

Vapour Space Flammability Measurements of High Ethanol (“E85”) and Low Ethanol (“E10”) Winter Automotive Fuels: Effects of Fuel Composition and Vapour Pressure

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ABSTRACT

This paper presents an experimental study of the vapour space flammability of Fuel Ethanol (a high-ethanol fuel for Flexible Fuel Vehicles, commonly known as “E85”) and gasoline containing up to 10% ethanol (commonly known as “E10”). The seasonal minimum vapour pressure limits in specifications for automotive spark ignition fuels are intended, in part, to minimize the formation of flammable mixtures in the headspace of vehicle fuel tanks. This is particularly important at subzero temperatures, where the headspace mixture may not be rich enough to prevent combustion in the presence of an ignition source such as a faulty electrical fuel pump. In the current study, the upper temperature limits of flammability were measured for field samples of “E85” and “E10”, and a series of laboratory-prepared blends of denatured ethanol, Before Oxygenate Blending (BOB) gasoline, and n-butane. The paper compares the measured flammability limits with the ambient temperatures of the field sampling locations, documents the relationship between vapour space flammability and vapour pressure, and discusses the requirements for achieving gasoline-like flammability performance at high ethanol levels.

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INTRODUCTION

The North American light duty vehicle fleet includes a substantial number of Flexible Fuel Vehicles (FFVs) which can operate using fuels containing up to 85% denatured ethanol. Such high ethanol fuel formulations are commonly identified as “E85”, but officially defined as “Fuel Ethanol”. When these vehicles are operated in climatic regions with very cold winter temperatures, the portion of denatured ethanol in the fuel is normally reduced to well below 85% in order to increase the portion of volatile hydrocarbons, thereby improving the volatility of the blend. This is necessary to provide adequate cold starting and driveability, as well as to avoid the formation of flammable mixtures in the fuel tank vapour space.

The volatility of the blend is specified in terms of vapour pressure, and measured by the ASTM D5191 Dry Vapour Pressure Equivalent (DVPE) test method. [Table 1](#) presents a comparison of the vapour pressure limits in the Canadian and U.S. automotive fuel ethanol standards for the four seasonal volatility classes of fuel. The minimum vapour pressure limits for each class are intended to ensure adequate volatility at low ambient temperatures (for cold starting, driveability, and the avoidance of flammable mixtures), while the upper vapour pressure limits are intended to avoid evaporative emissions and hot fuel handing problems.

Table 1. Canadian and U.S. Vapour Pressure Requirements for Automotive Ethanol Fuel

National Standard	Class 1 (I)	Class 2 (II)	Class 3 (III)	Class 4 (IV)
CAN/CGSB 3.512-2013	38-62 kPa	45-72 kPa	62-86 kPa	80-107 kPa
ASTM D5798-15	38-62 kPa	48-65 kPa	59-83 kPa	66-103 kPa

This paper is concerned primarily with the minimum vapour pressure requirements of Canadian winter fuels, Class III and Class IV, which are intended for 10% low-end design temperatures of $\leq -7^{\circ}\text{C}$ and $\leq -20^{\circ}\text{C}$ respectively. Canadian minimum vapour pressure limits are slightly higher than U.S. limits for Class III volatility (62 kPa versus 59 kPa), and substantially higher for Class IV volatility (80 kPa versus 66 kPa). The Canadian fuel ethanol standard (CAN/CGSB - 3.512 [1]) states that “The minimum vapour pressure limits specific to the respective volatility classes exist to help minimize the formation of a flammable mixture in the vapour space of the fuel tank at low temperature”. The U.S. standard specification for ethanol fuel blends for flexible-fuel automotive spark ignition engines (ASTM D5798 [2]) states that “The addition of hydrocarbon blendstock to fuel ethanol changes its volatility and can effect the flammability of fuel tank vapors”.

Appropriate seasonal vapour pressure limits can ensure that fuel tank vapour space mixtures are always too rich to be flammable so that it would be impossible for an ignition source (such as a faulty electric fuel pump) to cause a vehicle fire. However, there is limited information available about the actual temperature limits of flammability for real-world fuel ethanol blends, how these limits compare with those of the “status quo” that exists for low ethanol gasoline (“E10”), and the minimum vapour pressure values needed to achieve the desired temperature limits.

In the present study field samples of fuel ethanol (“E85”) and gasoline (“E10”) were tested for vapour pressure, ethanol content, and hydrocarbon composition. Throughout this paper, the term “E85” does not refer to the actual ethanol content of the fuel samples, but is used to identify fuel ethanol obtained from refuelling pumps that were labelled “E85”. Additional samples were prepared by blending denatured ethanol, winter Conventional Before Oxygenate Blending (CBOB) gasoline, and n-butane.

For each sample, the upper temperature limit of flammability (the temperature at and below which flammable mixtures were formed) was measured using a specialized test method in which small rectangular combustion chambers were refrigerated while filled to 5% volume with the test fuel (intended to simulate a vehicle fuel tank at its minimum fill level). Ignition was then attempted using a high energy spark and flammability was determined based upon the level of pressure rise from combustion. The paper compares the measured upper temperature limits of flammability with the ambient temperatures of the field sampling locations, documents the relationship between vapour space flammability and vapour pressure, and discusses the requirements for achieving gasoline-like flammability performance at high ethanol levels.

BACKGROUND

Flammability Limits

This paper is concerned with the upper temperature limit of flammability of gasoline and ethanol/gasoline blends. The upper temperature limit of flammability is the highest temperature at which the vapour/air mixture from a liquid fuel sample is flammable. Further increases in temperature will lead to a mixture that is too rich to be flammable. According to Rowley [3], there is currently no standardized method of determining the upper temperature limit of flammability. The study of upper temperature limits of flammability for gasoline and ethanol/gasoline blends using non-standard test methods includes the work of Persson et al [4], where fuel-air mixtures were prepared in refrigerated containers, and transferred to an “explosion chamber” where tests were conducted at room temperature.

The lower temperature limit of flammability is much more widely used, and is better known as the flash point. At temperatures below the flash point, the vapour/air mixture from a liquid fuel sample is too lean to be flammable. Flash point measurements using methods such as ASTM D93 and ASTM D7094 are the dominant means of assessing fire hazards during the storage, handling and transportation of flammable liquids, including critical situations such as the

transportation of hazardous goods by air. Another means of measuring the lower temperature limit of flammability is described in ASTM test method E1232 [5], where a glass test vessel is used to create a homogeneous fuel/air mixture.

The term “flammability limit” is most often used to describe the range of fuel/air concentrations that will support flame propagation. The upper (rich) and lower (lean) volume % concentration limits are frequently reported at 25 °C, and are also referred to as the upper and lower “explosive” limits. These limits have been published in a wide variety of sources, but not sources all report identical limits for flammable liquids. According to Catoire and Naudet [6], the International Chemical Safety Cards (ICSCs) and the National Institute for Occupational Safety and Health (NIOSH) are the major sources of reliable data.

The original sources for such data are rarely identified, but many of the published values are identical or very similar to those originally reported in the classic U.S. Bureau of Mines publications by Coward and Jones (Bulletin 503, 1952 [7]) and Zabetakis (Bulletin 627, 1965 [8]). Coward and Jones reported a range values for each chemical, obtained using a wide variety of apparatus designs and experimental conditions. The values typically used in current flammability limit compilations are the greatest upper concentration limits and the smallest lower concentration limits from Coward and Jones.

These values were obtained using a vertical glass tube of 5 cm inside diameter and 150 cm length, with the lower end closed and the upper end open. The mixture was ignited at the lower end, and was deemed to be flammable if the flame could propagate upwards the length of the tube. This configuration results in the widest flammability limits possible because the buoyancy of the hot gases assists flame propagation up the tube. Tests for flammable liquids were typically conducted with the mixture heated to 60 °C, rather than the 25 °C condition often reported in secondary sources.

As discussed by Zabetakis [8], the lower temperature limit of flammability can be calculated from the lower concentration limit of flammability and the vapour pressure curve of the flammable liquid in question. He referred to this as the “approximate flash point”. The approach is also discussed in ASTM E1232 as a means of estimating a safe temperature at which to begin ignition trials, in order to avoid the “energetic explosions” that could occur if the mixture was well within the flammable range.

Zabetakis cautioned that such calculations predict lower temperatures than the actual flash point. According to Rowley [3], the difference results from “the less than ideal conditions under which the flash point is determined”, particularly downward rather than upward flame propagation. It is noteworthy that calculated lower (or upper) temperature limits for common flammable liquids are not listed in any of the prominent sources of fire safety data. Flash point experiments are still used to identify the existence of flammability hazards.

Upper temperature limits of flammability can also be calculated from concentration limit data, using the upper concentration limit and the vapour pressure curve in this case. Comparisons between these calculations and measurements with the apparatus of the present study (using several pure hydrocarbons) have been reported by Cracknell et al [9]. The predicted upper temperature limits were 1-10 °C higher than the corresponding experimental results. This is not surprising, given that (like comparisons with the flash point) conditions for flame propagation in the apparatus are less ideal than those of upward propagation in a vertical flame tube. Nevertheless, it is believed that the apparatus used in the present study provides a good representation of vehicle fuel tanks, where significant horizontal and downward flame propagation would occur at the flammability limit. The following discussion addresses the differences between this apparatus and those of well-known standard test methods for upper and lower concentration limits of flammability.

Characteristics of the Apparatus used in the Current Study

The apparatus used in the current study was developed specifically to measure the upper temperature limit of flammability of gasoline and ethanol/gasoline blends. The design criteria included operation at temperatures as low as -40° C, the ability to withstand any explosive pressure rise that might occur (without the need for a pressure relief mechanism), and the ability to measure and record pressure/time data throughout the entire combustion event (rather than, for example, relying on visual observation of the combustion event or actuation of a pressure relief valve to identify flammability). The need to conduct replicate tests on a large number of fuel samples led to the use of relatively small combustion chambers so that up to 8 chambers (containing identical fuel samples or different fuel samples) could be tested during a single refrigeration cycle.

As discussed by Rowley [3], experimental determinations of flammability range are apparatus dependent. Critical factors include the direction of flame travel, the influence of quenching effects (as the flame encounters a vessel wall), and the criterion used to define flammability. Rowley discussed three standard test methods (for flammability concentration limits) in detail: The Bureau of Mines 5 cm x 150 vertical glass tube, the EN 1839 8 cm x 30 cm vertical glass tube, and the ASHRAE 12 L spherical flask.

In the current apparatus, the internal volume of the combustion chamber is 296 ml. The spark gap is located 14 mm below the “roof” of the chamber, 30 mm above the “floor”, and 62 mm/104 mm from the near and far horizontal walls respectively. Thus, the flame propagation leading to a pressure rise within the chamber is mainly horizontal and downward (as would be the case for common shapes of vehicle fuel tanks, which tend to be relatively flat). Based on the direction of flame travel alone, this would be expected to produce narrower flammability limits than any of the aforementioned test methods, all of which rely on upward flame propagation.

Initial wall quenching effects for horizontal and downward flame propagation in the apparatus would be similar to the vertical tube apparatus of the Bureau of Mines method (where the spark gap is 25 mm from the vertical tube walls) and the EN 1839 method (where the

spark gap is 40 mm from the vertical tube walls). Wall quenching effects would be expected to be much greater than those in the large ASHRAE 12 L spherical flask. Depending upon the location of the ignition source and the fuel tank geometry, wall quenching effects in the current apparatus are potentially greater than those in a vehicle fuel tank.

However, the criterion for flammability used in the current apparatus (a minimum pressure rise of 200 kPa) is substantially lower than the pressure rise values that actually occur with mixtures that are identified as flammable (typically 300-400 kPa, as shown later in Figure 7). Thus, it is believed that for flame propagation in the horizontal and downward directions, the minimum pressure rise criterion is exceeded before most of the flame front reaches the floor or vertical walls. If this is the case (this hypothesis has yet to be verified), wall quenching would have less impact on the results.

Considering the factors described above, it is clear that the apparatus used in the current study does not provide the widest possible flammability limits, so the upper temperature limits of flammability reported in this paper may be lower than those that could occur in vehicle fuel tanks. On the other hand, it is unlikely that the ideal conditions created by the standard test methods (central ignition and unimpeded vertical flame propagation) exist in most vehicle fuel tanks. Finally, it is noteworthy that the remainder of the paper will show that the upper temperature limits of flammability measured for winter gasoline samples were only slightly colder than the minimum ambient temperatures where the fuel was used. Thus, the measurements do not show a substantial safety margin for current practices in terms of the avoidance of flammable vapour space mixtures.

EXPERIMENTAL METHOD

Field Sampling

E85 and gasoline fuel samples were obtained over the winter season from a commercial facility in Ottawa and a fleet refueling facility in the Montreal geographic region (2013/2014). A second season of sampling was carried out at the Ottawa location (2014/2015). The fuel samples were obtained using apparatus and procedures derived from ASTM D5842 [10], the “Standard Practice for Sampling and Handling of Fuels for Volatility Measurements”. Fuel sample quantities of 2 litres were collected in 2.5 litre sampling containers to maintain the 70-85% fill volume range specified ASTM D5842. At least two containers were filled with each fuel sample in order provide separate sub-samples for flammability testing and for delivery to the laboratories that carried out the vapour pressure and chromatography measurements.

The sampling containers were chilled prior to sampling, and were transported and stored chilled once filled. 5 litres of fuel was “flushed” from the fuel dispenser into a waste container prior to any transfer of fuel to the sampling containers. Transfers of fuel from the fuel dispenser nozzles to the sampling containers were done using a nozzle extension apparatus (based on the recommendations of ASTM D5842).

Laboratory Blends

A set of laboratory fuel blends were prepared from denatured ethanol and winter grade Conventional Before Oxygenate Blending (CBOB) gasoline to produce samples containing denatured ethanol (E_d) levels of 0%, 10%, 20%, 30%, 50%, 75%, and 85% by volume. Additional E_d75 and E_d85 samples with improved volatility were prepared by replacing a portion of the CBOB in the blend with n-butane.

Denatured ethanol and CBOB were blended on a volumetric basis, with the mass of the components and final blend recorded. The blending process was carried out with the blend components and containers chilled to below -10°C in order to avoid vapour losses. In cases where n-butane was added, the butane container was also chilled to below -10°C , and the butane was bubbled through the chilled sample through a filter positioned at the bottom of the sample container. The additional butane content was calculated based upon the mass increase of the sample after the butane was added.

Fuel Analysis

The vapour pressure of all samples was measured using the ASTM D5191 Dry Vapour Pressure Equivalent (DVPE) method. The ethanol content of the E85 field samples was measured using the Gas Chromatograph (GC) analysis method of CAN/CGSB-3.0 No. 14.3. This method was also used to determine the hydrocarbon composition of the E85 field samples and the CBOB used in the laboratory blends. The ethanol content of the gasoline samples was measured using an infrared ethanol blend analyzer (Wilks InfraCal).

Vapour Space Flammability Measurements

The upper temperature limit of flammability for the samples was measured using an apparatus consisting of rectangular, closed chamber, constant volume combustion bombs that are refrigerated in an environmental test chamber. Each of the chambers has an internal volume of 296 ml, and is equipped with a modified spark plug, a pressure sensor, and thermocouples for measurement of the air and fuel temperatures. A fuel fill level of 5% was used, representing a worst-case vehicle fill level before refueling (i.e., “empty” or “refuel” light of the vehicle would be activated). The impact of different fill levels is discussed in a later section of this paper.

The combustion chambers are initially chilled to below 0°C . After the fuel is introduced and the combustion chamber is sealed, the chamber is refrigerated to the final test temperature. This typically results in a small vacuum in the chamber once the test temperature is reached. Atmospheric pressure is then re-established by briefly venting the chambers (thus, drawing air into the chamber). The fuel tank pressure in vehicles may be slightly greater than atmospheric pressure (which would tend to reduce fuel vaporization and raise the upper temperature limit of flammability) or slightly less than atmospheric pressure (which would tend to increase fuel vaporization and lower the upper temperature limit of flammability). The effect of pressure on the upper temperature limit of flammability has not been quantified with this apparatus.

In order to ensure adequate time for vapour/air mixing, the flammability test is conducted 3.5–4.0 hours after the sample is introduced into the combustion chamber. The environmental chamber has a powerful air circulation system that accelerates heat transfer from the combustion chambers. Thermal equilibrium (stable liquid and gas temperatures within the combustion chamber) is typically achieved within the first 1.5–2 hours.

Persson et al [3] have shown that even with true E85 (85% ethanol in the liquid phase), very little ethanol is present in the gas phase at low temperatures. For example, at -25°C , the fraction of ethanol in the gas phase was only about 5% (that is, only 5% of the fuel vapour was ethanol). Consequently, it is unlikely that gradient effects (due to the differing densities of gasoline hydrocarbons and ethanol vapours) would have affected the results.

In this study, 4 chambers were used at each temperature to permit replicate tests of a fuel sample. After conditioning the chambers to the test temperature, ignition of the mixture is attempted using a unique high energy ignition system. The occurrence of sufficient flame propagation to identify the mixture as flammable is determined by an increase in chamber pressure (due to combustion) that exceeds a threshold value of 200 kPa. The impact of the choice of pressure rise threshold is discussed later in this paper.

The ignition system used in the study discharged over 1 Joule of stored energy into an ignition coil, providing a 2 ms spark duration with a 50–100 mA saw-tooth current waveform. An even greater source of ignition energy might be provided by the electrical equipment in a vehicle fuel tank if the failure event led to heating and vaporization of electrical conductors (e.g., copper wiring glowing red hot and exploding). However, the upper temperature limits of flammability determined in the current study were based upon flame propagation limits (combustion pressure rise of less than 200 kPa) rather than ignition limits. At temperatures above the reported limits, the ignition energy was still sufficient to ignite the fuel-air mixture and produce small pressure rises from combustion. Thus, greater ignition energy would not be expected to change the upper temperature limits of flammability that were determined during the study.

Figure 1 shows examples of pressure rise measurements from an E85 fuel sample (55% actual ethanol content) over a temperature range of 3 degrees C. Each graph shows data from 4 consecutive tests using 4 different combustion bombs. At temperatures below the flammability limit (-29°C in this case), the pressure traces from individual tests were very consistent with peak values well above the aforementioned flammability threshold. In this case, the vapour space mixture of the sample was 100% flammable at -29°C .

At temperatures at or near the flammability limit, pressure traces with inflections or plateaus were typically encountered, and some tests would produce abnormally low peak pressure values. Such behavior occurred at -28°C with this sample. In this case, two tests produced peak pressure rise values well above the flammability threshold, while the peak pressure values of the other two tests were well below the flammability threshold. Thus, this series of tests showed a 50% probability of flammability at this temperature.