

Measurement of Vapor Pressures and Enthalpies of Vaporization of Gasoline and Ethanol Blends and Their Effects on Mixture Preparation in an SI Engine

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ABSTRACT

Global ethanol trade is forecast to increase 25-fold by 2020. Most of it will be blended with gasoline to make biofuel. However, blending ethanol with gasoline has a profound effect on the evaporation characteristics of the mixture. In particular, the thermodynamic properties of the blends can be significantly different than the constituents. A clear understanding of the blend's properties is essential for optimizing engine design, e.g. utilizing charge cooling effect.

Data available in the literature is very limited, considering ethanol-gasoline blends will be used as a fuel in large scale worldwide. In this work, comprehensive measurements of vapor pressures were carried out. The enthalpies of vaporization were derived from vapor pressure data using the Clausius-Clapeyron equation. Maximum vapor pressure occurs with 20% ethanol-gasoline blend at which a positive azeotrope is formed. The trend is different in enthalpy of vaporization. The results presented here contradict previous claims that the enthalpy of vaporization is a linear function of ethanol content. Such a trend is true up to 20%; the value then decreases a little and appears to flatten out between E30 and E60. After E60, it begins to increase again.

The ethanol-gasoline blends were tested in a port injected SI engine. The evaporation characteristic of the fuel was assessed by measuring the cycle-resolved temperature in the cylinder. The results have shown that low ethanol blends (0–30%) tend to evaporate readily, but the evaporative cooling is limited by the relatively low fuel flow rate (at fixed stoichiometry) and enthalpy of vaporization. High ethanol blends (>50%) with reduced vapor pressure cannot evaporate readily, but if they do vaporize, then they absorb large amounts of energy per unit mass. The implication of these competing effects is that maximum cooling is achieved using a blend with about 50% ethanol. A parameter “potential evaporative power” is introduced to estimate these effects.

INTRODUCTION

Global ethanol trade is forecasted to increase 25-fold by 2020 [1]. Most of it will be blended with gasoline to make biofuel. Recently, governments around the world have various legislations and subsidies promoting the use of biofuel. For example, all unleaded gasoline (ULG) sold in New Zealand will contain 3.4% of ethanol by 2012 [2]. Ethanol is seen as a renewable fuel that can reduce greenhouse gas emissions. For countries which are the net producer of ethanol, using ethanol as a fuel can reduce the dependence on oil imports, and also promote the local agricultural sector.

As pure fuel, ethanol is not volatile enough to be used under cold conditions. Brinkman *et al.* [3] and Gardiner *et al.* [4] reported cold starting difficulties with pure alcohol fuels. Blending it with gasoline can alleviate this problem. Such a blend is usually called by an E designation followed by two digits, which indicates the percentage of ethanol (by volume) in the fuel. For example, E85 has 85% ethanol and 15% gasoline. In some countries, it is also generally known as gasohol. However, blending ethanol with gasoline has a profound effect on the evaporation characteristics of the mixture. Ethanol and gasoline form an azeotrope when they are mixed together, which has significantly different properties than the original components. For instance, it has been widely reported that ethanol and gasoline blend has a higher vapor pressure than either component, causing an increase in evaporative emissions. Given that most of the ethanol will be blended with ULG to make fuel in the future, it is important to understand the effect of blending on fuel properties so as to optimize engine design and to control tailpipe and evaporative emissions.

There are only limited fuel properties of ULG-ethanol blends in the literature. Nan *et al.* [5, 6] measured specific heat of gasohol extensively over 78–320 K, and provided polynomial equations to model the specific heat as a function of temperature. Pumphrey *et al.* [7] and Balabin *et al.* [8] studied the vapor pressure of gasohol. Pumphrey *et al.* found that the Wilson equation could

predict the vapor pressure very accurately. Balabin *et al.* utilized the data to calculate the enthalpy of vaporization for blends with up to 20% ethanol. Other researchers [9, 10, 11] provided some fuel properties e.g. the density of gasohol used in their studies. This paper will focus on two thermodynamic properties: vapor pressure and enthalpy of vaporization. These properties are considered the most important for assessing the evaporation characteristics of different ULG-ethanol blends.

A total of 8 ULG-ethanol blends are considered. The methodology and apparatus for fuel properties measurements will be described. The results will be compared with published values, and discussed in relation to the azeotropic behavior. Finally, the effects of fuel properties on mixture preparation have been investigated in a port injected SI engine. In-cylinder temperatures were measured when the engine was motored with fuel injection. The principle of this thermometry and the results will be discussed. By analyzing suitable temperature parameters, the effects of fuel properties on mixture preparation will be examined, e.g. charge cooling during intake, evaporation in the compression stroke and liquid droplets entering the cylinder.

BASE FUEL PROPERTIES

The base fuel used in this study was New Zealand regular grade unleaded gasoline. Some fuel properties are given in Table 1.

Density @20°C [kg/L]	0.767 +/- 0.03
Reid Vapor Pressure (RVP) [kPa]	45–95
Research Octane Number (RON)	91 min.
Motor Octane Number (MON)	82 min.
Olefins [% v/v]	18
Aromatics [% v/v]	22–42
Oxygenates	0
Benzene [% v/v]	1 max.
Evaporated fraction @70°C [% v/v]	22–48
Evaporated fraction @100°C [% v/v]	45–68
Evaporated fraction @150°C [% v/v]	75 min.
Sulfur content	150 ppm max.

Table 1. Base fuel properties [12]

The fuel was stored in a 20-L sealed tank. Fuels for all tests were subsequently drawn from this tank, eliminating any change in composition due to refilling or evaporation.

This base fuel was blended with ethanol to form the fuel blends for experiments. The blending was done on a volume basis. For example, if 0.3 L of ethanol is mixed with 0.7 L of ULG, the mixture is referred to as E30. The ethanol is supplied by Anchor Ethanol in New Zealand. The feedstock for making this ethanol is whey [13], which is a by-product in dairy production. In contrast, bioethanol in the world is mainly produced using food crops such corn or sugar cane. Some properties of this ethanol is given in Table 2.

Density @20°C [kg/L]	0.7904
Normal boiling point [°C]	78.32
Normal freezing point [°C]	-114.1
Vapor pressure @20°C [kPa]	5.9
Dynamic Viscosity @20°C [mPa.s]	1.2
Molecular weight [kg/kmol]	46.07

Table 2. Some properties of ethanol used in experiments [14]

The ethanol as supplied was denatured by adding 2% methanol. Since methanol and ethanol belong to the same chemical family, their thermodynamic properties are similar. Density and vapor pressure measurements of this denatured ethanol agree with the published values of pure ethanol. Therefore, the effect of methanol is considered negligible.

Another issue is the hygroscopic nature of ethanol. Previous research has shown that a few percent of water in the ethanol can significantly alter the properties of a fuel after it has been blended with ULG [8]. Throughout the experiment, the density of ethanol had been monitored, it was always within 0.4% of the specification. Thus, it is concluded that no significant water absorption occurred.

BLENDS OF ULG AND ETHANOL

A total of 8 fuel blends were tested. They were mixed on a volume basis in 1-L batches. Ethanol and ULG were measured in separate measuring cylinders with graduation of 2 mL ensuring an accuracy of within 1 mL. The ethanol and gasoline were then poured into the same cylinder where they were mixed thoroughly. Blends were stored in 1-L sealed metal containers in a cool rooms between tests. Table 3 shows the blends prepared for testing.

Blend name	Ethanol content [% v/v]
E0	0
E10	10
E20	20
E30	30
E50	50
E60	60
E85	85
E100	100

Table 3. Blends used in experiments

IN-CYLINDER TEMPERATURE MEASUREMENT

Ethanol can absorb 2–3 times more latent heat per unit mass than ULG in the process of vaporization. When liquid fuel is being injected into the inlet manifold, it evaporates and absorbs heat from the intake air, manifold surface and the inlet valves. If the latent heat is predominantly supplied by air, the in-cylinder temperature will be lowered. Therefore, temperature measurements in the cylinder can be used to assess the evaporation characteristics of different fuel blends. Whilst fuel properties are often measured in steady state

where conditions are highly controlled, fuel evaporation in an engine is an inherently dynamic process. Besides fuel properties, fluid motion, spray droplet size, spray pattern, fuel film on the inlet manifold are some of the factors which determine the rate and completeness of evaporation. To investigate how different ULG-blends evaporate in a port-injected SI engine, a fast response thermometer was installed in the engine to measure the transient temperature within a cycle. As the probe was very fragile, the experiment was conducted under non-firing conditions. Similar studies conducted by Price *et al.* [15] in a direct injection SI engine found that the measurements could be used to indicate the quality of mixture preparation. Equipment, experimental procedures and results will be described later in this paper.

ENGINE APPARATUS

ENGINE

The engine used is a Ricardo E6 single cylinder research engine. It has a flat combustion chamber and a flat-top piston. The original carburetor system was replaced with a fuel injector system recently. The fuel injector was controlled by an Autronic ECU unit. The injection pressure was maintained at 276 kPa (gage), whilst the injection duration varies from 10–30 ms. The intake was connected to a Meriam laminar flow meter element, so that the air flow rate can be determined by measuring the pressure drop across the element. In-cylinder pressure was measured using a water-cooled piezo-electric pressure transducer (Kistler 601A) and a Kistler type 5011B charge amplifier. Apart from in-cylinder pressure, cyclic resolved temperature measurements were made in non-firing conditions. Details will be discussed in subsequent section.

A LabVIEW data acquisition system logged the high speed pressure and temperature data at every crank angle. It also recorded engine speed, torque, atmosphere pressure, humidity, oil pressure, and a few important temperatures of the intake air, coolant, exhaust and engine oil. The engine operating conditions and specifications are summarized in Table 4.

Type	4-Stroke
Combustion System	Port injected, spark ignition
Bore x Stroke	76.21 x 111.11 mm
Swept Volume	507 cm ³
Compression Ratio	7.0:1
Engine Speed	1500 rpm
Throttle position	WOT
Coolant temperature	60–65°C
Injector	Bosch pinto type
Fuel Pressure, gage	276 kPa (40 psi)
End of injection	TDC exhaust
Inlet valve opening (IVO)	7 CAD bTDC
Inlet valve closure (IVC)	36 CAD aBDC
Exhaust valve opening (EVO)	42 CAD bBDC
Exhaust valve closure (EVC)	7 CAD aTDC

Table 4. Engine specifications and operating conditions

VAPOR PRESSURE RIG

An ASTM standard test method D4953-99a “Standard Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)” [16] was adapted to measure the vapor pressures of fuel blends. The test method involved construction of two interlinking chambers with a pressure gage attached. A schematic of the test rig is shown in Figure 1. The standard prescribes measurements to be taken at 37.8°C, but in order to calculate enthalpy of vaporization, vapor pressure readings at different temperatures are required. Therefore instead of taking measurements at 37.8°C, readings were made at 30, 40, 50 and 60°C.

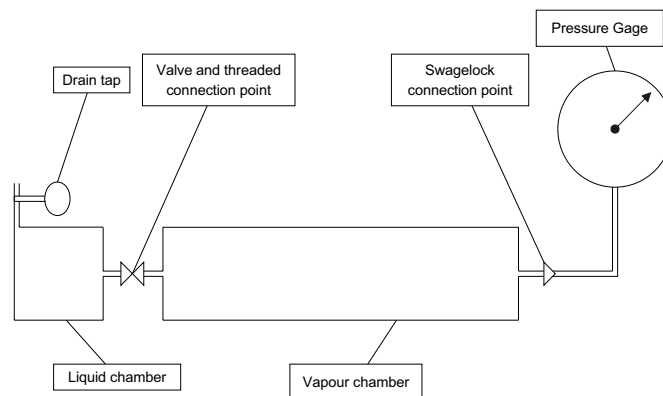


Figure 1. Schematics of the vapor pressure rig

Tests were repeated on different days and by different operators. It was found that readings were within 2 kPa, which was within acceptable limits as stated by the standard.

COLD WIRE THERMOMETRY

The in-cylinder temperature varies vastly and rapidly from ambient temperature to combustion temperature in millisecond timescales. In order to resolve features within an engine cycle, a sensor must have a response time in the range of milliseconds or better. A cold wire resistance thermometer is a good candidate. Its sensor is made up of a 5-μm platinum coated tungsten wire, which ensures minimal thermal inertia, and hence a fast response time. Price *et al.* [15] have established that such a sensor is fast enough to study the fuel injection event, as well as temperature changes in the cylinder due to compression.

The cold wire resistance thermometer does not measure the temperature of gas directly. What it measures is the resistance changes of the wire whose temperature-resistance relationship is monotonic. The probe was connected to a TSI Model 1745 constant current supply (normally used for an anemometer). This unit measured the resistance changes, and gave an output as a voltage. The principle of operation is discussed in detail

in [17]. A small electric current flows through the resistance wire. The higher the current, the stronger the signal but at a cost of increased sensitivity to velocity changes. The current was set to 0.986 mA, which is considered a good compromise between high signal-to-noise ratio and velocity interference. A good DC power supply was required to power the constant current supply because any electrical fluctuations, e.g. 100/120-Hz ripples, will show up in the measured temperature signal. A regulated DC power supply with very low ripple level was used. The temperature output was monitored in an isothermal environment, the resulting ripple due to the power supply was less than 0.15 K peak-to-peak.

The cold wire probe was installed in place of a spark plug using a specially designed adaptor. A diagram of the probe and the probe adaptor is in Figure 2. The adaptor was designed to locate the measurement point which was 3 mm above the combustion chamber surface. This was where the spark would have been located if the spark plug was there. The adaptor was in two halves which allowed the cold wire probe to be inserted safely with minimal risk of breaking the wire. The adaptor had a shield around the protruding wire element to protect it from fluid and accidental damage. Literature [18] suggested that it can withstand high speed gas flow (> 50 m/s), but not solid particles and liquid droplets impacting on it. In addition, the shield minimized the chance of wetting the probe with liquid fuel, or a wet bulb temperature would be measured.

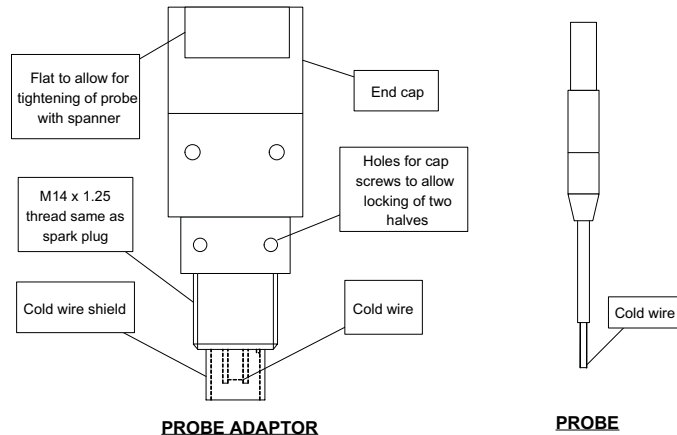


Figure 2. Schematic of the cold wire probe and adaptor

At the beginning of testing, it was unsure if the cold wire probe was strong enough to withstand the hostile environment in the cylinder, as well as potential damage from liquid fuel. The probe current was monitored throughout testing. Any wire breakage or drift in performance will firstly show in the current reading. Photos were taken of the probe after one run and after all testing had finished. As Figure 4 shows, it was able to withstand a significant amount of deposit without breaking. The probe current stayed constant at 0.986 mA, so no change in calibration had occurred.

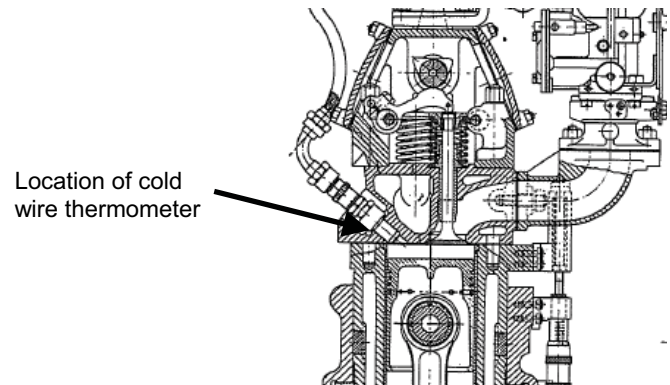


Figure 3. Location of the cold wire resistance thermometer in a cross sectional view of the Ricardo engine [19]



Figure 4. Photographs of the probe after one run (left) and after all testing was completed (right)

ENGINE TEST PROCEDURES

FUEL INJECTOR CALIBRATION

Ethanol is an oxygenate fuel, so it tends to lower the stoichiometric air-fuel ratio when it is blended with ULG. Table 5 summarizes the stoichiometric air-fuel ratio for various blends. To obtain a correct air-fuel mixture, fuel mass flow needs to be known and controlled. The fuel flow rate through a fuel injector is controlled primarily by the injection pressure and the injection duration. To a lesser extent the fuel flow rate is also controlled by fuel viscosity and temperature.

Fuel	Stoichiometric air-fuel ratio [m/m]
ULG	14.5
E10	13.9
E30	12.8
E50	11.7
E85	9.8

Table 5. Stoichiometric air-fuel ratio for different ethanol-ULG mixtures.