2013-01-9071
Published 11/20/2013
doi:10.4271/2013-01-9071
saefuel.saejournals.org

Analysis of Ethanol Fuel Blends

Teresa L. Alleman
National Renewable Energy Laboratory

ABSTRACT

In the last three years, three quality surveys on ethanol-blended fuels intended for use in flex-fuel vehicles have been published. Two of these surveys cover Flex-Fuel quality, and the third encompasses the quality of mid-level ethanol blends (MLEBs) from blender pumps. The purpose of these surveys was to report on the quality of the fuels and provide a snapshot in time of fuel quality.

This study examines the larger picture portrayed by these surveys and looks for broader trends in fuel quality. The analysis found that compliance with vapor pressure specification limits for Flex Fuel improved from 40% to 66% in Class 1, from 31% to 43% in Class 2, and from 12% to 30% in Class 3 between 2008 and 2010. Failures on other critical properties, such as acidity, pHe, water, and inorganic chloride were less than 6% in these studies.

The 2010 Flex Fuel samples readily met the ethanol content specification, with 88%, 92%, and 95% compliance for Classes 1, 2, and 3, respectively. In contrast, the 2008 Flex Fuel samples met the ethanol content specification only 28%, 58%, and 83% of the time for Classes 1, 2, and 3, respectively. Analysis of the MLEB data set revealed statistically identical vapor pressures for gasolines containing 10 vol% ethanol (E10) and E20 and E30 blends.

CITATION: Alleman, T., "Analysis of Ethanol Fuel Blends," *SAE Int. J. Fuels Lubr.* 6(3):2013, doi:10.4271/2013-01-9071.

INTRODUCTION

One of the United States Department of Energy goals is to reduce the amount of imported petroleum and petroleum products by 2.5 billion gallons a year annually [1]. This will not be accomplished with a single solution, but rather through multiple, diverse pathways. One potential solution is the use of domestically produced fuels, particularly those produced through renewable feedstocks. Currently, the most mature technology available for spark-ignited engines is the blending of fuel grade ethanol with gasoline.

Fuel grade ethanol is denatured with small amounts of hydrocarbons. The resulting blend is called denatured fuel ethanol or E98, which is 98 volume percent (vol%) ethanol, with the remaining 2 vol% being hydrocarbons to denature the fuel to make it unfit for consumption. ASTM International (ASTM) Specification D4806 [2] covers the quality of denatured fuel ethanol to be blended as transportation fuel. E98 is not used as a spark-ignited fuel because of its low vapor pressure, which causes starting and drivability issues, but is blended to lower concentrations with gasoline, depending on the intended market.

The United States produced 52.6 billion liters of fuel grade ethanol in 2011 [3]. The largest market for this fuel is the conventional gasoline market, where over 95% of the gasoline in the United States contains 10 vol% ethanol. Gasoline blends containing 10% ethanol must meet the requirements of ASTM D4814 [4]. The composition of fuels covered by ASTM D4814 is, in part, regulated by the Clean Air Act promulgated by the U.S. Environmental Protection Agency (EPA).

The Clean Air Act required the use of oxygenated gasoline to mitigate air pollution in certain regions of the United States. Depending on the severity of the pollution in a region, the EPA may mandate either wintertime-only oxygenate blending or year-round blending. While methyl *tert*-butyl ether (MTBE) was an early choice for oxygenate blending, ethanol is the preferred oxygenate in use today. The use of MTBE has substantially declined in the U.S. due to concerns about groundwater contamination, state bans, and the removal of the 2.0 weight percent oxygen content requirement for reformulated gasoline from Section 211(k) of the Clean Air Act, as enacted under the Energy Policy Act of 2005 [5,6]. The Renewable Fuel Standards have mandated the use of renewable fuel, which for all intents and purposes in the gasoline market, is ethanol. One way to meet the requirements in the Renewable Fuel Standard is through increased ethanol blending in gasoline.

Documents
Document Sharing Hub

Full document details: SAE 2013-01-9071

In 2011, the EPA granted a partial waiver to allow 15 vol % ethanol in gasoline in the United States [7]. This partial waiver allows introduction of 15 vol% ethanol in gasoline into commerce and permits use of the blended fuel in 2001 and newer cars, light-duty trucks, and sport utility vehicles. The waiver does not cover higher ethanol blends or the use of ethanol blends higher than 10% in motorcycles, off-road vehicles and equipment, or in model year 2000 and older cars, trucks and sport utility vehicles.

Higher level blends of ethanol in gasoline can be used in flex fuel vehicles (FFVs). FFVs are vehicles that can run on a wide range of gasoline-ethanol blends. These vehicles have special components in the engine that can withstand the corrosivity of high-ethanol content fuels and use feedback from the fuel gauge, exhaust oxygen sensor, knock sensor and in some cases a fuel composition sensor in the fuel line. This input is used to optimize computerized engine control of air/fuel ratio and spark timing [8].

Considerable confusion has surrounded the popular name of fuels meeting ASTM D5798 (properties summarized later in the paper) [9]. These fuels have historically been called “E85”, although they have never contained 85% ethanol. With the new specification revisions to reduce the ethanol content of these fuels, the fuels have been renamed as ethanol fuel blends. This term is used to describe D5798-compliant fuels, as separate from lower blends of ethanol in gasoline, such as mid-level ethanol blends or MLEBs. A more common term for the D5798 fuels is Flex Fuel. Because Flex Fuel has a much higher ethanol content than conventional gasoline, it is sold only at specialized dispensers. The number of these dispensers is growing rapidly, but is still small compared to conventional gasoline pumps [10].

Much work has been done on the emissions of FFVs. A recent study by Yanowitz and McCormick found a significant reduction in emission of carbon monoxide and nitrogen oxides from Tier 2 vehicles operating on 85 vol% ethanol compared to similar vehicles operating on certification gasoline. No significant impact on non-methane organic gases was observed [11].

The market for fuel grade ethanol is expanding through the use of so-called blender pumps that sell mid-level ethanol blends (MLEBs) for FFVs. MLEBs have ethanol content between 15 vol% and 50 vol%, between conventional gasoline (E10) and Flex Fuel. State incentives have led to an increasing number of blender pumps in the United States. Blender pumps provide another opportunity to blend ethanol into U.S. fuels, potentially increasing the volumes of fuel grade ethanol used.

FFV owners have proven to be reluctant to use Flex Fuel. While all of the reasons for this are unknown, reduced vehicle range may be a factor. The volumetric energy content of ethanol is roughly 30% less than typical gasoline (E10). Thus, blends containing high levels of ethanol, such as Flex Fuel, contain about 25% less energy than gasoline. This reduces the vehicle range and fuel economy by 25%. Many FFV owners find this to be unacceptable and could choose MLEBs to mitigate the impact on vehicle range while still increasing energy security (reduced petroleum content in the fuel) and reducing emissions.

MLEBs are dispensed through pumps that do the blending at the pump, rather than being blended at the petroleum terminal [12]. The parent fuels used in the blending will be conventional gasoline (almost always E10) and either Flex Fuel or E98. Although E98 is an option for blending, no stations are known to use E98 for these blends. Research shows that E98 has a greater range of flammability than gasoline or Flex Fuel and is thus a greater safety and handling risk [13]. This same work also shows that Flex Fuel blends produced from conventional gasoline and E98 would have vapor pressures below the minimum specified in D5798. It is likely that MLEBs produced from E98 and gasoline would also have substandard volatility, not to mention an increased risk for safety and handling due to the expanded flammability of E98.

This review paper looks at three recent surveys of ethanol fuels conducted by the U.S. Department of Energy's National Renewable Energy Laboratory in conjunction with the Coordinating Research Council (CRC). The first survey covered Flex Fuel quality and was reported in 2009. The second survey covered MLEBs from blender pumps, and the final survey covered Flex Fuel [14, 15, 16].

ASTM SPECIFICATIONS

To ensure the quality of fuels is consistent, ASTM publishes specifications for the quality of fuels and blendstocks. These standards are typically adopted by local, state, and federal agencies for fuel quality enforcement. For example, ASTM D4806 covers the properties of E98; ASTM D5798 covers Flex Fuels; and conventional gasoline, including E10, is covered under ASTM D4814. ASTM D7794 is the Standard Practice for blending MLEBs [17]. ASTM specifications change over time. The year of the most recent change is indicated by “-XX” after the specification number, where XX denotes the year of the change.

This report focuses on Flex Fuels, which are covered by ASTM D5798. A key to specification ASTM D5798 is the requirement for different volatilities, or volatility classes, depending on region and time of year. These volatility classes are set to ensure the fuel is fit-for-purpose and meets operability and drivability requirements year-round while the maximum vapor pressure limits evaporative emissions during hot weather.

The blending of ethanol in gasoline has a well-documented impact of the vapor pressure of the final mixture. In small amounts, less than about 20 vol%, the impact of adding ethanol on vapor pressure should be minimal. As the percentage of ethanol increases in a blend, the impact on vapor pressure is more pronounced [18]. A CRC study varied the ethanol content and vapor pressure of Flex Fuels in vehicles and determined the ability of vehicles to start and operate in cold ambient temperatures [19]. Results from this

AVA Documents
Document Sharing Hub
Full document details: SAE 2013-01-9071

Table 1. Comparison of ASTM D5798-09b, −10, and −11 specification limits

Property	Method	Year	Class 1	Class 2	Class 3	Class 4
Vapor pressure, kPa	D4953, D5190,or D5191	-09b	38-59	48-65	59-83	NA
		-10	38-59	48-65	59-83	NA
		-11	38-59	48-65	59-83	66-103
Ethanol, vol%	D5501	-09b	79-83	74-83	70-83	NA
		-10	68-83	68-83	68-83	NA
		-11	51-83	51-83	51-83	51-83
Methanol, max, vol%	D5501	All	0.5	0.5	0.5	0.5
Sulfur, max, mg/kg	D5453	All	80	80	80	80
Acidity, max, mass%	D1613	All	0.005	0.005	0.005	0.005
Solvent washed gum content, max, mg/100mL	D381	All	5	5	5	5
pHe	D6423	All	6.5-9.0	6.5-9.0	6.5-9.0	6.5-9.0
Unwashed gum content, max, mg/100mL	D381	All	20	20	20	20
Inorganic chloride, max, mg/kg	D7319 or D7328	All	1	1	1	1
Copper content, max, mg/L	D1688	All	0.07	0.07	0.07	0.07
Water content, max, mass%	E203 or E1064	All	1.0	1.0	1.0	1.0

NA = not applicable
pHe = acidity of high ethanol content liquids

study show that meeting minimum vapor pressure requirements for Flex Fuel is a critical parameter to ensure drivability and cold start for FFVs. Thus, it is imperative that Flex Fuel meets the vapor pressure requirements set forth in the specification.

A major change in ASTM D5798 was promulgated between the 2009 (−09) and 2010 (−10) versions of the specification. In ASTM D5798-09b and earlier versions, the minimum allowable ethanol content (as measured by ASTM D5501) varied with volatility class. Starting in ASTM D5798-10, the minimum allowable ethanol content dropped to 68 vol% across all volatility classes. Table 1 summarizes these changes. Difficulties have been noted in meeting minimum vapor pressure requirements, particularly in Class 3 Flex Fuel.

SAMPLE COLLECTION

In each Flex Fuel survey, samples were collected in the three volatility classes from public pumps around the United States. Stations were selected to cover a range of locations throughout the United States, and samples were collected from stations in the appropriate months for the desired volatility class.

The MLEB samples were geographically constrained by the location of blender pumps at the time of the survey, when all blender pumps were located in the midwestern United States. Installation of blender pumps is slowly being expanded into other areas of the country, although publically available lists of stations may not be current [20]. MLEB samples were collected in January 2009 (Class 3 Flex Fuel) and July 2010 (Class 1 Flex Fuel). To ensure blend accuracy, two liters of sample were purged before collection of each blend.

Blending of additional gasoline boiling range hydrocarbon into the ethanol (reduction in the minimum ethanol content) should make it easier for blenders to meet these requirements and provide on-specification fuels.

ASTM D5798-11 includes significant changes from the 2010 version. In 2011, the minimum ethanol content was further reduced to 51 vol%. This change, coupled with the addition of a fourth volatility class for the coldest winter areas, should further assist refiners and blenders in meeting the minimum vapor pressure specifications.

When a specification existed (for E10 or for Flex Fuel above the minimum ethanol content), the samples were analyzed by the ASTM test method in the specification. In the case of MLEBs, appropriate test methods were selected; however, ethanol at these blend levels fell outside the scope and precision of the methods at the time of the survey.

The error bars presented in Figures 2 and 3 use the applicable ASTM test method reproducibility as listed, regardless of whether scope and precision applies. It is well documented in the methods that precision may vary when outside the method scope, but the method precision is used for illustrative purposes.

RESULTS AND DISCUSSION

Flex Fuel

Ethanol content

In the 2009 Flex Fuel survey, samples were collected from July 2008 through July 2009. Samples were collected in Class 1 twice, once in July 2008 (47 samples) and again in

AVA Documents Document Sharing Hub

Full document details: SAE 2013-01-9071