

Properties of Ethanol Fuel Blends Made with Natural Gasoline

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S Supporting Information

ABSTRACT: This project looks at the potential of blending ethanol with natural gasoline to produce Flex-Fuels (ASTM D5798-13a) and high-octane, mid-level ethanol blends. Eight natural gasoline samples were collected from pipeline companies or ethanol producers around the United States. Analysis of the natural gasoline shows that the samples are 80–95% paraffinic, 5–15% naphthenic, 3% or less aromatics, and the balance olefins. The paraffins were typically pentane and isopentanes. The benzene content ranged from approximately 0.1 to 1.2 wt % such that blends of E30 or more would meet United States Environmental Protection Agency (U.S. EPA) limits for the benzene content in gasoline. The sulfur content in the natural gasoline ranged between 4 and 146 ppm. Assuming the lowest ethanol content in Flex-Fuel of 51 volume percent (vol %), a natural gasoline blendstock would be required to have 20 ppm sulfur or less for the finished fuel to meet the upcoming U.S. EPA Tier 3 gasoline sulfur limit. The research octane number (RON) (ASTM D2699-13) for the natural gasoline ranged from 67 to 72. Vapor pressure (ASTM D5191-13) ranged from 89 to 101 kPa. Two natural gasoline samples were selected for blending with ethanol. To make a 91 RON fuel (typical of U.S. regular gasoline), natural gasoline had to be blended with 30 vol % ethanol. Because of the high vapor pressure of these blendstocks, over 70 vol % ethanol could be blended into Flex-Fuel while still meeting the class 4 (wintertime) minimum vapor pressure requirement of 66 kPa. For blending of class 1 (summertime) Flex-Fuel, a minimum of 74 vol % ethanol was required to stay below the 62 kPa upper limit on vapor pressure. Modeling of vapor pressure using universal quasichemical functional-group activity coefficients (UNIFAC) and Wilson equation-based approaches provided good agreement with experimental data for most samples.

1. INTRODUCTION

Fuel-grade ethanol is a domestically produced gasoline blendstock that provides energy security and greenhouse gas emission and economic benefits.^{1,2} The vast majority of ethanol is blended as 10 volume percent (vol %) to produce E10, although E15 is allowable in 2001 and newer conventional vehicles.³ E10 gasoline is blended from ethanol and a gasoline blendstock for oxygenate blending or BOB. The concentration of the ethanol, excluding the required denaturing agent, must be at least 9 vol % and no more than 10 vol % of the gasoline. BOBs are complex blended products that, when blended with 10 vol % ethanol, meet the required specifications in D4814 for gasoline.

Flex-Fuel is a blend of ethanol and BOB, generally the same BOBs used to make conventional gasoline. Flex-Fuel has a lower energy density than E10 but often retails for the same price as E10.⁴ Without an economic incentive to purchase the fuel, few consumers purchase Flex-Fuel instead of regular gasoline, when given the option.

Mid-level ethanol blends (MLEBs) contain between 11 and 50 vol % ethanol and are a bridge between conventional gasoline and Flex-Fuel. MLEBs are currently produced from gasoline and fuel ethanol or gasoline and Flex-Fuel. With energy content more similar to E10, especially at lower blend levels, MLEBs give consumers additional choices at the fuel pump. An additional benefit from MLEBs may be the higher octane number of these blends compared to E10, which may enable future engine technologies.⁵

In the United States, more ethanol is produced domestically than can legally be blended in E10 (the so-called ethanol blend

wall). One potential solution to increase ethanol use is to blend Flex-Fuel and MLEBs with lower cost blendstocks than typical BOBs. This study examines one potential lower cost blendstock, natural gasoline (also called condensate), which is produced in abundance in the United States as a result of recent increases in crude oil and natural gas production.

The increase in U.S. domestic crude oil production from shale formations and improved recovery methods have been significant in the past decade.⁶ Along with increases in crude oil production, domestic natural gas production has also increased dramatically.⁷ Gas produced from some shale formations may be rich (or wet) and have high natural gas liquid (NGL) content. Current production of condensate in the United States, a component of NGLs found in rich gas, is estimated at $1.5 \times 10^8 \text{ m}^3$ annually compared to $9.7 \times 10^7 \text{ m}^3$ annually 10 years ago.⁸

Condensate, a component of NGLs, can come from two production sources, lease condensate or plant condensate. There is little chemical difference between lease and plant condensates beyond the definition. Lease condensate is recovered from the gas stream at the wellhead. Plant condensate remains in the gas until it is processed at gas-processing plants and is often called natural gasoline.

The Energy Policy and Conservation Act of 1975 generally prohibits export of crude oil and natural gas.⁹ Natural gas can be exported without restriction to Mexico and Canada and with

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regulatory approval to other countries. The Export Administration Act allows for limited exports of crude oil from Alaska's North Shore and Cook Inlet, some heavy California crude oils, crude oil exported to Canada that either remains in Canada or is refined and reimported back to the United States, and crude oil transported by the Trans-Alaskan Pipeline.¹⁰ These exceptions led to fewer than 1.1×10^4 m³ of crude oil per day exported in 2012.¹¹ Total U.S. imports for 2012 were 3.3×10^8 m³ of crude oil per day.¹² Once crude oil has been refined, there is no restriction on export; therefore, products such as finished diesel, gasoline, and gasoline blendstocks can be freely exported.

Export limitations become more complex when considering NGLs. NGLs include light hydrocarbons, such as ethane, propane, butanes, and pentanes, and higher hydrocarbons (pentanes plus). Ethane, propane, and butanes can also be exported without limitation. The pentanes plus fraction can be exported when it has been processed as natural gasoline but not when it is raw condensate. This has been broadly interpreted to mean condensate exports are prohibited. In June 2014, two companies sought and received approval from the U.S. Department of Commerce to export condensate.¹³

Without further approval for additional exports, there remains a glut of condensate in the U.S. market, and the price has dropped significantly.¹⁴ Traditional condensate markets, such as diluents for heavy Canadian crude oils and as a conventional gasoline blendstock, are not sufficient to consume all of the condensate on the market. One obvious solution could be to export condensate, particularly to Asia, where additional condensate is needed.¹³

Ethanol producers commonly use natural gasoline as a denaturant to render fuel-grade ethanol undrinkable, per Title 27 Part 19 Section 19.746 of the U.S. Code.¹⁵ Ethanol production in 2014 was just over 5.4×10^7 m³.¹⁶ Assuming all ethanol is denatured with natural gasoline at 2.5 vol %, this requires fewer than 1.3×10^6 m³ of natural gasoline annually as a denaturant (roughly 3.7×10^3 m³ per day).

With the huge increase in natural gasoline production, the cost has dropped, but the domestic market has not expanded. One area where condensate has traditionally been used, as a component of gasoline blendstocks, is shrinking rapidly. The growth of light domestic crude oil is pushing natural gasoline out of the refinery. Natural gasoline is also coveted as a diluent for heavy Canadian crude oil, although competition from other sources is also increasing.

This project looks at the potential of blending ethanol with natural gasoline to produce Flex-Fuels and high-octane MLEBs. For Flex-Fuel blending, the high vapor pressure of natural gasoline may limit whether the natural gasoline–ethanol blends can meet the requirements in ASTM International (ASTM) D5798-13a, "Standard Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines", for vapor pressure.

The inherently low research octane number (RON) of natural gasoline (well below 80) and high vapor pressure (about 90 kPa), especially compared to conventional BOBs, may be a limiting factor for MLEBs, particularly for summertime blending. Although this high blending vapor pressure may represent an opportunity for wintertime blending. Another issue is that ASTM D7794-14, "Standard Practice for Blending Mid-Level Ethanol Fuel Blends for Flexible-Fuel Vehicles with Automotive Spark-Ignition Engines", is currently limited to D4814 fuels (conventional gasoline) blended with

D4806 denatured fuel ethanol or D5798 Flex-Fuel, which would prohibit natural gasoline as the sole blendstock.

This project examines the properties when natural gasoline is blended with ethanol to produce MLEBs and Flex-Fuel. Common vapor pressure models were applied to the data to determine how the predicted vapor pressure compared to the measured data.

2. MATERIALS AND METHODS

A total of eight natural gasoline samples were collected from ethanol producers and pipeline companies. The samples were stored cold until needed for analysis. An undenatured ethanol sample was provided by an ethanol producer. The sample was denatured per the formulas provided by the Alcohol and Tobacco Tax and Trade Bureau using natural gasoline G, which was provided by an ethanol producer. Two BOBs were acquired from the manufacturers.

Specification D5798-13a includes limitations on the hydrocarbon blendstock used to make Flex-Fuel. Commonly, the blendstock is a BOB and not a finished gasoline or other hydrocarbon. The hydrocarbon blendstock must meet distillation, oxidation stability, and copper and silver strip corrosion requirements and report the vapor pressure. The natural gasolines were tested for all of these properties as well as simulated distillation, vapor pressure, aromatic content, sulfur content, and detailed hydrocarbon analysis (DHA). ASTM test method numbers are given with the results in Tables 1 and 2.

Natural gasoline–ethanol blends were prepared volumetrically. All blends, equipment, and containers were kept cold during blending, which was performed in a cold room. E51, E60, E70, and E83 blends were targeted to cover the range of allowable ethanol content in D5798-13a. Two MLEBs were made, an E30 and an E40, to round out the data set, as these blends are becoming increasingly popular offerings from so-called blender pumps. The actual ethanol content was verified by D5501-12e1, a gas chromatography method. The blends were evaluated for RON and vapor pressure. Additionally, heat of vaporization (HOV) was estimated from the sample composition obtained by DHA and ethanol content via D5501 and individual component HOV values.¹⁷

Measured vapor pressure results were compared to two vapor pressure models developed for ethanol blends made with more typical BOBs. The first model, by Reddy,¹⁸ used a universal quasichemical functional-group activity coefficients (UNIFAC) model of the blend components to estimate vapor pressures, followed by curve fitting of the model results to develop a readily usable mathematical function that approximates the UNIFAC results for BOBs of various vapor pressures combined with ethanol at various concentrations. The second model, described by Christiansen and co-workers¹⁹ but originally proposed by Pumphrey and co-workers,²⁰ is based on the Wilson equation with the gasoline blendstock included as a single pseudo-component. This model has been shown to be readily expandable to new components (other alcohols and oxygenates) and multiple components (mixed alcohols in hydrocarbon blendstocks). Both models estimate vapor pressure based on only two inputs, the volume concentration of ethanol and the vapor pressure of the blendstock. Supplemental Material 1 of the Supporting Information includes the description of the development of the Wilson equation, taken from Christensen and co-workers.¹⁹

3. RESULTS AND DISCUSSION

A DHA, per ASTM D6729-04 (reapproved 2009), was performed on the samples to determine the major components [the full DHA results are presented in Supplemental Material 2 of the Supporting Information, with one of the BOBs, a California reformulated BOB (CARBOB), also presented for reference]. All of the natural gasoline samples were between 80 and 95% paraffinic, 5 and 15% naphthenic, 3% or less aromatics, and the balance olefins. No oxygenates were

Table 1. Compound Class by DHA and Benzene Content (Weight Percent) for Natural Gasoline Samples by ASTM D6729-04 (Reapproved 2009) and Benzene by ASTM D5580-13^a

| property | ASTM method | sample | | | | | | | | |
|-------------------------|-------------|--------|-------|-------|-------|-------|-------|-------|-------|-----------------|
| | | A | B | C | D | E | F | G | H | CARBOB |
| paraffins (wt %) | D6729 | 37.7 | 40.7 | 40.9 | 39.1 | 48.4 | 45.0 | 45.5 | 41.0 | 7.0 |
| isoparaffins (wt %) | D6729 | 42.9 | 43.2 | 43.2 | 45.7 | 37.1 | 41.1 | 48.3 | 42.5 | 48.7 |
| total aromatics (wt %) | D6729 | 3.72 | 2.57 | 2.69 | 2.19 | 1.28 | 0.974 | 0.576 | 2.38 | 18.7 |
| | D5580 | 4.19 | 2.41 | 2.38 | 2.17 | 1.3 | 0.95 | 0.34 | 2.18 | NM ^b |
| benzene (wt %) | D6729 | 1.21 | 0.738 | 0.700 | 0.96 | 0.734 | 0.461 | 0.146 | 0.647 | 1.09 |
| | D5580 | 1.18 | 0.78 | 0.73 | 0.961 | 0.76 | 0.46 | <0.1 | 0.68 | NM |
| total naphthenes (wt %) | D6729 | 14.8 | 12.9 | 12.5 | 12.4 | 12.7 | 12.2 | 5.30 | 13.4 | 13.9 |
| olefins (wt %) | D6729 | 0.712 | 0.681 | 0.608 | 0.584 | 0.511 | 0.708 | 0.317 | 0.699 | 9.86 |
| unidentified (wt %) | D6729 | 0.113 | 0.030 | 0.025 | 0.019 | 0.055 | 0.031 | 0.037 | 0.000 | 1.83 |

^aNote that totals may not equal 100 because of rounding. ^bNM = not measured.

Table 2. Test Methods and Results for Natural Gasoline Sample Analysis

| property | method | A | B | C | D | E | F | G | H |
|---------------------------------------|---------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| vapor pressure (kPa) | D5191-13 | 95 | 90 | 91 | 89 | 100 | 100 | 90 | 91 |
| API gravity (deg) | D4052-11 | 78.3 | 81 | 80.9 | 81.1 | 82.1 | 82 | 83.6 | 80.5 |
| density at 15 °C (g/cm ³) | D4052-11 | 0.6738 | 0.6654 | 0.6655 | 0.6650 | 0.6618 | 0.6622 | 0.6571 | 0.6668 |
| copper corrosion | D130-12 | 1a | 1a | 1a | 1a | 1a | 1a | 1a | 1a |
| silver corrosion | D4814-11, Annex A-1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| RON | D2699-13b | 70.8 | 71.7 | 71.5 | 71.4 | 69.4 | 70.6 | 66.7 | 71.2 |
| MON | D2700-13b | 68.9 | 70.5 | 70.2 | 69.3 | 67.6 | 68.7 | 66.7 | 69.8 |
| stability, break (yes/no) | D525-12a | no | no | no | no | no | no | no | no |
| sulfur (ppm) | D5453-12 | 16.6 | 48.8 | 52.1 | 145.6 | 63.6 | 4.6 | 16.3 | 44.5 |
| lower heating value (kJ/kg) | D240-14 | 103.9 | 103.9 | 104.2 | 101.6 | 104.2 | 104.2 | 104.2 | 104.2 |
| distillation (°C) | D86-12 | | | | | | | | |
| initial boiling point (°C) | | 29.6 | 29.4 | 29.2 | 30.7 | 28.3 | 27.2 | 32.3 | 29.2 |
| T10 (°C) | | 39.2 | 39.4 | 39.1 | 40.1 | 40.1 | 38.2 | 40.8 | 39.8 |
| T50 (°C) | | 51.7 | 47.9 | 47.7 | 48.4 | 47.7 | 49.3 | 48.2 | 49.6 |
| T90 (°C) | | 100.1 | 86.7 | 86.5 | 86.4 | 77.4 | 81.6 | 88.1 | 89.4 |
| final boiling point (°C) | | 152.9 | 126.7 | 129.1 | 121.3 | 107.9 | 110.5 | 127.8 | 129.9 |
| distillation (°C) | D7096-10 | | | | | | | | |
| initial boiling point (°C) | | -3.7 | -3.1 | -2.7 | -2 | -43.5 | -17.6 | 22.3 | -3.3 |
| T10 (°C) | | 25.1 | 25.3 | 25.6 | 25.7 | 26.0 | 25.3 | 26 | 25.4 |
| T50 (°C) | | 36.2 | 35.8 | 35.9 | 36.0 | 35.9 | 36.3 | 36.0 | 36.0 |
| T90 (°C) | | 102.9 | 92.8 | 92.6 | 94.2 | 88.9 | 91.8 | 92.3 | 96.2 |
| final boiling point (°C) | | 144.5 | 137.1 | 137.5 | 137.7 | 125.3 | 133.7 | 138.6 | 138.1 |

found. Table 1 shows the compound classes for each sample. Benzene and total aromatics were measured by DHA and ASTM D5580-13. Aromatics were mainly composed of benzene and toluene and were low in all samples. Agreement was typically good between the methods. The United States Environmental Protection Agency (U.S. EPA) limits benzene content in conventional gasoline to less than 0.62 vol %, per D4814-13b. The U.S. EPA indicates that blends of E30 and E40 must meet the regulatory requirements for finished gasoline, including benzene limitations. For these samples, a 30 vol % blend with natural gasoline A would exceed the 0.62 vol % benzene maximum in D4814-13b. For this natural gasoline, at least 32 vol % ethanol would be needed to reduce the benzene to an acceptable level. All blends with natural gasoline D fell below the benzene maximum.

The majority of the paraffinic fraction came from compounds with seven or fewer carbon atoms. The samples were mostly *n*-pentane and isopentanes (accounting for approximately 50% of the samples), as shown in the data in Supplemental Material 2 of the Supporting Information. The samples differed by the diversity of isoparaffins identified, ranging from 21 unique

compounds to 49 (natural gasoline samples E and A, respectively). No consistent differences were observed between the samples collected from ethanol producers and pipeline companies.

Additional properties of the natural gasoline samples were measured and are reported in Table 2. The samples gave highly similar results when tested for density, copper and silver corrosion, and stability. The vapor pressures were between 83 and 103 kPa, with RONs of about 70 for all samples. The sulfur content ranged from 4.6 ppm in natural gasoline sample F to 146 ppm in natural gasoline sample D. The U.S. EPA regulates the sulfur content in finished gasoline and ethanol, and this has been interpreted that the sulfur content of MLEBs would need to meet the same limitations as conventional gasoline. Specification D5798-13a aligns with specification D4814-13b and includes a limit on sulfur of 80 ppm. A reduction in the gasoline sulfur content to 10 ppm starting in 2017 was recently announced as part of the Tier 3 gasoline rule.²¹ The new sulfur limits would require natural gasoline used as the hydrocarbon blendstock in Flex-Fuel to have 20 ppm sulfur or less (assuming an E51 blend). This level would have to be even lower if natural

gasoline was the sole hydrocarbon in a high-octane MLEB. However, when used only as a denaturant for ethanol, the sulfur content in natural gasoline could be as high as 330 ppm.

Table 2 shows the results for natural gasoline distillation by method D86-12. D86 was modified in 2007 to remove natural gasoline from the method scope. A more appropriate method to determine boiling characteristics of natural gasoline may be simulated distillation by method D7096-10. Currently, there is no correlation between D86 and D7096 for natural gasoline. As shown in Figure 1, the largest discrepancy between the

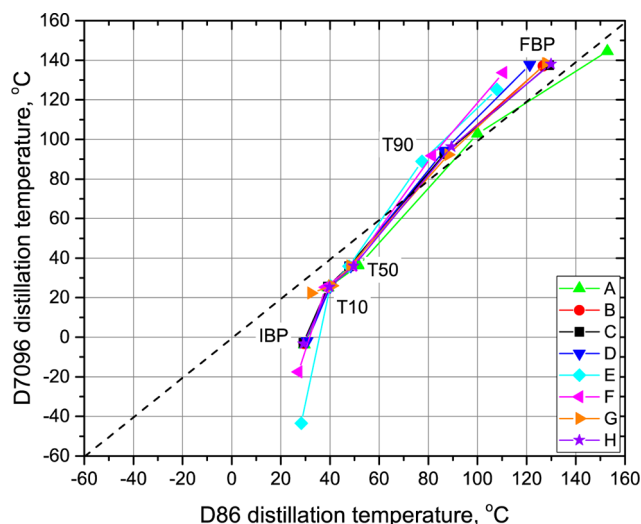


Figure 1. Comparison of D86 and D7096 (simulated distillation) for the natural gasoline samples.

methods for the natural gasoline samples is for the initial boiling point. The DHA confirmed that several samples had relatively high levels of low-boiling-point materials, such as propane and butanes, which are not differentiated in the D86-12 method. The requirements of D5798-13a include a maximum final boiling point of the hydrocarbon blendstock of 225 °C by D86; these natural gasoline samples readily met that requirement.

Two natural gasoline samples were selected to blend with ethanol: sample A, representing a blendstock that would comply with U.S. EPA Tier 3 requirements when blended with 51% ethanol, and sample D, representing a blendstock complying with the current U.S. EPA Tier 2 sulfur requirements, as well as the sample with the highest sulfur. D5501-12e1 results for actual ethanol content in the blends prepared are presented in Table 3. The ethanol content typically exceeded the target value by a few percent.

The tendency of a spark-ignited engine fuel to autoignite and cause knock is measured as the octane number, a critical performance parameter for spark-ignition engines. In the United States, the octane number at the retail pump is given as the average of two octane number measurements, RON (ASTM D2699-13b) and motor octane number (MON) (ASTM D2700-13b), and is known as the anti-knock index. The primary differences between the RON and MON measurements are intake temperature and engine speed in the test. RON is measured at a controlled lower intake temperature and engine speed, while MON controls the intake mixture temperature. Recent studies have demonstrated that MON is much less relevant in modern engines than was the case when these tests were introduced in 1932, and in fact,

Table 3. Measured Properties of Ethanol–Natural Gasoline Blends

| natural gasoline | target ethanol content | measured ethanol content (vol %) | vapor pressure (kPa) | RON | MON | sulfur (ppm) |
|------------------|------------------------|----------------------------------|----------------------|-------|-----------------|--------------|
| A | 0 | 0 | 95 | 70.8 | 68.9 | 16.6 |
| A | 30 | 30 | 94 | 94.3 | 86.5 | 11.62 |
| A | 40 | 40 | 90 | 98.8 | 87.7 | 9.96 |
| A | 51 | 54 | 86 | 102.9 | NM ^a | 7.64 |
| A | 60 | 65 | 81 | 104.4 | NM | 5.81 |
| A | 70 | 74 | 69 | NM | NM | 4.32 |
| A | 83 | 85 | 50 | NM | NM | 2.49 |
| D | 0 | 0 | 89 | 71.4 | 69.3 | 145.6 |
| D | 40 | 40 | 88 | 99.4 | 88.3 | 87.36 |
| D | 60 | 57 | 84 | 103.0 | NM | 62.61 |
| D | 60 | 63 | 79 | NM | NM | 53.87 |
| D | 70 | 71 | 65 | NM | NM | 42.22 |
| D | 83 | 84 | 49 | NM | NM | 23.30 |

^aNot measured because of insufficient sample available.

increasing MON at a constant RON may actually lower the fuel knock resistance.²²

Ethanol has a RON of approximately 110,¹⁹ significantly higher than typical U.S. gasoline at 91–93,²³ and, today, is commonly blended into sub-octane BOBs having RONs of approximately 84–88²⁴ to produce finished gasoline having an adequate octane number (in terms of the anti-knock index). The RON of MLEBs has been measured in a variety of research projects.^{5,23–27} Ethanol has a significant and nonlinear effect on the RON of the finished blend, with a diminishing effect on the RON as the ethanol content is increased. The RON of the final blend depends upon the starting RON of the BOB and increases rapidly to around 100–105 at E50, eventually reaching 110 at pure ethanol. Anderson and co-workers⁵ have considered the potential benefit of blending additional ethanol into gasoline. By blending more ethanol into BOBs to make a high-octane fuel, highly efficient advanced engine technologies can be enabled. This advanced engine technology employs direct fuel injection, which also benefits from the high HOV of ethanol, leading to evaporative cooling of the fuel–air mixture and enhanced knock resistance.

The published research has considered conventional BOBs, with RONs of approximately 84 and higher. Few studies report the effect of ethanol on the octane number when blended into a blendstock with significantly lower RON. Szybist and co-workers report results for blending of ethanol into a straight-run gasoline (SRG) (RON of 65) and *n*-heptane (RON of 0 by definition).²⁶ Anderson and co-workers also report on the properties of ethanol blended into a BOB with a RON of 82.²⁷

Figure 2 shows RON results for the ethanol–natural gasoline blends prepared for this study, ethanol blended with a CARBOB, and data from ref 26. The results indicate that, even for these low-RON blendstocks, the 91 RON level typical of finished regular gasoline would be met at approximately 30 vol % ethanol. However, the effect of the low blendstock RON is evident, as the 91 RON level is met for the sub-octane CARBOB at 10 vol % ethanol. The results presented here confirm results seen by the American Petroleum Institute in its study of mid-level ethanol blends, showing that RON increases rapidly with small additions of ethanol.²³ RON increases more slowly above about 50 vol % ethanol in the CARBOB because of the higher starting RON of the sample. The low-RON

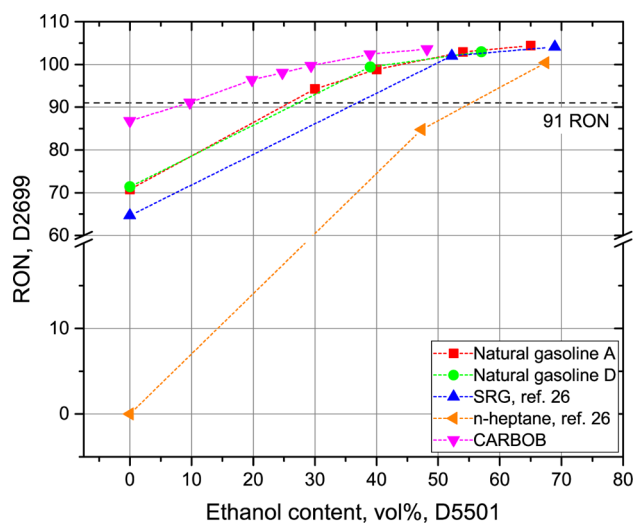


Figure 2. RON for ethanol–natural gasoline blends and other samples. Lines are for clarity and do not imply a curve fit.

natural gasoline blendstocks required more ethanol to reach the same RON levels.

Figure 3 shows results for measurement of HOV of ethanol blends with natural gasoline A. These data are very similar to

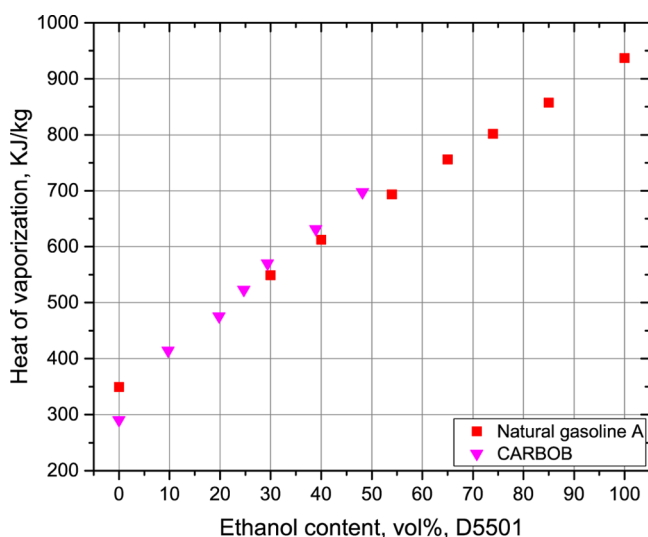


Figure 3. HOV of ethanol blends with natural gasoline A at 25 °C estimated by DHA. Results for CARBOB are shown for comparison.

HOV measured for CARBOB ethanol blends, indicating little difference in how hydrocarbon blendstocks affect this important knock resistance parameter. Blending ethanol at 50 vol % or higher can double the HOV of the fuel blend.

Octane sensitivity is defined as the difference between RON and MON. In modern engines, fuels with higher sensitivity generally exhibit higher knock resistance under many operating conditions.²² Paraffinic fuels have a sensitivity of near zero, and thus, sensitivity for the natural gasoline samples should be very low. The addition of aromatics, other non-paraffin hydrocarbons, or ethanol increases sensitivity. Figure 4 reports sensitivity for ethanol blends with natural gasolines A and D and a conventional gasoline blendstock along with literature results for SRG and *n*-heptane. The increase in octane sensitivity upon blending ethanol is very similar for all

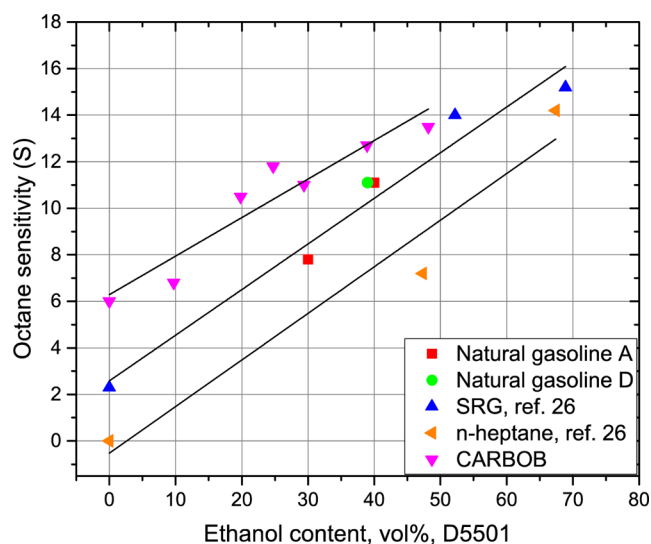


Figure 4. Octane sensitivity (*S*) for natural gasoline blends with ethanol. CARBOB is shown for comparison. Lines are shown for clarity.

blendstocks. The CARBOB increases sensitivity by about 6 with the addition of 30 vol % ethanol. Although the data are limited, by assuming that the SRG and natural gasoline are similar, an increase of 6 in sensitivity also requires the addition of about 30 vol % ethanol. However, the absolute value of sensitivity also depends upon the initial sensitivity of the blendstock; that is, a higher ethanol blend level is required to obtain a target level of sensitivity in natural gasoline compared to the conventional blendstock.

Minimum and maximum vapor pressure requirements are important performance properties for Flex-Fuel, which change depending upon the location and time of year. The vapor pressure requirements in D5798-13a are divided into four classes. The vapor pressure limits are set based on cold starting and driveability requirements^{28,29} as well as the need to control evaporative emissions in summer months. To give blenders maximum flexibility to meet the D5798-13a requirements, the ethanol content of Flex-Fuel can range between 51 and 83 vol %, as needed, to meet vapor pressure requirements.

For evaporative emissions control, the U.S. EPA limits gasoline vapor pressure to a maximum of 62 kPa from June 1 through September 15 for most areas of the country. As stated previously, it is widely believed that the U.S. EPA will require MLEBs to meet the same standards as conventional gasoline. Lower vapor pressure requirements exist for areas with ozone non-attainment and/or reformulated gasoline. Gasoline-ethanol blends with 10 vol % ethanol receive a 7 kPa (1 psi) waiver in conventional blends, although some limitations apply.³⁰ This waiver has not been granted to E15 blends.

Figure 5 shows results for vapor pressure of the ethanol–natural gasoline blends, the ethanol–SRG blend from ref 26, ethanol blended with the sub-octane CARBOB, and ethanol blended with a conventional wintertime BOB (or CBOB).

Classes 1 and 4 are the most common classes for Flex-Fuel, with the highest volumes sold throughout the year. The vapor pressures of the two natural gasolines, A and D, are 89 and 95 kPa, which could make it difficult to meet the lowest maximum vapor pressure for Flex-Fuel, and indeed, only the highest ethanol content blends were below the maximum 62 kPa class 1 requirement. Table 4 shows the range of the ethanol content

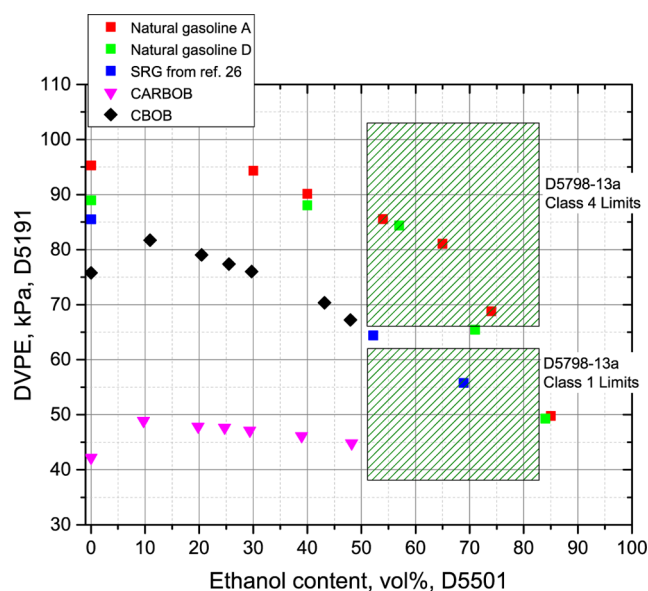


Figure 5. Vapor pressure (from ASTM D5191-13) for the ethanol–natural gasoline blends and other samples.

Table 4. Approximate Concentration of Ethanol Needed To Meet ASTM D5798-13a Vapor Pressure Limits for Flex-Fuel across All Classes

| | natural gasoline A | natural gasoline D | SRG from ref 26 |
|---------------------|--------------------|--------------------|-----------------|
| class 1: 38–62 kPa | E78–E83 | E74–E83 | E57–E83 |
| class 2: 48–65 kPa | E76–E83 | E71–E83 | E51–E83 |
| class 3: 59–83 kPa | E66–E80 | E61–E77 | <i>a</i> |
| class 4: 66–103 kPa | E51–E76 | E51–E71 | <i>a</i> |

^aVapor pressure requirements cannot be met with a blend of SRG and at least 51 vol % ethanol.

that would meet the vapor pressure requirements for each Flex-Fuel volatility class based on linear interpolation of the data for the two natural gasoline samples examined here. Notably, the SRG tested in ref 26 required 58 vol % ethanol to reduce its vapor pressure to below the maximum 62 kPa class 1 limit, a significantly lower amount than required for the natural gasoline samples.

Vapor pressure models can be used to help blenders determine the appropriate ratios of components to produce compliant blends directly without going through an iterative process of blending and testing. Figure 6 shows the predicted and measured vapor pressure of the natural gasoline–ethanol blends produced for this work for both MLEBs and Flex-Fuel. The Reddy¹⁸ and Pumphrey and co-workers²⁰ models closely align with each other and approximate the measured vapor pressure to within a maximum error of less than 7 kPa for the nine blends measured. In most cases, the difference between the measured result and the estimated result falls within the reproducibility of the method (approximately ± 2.75 kPa).

One sample deviates significantly from the models, the E65 in natural gasoline A. No additional amount of natural gasoline A remains to reblend and retest, but future work should consider whether this deviation is real and a significant nonlinearity in the curve or simply an analytical error.

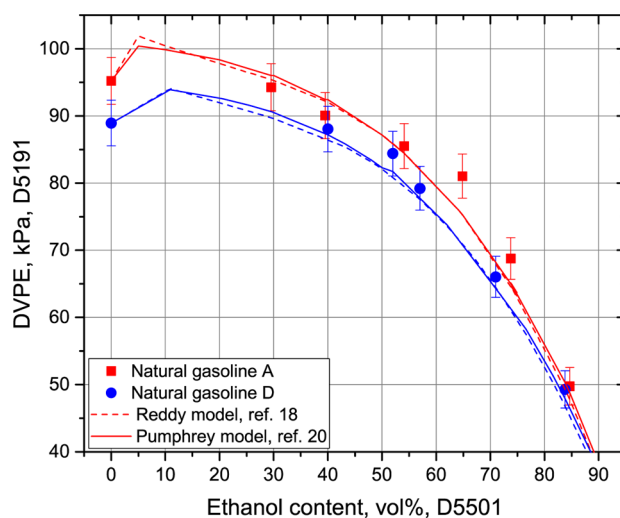


Figure 6. Measured and predicted vapor pressure for natural gasoline–ethanol blends. Error bars for the measured values represent the reproducibility of the ASTM D5191-13 method.

CONCLUSION

Eight natural gasoline samples were collected from pipeline companies or ethanol producers around the United States. Analysis of the natural gasolines shows that the samples are 80–95% paraffinic, 5–15% naphthenic, 3% or less aromatics, and the balance olefins. The paraffins were typically *n*-pentane and isopentanes. The RON for the natural gasoline ranged from 67 to 72. Vapor pressure (ASTM D5191-13) ranged from 89 to 101 kPa. The benzene content ranged from approximately 0.1 to 1.2 wt %, such that blends of E30 or more would meet U.S. EPA limits for the benzene content in gasoline. The sulfur content in the natural gasoline samples ranged from 4 to 146 ppm. If Flex-Fuels were produced with the minimum allowable ethanol content of 51 vol %, a natural gasoline blendstock would be required to have 20 ppm of sulfur or less for the finished fuel to meet the forthcoming U.S. EPA Tier 3 gasoline sulfur limit.

A 17 ppm sulfur natural gasoline and a 146 ppm sulfur natural gasoline were selected for blending with ethanol to produce Flex-Fuels and MLEBs. For knock resistance, the results indicate that, even for these low-RON blendstocks, the 91 RON level typical of finished regular gasoline in the United States would be met at approximately 30 vol % ethanol. The impact of ethanol blending on HOV was identical for a conventional BOB and ethanol–natural gasoline blends such that the blend HOV is twice that of the hydrocarbon blendstock at 50 vol % ethanol. For these high-vapor-pressure blendstocks, over 70 vol % ethanol could be blended with natural gasoline while still meeting the class 4 (wintertime) Flex-Fuel minimum vapor pressure requirement of 66 kPa. For blending of class 1 (summertime) Flex-Fuel, a minimum of 74 vol % ethanol was required to meet the 62 kPa maximum allowable vapor pressure. Modeling of vapor pressure using UNIFAC and Wilson equation-based approaches provided good agreement with experimental data.

ASSOCIATED CONTENT

Supporting Information

Details of Wilson equation-based vapor pressure modeling (Supplemental Material 1) and full DHA results (Supplemental Material 2) (PDF). The Supporting Information is available

free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.5b00818.

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Notes

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NOMENCLATURE

ASTM = ASTM International
 BOB = blendstock for oxygenate blending
 CBOB = conventional blendstock for oxygenate blending
 CARBOB = California reformulated blendstock for oxygenate blending
 DHA = detailed hydrocarbon analysis
 E_{xx} = blend of ethanol and hydrocarbon where *xx* is the volume percent ethanol in the blend
 HOV = heat of vaporization
 MLEB = mid-level ethanol blend
 MON = motor octane number
 NG = natural gasoline
 NGL = natural gas liquid
 ppm = parts per million
 RON = research octane number
 SRG = straight-run gasoline
 UNIFAC = universal quasichemical functional-group activity coefficients
 U.S. EPA = United States Environmental Protection Agency
 vol % = percent by volume

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