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Vice President
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From: Robert L. McCormick, National Renewable Energy Laboratory
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March 26, 2012

Re: **Discussion Document – Effect of Ethanol Blending on Gasoline RVP**

The United States Environmental Protection Agency (EPA) sets a maximum allowable Reid vapor pressure (RVP)[a] for gasoline and gasoline/ethanol blends in the summer months[b] in order to reduce evaporation of fuel from cars and from storage and transfer equipment. The addition of 10% ethanol to gasoline increases the RVP of the blend by about 1 psi. Beginning in 1992, nominal 10% ethanol (9-10 vol%, E10) summertime blends with gasoline were permitted a vapor pressure 1 psi greater than the normal EPA summer standards for conventional gasoline.[c] Higher level ethanol blends such as E15 have not received this waiver and are limited to an RVP of 9.0 psi in summer. Additionally, the 1-psi waiver does not apply to reformulated gasoline (RFG),[d] which must meet strict emission requirements that effectively limit RVP. In 2010 RFG comprised over a third of the gasoline sold in the U.S.

Over the next decade the federal Renewable Fuels Standard (RFS)[1] will require blending of 20 billion annual gallons more renewable fuel than used currently. Additionally, in 2011, EPA approved the use of up to 15% ethanol in gasoline (E15) as fuel for 2001 and newer model year light duty vehicles.[2] Thus, much of the future RFS mandated biofuel may be ethanol as E15, in particular ethanol produced from cellulosic biomass. Given the large potential market for E15, we have undertaken a review of vapor pressure regulations as well as the available data on the effect of ethanol at different blend levels on gasoline RVP.

The analysis demonstrates that the RVP impact of 15% ethanol is indistinguishable from that of 10% ethanol in gasoline for all volatility seasons and base hydrocarbon vapor pressures. For E20, effects are also indistinguishable for blends meeting the summer ozone season RVP requirements. However, a small reduction in RVP becomes apparent at vapor pressures over about 12 psi up to the maximum tested (about 16 psi) for E20. For E30, RVP is slightly lower

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[a] RVP, or what is more properly called the dry vapor pressure equivalent (DVPE), or more simply called vapor pressure, is the vapor pressure of a fuel measured at 100 °F (37.8 °C) in a vessel with a vapor/liquid volume ratio of 4:1 by ASTM D5191 or similar method. Because RVP is still commonly used in the industry the term is retained throughout this document.

[b] The summertime high ozone season has been determined by EPA to run from June 1 to September 15 at retail level and from May 1 to September 15 at terminals.

[c] Certain states have state implementation plan-approved RVP standard which do not provide for the 1.0 psi waiver (e.g. Maine, New York, Pennsylvania, Texas); or may have received EPA approval to opt-out of the 1.0 psi waiver provision per Section 1501(c) of the Energy Policy Act of 2005 [Clean Air Act 211(h)(5), as amended]. Additionally, Alaska, Hawaii, and U.S. territories are exempted from federal volatility regulations.

[d] RFG is a type of gasoline required since 1995 in cities with high smog levels. RFG differs from conventional U.S. gasoline, in that levels of certain components have been varied to reduce emissions of smog-forming and toxic pollutants.

relative to E10 for blends below about 9 psi, but significantly lower (over 1 psi) for blends with higher RVP. These results show that with respect to the regulation of gasoline vapor pressure for the summer ozone season, there is no technical reason for treating E10 differently from E15 or E20.

Background

Blending of ethanol into gasoline at 10 volume percent causes the RVP to increase by about 1 psi despite the fact that fuel grade ethanol has a lower vapor pressure than gasoline (see Figure 1). The low vapor pressure of fuel grade ethanol is caused by attractive forces between the ethanol molecules. The strongly electronegative oxygen atom in each ethanol molecule is attracted to the somewhat positive hydrogen atoms in other ethanol molecules. The attraction between ethanol molecules means that it has a stronger tendency to stay as a liquid and not vaporize into the more dispersed gaseous state. However, when blended into gasoline at relatively low concentrations the more numerous gasoline molecules disrupt the attractive forces between ethanol molecules and allow the ethanol to readily evaporate, raising the vapor pressure of the blend. Not surprisingly this increase in vapor pressure with ethanol is more marked with the lower RVP hydrocarbon blendstocks. This would be true with the addition of any component which raises vapor pressure, as the final pressure is a weighted average of the pressure contributions of all of the components. As ethanol content is increased above about 20% the vapor pressure increase becomes less, and above about 50% ethanol vapor pressure for the blend is less than that of the gasoline.

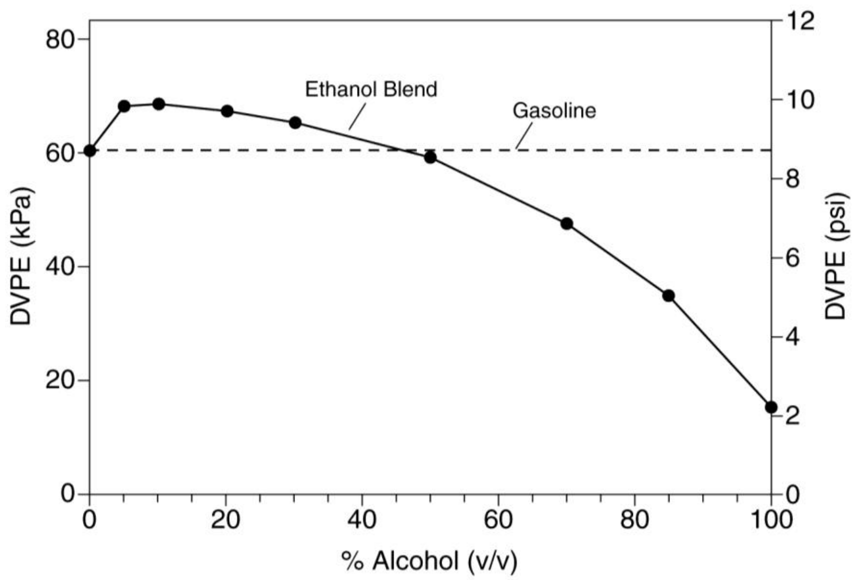

Figure 1. Effect of ethanol blending on vapor pressure of gasoline.

When ethanol was first permitted as an additive in gasoline at concentrations of up to 10% in 1979, its effect on vapor pressure was not regulated.[3] In 1992, new EPA regulations (40 CFR 80.27) provided a 1-psi waiver for ethanol blends that contained between 9 and 10 percent ethanol.   Most, but not all, of the state-set RVP standards also allow a 1-psi waiver for blends of 9 to 10 percent ethanol.[4,5] The purpose of the 1-psi waiver was to support the emerging ethanol industry. At that time EPA believed it would be difficult to economically justify a separate storage and distribution system for the small amount of lower vapor pressure gasoline needed for

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ethanol blending, with the result that low RVP gasoline blendstock for ethanol blending would not be made available.[6] The waiver allowed E10 to be made with the same gasoline distributed as finished fuel to be used without ethanol addition. Allowing vapor pressure to increase also lets refiners keep volatile components in the gasoline. This is estimated by the U.S. Energy Information Administration (EIA) to provide a 2 to 3% increase in conventional gasoline volume.[7]

In 1995 RFG was introduced in a number of cities throughout the U.S. Since 1998 RFG formulation has been based on the “complex” model which relates fuel properties to emissions and is used to show that a given formulation will produce the required emission reductions.[8] In the complex model there are no specific limits on RVP, it is a model variable. However, high RVP fuels are not able to meet the required emission reductions so that in practice RFG has lower RVP than most other forms of gasoline. The use of RFG rapidly expanded and in the 2010 RFG Survey Data from EIA[9] it was reported that about one-third of the gasoline sold (47.2 billion gallons) was RFG and the other two-thirds were conventional gasoline (90.7 billion gallons).

The summer 2011 Alliance of Automobile Manufacturers’ (AAM) survey of 430 gasoline stations found that 94% were selling nominal E10 gasoline, including all but one of the 80 surveyed gasoline stations that were selling gasoline with the lowest RVP, 7.0 psi or less (see Figure 2). This suggests that low RVP gasoline blendstock, necessary to meet the strictest RVP standards or to formulate RFG with the inclusion of 10% ethanol, is available in sufficient quantities for a large portion of the US market. However, such blendstocks are produced by removing light ends, reducing the volume of gasoline available.[7] Note that these blendstocks may not have adequately low RVP for blending with 15% ethanol, which has a more strict RVP requirement.

With two-thirds of the U.S. fuel supply incorporating ethanol but not subject to the stricter effective RVP limits imposed by the complex model on RFG, removing the 1-psi waiver would result in a significant reduction in average vapor pressure and a consequent reduction in volatile organic carbon (VOC) emissions. The scale of emissions change will depend on ambient conditions and the overall emissions impact can only be estimated. However, according to a recent Coordinating Research Council (CRC) analysis using EPA’s MOVES air emissions model,[10] reducing summer RVP by 1 psi in Cook County, Illinois (Chicago and vicinity), will reduce evaporative VOC emissions by about 5% and total emissions (tailpipe plus evaporative) by about 2.5%.

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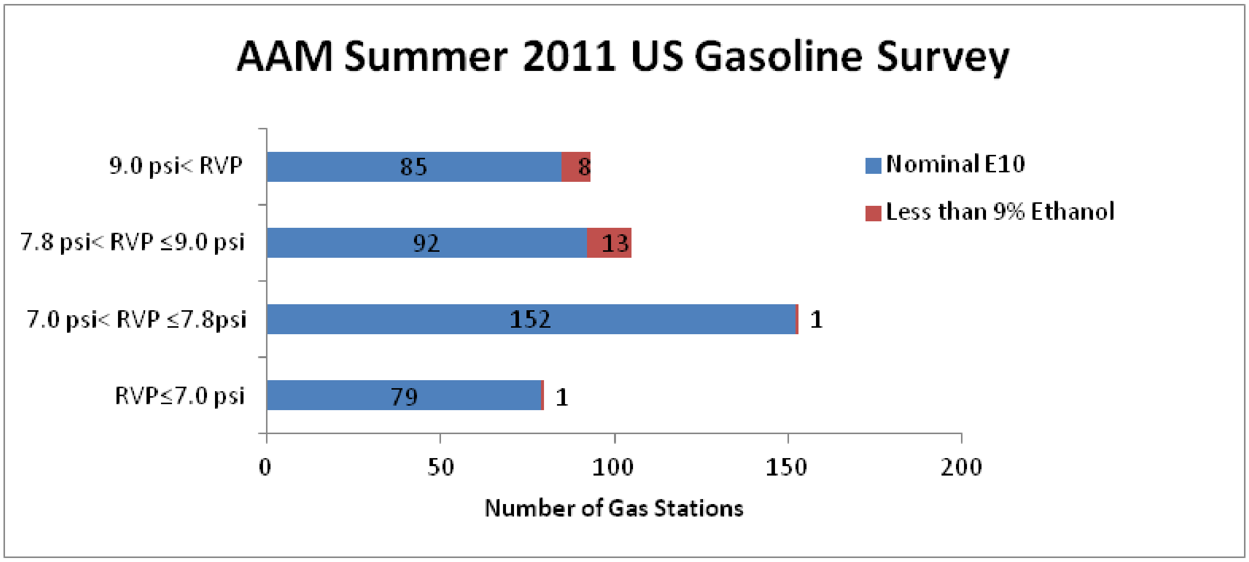

Figure 2. AAM summer 2011 US gasoline survey; results from 430 gasoline stations showing proportion selling E10.[11]

Experimental Results

The American Petroleum Institute has tested the effect of added ethanol on the vapor pressure of 71 ethanol-free gasolines.[12] The testing was done on a wide range of gasolines and blendstocks, as shown in Table 1, and the level of ethanol considered included volumetric concentrations of 0, 10, 12.5, 15, 20 and 30%. Various other researchers[13,14,15,16,17,18] have measured the effect of ethanol addition on a much smaller number of gasolines. The results of these studies have been combined in the graphs below and appear to be consistent with the API results.

Figure 3 shows how blending of 10% ethanol affects the RVP of the gasolines and blendstocks considered in this analysis. It was apparent that the results fell into two ranges. For blendstocks with RVP of about 9 psi or higher, blending of 10% ethanol increases RVP by slightly less than 1 psi on average. However, for lower RVP blendstocks 10% ethanol causes a larger increase in RVP, and this increase grows larger as the base blendstock RVP is lowered. In blendstocks intended for the lowest RVP gasolines (<6 psi base blendstock RVP) the average increase from E10 is over 1.5 psi, and in some cases can be over 2.0 psi.

An interesting feature of Figure 3 is that at the same base hydrocarbon RVP level, different blendstocks can have a range of RVP response to 10% ethanol. Even above 9 psi there are a few blendstocks that yield significantly more or less than the 1-psi RVP increase. The range of vapor pressure impacts for the same concentration of ethanol in different base hydrocarbons is much larger than the range in vapor pressure impact caused by changing the ethanol content from 10% to 15%, 20% or even 30% using the same base hydrocarbon – as can be seen by comparing Figure 3 with Figures 4 through 6, below. This is attributed to the proportion of different compounds in the base gasoline, each of which will be more or less repelled by the polar ethanol molecules. With greater repulsion, there will be higher vapor pressure. For example, researchers have found that the higher the content of saturated hydrocarbons or paraffins, the higher the vapor pressure of the resultant alcohol-hydrocarbon blend.[19]

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Table 1. Base Stock Sample Distribution and Range of Volatility Properties, API Study

		Sample Counts			Selected Volatility Characteristics				
	States	**RUL[a]**	**PUL[b]**	**Total**	**Vapor Pressure (psi)**	**T10 (F)**	**T50 (F)**	**T90 (F)**	**TV/L=20 (F)**
ASTM Class AA	TX, PA, UT, TN	5	6	11	6.4 – 7.6	130 – 156	213 – 231	306 – 347	147 – 170
ASTM Class A	TX, WV, AR, SD	5	5	10	7.5 – 8.2	124 – 146	202 – 240	312 – 332	141 – 160
ASTM Class B	NE, SD, UT	4	3	7	8.9 – 11.0	119 – 134	194 – 222	29 – 333	128 – 153
ASTM Class C	TX, AL, LA, OK	3	4	7	8.3 – 12.3	110 – 132	200 – 230	320 – 351	126 – 147
ASTM Class D	TX, AL, NC	4	4	8	11.0 – 13.2	105 – 116	191 – 229	315 – 338	123 – 130
ASTM Class E	AK, SD, WV, UT, WA, IA	6	6	12	11.0 – 13.8	100 – 125	176 – 228	262 – 317	110 – 134
Refiner-supplied Summer BOBs	TX, NJ, IL, CA	3	7	10	4.8 – 7.0	139 – 163	197 – 235	310 – 335	156 – 173
Refiner-supplied Winter BOBs	TX, IL	1	2	3	10.9 – 11.7	109 – 120	193 – 229	296 – 346	120 – 134
CRC Fuels		3	0	3	13.9 – 14.7	93 – 96	143 – 171	269 – 279	104 – 109
TOTALS		**34**	**37**	**71**					

[a]Regular unleaded gasoline, [b]Premium unleaded gasoline.

Figure 4 compares E10 RVP with E15 RVP in the same base hydrocarbon. At higher blend RVP the E15 values tend to be slightly lower, however this effect averages only 0.1 psi, which is within the repeatability of the RVP test method and may not be statistically significant. In a given hydrocarbon base fuel, blending of 10% and 15% ethanol will have essentially the same effect on RVP.

Figures 5 and 6 show similar plots comparing the RVP of E10 with that of E20 and E30. At low base fuel RVP, E20 results are virtually identical to those of E10, but there appears to be a small but significant reduction in RVP for blends above about12 psi, in some cases by as much as half a psi. For E30 the RVP reduction is larger with an average reduction of 0.6 psi relative to blending of E10. In a few cases the RVP reduction is greater than 1 psi, although only for RVPs above 10 psi.

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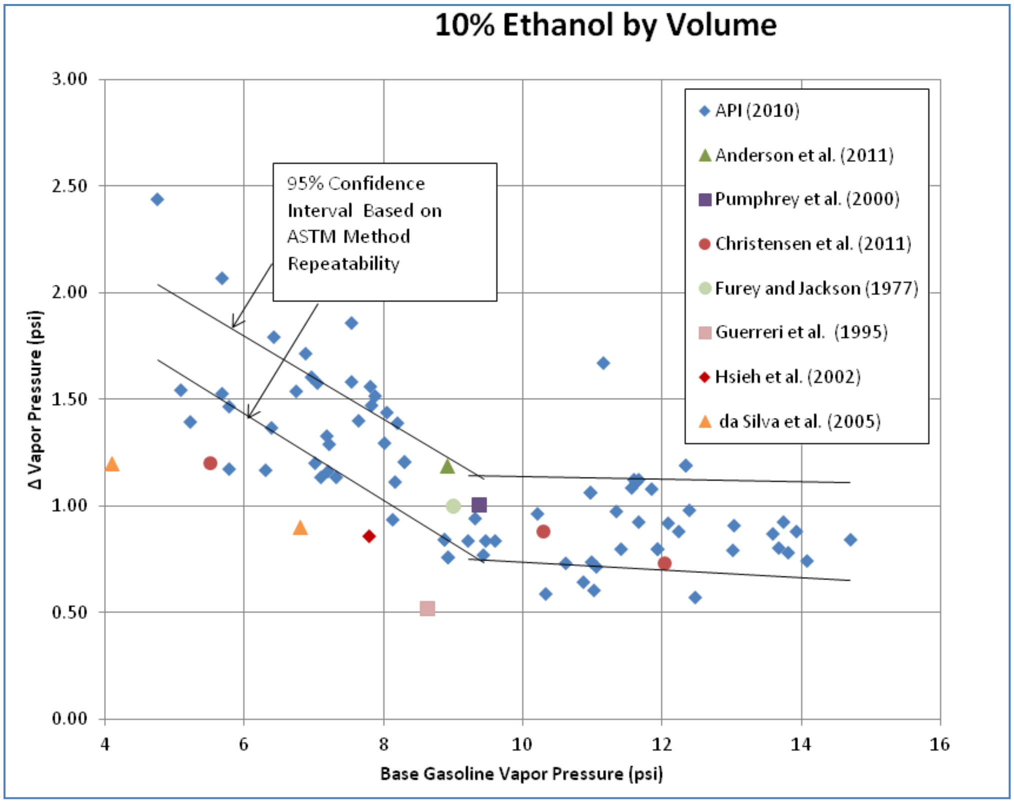

Figure 3. Change in RVP for blending 10% ethanol into gasolines and blendstocks with a range of RVP, showing confidence interval.[e]

[e] ASTM defines repeatability as the interval between two measured values made at the same laboratory, at which there is a 5 percent chance that the measured difference is due to random chance as opposed to an actual difference. The 95% confidence interval around any single datapoint is +/- the repeatability According to ASTM, Method D5191 repeatability = .006*(RVP+23.2). For the range of samples shown in Figures 3 through 6, calculated repeatability ranged from 0.18 psi to 0.23 psi. However, in Figure 2, the y-axis value is the difference of two measurements and the uncertainty of the difference between two independent values is the quadratic sum of the individual uncertainties = $s(a-b)=\mathrm{sqrt}((a^2)+(b^2))$; for this graph the repeatability is 0.26 to 0.33. The high and low point of the confidence interval range was calculated for each datapoint and then a regression was calculated for all the high points and all the low points. Thus, if the Δ vapor pressure was only dependent on the base gasoline vapor pressure, we would expect only 5% of the API datapoints to fall outside the confidence interval shown.

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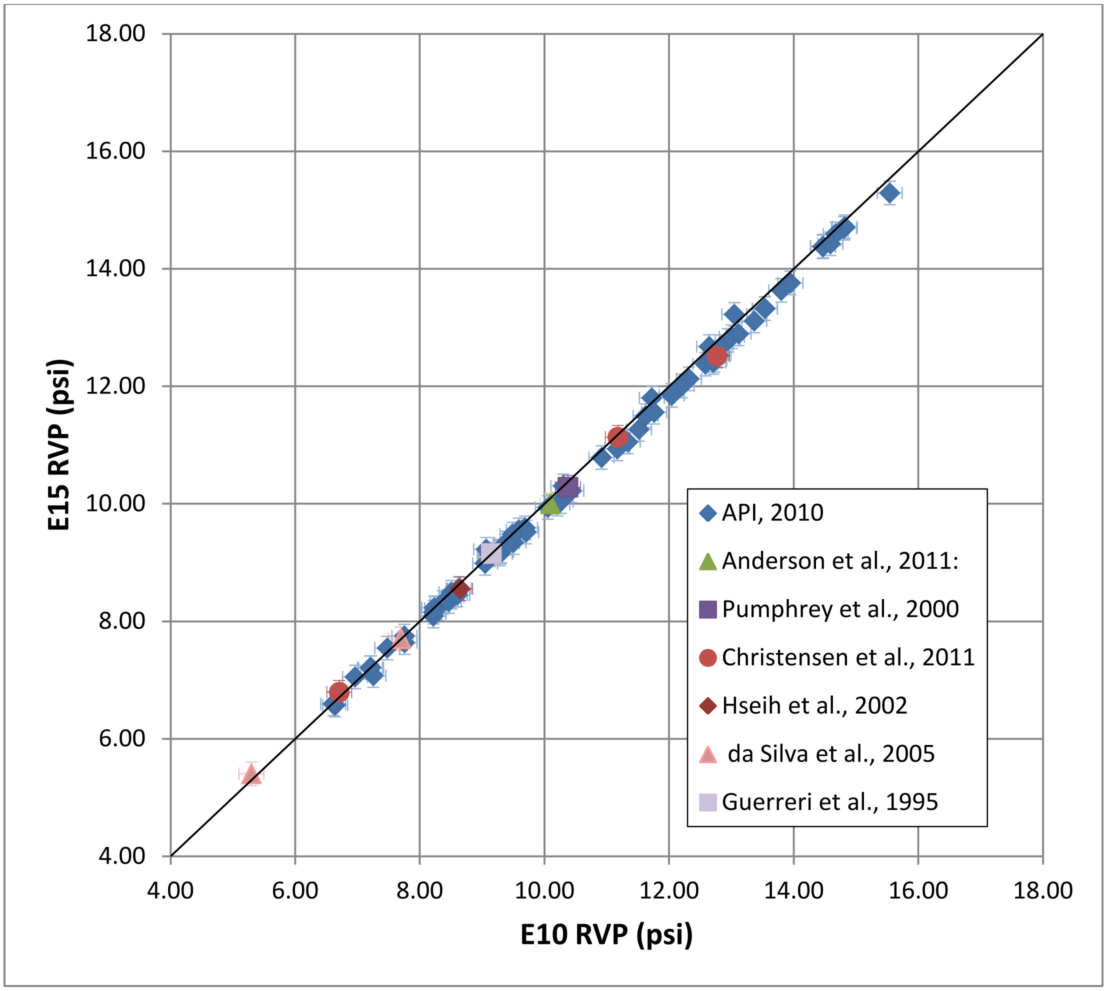

Figure 4. RVP results for E15 and E10 blended into the same base fuel. Error bars equal to repeatability of ASTM method.

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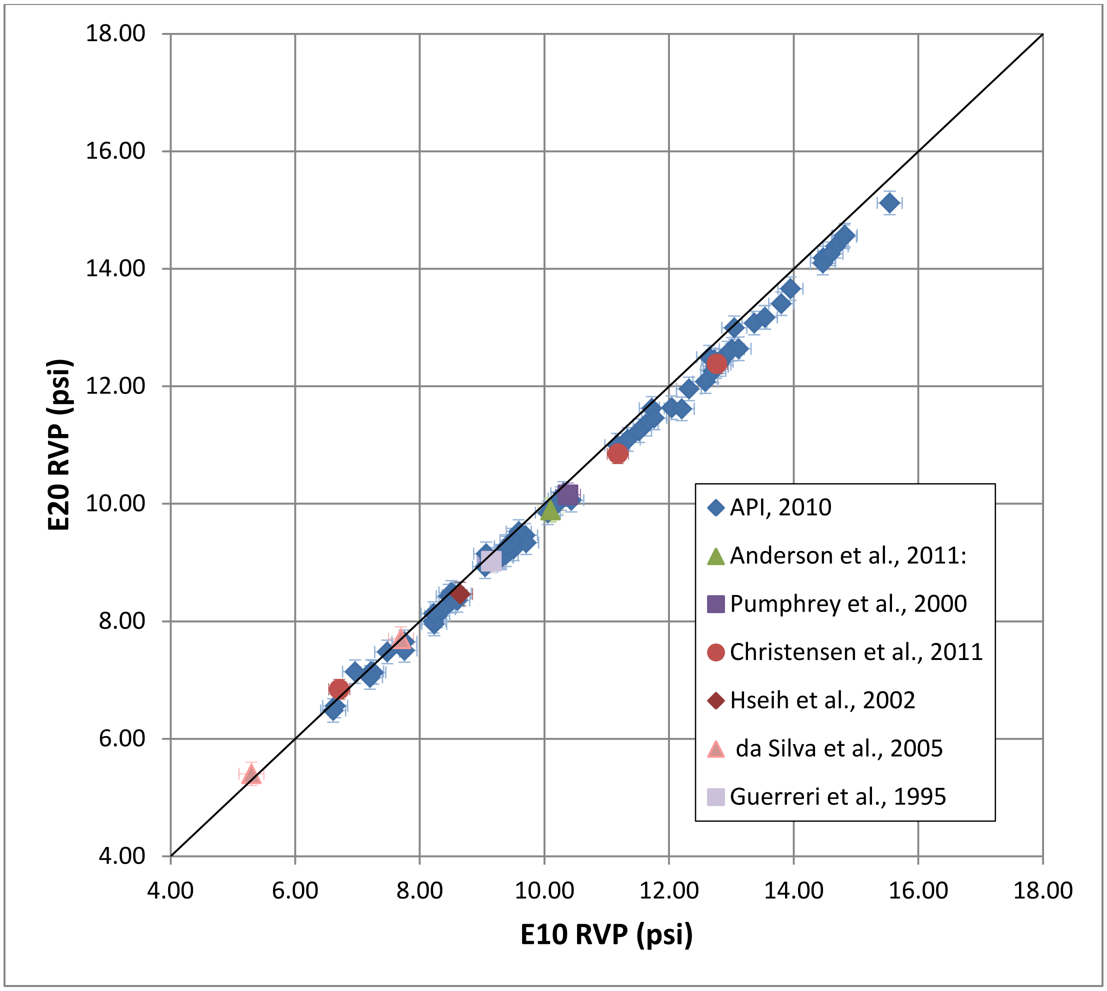

Figure 5. RVP results for E20 and E10 blended into the same base fuel. Error bars equal to repeatability of ASTM method.

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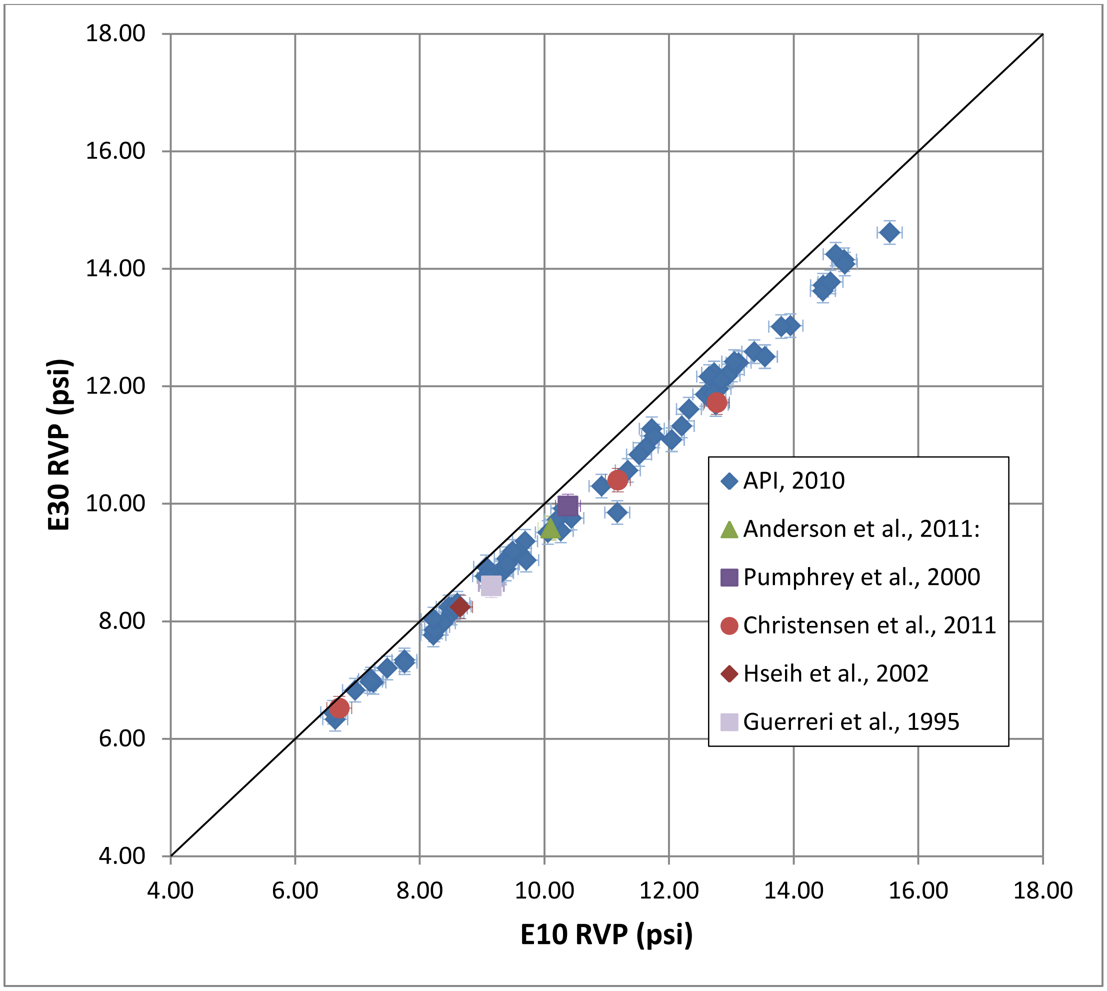

Figure 6. RVP results for E30 and E10 blended into the same base fuel. Error bars equal to the repeatability of the ASTM method.

Conclusions

The addition of 10% ethanol to gasoline is known to increase RVP by 1 psi or more. Nonetheless, E10 gasoline blends are meeting the most restrictive RVP standards, below 7.0 psi, throughout the U.S. The RVP impact of blending 10% and 15% ethanol is indistinguishable for all volatility classes. The RVP impact of blending 20% ethanol is indistinguishable from E10 for summer ozone season gasoline. Thus, from a vapor pressure perspective, there is little reason to treat E15 to E20 blends differently from E10. In areas employing the 1-psi waiver, blending of ethanol at levels other than 9-10% requires a different blendstock because of the more restrictive vapor pressure requirements for these blends. This is true even though an E15 blend in a given hydrocarbon blendstock would have the same RVP as an E10 blend. Eliminating the 1-psi waiver would reduce evaporative VOC emissions from non-RFG fuel by about 5%; however this would likely decrease the available gasoline supply by removing some of the higher volatility components.

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