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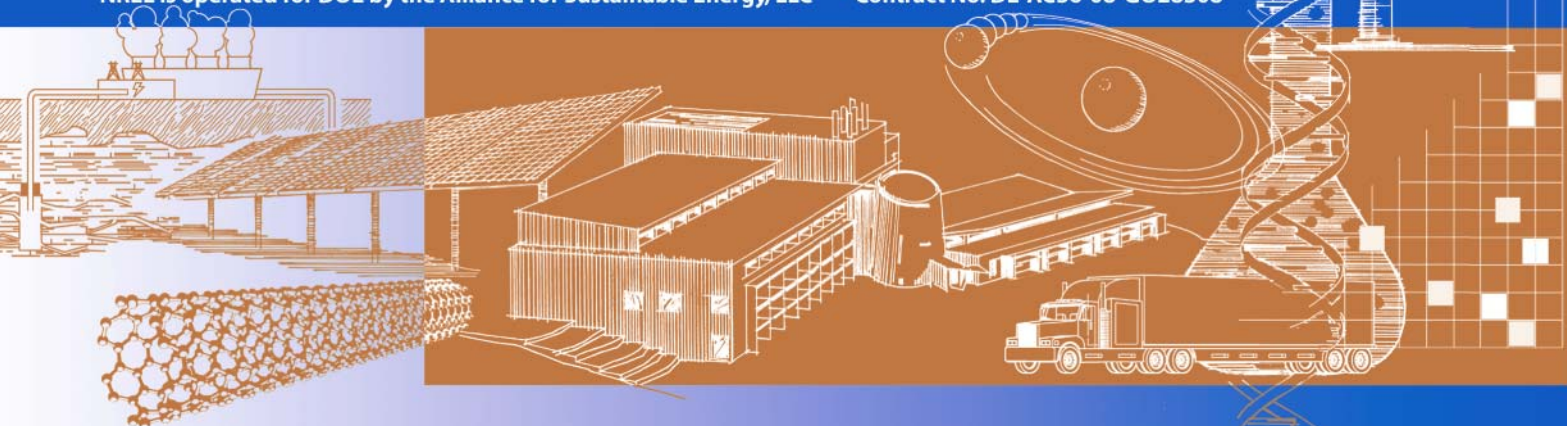
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An Experimental and Modeling Study of the Flammability of Fuel Tank Headspace Vapors from High Ethanol Content Fuels

D. Gardiner, M. Bardon, and G. Pucher
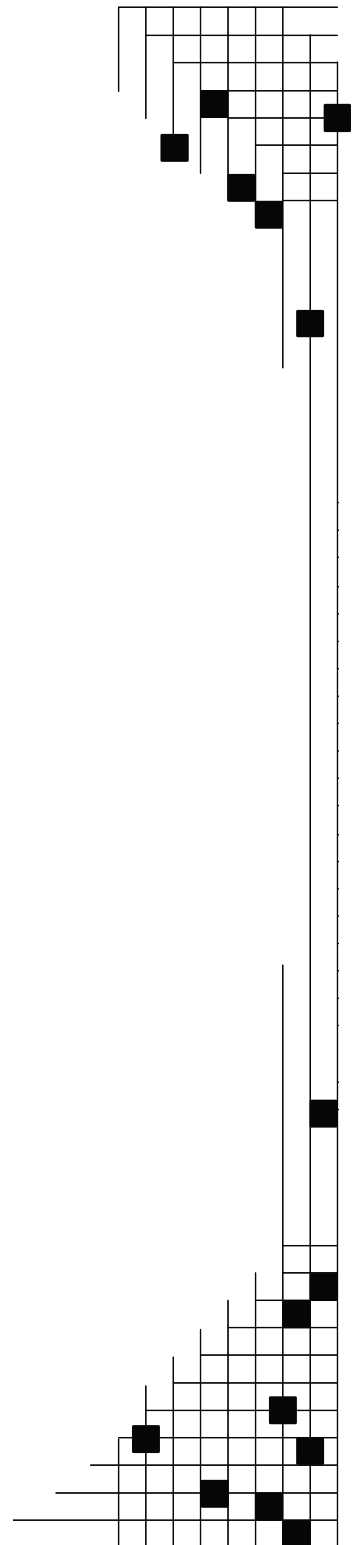*Nexum Research Corporation*
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Executive Summary

Background

Gasolines and alcohol/gasoline blends are mixtures of hundreds of individual pure compounds. An important result is that the composition of the headspace vapors in a fuel tank depends on both ambient temperature and how much liquid fuel is left in the tank. Light volatile fractions evaporate first, followed progressively by the heavier molecular weight compounds in the fuel. The compositions of liquid and vapor phases vary continuously as the fuel evaporates. Air is also present in a vented or pressure-equilibrated tank, mixed with the fuel vapor in the headspace.

Gasoline is so volatile at most ambient temperatures that the headspace vapors in the 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. Similarly, when refueling a nearly empty tank at very cold temperatures, the headspace vapors are expelled as a plume of fuel vapor and air as the liquid enters the tank, producing a flammable plume. An ignition source within that plume could lead to a flame travelling back down into the tank and causing an explosion. 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. Suitable precautions to deal with flammable vapors would therefore be necessary to avoid fires and explosions if pure ethanol were used as a fuel.

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. 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 to ensure that consumers and fuel handlers can be protected from significant unexpected risks or appropriately advised if special precautions are needed. Depending on the level of increased risk, if any, it might also be appropriate for auto manufacturers and fuel suppliers to implement modifications to mitigate hazards in vehicles or fuel-handling equipment.

Objectives of the Work Reported

The tests and mathematical modeling carried out in this project were aimed at helping quantify differences between candidate E85 (approximately 85% ethanol, 15% gasoline) blends and gasolines with respect to flammability hazards related to fuel tanks and refueling processes. The following were specific tasks:

1. Develop the experimental apparatus and testing protocols needed to evaluate the flammability of fuel tank headspace vapors under representative, small-scale laboratory conditions.

2. Test a series of fuel blends supplied for the work and selected as representative candidate commercial E85 fuel blends or as gasolines and denatured ethanol to be used for comparison.

3. Analyze the test results and draw conclusions relevant to the flammability observed.

4. Develop mathematical models for the fuel tank tests based on existing simulation techniques previously shown to have been successful for alcohol/gasoline blends. Use the models to predict flammability of the fuels tested in the experimental work, and evaluate the utility of such modeling to assess fuel tank combustion hazard scenarios.

5. Carry out preliminary analysis of the flammability risks associated with vapor/air plumes emitted from fuel tanks during refueling.

Principal Results

1. A test process using multiple small, closed test chambers fitted with spark plugs and pressure transducers was developed. It was found to be an effective means of comparing the flammability of numerous fuel samples in a relatively short period. All tests reported corresponded to a tank having 5% of its volume filled with liquid fuel and the remainder with fuel vapor and air at ambient conditions. By attempting to ignite the mixture at different test temperatures varying from room temperature to as low as -30ºC (-22ºF), the range of temperatures for which the headspace vapor was flammable was determined for all 10 test fuels.

2. Seven E85 fuel blends, two types of gasoline, and denatured ethanol were compared. Headspace vapors for the two gasolines became flammable when the temperature dropped to approximately -19ºC (-2ºF) and -25ºC (-13ºF) or lower. The E85 blends, on the other hand, produced flammable vapors at temperatures below values ranging from -2ºC (28ºF) to -22ºC (-8ºF). Denatured ethanol was found to be flammable at room temperature and all temperatures down to approximately -6ºC (22ºF).

3. Three E85 fuels that were blends of denatured ethanol and natural gasoline had flammability behavior similar to the summer gasoline tested.

4. The limit temperature for flammability of the E85 and gasoline test fuels often corresponded to the ranking to be expected from their dry vapor pressure equivalent (DVPE, i.e., vapor pressure at 100ºF in the ASTM standard apparatus used for that test). However, there were exceptions. DVPE alone did not predict the ranking of the fuels correctly in all cases. A more volatile fuel at 38ºC (100ºF) is not necessarily more volatile at -29ºC (-20ºF).

5. In general, E85 is flammable at low temperatures, whereas denatured ethanol is flammable at warmer temperatures. If both types of fuels are stored in separate tanks at the same location, there is a wide range of ambient temperatures for which one or both of the tanks' headspace vapors will be flammable. This is relevant to the issue of splash blending of ethanol and gasoline at refueling stations and the mixing of ethanol with gasoline by consumers themselves.

6. The mathematical modeling confirmed that DVPE by itself does not reliably rank the low-temperature flammability hazards of fuel tank headspace vapors when comparing conventional gasolines with alcohol blends or even comparing among alcohol blends. Differences in gasoline distillation characteristics, particularly as they represent the more volatile light ends, must be accounted for to obtain reliable comparisons.

7. Existing mathematical models for gasoline primers can be used for some alcohol blend comparisons, provided that both DVPE and distillation data of the model used are reasonable approximations of the actual primer's characteristics. Matching DVPE alone is insufficient.

8. At any given temperature, fuels that are more volatile produce longer plumes during refueling and represent greater hazards.

9. For the more dangerous situation of a flammable plume adjacent to flammable tank headspace vapors, the size and location of the plume is important. Some cases might have plume lengths of such a size as to present a serious hazard of ignition and subsequent tank explosion, whereas others might have plumes short enough to preclude ignition by typical ignition sources found in the immediate vicinity of the refueling equipment. This aspect was not assessed in detail in this project.

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I. Experimental Study

1. 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 present study, the objective was to determine the flammability of the headspace vapors from different fuels. 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.

2. Apparatus and Test Procedures

2.1 Flammability Test Chambers

Nine 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 chambers were based on modified cast-aluminum electrical junction boxes. A lid was fabricated from

aluminum plate to mount a spark plug and two ball valves. The interior volume of the chambers was 296 mL.
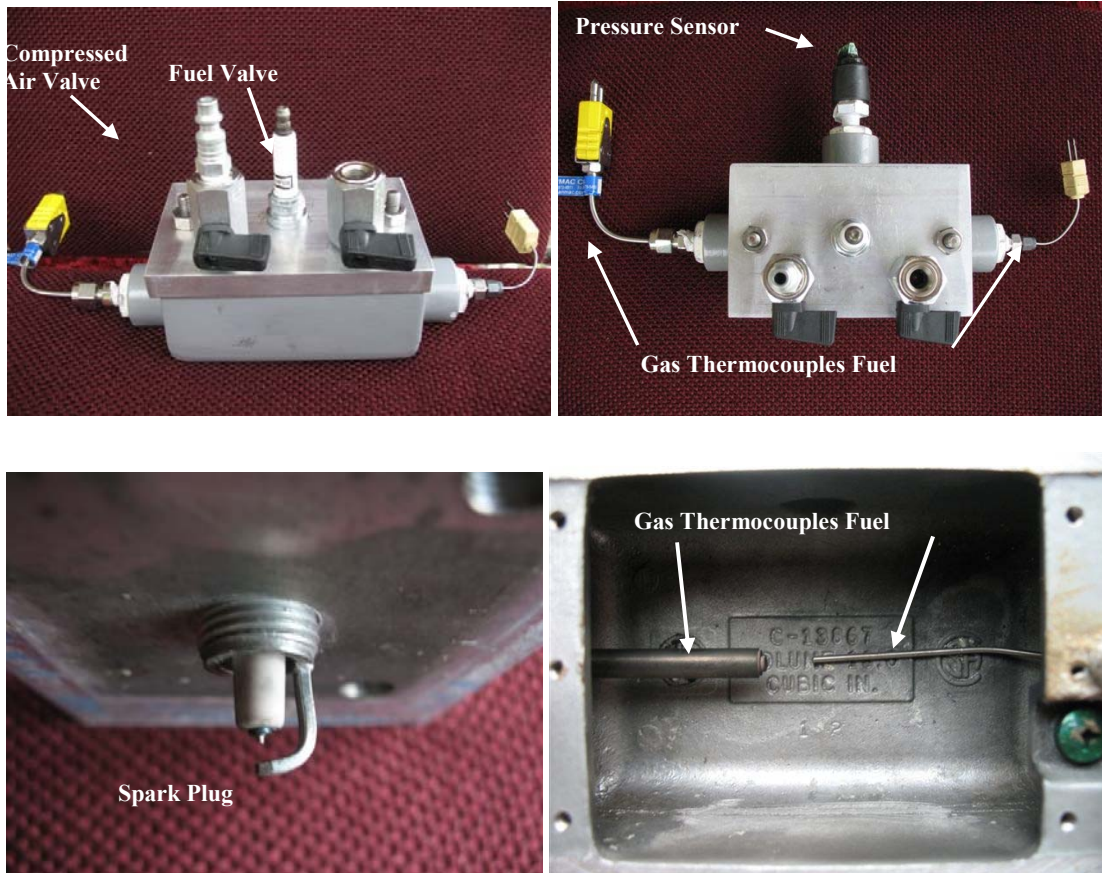
Figure 1. Flammability Test Chamber

The existing pipe thread fittings in each box were used to install the pressure sensor and thermocouples. 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 behavior 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 signals from the pressure sensor, the thermocouples, and the trigger signal from the ignition system (which showed the timing of the spark) were recorded with a Daqbook 100 16-bit data acquisition system. Signal conditioning modules that were part of this system were used for the thermocouple voltages (providing ice point compensation, amplification, and linearization) and to provide differential amplification for the pressure sensor output voltage.

Each chamber was equipped with ball valves, one of which was connected to a compressed-air fitting. The valve without the fitting was used when fuel was loaded into the chamber with a syringe. The chamber was purged between tests by blowing compressed air through the other valve while the fuel valve was open to vent the purged fuel and air. It was then leak tested by closing the fuel valve and pressurizing the chamber to 550 kPa (80 psi).

2.2   Ignition Apparatus

The ignition source for the experiments was composed of an automotive spark plug and a laboratory programmable ignition system. 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 spark plug had an internal resistor to reduce electromagnetic interference (like most modern spark plugs) and was used in combination with a resistive interference suppression ignition cable. These measures made it possible to record noise-free pressure and thermocouple signals.

The programmable ignition system (Figure 2) was a proprietary design produced by Nexum Research Corp. The system uses current sensing and closed-loop control to produce repeatable spark-current waveforms at current levels and durations programmed by the user. The details of the spark characteristics used for the experiments are discussed in the results section of this report. The ignition system was located outside the cold chamber, and the ignition cables from the test chambers were extended through the chamber wall to the outside of the chamber near the ignition coil. The appropriate cable for the chamber being tested was connected to the coil prior to the ignition attempt.
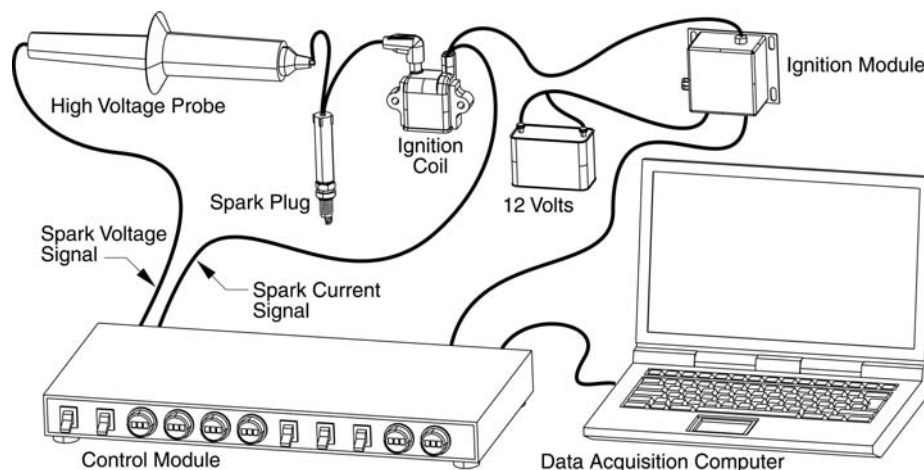
Figure 2. Programmable Ignition System

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2.3   Test Procedure

The experiments were carried out in a refrigerated engine testing cell. During most of the experiments, all nine test chambers were chilled together. During some tests, the same type of fuel was used in each chamber. In other cases, a different fuel was used in each chamber, or three fuels were tested (three chambers for each fuel). 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.* [1], 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.

Before each test, fuel at room temperature was extracted with a syringe from one of the 20-L 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.   Results and Discussion

3.1   Delivered Ignition Energy

An example of the current waveform of the spark is shown in Figure 3. This spark required almost 1 J of stored energy from the capacitor that was discharged through the primary winding of the ignition coil. This is an order of magnitude higher than a typical automotive ignition system. However, only a fraction of this energy was delivered across the spark plug gap to ignite the mixture owing to various losses in the ignition circuit.
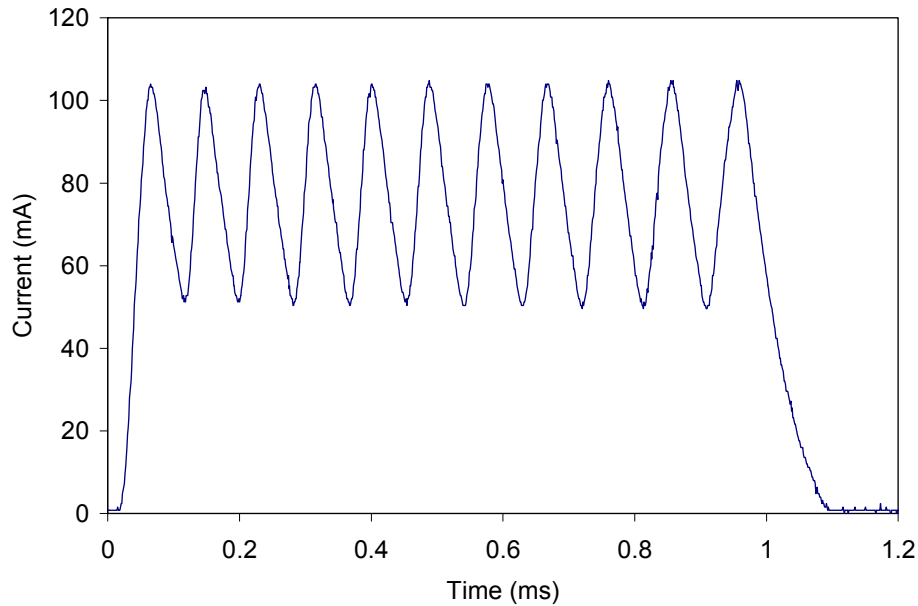
Figure 3. Example of the Current Waveform of the Spark

Resistive losses in the coil windings, ignition cable, and spark plug resistor are proportional to the square of the spark current (I^2R losses), thus sparks in which the current is maintained at a relatively high level throughout the discharge period are inherently inefficient. Furthermore, spark discharges at atmospheric pressure deliver much less energy across the spark plug gap than do discharges at elevated pressures (such as in a running engine [2]) because the effective resistance of the gas between the electrodes is low compared with the external resistance of the ignition circuit.

In the present study, the ignition energy delivered to the spark gap was calculated based on measurements of the spark current and voltage. The spark current measurement was provided by the programmable ignition system, which uses a current-sensing resistor in the current loop from the secondary winding of the ignition coil. The spark voltage was measured using a Tektronix 6015 1000:1 high-voltage probe attached to the spark plug terminal. The voltage and current values were recorded with a Tektronix TDS 2014 oscilloscope and transferred to a PC for analysis.

The delivered energy was calculated as the integral of the spark power. Because the measured voltage included the voltage drop across the spark plug resistor, the power dissipated in the resistor (I^2R) was subtracted from the total power so that only the power dissipated between the electrodes was included in the calculation.

Spark voltage and current measurements were made with a spark plug installed in a test chamber at atmospheric pressure and without fuel. The apparatus was installed in the cold chamber, and experiments were carried out at temperatures ranging from +18°C to -20°C. The results of the energy calculations are shown in Figure 4.

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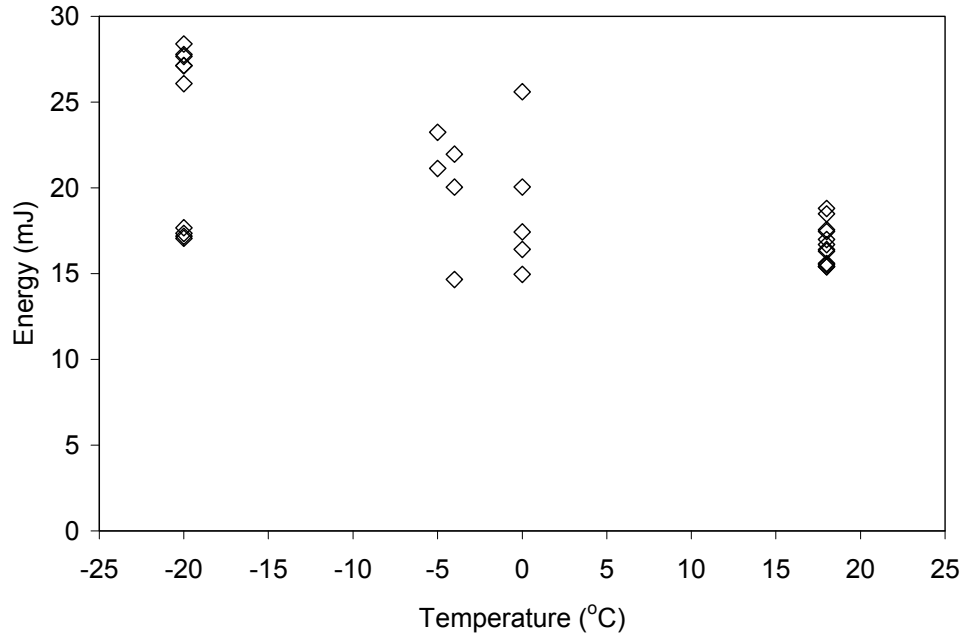
Figure 4. Effect of Ambient Temperature on Delivered Spark Energy

The delivered ignition energy was 15–20 mJ at room temperature but showed a greater variation between sparks as the temperature became lower. In some cases, energy levels greater than 25 mJ were obtained. This is consistent with the higher gas density at lower temperatures.

The ignition energy provided in this study was greater than would be delivered by a standard automotive system at atmospheric pressure [2], and such systems are commonly used for determining the explosive limits of gases and vapors [3]. Thus, it was concluded that the ignition system used in the present study was more than adequate to ignite any fuel-air mixtures that were actually flammable (i.e., capable of flame propagation after ignition).

3.2   Pressure and Temperature Measurements with Denatured Ethanol at Room Temperature

Figures 5–7 show results from tests in which all nine chambers were loaded (5% fill level) with denatured ethanol and ignited at room temperature. As discussed further in this report, denatured ethanol was flammable at this temperature and could be ignited with 100% reliability. These figures and the following discussion are presented to illustrate the raw measurements used to produce the upcoming flammability plots for the test fuels.
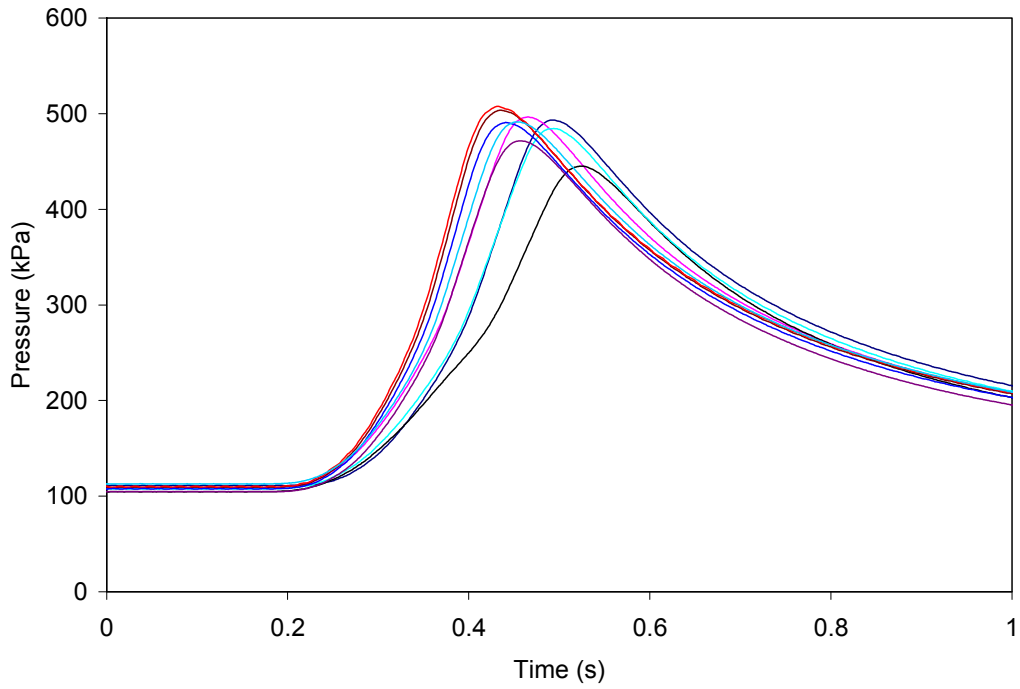
Figure 5. Pressure Rise during Combustion of Denatured Ethanol at 18°C
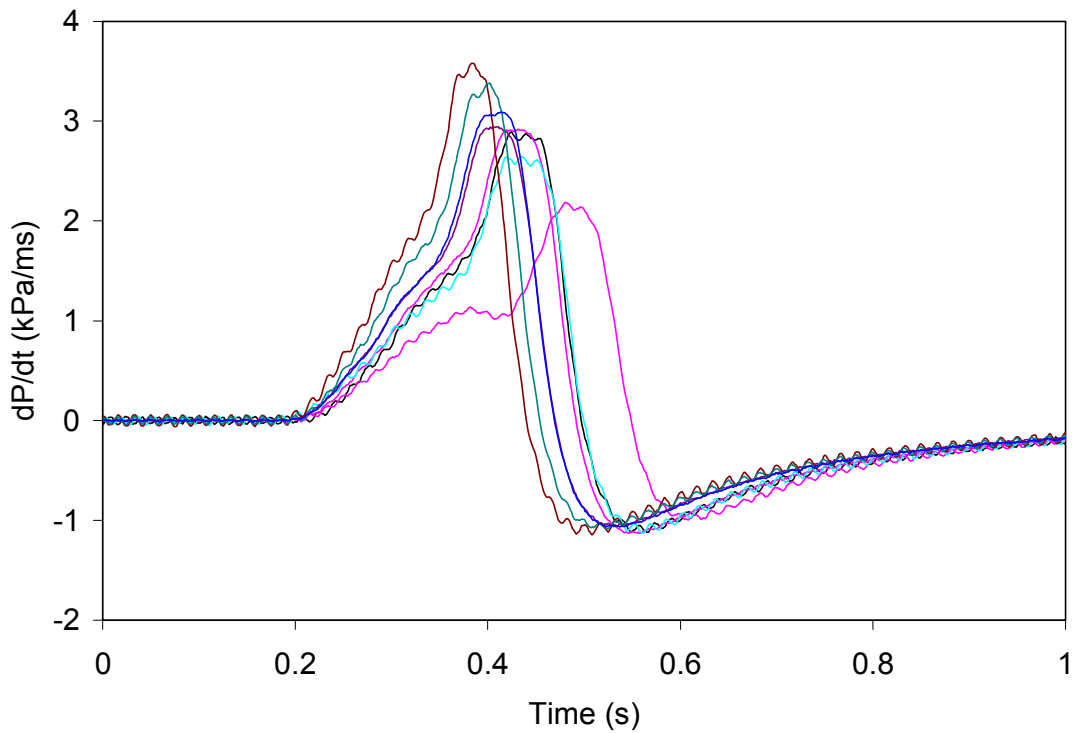
Figure 6. Rate of Pressure Rise during Combustion of Denatured Ethanol at 18°C
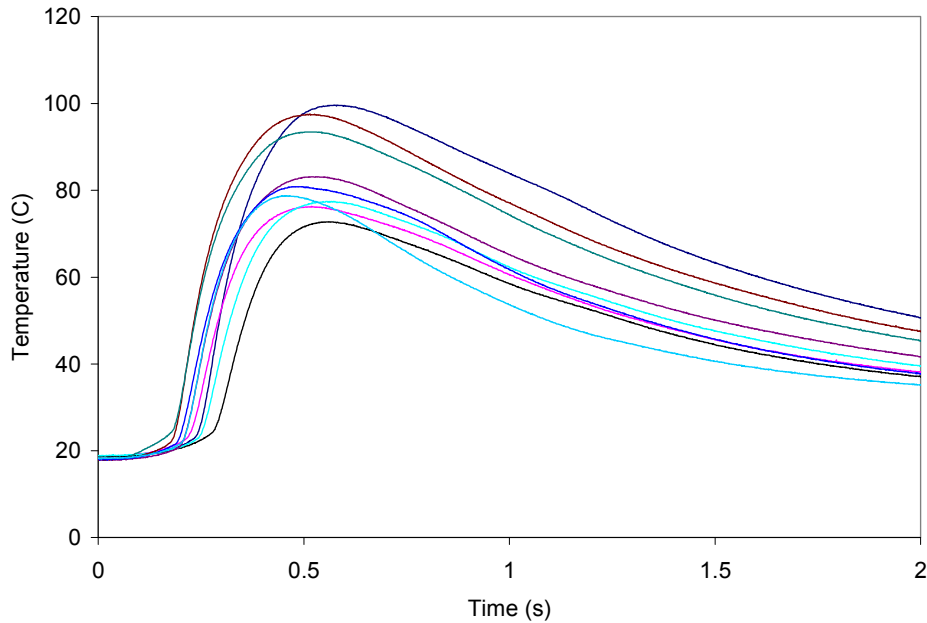
Figure 7. Temperature Rise during Combustion of Denatured Ethanol at 18°C

Figure 5 shows overplots of the absolute pressure in the chambers following ignition. Such pressure records were used to generate the maximum pressure rise data (p_{max}-p_{min}) for each fuel. Those data were later used to determine whether the fuel was flammable at a given temperature.

The peak pressure levels were similar for these tests under identical conditions. However, there were greater differences in the details of the pressure-time history, as some examples took longer than others to reach a given pressure level. These differences are accentuated in plots showing the rate of pressure rise in Figure 6. These curves were obtained by differentiation of the pressure plots. As discussed earlier, the rate of pressure rise provides a relative indication of the burning rate of the fuel-air mixture in the chamber.

Figure 7 shows overplots of the temperature signal from the fast-response gas temperature thermocouple in the chamber. Unlike the pressure signal, the temperature signal is a point measurement that is sensitive to the location of the thermocouple junction. Consequently, the thermocouple signal is affected by the direction of the flame movement so that similar burning rates might produce different temperature/time profiles. Because of this, the gas temperature signals were less consistent than the pressure signals; therefore, the pressure signals were used for all the remaining analyses.

3.3 Pressure Rise and Rate of Pressure Rise Results for the Test Fuels at Different Ambient Temperatures

In the following analysis, the test fuels have been divided into two groups to improve the clarity of the graphs. The first group consists of four fuels (designated E85G, E85R, E85W, and E85Y) that were originally blended for a vehicle study [4]. These fuels all contained volume percentages of ethanol approaching 85% (80.7%–82.3%) and contained different grades of CARBOB base gasoline or pump gasoline as the main blending component. These fuels are

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referred to as "gasoline E85 blends" in the remainder of the report. In addition, isopentane and toluene were added to some fuels. In essence, these were "near" E85 (approximately 85% ethanol, 15% gasoline) fuels in which custom tailoring of the composition of blended hydrocarbons was used to obtain the desired volatility characteristics.

The second group of three fuels (E85A, E85B, and E85C) were all blends containing only denatured ethanol and natural gasoline (natural gas condensate). Thus, these fuels are referred to as "natural gasoline E85 blends" in the remainder of the report. The ethanol volume percentage of these fuels ranged from 69.4% to 79.1%. The desired volatility was achieved by varying the ratio of ethanol to natural gasoline such that the most volatile blend (E85C at 69.4% ethanol) had substantially lower ethanol content than the gasoline blends in the first group.

Each graph also shows the results for a reference gasoline (used in the Chevron study) and pure natural gasoline. The reference gasoline had summer-grade volatility characteristics, whereas the natural gasoline (which is not sold commercially as a vehicle fuel) had greater volatility comparable to commercial winter-grade gasoline blends. Thus, these fuels represented the two extremes (in terms of volatility) that could exist for gasoline.

The pressure rise results for the gasoline E85 blends are shown in Figure 8. Values of zero indicate cases in which the vapor failed to ignite. The results were clearly binomial in nature, as all the experimental results were either above 680 kPa or below 100 kPa. It is proposed that the upper values represent cases of complete or substantially complete flame propagation. The vapor was, therefore, flammable in these cases. The non-zero lower values are believed to represent cases of partial flame propagation. In these cases, the vapor could be ignited by the high-energy ignition system but was not, by this definition, flammable.
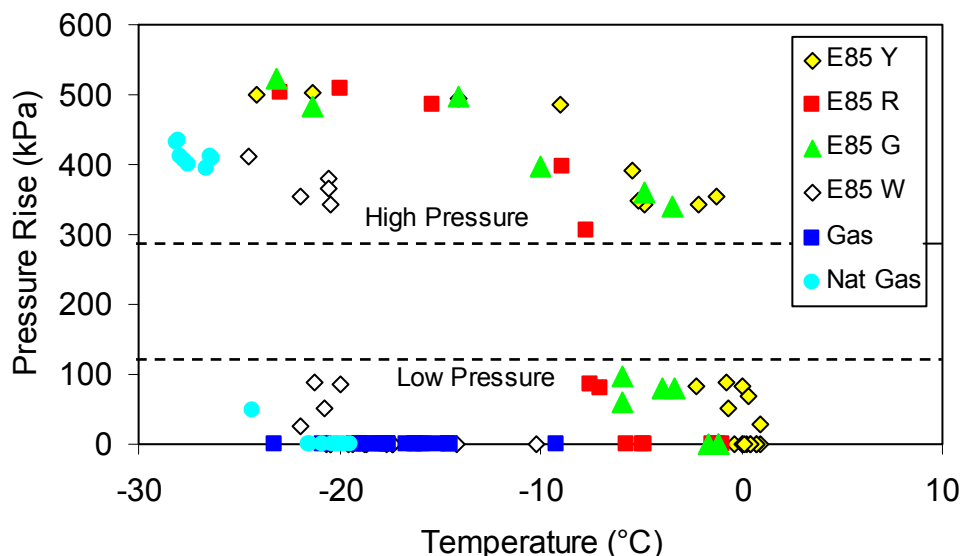
Figure 8. Pressure Rise Comparison for Gasoline E85 Blends

Further evidence that there were cases of partial flame propagation can be seen in the rate of pressure rise results of Figure 9. For the cases in the high-pressure group, the rate of pressure rise fell with increasing temperature, and this effect was greater than the effect of temperature on the

peak pressure rise. The results corresponding to those giving low peak pressures are identified on the graph. These cases resulted in rates of pressure rise less than 1 kPa/ms.
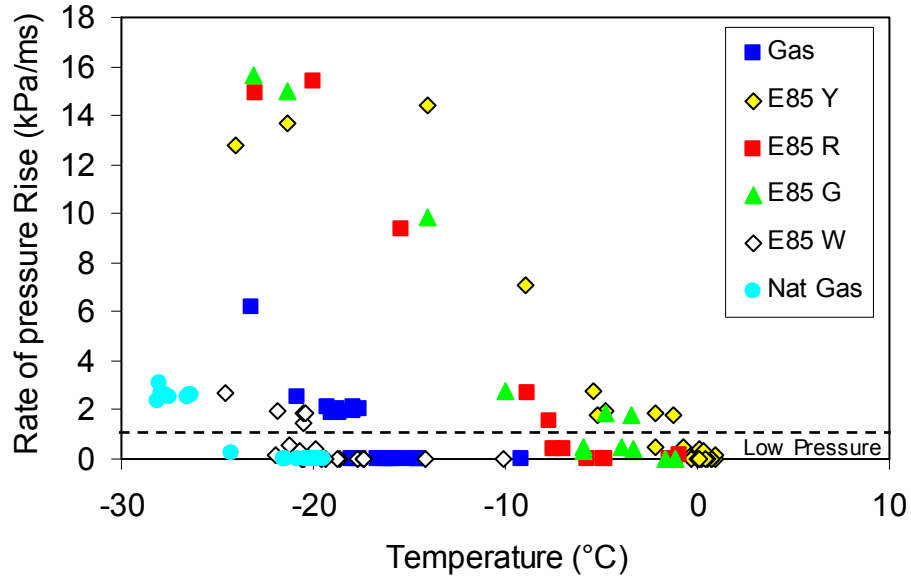
Figure 9. Rate of Pressure Rise Comparison (Gasoline E85 Blends)

Similar behavior can be seen in the results for the natural gasoline blends, shown in Figures 10 and 11. The binomial nature of the results was more pronounced for these fuels.
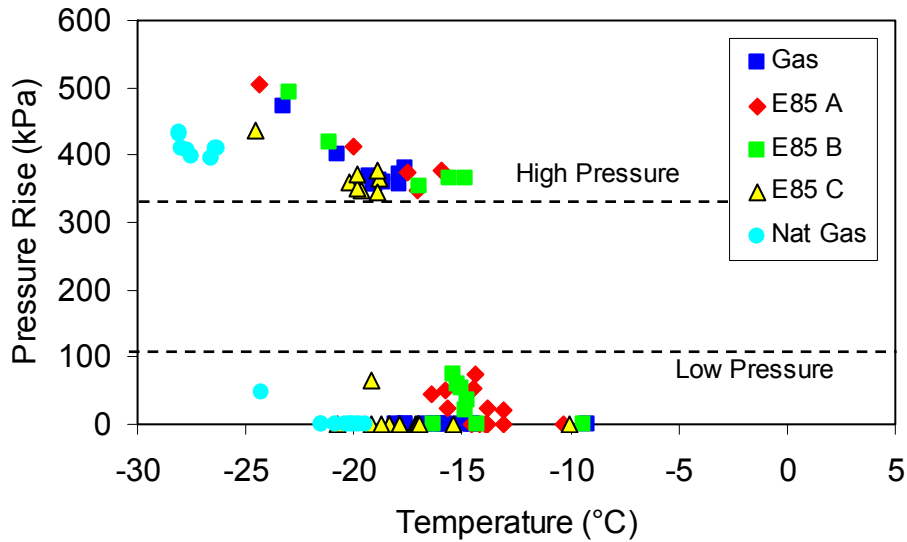
Figure 10. Pressure Rise Comparison for Natural Gasoline E85 Blends
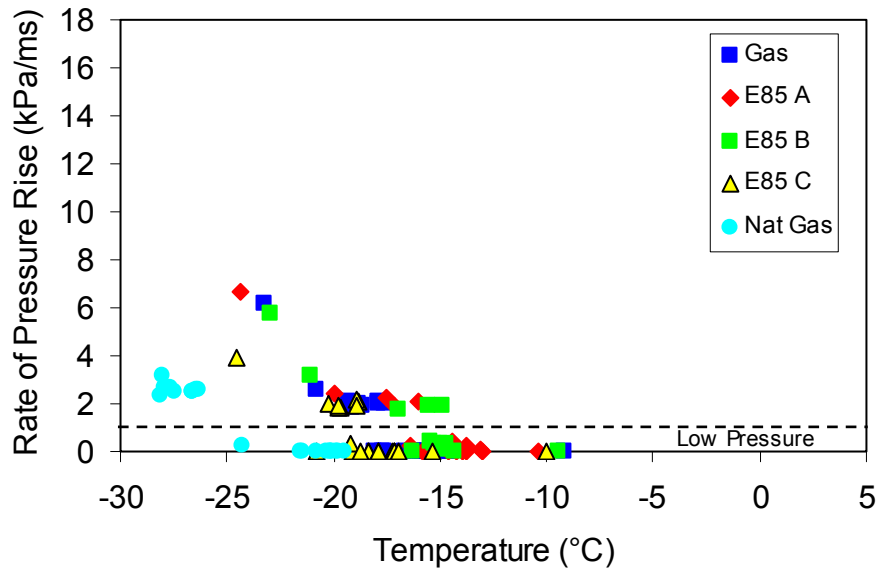
Figure 11. Rate of Pressure Rise Comparison for Natural Gasoline E85 Blends

Returning to Figure 8, three of the four gasoline E85 blends (E85G, E85R, and E85Y) were flammable at substantially higher temperatures than the reference summer-volatility gasoline. The exception was the E85W fuel, which was blended with winter-volatility gasoline and isopentane (see Appendix A). This fuel gave results midway between those of the summer-volatility gasoline and the high-volatility, natural gasoline. The vapor pressure of this fuel (58.8 kPa dry vapor pressure equivalent [DVPE]) was slightly higher than that of the summer gasoline (53 kPa DVPE) but much lower than that of the natural gasoline (81.7 kPa DVPE).

The rate of pressure rise results in Figure 9 show that, for cases in which all the fuels were flammable (circa -20°C), the peak rates of pressure rise were much higher with the E85G, E85R, and E85Y gasoline E85 fuels. In practice, this would represent a risk of a more destructive incident (i.e., a more violent explosion) if the vapors were ignited. On the other hand, the peak pressure rise rates for E85W were no higher than those of the test gasoline blends.

Referring to Figure 10, the peak pressure rise results at a given temperature for the natural gasoline E85 fuels were similar to those for the summer-volatility gasoline. The rate of pressure rise results in Figure 11 were similar as well. Thus, it is likely that these E85 fuels would not pose fire and explosion risks substantially greater than those of a summer-volatility gasoline in use below its intended ambient temperature range.

The results in Figures 8–11 give a qualitative indication of the relative flammability of the different fuel blends. For quantitative comparisons, it was necessary to derive a single value representing the upper flammability limit temperature for each fuel. This was accomplished via statistical analysis of the peak pressure rise data using a PROBIT technique [5]. The use of this digital technique was justified by the binomial nature of the data.

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

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(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 temperature at which there was a 50% probability (at 95% confidence) of a high-pressure event was determined. This temperature was used to define the upper flammability limit of the fuel. An example of this process for one of the fuels is shown in Figure 12. The analysis also provided the standard deviation for the limit temperature. This value was used, along with the errors inherent in the experimental temperature measurements, to calculate error bars for the limit values.
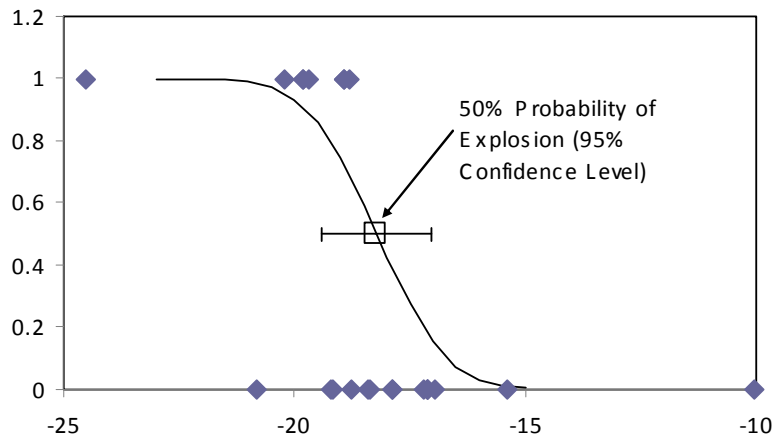
Figure 12. Digital Curve Fit to Establish 50% Flammability Limit Temperature

The results of the upper flammability limit analysis are plotted versus the vapor pressure of the fuels in Figure 13. The limit temperature was strongly related to the DVPE, but vapor pressure alone would not correctly predict the ranking of the fuels in all cases. Natural gasoline blends E85A and E85B had limit temperatures only slightly higher than the summer-volatility gasoline, but their DVPE values were higher than that of the gasoline.
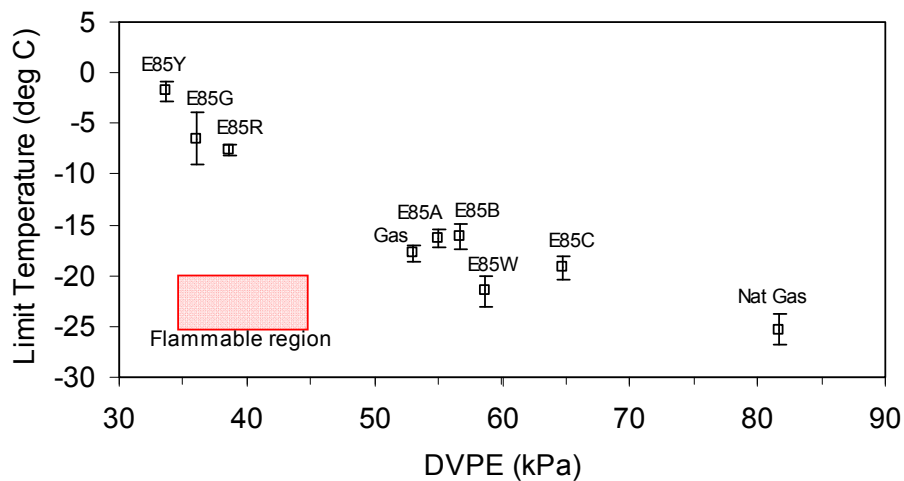
Figure 13. Upper Flammability Limit as a Function of Vapor Pressure for E85 Fuels and Reference Gasoline Blends

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Only two of the E85 fuels (E85C and E85W) had limit temperatures lower than the summer-volatility gasoline. It is interesting to compare how this was achieved in each case. The natural gasoline blend E85C contained only 69.4% ethanol and had a DVPE value more than 16 kPa higher than the gasoline. This gave a limit temperature about 1.5°C lower than the gasoline.

E85W had an ethanol content of 81.4%. The remainder of this fuel was high-volatility commercial gasoline (94.8 kPa DVPE) and crude isopentane. E85W had a DVPE value only 5.9 kPa greater than the summer-volatility gasoline, but its limit temperature was lower by almost 4°C. Thus, this fuel was noteworthy in its potential to provide good safety margins for flammability while maintaining high ethanol content and not requiring excessively high vapor pressure.

The DVPE values for E85W that were measured after the conclusion of the experiments (and used on Figure 13) were virtually identical to those originally provided by the source of the fuel. This might suggest that this fuel was not highly sensitive to volatility loss ("weathering") during storage or transfers between containers.

3.4   Lower Flammability Limit of Denatured Ethanol

As discussed earlier, no upper flammability limit was established for the denatured ethanol evaluated in the study. This fuel was flammable at room temperature, and no tests were conducted at elevated temperatures. Instead, the denatured ethanol approached its lower (lean) flammability limit as the ambient temperature was lowered and eventually would not ignite if it was too cold.

Figures 14 and 15 show the results for the peak pressure rise and rate of pressure rise for the flammability experiments with denatured ethanol. In Figure 15, the rate of pressure rise was substantially below the maximum values when the ambient temperature approached 20°C. This indicates that this fuel was nearing the upper flammability limit at this temperature.
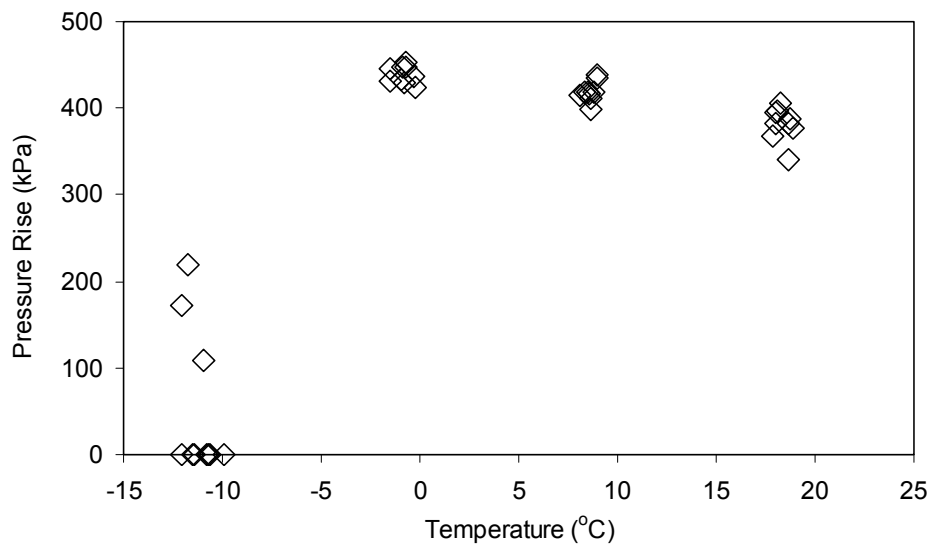
Figure 14. Pressure Rise Results for Denatured Ethanol

13
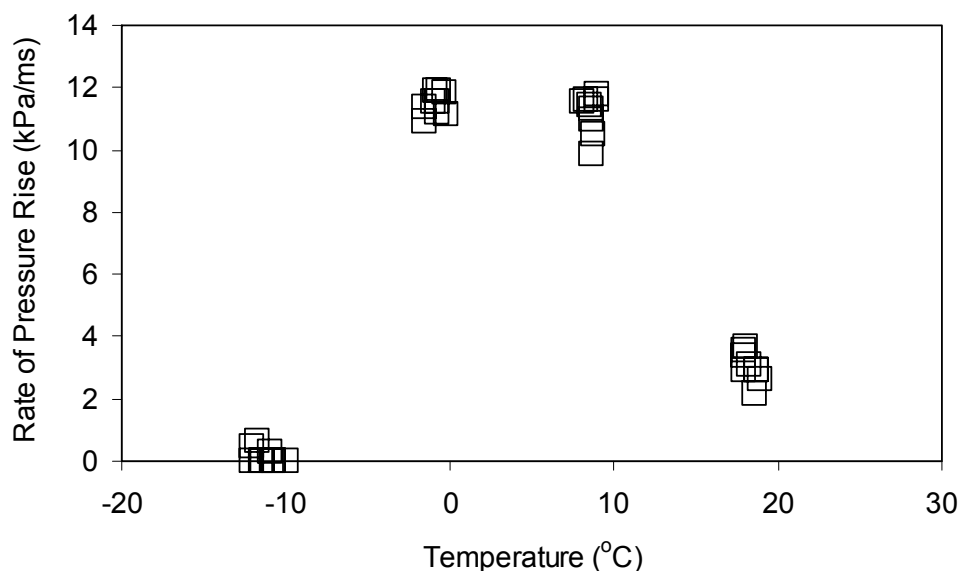
Figure 15. Rate of Pressure Rise Results for Denatured Ethanol

If E85 is blended at the refinery or fuel supply facility, the public would not be exposed to denatured ethanol alone at service stations. However, one possible scenario for the use of E85 fuels involves blending ethanol and gasoline at the service station pump, rather than delivering pre-blended E85 to the service station. In a pump-blending approach, denatured ethanol would be stored onsite in its own storage tank. It would be blended at the pump with commercial gasoline (from one of the other storage tanks) to make E85 for flexible-fuel vehicles.

This approach would result in E85 fuels that do not comply with the minimum vapor pressure specifications of ASTM D5798. The volatility of the gasoline available at the service station during a given season would be too low to produce specification-complying fuel if the gasoline was blended with denatured ethanol at 15% by volume. Nevertheless, dispenser blending is being promoted by some organizations for economic reasons. Furthermore, blending of ethanol and gasoline by "amateurs" and small organizations is known to exist, so there are isolated cases in which the onsite blending scenario would be applicable.

The fuel resulting from such an approach might, in some cases, resemble the E85Y of the present study. This fuel was a blend of denatured ethanol and summer-grade CARBOB base gasoline. In Figure 16, the pressure rise results from both of these fuels are plotted together. Throughout the temperature range shown, the headspace vapors of at least one of the two fuels would always be flammable.

14
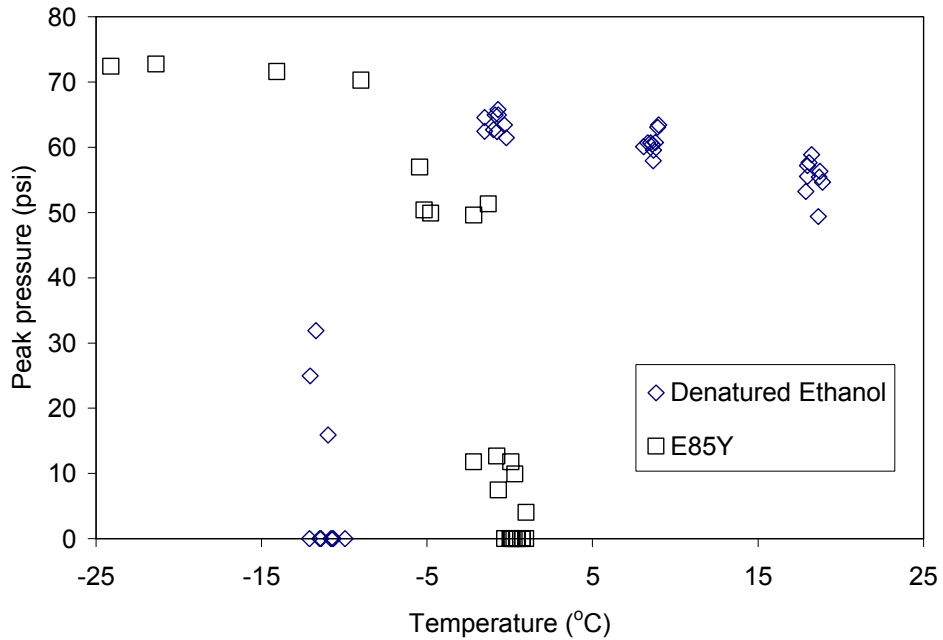
Figure 16. Pressure Rise Comparison for Denatured Ethanol and E85Y

In Figure 17, the temperature limits from the PROBIT analysis are depicted to show the regions of flammability (in terms of ambient temperature) if both fuels were present. There is a temperature region where both the denatured ethanol vapor (in the storage tank) and the E85 vapor (in the vehicle tank) could be flammable simultaneously.
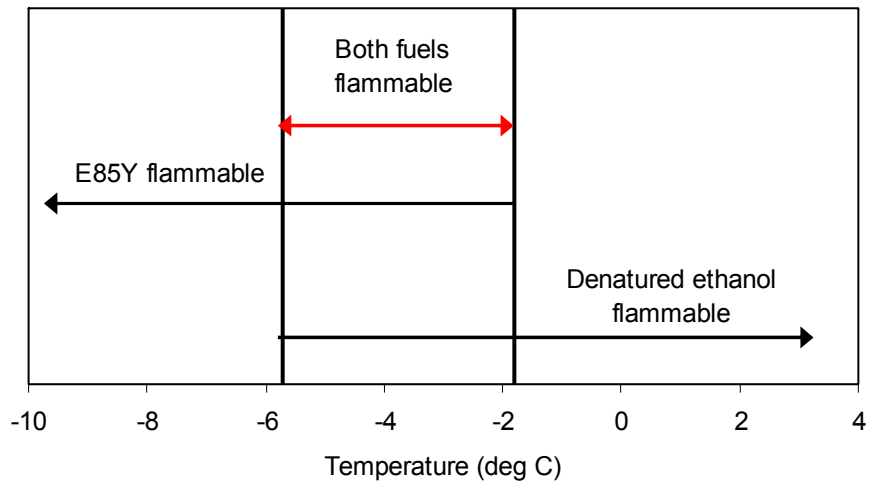
Figure 17. Flammability Limits of Denatured Ethanol and E85Y

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4. Conclusions and Recommendations from the Experimental Study

1. Experiments were carried out to determine the flammability of fuel tank headspace vapors as a function of temperature. Seven E85 fuel blends, two types of gasoline, and denatured ethanol were compared. For gasoline and E85, the fuels were flammable below a given critical temperature, as the vapor was too rich to be flammable at temperatures exceeding this value. Denatured ethanol was found to be flammable at room temperature and was not flammable below a critical temperature because the vapor was too lean.

2. Three E85 fuels that were blends of denatured ethanol and natural gasoline (containing 69.4%–79.1% ethanol) had flammability behavior similar to the test gasoline with summer-volatility characteristics. Three fuels that were blends of denatured ethanol and different commercial gasoline components (containing 80.7%–82.3% ethanol) were flammable up to substantially higher temperatures than the summer-volatility test gasoline. One fuel (81.4% ethanol) containing high-volatility commercial gasoline and isopentane had a limit temperature for flammability significantly lower than that of the summer-volatility test gasoline but higher than that of the high-volatility natural gasoline.

3. The limit temperature for flammability of the E85 and gasoline test fuels was strongly related to their vapor pressure inspections (DVPE), but DVPE alone did not predict the ranking of the fuels correctly in all cases.

4. In general, E85 is flammable at low temperatures, whereas denatured ethanol is flammable at warmer temperatures. If both types of fuels are stored at the same location, there is a wide range of ambient temperatures for which one or both of the fuels will be flammable.

5. The E85 fuels used in the study represented a wide range of blending options but did not provide a blend matrix in which critical parameters (such as ethanol content, vapor pressure, and hydrocarbon composition) were varied in a systematic manner. It is recommended that such a fuel blend matrix be designed for future experimental work.

6. The study addressed the flammability of tank headspace vapors using a strong, reliable ignition source. The relative hazards posed by weaker sparks that represent actual potential ignition sources should also be investigated.

7. All the experiments were carried out using a relatively low (5%) tank fill level, as this represented a worst-case scenario for potential flammability. The effect of fill level on flammability should also be investigated.

8. The experimental approach used in the present study (involving multiple small, closed test chambers and pressure rise measurements) was found to be an effective means of comparing the flammability of numerous fuel samples in a relatively short period. However, further refinements to the apparatus and experimental technique are needed before it can be recommended as standard test practice.

II. Mathematical Modeling Study

5.   Background

5.1   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:

$$P_{sat} = C_1 \exp(-C_2 / T) \tag{1}$$

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.

Modeling 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:

$$P_{fuel\,sat} = \sum_{i=1}^{i=N} X_i P_{i\,sat} \tag{2}$$

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 2 can then be used to find the vapor pressure of the blend at some given mass fraction evaporated (e.g., 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, and the exact composition of each blend to be evaluated must be known.

For many practical analyses, a simple and fast model is needed to allow blend volatility to be calculated. It has been shown [6,7] that hydrocarbon blends such as gasoline can be modeled 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:

$$P_{sat} = f_1 \exp(-f_2 / T) \tag{3}$$

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 3 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 6 and 7 showed how the functions can de derived using only the ASTM distillation data [8] for the mixture and its specific gravity.

Despite the drastic simplification of using Equation 3 to represent the complex evaporative behavior of a hydrocarbon mixture, experimental measurements [9] showed that this method gave satisfactory predictions of vapor pressure over a range of temperatures from 0ºC to 40ºC. Subsequent measurements to temperatures as low as -40ºC showed that the method worked well over the entire range of interest (-40ºC to +40ºC) for ambient conditions in North America.

5.2   *Volatility Characteristics of Gasoline/Alcohol Blends*

Based on the success of this simplified approach to modeling hydrocarbon blends, the method was extended to encompass blends of methanol or ethanol with gasoline. The approach [10] 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 3), and the alcohol, represented by the Clausius-Clapeyron equation (Equation 1) as usual for pure compounds.

Such blends are somewhat more complicated to model than those involving only hydrocarbons, because mixtures of strongly polar compounds such as alcohols do not form ideal mixtures with non-polar compounds such as hydrocarbons. Thus, Raoult's Law (Equation 2) does not apply as written, and a modification to account for the non-ideality of the resulting alcohol/hydrocarbon mixture was used. For a blend such as 85% methanol and gasoline (M85), this has the following form:

$$P_{M85} = \gamma_g X_g P_{gsat} + \gamma_m X_m P_{msat}$$

where

P_{M85} = equilibrium saturation pressure of the M85 mixture

γ_g = activity coefficient for gasoline in the blend

γ_m = activity coefficient for methanol in the blend

X_g = mole fraction of gasoline in the liquid phase

X_m = mole fraction of methanol in the liquid phase

P_{gsat} = saturated vapor pressure of the gasoline

P_{msat} = saturated vapor pressure of the methanol

Note that X_g and X_m as well as P_{gsat} vary continuously as the fuel evaporates. Furthermore, at any point in the evaporation process, when the overall vapor fraction VF_{M85} is some fixed value (between 0 and 1), say 0.4, the vapor fraction of the gasoline component VF_g is different from that of the methanol VF_m and both are different than VF_{M85}. Representative values for the two activity coefficients were determined for use with gasoline alcohol blends as part of that and subsequent work. Since the mole fractions of each of the two components in the liquid phase are not known *a priori* for some overall value of vapor fraction for the blend, iteration is required to determine the vapor pressure and other volatility characteristics needed, such as the molecular weight of the vapor phase. This makes the model more complex to use but again vastly simpler than the more rigorous methods. Experimental measurements over the temperature range –40ºC to +40ºC again showed that the model works satisfactorily for predicting the volatility properties of such pseudo-binary alcohol/gasoline blends [10].

The original work summarized above was motivated at the time by the need to predict the comparative cold-starting behavior of fuels, particularly alcohol/gasoline blends. To evaluate the performance of light refinery streams as cold-starting primers for alcohol blends, vapor pressure measurements were also carried out on high-methanol mixtures primed with either gasoline or a representative light isocrackate (LIC). The model was shown to give good predictions for this type of hydrocarbon primer as well [11].

5.3   Flammability Characteristics of Gasoline/Alcohol Blends

Based on the success of the volatility predictions for alcohol/hydrocarbon blends, the model was used to predict the flammability of fuel tank headspace vapors. Under most conditions at moderate ambient temperatures, the vapor/air mixture in the headspace of a gasoline fuel tank is too rich to burn, despite what Hollywood action movies would lead the public to believe. As the fuel level decreases in a fuel tank during use, the vapor pressure decreases, and the vapor/air mixture in the tank becomes progressively less rich. At sufficiently low temperatures and a nearly empty tank, the vapor-air mixture eventually falls into the flammable range and then presents a potential explosion hazard. For winter-grade gasolines, this temperature occurs is quite low and historically has not been considered a serious risk. Alcohol/gasoline blends tend to be more sensitive to this effect of low fill level because there is a smaller total amount of the most volatile hydrocarbon components in the original fuel compared with 100% gasoline.

However, alcohol/gasoline blends are less volatile than gasolines and have different stoichiometries. As a result, the content of the headspace above the liquid fuel in the tank can present a hazard at ambient temperatures much higher than required for their gasoline

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counterparts. The fuel volatility model described above was therefore evaluated to determine if it could be used to reliably assess fuel tank hazards with various alcohol/gasoline blends [1,12–15].

In those studies, the volatility model was used to assess composition at any given temperature and fuel fill level in a tank. Published, well-recognized flammability data [16] and the LeChatelier mixing rule [17] were used to evaluate the resulting flammability of the vapor phase. Results were satisfactory, and it was shown that this method can be used to predict the hazards associated with fuel tank vapor/air mixtures [1,12–15].

The above techniques for predicting vapor-phase properties and their flammability were used in the present study, focusing on comparisons between specific primed ethanol blends.

6.   Scope of the Present Modeling Study

Because of the limited nature of this study, and the data available on primers used in the various blends, it was not possible to create models of the hydrocarbon components in each blend in accordance with the full modeling technique described in the references cited above. Instead, a number of existing models for representative gasoline primers were used. These existing models covered representative low-, medium-, and high-volatility gasolines, Indolene, and LIC, all resulting from the previous work. The following were the goals:

1. Determine to what extent off-the-shelf gasoline or LIC models could be used to predict, *a priori*, the flammability of the blends in the study (which had various commercial gasolines and gasoline components as primers) without modeling the specific primers in detail.

2. Determine what level of improvement over the *a priori* predictions could be obtained using the off-the-shelf gasoline models "tuned" by using the measured values of vapor pressure (DVPE [18]) at the standard Reid vapor pressure (RVP) conditions (100ºF and vapor/liquid ratio of 4:1) [19] to adjust the calculated vapor pressures as a means of improving predicted flammability.

3. Make recommendations about the potential for improving predictions by using the measured distillation data [8] and specific gravity of the actual hydrocarbon primer used in a given blend instead of the existing off-the-shelf gasoline models.

7.   Models Used to Represent the Fuels Tested Experimentally

7.1   Gasoline Primer Simulations

The off-the-shelf primers used for this study are listed below. The references cited in each case provide the polynomial expressions used in the model and the coefficients used in the polynomials for that particular primer.

- Low-volatility gasoline [6] (LowVol) RVP = 4.24 psi (29.3 kPa)
- Indolene [6] (Ind) RVP = 8.21 psi (56.6 kPa)
- Medium-volatility gasoline [11] (MedVol) RVP = 11.45 psi (79.0 kPa)
- Light isocrackate [11] (LIC) RVP = 11.5 psi (79.5kPa)

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- High-volatility gasoline [6] (HighVol) RVP = 15.1 psi (104 kPa)

7.2 Ethanol Vapor Pressure

The ethanol vapor pressure was modeled using the Antoine Equation:

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

> The values of the coefficients used for ethanol were taken from Wilhoit and Zwolinski [20].

7.3 Selection of Existing Primer Models for Each Test Blend

Appendices A–J show the 10 test fuels, some of their pertinent property data, the off-the-shelf primer models selected for use with that fuel blend, and the reasons for those particular selections.

8. Results of the Modeling

Mathematical modeling of the flammability hazard associated with fuel tank headspace vapors was carried out to help answer several questions:

1. To what extent can DVPE [18] be used to rank fuels in order of flammability?
   - DVPE reflects the volatility of a fuel at 100ºF and is usually readily available. Therefore, it would be the easiest property to use in comparing, qualitatively, the volatility and hence the flammability of the fuel vapor/air mixture in a tank at low ambient temperatures. Gasolines and alcohols cannot be compared to each other on this basis owing to their differences in volatility behavior with temperature. However, blends having a similar alcohol content, such as E85, might be expected to behave more similarly and therefore be more amenable to comparisons simply based on DVPE.

2. To what extent can the existing gasoline models be used to rank fuels in order of flammability?
   - The full computational procedure described in the references [6,7] is complex and requires that the D86 distillation data and specific gravity of the hydrocarbon primer be known before it is added to the alcohol. Because the previous work examined five gasolines of varying volatility, it would be simple and convenient if the models already known for those samples could be used to represent other similar candidate primers in E85 blends.
   - There were two aspects to this part of the study. The first was simply an *a priori* prediction in which the primer of the candidate blend was modeled using the off-the-shelf model that seemed to best reflect its volatility characteristics. The second stage was to see if some slight tuning of the off-the-shelf model to fit the measured DVPE of the alcohol blend could give significantly better results for predicting low-temperature flammability.

3. To what extent can the existing gasoline models be used to predict the actual temperature flammability limits for new candidate blends?
   - Both *a priori* and tuned versions of the models were to be examined in this regard.

8.1   Initial Predictions without Tuning the Model

Modeling runs were carried out in two steps. The first step simply used the measured ethanol content of each blend along with whichever off-the-shelf hydrocarbon model seemed to best reflect the nature of the primer in the blend. Appendices A–K describe the reasons for the selection of the particular off-the-shelf gasoline primer used to model each fuel blend.

The following table compares these initial predictions to the flammability data measured in the experimental part of this study. The fuels are listed in rank order of measured flammability by temperature. The DVPE of each fuel is also shown to illustrate how DVPE fares in ranking the flammability of these fuels.

Table 1. Measured Temperature Flammability Limits and Initial Predictions

Fuel Blend	Measured Flammability Limit[1] (ºC)	Initial Flammability Limit Prediction (ºC)	DVPE[3] [18] (psi)	Predicted DVPE [with Primer shown] (psi)
Yellow	-1.8 +/- 0.47	+15.1	4.87	4.22 [LowVol]
Green	-6.49 +/- 2.05	+0.5	5.24	5.71 [Ind]
Red	-7.6 +/- 0.01	+1	5.60	6.05 [Ind]
Type B	-16.1 +/- 0.78	-13.5	8.22	8.66 [LIC]
Type A	-16.33, +/- 0.32	-12	7.98	8.29 [LIC]
Blue	-17.78 +/- 0.28	-11.5	7.69	8.21 [Ind]
Type C	-19.25 +/- 0.69	-16.5	9.37	9.57 [LIC]
White	-21.56 +/- 0.98	-10.5	8.54	7.92 [LIC]
Natural Gasoline	-25.3 +/- 1.02	-20.5	11.85	11.5 psi [LIC]
Denatured Alcohol	-5.73 +/- 4.23 (lean limit)[2]	-15.5	2.97	[LIC]

[1]These are the rich temperature limits, i.e., the mixture in the tank is too rich to support combustion until the ambient temperature falls to this value. At that point, the mixture becomes flammable and remains so until continued cooling takes it to the lean limit of flammability at some lower temperature that was not measured in this study.
[2]Ethanol is flammable at room temperature, so this was the temperature at which it ceased to be flammable, i.e., the lean limit. The rich limit lies above room temperature and was not measured in this study.
[3]Values measured by the Alberta Research Council.

8.2   Conclusions from this Initial Modeling

Several observations and conclusions can be drawn from the results shown in Table 1:

1. The ranking of the Blue fuel (a commercial gasoline) compared with the E85 blend of similar DVPE (Type A) illustrates the well-known observation that gasolines and alcohols behave differently at low temperatures. Despite its slightly lower DVPE, the Blue fuel becomes flammable at a lower temperature than the Type A E85. The effect of temperature on volatility is different for the two blends, and the more volatile fuel at 100°F is less volatile at cold temperatures and becomes flammable under warmer ambient conditions in a fuel tank. A simple comparison of DVPE as an indicator of low-temperature flammability would be misleading.

2. As might be expected intuitively, alcohol blends that are more volatile at DVPE conditions generally translate into safer fuels, i.e., higher DVPE fuels do not become flammable until lower ambient temperatures are reached. However, there are notable exceptions in which the DVPE fails to order flammability correctly. Although the order of Types A and B are reversed compared with their DVPE ranking, the experimental uncertainty gives them approximately the same measured flammability limit, so too much significance should not be placed on that comparison. However, the White fuel has a significantly lower DVPE than Type A but does not become flammable until a lower temperature, i.e., it is safer in that sense despite its lower DVPE. Thus, even when comparing alcohol blends to each other rather than to gasolines, the use of DVPE to assess low-temperature flammability can lead to significant errors.

3. The *a priori* models predict measured DVPE reasonably well. However, like the DVPE, they also do not reliably rank the flammability of the various blends in the measured order. In fact, they are arguably worse overall in correlating flammability than DVPE, because the White fuel is even further out of the measured rank order of flammability. Simply using off-the-shelf models of similar DVPE is not sufficient to assess low-temperature flammability of a particular fuel blend reliably.

4. As noted above, the rich temperature flammability limits predicted *a priori* by the off-the-shelf models are close in some cases and far from measured values in others, i.e., results are not generally encouraging viewed as a whole. However, a closer examination shows that the only cases in which the prediction can be said to be satisfactory involve Types A, B, and C and the "Natural Gasoline" (which was itself the primer for blends A, B, and C). This is also the case in which the D86 data for the primer used in those fuels was known, so the predictions could use a primer that was demonstrably similar, albeit not identical, to the primer actually used in the tested blends. For Types A, B, and C and Natural Gasoline, the predicted flammability limits are reasonably close to measured values, but the predicted rich flammability limits are all slightly warmer than measured values. Although the D86 for the Blue gasoline was also known, there was no off-the-shelf primer model that was a good fit to those data.

8.3 Tuning the Off-the-Shelf Models

The second step was to determine whether more useful modeling results for low-temperature flammability could be obtained using the off-the-shelf mathematical models if they were tuned to predict exactly the measured DVPE of either the actual primer, if known, or the DVPE of the alcohol blend if the primer DVPE itself was unknown. This technique was evaluated for two classes of results:

1. Yellow was studied as a sample of a blend in which the DVPE of the primer alone was known (4.8 psi [33.1 kPa]) and could be matched fairly well by one of the off-the-shelf models—in this case "Low Volatility Gasoline" (4.24 psi [29.3 kPa]).

2. Types A,B, and C and their known primer, Natural Gasoline, were studied as examples of the case in which the actual distillation data of the primer were reasonably well matched by one of the off-the-shelf primer models—in this case LIC (11.5 psi [79.5kPa]).

For each model, these tuned versions were run to determine whether there was any significant improvement over the *a priori* versions.

Table 2. Results for the Models Tuned to Match DVPE

Fuel Blend	Measured Flammability Limit (ºC)	*A Priori* Flammability Limit Prediction (ºC)	Tuned Flammability Limit Prediction (ºC)	Primer Model used
Yellow	-1.8 +/- 0.47	+15.1	+11.5	LowVol
Type B	-16.1 +/- 0.78	-13.5	-14.5	LIC
Type A	-16.33 +/- 0.32	-12	-13.5	LIC
Type C	-19.25 +/- 0.69	-16.5	-17.5	LIC
Natural Gasoline	-25.3 +/- 1.02	-20.5	-20.9	LIC

As seen in Table 2, tuning the off-the-shelf model for the Yellow fuel blend improved the predicted rich flammability limit somewhat and moved it in the correct direction. However, the predicted limit was still substantially higher than the measured value. It is apparent that simply matching the DVPE of the gasoline primer is insufficient to give an adequate representation of a primer having different distillation characteristics. The difference in volatility behavior at temperatures other than the 100°F used in the DVPE test is significant and cannot be simulated merely by adjusting DVPE of an off-the-shelf model that has full distillation data that might not match the actual primer.

The results for the case in which the off-the-shelf model for LIC was tuned so that its DVPE matched that of the Natural Gasoline were slightly better. However, the tuning required was small because the DVPE of the LIC was already close to that of the Natural Gasoline. Again, the

changes were in the correct direction, but the improvement was small and still left discrepancies. Figure 18 compares the distillation data of the Natural Gasoline with those of the LIC used to simulate it.
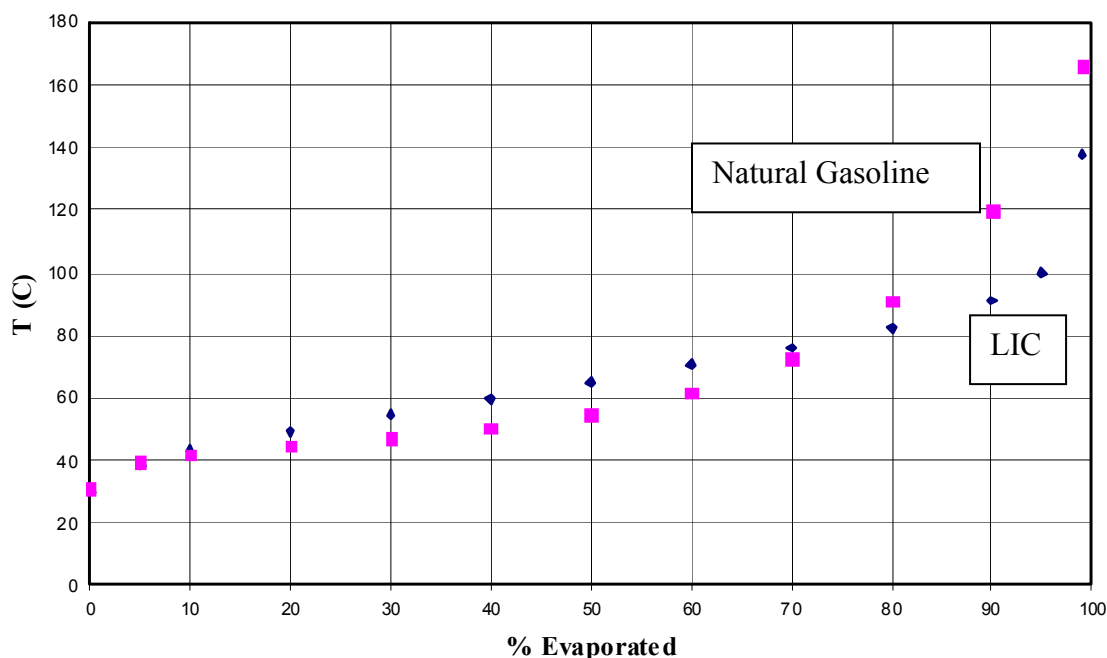
Figure 18. Distillation Data for LIC and Natural Gasoline

At low temperatures, there is little ethanol in the vapor phase. As a result, the flammability of the blend depends primarily on the mass of hydrocarbon components there. This is turn is a direct function of the hydrocarbon vapor pressure. The lightest, most volatile components in the fuel have the greatest influence, with higher boiling fractions having progressively less impact because their contributions to total vapor pressure are smaller. This graph shows that the lightest (i.e., most volatile) components in the Natural Gasoline have similar volatility to those of the LIC and would have a similar effect on flammability. However, the next most volatile fractions (seen here as the range from about 15%–70% evaporated on the distillation curve) are more volatile in the Natural Gasoline than in the LIC. The slight discrepancies in the predicted flammability limits when LIC was used to simulate the Natural Gasoline primer can be attributed to these more volatile fractions in the real primer.

8.4 Conclusions from the Tuned Modeling

1. Tuning an off-the-shelf model selected based on DVPE alone but not necessarily reflecting the actual hydrocarbon components of the real primer does not give reliable results.

2. With a model that has both DVPE and distillation data that are reasonable representations of the actual primer, *a priori* results are already satisfactory. Simply tuning the model to match primer DVPE creates little improvement.

9. Conclusions from the Fuel Tank Flammability Modeling

1. DVPE by itself does not reliably rank the low-temperature flammability hazards of fuel tank headspace vapors when comparing conventional gasolines with alcohol blends or comparing among alcohol blends. Differences in distillation characteristics, particularly as they represent the more volatile light ends, must be accounted for to obtain reliable comparisons.

2. Existing mathematical models for gasoline primers can be used for some alcohol blend comparisons, provided that both DVPE and distillation data of the model used are reasonable approximations of the actual primer.

3. For confident use of these modeling techniques, the actual primer distillation data should be used to create the models [6,7]. The resulting alcohol blend models [1,9–15] will then be based on a faithful representation of their hydrocarbon components.

4. The present study has shown that the modeling techniques used appear to give good predictions provided the primer model is a good match for the actual gasoline primer used in the alcohol blend. It would be desirable to carry out further studies of varied candidate E85 blends for which the full primer information is known. Such a study could allow conclusions to be drawn about the accuracy and reliability of this modeling technique for making flammability hazard predictions when assessing future candidate alcohol blends.

5. The mathematical model, in principle, could be used to predict tank safety more reliably than DVPE alone, but it is too complex for routine use in the field. However, further study using the model might permit a simpler correlation to be developed for field use that is more reliable than DVPE alone.

10. Plumes of Flammable Vapor Emitted from Vehicle Fuel Tanks during Refueling

10.1 Background

When a fuel tank is being refilled, the headspace vapors present in the tank before fueling begins are progressively expelled out the filler neck. They flow out of the tank at approximately the same volumetric flow rate as that of the liquid fuel entering the tank and have the same properties at the exit as the headspace vapors. In many areas of the United States, service stations are equipped with vapor recovery systems at the fill nozzle that prevent the headspace vapors from being released to the atmosphere. All new passenger cars and trucks sold in the United States are equipped with onboard refueling vapor recovery systems. These emission control systems should also prevent the formation of flammable mixtures outside the tank during refueling.

However, this technology might not be present or effective in some cases, such as the filling of portable fuel containers, older vehicles (amateur E85 conversions are known to exist), and trailered marine craft. If the vapor expelled from the fuel tank is not captured in some way, it will produce a plume of fuel-air mixture that flows outward and entrains air from the surroundings as it flows downstream. The fresh air being entrained progressively into the plume as it moves downstream dilutes the mixture and steadily reduces the fuel-air ratio inside the plume itself.

Figure 19 shows the case of such a plume produced while refueling a vehicle in the presence of a crosswind.
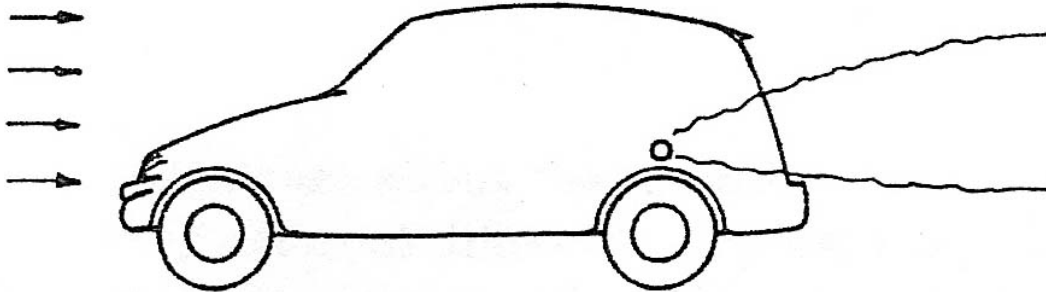
Figure 19. Plume of Fuel-Air Vapor Expelled during Refueling

Depending on the presence or absence of an ambient wind, wind velocity, and rate of refueling, the plume might be vertical or blown downwind as shown in Figure 19. It is subject to shear forces at its boundary that entrain ambient air and buoyancy forces that might change the shape and direction of the plume. Within the plume, there is diffusion of the entrained air toward the core, dependant upon the turbulence intensity, mixture properties, and rate of air entrainment. Figure 20 shows the typical concentration profile of a component such as fuel vapor within the plume as it is progressively diluted.

Transverse

Distance

Downstream Distance
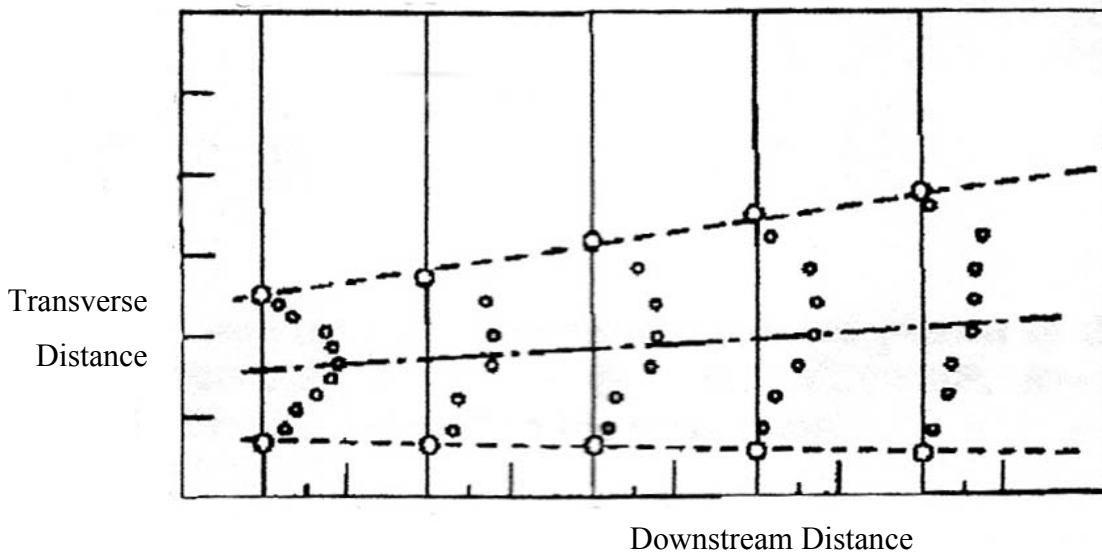
Figure 20. Typical Fuel Concentration Profiles in the Plume [21]

As the plume moves downstream, the fuel concentration decreases. The mixture within the plume might be more or less uniform depending on turbulence intensity and rate of air entrainment.

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The details of the fuel concentration and plume dynamics can vary considerably, depending on the flow field fluid dynamics. However, some useful general conclusions can be deduced without analyzing the details of the flow. Overall, there are two different scenarios possible with respect to potential fire and explosion hazards.

Case 1. Rich Tank Headspace Vapors.   The first scenario occurs when the tank headspace vapors are above the rich limit of flammability. This is the normal case at warm ambient temperatures when the fuel is gasoline or an alcohol/gasoline blend. In this case, the plume is too rich to burn at the tank exit, but falls into the flammable region as entrained air dilutes it. Further air entrainment downstream eventually dilutes the mixture enough so that it passes the lean limit of flammability and thus becomes too lean to support combustion beyond that point. Therefore, there is a segment of plume inside which the mixture is flammable. A spark or other ignition source within this area would lead to a flame propagating throughout the flammable portion of the plume, including backward toward the tank. This is clearly a hazard because it could ignite other materials in the area or cause injuries to anyone within that region. However, the vapors inside the filler neck and the headspace vapors cannot be ignited because they are above the rich flammability limit, so the tank will not explode under this scenario. In general, fuels that are more volatile produce longer flammable plumes, and gasoline is more hazardous in this regard than alcohol blends [21].

Case 2. Flammable Tank Headspace Vapors. This scenario is more hazardous than the previous scenario. The vapors in the plume expelled from the tank are flammable immediately at the exit and remain so until the point downstream at which the mixture is sufficiently diluted by entrained air so that it falls below the lean flammability limit. As in Case 1, an ignition source within the flammable portion of the plume would lead to a flame propagating throughout the flammable portion of the plume, including backward toward the tank. In this case, however, the flame would propagate all the way back to the tank filler neck. Because the headspace vapors are themselves flammable, the flame would not stop at the tank entrance but would continue to propagate into the tank itself, producing an explosion, rupture of the tank walls, and violent dispersion of the liquid fuel to create a substantial fire.

10.2 Analysis

As mentioned above, the actual fluid mechanics of the plume are complex and depend up a number of factors. However, some general conclusions can be drawn based on the common aspects found in any of the possible plume types.

The rate of air entrainment depends on the details of the flow field. However, for any of the candidate fuels of interest, the fluid properties responsible for the fluid dynamics of the plume are very similar because they are close to those of air at ambient temperature. As a result, regardless of what factors affect the shape and evolution of the plume, they are essentially the same for any of the candidate fuels. The rate of entrainment of ambient air into the plume depends on the flow field and at any point is given by

$$\frac{d\dot{m}_{air}}{d\xi}\bigg|_{\xi} = fn(flowfield)$$

(4)

where ξ is the curvilinear coordinate along the plume length with its origin at the tank filler neck and $\dot{m}_{air}$ is the mass flow rate of the air within the plume at any cross section normal to the axis of the plume. The mass flow rate increases steadily owing to entrainment of ambient air into the plume, whereas the mass flow rate of fuel vapor at any cross section is constant and equal to that at the filler neck for a steady rate of flow of liquid fuel into the tank.

The fact that the fuel flow rate is constant means that all air entrained along the plume length reduces the fuel-air ratio by a characteristic amount regardless of the fuel concerned. The rate of change of the flammability of the plume depends strongly on the flow field but is the same for all the candidate fuels.

Equation 1 can be recast to express the overall fuel-air equivalence ratio, ϕ, of the mixture at any point along the plume location, where

$$\phi = \frac{f_{actual}}{f_{stoich}}$$

(5)

and

$$f = \frac{\dot{m}_{fuel}}{\dot{m}_{air}}$$

(6)

And f_{stoich} is the value of f for a stoichiometric mixture for the fuel in question.

With these definitions, a value of ϕ greater than 1 signifies a rich mixture and less than 1 signifies a lean mixture. This is a particularly convenient convention because, for all the fuels in question, the rich and lean flammability limits occur at virtually the same values of ϕ. Expressing $\dot{m}_{air}$ in terms of ϕ:

$$\dot{m}_{air} = \dot{m}_{air}\frac{\dot{m}_{fuel}}{\dot{m}_{fuel}} = \frac{\dot{m}_{fuel}}{\phi \cdot f_{stoich}}$$

(7)

Differentiating Equation (4) allows us to recast Equation (1) as follows:

$$-\frac{\dot{m}_{fuel}}{f_{stoich}}\frac{d\phi}{\phi^2} = fn(flowfield)$$

(8)

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The function on the right in Equation (5) depends on the details of the flow field. However, it is a positive function and is nearly constant for many cases of interest. For example, the rate of entrainment in a turbulent jet in still air is constant and that in a turbulent jet in a cross flow (such as shown in Figure 19) is only a very weak function of distance along the plume [17]. In a case in which the function is a constant, Equation (5) can be integrated, giving the following:

$$\phi_\xi = \frac{\phi_1}{1 + const \times (\xi - \xi_1)} \qquad (9)$$

where state 1 is at the start of the plume (i.e., at the exit of the filler neck) when the plume properties are still those of the headspace vapors. $(\xi - \xi_1)$ is the distance downstream along the curved shape of the plume.

Equation (9) shows that the equivalence ratio and hence the flammability of the mixture at any location along the plume has the shape shown in Figure 21.
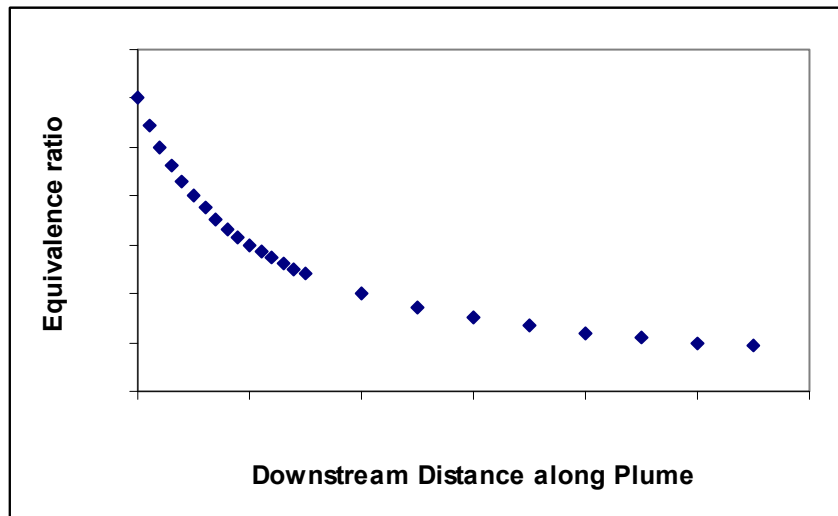
**Figure 21. Decrease in Equivalence Ratio in the Plume
Downstream of the Fuel Tank**

The two flammable plume scenarios described above now can be visualized as shown in Figures 22 and 23. The distance L_f shows the flammable portion of the plume. In Figure 22, there is a rich section just downstream of the filler neck before the plume becomes flammable.
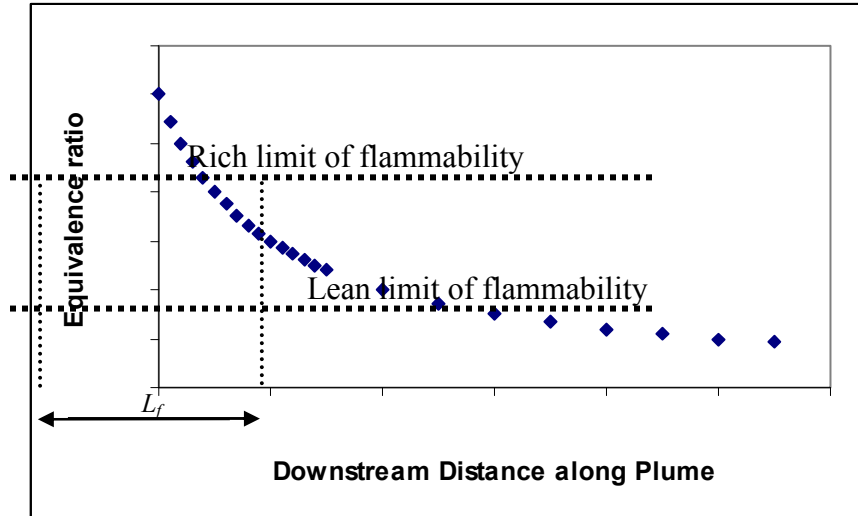
Figure 22. Flammable Region in the Plume for Case 1: Headspace Vapors above the Rich Limit of Flammability
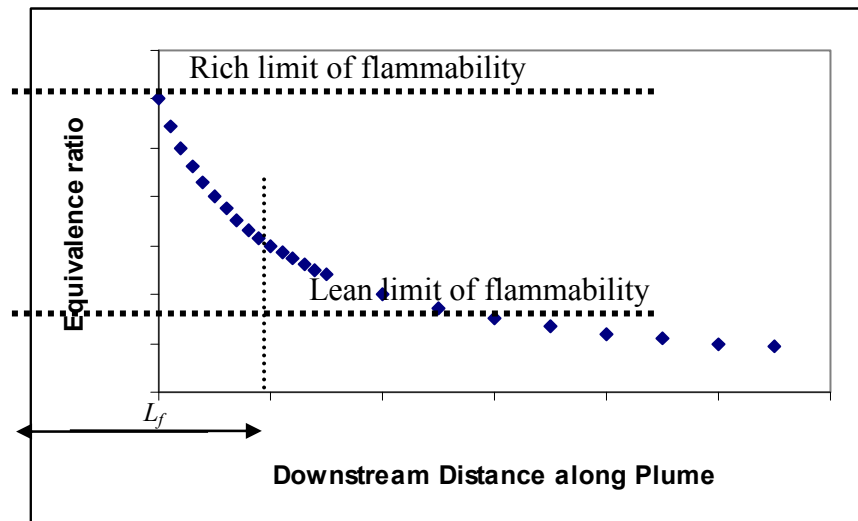
Figure 23. Flammable Region in the Plume for Case 2: Headspace Vapors Flammable

In Figure 23, the distance L_f again shows the flammable portion of the plume. However, in this case, the flammable part of the plume is adjacent to the tank and the headspace vapors are themselves also flammable.

The size and shape of the plume, as well as the rate of decrease of equivalence ratio ϕ downstream inside it, depend on the particular flow field conditions. However, the general relationship in Equation (9) and the models for fuel blend volatility allow a limited quantitative comparison to be made between the relative flammability hazards of the candidate fuel blends.

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In the following illustrative comparison, an arbitrary value was used for the constant in Equation (9) so this equation could be used to compare the plume lengths of four fuels at both low and high ambient temperatures and draw general conclusions. The particular values given are of no significance except to define the relative sizes of the plumes with respect to each other. A detailed flow field model (still air, cross winds of various magnitudes, buoyancy effects, laminar or turbulent conditions, etc.) would need to be created to determine air entrainment rates and hence actual plume lengths in absolute terms. Different quantitative values would be found for any particular flow conditions, but the general trend is expected to be consistent with Figure 24.

The results shown in Figure 24 were derived using the mathematical models used in the simulation of the Natural Gasoline and each of the three blends produced by mixing it with ethanol in various proportions, i.e., Type A, Type B, and Type C. The measured DVPE and the simulations both ranked these fuels, based on increasing volatility, as Type A, B, and C then Natural Gasoline (see Table 1). The relative plume lengths were evaluated at +20ºC (representing Case 1: rich headspace vapor) and -20ºC (representing Case 2: flammable headspace vapor).
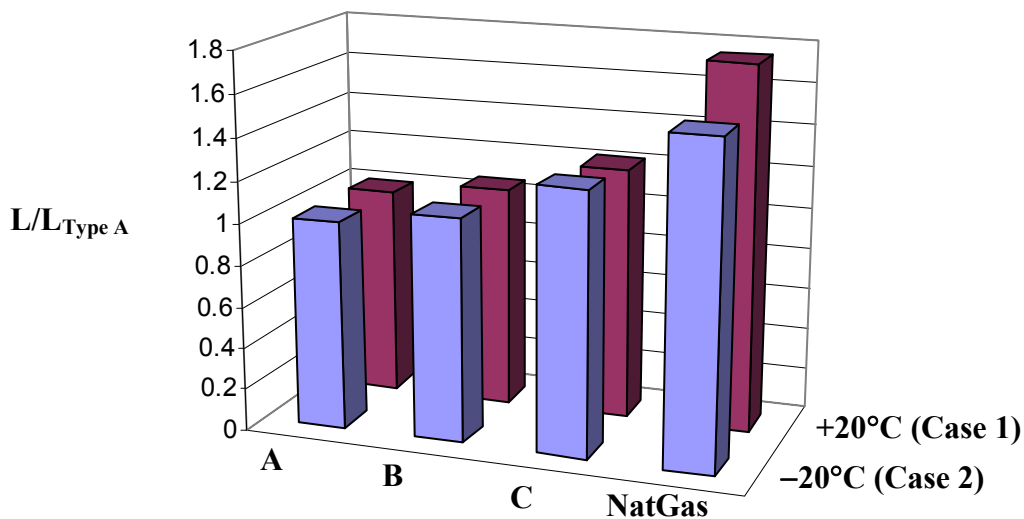
Figure 24. Relative Flammable Plume Lengths

10.3   *Conclusions from the Plume Modeling Study*

The following qualitative conclusions are drawn from this study:

1. Fuels that are more volatile produce longer plumes in both Case 1 and Case 2 scenarios. Usually, fuels that are more volatile at DVPE conditions are also more volatile at low temperatures, but this is not always the case, as previous studies have shown [11]. Nevertheless, at any given temperature, the more volatile fuel at that temperature will produce the longest flammable plume and represent the greatest hazard.

2. For the more dangerous situation of Case 2 (a flammable plume adjacent to flammable tank headspace vapors), the size and location of the plume is important. It was beyond the scope of this study to examine the range of fluid mechanics scenarios applicable to the various practical cases of interest for refueling. However, some preliminary work carried out here, coupled with the results of one previous study of a refueling plume in a crosswind, suggest that some cases might have plume lengths of such a size as to present a serious hazard of ignition and subsequent tank explosion [21]. Other cases might have plumes short enough to preclude ignition by typical ignition sources found in the immediate vicinity of refueling equipment. A thorough quantitative assessment is needed of the various flow regimes possible during refueling to establish the actual sizes of the flammable plumes possible under different conditions. This assessment should consider buoyancy effects, still air, crosswinds of various magnitudes, the variability of refueling rates and equipment geometries, etc. Mathematical models already exist in the fluid mechanics literature for many of these possibilities, but some experimental confirmation of their applicability and reliability for this purpose will be needed.

III. Overall Conclusions and Recommendations

11.   Experimental Conclusions

1. Experiments were carried out to determine the flammability of fuel tank headspace vapors as a function of temperature. Seven E85 fuel blends, two types of gasoline, and denatured ethanol were compared. For gasoline and E85, the fuels were flammable below a given critical temperature, as the vapor was too rich to be flammable at temperatures exceeding this value. Denatured ethanol was found to be flammable at room temperature and was not flammable below a critical temperature when the vapor became too lean to be flammable.

2. Three E85 fuels that were blends of denatured ethanol and natural gasoline (containing 69.4%–79.1% ethanol) had flammability behavior similar to the test gasoline with summer-volatility characteristics. Three fuels that were blends of denatured ethanol and different commercial gasoline components (containing 80.7%–82.3% ethanol) were flammable up to substantially higher temperatures than the summer-volatility test gasoline. One fuel (81.4% ethanol) containing high-volatility commercial gasoline and isopentane had a limit temperature for flammability that was significantly lower than that of the summer-volatility test gasoline but higher that that of the high-volatility natural gasoline.

3. The limit temperature for flammability of the E85 and gasoline test fuels was strongly related to their vapor pressure specifications (DVPE), but DVPE alone did not predict the ranking of the fuels correctly in all cases.

4. In general, E85 is flammable at low temperatures, whereas denatured ethanol is flammable at warmer temperatures. If both types of fuels are stored in separate tanks at the same location, there is a wide range of ambient temperatures for which one or both of the tanks' headspace vapors will be flammable.

5.   The experimental approach used in the present study (involving multiple small, closed test chambers and pressure rise measurements) was found to be an effective means of comparing the flammability of numerous fuel samples in a relatively short period.

11.1   Conclusions on the Mathematical Modeling of Fuel Tank Flammability

1.   DVPE by itself does not reliably rank the low-temperature flammability hazards of fuel tank headspace vapors when comparing conventional gasolines with alcohol blends or comparing among alcohol blends. Differences in distillation characteristics, particularly as they represent the more volatile light ends, must be accounted for to obtain reliable comparisons.

2.   Existing mathematical models for gasoline primers can be used for some alcohol blend comparisons, provided that both DVPE and distillation data of the model used are reasonable approximations to those of the actual primer. Matching DVPE alone is insufficient.

3.   Within the constraints of the present study, the modeling techniques used gave reasonable predictions of headspace vapor flammability, provided the primer model was a good match for the actual gasoline primer used in the alcohol blend.

11.2   Conclusions on the Mathematical Modeling of Plumes Emitted During Refueling

1.   Fuels that are more volatile at the temperature of interest produce longer plumes during refueling and represent greater hazards. Usually, fuels that are more volatile at DVPE conditions are also more volatile at low temperatures, but this is not always the case, as previous studies have shown.

2.   For the more dangerous situation of a flammable plume adjacent to flammable tank headspace vapors, the size and location of the plume is important. It was beyond the scope of this study to examine the range of fluid mechanics scenarios applicable to the various practical cases of interest for refueling. Some cases might have plume lengths of such a size as to present a serous hazard of ignition and subsequent tank explosion, whereas others might have plumes short enough to preclude ignition by typical ignition sources found in the immediate vicinity of refueling equipment.

IV. Recommendations

1.   The E85 fuels used in the current study represented a wide range of blending options but did not provide a blend matrix in which critical parameters (such as ethanol content, vapor pressure, and hydrocarbon composition) were varied in a systematic manner. It is recommended that such a fuel blend matrix be designed for future experimental work.

2.   The current study addressed the flammability of tank headspace vapors using a strong, reliable ignition source. The relative hazards posed by weaker sparks that represent actual potential ignition sources should also be investigated.

3. In the current study, all the experiments were carried out using a relatively low (5%) tank fill level, as this represented a worst-case scenario for potential flammability. The effect of fill level on flammability should also be investigated.

4. Although the experimental approach used in the present study was found to be effective, further refinements to the apparatus and experimental technique are needed before it can be recommended as standard test practice.

5. For confident use of these modeling techniques for the flammability of fuel tank headspace vapors, the actual primer distillation data should be used to create the models. The resulting alcohol blend models will then be based on a faithful representation of their hydrocarbon components.

6. Further studies are needed of varied candidate E85 blends for which the full primer information is known. Such a study could then allow well-founded conclusions to be drawn about the accuracy and reliability of this modeling technique for making predictions of fuel tank flammability hazards of candidate alcohol blends.

7. The mathematical model, in principle, could be used to predict tank safety more reliably than DVPE alone, but it is too complex for routine use in the field. Further study should be undertaken using the model to determine if a correlation could be developed that would be simple enough for field use but more reliable than DVPE alone.

8. A thorough quantitative assessment is needed of the various flow regimes possible during refueling to establish the actual sizes of the flammable plumes emitted from the tank under different conditions. This assessment should consider buoyancy effects, still air, crosswinds of various magnitudes, the variability of refueling rates and equipment geometries, etc. Mathematical models already exist in the fluid mechanics literature for many of these possibilities, but some experimental confirmation of their applicability and reliability for this purpose will be needed.

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Appendix A. Yellow Fuel Blend

Properties and Supplementary Information

Table A-1. Characteristics of the Primer Used in this Blend Formulation
(blending data supplied by Lew Gibbs, Chevron Products Company, Richmond, CA)

HC Category	Mass% by GC	Mass% in HC
Paraffins	2.16	13.0
Iso-paraffins	8.31	50.2
Olefins	0.6	3.6
Naphthenes	1.56	9.4
Aromatics	3.93	23.7
Unknowns	0.13	
Ethanol	82.31	
Methanol	0.04	
Total	99.0	100
Water	0.992	

DVPE (kPa)	DVPE (psi)	NREL (psi)	EtOH (vol%)	NREL (vol%)	NREL (mass%)
33.6	4.87	4.92	80.96	82.29	83.86

Note: Unless otherwise noted, properties shown are values measured by the Alberta Research Council subsequent to the flammability testing at the Nexum Laboratory.

FR44986 (Yellow blend) was 85 vol% EtOH and 15 vol% 4.80 psi (33.1kPa) CARBOB (summer-grade CARBOB).

CARBOB is the base gasoline used in California for ethanol blending to make California Phase 2 reformulated gasoline when ethanol is added at 5.7 vol%.

Existing Hydrocarbon Model used in the initial simulations: Low Volatility Gasoline [6] RVP = 4.24 psi (29.3 kPa). This primer has a similar DVPE to the summer CARBOB.

Appendix B. Green Fuel Blend

Properties and Supplementary Information

Table B-1. Characteristics of the Primer Used in this Blend Formulation
(blending data supplied by Mr. Lew Gibbs, Chevron Products Company, Richmond, CA)

HC Category	Mass% by GC	Mass% in HC
Paraffins	2.01	14.1
Iso-paraffins	6.9	48.4
Olefins	0.88	6.2
Naphthenes	1.69	11.9
Aromatics	2.78	19.5
Unknowns	0.1	
Ethanol	84.95	
Methanol	0.04	
Total	99.4	100
Water	0.693	

DVPE (kPa)	DVPE (psi)	NREL (psi)	EtOH (vol%)	NREL (vol%)	NREL (mass%)
36.1	5.24	7.31	83.58	80.67	82.9

Note: Unless otherwise noted, properties shown are values measured by the Alberta Research Council subsequent to the flammability testing at the Nexum Laboratory.

FR45039 (Green) was a mixture of several blends of E85 to make a 7 psi (48.3 kPa) E85, which makes the composition difficult to determine. It contains all the hydrocarbon components except for the 4.80 psi (33.1 kPa) CARBOB (i.e., it presumably contains 5.92 psi [40.8 kPa] CARBOB, 10.66 psi [73.5kPa] CARBOB, toluene, and crude isopentane).

CARBOB is the base gasoline used in California for ethanol blending to make California Phase 2 reformulated gasoline when ethanol is added at 5.7 vol%.

Existing hydrocarbon model used in the initial simulations: Indolene [6] RVP = 8.21 psi (56.6 kPa).

Appendix C. Red Fuel Blend

Properties and Supplementary Information

Table C-1. Characteristics of the Primer Used in this Blend Formulation
(blending data supplied by Mr. Lew Gibbs, Chevron Products Company, Richmond, CA)

HC Category	Mass % by GC	Mass % in HC
Paraffins	2.36	13.9
Iso-paraffins	8.39	49.5
Olefins	0.71	4.2
Naphthenes	1.61	9.5
Aromatics	3.89	22.9
Unknowns	0.12	
Ethanol	82.27	
Methanol	0.04	
Total	99.4	100
Water	0.65	

DVPE (kPa)	DVPE (psi)	NREL (psi)	EtOH (vol%)	NREL (vol%)	NREL (mass %)
38.6	5.60	5.6	80.78	80.74	82.42

Note: Unless otherwise noted, properties shown are values measured by the Alberta Research Council subsequent to the flammability testing at the Nexum Laboratory.

FR44987 (Red) was 85 vol% EtOH, 11.9 vol% 5.92 psi (40.8 kPa) CARBOB, 2.5 vol% 10.66 psi (73.5 kPa) CARBOB, and 0.5 vol% toluene.

CARBOB is the base gasoline used in California for ethanol blending to make California Phase 2 reformulated gasoline when ethanol is added at 5.7 vol%.

Existing hydrocarbon model used in the initial simulations: Indolene [6] RVP = 8.21 psi (56.6 kPa).

Appendix D. White Fuel Blend

Properties and Supplementary Information

Table D-1. Characteristics of the Primer Used in this Blend Formulation
(blending data supplied by Mr. Lew Gibbs, Chevron Products Company, Richmond, CA)

HC Category	Mass% by GC	Mass% in HC
Paraffins	3.78	23.8
Iso-paraffins	6.64	41.9
Olefins	1.25	7.9
Naphthenes	1.42	9.0
Aromatics	2.77	17.5
Unknowns	0.08	
Ethanol	83.42	
Methanol	0.04	
Total	99.4	100
Water	0.65	

DVPE (kPa)	DVPE (psi)	NREL (psi)	EtOH (vol%)	NREL (vol%)	NREL (mass%)
58.9	8.54	8.57	81.4	82.12	84.13

Note: Unless otherwise noted, properties shown are values measured by the Alberta Research Council subsequent to the flammability testing at the Nexum Laboratory.

FR44927 (White) was 85 vol% EtOH, 11.4 vol% 13.75 psi (94.8 kPa) commercial gasoline, and 3.6 vol% crude isopentane.

The commercial gasoline was from a Rocky Mountain refinery chosen so as to get a winter grade with a high vapor pressure (13.75 psi [94.8 kPa]) that did not contain ethanol.

The crude isopentane was obtained from a refinery sphere and contains butane and other hydrocarbons. The batch used was not inspected, but an earlier batch had an estimated vapor pressure of 22 psi (151.7 kPa).

Existing hydrocarbon model used in the initial simulations: High Volatility Gasoline [6] RVP = 15.1 psi (104 kPa).

Appendix E. Blue Fuel Blend

Properties and Supplementary Information

Table E-1. Characteristics of the Primer Used in this Blend Formulation
(blending data supplied by Mr. Lew Gibbs, Chevron Products Company, Richmond, CA)

HC Category	Mass% by GC	Mass% in HC
Paraffins	8.29	8.4
Iso-paraffins	53.85	54.6
Olefins	6.52	6.6
Naphthenes	8.71	8.8
Aromatics	21.33	21.6
Unknowns	1.3	
Ethanol	0	
Methanol	0	
Total	100.0	100
Water	0	

DVPE (kPa)	DVPE (psi)	NREL (psi)	EtOH (vol%)	NREL (vol%)	NREL (mass%)
53	7.69	7.98	0	0	0

	D86 (ARC) °C	D86 (ARC) °F	D86(NREL) °F
IBP	36.2	97.16	95.3
5	52.6	126.68	126.3
10	59	138.2	137.8
20	68.2	154.76	155.4
30	77.3	171.14	172.4
40	86.5	187.7	190
50	95.5	203.9	206.4
60	103.8	218.84	222
70	112.2	233.96	237.2
80	123.4	254.12	257.5
90	145.7	294.26	298
95			331.3
EP	186	366.8	342.3
Residue	1.3		3.3
loss	0.7		0.7

Note: Unless otherwise noted, properties shown are values measured by the Alberta Research Council subsequent to the flammability testing at the Nexum Laboratory.

FR44928 (Blue) was 59.1 vol% 5.92 psi (40.8 kPa) CARBOB and 40.9 vol% 10.66 psi (73.5 kPa) CARBOB.

The Blue fuel was a gasoline reference with which to compare the driveability performance of the various E85s. The summertime federal vapor pressure limits are 7.8 psi and 9.0 psi, depending on location and emissions compliance.

CARBOB is the base gasoline used in California for ethanol blending to make California Phase 2 reformulated gasoline when ethanol is added at 5.7 vol%.

Existing hydrocarbon model used in the initial simulations: Indolene [6] RVP = 8.21 psi (56.6 kPa) chosen as a representative commercial gasoline of similar DVPE.

Appendix F. "Natural Gasoline" Fuel Blend

Properties and Supplementary Information

Table F-1. Characteristics of the Primer Used in this Blend Formulation
See above D86 data

HC Category	Mass % by GC	Mass % in HC
Paraffins	28.41	28.9
Iso-paraffins	51.38	52.3
Olefins	3.41	3.5
Naphthenes	10.63	10.8
Aromatics	4.39	4.5
Unknowns	1.44	
Ethanol	0.34	
Methanol	0	
Total	100.0	100
Water	0	

DVPE (kPa)	DVPE (psi)	NREL (psi)
81.7	11.85	

	D86 (ARC) °C	D86 (ARC) °F
IBP	31.1	87.98
5	39.8	103.64
10	41.9	107.42
20	44.6	112.28
30	47.1	116.78
40	50.3	122.54
50	54.9	130.82
60	61.8	143.24
70	72.9	163.22
80	90.9	195.62
90	119.8	247.64
95		
EP	166	330.8
Residue	1.1	
loss	0.7	

Note: Unless otherwise noted, properties shown are values measured by the Alberta Research Council subsequent to the flammability testing at the Nexum Laboratory.

Existing hydrocarbon model used in the initial simulations: Light Isocrackate [11] RVP = 11.5 psi (79.5kPa). Although not exactly the same, "Natural Gasoline" is more similar in composition and D86 characteristics to LIC (Appendix K) than to a commercial gasoline.

Appendix G. Type A Fuel Blend

Properties and Supplementary Information

Table G-1. Characteristics of the Primer Used in this Blend Formulation

HC Category	Mass% by GC	Mass% in HC
Paraffins	5.12	29.9
Iso-paraffins	9.02	52.7
Olefins	0.38	2.2
Naphthenes	1.86	10.9
Aromatics	0.72	4.2
Unknowns	0.39	
Ethanol	81.64	
Methanol	0.04	
Total	99.2	100
Water	0.867	

DVPE (kPa)	DVPE (psi)	NREL (psi)	EtOH (vol%)	NREL (vol%)
55	7.98	7.75/7.87	79.12	79.25

Note: Unless otherwise noted, properties shown are values measured by the Alberta Research Council subsequent to the flammability testing at the Nexum Laboratory.

Existing hydrocarbon model used in the initial simulations: Light Isocrackate [11] RVP = 11.5 psi (79.5 kPa). This was selected because the Type A blend was understood to have been blended using the "Natural Gasoline" (Appendix F). Although not exactly the same, "Natural Gasoline" is more similar in composition and D86 characteristics to LIC [Appendix K] than to a commercial gasoline.

Appendix H. Type B Fuel Blend

Properties and Supplementary Information

Table H-1. Characteristics of the Primer Used in this Blend Formulation

HC Category	Mass% by GC	Mass% in HC
Paraffins	5.71	29.8
Iso-paraffins	9.96	52.0
Olefins	0.43	2.2
Naphthenes	2.17	11.3
Aromatics	0.87	4.5
Unknowns	0.58	
Ethanol	79.45	
Methanol	0.04	
Total	99.2	100
Water	0.844	

DVPE (kPa)	DVPE (psi)	NREL (psi)	EtOH (vol%)	NREL (vol%)
56.7	8.22	9.38	76.73	76.08/76.93

Note: Unless otherwise noted, properties shown are values measured by the Alberta Research Council subsequent to the flammability testing at the Nexum Laboratory.

Existing hydrocarbon model used in the initial simulations: Light Isocrackate [11] RVP = 11.5 psi (79.5 kPa). This was selected because the Type A blend was understood to have been blended using the "Natural Gasoline" (Appendix F). Although not exactly the same, "Natural Gasoline" is more similar in composition and D86 characteristics to LIC (Appendix K) than to a commercial gasoline.

Appendix I. Type C Fuel Blend

Properties and Supplementary Information

Table I-1. Characteristics of the Primer Used in this Blend Formulation

HC Category	Mass% by GC	Mass% in HC
Paraffins	7.6	29.4
Iso-paraffins	13.49	52.1
Olefins	0.74	2.9
Naphthenes	2.89	11.2
Aromatics	1.15	4.4
Unknowns	0.61	
Ethanol	72.76	
Methanol	0.04	
Total	99.3	100
Water	0.763	

DVPE (kPa)	DVPE (psi)	NREL (psi)	EtOH (vol%)	NREL (vol%)
64.6	9.37	10.03	69.44	72.58/70.72

Note: Unless otherwise noted, properties shown are values measured by the Alberta Research Council subsequent to the flammability testing at the Nexum Laboratory.

Existing hydrocarbon model used in the initial simulations: Light Isocrackate [11] RVP = 11.5 psi (79.5kPa). This was selected because the Type A blend was understood to have been blended using the "Natural Gasoline" [Appendix F]. Although not exactly the same, "Natural Gasoline" is more similar in composition and D86 characteristics to LIC [Appendix K] than to a commercial gasoline.

Appendix J. "Denatured Alcohol" Fuel Blend

Properties and Supplementary Information

Table J-1. Characteristics of the Denaturant Used in Modeling this Blend Formulation

HC Category	Mass% by GC	Mass% in HC
Paraffins	0.51	30.9
Iso-paraffins	0.88	53.3
Olefins	0.02	1.2
Naphthenes	0.2	12.1
Aromatics	0.04	2.4
Unknowns	0.15	
Ethanol	97.18	
Methanol	0.04	
Total	99.0	100
Water	1.025	

DVPE (kPa)	DVPE (psi)	NREL (psi)	EtOH (vol%)
20.5	2.97		96.86

Note: Unless otherwise noted, properties shown are values measured by the Alberta Research Council subsequent to the flammability testing at the Nexum Laboratory.

Existing hydrocarbon model used in the initial simulations: Light Isocrackate [11] RVP = 11.5 psi (79.5kPa). This was selected because the ethanol denaturant was understood to have been the "Natural Gasoline" (Appendix F). Although not exactly the same, "Natural Gasoline" is more similar in composition and D86 characteristics to LIC [Appendix K] than to a commercial gasoline.

Appendix K. Fuel Properties for Off-the-Shelf Mathematical Gasoline Models

Table K-1. Reid Vapor Pressures [21]

D86[3] Data

Volume % Recovered	Low-Volatility Gasoline		Indolene		Medium-Volatility Gasoline		Light Isocrackate		High-Volatility Gasoline	
	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
0	41	106	30	86	30	86	30	86	22	72
5					39	102	39	101		
10	72	162	57	135	46	114	43	110	36	97
20	83	181	76	169	57	135	49	121	47	117
30	93	199	90	194	71	160	55	130	61	142
40	103	217	99	210	87	188	60	139	76	169
50	114	237	107	225	101	214	65	149	91	196
60	126	259	116	241	119	246	71	159	105	221
70	141	286	127	261	136	276	76	169	116	241
80	158	316	142	288	150	302	82	180	125	257
90	186	367	164	327	184	364	91	196	141	286
95					209	408	100	212		
EP	244	471	198	388	220	428	138	280	184	363
Residue/Loss	unknown		unknown		3%		1%		unknown	

Low-Volatility Gasoline [6] RVP = 4.24 psi (29.3 kPa)

Indolene [6] RVP = 8.21 psi (56.6 kPa)

Medium-Volatility Gasoline [11] RVP = 11.45 psi (79.0 kPa)

Light Isocrackate [11] RVP = 11.5 psi (79.5kPa)

High-Volatility Gasoline [6] RVP = 15.1 psi (104 kPa)

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14. ABSTRACT *(Maximum 200 Words)*
An experimental and modeling study was done to determine the flammability of fuel tank headspace vapors as a function of ambient temperature for seven E85 (85% ethanol, 15% gasoline) fuel blends, two types of gasoline, and denatured ethanol at a low tank fill level. Samples in small, closed chambers were tested simultaneously in a cold chamber to determine flammability and pressure rise when ignited by a strong electric spark. Gasoline and E85 fuels were flammable below a critical temperature; above it, the vapor was too rich to burn. Denatured ethanol was flammable at room temperature and colder, down to a critical temperature; below it, the vapor was too lean to burn. The flammability limit temperature of the E85 and gasoline fuels related to the dry vapor pressure equivalent (DVPE), but DVPE did not reliably rank the low-temperature flammability hazards of fuel tank headspace vapors when conventional gasolines were compared with alcohol blends.

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E85; ethanol blends; fuel flammability studies; ethanol emissions; fuel tank vapors; gasoline vapors; denatured alcohol vapors

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