

Calculation of Heating Value for Gasoline Containing Ethanol

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ABSTRACT

Ethanol for use in automotive fuels can be made from renewable feedstocks, which contributes to its increased use in recent years. There are many differences in physical and chemical properties between ethanol and petrochemicals refined from fossil oil. One of the differences is its energy content. The energy content, or heating value, is an important property of motor fuel, since it directly affects vehicle fuel economy. While the energy content can be measured by combustion of the fuel in a bomb, the test is time-consuming and expensive. It is generally satisfactory and more convenient to estimate that property from other commonly-measured fuel properties. Several standardized empirical methods have been developed in the past for estimating the energy content of hydrocarbon fuels such as gasoline, diesel fuel, and jet fuel. However, the addition of ethanol to gasoline has become very common in some countries, and most of the estimation methods developed for hydrocarbon fuels are not satisfactory for use with gasoline-ethanol blends, especially blends containing more than about 10 volume-percent ethanol. This paper summarizes heating value test results from recently collected retail samples of gasoline-ethanol blends in the U.S. for E10 and E85 blends and in Brazil for E20 and E100 blends, as well as laboratory blends of different levels of fuel ethanol. The heating values obtained by different standardized test methods are compared and discussed. New empirical equations are proposed for gasoline fuel blends containing ethanol.

INTRODUCTION

A fuel's energy content is an important factor affecting vehicle power output and fuel consumption. The lower heating value of a fuel is defined as the amount of heat released by combusting in oxygen a specified quantity (initially at 25°C) with all of the products being gaseous, which assumes the latent heat of vaporization of water in the reaction products is not recovered. The higher heating value (or gross calorific value or gross energy) of a fuel is defined as the amount of heat released by a specified quantity (initially at 25°C) once it is combusted and the products have returned to a temperature of 25°C, which takes into account the latent heat of vaporization of water in the combustion products [1].

For internal combustion engines, energy contained in water vapor cannot be practically recovered. Thus, it is more appropriate to use LHV in automotive applications. In this paper, the terms HOC (heat of combustion) or heating values all refer to lower heating values. Standard ASTM test methods [2-3] have been developed to measure the energy content of liquid fuels by burning a weighed sample of the fuel in the presence of oxygen in a calorimeter. The increase in temperature is used to calculate the energy content in mass units of mega- joules per kilogram (MJ/kg). Additional discussion can be found in SAE J1498 [4].

Most natural gas furnaces are non-condensing; the water vapor produced by combustion goes up the chimney. But a few high efficiency condensing furnaces are marketed. For these it is appropriate to use the high heating value of the gas.

There is much information in the literature concerning the higher heating values for fuels like coal, other fossil fuels, and biomass. Most of the calculations of heating values from elemental composition were derived for higher heating values. The higher heating values are related to lower heating values by the following [5]:

$$\text{HHV}=\text{LHV}+(\text{mH}_2\text{O}/\text{mf})\text{hfgH}_2\text{O}$$

Where $\text{mH}_2\text{O}/\text{mf}$ is the ratio of mass of water produced to mass of fuel burned and h is heat of vaporization of water at the temperature and pressure of the products.

Or as in reference [2],

$$\text{LHV}=\text{HHV}-0.2122*H$$

H is mass percentage of hydrogen in the sample.

Since the energy content of gasoline and gasoline-alcohol blends are not routinely measured, it is useful to be able to estimate the energy content from other commonly-measured fuel properties. There is an empirical linear relationship between density and energy content for gasolines that do not contain alcohols or ethers [6] and this correlation is often sufficient for routine work. It can also be extended to other hydrocarbon fuels. The accuracy and precision can be improved by including other commonly-measured fuel properties in the correlation. There are two standard ASTM procedures [7-8] for estimating energy content from API gravity [9-10] (a measure of fuel density) and aniline point [11] (an indication of the aromaticity of the fuel), but aniline point is rarely measured for gasoline.

In the 1970s, the U.S. Air Force evaluated eight correlation methods to estimate the energy content of aviation fuels [12]. These equations were developed by regression analysis of commonly-measured fuel properties against energy content measured in a bomb calorimeter. Six of the eight methods used API gravity and aniline point. The other two used API gravity, distillation temperatures [13], and aromatic content [14]. The precision of those two methods was found to be superior to that of the actual measurement of energy content in a calorimeter.

This last equation was subsequently standardized by ASTM as D3338, "Standard Test Method for Estimation of Net Heat of Combustion of Aviation Fuels" [15]. It uses the density, distillation temperatures, and aromatic content of the fuel. A correction factor for the fuel sulfur content is also applied. These properties are commonly measured on most fuels.

Although the equation in D3338 for estimating energy content was developed for aviation fuels, it can also be used for other similar hydrocarbon fuels, including gasolines and diesel fuels. The U.S. Environmental Protection Agency

specifies this method for estimating the energy content of test fuels used to measure vehicle fuel economy [16].

D3338 is applicable only to all-hydrocarbon fuels, whereas a majority of gasolines in the U.S., as well as in some other countries, now contain ethanol. Ethanol has only about 60-65 percent as much energy per kilogram as gasoline. Therefore, a modification is needed to account for the ethanol. For this project, the D3338 equation was used for the gasoline (hydrocarbon) portion of the fuel only, excluding the ethanol. To accomplish this, the density and the aromatics content of the gasoline portion of the fuel were calculated, based on the concentration of ethanol in the complete fuel and the properties of pure ethanol. Although the distillation characteristics of the base gasoline cannot be derived in this manner, the effect of distillation is small.

Besides D3338, there are a number of other empirical equations to calculate heating values of fuels [17,18,19,20]. Most of these equations were derived from the composition of the fuel, particularly for higher heating value calculations for coal and recently for biomass. An equation developed jointly by SGS and BMW from fuel elemental composition has been used commonly among automotive companies for lower heating value calculations for market fuel surveys [21]. However, all those empirical equations are displaying more deviations now that gasoline contains more and more ethanol. This paper summarizes test results from recently collected retail samples of gasoline-ethanol blends in the U.S. for E10 and E85 blends and in Brazil for E20 and E100 blends, as well as laboratory blends of different levels of fuel ethanol with certification gasolines. The heating values obtained by different methods are compared and discussed. New empirical equations are proposed for gasoline fuel blends containing ethanol.

EXPERIMENTAL

A total of nine fuels were prepared by blending different amounts of ethanol into two gasolines. The US Tier 2 and Euro IV certification gasolines were used as standard base fuels. The base fuel properties are listed in Table 1 and the blended fuel properties are listed in Table 2. Out of the nine blends, fuels A, B, F and H were blended with Euro IV base gasoline and the rest of the blends were made with Tier 2.

The blended fuels were then speciated for detailed hydrocarbon composition and ethanol content analysis by ASTM D6729, heating value determination by ASTM D240, and other common gasoline tests as shown in Table 1. Elemental analysis for carbon and hydrogen was also performed on the fuels by ASTM D5291, and oxygen was determined by ASTM D5622.

Table 1. Properties of standard fuels being used

Properties	Test Methods	RFG Tier 2 Fed Cert Gasoline	Euro IV Cert Gasoline
LHV MJ/kg	ASTM D240	43.205	43.049
Density Rel@15.6°C	ASTM D4052	0.7431	0.7494
Sulfur ppm	ASTM D5453	27	3
T10 °C	ASTM D86	52.2	49
T50 °C	ASTM D86	106.4	100.4
T90 °C	ASTM D86	159.7	161.8
Aromatics v%	ASTM D1319	28.7	33
Olefins v%	ASTM D1319	0.9	0.6
Saturates v%	ASTM D1319	70.5	66.5
C wt%	ASTM D5291	86.53	86.84
H wt%	ASTM D5291	13.47	13.16
O wt%	ASTM D5622	<0.05	<0.05

Consideration was given to whether the precision method for heating value measurement, ASTM D4809, should be used instead of D240 in this project. The repeatability is 0.091 and 0.13 for D4809 and D240, respectively. The reproducibility is 0.45 and 0.40 for D4809 and D240, respectively. Since all the heating value measurements reported in this paper were performed in one lab, which did not have the capability to run D4809. D240 was considered acceptable. Furthermore, the repeatability from the other measured properties in the empirical equations may contribute greater errors than the two methods themselves.

Other fuel properties were tested according to corresponding ASTM methods as listed in [Table 1](#). All tests were performed at ISO17025 accredited labs.

Table 2. Properties of blended fuels

Fuel ID	A	B	C	D	E	F	G	H	I
D240 LHV MJ/kg	41.28	39.63	38.04	36.42	33.21	33.17	29.21	29.19	24.18
Paraffin wt%	1.27	1.21	4.18	3.52	2.21	2.54	1.32	0.72	0.00
i-Paraffins wt%	38.58	34.22	32.38	27.05	16.58	17.95	6.96	7.45	0.00
Aromatics wt%	40.45	35.93	30.66	26.18	17.78	17.03	5.31	5.70	0.00
Mono-Aromatics wt%	39.46	35.05	29.82	25.41	17.32	16.54	5.15	5.55	0.00
Naphthalenes wt%	0.23	0.20	0.27	0.21	0.02	0.13	0.04	0.03	0.00
Naphtheno/Olefino-Benz wt%	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.00	0.00
Indenes wt%	0.74	0.66	0.55	0.55	0.44	0.34	0.12	0.12	0.00
Naphthenes wt%	9.25	8.17	2.43	2.02	1.39	1.37	0.65	1.64	0.00
Mono-Naphthenes wt%	9.25	8.17	2.43	2.02	1.39	1.37	0.65	1.64	0.00
Olefins wt%	0.07	0.06	0.25	0.17	0.12	0.13	0.04	0.02	0.00
n-Olefins wt%	0.04	0.03	0.07	0.07	0.04	0.04	0.01	0.01	0.00
Iso-Olefins wt%	0.03	0.02	0.17	0.09	0.08	0.08	0.03	0.02	0.00
Naphtheno-Olefins wt%	0.01	0.01	0.02	0.01	0.00	0.01	0.00	0.00	0.00
Ethanol wt%	9.88	19.99	29.38	40.43	61.63	60.56	84.77	84.26	95.00
Unidentified wt%	0.49	0.44	0.72	0.62	0.30	0.43	0.94	0.21	0.00
Density Rel @15.6°C	0.755	0.758	0.758	0.762	0.773	0.773	0.786	0.788	0.816
T10 °C	48.6	49.6	54.4	56.3	61.8	62	73.2	72.7	
T50 °C	82.3	73.3	74.6	75	76.3	76.3	77.7	77.7	
T90 °C	161.7	158.7	149.1	140.9	79.5	79.5	78.6	78.6	
Sulfur ppm	3.62	3.58	19.37	15.49	10.36	10.17	4.11	1.93	
C wt%	83.17	79.49	76.14	72.32	65.42	64.61	57.12	57.17	52.11
H wt%	13.12	13.13	13.37	13.30	13.19	13.06	13.20	13.15	13.98
O wt%	3.71	7.39	10.49	14.38	21.38	22.33	29.69	29.68	33.90

RESULTS AND DISCUSSION

A. Heating values for gasoline containing 10% or less ethanol

As we know, ethanol has lower energy content than gasoline and therefore gasoline containing ethanol would have lower heating values compared to gasoline itself. However, using D3338 to calculate the heating values currently from US market would indicate that fuels with high ethanol content (the E9 - E11 fuels in [Figure 1](#), for example) have higher energy content than gasolines of similar density with no ethanol (E0), which is incorrect. [Figure 1](#) shows the heating values by D3338 from the US market gasoline in 2007. Since the actual energy contents of the fuels were not measured, the calculated energy contents are plotted against density. All data are segregated into five groups based on the ethanol contents.