

Calculation of Heating Value for Diesel Fuels Containing Biodiesel

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ABSTRACT

Biodiesel, a fuel comprised of mono-alkyl esters of long-chain fatty acids also known as Fatty Acid Methyl Esters (FAME), derived from vegetable oils or animal fats, has become an important commercial marketplace automotive fuel in the United States (US) and around the world over last few years. FAME biodiesels have many chemical and physical property differences compared to conventional petroleum based diesel fuels. Also, the properties of biodiesel vary based on the feedstock chosen for biodiesel production. One of the key differences between petroleum diesel fuels and biodiesel is the energy content. The energy content, or heating value, is an important property of motor fuel, since it directly affects the vehicle fuel economy. While the energy content can be measured by combustion of the fuel in a bomb calorimeter, this analytical laboratory testing is time consuming and expensive. It would be more convenient to estimate the energy content 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, with the addition of biodiesel to petroleum diesel fuel, the estimation methods developed for hydrocarbon diesel fuels are not very accurate for use with biodiesel blends. This paper summarizes heating value test results from different biodiesel blends representing the most common biodiesel feedstocks. New lower heating value predictive model equations are proposed for diesel fuel blends containing biodiesel and the results from standardized measurement tests are compared to the calculated values. This paper expands the scope of the empirical equations proposed in the SAE paper 2010-01-1571 for gasoline-ethanol blends to cover diesel fuel blends containing biodiesel.

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INTRODUCTION

A fuel's energy content is an important factor affecting vehicle power output and fuel consumption. The lower heating value (LHV) of a fuel is defined as the amount of heat released by combusting a specified quantity of fuel (initially at 25°C) in oxygen with all of the products being gaseous and in which the latent heat of vaporization of water in the reaction products is not recovered (water remains as vapor). 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 and latent heat of vaporization of water is recovered by condensation of water vapor 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. 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 such applications it is appropriate to use the higher heating value of the gas. In this paper, the terms heat of combustion or heating value refer to lower heating value. Standard ASTM test methods 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 (2,3). The increase in temperature is used to calculate the energy content in mass units of megajoules per kilogram (MJ/kg). Additional information on standardized procedures for determining the heat of combustion of fuels can be found in SAE J1498 (4).

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):

$$\text{HHV} = \text{LHV} + (m_{\text{H}_2\text{O}}/m_{\text{F}})h_{\text{fgH}_2\text{O}}$$

where $m_{\text{H}_2\text{O}}/m_{\text{F}}$ 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 LHV is related to HHV as defined in reference (2)

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

where H is mass percentage of hydrogen in the sample.

Since the energy contents of diesel fuel and biodiesel 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 fuels that do not contain oxygenated compounds and this correlation is often sufficient for routine work (6). It can also be extended to other hydrocarbon fuels. The accuracy and precision of this correlation can be further 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 not routinely measured for diesel fuel.

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 for most fuels.

Although the equation in ASTM D3338 for estimating energy content was developed for aviation fuels, it can also be used for other similar hydrocarbon fuels, including gasoline 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).

ASTM D3338 is applicable only to non-oxygenated fuels, whereas some diesel fuels in the U.S., as well as in some other countries, now contain biodiesel. Typical biodiesel (B100) has only about 90 percent as much energy per kilogram as petroleum diesel fuel. Therefore, a modification to the predictive energy content equation is needed to account for the biodiesel. For this project, the ASTM D3338 equation was used for the diesel fuel (hydrocarbon) portion of the fuel only, excluding the biodiesel. To accomplish this, the density and aromatic content of the diesel fuel portion of the fuel blend were calculated, based on the concentration of biodiesel in the complete fuel and properties of the biodiesel. Although the distillation characteristics of the base diesel fuel cannot be derived in this manner, the effect of distillation temperatures on the calculation of energy content by D3338 is small.

Besides ASTM D3338, there are 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 the fuel's elemental composition has been commonly used among automotive companies for lower heating value calculations for market fuel surveys (21). However, the common empirical equations have poor precisions for diesel fuels containing biodiesel as discussed in this study similar to gasoline fuels containing ethanol (22). This paper summarizes test results for heating values from recent retail fuel surveys of diesel fuels and biodiesel blends in the U.S., as well as laboratory blends of different types and levels of biodiesel with emissions certification diesel fuels. The heating values obtained by different methods are compared and discussed. New empirical equations for calculation of heating values are proposed for biodiesel blended diesel fuels.

EXPERIMENTAL

This study included five biodiesel fuels representing the common commercial feedstock for biodiesels and five ultralow sulfur petroleum diesel fuels. The biodiesel types were Soy Methyl Ester (SME), Rapeseed Methyl Ester (RME), Corn Methyl Ester (CME), Animal Fat Methyl Ester (AME) and Waste Vegetable Oil Methyl Ester (WVOME). The common properties for the base diesel fuels and the biodiesels (B100) were retested according to standard ASTM methods. The key properties for the diesel fuels are listed in [Table 1](#) while the key properties and fatty acid profiles for biodiesels (B100) are shown in [Table 2](#) and [Table 3](#) respectively. FAME content for SME, RME and CME was >90 wt% while for AME it was 86 wt% and for WVOME it was just 43 wt%. Certificate of analysis obtained for these samples showed that they met the requirements of ASTM

Table 1. Diesel fuels characterization.

Property	Test Method	Units	US Certification	Euro IV Certification	Tar Sands	Swedish Class-I	ULSD Mid-Cetane
Cloud Point	ASTM D5771	°C	-23	-23	-31	-44	-31
Sulfur	ASTM D7039	ppm	12	38	3	11	14
Water Content	ASTM D6304	mg/kg	31	25	50	15	22
Density@ 15°C	ASTM D4052	g/l	851.2	836.3	838.9	808.9	838.8
Distillation, T10	ASTM D86	°C	215.7	186.7	200.0	197.2	204.4
Distillation, T50	ASTM D86	°C	259.5	275.6	247.2	223.9	240.0
Distillation, T90	ASTM D86	°C	304.3	326.1	303.3	268.9	312.2
LHV	ASTM D240	MJ/kg	42.75	42.99	42.91	43.45	42.87
Carbon	ASTM D5291	wt%	86.71	86.51	86.12	85.31	86.98
Hydrogen	ASTM D5291	wt%	13.15	13.82	13.68	14.32	13.5
Oxygen	ASTM D5291	wt%	0.14	0.00	0.00	0.00	0.00
Aromatics	ASTM D1319	vol%	27.4	13.1	16.3	3.5	20.9

Table 2. Biodiesel fuels characterization.

Property	Test Method	Units	SME	RME	CME	AME	WVOME
Cloud Point	ASTM D5771	°C	0	-5	-3	5	1
Pour Point	ASTM D5950	°C	- 1	-12	-5	3	-4
Sulfur	ASTM D7039	ppm	0	1	4	7	3
Oxidation Stability, Rancimat IP	EN14112	hours	3.0	7.9	4.2	8.5	6.8
Acid Number	ASTM D664	mg KOH/g	0.2	0.2	0.3	0.1	0.1
Water Content	ASTM D6304	mg/kg	400	254	240	166	269
Density @15°C	ASTM D4052	g/l	885.1	882.2	886.4	883.7	883.8
Distillation, T10	ASTM D1160	°C	346	349	346	342	347
Distillation, T50	ASTM D1160	°C	350	351	350	348	351
Distillation, T90	ASTM D1160	°C	353	353	353	354	356
LHV	ASTM D240	MJ/kg	37.24	37.42	37.11	37.33	37.28
Carbon	ASTM D5291	wt%	76.95	76.98	77.19	77.06	77.00
Hydrogen	ASTM D5291	wt%	11.92	12.02	11.90	11.92	11.98
Oxygen	ASTM D5291	wt%	11.13	11.00	10.91	11.02	11.02

D6751 for B100. Since, ASTM D6751 does not specify FAME content limit and these were commercial samples, they were considered acceptable for the scope of this study. A separate study to understand the lower FAME content especially in WVOME is underway. The US certification diesel (EPA Generic 40CFR 86.113-07) and Euro IV certification diesel fuels were further selected as standard base fuels to prepare a total of fourteen blends of different types and concentrations of biodiesels as described in [Table](#)

4. The types of biodiesel blends and their key properties are listed in [Table 5](#). Consideration was given to whether the better precision method for heating value measurement, ASTM D4809, should be used instead of ASTM D240 method in this project. The repeatability is 0.091 and 0.13 for ASTM D4809 and ASTM D240, respectively. The reproducibility is 0.45 and 0.40 for ASTM D4809 and ASTM D240, respectively. Since all the heating value measurements reported in this paper were performed in one lab, which did

Table 3. Fatty acid characterization of biodiesel fuels.

Biodiesel	Fatty Acid Composition (wt%)				
	SME	RME	CME	AME	WVOME
C14:0	0.16	0.05	0.04	0.57	0.4
C14:1	0.00	0.00	0.00	0.06	0.00
C16:0	10.07	4.24	9.24	13.54	7.28
C16:1	0.31	0.20	0.09	1.46	0.35
C18:0	4.68	1.64	2.49	6.70	3.64
C18:1	21.43	54.90	22.99	33.08	0.00
C18:2	49.02	20.33	52.55	26.67	25.46
C18:3	6.51	8.58	2.47	2.23	2.69
C20	0.54	1.71	0.49	0.97	0.58
C22:0	0.34	0.37	0.23	0.20	0.61
C22:1	0.03	0.36	0.00	0.05	0.00
> C22	0.18	0.38	0.19	0.24	1.44

Table 4. Biodiesel blends used for this Study.

US B5-SME	5 vol% blend of SME in US Tier 2 Cert Diesel
US B20-SME	20 vol% blend of SME in US Tier 2 Cert Diesel
US B50-SME	50 vol% blend of SME in US Tier 2 Cert Diesel
US B5-RME	5 vol% blend of RME in US Tier 2 Cert Diesel
US B20-RME	20 vol% blend of RME in US Tier 2 Cert Diesel
US B50-RME	50 vol% blend of RME in US Tier 2 Cert Diesel
US B5-CME	5 vol% blend of CME in US Tier 2 Cert Diesel
US B20-CME	20 vol% blend of CME in US Tier 2 Cert Diesel
US B50-CME	50 vol% blend of CME in US Tier 2 Cert Diesel
US B20-AME	20 vol% blend of AME in US Tier 2 Cert Diesel
US B20-WVOME	20 vol% blend of WVOME in US Tier 2 Cert Diesel
EU B20-SME	20 vol% blend of SME in Euro 4 Ref Diesel
EU B20-RME	20 vol% blend of RME in Euro 4 Ref Diesel
EU B20-CME	20 vol% blend of CME in Euro 4 Ref Diesel

not have the capability to run ASTM D4809, ASTM D240 was utilized for this work. Furthermore, the repeatability from the other measured properties in the empirical equations may contribute greater errors than the two methods themselves.

RESULTS AND DISCUSSION

A. Heating Values for Diesel Fuels Containing Biodiesel

Typical commercial biodiesel has lower energy content compared to regular petroleum diesel fuel and hence diesel

fuel containing biodiesel is expected to have lower energy content compared to diesel fuel itself. [Figure 1](#) shows the relationship between calculated heating values as per ASTM D3338 method and density for US market place diesel and biodiesel blends samples from 2008 winter and 2011 summer diesel survey. The biodiesel content in the survey samples varied from 0 to 46.1 vol%. The data was segregated in five distinct groups based on the biodiesel content to determine if there was a correlation between the heating values calculated by ASTM D3338 and the biodiesel content. Since the biodiesel type in the fuel survey samples was not known, it was assumed that all blends were made from SME biodiesel.