

Heat of Vaporization Measurements for Ethanol Blends Up to 50 Volume Percent in Several Hydrocarbon Blendstocks and Implications for Knock in SI Engines

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ABSTRACT

The objective of this work was to measure knock resistance metrics for ethanol-hydrocarbon blends with a primary focus on development of methods to measure the heat of vaporization (HOV). Blends of ethanol at 10 to 50 volume percent were prepared with three gasoline blendstocks and a natural gasoline. Performance properties and composition of the blendstocks and blends were measured, including research octane number (RON), motor octane number (MON), net heating value, density, distillation curve, and vapor pressure. RON increases upon blending ethanol but with diminishing returns above about 30 vol%. Above 30% to 40% ethanol the curves flatten and converge at a RON of about 103 to 105, even for the much lower RON NG blendstock. Octane sensitivity ($S = \text{RON} - \text{MON}$) also increases upon ethanol blending. Gasoline blendstocks with nearly identical S can show significantly different sensitivities when blended with ethanol. HOV was estimated from a detailed hydrocarbon analysis (DHA) as well as using a differential scanning calorimetry/thermogravimetric analysis (DSC/TGA) method. The DHA method allows relatively straight-forward estimation of fuel composition and temperature effects, and errors are estimated at less than 10%. The DSC/TGA produces results in good agreement with DHA, and can provide HOV as a function of fraction evaporated. A striking feature of the HOV results was the insensitivity of HOV to the hydrocarbon blendstock for temperatures up to 150°C - all four hydrocarbon blendstocks had essentially the same HOV in kJ/kg and exhibited the same HOV response to blending with ethanol. HOV is much less variable than RON or S . HOV at 20% evaporated from the DSC/TGA experiment appeared to be unaffected by ethanol content while HOV at 50% evaporated increased monotonically with ethanol content.

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INTRODUCTION AND BACKGROUND

The introduction of more stringent standards for fuel economy as well as greenhouse gas emissions [1] is driving research to increase the efficiency of spark ignition (SI) engines. Approaches for increasing SI engine efficiency include increased compression ratio, direct injection (DI), turbocharging, downsizing, and down-speeding. Higher octane number (more highly knock resistant) fuels allow improved combustion phasing and operation at higher loads at the same engine speed, while also allowing the higher in-cylinder temperature and pressure generated by increased compression ratio and turbocharging which are critical for downsizing and down-speeding [2,3,4]. At the same time, renewable fuel usage is mandated to increase in the United States under the Renewable Fuel Standard [5], and globally under laws enacted in other countries. Ethanol, the most commonly used renewable fuel, has a research octane number (RON) of approximately 110 [6] compared to typical U.S. regular gasoline at 91-93 [2]. Accordingly, high octane number ethanol blends containing from 20 volume percent (vol%) to 40 vol% ethanol are being extensively

studied [3, 7,8,9,10]. A unique property of ethanol is its high heat of vaporization (HOV), which significantly increases charge cooling for DI engines, providing additional knock resistance.

The tendency of a spark-ignited engine fuel to autoignite and cause knock is measured as the octane number, a critical performance parameter for SI engines. In the United States, octane number at the retail pump is given as the anti-knock index, the average of two octane number measurements: research octane number (RON) (ASTM D2699-13b) and motor octane number (MON) (ASTM D2700-13b). The primary differences between the RON and MON measurements are fuel-air charge temperature and engine speed, with the RON test using a comparatively low fuel-air charge temperature (that is dependent on the fuel's latent heat of evaporation) and slower engine speed while the MON test is conducted at a significantly higher fuel-air charge temperature (149°C) and faster engine speed. Recent studies have demonstrated that MON is correlated with different effects in modern engines than was the case when these tests were introduced in 1932, and in fact increasing MON at constant RON may actually lower the fuel knock resistance. The

difference between RON and MON is called sensitivity, $S = \text{RON} - \text{MON}$, and represents the sensitivity of the fuel autoignition kinetics to the unburned gas temperature [8]. Kalghatgi [12], and Mittal and coworkers [13] have shown that fuels with higher S have slower autoignition kinetics at lower temperatures and faster autoignition kinetics at higher temperatures, compared to fuels with lower S .

Given the high RON of ethanol, it is commonly blended into a sub-octane blendstock for oxygenate blending having RON of approximately 84 to 88 [14] to produce finished gasoline having adequate knock resistance (in terms of the anti-knock index). The RON of blends above E10 has been measured in a variety of research projects [14,15,16,17]. Ethanol has a non-linear effect on the RON of the finished blend, with diminishing effect as the ethanol content is increased. The increase in RON depends on the starting RON of the blendstock, but increases to around 100 to 105 at E50. Ethanol exhibits a MON of 90 ($S=20$) and imparts sensitivity to hydrocarbon blendstocks with low S .

Fuel knock resistance for DI engines is enhanced by the fact that the fuel-air charge is cooled in the cylinder as the fuel evaporates, reducing the end-gas temperature. This is a major advantage of DI over other SI engine fuel systems and is important regardless of fuel type. However, at 25°C, the HOV of gasoline boiling range hydrocarbons is 350 to 400 kJ/kg while that of ethanol is 924 kJ/kg [3,18]. Because ethanol supplies some oxygen and reduces the amount of air required to burn the fuel, this heat of vaporization advantage is even greater when considered on a per kilogram of stoichiometric mixture basis where the value for hydrocarbon is 22 kJ/kg while that for ethanol is 92 kJ/kg [3]. There is experimental evidence that RON is affected by the HOV of the fuel [19]. However it is not clear that RON captures the full cooling experienced by the intake charge in a DI engine. At E30, this cooling effect may provide the equivalent of 5 to 10 RON units of knock resistance [20].

HOV is also a factor in vehicle driveability. If the fuel requires a higher amount of heat to vaporize at the same temperature, it will not vaporize as readily, in effect, acting like a fuel with a higher T10, T50, or T90 or will be more difficult to vaporize under cold start conditions [21]. The use of an estimation of the amount of heat needed to evaporate sufficient fuel to form an ignitable air-fuel-vapor mixture has been proposed as a fuel property parameter for predicting cold weather driveability [22].

A large database of HOV values for pure compounds has been published [23]. Users of this database are cautioned to carefully examine the source of the data as the database is all inclusive and includes values measured using poorly accurate methods as well as values that upon investigation were not measured, but predicted using various methods. However, the database does contain much high quality data that was measured using many different methods, but which primarily involve either direct or indirect measurement of vapor pressure as a function of temperature. The Clausius-Clapeyron equation is then integrated under the assumption that HOV is constant over a small temperature range and solved for HOV:

$$\ln P = A - \text{HOV}/RT \quad (1)$$

where P is pressure, A is a constant of integration, R is the ideal gas constant, and T is temperature. Data for ethanol and several hydrocarbon components of gasoline are shown in Figure 1. HOV decreases as temperature increases attaining a value of zero at the critical temperature. This effect is much larger for ethanol than for the hydrocarbon components. At 25°C, the HOV for ethanol is 924 kJ/kg while that for most hydrocarbon components of gasoline is between 350 to 400 kJ/kg.

Methods for measuring HOV of complex mixtures like gasoline are not well developed. Early studies measured vapor pressure as a function of temperature and applied the Clausius-Clapeyron equation [24, 25]. However, for broad boiling range mixtures like gasoline, the vapor pressure is determined by the most volatile components. For example, several different studies have shown that the initial boiling fractions or container headspace are enriched in the most volatile butane and pentane components of gasoline [26, 27]. This will result in significant errors in the HOV measurement, especially for blends with ethanol given its much higher HOV than gasoline hydrocarbon components.

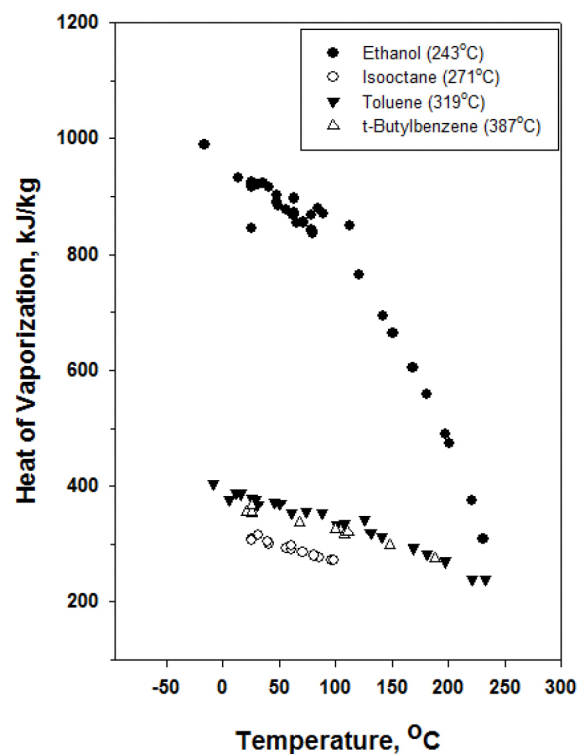


Figure 1. HOV of ethanol and several hydrocarbon components of gasoline, data from Chickos and Acree [23]. Values in parenthesis are the compound's critical temperature where HOV=0.

In principle, differential scanning calorimetry (DSC) could be used to measure gasoline HOV, although we have found no examples of this in the literature [28]. Detailed hydrocarbon analysis (DHA) by gas

chromatography has been used to estimate a number of gasoline properties such as the distillation curve from the pure component boiling points [29] and the octane number from pure component octane numbers [30]. This approach could also be used for estimating HOV. A correlation gas chromatography method has been used to estimate HOV for complex fuel mixtures [31]. This method is an indirect measurement of vapor pressure as a function of temperature for each component of the mixture, and then the Clausius-Clapeyron equation is applied to each component of the mixture.

Our objective has been to develop a clear understanding of how to measure HOV and how to quantify knock resistance for ethanol gasoline blends. Blends of ethanol at nominal 10, 20, 25, 30, 40, and 50 vol% were prepared with three gasoline blendstocks and a natural gasoline (NG). NG is also known as natural gas condensate and is a byproduct of natural gas production consisting primarily of pentanes. Performance properties and composition of the blendstocks were measured. A similar set of properties were measured for the ethanol blends, including RON, MON, net heating value, density, distillation curve, and vapor pressure. HOV was measured by DSC/TGA and estimated from DHA.

METHODS

Fuels

Gasoline blendstocks were obtained from petroleum refiners or local suppliers. These include a wintertime conventional blendstock for oxygenate blending (wCBOB), a California Air Resources Board reformulated blendstock (CARBOB), and a summer class AA blendstock from an ozone non-attainment area (sCBOB). An NG sample was obtained from a mid-stream company. Chemical-grade anhydrous ethanol was used. With the exception of blends in sCBOB, which were prepared volumetrically at room temperature, blending was performed using fuel that had been stored in a freezer overnight prior to blending. Using the densities of the base fuel and of the ethanol, the weight of each component needed to reach the target volume percent was calculated for each blend level and the fuel was blended by weight. Volume percent was measured by gas chromatography using ASTM Method D5501 for all blends. Samples were stored in a freezer in glass or aluminum containers with care to avoid excess headspace.

Fuel Properties

ASTM methods were used as written for most fuel properties. RON and MON tests were conducted at Southwest Research Institute.

DHA was performed by ASTM method D6729. In brief, a gas chromatograph equipped with a flame ionization detector and a cryogenic oven cooling valve was utilized for analysis. A Rtx-100 DHA (Restek, Bellefonte, PA) column of dimensions 100 m × 0.25 mm, 0.5 µm film thickness was used for separation of the hydrocarbons. The helium carrier gas was set to a flow rate of 2 mL/min in constant flow mode. The oven was programmed as follows: 0°C for 15 minutes, followed by a ramp of 1°C/min to 50°C, then 2°C/min to 130°C, then 4°C/min to 270°C with a 5 min hold. The flame ionization detector was set to 300°C, and the flow rates

were: 40 mL/min for hydrogen, 450 mL/min for air, and 30 mL/min for nitrogen. The injection port was set to 250°C, and samples were injected neat at 0.2 µL with a split ratio of 200:1. In order to identify the individual components, a certified hydrocarbon standard provided by Separation Systems (Gulf Breeze, FL) was used to determine individual hydrocarbon retention times for generation of DHA reports with its Hydrocarbon Expert 5 (HCE5) software. Once the components were identified and quantified, an Excel spreadsheet listing each component and the mole percent (mol%) present was generated. Because there were a few hundred components we eliminated any component that was <0.05 mol% which resulted in less than a 5% total reduction in sample.

HOVs of individual compounds were predicted at given temperatures following the method proposed by Reid, Prausnitz, and Poling [32]:

$$\frac{HOV}{RT_c} = 7.08(1 - T_r)^{0.354} + 10.95\omega(1 - T_r)^{0.456} \quad (2)$$

where HOV is the heat of vaporization, R is the gas constant (0.008314 kJ/mol K), T_c is the critical temperature, T is the desired temperature, T_r is the reduced temperature (T/T_c), and ω is the acentric factor. Critical temperature and acentric factor for individual compounds were taken from literature sources [33, 34].

The predicted HOVs in kJ/mol were multiplied by the mol% of each component present and then totaled. This value was divided by the total mol% of the sample (after removal of the minor components) and then divided by the average molecular weight of the gasoline (this value is also calculated by the HCE5 software) to give the HOV in kJ/kg. For ethanol blends the ethanol content measured by ASTM method D5501 and the predicted HOV of ethanol at the given temperature were factored into this calculation.

HOV was measured using a DSC/TGA method. A DSC/TGA Q600 (TA Instruments, Newcastle, DE) was used for all experiments. The instrument was calibrated using sapphire as a standard for heat flow and alumel and nickel as standards for weight loss. The instrument's cell constant was further calibrated using deionized water. Water was run three times and the HOVs were calculated and averaged. The average was compared to the reported literature value for water and the literature value/measured value ratio was calculated. All subsequent sample measurements were adjusted by this value.

Samples were prepared by storing them in a container with dry ice to limit evaporation during transfer to the sample pan. The sample was injected via microliter syringe into a 50 microliter aluminum pan (Mettler Toledo part# ME-51119872) with 75 µm laser drilled pin-hole aluminum lids (TA Instruments part# 900860.901) and a sample transfer time of 30 seconds. The experiment was initiated immediately upon loading of the sample into the instrument at a constant temperature of 23°C and nitrogen flow of 100 mL/min.

The heat flow values were corrected for zero heat flow by subtracting the baseline value measured after the sample had evaporated from the measured heat flow at each point. Heat flow at each point was then corrected for the cell constant determined from calibration of the

instrument with deionized water. The DSC data were plotted as heat flow (in milliwatts) versus time (see example in Figure 2), and the area under the curve was estimated using the trapezoid method. This corrected area under the curve is the total heat flow to the sample in millijoules required for evaporation. This value was divided by the total mass of the sample to give the sample total HOV. The HOV of pure ethanol was measured as 936 kJ/kg which is within 1.3% of the 924 kJ/kg value commonly reported in the literature [3, 18]. The heat flow and TGA (sample mass) data were combined to estimate a HOV as a function of mass fraction of sample evaporated.

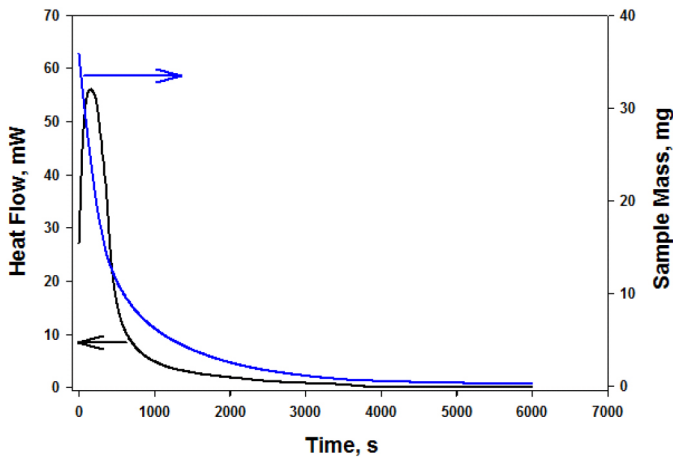


Figure 2. Heat flow (baseline corrected) and mass loss curves from the DSC/TGA experiment for 30 vol% ethanol in CARBOB.

RESULTS AND DISCUSSION

Fuel Properties

Paraffin, isoparaffin, aromatic, naphthene, and olefin (PIANO) analyses from the detailed hydrocarbon analysis of the hydrocarbon blendstocks are reported in Table 1. The wCBOB and sCBOB have about 25 vol% aromatics - in the range typical for gasoline in North America, while the CARBOB would be considered low aromatic content gasoline [35]. The NG is almost entirely paraffinic. Table A-1, A-2, A-3, A-4 in the Appendix present the properties of the hydrocarbon blendstocks as well as their ethanol blends. Our intent was to have blendstocks covering a broad range of properties, especially volatility, available in the market today. The blendstocks have vapor pressure as dry vapor pressure equivalent (DVPE) ranging from 6.1 psi (42 kPa) to 13.8 psi (95 kPa) and T90 ranging from 100°C to 172°C. Note that actual ethanol content differed somewhat from nominal (or target) values, especially for the 40% and 50% blends.

Figure 3 shows RON as a function of ethanol content. While the blendstocks have RON values that differ by up to 23 RON units, above 30% to 40% ethanol the curves converge at a RON of 103 to 105, even for the much lower RON NG sample. Figure 4 shows octane sensitivity (S) which increases significantly as ethanol is blended into the various blendstocks. Unlike RON, which appears to converge at a single or narrow range of values for high ethanol content, there are significant differences in S at high ethanol levels. Gasoline blendstocks with nearly identical S can show significantly different sensitivities when blended with ethanol.

Table 1. PIANO analysis (ASTM D6729) and volatility properties for the hydrocarbon gasoline blendstocks.

Group	wCBOB	CARBOB	sCBOB	NG
Paraffin, vol%	9.59	7.65	11.5	37.7
I-Paraffins, vol%	56.1	53.6	47.9	42.9
Aromatics, vol%	25.8	15.6	23.7	3.72
Naphthenes, vol%	4.71	13.0	7.8	14.8
Olefins, vol%	3.60	8.09	8.4	0.712
Average Molecular Weight (DHA)	96.3	100.5	95.9	80.2
C, wt% (DHA)	85.9	85.6	86.1	84.1
H, wt% (DHA)	14.1	14.4	13.9	15.9
DVPE, kPa (ASTM D5191)	76	42	46	95
T ₁₀ , °C (ASTM D86)	43	65	61	39
T ₅₀ , °C (ASTM D86)	101	106	98	52
T ₉₀ , °C (ASTM D86)	172	156	154	100

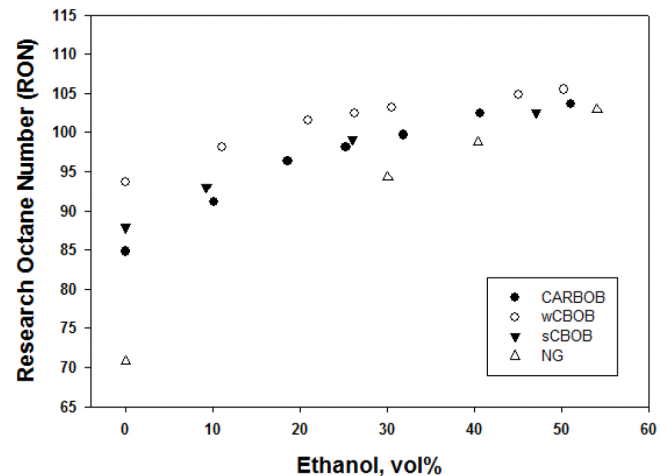


Figure 3. RON measured for ethanol-gasoline blends.

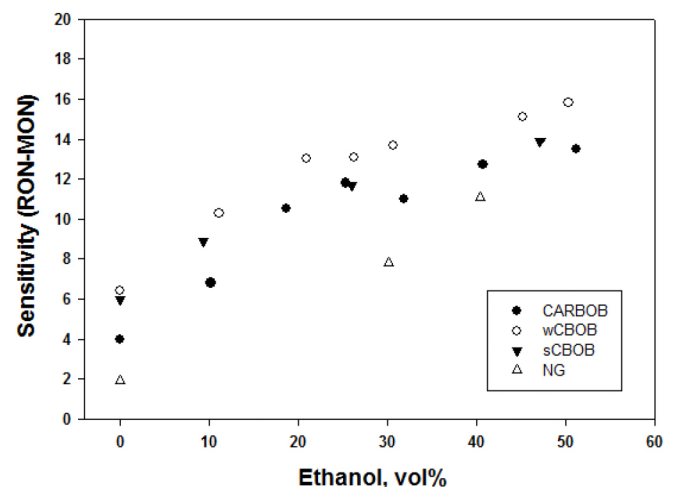


Figure 4. Octane sensitivity for ethanol-gasoline blends.