

Estimation of Elemental Composition of Diesel Fuel Containing Biodiesel

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ABSTRACT

Carbon, hydrogen and oxygen are major elements in vehicle fuels. Knowledge of fuels elemental composition is helpful in addressing its performance characteristics. Carbon, hydrogen and oxygen composition is an important parameter in engine calibration affecting vehicle performance, emissions and fuel economy.

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 oxygen content. Typical oxygen content in pure biodiesel (B100) is about 11 weight % while conventional ultra-low sulfur petroleum diesel fuel has negligible oxygen content. High oxygen content of biodiesel impacts its characteristics compared to petroleum diesel.

A previous paper (SAE2013-01-1139) discussed the change in energy content of diesel fuel containing biodiesel primarily due to its high oxygen content and the estimation of net heating values from common fuel properties. This paper is a continuation of the previous study and will discuss the estimation of elemental composition of biodiesel blended diesel fuels from common fuel properties. While the carbon, hydrogen, and nitrogen contents can be measured by combustion of the fuel in a tube and then quantifying the combustion products as described in ASTM D5291 or E191, the test is time-consuming and expensive. The repeatability of the method is also marginally satisfactory.

It is generally satisfactory and more convenient to estimate the elemental composition from other commonly-measured fuel properties. Several standardized empirical methods have been developed in the past for estimating the hydrogen content of hydrocarbon fuels. However, the addition of oxygenated biodiesel fuel to diesel has become very common in many countries, and most of the estimation methods developed for hydrocarbon fuels do not provide accurate results for biodiesel blends, especially blends containing more than about 5 volume-percent biodiesel.

This paper summarizes compositional data from recently collected retail samples from US market place, as well as laboratory blends containing different concentrations of biodiesels made from various types of biodiesels representing the most common feedstock.

The compositional data obtained by different standardized test methods is compared and discussed. New empirical methods and equations are proposed for diesel containing biodiesel blends.

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INTRODUCTION

Biodiesel has become an important commercial marketplace fuel in the United States (US) over last few years and

its use is expected to increase. The low Greenhouse Gas renewable fuel goals established in the Energy Independence and Security Act of 2007 (EISA) resulted in the development of the Renewable Fuels Standard (RFS) in February 2010.

that specifically requires a renewable component in US diesel fuel.

Fatty Acid Methyl Ester (FAME), biodiesel, is a particularly attractive renewable fuel since it can be synthesized with common feedstock's like soybean oil, animal fat and yellow grease at a competitive cost compared to other green diesel alternatives [1]. Biodiesel is produced by chemical reaction of fat or vegetable oil with lower chain alcohol in presence of base catalyst such as sodium hydroxide or potassium hydroxide [2]. The most common alcohol used for biodiesel production is methanol while ethanol is also used sometimes.

The RFS2 program, consistent with the US Environmental Protection Agency's (EPA) announcement, requires a minimum of 800 million gallons of biomass-based diesel in 2011, which includes biodiesel [3]. In addition to the Federal RFS2 program, state and local biodiesel blending mandates is also predicted to increase utilization of biodiesel [4]. For example, California's low-carbon fuel standard (LCFS) rule enacted to reduce carbon intensity in transportation fuels as compared to conventional petroleum fuels, favors use of biodiesel fuel [5] while Illinois state provides tax incentives to use biodiesel fuel[6].

Currently, in the US on-highway ULSD fuel allows up to 5 volume % biodiesel use as per the ASTM D 975 diesel fuel specification. ASTM D7467 is the standard for B6-B20 blends and facilitates use of biodiesel beyond 5 volume percent. OEMs support for use of biodiesel in their vehicle is increasing. All major OEMs producing diesel vehicles for the U.S. market support at least B5 and lower blends, and many manufacturers now support B20 or higher biodiesel blends in at least some of their equipment [7].

The increase use of biodiesel as marketplace fuel warrants knowledge of basic properties of biodiesel and biodiesel blended fuels for use as automotive fuel. Some of the fuel properties which are not part of the standard specification requirements are not commonly measured and are not reported on the certificate of analysis for the batch of fuel. For such properties it is useful to have ability to estimate the values from other commonly-measured fuel properties. The elemental composition of the fuel is one such property not tested frequently but knowledge of this property is important in several applications. For example, the hydrogen content is needed to calculate the lower (or net) heating value of a fuel from its measured higher (or gross) heating value [8]. The fuels carbon composition along with its energy density and the impact of engine efficiency plays critical role in overall vehicle CO₂ emissions[9].

ASTM Test Methods D1018 [10], D3701 [11], and D4808 [12] can be used to measure the mass-percent hydrogen in petroleum fuels. If the fuel is composed only of hydrocarbons, the carbon content is determined simply by subtracting the mass-percent hydrogen from 100. ASTM D5291 [13] can be used to measure the carbon, hydrogen, and nitrogen contents of fuel. The apparatus described in

specification ASTM E191 [14] can be used in a laboratory method to measure the carbon and hydrogen contents of fuel. For elemental composition measurement, sulfur content of fuel had been vital however since diesel sulfur levels have been reduced significantly in recent years, the effect of sulfur is essentially negligible. The increasing usage of biodiesel in diesel fuel increases the oxygen content of the fuel. Therefore, the major elements in today's marketplace diesel fuels are carbon, hydrogen, and oxygen.

The methods mentioned above for measuring hydrogen content are time-consuming and expensive, and therefore it is useful to be able to estimate the hydrogen content from other commonly-measured fuel properties. In the 1970s, the U.S. Air Force evaluated five correlation methods to estimate the hydrogen content of aviation fuels [15]. These equations were developed by regression analysis of commonly-measured fuel properties against measured hydrogen content. One of the methods uses API gravity [16,17] (a measure of fuel density) and aniline point [18] (an indication of the aromaticity of the fuel). There are four other methods, developed by Chevron Research Company, that uses API gravity, distillation temperatures [19], and aromatic content [20]. One of these four methods was subsequently standardized by ASTM as D3343, "Standard Test Method for Estimation of Hydrogen Content of Aviation Fuels" [21]. It provides a method for estimating the hydrogen content of hydrocarbon fuels using density, distillation temperatures, and aromatic content. These properties are commonly measured on most fuels.

Although the Air Force was primarily interested in evaluating the estimation methods for their applicability to JP-4 and Jet A fuels, the fuels used to develop the equation in D3343 included commercial jet fuels, pure hydrocarbons, special solvents, and high temperature fuels. Based on the ranges of the individual properties of the fuels used in the study (see D3343), the equation in D3343 is useful for other fuels such as automotive gasoline and diesel fuels. D3343 is applicable only to all-hydrocarbon fuels, whereas a many diesel samples in the U.S., as well as in some other countries, now contain biodiesel. Therefore, a modification is needed to account for the biodiesel. Using the procedure similar to that described in a previous SAE paper on the estimation of fuel energy contents [22], the equation in D3343 for hydrogen content can be modified to be applicable for biodiesel and biodiesel blended fuels.

This paper summarizes the test results of biodiesel and biodiesel blended fuels for hydrogen composition measured by reference method ASTM D5291 and compares these to the values calculated by existing empirical equation as per ASTM D3343 method. The empirical equation described in ASTM D3343 is modified for calculation of hydrogen content in biodiesel blended fuels. Also, a new empirical method based on commonly measured fuel properties is proposed as a quick and easy way for determination of hydrogen of biodiesel blended fuels.

EXPERIMENTAL

This study included five biodiesel fuels representing the common commercial feedstock for biodiesels and five ultralow sulfur petroleum diesel fuels. The certification fuels were selected as part of diesel test fuels matrix and also as base diesels for biodiesel blend components since they were readily available in required quantities. Also, the values for the properties of certification diesels (US and European) relevant for this study such as sulfur content, distillation profile, aromatic content were found to be within the range that is seen in the commercial fuels for the respective markets. This information is available based on the fuel surveys for the respective regions by independent agencies. Thus, these fuels could be regarded as representative for their markets.

Table 1. Diesel fuels characterization.

Property	Test Method	Units	US Certification	Euro IV Certification	Tar Sands	Swedish Class-I	US 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
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

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](#). Certificate of analysis obtained for these samples showed that they met the requirements of ASTM D6751 for B100. 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 3](#). The types of biodiesel blends and their key properties are listed in [Table 4](#) and [Table 5](#). Elemental analysis for carbon and hydrogen was also performed on the experimental samples including B100 and biodiesel blended fuels by ASTM D5291. The oxygen content for the samples was then calculated based on the results of ASTM D5291.

Table 2. Biodiesel Fuels Characterization.

Property	Test Method	Units	SME	RME	CME	AME	WVO ME
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
C	ASTM D5291	wt%	76.95	76.98	77.19	77.06	77.00
H	ASTM D5291	wt%	11.92	12.02	11.90	11.92	11.98
O	ASTM D5291	wt%	11.13	11.00	10.91	11.02	11.02

Table 3. 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