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## Vapor Pressures of Alcohol–Gasoline Blends

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Reid vapor pressures (RVPs) were determined for alcohol–gasoline blends containing 5–85% by volume of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *i*-butanol (2-methyl-1-propanol), and *t*-butanol (2-methyl-2-propanol). The results are compared to literature data. Most alcohols form near-azeotropic mixtures with hydrocarbons in gasoline that affect the vapor pressure of the blend in a non-ideal manner. In addition, vapor pressures of dual-alcohol blends with gasoline containing a range of ethanol and 1-butanol volume percentages were determined. We demonstrate a simple method to prepare dual-alcohol–gasoline blends with RVPs indistinguishable from that of the base gasoline. It may be advantageous to use alcohols in addition to ethanol in the form of dual- or multi-alcohol blends as these become available in larger scale in the future.

### 1. Introduction

Prompted by concern about climate change and energy security, during recent years, there has been an increasing interest in using automotive fuels derived from biomass.<sup>1</sup> In the U.S., the Renewable Fuel Standard established by the Energy Independence and Security Act of 2007 mandates the use of 36 billion gallons (136 billion liters) of renewable fuel by 2022, corresponding to replacement of approximately 17% of projected gasoline use for light-duty vehicles in 2022.<sup>2</sup> In Europe, the Renewable Energy Directive calls for 10% use of renewable energy in the transportation sector by 2020.<sup>3</sup> In 2008, Brazil produced 6.5 billion gallons (25 billion liters) of ethanol, corresponding to 37% of global ethanol fuel demand<sup>4</sup> and more than 50% of the country's light-duty vehicle fuel consumption,<sup>5</sup> and the use is projected to grow in the future.

Biofuels used today are primarily first-generation biofuels made from food crops (e.g., ethanol from sugar cane, corn, or sugar beet; biodiesel from oil seeds, such as soybean or rapeseed, or from animal fats). Approximately 85% of the total global volume of biofuels produced in 2007 came from ethanol produced by the fermentation of sugars.<sup>6</sup> To reduce competition with food crops and increase the yields per hectare, second-generation biofuels are being developed. Second-generation

alcohol biofuels can be produced from biomass via either biotic routes (e.g., pretreatment of cellulose and hemicellulose to release sugars that can be fermented to give ethanol,<sup>7</sup> butanol, or higher alcohols<sup>8</sup>) or abiotic routes [e.g., gasification followed by thermochemical synthesis, giving a mixture (typically C<sub>1</sub>–C<sub>4</sub>) of alcohols].

Most light-duty vehicles produced today are not capable of running on pure alcohols, and therefore, most alcohol biofuels are blended with gasoline. In Brazil, the ProAlcool launched in 1975 made it mandatory to blend 20–25% anhydrous ethanol into gasoline and vehicles were built to be compatible with these blends.<sup>9</sup> Dedicated vehicles were also built that ran exclusively on 100% hydrous ethanol, which contains 5–7% water.<sup>10</sup> Brazilian ethanol production has increased 60% since the introduction of the ProAlcool program, and by 2007, approximately 86% of new cars manufactured in Brazil were flexible fuel vehicles (FFVs).<sup>11</sup> Brazilian FFVs can run on any blend containing from 0% ethanol (E0) to 100% ethanol (E100), including hydrous ethanol. Alcohol blend percentages in gasoline are commonly expressed as volumetric percentages; this convention is also used here unless otherwise specified.

In Europe, low-level blends of methanol with gasoline were sold during the 1980s and early 1990s. FFVs capable of running on methanol blends with gasoline were introduced into the U.S. in the early 1990s. By the late 1990s, ethanol had emerged as the predominant alcohol for blending with gasoline and FFVs were developed for ethanol blends. As of 2008, there were approximately 7 million FFVs in the U.S.<sup>12</sup>

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The most common biofuel in the U.S. is ethanol blended into gasoline at up to 10% by volume (E10). Blends with 85% denatured ethanol by volume (E85) are also available. In practice, the denaturant used in ethanol is gasoline; thus, the actual ethanol content in summer-grade E85 is approximately 79% (v/v), while that in winter-grade E85 is kept as low as 70% (v/v) to improve cold starting.<sup>13</sup> The use of ethanol blends greater than 10% requires some engine and fuel system modifications. FFVs are currently the only vehicles available in the U.S. that are designed to use blends from E10 to E85.

With the development of second-generation biofuels, it is possible that alcohols other than ethanol will enter the market. The butanol isomers have higher energy density, lower vapor pressures, and greater compatibility with engine materials than ethanol<sup>14–16</sup> and, hence, are attractive potential biofuels. Prior to the introduction of new alcohol gasoline blends, detailed knowledge of their physical and chemical properties, performance in engines, and impact on materials and emissions is needed, as previously accomplished for more widely used oxygenates, such as ethanol and methyl tertiary butyl ether (MTBE).<sup>17,18</sup>

Vapor pressure is an important property of automotive gasoline fuels. The vapor pressure can affect proper cold starting of the engine, vapor lock tendency in older engines without fuel injection (e.g., carbureted engines), and quality of starting in engines with fuel injection.<sup>17–19</sup> Vapor pressure is also a critical factor in meeting evaporative emission requirements. Gasoline standards in the U.S.<sup>20,21</sup> and globally<sup>22</sup> specify allowable vapor pressures depending upon the type of fuel and ethanol content, geographic location, and season.

The vapor pressure most often reported is the Reid vapor pressure (RVP), which is defined as the vapor pressure measured at 100 °F (37.8 °C) in a chamber with a vapor/liquid volume ratio of 4:1 while following a method-specific procedure. Test methods for measuring the RVP of gasoline have evolved to improve accuracy, precision, and speed. American Society for Testing and Materials (ASTM) method D323,<sup>23</sup> first adopted in 1930 and based on the original 1927 method developed by Reid, is not applicable for use

with many oxygenated compounds, such as alcohols, because of trace amounts of water present in the test.<sup>19</sup> ASTM D4953<sup>24</sup> provided a modification to the test to allow for the measurement of the vapor pressure in gasoline with oxygenates. ASTM methods D5191<sup>25</sup> (equivalent to European method EN 13016-1), D5190,<sup>26</sup> and D5482<sup>27</sup> involved additional automation, smaller sample volumes, and greater precision. The method used in the present study, ASTM method D6378<sup>28</sup> is a further improvement that eliminates the need for sample cooling and air saturation before the test, increasing speed, reducing losses of highly volatile compounds, and improving accuracy.<sup>28</sup> This method was recently approved for inclusion as an alternative vapor pressure test method in the ASTM D4814 automotive fuel specification.

With the “triple expansion” method used in ASTM D6378, the vapor pressure determined for the fuel excludes any pressure contributions from dissolved air in the fuel. This approach is different from the earlier methods that measure the total vapor pressure of fully air-saturated samples. Systematic differences in results are to be expected from the various vapor pressure methods, and to make this clear, the results are identified differently. Correlations are used to provide interchangeability. For example, the result obtained with ASTM D323 is RVP by definition. ASTM D4953 has two different procedures: Procedure A is essentially identical to D323 but without water, giving results identified as “dry vapor pressure” that should be indistinguishable from RVP. Procedure B involves other test modifications and yields the “dry vapor pressure equivalent” (DVPE); a correlation equation is applied to provide results equivalent to procedure A. ASTM D5191 data are also adjusted using a correlation to give DVPE. Vapor pressure regulations specified by the U.S. Environmental Protection Agency (EPA) and the California Air Resources Board (CARB) are based on ASTM D5191. However, different equations are used to correlate the measured total chamber pressure to equivalence with earlier tests: EPA to DVPE (D5191) and CARB to RVP (D323).<sup>28</sup> Finally, the result obtained using method D6378 is identified as VP<sub>x</sub>, where *x* is the vapor/liquid ratio (e.g., VP<sub>4</sub>), but correlations allow for estimates of DVPE (D5191) as well as EPA DVPE and CARB RVP.

The above ASTM methods use a defined vapor/liquid ratio. While the vapor pressure is independent of the vapor/liquid ratio for a pure compound, this is not true for mixtures, such as gasoline. Even highly volatile compounds that are present at small concentrations can contribute greatly to the vapor pressure, but their impact on the measured vapor pressure is progressively reduced with an increasing vapor/liquid ratio.

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The vapor pressure of an ideal mixture can be expressed by Raoult's law as shown in eq 1, where  $P$  is the vapor pressure of the mixture,  $P_i$  is the vapor pressure of compound  $i$ , and  $x_i$  is the mole fraction of compound  $i$ .

$$P = \sum P_i x_i \quad (1)$$

When blending alcohols with gasoline, especially the shorter chain alcohols, methanol and ethanol, the blend exhibits reductions in distillation temperatures and does not behave like an ideal mixture, because of the formation of a near-azeotropic mixture.<sup>29–31</sup> These non-ideal mixtures also have higher vapor pressures than would be predicted by Raoult's law.<sup>32,33</sup> This effect is particularly noticeable when a small amount of alcohol (a few volume percent) is blended into gasoline, because the blend has a vapor pressure higher than either the gasoline or the alcohol alone. The effect is often represented through the use of non-unity activity coefficients for each component,  $\gamma_i$ , as shown in eq 2.

$$P = \sum \gamma_i P_i x_i \quad (2)$$

For example, with data from Bennett et al.,<sup>34</sup> Harley et al.<sup>35</sup> found that the activity coefficient for ethanol in reformulated gasoline was 7.0 for gasoline containing 3% (m/m) ethanol but the activity coefficient decreased with an increasing ethanol content. The equilibrium headspace vapors above the gasoline contained the most volatile hydrocarbons (butane, pentane, and hexane isomers) and ethanol. Activity coefficients of the gasoline hydrocarbons were 1.0–1.2 in the absence of ethanol but increased to 1.4–1.7 when the gasoline contained 3–10% (m/m) ethanol.

With the expected increasing use of bioalcohols in gasoline blends and the possibility that alcohols other than ethanol and methanol will be used, it is important to have an accurate understanding of the vapor pressures of such blends. We report the results of a systematic study of the vapor pressures of mixtures of methanol, ethanol, 1- and 2-propanol, and 1-, 2-, *i*-, and *t*-butanol with gasoline. This work complements our recent study of the distillation curves for these alcohol–gasoline blends.<sup>31</sup>

## 2. Experimental Section

Haltermann (Channelview, TX) EEE is a standard gasoline used in the U.S. Federal Test Procedure (FTP) to certify vehicles for compliance with emission regulations and was used as the base gasoline in this study. EEE gasoline is specified to have a RVP of 60–63 kPa (8.7–9.1 psi). As determined by gas chromatography analysis (Southwest Research Institute, San Antonio, TX), the fuel contained (by weight) 6.0% paraffins, 48.4% iso-paraffins, 41.2% aromatics, 3.4% naphthenes, 0.07% olefins, and 0.9% unidentified compounds. The top five most abundant compounds (by weight) were as follows: 22% toluene, 16%

**Table 1. Physical Properties<sup>a</sup> of the Gasoline and Alcohols Used in This Study**

	molecular weight (g/mol)	RVP (kPa)	density at 20 °C (g/mL)	normal boiling point (°C)
EEE gasoline	98.5 <sup>b</sup>	60–62 <sup>c</sup>	0.741 <sup>c</sup>	n/a <sup>d</sup>
methanol	32.04	32.0	0.791	64.6
ethanol	46.07	16.0	0.789	78.3
1-propanol	60.10	6.2	0.804	97.2
2-propanol	60.10	12.4	0.786	82.3
1-butanol	74.12	2.2	0.810	117.8
2-butanol	74.12	5.3	0.807	99.6
<i>i</i> -butanol	74.12	3.3	0.802	107.9
<i>t</i> -butanol	74.12	12.2	0.787	82.4

<sup>a</sup> Data from ref 36, unless otherwise noted. <sup>b</sup> Weighted average from known hydrocarbon speciation. <sup>c</sup> Measured. <sup>d</sup> See ref 31 for D86 distillation temperatures of EEE gasoline.

2-methylbutane, 10% 2,2,4-trimethyl pentane, 6% 1,2,4-trimethylbenzene, and 4% 2,3,4-trimethylpentane.

The alcohols used were methanol (99.8% purity, <0.002% water per manufacturer specification), ethanol (99.5+%, <0.05% water), 1-propanol (99.7%, <0.005% water), 2-propanol (99.5%, <0.003% water), 1-butanol (>99.4%, <0.1% water), 2-butanol (99.5%, <0.005% water), *i*-butanol (99.5%, <0.05% water), and *t*-butanol (>99%, <0.1% water). All were obtained from either Sigma-Aldrich or Acros Organic Chemicals.

For each alcohol, blends containing 5, 10, 20, 30, 50, or 85% (v/v) of the alcohol in the base gasoline were typically prepared. The blends are referred to using identifiers consisting of one or more letters denoting the type of alcohol followed by the volume percent unless otherwise noted, e.g., E5, E10, E20, E30, E50, and E85 in the case of ethanol. E0 denotes gasoline without alcohols. Vapor pressures of the pure alcohols were also measured.

In addition, dual-alcohol blends (containing ethanol and 1-butanol in equal volumetric proportions) were prepared containing a total alcohol content of 10, 20, 30, 50, 85, or 100% (v/v). Three additional dual-alcohol blends were prepared with total alcohol content of 10, 20, or 30% (v/v) but with ethanol and butanol in such proportions as to match the RVP of the base gasoline, namely, 1:4.6, 1:1.5, and 1:0.6 (v/v) ethanol/1-butanol.

All blends were prepared gravimetrically at room temperature using alcohols (as received) and gasoline at 4 °C, with the only exception being *t*-butanol, which is a solid at room temperature and was kept in a warm water bath at 30 °C prior to and during blending. The blends were then stored at 4 °C in sealed 62 mL glass containers containing 45 mL of blended fuel. Volume percentages at 20 °C were calculated using densities of the alcohols<sup>36</sup> and gasoline (Table 1), assuming no change in volume after mixing. This assumption is expected to have minimal impact on results (e.g., ethanol–gasoline mixtures showed less than 0.6% volume increase<sup>18</sup>). Molar percentages were calculated using the known or estimated molecular weights shown in Table 1. The molecular weight of the base gasoline was calculated as the weighted average of the molecular weights of the known hydrocarbon composition.

Vapor pressures of the gasoline, pure alcohols, and their blends were determined using a MINIVAP VPSH instrument (Grabner Instruments, Vienna, Austria) that operates according to ASTM method D6378.<sup>28</sup> Samples were drawn into the instrument via a small, manufacturer-supplied inlet tube. Triplicate vapor pressure determinations were made for each blend at RVP conditions [37.8 °C (100 °F) and 4:1 vapor/liquid ratio]. The measurement is performed such that the reported vapor pressure excludes the impact of dissolved air in the fuel. The method states that the results thus obtained are to be identified as VP<sub>4</sub>, indicating the 4:1 vapor/liquid ratio used in the test. The VP<sub>4</sub> results were adjusted to give “predicted DVPE” values consistent with those from

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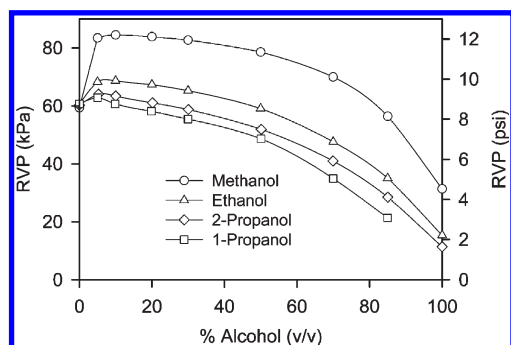
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**Figure 1.** RVPs (predicted DVPE) of blends of the  $C_1$ – $C_3$  alcohols with gasoline.

ASTM method D5191 using the manufacturer-provided correlation (i.e., predicted DVPE =  $VP_4 - 1.027$  kPa).<sup>37</sup> Measured  $VP_4$  values below 7 kPa were excluded, consistent with the test method minimum specified in ASTM D6378 and based on a comparison of results to literature values for the pure alcohols.

According to ASTM D6378, samples should be prepared in a 1 L flask filled 70–80% with sample and only one vapor pressure determination should be made with each prepared sample. To minimize waste, this method was modified in the present study by reducing the prepared sample volume and making multiple (up to three) measurements with each sample. Because the VPSH instrument method requires only 10 mL of sample for each measurement, approximately 45 mL of each blend was prepared in each 62 mL container, maintaining the sample/headspace volume ratio specified in the ASTM methods.<sup>28</sup> Vapor pressure measurements using M10 blends with both large (700–800 mL in 1 L bottles) and small (45 mL in 62 mL vials) samples and with multiple determinations on each sample confirmed no appreciable difference in the determined  $VP_4$  values (the difference between measurements was less than 1%).

Evaporative losses were minimized during the measurement by keeping the sample vial in an ice bath and covering the opening with aluminum foil while the sample was drawn into the instrument. The container was sealed and stored in the ice bath between measurements.

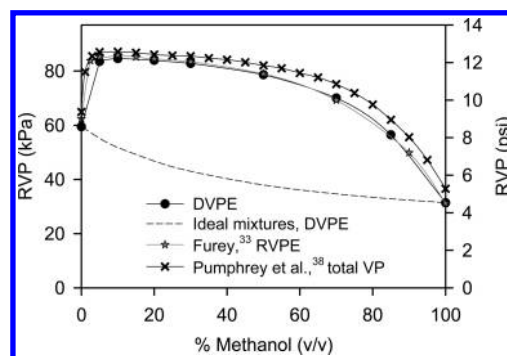
Gasoline density was measured using an Anton Paar (Graz, Austria) model DMA 35 portable density meter.

### 3. Results and Discussion

Vapor pressures from blends of the  $C_1$ – $C_4$  alcohols with gasoline were measured according to ASTM method D6378 [i.e., at 37.8 °C (100 °F) and with 4:1 vapor/liquid ratio]. Results thus obtained, identified as  $VP_4$  values per ASTM D6378, are provided in Tables S-1–S-9 in the Supporting Information. Predicted DVPE values for these blends (shown in Figures 1–7) were calculated from the  $VP_4$  values as previously described. For clarity of presentation, we hereafter use the term “RVP” when discussing our predicted DVPE data and DVPE, RVPE, or true RVP data reported by others.

The measured RVPs for methanol, ethanol, and 2-propanol were within 2% of the literature values listed in Table 1 (the vapor pressures for the other alcohols were below the test method minimum of 7 kPa). The RVP of the base gasoline was measured with each set of alcohol blends and was relatively constant over the duration of the study (60.2–61.7 kPa).

**3.1. Methanol Blends.** As can be seen in Figure 1, the addition of relatively small amounts of methanol to gasoline increases the RVP by more than 30%, resulting in values that are higher than those of the base gasoline (61 kPa) and pure



**Figure 2.** RVPs (predicted DVPE) of methanol–gasoline blends compared to RVPE values obtained by Furey<sup>33</sup> and total vapor pressures by Pumphrey et al.<sup>38</sup> The dashed line shows what would be predicted for the ideal behavior of these blends.

methanol (31 kPa). The highest RVP (84 kPa) is observed for a blend containing 10% (v/v) methanol. The RVPs of the methanol blends are higher than those of the base gasoline for methanol concentrations up to approximately 80% (v/v).

In Figure 2, these results are compared to those for hypothetical ideal mixtures of gasoline and methanol calculated using eq 1. Note that the curve for ideal mixtures would be a straight line if plotted versus the alcohol mole fraction. The methanol–gasoline mixtures deviate from this line and are clearly non-ideal. This phenomenon is ascribed to interference by the nonpolar hydrocarbons in gasoline with the intramolecular hydrogen bonding between the polar methanol molecules<sup>33</sup> and interference by methanol with molecular interactions between the hydrocarbons. Furey<sup>33</sup> found the increase in RVP because of methanol addition to gasoline to be essentially independent of the base gasoline RVP.

As shown in Figure 2, our results agree very well with those obtained by Furey.<sup>33</sup> However, the RVPs measured in the present work are consistently 2–6 kPa lower than those reported by Pumphrey et al.<sup>38</sup> The vapor pressure for methanol reported by Pumphrey et al. (36.4 kPa) is also considerably higher than literature values (31–32 kPa)<sup>33,36,39</sup> and the value determined in the present study (31.2 kPa). However, Pumphrey et al. did not attempt to determine a RVP-equivalent result (e.g., DVPE per ASTM D5191).<sup>40</sup> Thus, their reported data should be considered uncorrected total vapor pressures that include the effect of dissolved air in the samples and are biased high compared to RVP-equivalent values. We ascribe the difference between the vapor pressures reported by Pumphrey et al. and those from the present work to the contribution of dissolved air in the samples.

**3.2. Ethanol Blends.** The trends in RVP observed for ethanol blends in gasoline are similar to those observed for methanol blends. The magnitude of the increase in vapor pressure is less with ethanol addition (Figure 1), consistent with its lower vapor pressure and lower polarity as compared to methanol. As with the methanol blends, the highest RVP (68 kPa) is observed when 10% (v/v) ethanol is added to the gasoline. At ethanol concentrations up to approximately 45% (v/v), the observed RVPs are higher than that of the base gasoline.

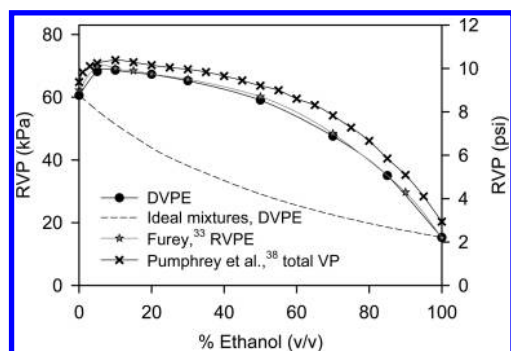
As shown in Figure 3, our results are in excellent agreement with those reported by Furey<sup>33</sup> over the full range of ethanol concentrations, while those of Pumphrey et al.<sup>38</sup> are 2–7 kPa

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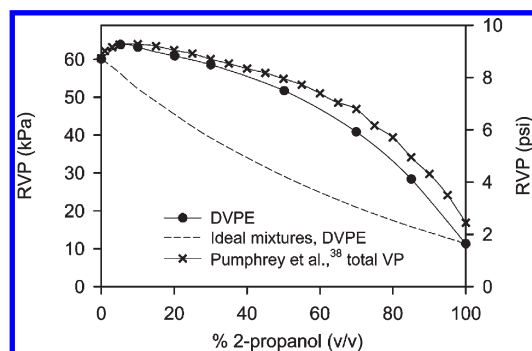
**Figure 3.** RVPs (predicted DVPE) of ethanol–gasoline blends compared to RVPE values obtained by Furey<sup>33</sup> and total vapor pressures by Pumphrey et al.<sup>38</sup> The dashed line shows what would be predicted for the ideal behavior of these blends.

higher. Again, differences are likely due to the contribution of dissolved air in the data reported by Pumphrey et al. The observation of maximum RVP at 10% (v/v) ethanol is consistent with several studies,<sup>32,38,41</sup> whereas others<sup>33,42</sup> have observed the maximum at lower concentrations, such as 4–5% ethanol. However, the actual RVP variation across the range of 5–10% (v/v) ethanol is relatively minor. The observed difference may reflect the different chemical compositions of the gasolines tested. Contrary to findings with methanol,<sup>33</sup> the RVP increase with ethanol addition to gasoline has been found to be gasoline-dependent, with greater RVP increases observed for base gasolines with lower RVP<sup>18</sup> or greater saturated hydrocarbon content.<sup>43</sup>

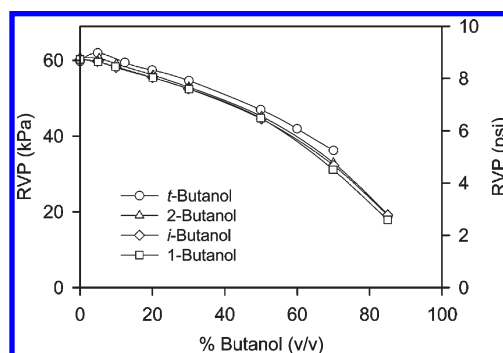
**3.3. Propanol Blends.** For the two propanol isomers, the highest RVPs are observed when 5% (v/v) propanol is blended with gasoline (Figure 1). The RVPs for the 2-propanol blends are slightly higher than those of the 1-propanol blends, consistent with the higher vapor pressure of 2-propanol (12.4 kPa) than 1-propanol (6.2 kPa). The RVPs of the propanol–gasoline blends are higher than that of the base gasoline when they contain less than approximately 25% (v/v) 2-propanol or 10% (v/v) 1-propanol. As was observed for methanol and ethanol, the addition of approximately 50% (v/v) 2-propanol to gasoline results in the greatest deviation from the ideal behavior in absolute terms (Figure 4).

The RVPs determined for the 2-propanol blends are compared to those reported by Pumphrey et al.<sup>38</sup> in Figure 4. The maximum RVP in the present study is found at a slightly higher 2-propanol concentration [10% (v/v) versus 5%], but the difference in vapor pressure between these concentrations is minor (1% or less) in both studies. The increasing deviation between our data and those reported by Pumphrey et al. with increasing 2-propanol concentration is likely due to the reporting of the total vapor pressure (as discussed above) combined with a lower RVP of their base gasoline.<sup>38</sup>

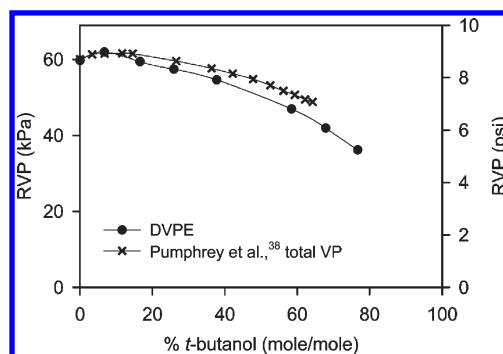
**3.4. Butanol Blends.** The RVPs of blends of the four butanol isomers with gasoline are shown in Figure 5. Except for a minor RVP increase for 5% (v/v) *t*-butanol, the addition of the butanol isomers resulted in a decrease in RVP with an increasing butanol concentration, consistent with the lower vapor pressures of the butanol isomers (Table 1). The data for *t*-butanol are similar to those obtained by



**Figure 4.** RVPs (predicted DVPE) of 2-propanol–gasoline blends compared to total vapor pressures obtained by Pumphrey et al.<sup>38</sup> The dashed line shows what would be predicted for the ideal behavior of these blends.



**Figure 5.** RVPs (predicted DVPE) of the blends of the butanol isomers with gasoline.



**Figure 6.** RVPs (predicted DVPE) of *t*-butanol blends compared to total vapor pressures obtained by Pumphrey et al.<sup>38</sup> Results are expressed as mole percentage to allow for this comparison.

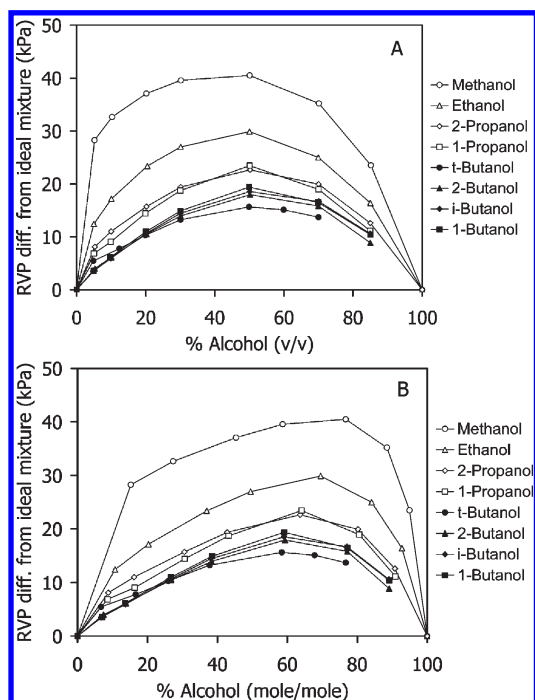
Pumphrey et al.<sup>38</sup> (Figure 6) with the caveats discussed earlier. Pumphrey et al. observed the maximum RVP at a somewhat higher *t*-butanol concentration [12% (mol/mol)] as compared to the present study [7% (mol/mol), equal to 5% (v/v)], but the actual increase in vapor pressure in both studies was minor (approximately 2 kPa).

The measured RVPs of the butanol–gasoline blends are somewhat higher than what would be expected for ideal mixtures. This effect, however, is considerably less than with the more polar C<sub>1</sub>–C<sub>3</sub> alcohols, as shown in Figure 7. Figure 7 shows the RVP deviation from ideality as a function of the alcohol concentration, thus factoring out differences in the RVPs of the alcohols and the base gasoline. The addition of each alcohol resulted in a maximum deviation from ideality at a volumetric concentration of approximately 50%. The dependence of vapor partial pressures, however, is typically related to molar

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(42) Balabin, R. M.; Syunyaev, R. Z.; Karpov, S. A. *Fuel* **2007**, *86*, 323–327.

(43) Mužíková, Z.; Pospíšil, M.; Šebor, G. *Fuel* **2009**, *88*, 1351–1356.

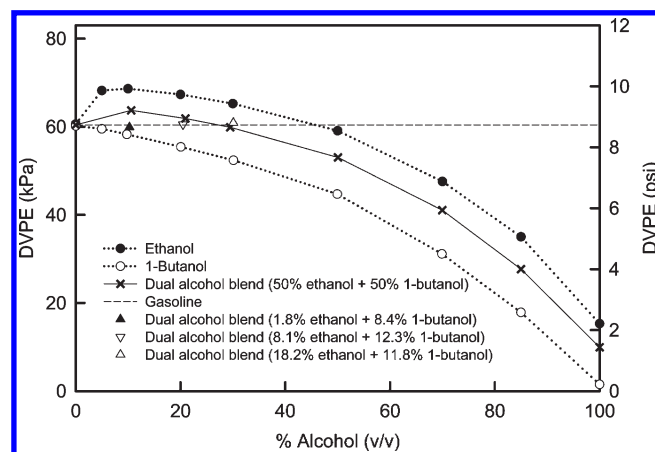


**Figure 7.** RVP difference from that predicted for ideal mixtures for all single-alcohol blends with gasoline, plotted versus both (A) volumetric and (B) molar alcohol concentration.

composition, as reflected in Raoult's law. In molar terms, 50% alcohol by volume corresponds to molar concentrations of 77% methanol, 70% ethanol, 64% propanol, and 59% butanol. The departure from ideality appears to relate more closely to the volumetric displacement and resulting surface coverage by the alcohols. This appears consistent with the two mechanisms discussed earlier: (1) interference with hydrogen bonding between polar alcohol molecules by the nonpolar hydrocarbons and (2) interference with hydrocarbon interactions because of the polar alcohol.

In particular, the difference between the blends with 2-propanol and *t*-butanol is noteworthy, because the RVPs and boiling points of these alcohols are approximately equal (within 2%, Table 1). As seen in Figure 7, for any given volumetric concentration, the more polar 2-propanol produces as much as a 50% greater deviation from ideality than does *t*-butanol. This difference highlights the importance of alcohol polarity on the RVP impact for alcohol–gasoline blends.

**3.5. Dual-Alcohol Blends.** The RVPs of several dual-alcohol blends of ethanol and 1-butanol in gasoline are shown in Figure 8, along with corresponding single-alcohol (ethanol or 1-butanol) blends for comparison. The RVPs of dual-alcohol blends containing ethanol and 1-butanol in equal volume proportions lie approximately midway between those of the two single-alcohol blends containing the same total alcohol volume concentration. Thus, the vapor pressure of this dual-alcohol blend can be approximated as the simple volumetric average of two single-alcohol blends. For example, the RVP of a blend containing 10% (v/v) ethanol and 10% (v/v) 1-butanol can be estimated as the simple average of the RVPs of a blend containing 20% (v/v) ethanol and another containing 20% (v/v) 1-butanol. This possibility of blending fuels for RVP based on volumetric alcohol composition rather than molar composition is likely related to the earlier observation that RVP deviations from non-ideality are also volume-based.



**Figure 8.** RVPs (predicted DVPE) of single- and dual-alcohol blends in gasoline with different relative proportions of ethanol and 1-butanol.

By changing the proportions of the two alcohols, a dual-alcohol blend in gasoline can be formulated that has a certain desired RVP. This may have a significant practical benefit for mitigating the RVP increase resulting from the addition of methanol and ethanol to gasoline. The advantages of such multi-alcohol fuels have been recognized, e.g., U.S. EPA approval of the “DuPont waiver”, which allows for higher methanol concentrations in gasoline when blended with ethanol, propanol, or butanol.<sup>17</sup> Presently, fuel suppliers may need to adjust the hydrocarbon composition of the base gasoline for ethanol blends to satisfy RVP requirements.

Using the dual-alcohol approach, the proportions of the two alcohols in gasoline could be adjusted to produce a blend that has the same RVP as the base gasoline as follows. First, establish the total concentration of alcohol desired in the dual-alcohol blend [ $C_{\text{tot}}$ , % (v/v)]. Second, prepare two single-alcohol blend samples, each containing  $C_{\text{tot}}$  of the single alcohol in gasoline (e.g., for  $C_{\text{tot}} = 10\%$ , prepare E10 and 1-Bu10) and measure their respective RVPs. Third, linearly interpolate between the RVPs of these two blends to arrive at the required concentrations of the two alcohols in the dual-alcohol blend that yields the same RVP as the base gasoline. This is performed according to the following equation:

$$C_i = \left( \frac{P_{\text{gasoline}} - P_j(C_{\text{tot}})}{P_i(C_{\text{tot}}) - P_j(C_{\text{tot}})} \right) C_{\text{tot}} \quad (3)$$

where  $C_i$  is the volume fraction of alcohol  $i$ ,  $P_{\text{gasoline}}$  is the RVP of the base gasoline, and  $P_i(C_{\text{tot}})$  and  $P_j(C_{\text{tot}})$  are the RVPs of the single-alcohol blends of alcohols  $i$  and  $j$ , respectively, at a volume fraction,  $C_{\text{tot}}$ , that is equal to the desired total alcohol volume fraction in the dual-alcohol blend. When the RVPs have not been measured at precisely the desired total volume fraction, the values are estimated by linear interpolation of the RVP curves of the single-alcohol blends (e.g., the RVP for E10 is estimated by linear interpolation from the RVPs measured for E5.0 and E10.1).

To test this approach, we estimated the concentrations of ethanol and 1-butanol that would produce dual-alcohol–gasoline blends containing 10, 20, or 30% (v/v) alcohol having the same RVP as the base gasoline [2.0% (v/v) ethanol + 8.0% 1-butanol, 8.3% ethanol + 11.7% 1-butanol, and 18.6% ethanol + 11.4% 1-butanol, respectively]. The measured RVPs of the resulting blends are indicated as triangles in Figure 8 and



are indistinguishable from the base gasoline. As reported previously,<sup>43,44</sup> mixing such a dual-alcohol blend with gasoline having the same RVP (but containing no alcohol) often results in a mixture with increased RVP. This is seen in Figure 8 where a dual-alcohol blend with 10% alcohol has a higher RVP than the dual alcohol blend containing 20% alcohol. The 10% dual-alcohol blend can be regarded as an equal-volume mixture of the 20% dual-alcohol blend and gasoline containing no alcohol.

This finding for dual-alcohol blends is similar to the findings of our recent study of the distillation curves of alcohol–gasoline blends.<sup>31</sup> In that study, the distillation curves of dual-alcohol blends containing 10% of each of two alcohols were found to be intermediate to the distillation curves of the two single-alcohol blends at 20% concentration. For example, the distillation curve for E10/1-Bu10 (i.e., 10% ethanol and 10% 1-butanol) was intermediate to the curves for E20 and 1-Bu20. Furthermore, the E10/1-Bu10 distillation curve more closely followed the curve for the base gasoline than E20, 1-Bu20, or even E10 and 1-Bu10. The use of multiple alcohols can therefore be useful by providing flexibility in how the addition of alcohols impacts RVP and distillation behavior, with the potential to minimize any such impacts.

**3.6. Implications.** Increasingly stringent evaporative emission regulations for light-duty vehicles are likely to ensure that efforts to control gasoline vapor pressure continue. This may be complicated by future increases in renewable fuel use. In the U.S., the revised Renewable Fuel Standard mandates greater use of biofuels,<sup>2</sup> likely accomplished through blending ethanol in gasoline but possibly by other alcohols as well. These higher blending volumes and the resulting impacts on fuel volatility may make the use of alcohols other than ethanol more attractive.

In the U.S., the federal government (EPA) and some state governments regulate the properties of commercial gasoline as a means to control evaporative emissions. To do so, these regulations typically specify a maximum RVP that varies by location and season, consistent with the objective of controlling evaporative emissions. Most areas have a 62 kPa (9.0 psi) limit, whereas other areas are limited to 54 kPa (7.8 psi) or 48 kPa (7.0 psi).<sup>20</sup> There is recognition that ethanol added at low concentrations increases the RVP of gasoline; thus, the EPA allows for a RVP waiver for 6.9 kPa (1 psi) for gasoline containing 9–10% (v/v) ethanol in certain locations.<sup>18</sup> ASTM specification D4814 for gasoline<sup>21</sup> also gives maximum RVP values that depend upon geography and season, ranging from a limit of 54 kPa maximum for Class AA gasoline to 103 kPa maximum for Class E gasoline.

On the other hand, engine operation (cold weather starting and warm-up) can suffer if fuel vapor pressure is too low.<sup>22</sup> Port fuel-injected (PFI) engines can be sensitive to low RVP gasoline, but direct-injection engines are mostly insensitive. This consideration is recognized in gasoline specifications issued by automobile manufacturers,<sup>22</sup> in which RVP limits are given as both minimum and maximum values (e.g., 45–60 kPa for Class A gasoline and 55–70 kPa for Class B gasoline). Likewise, because low vapor pressure can be an issue for gasoline with high ethanol content, ASTM specification D5798<sup>13</sup> for E85 also gives both maximum and minimum RVP limits. For example, Class 1 E85 [summer-grade, minimum 79% (v/v) ethanol] should have a RVP of

38–59 kPa, whereas Class 3 E85 [winter-grade, minimum of 70% (v/v) ethanol] should have a RVP of 66–83 kPa. Increasing adoption of direct-injection engine technology could help mitigate the potentially adverse impact of low RVP resulting from high-level alcohol content.

As shown here, the type of alcohol and its concentration has a profound impact on the vapor pressure of an alcohol–gasoline blend. The low-molecular-weight alcohols can greatly increase RVP at the low blending percentages currently in use for ethanol (e.g., E10). In such cases, blending using a base gasoline with a lower RVP may be needed to meet RVP regulations, but this can be limited by other volatility constraints.<sup>18</sup> Methanol poses a greater challenge than ethanol in this respect. Propanol and butanol isomers are attractive at low blending concentrations because they have less RVP impact than ethanol.

Once the gasoline pool is saturated with E10, higher alcohol concentrations will be needed in the form of so-called “mid-level blends” (e.g., E15–E30) and/or high-level blends (E70–E85).<sup>2</sup> For mid-level blends of ethanol and methanol, the RVP declines with an increasing alcohol content and eventually matches that of the base gasoline (at approximately E50 and M80). High-level blends, e.g., E85, can have RVPs considerably lower than some base gasolines. Mid-level blends containing propanol and butanol isomers would also have RVPs lower than some base gasolines without reformulation, and their use in high-level blends may be problematic.

Blends using more than one alcohol were shown to be a possible solution to mitigating RVP impacts for both low- and mid-level alcohol content in gasoline. For example, alcohols that usually result in an increase in RVP when blended with gasoline in small amounts (methanol, ethanol, and propanols) can be combined with alcohols that would generally cause a decrease in RVP when blended with gasoline (e.g., butanols). The overall effect would be a blend with a RVP close to that of gasoline.

The butanol isomers have been recognized as attractive gasoline-blending components, given their fungibility with gasoline (primarily their reduced sensitivity to water-induced phase separation<sup>45</sup>). In comparison to ethanol, the butanol isomers may also be attractive because of their lower RVP impact at low blending concentrations with gasoline. Given that the four butanol isomers have a fairly similar impact on RVP, differences in other properties (e.g., octane number enhancement) may determine the selection of preferred isomers for gasoline blending.

#### 4. Conclusions

We present a large body of self-consistent data concerning the RVPs of alcohol–gasoline mixtures that are of potential importance as future biofuel blends. While the effect of methanol and ethanol on the RVP of gasoline is well-understood, the data presented here can be used to guide efforts to meet industry RVP specifications using higher alcohols.

The RVP of the base gasoline was higher than that of the C<sub>1</sub>–C<sub>4</sub> alcohols. The alcohols and hydrocarbons in the gasoline formed non-ideal mixtures with RVPs that were higher than would be expected for ideal mixtures. Blends of methanol and ethanol have RVPs higher than the base gasoline over a wide concentration range. The highest RVPs were observed

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with relatively low concentrations (5–10%, v/v) of these alcohols. The propanols and *t*-butanol had RVPs higher than the base gasoline only at 5–10% (v/v) concentration. The other three butanol isomers decreased the RVP when added to the base gasoline at any concentration. The propanols and butanols may be more attractive blending components than ethanol at low to medium blending concentrations (10–30%, v/v) because of their lesser impact on RVP. At high blending concentrations (70–85%), however, the propanols and butanols may produce problematically low RVPs.

When more than one alcohol is added to gasoline, it is possible to offset the RVP changes and obtain a blend with a RVP equal to that of the base gasoline. This avoids the RVP

increase or decrease associated with the use of only one alcohol. As an example, a simple method is demonstrated to prepare dual-alcohol–gasoline blends with RVPs indistinguishable from that of the base gasoline using ethanol and 1-butanol.

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**Supporting Information Available:** Tables of the vapor pressure (VP<sub>4</sub>) data. This material is available free of charge via the Internet at <http://pubs.acs.org>.