0.7610 | 0.7584 | 0.7205 | 0.7128 | 0.7933 |
| D5191 ASTM DVPE, psi | 6.14 | 7.81 | 9.02 | 10.12 | 10.49 | 12.94 | 12.94 | -- |
| D5501 EtOH, Vol % | 83.81 | 75.49 | 68.38 | 59.57 | 56.49 | 15.34 | N.D. | 96.98 |
| D5501 MeOH, Vol % | 0.04 | 0.03 | 0.03 | 0.02 | 0.02 | <0.03 | N.D. | 0.04 |
| E1064 H2O, Wt % | 0.68 | 0.61 | 0.58 | 0.51 | 0.49 | 0.316 | -- | 0.74 |
| D86 IBP, °F | 118.5 | 107.4 | 96.8 | 93.2 | 90.7 | 84.1 | 78.4 | -- |
| D86 T 10 Evaporated, °F | 165.6 | 161.3 | 154.1 | 146.6 | 144.2 | 116 | 110.5 | -- |
| D86 T 20 Evaporated, °F | 169.0 | 167.5 | 164.1 | 161.5 | 159.9 | 136.5 | 140 | -- |
| D86 T 30 Evaporated, °F | 170.4 | 169.6 | 167.1 | 165.4 | 164.6 | 151.8 | 179.2 | -- |
| D86 T 50 Evaporated, °F | 171.6 | 171.9 | 170.3 | 169.0 | 168.4 | 163.4 | 223.9 | -- |
| D86 T 70 Evaporated, °F | 172.2 | 173.1 | 172.2 | 171.8 | 171.3 | 238.7 | 245.9 | -- |
| D86 T 90 Evaporated, °F | 173.1 | 174.7 | 174.6 | 175.2 | 175.2 | 303.7 | 313.9 | -- |
| D86 End Pt, °F | 252.1 | 343.8 | 353.5 | 358.5 | 361.1 | 378 | 386.2 | -- |
| D86 Recovery, Vol % | 98.4 | 97.8 | 97.8 | 97.3 | 97.5 | 96.4 | 97.1 | -- |
| D86 Residue, Vol % | 0.8 | 0.9 | 1.0 | 1.0 | 1.1 | 0.9 | 0.9 | -- |
| D86 Loss, % | 0.7 | 1.2 | 1.1 | 1.5 | 1.2 | 2.7 | 2.0 | -- |
| D86 E 200, % | 98.9 | 98.0 | 96.7 | 95.3 | 94.4 | 59 | 36.1 | -- |
| D86 E 300, % | not appl | 98.1 | 96.7 | 95.4 | 94.5 | 89.5 | 87.7 | -- |

**Table 2**: Properties of Fuels Containing Low Vapor Pressure Winter Gasoline (12.04 psi/83.0 kPa DVPE)

| Product | E83 | E75 | E68 | E60 | E55 | E15 | E0 | EtOH |
|---|---|---|---|---|---|---|---|---|
| Sample ID | 3192177 | 3192176 | 3192175 | 3192162 | 3192161 | 3192160 | 3192158 | 3192156 |
| D4052 Specific Gravity at 60°F | 0.781 | 0.769 | 0.7629 | 0.7638 | 0.7605 | 0.6915 | 0.7185 | 0.7938 |
| D5191 ASTM DVPE, psi | 6.59 | 7.5 | 8.53 | 9.46 | 9.98 | 12.35 | 12.04 | -- |
| D5501 EtOH, Vol % | 80.45 | 73.05 | 65.95 | 58.28 | 54.55 | 14.36 | -- | 97.05 |
| D5501 MeOH, Vol % | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | -- | 0.05 |
| E1064 H2O, Wt % | 0.744 | 0.724 | 0.689 | 0.605 | 0.638 | 0.232 | 0.033 | 0.986 |
| D86 IBP, °F | 109.7 | 101.7 | 98.6 | 92 | 89.2 | 80.8 | 76.9 | -- |
| D86 T 10 Evaporated, °F | 161.9 | 157.1 | 149.5 | 142.5 | 135.4 | 114.2 | 109.2 | -- |
| D86 T 20 Evaporated, °F | 168 | 166.9 | 162.9 | 158.7 | 157.1 | 134.3 | 136.1 | -- |
| D86 T 30 Evaporated, °F | 169.9 | 169.6 | 167.1 | 164.5 | 164 | 148.9 | 170.2 | -- |
| D86 T 50 Evaporated, °F | 171.5 | 172.1 | 170.6 | 168.9 | 169.1 | 161.2 | 219.6 | -- |
| D86 T 70 Evaporated, °F | 172.1 | 173.2 | 172.5 | 171.6 | 172.3 | 238.1 | 248 | -- |
| D86 T 90 Evaporated, °F | 172.8 | 174.7 | 174.4 | 174.5 | 176.3 | 310 | 318.2 | -- |
| D86 End Pt, °F | 310.5 | 346.1 | 355.2 | 360.8 | 362.2 | 381.5 | 388 | -- |
| D86 Recovery, Vol % | 97.9 | 97.7 | 97.8 | 98 | 96.9 | 97.3 | 96.4 | -- |
| D86 Residue, Vol % | 0.7 | 1 | 1.1 | 1 | 1 | 0.9 | 1.1 | -- |
| D86 Loss, % | 1.4 | 1.3 | 1.1 | 1 | 2.1 | 1.8 | 2.5 | -- |
| D86 E 200, % | 98.6 | 97.6 | 96.5 | 94.8 | 93.8 | 60 | 39.9 | -- |
| D86 E 300, % | 98.7 | 97.7 | 96.6 | 95 | 94.4 | 88.5 | 86.5 | -- |

**Table 3**: Properties of Fuels Containing High Vapor Pressure Winter Gasoline (14.68 psi/101.2 kPa DVPE)

| Product | E83 | E75 | E68 | E60 | E55 | E15 | E0 | EtOH |
|---|---|---|---|---|---|---|---|---|
| Sample ID | 3192184 | 3192183 | 3192182 | 3192181 | 3192180 | 3192179 | 3192178 | 3192156 |
| D4052 Specific Gravity at 60°F | 0.7775 | 0.7731 | 0.7693 | 0.7612 | 0.7669 | 0.6436 | 0.6582 | 0.7938 |
| D5191 ASTM DVPE, psi | 7.47 | 9.34 | 10.26 | 11.66 | 12.07 | 14.72 | 14.68 | -- |
| D5501 EtOH, Vol % | 81.48 | 74.21 | 67.87 | 58.11 | 54.62 | 13.7 | -- | 97.05 |
| D5501 MeOH, Vol % | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | -- | 0.05 |
| E1064 H2O, Wt % | 0.798 | 0.711 | 0.673 | 0.607 | 0.563 | 0.283 | 0.049 | -- |
| D86 IBP, °F | 105 | 94.1 | 92.9 | 87.1 | 85.8 | 78.3 | 73.5 | -- |
| D86 T 10 Evaporated, °F | 160.8 | 147.7 | 136.9 | 126.3 | 124.9 | 104.6 | 95.3 | -- |
| D86 T 20 Evaporated, °F | 169.4 | 164.1 | 159.9 | 150.8 | 146.6 | 118.4 | 112.2 | -- |
| D86 T 30 Evaporated, °F | 171.4 | 168.6 | 167.1 | 162.9 | 160.1 | 132.9 | 132.9 | -- |
| D86 T 50 Evaporated, °F | 172.7 | 171.2 | 171.3 | 170.5 | 168.8 | 154.2 | 185.6 | -- |
| D86 T 70 Evaporated, °F | 173.1 | 172.1 | 172.6 | 173 | 172 | 193.8 | 240.5 | -- |
| D86 T 90 Evaporated, °F | 174 | 173.5 | 174.4 | 175.5 | 175 | 302.5 | 308.3 | -- |
| D86 End Pt, °F | 266.3 | 336.9 | 345.4 | 349.1 | 353.9 | 365.8 | 366.5 | -- |
| D86 Recovery, Vol % | 97.7 | 98.5 | 97.5 | 97.1 | 97.7 | 97.4 | 97 | -- |
| D86 Residue, Vol % | 0.9 | 0.6 | 0.8 | 1.1 | 0.8 | 0.9 | 0.9 | -- |
| D86 Loss, % | 1.4 | 0.9 | 1.7 | 1.8 | 1.2 | 1.7 | 2.1 | -- |
| D86 E 200, % | 98.8 | 98.1 | 97.4 | 95.1 | 94.4 | 70.3 | 55.2 | -- |
| D86 E 300, % | not appl | 98.2 | 97.5 | 95.4 | 95 | 89.4 | 88.1 | -- |

# Appendix B: Recommendations Regarding Fuel Samples for Future Flammability Tests

The headspace flammability project has provided information both to guide the development of specifications for ethanol/gasoline blends, and to reveal the potential hazards and consequences if such specifications are not adhered to. To this end, there has been some discussion of the possibility of obtaining additional "real world" "E85" samples (from an NREL/CRC survey, or otherwise) for comparisons with the laboratory fuel samples that have been evaluated thus far. However, examination of the 2008/2009 NREL/CRC survey of "E85" fuels shows that a very wide range of fuel properties were encountered in the field samples for all three classes of "E85". Thus, no "typical" fuel existed, so a large number of these samples would need to be tested to properly characterize the headspace flammability of in-use fuels.

***The following discussion presents the rationale for an alternative approach in which laboratory fuel blends would be used to represent the range of possible in-use fuel blends. It is proposed that further data obtained from a strategically chosen fuel matrix (with systematic variation of critical blend parameters) will ultimately provide the best value for enhancing knowledge about flammability hazards and facilitating the prediction of flammability characteristics through mathematical modeling.***

The tests conducted so far with laboratory blends provided by Marathon have covered three levels of base gasoline vapor pressure (nominally 12, 13, and 15 psi), intended to represent low, typical, and high values for winter gasoline. Nominal ethanol content levels of 0%, 15%, 55%, 60%, 75%, and 83% have been used for the blends. Measurements of the actual vapor pressure value (DVPE) and ethanol volume percentage have been supplied by Marathon for each blend.

The experimental results obtained thus far in the study have demonstrated that the vapor pressure of the gasoline used to produce the ethanol blended fuel has a pronounced effect on its headspace vapor flammability. As shown in Figure 1, the plotting the vapor pressure of each blend versus its ethanol content reveals a unique curve for each of the three base gasoline vapor pressure levels.

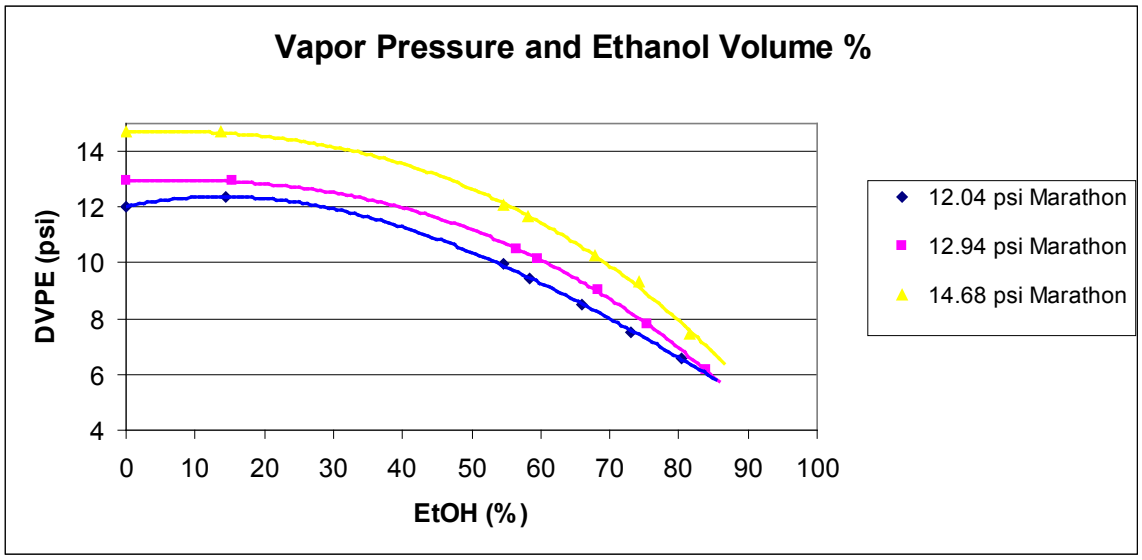


**Figure B-1: Relationship of Vapor Pressure and Ethanol Content for Marathon Blend Samples**

The CRC fuel survey measured the ethanol content and vapor pressure of the "E85" samples that were collected. The vapor pressure of the gasoline originally used to blend these fuels was not known. However, it is possible to gain some insight into the approximate gasoline vapor pressure levels for the CRC "E85" blends by plotting the vapor pressure versus ethanol content, and comparing these data points with the three Marathon vapor pressure curves.

Figure 2 compares the CRC data for Class 3 fuels with the Marathon curves. It can be seen that most of the data points for the CRC samples fall within the bounds of the upper (14.68 psi) and lower (12.04 psi) Marathon curves. This suggests that the gasoline originally uses to blend these CRC fuels probably ranged somewhere between about 12 psi and 15 psi. Thus, we can conclude that the Marathon laboratory blends tested thus far have provided a good representation for the majority of "real world" ethanol/gasoline blends likely to be produced with available winter gasoline.

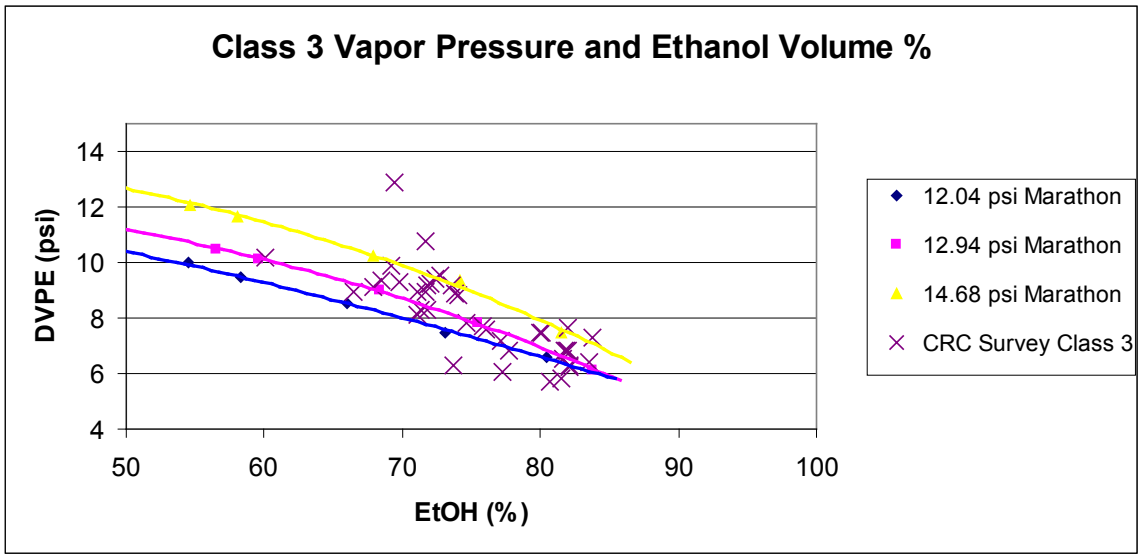


**Figure B-2: Comparison of Marathon Laboratory Blends and CRC Survey Class 3 Samples**

The two CRC samples that fall above the Marathon curves exhibit unusually high vapor pressure values relative to their indicated ethanol content. The lower of the two (in terms of vapor pressure) may simply have been blended with gasoline having an unusually high vapor pressure value. Inspection of the D86 results for this sample (ID#54833) shows a relatively low initial boiling point (94 deg F), but typical T50, T90, and FBP values.

However, the higher vapor pressure "E85" sample (ID#54815) had unusually low IBP and T50 values, and unusually high T90 and FBP values. Since the T50 temperature for this sample (161 deg F) was lower than the boiling point of ethanol (173 deg F), it does not seem possible that it could contain close to 70% ethanol, as indicated.

The data points of four samples (***10% of the Class 3 samples*** collected in the CRC survey) fell below the Marathon curve for 12 psi gasoline. This is evidence that, during the Class 3 season, at least some of the gasoline used to produce ethanol/gasoline blends may have vapor pressure levels substantially below 12 psi. ***Thus, it is recommended that testing of laboratory blends made from gasoline with lower vapor pressure levels (than those of the Marathon blends tested thus far) be considered for future directions.***

Figure 3 shows a similar comparison using the data for the Class 2 samples from the CRC survey. The results are very similar to those of Figure 2, with the majority of samples within the bounds of the Marathon curves. This suggests that the Class 2 samples collected in the CRC survey were blended with gasoline having a range of vapor pressure levels similar to that of the Class 3 blends. It appears that the difference between the Class 3 and the Class 2 samples was, in general, lower ethanol content for the latter.

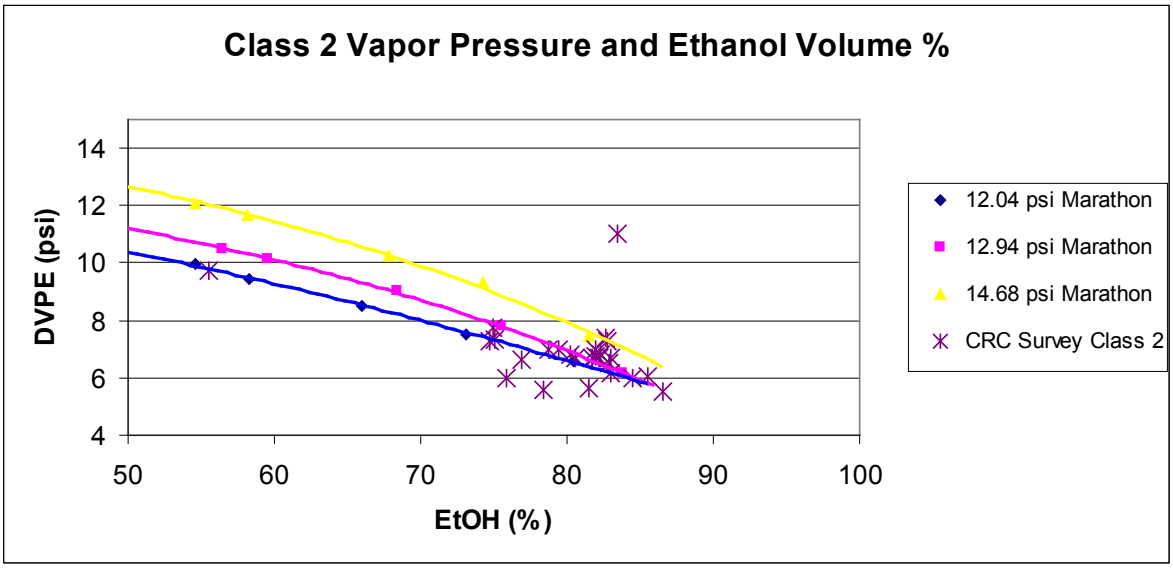


**Figure B-3: Comparison of Marathon Laboratory Blends and CRC Survey Class 2 Samples**

The single sample falling above the 14.68 psi Marathon curve (ID#54845) had unusually low D86 IBP and T50 values, and unusually high T90 and FBP values, similar to case of the anomalous Class 3 sample (ID#54815) discussed earlier. Thus, there should be similar uncertainties regarding the actual ethanol content of this sample.

Again, four of the Class 2 samples (in this case, *15% of the samples* collected) fell below the 12.04 psi Marathon curve. *As discussed earlier, this show a possible need for further testing of laboratory blends made from gasoline with vapor pressure levels below 12 psi.*

Figure 4 shows a comparison between the Marathon blends and the Class 1 samples from the CRC survey. Thus far, "E85" headspace vapor flammability concerns have focused upon relatively cold ambient temperatures and the Class 3 fuels that would be expected to be used under these conditions. However, some of the summer fuels collected in the CRC survey had extremely low vapor pressure levels and extremely high ethanol levels.

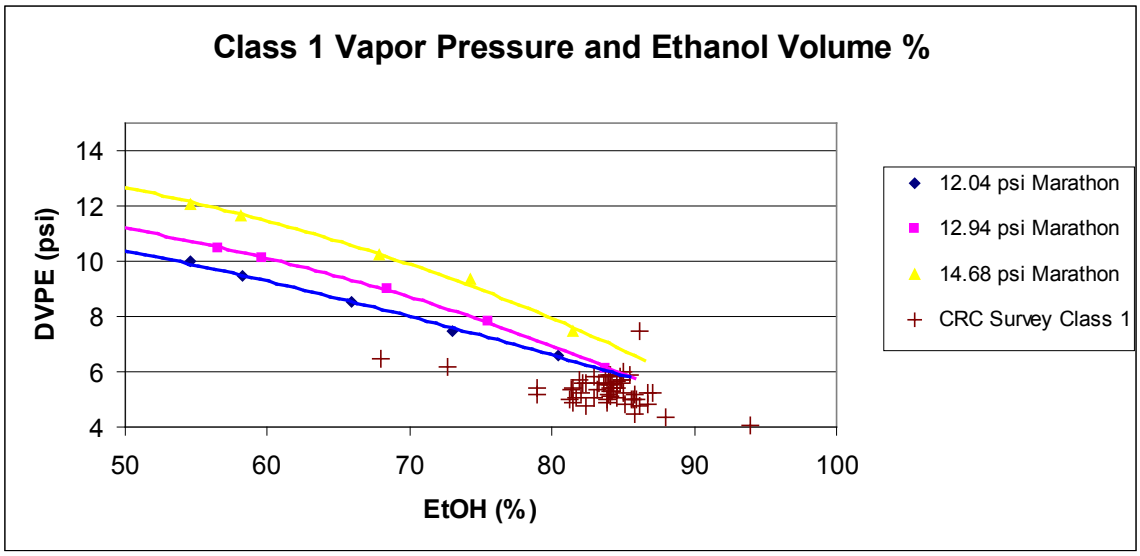


**Figure B-4: Comparison of Marathon Laboratory Blends and CRC Survey Class 1 Samples**

It can be seen that one "E85" sample had an ethanol content of almost 95%, and thus was essentially denatured ethanol. Numerous samples had vapor pressure values of less than 4.5 psi. In comparison, the "worst" fuel tested thus far in the flammability project was a Phase 1 sample with a DVPE value of about 5 psi, and a flammability limit of -2 deg C. Thus, it is likely that the flammability limits for some of the low vapor pressure CRC samples could lie above the freezing point, and flammability risks could exist at temperatures where Class 1 or Class 2 fuels are used. ***Therefore, it is recommended that flammability testing be carried out on laboratory blends made with low vapor pressure gasoline such that the resulting blends fall within the range indicated by the least volatile Class 1 fuels shown in Figure 4.***

As a first step for planning appropriate blends for future tests of Class 2/3 and Class 1 fuels, it is suggested that Marathon be asked to produce a series of blends with low vapor pressure base gasolines for the purpose of "vapor pressure mapping" only. The suggested matrix would be comprised of two nominal ethanol content levels (75% and 85%), and gasoline vapor pressure levels of 7, 8, 9, 10 and 11 psi. The vapor pressure and actual ethanol content of these blends would be measured, allowing data points from these fuels to be added to Figures 2-4.

Analysis of these plots would make it possible to select the gasoline vapor pressure levels needed to cover the range of samples seen in the CRC survey but not represented by the laboratory blends tested thus far. Based on this analysis, the selected gasoline vapor pressure levels would be used to produce new blends (E0, E15, E55, E60, E68, E75, E83 as before) for flammability testing.

***It should be noted that the blends seen in the CRC survey (obtained from refueling locations) do not represent the "worst case scenario" for what might be present in vehicle fuel tanks. This is because vehicle tanks may contain "out of season" fuel, or fuel that has lost vapor pressure due to "weathering". Thus, it is proposed that extending the flammability testing to fuels blended with low vapor pressure gasoline is an important future direction for establishing the "real world" risks associated with ethanol/gasoline blends.***

# Appendix C: Summary of the Models for the Volatility and Flammability of Ethanol-Gasoline Blends

**Volatility Characteristics of Gasolines**

For a pure compound such as a single-component hydrocarbon, the composition and hence molecular weight of the vapor and liquid phases are constant and identical regardless of how much has evaporated, and the vapor pressure and enthalpy of evaporation are functions only of temperature.

The vapor pressure of pure compounds can be adequately described for most practical purposes by a simple equation such as the classical Clausius-Clapeyron equation, as follows:

$$P_{sat} = C_1 \exp(-C_2 / T) \qquad \text{(C1)}$$

where

$P_{sat}$ = equilibrium saturation pressure
$T$ = absolute temperature
$C_1$ and $C_2$ = constants for any given pure substance

On the other hand, commercial gasolines and other refinery products are mixtures of hundreds of individual pure hydrocarbon compounds. As a result, the compositions of the liquid and vapor phases vary continuously as the fuel evaporates. Light volatile fractions evaporate first, followed progressively by the heavier molecular weight compounds in the fuel.

Modelling real fuels can in principle be done by expressing the vapor pressure of each of the hundreds of components using Equation 1 with the constants applicable for each component, and then combining all components using Raoult's Law for ideal mixtures, namely:

$$P_{fuel\ sat} = \sum_{i=1}^{i=N} X_i P_{i\ sat} \qquad \text{(C2)}$$

where

$P_{fuel\ sat}$ = total vapor pressure of the hydrocarbon blend
$X_i$ = mole fraction of component $i$ in the liquid phase of the blend at equilibrium
$P_{i\ sat}$ = equilibrium saturation pressure of component $i$ alone

In practice this requires the detailed composition of the fuel blend to be known, and the constants $C_1$ and $C_2$ for each component to be available. Equation C2 can then be used to find the vapor pressure of the blend at some given mass fraction evaporated, (say 20%). However, iteration is required because the mole fractions of each compound in the two phases are different from each other and are no longer the same as that of the initial mixture before evaporation occurred. A computer model can be developed on this basis, but the code for such a model tends to be large and relatively slow. More importantly, the exact chemical composition of each blend to be evaluated must be known. The gas chromatograph (GC) data for fuels in the field is often not

available, whereas ASTM distillation data and specific gravity are usually known. Non-ideal mixtures, such as blends of gasoline and ethanol, further complicate the process, and equation C2 is no longer valid for non-ideal blends.

For many practical analyses, a simple and computationally fast model is needed to allow blend volatility to be calculated. It has been shown in various previous publications [9,14,15] that hydrocarbon blends such as gasoline can be modelled quite satisfactorily for many purposes by describing their vapor pressure and other properties using the form of the Clausius-Clapeyron equation but using appropriate polynomial functions instead of the two constants $C_1$ and $C_2$ as follows:

$$P_{sat} = f_1 \exp(-f_2 / T) \qquad \text{(C3)}$$

where

$P_{sat}$ = equilibrium saturation pressure
$T$ = absolute temperature
$f_1$ and $f_2$ = functions of the extent of evaporation defined by $VF$ where
$VF$ = mass fraction of the mixture in the vapor phase

Equation C3 essentially separates the effects of temperature, expressed directly in the exponential term of this Clausius-Clapeyron format, from the extent of evaporation, contained exclusively within the functions $f_1$ and $f_2$. These latter two functions can be expressed as polynomials in the vapor fraction, $VF$. References 14 and 15 showed how the functions can be derived using only the ASTM D86 distillation data for the mixture and its specific gravity. The following is a brief summary.

**Determination of the function $f_2$**

For pure, single component hydrocarbons

$$f_2 = \Delta H / R \qquad \text{(C4)}$$

where
$\Delta H$ = molal enthalpy (J/mol) of evaporation
$R$ = universal gas constant (8.314 J/mol K)

For the multi-component gasoline, the mean value (J/mol) of molal enthalpy for the vapor present at the specified $VF$ is used instead[14]. This mean value can be found by integrating the values at each boiling temperature from $VF$ =0 up to the desired value of $VF$ and averaging. The resulting average $\Delta H$ for the vapor phase of the gasoline is used to calculate the value of $f_{2\,\mathrm{at}}$ at that $VF$ using equation C4.

**Molecular Weight M**

Reference 15 presents a method of estimating the molecular weight of a component boiling at any given temperature on the D86 curve. The overall specific gravity of the gasoline is

required for this calculation. For the present model the value of mean vapor phase molecular weight at any value of *VF* is needed, and can again be found by integrating the values at each boiling temperature from *VF* =0 up to the desired value of *VF* and averaging.

**Summary of the Bridgemann Correlation as used in Reference 14**

Consider an equilibrium mixture of air and gasoline vapor such that the partial pressure of the air plus that of the fuel vapor above the liquid produces a total pressure of 1 atmosphere. Essentially, the Bridgemann technique utilized in the model and described in Reference 14 provides a means of estimating, for any gasoline whose ASTM distillation curve is known, the temperatures at which the air/fuel mass ratio will be 16:1 for mass fractions evaporated, *VF*, varying from 0 (start of evaporation) to 1 (fully evaporated). This transforms the non-equilibrium, volume-based ASTM distillation curve into a curve on which each point corresponds to an equilibrium condition for the air/fuel vapor mixture in which pressure is 1 atmosphere, the air/fuel mass ratio is 16:1 and any value of mass fraction vaporized, *VF*, has a corresponding temperature.

Bridgemann's correlation method for estimating this *VF* /temperature curve can be summarized as follows:

For 0< *VF* <1

$$C_{VF} = 39 + \log_{10}\left[\frac{1-VF}{0.5}\right] \times \sqrt{460S} \qquad \text{(C5)}$$

where

$C_{VF}$ = a constant for that selected value of *VF*

*S*= slope of ASTM distillation curve at a volume % evaporated = 100* *VF* (e.g. for *VF* of 0.5, the slope of the D86 curve at 50% evaporated is used)

The 16:1 temperature for this *VF* is then given by

$$t_{16} = \left[t_{ASTM} - (136.6 - C_{VF})\right]/1.5 \qquad \text{(C6)}$$

where

$t_{16}$ = the temperature (°C) at which this *VF* produces a 16:1 air/vapor mixture at atmospheric pressure

$t_{ASTM}$ = the temperature (°C) of the D86 curve at vol% evaporated =100* *VF*

For *VF* =0

$$C_{VF=0} = 39 - 10\sqrt{S_{ASTM10\%}} \qquad \text{(C7)}$$

$$t_{16} = \left[t_{ASTM10\%} - (136.6 - C_{VF=0})\right]/1.5 \qquad \text{(C8)}$$

where

$t_{ASTM10\%}$ = the 10% evaporated boiling temperature from the D86 data

$S_{ASTM\,10\%}$ = the slope of the D86 curve at 10% evaporated

For $VF = 1$

$$C_{VF=1} = 39 - 10\sqrt{S_{ASTM\,90\%}} \quad \text{(C9)}$$

$$t_{16} = \left[t_{ASTM\,90\%} - (136.6 - C_{VF=1})\right]/1.5 \quad \text{(C10)}$$

where

$t_{ASTM\,90\%}$ = the 90% evaporated boiling temperature from the D86 data

$S_{ASTM\,90\%}$ = the slope of the D86 curve at 90% evaporated

**Determination of the function $f_1$**

With the value of $t_{16}$ known for each value of *VF*, mean vapor phase molecular weight *M* determined using the method as described in reference 15 (as for $\Delta H$, the mean value up to the specified *VF* must be used) and $f_2$ at this *VF* known, the ideal gas law and equation C3 can be used to find the value of $f_1$ for this value of *VF*. See reference 15 for details.

Carrying out all the computations necessary to determine $f_1$ and $f_2$, mean *M* and mean $\Delta H$ of the vapor phase present at that value of *VF* is not trivial. However, once determined, polynomial curves can be fitted to those values and equation C3 can then be easily used in larger models and analyses, such as the determination of flammability. In Phase 2 this version of the gasoline model was updated from earlier Fortran software and set up as an Excel™ spreadsheet so as to allow the coefficients for polynomial functions to be determined for $f_1$, $f_2$ and *M*.

A more sophisticated method for determining *M* and $\Delta H$, was originally published in Reference (9). This involved an iterative approach to estimate the different instantaneous temperatures of liquid and vapor phases during the D86 distillation process for a gasoline. In Phase 3 reported here, the original Fortran program written for that later work was used to derive the functions for each base gasoline of the present study, in an attempt to improve the capability of the gasoline model to predict DVPE. For the gasolines used in this study it performed slightly better; however, the main limitation for this work aimed at ethanol/gasoline blends lies in the method for determining the effects of the non-ideality of these mixtures of polar and non-polar molecules.

**Comments on the Accuracy of the Gasoline Volatility Model**

Vapor pressure is very sensitive to the light ends of the gasoline. It is surprising that a model using only the D86 distillation data and specific gravity performs as well as this one has been shown to do for a wide variety of gasolines. However, its limitations should be kept in mind. Rather extensive software is written to generate the polynomial equations for $f_1$ and $f_2$, mean *M* and mean $\Delta H$ based on D86 and specific gravity inputs. Once the coefficients for those variables are determined the model becomes easy to use. Its main advantage is that detailed GC data is not required. Being based on the distillation curve, it tends to underestimate the effect of light ends which are very important for other properties such as DVPE, but are only coarsely

reflected in the front end of the D86 curve. Minor differences in front end D86 temperatures, or loss of light ends during handling can materially affect the DVPE and the flammability of the fuel vapor.

In Phase 2 of this work, and again in this present study, the model coefficients were generated for the base gasoline from the distillation and specific gravity data. The model was then used to predict DVPE as a test of the accuracy of this part of the blend model. To better reflect the volatility of the base gasoline, a constant multiplier was applied to the predicted vapor pressure in equation C3, so as to align the model predictions under DVPE conditions (4:1 vapor/liquid volume ratio, and T=100°F) to the actual measured DVPE. This factor was then used consistently when incorporating the gasoline model into the larger gasoline/ethanol blend model, assuming that vapor pressure at any temperature would be equally affected. This is not strictly correct, but was the only method possible within the limited resources available for modelling in this study.

Despite the drastic simplification of using equation C3 to represent the complex evaporative behaviour of a hydrocarbon mixture, experimental measurements [19] have shown that this method gave quite satisfactory predictions of hydrocarbon vapor pressure over a range of temperatures from 0ºC to 40ºC. Subsequent measurements to temperatures as low as -40ºC showed that the method gave measured vapor pressures within experimental error over the entire range from -40ºC to +40ºC that is of interest for ambient conditions in North America [20]. In the present study, the gasoline model as used here predicted DVPE for the base gasolines within 4-11% of the measured values.

**Volatility Characteristics of Ethanol**

The ethanol vapor pressure is modelled using the Antoine Equation.

$$\log_{10} P_{sat\ ethanol} = A - B/(C + T) \qquad \text{(C11)}$$

The values of the coefficients used for ethanol were taken from Wilhoit and Zwolinski [16].

**Modelling Gasoline/Alcohol Blends**

The approach [4] was to treat any blend of an alcohol with a hydrocarbon as if it were a pseudo-binary mixture, that is, a mixture of a single hydrocarbon component represented by the model described above (Equation C3), and the ethanol, represented by the Antoine equation.

Mixtures of hydrocarbons, such as gasoline, are made up of non-polar molecules and conform to Raoult's Law quite well. However, alcohols consist of strongly polar molecules. This leads to large deviations from the behaviour predicted by Raoult's Law when alcohols are mixed with hydrocarbons. Thus Raoult's Law (Equation C1) does not apply as written and a modification to account for the non-ideality of the resulting alcohol/hydrocarbon mixture must be used. By convention, this has the following form for a blend such as ethanol and gasoline (designated below in the form EX where X is the volume% of ethanol in the blend):

$$P_{EX} = \gamma_g X_g P_{gsat} + \gamma_{EtOH} X_{EtOH} P_{EtOHsat} \quad \text{(C12)}$$

where

| | |
|---|---|
| $P_{EX}$ | = equilibrium saturation pressure of the EX mixture |
| $\gamma_g$ | = activity coefficient for gasoline in the blend |
| $\gamma_{EtOH}$ | = activity coefficient for ethanol in the blend |
| $X_g$ | = mole fraction of gasoline in the liquid phase |
| $X_{EtOH}$ | = mole fraction of ethanol in the liquid phase |
| $P_{gsat}$ | = saturated vapor pressure of the gasoline |
| $P_{EtOHsat}$ | = saturated vapor pressure of the ethanol |
| $X$ | = percent ethanol in the blend e.g. E55 contains 55% ethanol |

Note that $X_g$ and $X_{EtOH}$ as well as $P_{gsat}$ vary continuously as the fuel evaporates. Furthermore, at any point in the evaporation process, when the overall mass fraction vaporized is some given value between 0 and 1, say 0.4, the mass fraction of gasoline vaporized is different from the mass fraction of ethanol vaporized, and neither is equal to the overall value of 0.4 in this example. Since the mole fractions of each of the two components in the liquid phase are not known *a priori* for any given overall value of mass fraction vaporized, iteration is required to determine the vapor pressure and other volatility characteristics needed, such as the molecular weight of the vapor phase. This latter is needed, as well as the partial pressures of the two components, as part of the determination of vapor phase flammability.

In order to model the vaporization behaviour of such a blend and the resulting flammability of the vapor phase above the liquid in a fuel tank, representative values for the two activity coefficients must be determined for use in this binary model. In this phase of the work, the Margules two-suffix equation was used, in the form described in Reference 4.

This has the form:

$$\gamma_{gasoline} = e^{\frac{AX_{ethanol}^2}{T}} \quad \text{(C13)}$$

$$\gamma_{ethanol} = e^{\frac{AX_{gasoline}^2}{T}} \quad \text{(C14)}$$

where

$\gamma_{gasoline}$ = activity coefficient of the gasoline
$\gamma_{ethanol}$ = activity coefficient of the ethanol
$A$ = the Margules 'constant'
$X_{gasoline}$ = mole fraction of gasoline remaining in the liquid at equilibrium
$X_{ethanol}$ = mole fraction of ethanol remaining in the liquid at equilibrium

The following expression was used for the value of A, as presented in Reference (4):

$$A = C_1 + C_2 \times \left( \frac{X_{ethanol}}{1 - X_{ethanol}} \right) \quad \text{(C15)}$$

This skews the non-ideality effects so they are no longer symmetrical between the two fuels, but rather have a stronger impact on gasoline vapor pressure in the high ethanol blends than in the lower ethanol blends. This had previously given better results in modelling the data available on various methanol and ethanol blends. In that original work [4], the measured vapor pressures of various blends of methanol and ethanol were used to derive values of $C_1$ and $C_2$ of 600 and 5.25, respectively. These were values that gave reasonable results for a broad range of methanol and ethanol blends with gasoline.

In Phase 2 of the present study, only high alcohol blends had sufficient data on the base gasoline to allow use of the model. Since measured DVPE was available for those high ethanol blends, those values were used to estimate a value of A so as to make the predicted DVPE match the measured values better than occurred when the earlier published values [4] were used in the model. It was found that a good fit to the DVPE values of the high ethanol blends studied in Phase 2 could be obtained using values for $C_1$ and $C_2$ of 600 and -2.27, respectively. These values of the two constants were then used in the model to predict the low temperature flammability of the blends under study in Phase 2, with reasonable success.

Since DVPE for all the blends used in the present phase of the work was provided, the values of A for each blend could be determined for DVPE conditions (100 °F). Using these values of A essentially matched the model prediction to the measured DVPE of each individual ethanol/gasoline blend. A curve was fitted to these discrete values of A so that any other blend could be studied. All predictions presented in this report used those values of A, derived at DVPE conditions but used for low temperature predictions.

**Modelling the Flammability Characteristics of Gasoline/Alcohol Blends**

The volatility model allows the composition of the vapor phase to be determined at any given temperature and fuel fill level in a fuel tank. Using published flammability data for the gasoline and ethanol [10], combined using the LeChatelier mixing rule, then allows the resulting flammability of the vapor phase to be determined. Details of the calculation methods used are provided in Reference 12.