Fuel 243 (2019) 630–644

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Review article

Measuring and predicting the vapor pressure of gasoline containing oxygenates

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ARTICLE INFO

Keywords:
Gasoline
Reid vapor pressure
Oxygenate
Biomass
Oxygenate-gasoline blends

ABSTRACT

This review describes the measurement and prediction of volatility characteristics, especially Reid vapor pressure, of gasoline blended with oxygenates such as those that could be derived from biomass. Including more advanced biofuels containing oxygen in gasoline affects critical fuel properties related to the volatility of the blended fuel. The vapor pressure of oxygenate-gasoline blends typically exhibits non-ideal behavior requiring updated measurement and prediction tools to ensure the resulting fuel meets all safety and performance specifications. This review, the first covering the measurement, prediction and impact on vapor pressure of oxygenates other than alcohols, discusses the suitability of established methods to measure Reid vapor pressure in blends containing oxygenates. The review then surveys methods used to predict vapor-liquid equilibria along with a description of suitability of these methods for use on gasoline-oxygenate blends. Finally, the outputs of a series of models are compared to Reid vapor pressure measurements for a series of oxygenates in a real gasoline to illustrate the potential and shortcomings of the models.

1. Introduction

This review provides a historical perspective on gasoline vapor pressure and the impact of blending biomass-derived blendstocks (bio-blendstocks) into petroleum-based fuels. The review includes a description of up-to-date methods used to measure and predict fuel vapor pressure, particularly the vapor pressure of gasoline at 100°F, commonly called the Reid vapor pressure (RVP). We also include a preliminary description of the impact of new oxygenate gasoline additives on the vapor pressure of gasoline, a literature review, new measurements, and comparison with the theoretical modeling results obtained through readily available thermodynamic packages. As far as the authors are aware, this is the first review covering the volatility behavior of oxygenates other than alcohols, including comparisons of model predictions and measurements.

This review is motivated by renewed interest in non-traditional bio-blendstocks (*i.e.*, new oxygenates and mixtures containing more oxygen) and the increasing importance of bio-blendstocks in reducing petroleum consumption and greenhouse gas emissions. The United States consumes 7 billion barrels of petroleum annually [1], approximately 20% of the oil utilized globally [2]. The transportation sector uses 70% of the 7 billion barrels consumed annually, an increase of nearly 3% since 2005 [1]. Consumption is driven in large part by the approximately 260 million passenger vehicles on the road, 80% of which are fueled by gasoline [3]. Carbon dioxide formed by the combustion of petroleum fuels is a major contributor to man-made global warming [4]. Price volatility harms the economy as increases in the price of oil result in monetary inflation and decreased economic growth. However, decreases in the price of oil do not have as great a stimulatory effect [5]. Thus, the production of alternative liquid transportation fuels may provide substantial benefits to the economy.

Biofuels, in a broad sense, are fuels generated from living or recently living organisms. Such fuels can be cheap [6] and abundant, and can be transformed directly into drop-in liquid transportation fuels such as gasoline, diesel, and jet fuel. Biomass includes algae, sugars (from corn or sugar cane), and low-value or waste plant material, such as corn

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https://doi.org/10.1016/j.fuel.2019.01.137
Received 1 January 2018; Received in revised form 10 January 2019; Accepted 27 January 2019
Available online 19 February 2019
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stover or forest residues, and whole energy plant products such as switchgrass or *miscanthus*. Grasses, woods and other terrestrially grown resources are often referred to as "lignocellulosic biomass" and are comprised primarily of cellulose, hemicellulose, and lignin [7]. When transformed from biomass into biofuels, biofuels hold a major advantage over fossil fuels because their combustion is carbon neutral, in the sense that they release the same amount of carbon dioxide as that absorbed by the growing plants. Hence there is no net increase in the amount of carbon dioxide in the atmosphere [8]. Additionally, biofuels can displace fossil fuels, offering a route to reduced dependence on foreign oil. They also have the potential for greater geographic distribution since the biomass sources are not as concentrated as oil.

Biomass-to-fuel conversion processes typically produce single compounds or mixtures including a significant concentration of oxygenates. These may include various functional groups, but alcohols, typically ethanol, are the most widely used. Conversion of all of the oxygenates to hydrocarbons is technically feasible by deep hydrotreatment methods, but impractical due to the high cost [9]. Moreover, the complete elimination of oxygenates may not be optimal because certain oxygenates can provide benefits such as improved fuel properties. For example, oxygenates may improve fuel properties such as resistance to autoignition in gasoline (measured as increased Research Octane Number, or RON). In many cases, complete deoxygenation of lignocellulose-derived biofuels will degrade the resistance to autoignition, or lower the RON, by converting all the aromatics to low-RON naphthenes [10].

The addition of oxygenates may also affect refinery economics. Oxygenates may increase or decrease the vapor pressure of the fuel (discussed in more detail below), which in turn changes the amount of high volatility, low-cost components that may be added. Specifically, more low-cost butane can be incorporated to increase octane in winter blends in northern states. In the summer, the butane content must be lowered to meet the RVP specification, which in turn requires the use of higher cost components, such as isoparaffins, to meet the required minimum octane rating. From the refiner's perspective, the key factor in blending profitability is the spread between gasoline and butane price. Addition of butane will result in reduced cost for the refiner and increased profit at a fixed gasoline selling price. As an example, two refiners located in Wisconsin blended 2.6 million gallons and 4.3 million gallons of butane into gasoline at levels as high as 4.8 vol% between September and March. At the time, the gasoline-butane spread was $1.5/gallon, resulting in profits of $4 million dollars and $6.5 million dollars, respectively [11].

1.1. Fuel volatility specifications

The volatility of liquid fuels such as gasoline is critical for combustion efficiency and reduced emissions. Combustion in an internal combustion engine occurs when a controlled mixture of fuel vapor and air is introduced into the cylinder and compressed to the point of ignition (diesel), or compressed and ignited with a spark (spark ignition). In a gasoline engine, typically spark ignited, the fuel is vaporized during the injection process. Vapor formation is dependent on the rate and extent of fuel evaporation, which is in turn dependent on the chemical composition of the fuel droplet.

Aspects of the volatility of gasoline are expressed by a number of different measures, including distillation curves (which includes T_{10}, T_{50} and T_{90} or the temperature at which 10%, 50% and 90% of the fuel has evaporated), drivability index, vapor pressure at 100°F, vapor/liquid ratio, and vaporization enthalpy [12]. To ensure the safety and quality of the fuel supply, the volatility of gasoline and gasoline-oxygenate blends is regulated by various government agencies. Largely because of season and location, there is not a uniform set of gasoline volatility specifications. Instead, these requirements encompass a wide range of values. For RVP, US requirements range from 54 to 103 kPA (7.8–15 psi). Vapor lock protection requires a minimum temperature at which the vapor-liquid ratio is 20 that ranges from 54 to 35 °C (129 to 95°F) [13]. These varying requirements mean that the fuel composition is geographically and seasonally variable. The United States Environmental Protection Agency (EPA) provides a 1 psi "waiver" for the RVP of blends of conventional gasoline with 9–10 vol% ethanol, *i.e.*, an increase in the maximum RVP for E10 gasoline. In the US, the volatility specifications in ASTM D4814 cover oxygenates such as alcohols and ethers when that oxygenate is not the primary component of the fuel [14].

The European Committee for Standardization (CEN) summarizes test methods in *EN 228 Automotive Fuels – Unleaded petrol – Requirements and test methods* [15,16], with regulations described in Directive 2009/30/EC. The EU currently requires a maximum fuel vapor pressure of 60 kPa (8.7 psi) during summer. Some Member States have a derogation easing the standard for blends with ethanol, allowing vapor pressures up to 70 kPa (1.4 psi) in summer (similar to the US EPA "1 lb waiver") for fuel with 10% bio-derived ethanol by volume.

These requirements balance two competing needs. First, a high vapor pressure fuel is required to start the engine and operate efficiently at colder winter temperatures. Second, when temperatures are higher in the summer or at higher altitudes, a higher vapor pressure can result in the gasoline vaporizing in the fuel line and interrupting fuel flow, a phenomenon known as "vapor lock" [17]. This condition could result in the engine running rough or stalling completely, requiring that the vehicle cool down before restarting is possible. Vapor lock can also occur at the fuel pump, causing cavitation in the pump and loss of fluid flow. Although motorcycles and older carbureted engines can still suffer vapor lock, the advent of pressurized fuel injection lines where the fuel pump is located in the fuel tank has eliminated the potential for vapor lock in most modern vehicles.

1.2. Impact of oxygenates on volatility

The presence of oxygenates changes the volatility behavior of a fuel. While the distillation behavior of hydrocarbons is well understood, the addition of oxygenates complicates the behavior of mixtures by introducing non-ideal interactions such as those between polar and nonpolar compounds. Many reviews and studies, including those by Andersen et al., Pumphrey et al., and King and Furey, describe a large number of experimental results and models developed to predict the non-ideal RVP behavior of alcohols blended into petroleum base fuels [18–23,30–32,19,24–26]. However, there is much less information describing the interaction of other oxygenates [9] and how they affect final blend properties.

Optimizing fuel composition for increased engine efficiency and reduced emissions trades off among many characteristics. Decreasing volatility by reducing the amount of light, or low-boiling, chemical constituents of gasoline (pentanes and smaller) can also result in a decreased RON [27]. The midrange of the distillation curve is the region with temperatures between which 20% and 90% evaporation occurs (T_{20}-T_{90}). However, decreasing the midrange (T_{20} to T_{90}) to lower T_{20} and T_{90} values can result in faster starting, smoother running, higher short-trip fuel economy, greater power, and better acceleration. The tail end of the distillation curve is found at temperatures above 90% evaporation. These are the least volatile compounds in the gasoline, and modifying this part of the curve downward can result in greater fuel efficiency once the engine is warm, fewer deposits in the engine, lower fuel contamination of the lubricating oil, and lower volatile organic compound (VOC) emissions in the exhaust. There is little variation in the tail end of the distillation curve between the classes of gasolines to avoid excessively high T_{90} values, thereby ensuring a consistent distillation cutoff when gasoline range fuels are produced from petroleum.

The impact of added oxygenates on gasoline volatility is also important for fuel transfer and storage. For the safe storage of gasoline fuel with flashpoints of −45C, it is important that the vapor pressure be

sufficiently high to keep the fuel fraction outside of the flammability limits in the headspace of the fuel tank [28–30]. The evaporation of VOCs from gasoline occurs during all stages of the fuel's life cycle, including refining, commercial handling, transportation, storage, and final distribution at a fueling center [31]. VOCs can have a significantly detrimental effect on human health and are ozone precursors. As will be discussed further in this review, the oxygenate content of prospective gasolines containing some bio-blendstocks can significantly affect fuel volatility and hence change the environmental impact of the use of a particular biofuel.

1.3. Predicting the vapor pressure of oxygenate blends

The measurement of the vapor pressure of the fuel candidate mixture according to an established and appropriate standard method is the best means to determine the suitability of a given blend as a fuel blendstock. However, such measurements are not always possible in the early stages of material development where sample sizes are often limited. This is particularly true when screening biomass-derived fuel candidates generated by biochemical routes [32]. Current models to predict RVPs of mixtures do much more poorly when oxygenates other than alcohols are blended into hydrocarbon fuels due to the non-ideal blending behavior. Therefore, improved understanding of the blending behavior of oxygenates is essential to enable rapid biofuel candidate discovery. Advances in the modeling of these non-ideal systems can be expected to improve vapor pressure predictions for new mixtures incorporating unique chemical group contributions. In a study on the effect of additives and blendstocks on RVP [33], the authors determined that UNIFAC-based models show limited applicability in predicting the RVP of gasoline mixtures with materials that show a significant degree of hydrogen bonding, such as lower alcohols (methanol, ethanol, propanol, 2-methyl-1-propanol), because these conventional models don't take the intermolecular interactions in these mixture explicitly into account.

The rest of this paper is organized as follows. We discuss methods of measuring vapor pressure in Section 2, including early versions developed in the 1920 s and including the current ASTM standards and specifications. This is followed in Section 3 by a description of the effect of oxygenates on gasoline volatility, including the specific RVP behavior of oxygenates in oxygenate-gasoline blends. Next, Section 4 reviews theoretical approaches to modeling the vapor pressure of gasoline-oxygenate blends, including a comparison of modeling approaches compared to experimental measurements. Finally, Section 5 presents new data collected in this work that illustrates the effect that oxygenate bio-blendstocks of various compositions and concentrations have on the RVP of gasoline. An ASPEN Plus-based estimation method was used to calculate various thermodynamic property models (*i.e.*, statistical associating fluid theory [SAFT], SRKKD, BK10, cubic-plus association [CPA], non-random two liquid theory [NRTL], Wilson, UNIFAC, and UNIFAC-DMD) to estimate the RVP of oxygenate blends. The estimates are compared to a series of new vapor pressure data for several oxygenates in a gasoline fuel.

2. Vapor pressure measurement methods

Fuel vapor pressure measurement science and technology dates back more than 100 years. The measurement of fuel vapor pressures started in the early 1900s with liquefied petroleum gas storage and handling because vapor pressure is invariably tied to pressure vessel and safety valve operation. Many methods have been developed in the intervening years to address practical challenges that arise including contamination by water, dissolved air, sample size, and the loss of the more volatile components in a sample. We summarize many of these methods, focusing on those used in the United States, but recognize that parallel methods have been developed and adopted worldwide. The methods described in this section are summarized in Table 1.

Table 1
Comparison of vapor pressure measurement method for automotive gasoline performed at 37.8 °C (100°F) and at vapor-to-liquid ratio of 4:1.

ASTM Standard	Year	Test method	Scope and applicability	Vapor pressure range kPa (psi)	Sampling prep requirement	Result output	Sample size (chamber vol.)	Reproducibility/accuracy‡ kPa (psi)
D323 Proc. A	1920-	Reid method, with prior sample cooling and air saturation	No oxygenates, except MTBE	35–100 (5.08–14.5)	Cooling to 0 °C (32°F) and air saturation required	Reid Vapor pressure (RVP)	100 cc	5.2 (0.75)
D323 Proc. B	1920-	Reid method, semi-automatic	No oxygenates, except MTBE	35–100 (5.08–14.5)	Cooling to 0 °C (32°F) and air saturation required	Reid Vapor pressure (RVP)	100 cc	4.5 (0.65)
*D4953 Proc. A	1989	Dry Reid method	Oxygenated gasoline	35–100 (5.08–14.5)	Cooling to 0 °C (32°F) and air saturation required	Dry Vapor Pressure Equivalent (DVPE)	100 cc	5.52 (0.80)
*D4953 Proc. B	1989	Dry Reid method, semi-automatic	Oxygenated gasoline	35–100 (5.08–14.5)	Cooling to 0 °C (32°F) and air saturation required	DVPE	100 cc	2.90–5.38 (0.42–0.78)
*D5191	1991	Mini method, automatic, vacuum	Oxygenated gasoline	7–130 (1.02–18.85)	Cooling to 0 °C (32°F) and air saturation required	Total chamber pressure –correlated to DVPE	1–10 cc	2.87–3.65 (0.42–0.53)†
*D5482	1993	Mini method, automatic, atmospheric	Oxygenated gasoline	7–110 (1.02–15.95)	Cooling to 0 °C(32°F) and air saturation required	Total chamber pressure–correlated to DVPE	1–10 cc	2.69–4.14 (0.39–0.60)
*D6378	1999	Triple expansions	Oxygenated gasoline	7–150 (1.02–21.76)	No prior cooling or drying necessary	Total vapor pressure: VPx-can be correlated to both DVPE and RVPE	5–15 cc	1.63 (0.24)

*These methods were specified by ASTM D4814 for measuring vapor pressure of oxygenated gasoline.
†Reproducibility is defined as 0.0161*(DVPE + 18 psi or 124 kPa). For gasoline AA fuel (RVP of 7.83 psi or 54 kPa), calculated reproducibility is 0.42 psi (2.87 kPa), and for Gasoline E (14.94 psi or 103 kPa), 3.65 kPa.
‡Reproducibility is based on comparison of multiple laboratory measurements.

2.1. Original Reid and dry Reid methods

In the 1920s the U.S. Bureau of Mines recognized the need for an improvement over the "vapor tension" method then employed (a pressure gauge on a length of 2 in pipe). A competition was held that eventually led to ASTM D323 [34]. This method was originally used for so-called "natural gasoline," which is a mixture of liquid hydrocarbons extracted from natural gas and then processed from the casing-head (the mouth or opening) of an oil well for blending with refinery gasoline. [35]. Thus the original method is called "Standard Test Method for Vapor Pressure of Natural Gasoline Reid Method" [36]. The original ASTM D323 method has been updated over the course of nearly a century with minor revisions dating back to the original version in 1927 [25]. The most recent update to ASTM D323 was approved in 2015. ASTM D323 is only approved for use with non-oxygenated gasoline with exception of methyl tert-butyl ether (MTBE) present as an additive [36]. Historically, revisions to ASTM D323 included improved and up-to-date procedures that increased the accuracy and precision based on the gasoline formulation. Therefore, it is pertinent to refer to the most up-to-date version prior to performing this measurement because the formulation may change.

ASTM D323 measures gasoline/petroleum products in a sealed chamber with a vapor-to-liquid volume ratio of 4-to-1 at 37.8 °C (100°F). The vapor pressure in the chamber using a pressure gauge is the RVP and is reported in kPa or psia. Notably, this method also requires samples to be initially cooled and saturated with air at 32°F prior to introduction to the sealed chamber, which is already heated to 100°F prior to pressure read-out. This method requires careful handling of the volatile sample to ensure high accuracy readings. Further discussion of the sample handling has been standardized in D4057 [37].

An example of the complex regulatory environment surrounding Reid vapor pressure measurements is described in the California Air Resources Board (CARB, a regulatory agency in the United States) Phase 3 requirements. These requirements specify a range of acceptable RVP values, which are to be measured via ASTM D323-58, or 13 California Code of Regulations 2297, or ASTM D6378-08 [38]. This is problematic because ASTM D323 (Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)) is not designed to test oxygenated fuels, and the presence of trace amounts of water is not accounted for in the method, which may lead to inaccurate measurements. Other ASTM vapor-pressure measurements have been developed and reviewed for applicability to oxygenated blends [39]; ASTM D4814 is the governing document specifying acceptable methods for measuring the vapor pressure of spark-ignition engine fuel [13]. This standard specifies the use of D4953, D5191 (equivalent to EN 13016-1 in Europe), D5482, or D6378 for vapor pressure measurements of oxygenated blends (discussed in detail in Section 2). Vapor pressures are often reported as "RVP," even when the actual measurement is a dry vapor pressure equivalent (DVPE) [18,19,25 40]. These two are often used interchangeably, but are not in practice and may mislead. For example, an inconsistency in RVP measurements between Pumphrey et al. [19] and with Andersen et al. [25] was observed, with the difference attributed to the presence of saturated air in the samples analyzed by Pumphrey et al. Andersen et al reports DVPE.

The impact on vapor pressure of trace amounts of water is often neglected. Chevron's Motor Gasoline Technical Review [41] reports water solubility in gasoline as up to 150 ppm, and up to 600 ppm with oxygenated fuels. For gasoline containing ethanol, water solubility may be as high as 6000–7000 ppm (0.6–0.7 wt%) at 21 °C (70°F). Timpe and Wu showed that for three gasoline blends containing 10 vol% ethanol, adding 0.2 wt% water increased the vapor pressure by about 1.4 kPa (0.2 psi) and 0.4 wt% water increased the vapor pressure by about 2.1 kPa (0.3 psi) [42]. Given the increased water solubility of oxygenates, the amount of water should be accounted for in the measurement.

ASTM method D4953 was developed in 1989 after a series of inter-laboratory tests with different fuels determined a new method was necessary to replace the Reid method for oxygenated gasoline [43]. ASTM D4953 uses an identical equipment setup as method D323, yet it is suitable for measuring the vapor pressure of gasoline-oxygenate blends because it accounts for the presence of water-vapor pressure by first eliminating moisture from the measurement chamber. The modification to the procedure requires that the interior surfaces of the liquid and vapor chambers be free of water. The procedure reports a DVPE, which is used interchangeably with RVP because there is no relative bias between this method and D323. Protocols for handling of the samples prior to measurement with D323 and D4953 are specified by the standard D4057 [37].

2.2. Miniaturized methods

In the early 1990s, faster and automated vapor pressure measurement methods were developed that require smaller sample volumes and are applicable to oxygenated gasoline fuels. One such method, ASTM D5191 [44], uses a miniaturized apparatus requiring about 10% of the sample volume required by ASTM D323 or D4953. ASTM D5191 is the most widely used method in the US for regulatory compliance and is equivalent to IP 394 (UK), AFNOR M07-079, and EN 13016-1.

ASTM D5191 reports a vapor pressure number that is related to that obtained by ASTM D4953 by the linear relationship $DVPE_{D4953} = 0.965 \times DVPE_{D5191} - 3.78\ kPa\ (0.55 psi)$. The D5191 measurement may also be converted to an RVP equivalent (RVPE) as measured by ASTM D323 using the linear relationship$RVPE_{D323} = 0.972 \times DVPE_{D5191} - 4.93\ kPa (0.72\ psi)$. Of course, the accuracy of each measurement is different, even though the results can be related to each other. ASTM D5191 differs from methods ASTM D323 or D4953 by preparing the sample chamber under vacuum to ensure it is free of air or moisture prior to the introduction of the sample. Careful saturation of the sample with air three times is specified for D323, D4953 and D5191.

ASTM D5482 is similar to ASTM D5191 in that it is performed in a miniaturized apparatus, but it is performed at atmospheric pressure [45]. This method may result in higher error resulting from the potential for moisture in the testing chamber. Inter-laboratory testing showed that the final accuracy for D5482 is slightly lower than D5191.

In 1999, ASTM D6378 was developed and approved to address issues arising from volatile components in the fuel while eliminating the need for air saturation and chilling of samples [46]. This method differs considerably from other vapor pressure methods, most notably in how the sample chamber accommodates pressure measurements at different volumes. After the measurement chamber is sealed, an expansion is performed in three distinct steps to a final volume of four times that of the test specimen. The pressure is observed and recorded after each step. The partial pressure of air is calculated from the observed pressure during the three-expansion step. The final vapor pressure at the third step is reported as "VP_4." VP_4 is calculated by subtracting the partial pressure of air that has been corrected for the test temperature. All parameters (volume from expansion steps, pressure, and calculations) are performed automatically by the testing instrument. ASTM D6378 is notable as one of the accepted methods for RVP measurement by California Air Resource Board and was used exclusively for measurement of the "RVP" of the alcohol-gasoline mixture blend study [25]. In terms of improvements and differences, D6378 has the broadest range of measurable vapor pressures from 7 to 150 kPa. Additionally, the three separate expansions account for the contribution of air in the chamber and dissolved in the fuel, relieving the necessity to saturate the fuel with air prior to making the measurement. As a result, the final reproducibility of this technique proved to be better than the preceding volatility measurement methods with reproducibility measured at 1.63 kPa [39]. The value determined via D6378 is related to that determined by ASTM D5191 by $DVPE_{D5191} = DVPE_{D6378} - 0.15\ psi (1.027\ kPa)$ and ASTM D4953 by

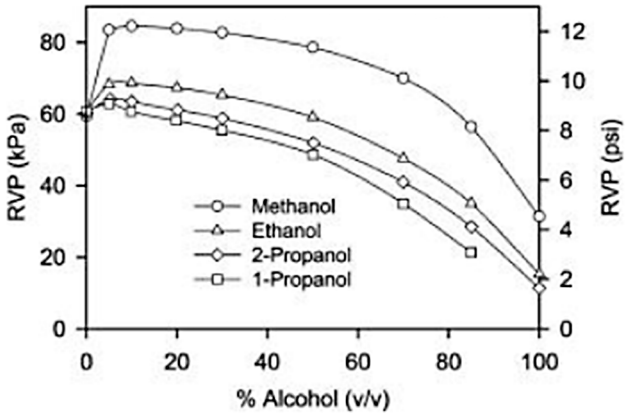


Fig. 1. Measured RVP (predicted DVPE) of blends of the C1-C3 alcohols with gasoline measured using ASTM D6378. Reprinted with permission from V.F. Andersen, J.E. Anderson, T.J. Wallington, S.A. Mueller, O.J. Nielsen, "Vapor pressures of alcohol-gasoline blends," *Energy and Fuels* 24 (2010) 3647–3654. Copyright 2010 American Chemical Society.

$$DVPE_{D4953} = 0.956 \times DVPE_{D6378} DVPE_{D6378} - 0.35\ psi (2.39\ kPa).$$

3. Volatility of gasoline and oxygenated additives

Gasoline is a volatile and complex mixture of hydrocarbons that is compatible with spark-ignition, internal combustion engines. Gasoline is a fungible commodity due to its fuel properties rather than its specific chemical components, and it primarily consists of straight, branched and cyclic alkanes, alkyl-monoaromatics, alkenes, and oxygenates. A very nice summary can be found in Simmons and Potter [47]. In addition to hydrocarbons ranging from C4-C12, all boiling at temperatures of less than about 200 °C [48], gasoline includes small amounts of additives, such as detergents, antiknock agents that enhance octane number, corrosion inhibitors, antioxidants, and stabilizers in the form of metal deactivators [41,49,50].

The use of oxygenates in gasoline has grown with the increasing demand for higher octane and renewable fuels. There is a long history of ethanol blending into gasoline; in the US, this history dates back to the 1930s in Nebraska. An early study of the effect of ethanol blending on fuel volatility (evaporative and tailpipe emissions) in conventional gasoline was performed by Furey et al. [20,51]. The authors also looked at MTBE blending in this study. Furey et al found that ethanol exhibits non-ideal liquid mixing behavior, and the resulting vapor pressure of the mixture was not linearly proportional to the additive concentration.

There are two main factors identified in the literature accounting for the non-ideal behavior of blending of shorter chain alcohols in gasoline. These factors are discussed extensively by Andersen et al. [25]. First the short-chain alcohols can form an azeotrope with gasoline. This has been attributed as the primary reason for increased RVP at low alcohol concentrations [18–23,25,51]. Second, the strong hydrogen bonding results in changes in the behavior of the alcohol molecules, as the nonpolar hydrocarbons interfere with the intramolecular hydrogen bonding between the polar alcohol molecules. An early set of observations of this non-ideal behavior was made by Furey in 1985 [Furey 1985]. In work by Dixon [52] and Von Solms et al. [53], methanol in its pure state was observed to form tetramers due to strong hydrogen bonding, which depresses volatility for neat methanol. However, when blended with hydrocarbons in gasoline, the tetramers are disrupted, and the methanol tends to behave more as single molecules, leading to higher vapor pressure due to the lower molecular weight of single methanol molecules compared to the clusters. The current state of understanding regarding the effects on RVP upon blending with gasoline are discussed in the remainder of this section.

Although much of the focus on oxygenates for fuels has centered on alcohols and MTBE, other functional groups may be suited for blending in gasoline. Other oxygenates exhibit non-ideal behavior as well. Generally, increasing polarity corresponds to increasing non-ideal behavior, and thus, fuel volatility that behaves nonlinearly [54]. One consequence is that as the relative number of carbons increases, the behavior of the molecule becomes more like its hydrocarbon counterparts [54]. Below is a brief discussion of the RVP impact on gasoline of major functional groups derived from biomass, including alcohols, ethers, esters, ketones, and furans.

3.1. RVP trends: alcohols

Alcohols strongly affect RVP, with the strength of the impact dependent on chemical structure and concentration. Neat alcohols typically have low RVP (lower than gasoline) but can nonetheless increase the volatility of gasoline when blended at low to medium blending concentrations due to effects described in Section 3.1 Ethanol and methanol have both been widely studied and used in the fuel industry [18,25]. Addition of a relatively small amount of methanol (< 10% v/v) to gasoline (EEE; RVP = 61 kPa) increases the RVP by more than 30%, even though pure methanol has a low RVP (31 kPa). This effect has been found to be essentially independent of base fuel composition [25]. However, the RVP increase when ethanol is added is dependent on the composition of the base gasoline, with greater RVP increases observed for base gasolines with lower RVP [55] or greater saturated hydrocarbon content [56].

The effects of larger alcohols on vapor pressure have also been studied. As expected, increasing the chain length on the alcohol decreases the RVP impact, as observed in several references including Andersen et al. [25] and Christensen et al. [9]. In both low-volatility blendstock, as well as in certification gasoline that is used for emissions testing (gasoline EEE) [18,25], RVP increased for blends containing less than 25 vol% 2-propanol or 10 vol% 1-propanol. Fig. 1 compares results from Andersen et al [25] for methanol, ethanol, 1-propanol and 2-propanol. Andersen et al. found that 1-propanol, isopropanol and tert-butanol also increased the vapor pressure of the blended fuel [25]. Extrapolating from these results, as the chain length continues to increase, at some point, no RVP increase will be observed. As an example, no RVP increase was observed for di-tert-butoxypropanol in reference 19 [57]. Butanols [25], pentanol [9] and other larger alcohols have been studied as well. For example, Christensen et al. [9] determined that when butanol or pentanol is blended with low RVP base fuels, the resulting blended fuel RVP meets the specification for flex fuel vehicles (*i.e.*, no waiver is required), with only a minor RVP increase for a 5 vol % t-butanol blend.

The RVP impact of blending multiple alcohols into a hydrocarbon fuel appears to behave as a linear combination of the expected behavior of the individual alcohols. Fig. 2 shows the smaller increase in RVP when a 50:50 mixture of 1-butanol and ethanol is blended with gasoline as compared to the single alcohol blends with gasoline [25]. Three individual 1-butanol:ethanol blends are also made that match the RVP of the base gasoline. Blending two or more alcohols offers significant potential advantages in increasing the renewable content of our fuel stream with minimal emissions impact compared to using ethanol or methanol singly. This could also provide flexibility throughout the supply chain in meeting RVP requirements.

Christensen et al. [9] examined the effect of linear C_2-C_5 alcohols on three hydrocarbon blendstocks for oxygenate blending (BOBs). Ethanol addition resulted in an RVP increase in all three BOBs. Butanol and pentanol addition resulted in a decrease in vapor pressure in all three BOBs. 2-Propanol increased the RVP of the lowest vapor pressure BOB, and decreased the RVP of the other two BOBs. This is consistent with the observations described above, where a similar phenomenon was seen for methanol and ethanol, *i.e.*, lower RVP base fuels are more prone to an increase upon addition of alcohols.

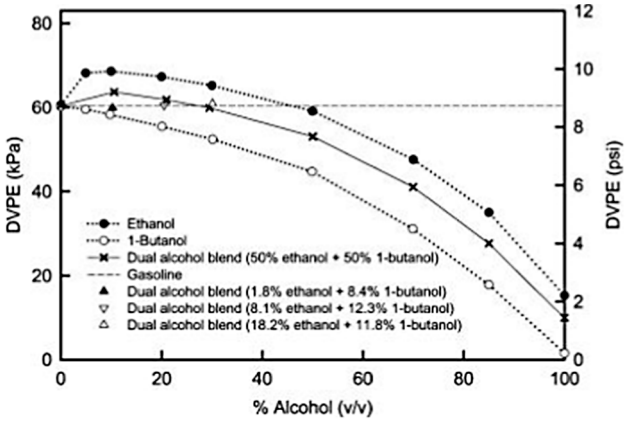


Fig. 2. Measured RVP (predicted DVPE) from ASTM D6378 of single- and dual-alcohol blends in gasoline. Reprinted with permission from V.F. Andersen, J.E. Anderson, T.J. Wallington, S.A. Mueller, O.J. Nielsen, "Vapor pressures of alcohol-gasoline blends," *Energy and Fuels* 24 (2010) 3647–3654. Copyright 2010 American Chemical Society.

3.2. RVP trends: ethers

Most of the literature on ethers focuses on the effects of MTBE and ETBE in gasoline due to their previous use in the US and ongoing use elsewhere. MTBE, in particular, has been well studied [58]. Adding MTBE to gasoline results in increased RVP. However, it displays more ideal behavior (see Section 4 for a detailed discussion of ideal behavior) with a linear dependence on MTBE content, in contrast to ethanol's strongly nonlinear behavior [12]. ETBE increases RVP much less significantly, with only a slight (< 10% absolute) change observed at concentrations up to 25%. Da Silva et al. observed a dependence of the base fuel composition on the RVP change for MTBE and ETBE. The observed RVP increase upon addition of MTBE was much higher in a highly paraffinic blendstock than in a more aromatic blendstock [12]. ETBE showed a modest increase in the paraffinic blendstock and a decrease in the RVP in the more highly aromatic blendstock.

Other ethers have also been evaluated by McCormick and coworkers. 2-methyl tetrahydrofuran (or 2-methyloxolane) is a cyclic ether with promise for use as a bio-derived fuel. This ether decreased the RVP of several BOBs upon blending at levels up to 12 vol% [9]. McCormick et al. [59] also looked at anisole (methoxybenzene or methyl phenyl ether). Anisole decreased the measured RVP when blended into a BOB, exhibiting linear (ideal) behavior.

3.3. RVP trends: esters

McCormick and coworkers measured the RVP of several esters – methyl acetate, ethyl acetate, butyl acetate, and ethyl butyrate – at 10%, 20% and 30% by volume in a reformulated BOB. Like alcohols, small esters also exhibited non-ideal behavior, though the behavior is quantitatively and qualitatively different from the alcohols [59]. Methyl acetate causes a continuous sublinear increase in RVP up to at least 30 vol%. Increasing chain length leads to more ideal behavior such that for molecules as large as butyl acetate or ethyl butyrate, an essentially linear decrease in RVP is observed. Ethyl acetate increases the vapor pressure of gasoline only slightly (although still nonlinearly with concentration). This difference in blending behavior between the esters and the alcohols points towards a different explanation for the observed effects on RVP. Dilution of the lighter alcohols results in breaking the intermolecular hydrogen bonds between the solute molecules, facilitating alcohol volatilization and thus increasing the vapor pressure. Ester hydrogen bonding is weaker, and thus this effect is either weaker or not observed, and the increase in vapor pressure in the case of methyl acetate and ethyl acetate is due in part to their own high volatility. No further explanation for the origin of the nonlinear behavior was given, although the decreased dipole of the esters compared to the alcohols will increase van der Waals interactions with the fuel molecules in the BOB. Dabbagh et al. [60] also reported a smaller increase in RVP with addition of methyl acetate and ethyl acetate compared to ethanol. Finally, Christensen et al. [9] measured the RVP impact of blending three levulinic acid esters – methyl levulinate, ethyl levulinate, and butyl levulinate – and methyl pentanoate into several BOBs. These esters are all large enough that no increase in RVP was observed for the levulinates at up to 8 vol%, or for methyl pentanoate at blend levels up to 22 vol%.

3.4. RVP trends: ketones

The effect of blending several ketones on gasoline RVP was also examined by McCormick et al. [59]. Except for 2-butanone, the lightest ketone in the series, a steady decrease in RVP was observed with increasing ketone concentration in gasoline. 2-butanone showed substantial increase in RVP. Ketones, particularly acetone and 2-butanone, may interact unfavorably with elastomers in the fuel system and cause swelling [61]. Some ketones may also show elevated tendency for gum formation at high engine loads [40].

3.5. RVP trends: furans

McCormick et al. [59] also looked at a mixture of furans (2-methylfuran and 2,5-dimethylfuran) which can be generated by chemical conversion of sugars. Like anisole above, the furan mixture showed a steady decrease in RVP of gasoline with increasing blending level in gasoline. At 5 vol% in gasoline, 2-methylfuran showed an increase in RVP. Despite promising fuel properties, the furans studied in this work have known issues with oxidative stability [62]. Some of these results are summarized in Table 2.

4. Thermodynamic models and descriptions

Predicting the vapor pressure of a system at a given temperature

Table 2
Effect on RVP of 10% oxygenate blended into low RVP California Reformulated Gasoline Blendstocks for Oxygenate Blending (CARBOB). From data presented in Christensen et al. [9] and McCormick et al. [59].

Group	Oxygenate	RVP Impact
Alcohols	ethanol	+ +
	1-propanol	No change
	2-propanol	–
	1-butanol	–
	2-butanol	–
	2-methyl-1-propanol	–
	I-butanol	–
	1-pentanol	–
	3-methyl-1-butanol	–
Esters	methyl acetate	+ +
	ethyl acetate	+
	butyl acetate	–
	ethyl butyrate	–
	ethyl levulinate	No change
	ethyl levulinate	–
	butyl levulinate	–
	methyl pentanoate	–
Furans	2-methylfuran	+
	2,5-dimethylfuran	–
	2-methyltetrahydrofuran	–
Ketones	2-butanone	+
	2-pentanone	–
	cyclopentanone	–
	2,4 dimethyl-3-pentanone	–

requires an accurate prediction of the vapor-liquid equilibrium at the condition, which is determined by the system thermodynamics. Thermodynamics provides the foundation by which equations of state (EoS) can be used to present phase equilibria of a given system, over a wide range of temperatures and pressures, and to derive accurate physical properties of that system, including vapor pressure. Initially EoS were used for systems which could be deemed ideal, *i.e.*, predominantly pure compounds or simple mixtures of nonpolar molecules which are well represented by van der Waals forces of repulsion and dispersion, and other weak electrostatic forces. In the last few decades, more sophisticated models have been proposed taking into account inter- and intramolecular interactions that can more accurately take into account intermolecular associating forces such as coulombic forces, strong polar forces, complexing forces, forces associated with chain flexibility, induction forces, etc. These models include early efforts by Soave (1972) and Peng and Robinson (1976) and are reviewed in [63]. Since the focus of this review is on the volatility—especially the vapor pressure—of fuel mixtures containing oxygenates, this section focuses on theoretical approaches to predict the vapor pressure of a gas in equilibrium with a liquid.

4.1. Vapor pressure thermodynamics

Prior to working with mixtures, the vapor pressures of individual components within a mixture can be considered individually. The vapor pressure of a pure component is often referred to as its saturation pressure. The temperature dependence of the vapor pressure of a pure component can be calculated using one of the well-known Antoine [64] (based on a modified Clapeyron equation approach), Riedel (based on a statistical method for nitrogen and argon) [65], or Wagner [66] equations. Once the necessary empirical parameters are determined for a given compound, these equations can be used to calculate vapor pressures over a large temperature range for a large number of very different compounds.

In a mixture, the relative fractions of any given component in equilibrium between the vapor and liquid phases reflects the degree of volatility of that component relative to the other components. A more volatile component will have a greater concentration in the vapor phase relative to its concentration in an equilibrium liquid phase than a less volatile component. This differential volatility among the parts of a mixture serves as the basis for separations using distillation.

In ideal mixtures, the thermodynamic properties of a fluid are directly proportional to composition. This relationship is described by Raoult's law, given in equation $P = x_i P_i^{sat}$ where y_i is the vapor phase mole fraction of component i, P is the vapor pressure, x_i is the liquid phase mole fraction, and P_i^{sat} is the saturation pressure of the pure component i at the same temperature. The relationship between the compositions of equilibrium vapor and liquid phases in ideal mixtures does not change with changing composition, and can be readily calculated from a measurement of the vapor pressure of the mixture and the saturation pressures of each pure component.

An ideal solution is one in which the sizes, shapes, and interactions of unlike species are the same. Like an ideal gas, there is no change in volume on mixing relative to the simple sum of the pure component values, and no heat released by mixing. Unlike an ideal gas, molecules in an ideal solution are presumed to take up space and have long-range interactions. Solutions of similarly sized nonpolar hydrocarbons exhibit nearly ideal behavior because of the similarity of like and unlike interactions between molecules. An example of a mixture that approaches ideal solution behavior is n-hexane and n-heptane, which are similarly sized linear alkanes that both interact through weak van der Waals forces. Dilute solutions, where the concentration of one component is very high, can also approximate ideal solution behavior due to a very low number of unlike interactions.

Non-ideal mixtures include large differences in the interactions among components. For example, the components could have very different sizes, or have very different intermolecular interactions. In the vapor phase, non-ideality also results at high pressures, where the distance between molecules is relatively small and the molecules are likely to interact. A mixture containing both polar molecules and nonpolar molecules exhibits non-ideal solution behavior. A non-ideal mixture of ethanol, a hydrogen-bonding molecule, and n-hexane, a nonpolar alkane that interacts primarily through van der Waals forces, exhibits large deviations in vapor pressure from that expected from an ideal solution. Gases close to their critical pressures also behave non-ideally.

The result of non-ideality in mixtures of fluids is that the relationship between composition and pressure is no longer linear, and composition-dependent corrections must be added to Raoult's law. These additions are the vapor phase fugacity coefficient, ϕ_i, and the liquid phase activity coefficient, γ_i, leading to the expression $f_i y_i P = \gamma_i x_i \phi_i P_i^{sat}$. $\hat{\phi}_i$is a fugacity coefficient of a component in a mixture. The degree of vapor phase non-ideality is described by $\phi_i f_i$, while γ_i reflects the degree of liquid phase non-ideality. When this equation is used in the calculation of vapor-liquid equilibrium (VLE), the vapor phase is sometimes assumed to behave ideally, so that f_i is equal to 1. Under conditions of moderate to high pressure, it is necessary to use experimental data for the system, a generalized correlation function, or an equation of state to calculate f_i. These first two methods are purely empirical, while the last may also include some theoretical aspects, such as in the virial equation of state. The value of γ_i is needed to calculate VLE in nearly all real systems, and can be found from an activity coefficient model or, less accurately, an equation of state. Activity coefficient models may be purely empirical and based on known trends in experimental data, or they may be based on a combination of theoretical and empirical considerations. For example, the Margules equation was proposed because it is the simplest mathematical expression capable of reproducing the known endpoint behavior of the activities of species in solution [67]. In contrast, the universal quasi-chemical equation (UNIQUAC) combines a microscopic understanding of solution behavior with empirical parameters that must be fit to experimental data to calculate γ_i [68].

4.2. Approaches to modeling vapor pressure and VLE

There are numerous benefits of modeling VLE of mixtures, and thus vapor pressure, to applications like gasoline blending and industrial process design. In the absence of robust models, it would be necessary to collect vapor pressure data for every composition and condition being explored. Such a process would be time-consuming and expensive. Instead, models are used to correlate and predict VLE data, allowing for the efficient use of resources in industrial processes. These relationships can be used to optimize the composition of gasoline consisting of different blended fractions without the need for extensive experimental testing. Fuel blends can be optimized for cost while meeting both consumer and regulatory requirements for the final product's physical and chemical properties. A detailed description of thermodynamic models used to describe the behavior of petroleum products in industrial and research applications can be found elsewhere [69,70].

The most data-intensive and narrowly applicable models are empirically-derived correlations. This approach relies on the idea that simple interpolation between data points provides a satisfactory, continuous description of VLE in those parts of the phase diagram that have not been explicitly sampled. Such relationships cannot reliably be used to extrapolate beyond the boundaries of the experimental data used in the correlation. However, they are an efficient way of expressing the correlations contained in experimental data when referring to tables of experimental data is undesirable.

Semi-empirical activity coefficient models reduce the amount of data necessary to model VLE by presenting a good description of system

behavior with changes in composition, temperature, or pressure without requiring additional data to be collected for all conditions of interest. The conditions under which the results of semi-empirical models may be extrapolated depend on the form of the model. Semi-empirical models are derived from fluid-phase thermodynamics and can be parameterized using either experimental data alone or a combination of experimental data and the results of more robust predictive models. In contrast to purely empirical correlations, semi-empirical models may yield reasonable descriptions of VLE behavior outside of the limits of the experimental data used in their parameterization. For example, as described for the Wilson equation and UNIQUAC model below [71], VLE behavior in multicomponent systems may be predicted by semi-empirical models using only VLE data collected in binary systems.

Three related semi-empirical activity coefficient models that have been used with particular success in the correlation of VLE data of alcohols in nonpolar solvents are the Wilson equation, the NRTL model, and the universal quasi-chemical equation (UNIQUAC) [71]. All are examples of local composition models, where a theoretical understanding of fluid-phase behavior arises from the consideration of the impact of microscopic volumes of heterogeneity in the composition of the fluid on the energetics of unlike interactions. The Wilson equation was developed first and has two adjustable parameters (related to pure component molar volumes and to characteristic energy differences) that are largely independent of temperature. This allows the Wilson equation to be used in the extrapolation of VLE to different temperatures, although this model fails in systems that exhibit phase separation. The NRTL model, developed next, has three adjustable, temperature-dependent parameters. However, unlike the original Wilson equation, the NRTL model can describe liquid-liquid equilibrium. Finally, the UNIQUAC model requires two parameters and, like the Wilson model, is able to be extrapolated to a limited range of different temperatures. The UNIQUAC equation also forms the basis for the UNIQUAC Functional-group Activity Coefficients (UNIFAC) group-contribution model. All of these models have been used to predict multicomponent VLE systems based on binary VLE data.

Semi-empirical group-contribution activity coefficient models have the potential to reduce the need for experiment even further, as well as serve a predictive function in systems containing molecules for which experimental data has not yet been collected. Group-contribution methods are based on the premise that the thermodynamic properties of complex molecules may be approximated by taking into account contributions from the functional groups making up those molecules. This allows for the estimation of activity coefficients of molecules based solely on their structures. The UNIFAC group-contribution model has the greatest immediate relevance to industrial applications due to its widespread use. However, recent developments in SAFT models have proved promising for predicting thermodynamic properties of molecules not used in the parameterization of the model.

4.2.1. Empirical models for vapor pressure in oxygenate-gasoline blends

Empirical models relating RVP and oxygenate concentration are of particular interest in industrial applications due to their simplicity when compared with semi-empirical models. They consist of simple relationships that rely only on the known vapor pressure of the components and the final composition of the mixture.

In 1985, Furey suggested a simple relationship to describe the RVP of ethanol-gasoline blends with 0.2–2 vol% alcohol, $RVP = kC^n$, where C is the concentration of the alcohol, and k and n are constants unique to the specific gasoline and alcohol in the mixture [51]. While not used practically, this relationship shows the potential for a very large impact of alcohol concentration on the vapor pressure of gasoline when introduced even at low concentrations. The vapor pressure of gasoline blends is particularly sensitive to small amounts of short-chain alcohols, as shown in Section 3.

The California Environmental Protection Agency has developed the California Model for California Reformulated Gasoline Blendstocks for Oxygenate Blending (CARBOB), which is applicable to blends containing less than 10 vol% ethanol, $RVP_{FG} = 1.446 + 0.961RVP_{CARBOB}$, where RVP_{FG} is the RVP of the final gasoline product, and RVP_{CARBOB} is the RVP of the initial CARBOB, both in psi [72]. While this linear relationship is straightforward to calculate, it does not describe the impact of ethanol on the vapor pressure of gasoline BOBs at higher ethanol concentrations. Following the rapid increase in vapor pressure up to approximately 10 vol% ethanol, the vapor pressure begins to level out, and a more complex correlation is needed to capture this behavior.

In 2010, Andersen et al. [25] suggested an equation that could be used to calculate the relative amounts of alcohol-containing fuels that must be mixed to equal the vapor pressure of the original BOB, given a desired alcohol concentration in the final product using a linear approximation.

4.2.2. Semi-empirical models for vapor pressure and VLE

Much of the work in the literature correlating VLE data for fuel-relevant molecules, where at least one component is an octane-enhancing oxygenate, has focused on binary and ternary systems. The best results are obtained when the Wilson equation or the UNIQUAC model are used to correlate these data. However, the results of these models are often compared with other, potentially less effective models such as a simple equation of state. A detailed description of these models and their application can be found in Walas [71].

In an SAE report from 1994, Chen et al. proposed the use of a 10-component fuel surrogate, modeled using the Peng-Robinson equation of state, and binary interaction coefficients to describe the volatility characteristics of gasoline [73]. The proposed 10-component fuel surrogate was designed to recreate the distillation behavior of real fuels by including a variety of both light and heavy compounds. The distillation curve, RVP, and vapor composition data for several fuel surrogates with and without oxygenates were compared with the results of the Peng-Robinson equation of state model. This approach provided a very good fit to experimental data for fuel surrogates without oxygenates. However, the model was less accurate in systems containing the oxygenates MTBE and methanol.

The VLE of binary and ternary systems containing ethers, alcohols, linear and branched alkanes, alkenes, and cyclic hydrocarbons were explored by Spanish researchers in a series of related publications beginning the in mid-1990s (for example, see [74–77] for early and recent examples). The shared method used in these papers was to collect binary and sometimes ternary VLE data (P-x and P-x-y data) for varying groupings of these fuel-relevant molecules. These data were then correlated using some combination of the following models: the Margules equation, the Wohl equation, the Wilson equation, the NRTL model, and the UNIQUAC model. Non-ideal behavior in the vapor phase was quantified by using the virial equation of state. In general, the Wilson equation and the UNIQUAC model were found to provide the best fit to binary data and were the most effective at predicting the behavior of ternary systems from binary interaction coefficients in systems containing ethers and alcohols in the presence of fuel-relevant hydrocarbon molecules.

Ternary ETBE-containing systems were investigated in two papers comparing the results of using binary interaction parameters in the Redlich-Kister equation, the Wilson equation, the NRTL model, and the UNIQUAC model to predict the behavior of ternary systems. The vapor phase was assumed to behave ideally. The success of these models was compared with the results of using the UNIFAC method to predict vapor pressures [78,79]. Bubble-point and dew-point pressures were most accurately reproduced by the UNIQUAC model in the ETBE/hexane/heptane system, while the Wilson equation was most accurate in the ETBE/octane/heptane system. Both of these models performed better than the NRTL model. The UNIFAC method was the least accurate model in both ternary systems, but was still within 7% of the experimental values.

Mejia et al. characterized the volatility of mixtures of ethers, alcohols and alkanes through the collection of VLE data (T-x-y data) for ETBE/propanol, TAME/hexane, and TAME/ethanol/hexane systems [80–82]. The Wohl equation, Wilson equation, NRTL model, and UNIQUAC model were used to correlate the VLE data in both binary systems. All of these models were able to describe the thermodynamic properties of the binary systems well. Binary interaction parameters were then used to predict VLE in the ternary TAME/ethanol/hexane system using the Wilson equation, the NRTL model, and the UNIQUAC model. While all models provided a good estimate of bubble- and dew-point pressures of the ternary system, the Wilson equation included the smallest deviation from the experimentally determined values.

Pumphrey et al. used a pseudo-binary approach to model the VLE of real gasoline-alcohol mixtures, and compared to experimental data [19]. The study covered blends of gasoline and varying concentrations of a single alcohol, including methanol, ethanol, isopropanol, or t-butanol. These solutions were treated as pseudo-binary mixtures, where gasoline is considered to behave as a single component, and the added alcohol is the second component. The Margules, van Laar, and Wilson equations were used to model the vapor pressures of these gasoline/alcohol mixtures using parameters derived from the infinite dilution activity coefficients of the gasoline pseudo-component and the added alcohol. The Wilson equation was found to provide a good fit to the experimental vapor pressure data, within approximately 5%, while the Margules and van Laar equations were off by as much as 25% in the gasoline/methanol system. These results suggest that creating a gasoline model of high complexity may not be necessary to be able to predict RVP changes with composition using a minimum of experimental data.

Hull et al. measured VLE data (P-x-y data) for binary mixtures of ethanol/isooctane, 1-butanol/isooctane, and ethanol/o-xylene at different temperatures using a novel headspace gas chromatography method [83]. The Flory-Scatchard model, the Wilson equation, the NRTL model, and the UNIQUAC model were then used to correlate the data. All models were found to describe the binary VLE data with similar degrees of accuracy, with the UNIQUAC model performing the worst. The Wilson model, although effective at describing VLE data, was considered to be impractical for applications in gasoline blending due to its inability to describe liquid-liquid phase separation. The use of the NRTL and Flory-Scatchard models over the UNIQUAC model is suggested, due to their simplicity and accuracy.

A number of efforts have extended the UNIQUAC framework by including group-contribution methods to improve the applicability to new components. An early example is a study by Reddy to improve prediction of evaporative losses in gasoline/alcohol mixtures. In this work, Reddy modeled the volatility of a 34-component fuel surrogate and varying amounts of different alcohols (methanol, ethanol, and t-butanol) using the UNIFAC method [84]. Vapor phase non-ideality was quantified using the Redlich-Kwong equation of state. The results of this model were then compared with experimental measurements of the mass loss due to evaporation in equivalent experimental systems, rather than more traditional volatility measurements like vapor pressure. The calculated and experimental evaporative losses were found to be in good correspondence. Reddy extended this method to ethanol-gasoline blends with arbitrary ethanol content (0–100%) [85] and validated through comparison with the results of RVP measurements of blends containing two different types of ethanol-containing, commingled fuels.

The predictive capabilities of three different UNIFAC-based models in blended gasolines were studied by Hatzioannidis et al. in 1998 [33]. The impact of different concentrations of various alcohols, ethers, ketones, amides, amines, and esters on the RVP of a 5-component gasoline surrogate was experimentally measured using ASTM D5191. Three previously published relationships integrating modifications to the original UNIFAC model were used to predict the RVP for each mixture, where the vapor phase non-ideality was determined from the viral equation of state. It was determined that all UNIFAC models were, on average, able to predict the RVP within an average uncertainty of approximately 2%. However, their performance was poor for systems including alcohols, which are hydrogen-bonding additives. The errors in those systems were much greater (more than 5%) than in systems containing non-hydrogen-bonding additives.

4.2.3. Statistical associating fluid theory (SAFT)

Recent breakthroughs in the theories predicting vapor pressure came through developments in statistical mechanics and the ubiquity of computational resources that allowed for additional insights gained from molecular simulations. SAFT is an accurate method for systems comprised of associating fluids for a large variety of molecular classes including hydrocarbons, polymers, liquid crystals, ionic liquids, and inhomogeneous fluids [3–7]. Initially developed by Chapman et al. 1990 and Huang and Radosz 1990 from theory originating from the thermodynamic perturbation theory of Wertheim [8–11] and the perturbed hard chain theory developed by Prauzintz, SAFT has proven a useful methodology for incorporating EoS to describe associating fluids.

SAFT has several variants that can be applied as appropriate to a given system. The SAFT-γ variant has been shown to provide a very accurate description of the fluid-phase behavior for chemical families containing CH_3, CH_2, CH_3CH, ACH, $ACCH_2$, CH_2═, CH═, OH, COOH and C═O groups [12], (where AC denotes aromatic carbons). γ denotes that the segments in the system are fused rather than represented as tangential to one another [13]. The SAFT-γ-mie variant has been successfully used to predict vapor pressure. SAFT-γ-mie uses the principle that a system can be described by homonuclear or heteronuclear mie segments to create a fused chain, whereby mie represents mie potentials (*i.e.,* a generalized Lennard-Jones form with a variable repulsive and attractive exponent) [14]. The full theory behind SAFT-γ-mie is given elsewhere [1,15]. Briefly, the EoS used for SAFT-γ-mie employs the Helmholz energy to take into account free energy contributions as given by Eq. (1) below:

$$\frac{A}{Nk_BT} = \frac{A^{ideal}}{Nk_BT} + \frac{A^{mono}}{Nk_BT} + \frac{A^{chain}}{Nk_BT} + \frac{A^{assoc}}{Nk_BT} \quad (1)$$

where A^{ideal} is the ideal Helmholz energy contribution that accounts for the rotational, vibrational, and translational contributions to the kinetic energy of a segment, A^{mono} represents the free energy that would exist between the segments in their monomeric form, A^{chain} is the contribution to the free energy for the formation of molecules from fused segments and A^{assoc} is the contribution from association between the molecules, N is the total number of molecules, k_B is the Boltzmann constant, and T is the absolute temperature. Once A is known, the vapor pressure is determined via the partial derivative as follows:

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} \quad (2)$$

Studies have shown promise in predicting the vapor pressure of oxygenates with low percentage average absolute deviations (% AAD). Lymperiades et al., used SAFT-γ-mie to evaluate several functional groups such as n-alkanes, branched alkanes, alkylbenzenes, olefins, carboxylic acids, alcohols, ketones, and amines [13,19]. For pure components, the approach was highly predictive for all chemical classes, with %AAD being within < 5% of experimental values in all cases. Papaioannou (2014) further refined the SAFT-γ-mie methodology to predict the vapor pressure of n-alkanes with %AAD of 1.55% for nine n-alkanes, and six different alkyl esters with %AAD of 0.83%.

Several studies have focused on mixtures of compounds relevant to the oil and gas industry (*e.g.*, for the purposes of oil recovery). These systems can give insight and parameters pertinent to systems relevant to the transportation fuel industry. Most studies start by studying pure component mixtures with simple SAFT, with later work expanding the number and complexity of compounds under study by new incorporating SAFT variants with increasing complexity. An early study

(2004) by Sen Li, et al. [20] evaluated the VLE of sixteen binary and nine ternary mixtures of alcohols, hydrocarbons, water and carbon dioxide via SAFT, and used a root mean square deviation from experimental data to evaluate the predictions, with deviations being somewhat large.

Subsequent studies improved on the Sen Li results by including further terms to the theory. Al-Saifi et al. [86] evaluated a large array of water-alcohol-hydrocarbon ternary systems by applying three dipolar theories (Jog and Chapman (JC) [22–25], Gross and Vrabec (GV) [26]) and Economou (KSE) [27]) to the perturbed-chain statistical association fluid theory (PC-SAFT) where different classes of alcohols were considered, including glycols. While hydrogen-bonding interactions are greater contributors to associations between molecules, the inclusion of the dipolar terms allows for fluids which have permanent dipole moments such as water and alcohols to be represented when calculating phase behavior. All of the dipole systems could satisfactorily predict the VLE for water-hydrocarbon systems at moderate temperatures, with lesser agreement with experimental data at 149 °C. Alcohol water systems behaved better with the JC polar model, while the glycol-water binary systems compared well with experiment throughout. For alcohol-hydrocarbon binary systems, the JC generally performed the best, for a large range of temperatures.

Lobanova et al. (2008) [28] evaluated binary and ternary mixtures comprising of *n*-alkanes, water and carbon dioxide. They developed accurate pure component and binary interaction parameters that could be used by the SAFT-γ-mie equation of state, coupled to molecular simulations to develop accurate vapor-liquid equilibria for the binary and ternary systems. In a most recent development, Papaioannou (2016) [29] used SAFT-γ-mie specifically to study yet more complex systems relevant to the oil and gas industry that include carbon dioxide, water, methanol, aromatics and alkanes, in ternary systems, and obtained excellent agreement with experiment. The approach used in this study provided universally good predictions for fluid-phase equilibria and represents the most recent thinking for methodologies to predict vapor pressure of the types of molecules described in this review.

5. Comparison of models and experimental results

This section describes the results of measurements on a test set of oxygenate blendstocks blended into a base fuel, and compares them to the outputs of a series of models to evaluate the accuracy of these models. The models were chosen to cover much of the territory discussed in Section 4, and are widely available as an integrated feature of commercially available process simulation software such as ASPEN Plus (Aspen Technology, Inc.) or CHEMCAD (Chemstations, Inc.). Heuristic methods for matching a mixture of components with the best thermodynamic model are available in the literature and in the software and take into account the outcomes of the modeling discussions from Section 4. For gasoline-only blendstocks, the heuristic models generally suggest the equation-of-state models (*e.g.*, Soave-Redlich-Kwong/SRK, Braun K10, Peng-Robinson). When polar molecules such as ethanol or other oxygenates are added to gasoline, the heuristic method suggests the use of activity coefficient models (*e.g.,* Wilson, NRTL, UNIQUAC, UNIFAC) when polar molecules such as ethanol or other oxygenates are added to gasoline.

As described in Section 4, models used for VLE calculations typically require binary interaction parameters (BIPs) for every pair of molecular species in the liquid. Experimental VLE data are used, when available, to mathematically determine the optimal BIPs. However, given the large number of components in gasoline (200+), many interaction parameters are not available in the software databases. In these cases, the BIPs can either be set to zero or estimated using a UNIFAC functional-group contribution model. The total number of BIPs necessary to describe a system is equal to the square of the number of components. For a typical gasoline with over 200 components, there are over 40,000 BIPs, which can overwhelm the available memory in workstations used to run the software. For this reason, a representative subset of components was judiciously selected to represent the gasoline mixture of interest without losing fidelity in the estimated RVP.

5.1. Comparison of model and experimental surrogate hydrocarbon mixture vapor pressure

A simple hydrocarbon mixture reported originally in Campbell [87] and used by Vazquez-Esparragoza et al. [88], was used to evaluate the models available in both ASPEN Plus (Version 8.8) and CHEMCAD (Version 7) as a test case. An evaluation of commonly used models was performed to compare estimated results with experimental data for the RVP and true vapor pressure (TVP; defined as the equilibrium partial pressure exerted by a volatile organic liquid as a function of temperature as determined by the test method ASTM D2879) of a 6-component hydrocarbon liquid composed of isobutene (6.4%), isopentane (7.9%), *n*-butane (12.0%), n-pentane (5.3%), *n*-hexane (17.6%) and *n*-heptane (50.7%). Fig. 3 shows the results for RVP and TVP estimates made using a full set of models in ASPEN Plus and CHEMCAD. The RVP for the light hydrocarbon mixture was measured using a method that appears to follow ASTM D-323 (although not explicitly stated by the author). The TVP value reported by Campbell was read from a graph correlating TVP to RVP. The RVP and TVP values were 124.1 kPa (18.0 psi) and 134.4 kPa (19.5 psi), respectively.

This comparison leads to useful insights:

(1) First, the ASPEN RVP-ASTM property is independent of model selected by the user. This built-in ASPEN Plus property is recommended for hydrocarbons in the gasoline boiling range. Its estimations are within 2% of the measured RVP value in this evaluation.
(2) Second, the SRK models in ASPEN and CHEMCAD agree well for TVP and RVP.
(3) Third, the CHEMCAD Wilson model did not predict RVP well, but made a more accurate prediction of TVP. Using UNIFAC to estimate missing BIPs improved the RVP to within 2% of the experimental value.
(4) Fourth, the default CHEMCAD method for calculating the RVP property is based on iteratively performing a flash calculation and adjusting the pressure until the calculated vapor-to-liquid volume flow ratio equals four. This mimics the ASTM D5191 method that uses a 4:1 vessel volume-to-liquid sample volume and measuring the resulting pressure at 37.8 C (100 F).

From this analysis, it is evident that most of the models perform reasonably well at estimating the RVP. The inability to select the thermodynamic model for the RVP calculation in ASPEN Plus raised a concern for mixtures containing polar components. Therefore, an alternate method was developed in ASPEN Plus to compensate for this attribute.

5.2. Comparison of vapor pressure estimated by ASPEN model and experimental results for gasoline-oxygenate mixture

We followed the RVP comparisons of the surrogate with model outputs and experimental results for oxygenate-gasoline blends. We used a CARBOB, provided by Intertek, Inc., as the base fuel for a systematic evaluation of the RVP changes resulting from blending selected oxygenates. The CARBOB was analyzed according to ASTM D6730, detailed hydrocarbon analysis (DHA), to provide the basis for building a surrogate to model the CARBOB. Finally, a simple process flowsheet was developed in ASPEN Plus to mimic the D5191 method in the same fashion that CHEMCAD calculates the RVP, overcoming the limitations of the default RVP model in Aspen Plus and the inability to select the thermodynamic model being used. The flowsheet is shown in Fig. 4. The flowsheet allows for a user-defined hydrocarbon mixture (in this

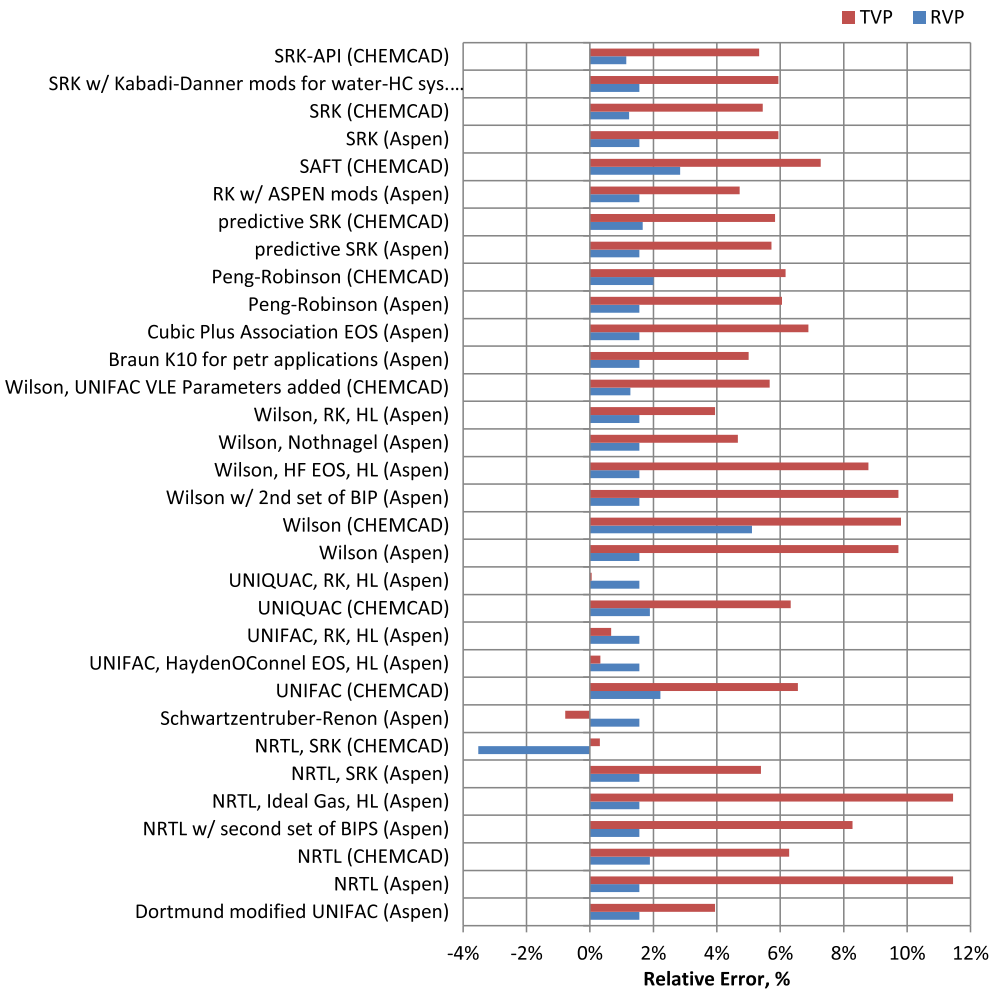


Fig. 3. Relative errors for the RVP and TVP estimated values reported as physical property results in ASPEN Plus and CHEMCAD. The model name given first in each line is the primary model method being used to estimate the RVP based on liquid phase properties. When a second (and third) model is listed, these refer to additional models used for the vapor phase calculations or limited vapor solubility in the liquid phase, if applicable. Some models were not available in both ASPEN Plus and CHEMCAD. Model/method abbreviations: SRK = Soave-Redlich-Kwong; API = American Petroleum Institute; HC = hydrocarbon; SAFT = statistical associating fluid theory; RK = Redlich-Kwong; EOS is equation of state; NRTL = non-random two liquid theory; HF EOS = hydrogen fluoride equation of state for molecules that oligomerize in the vapor phase; BIP = binary interaction parameters; UNIQUAC = universal quasi-chemical equation; UNIFAC = UNIQUAC functional group activity coefficients; HL = Henry's Law (no HL components were specified).

case CARBOB) to be mixed with another user-defined oxygenate mixture. A design specification method in ASPEN adjusts the oxygenate flowrate to achieve a desired oxygenate blend fraction (*e.g.*, 10 vol% ethanol, also known as E10). Other oxygenates can be added to this stream to create other blends. The water stream shown is for adding small amounts of water to evaluate the influence of water on the RVP and possibly liquid phase separation. The EXAIR stream is for removing excess air in situations where the influence of saturating the CARBOB with air is of interest (air stream into the process is not shown). The mixture is split into two identical streams to allow using both a 2-phase (vapor-liquid) and 3-phase (vapor-liquid-liquid) calculation method. In the 2-phase flash (FL200), the temperature is set to 37.8 °C (100°F as shown in Fig. 4), and then the pressure is varied using a design specification until the volumetric flow of the vapor stream is 4 times the volumetric flow of the liquid stream. The final pressure that achieves this ratio is defined as the RVP for this estimation method.

A 2-phase calculation block is used in FL200 (Fig. 4) such that there is no prediction for liquid phase separation in cases where the mixture is highly non-ideal. The FL200-3 block performs a rigorous calculation that allows for liquid phase separation if the underlying estimation methods determine this better minimizes the Gibbs free energy of the system. When a second phase is predicted, there are flows from both liquid streams leaving FL200-3, and only a single stream with flow when the system has a single liquid phase predicted.

The CARBOB DHA identified more than 226 components. Sixty-four of the 226 components accounting for 2.1% of the sample mass were not identified. Of the 162 components remaining, 136 were available in the ASPEN Plus component database. Accounting for the components not identified and unavailable in the ASPEN Plus database, the final distribution of components is paraffins (12.2%), isoparaffins (64.5%), aromatics (15.9%), naphthenes (1.5%), and olefins (3.7%).

Modeling 136 components leads to slow model convergence on an average desktop workstation. Although computer dependent, the computer used for this analysis could not accommodate robustly all 13 components. A subset of components was created by removing components until the model would work well on a desktop computer; this resulted in removing components with less than 0.1 wt% abundance leaving 122 components. This approach removed some of the high-boiling compounds, most of which are aromatic. The distillation curve (Fig. 5) for this mixture showed this effect clearly as there was less high-boiling-point material. Other approaches could be used as well.

Once the composition was established for the model, the ASPEN model was used to estimate the RVP for the CARBOB and the oxygenate/CARBOB mixtures using several thermodynamic models to compare to experimental measurements. The RVP was measured experimentally using ASTM D6378 after blending at 10 vol%, 20 vol% and 30 vol% with ethyl butyrate, butyl acetate, isopropyl acetate, anisole, 1,2-isopropylidene-glycerol, and 2,2,4-trimethyl-1,3-dioxolane. The results and molecular structures of the oxygenates are shown in Fig. 6.

Fig. 6 also shows the magnitude of the differences in estimated and measured values. The comparison between the models are also shown graphically in Fig. 7.

The estimates for these models are in relatively good agreement with experimental measurements. The average absolute difference between estimate and measurement is between 0.12 psi for the UNIFAC model and 0.21 for the NRTL model. Note that the UNIFAC models could not estimate RVP for the dioxolane mixture because the ASPEN Plus database does not contain the required functional-group

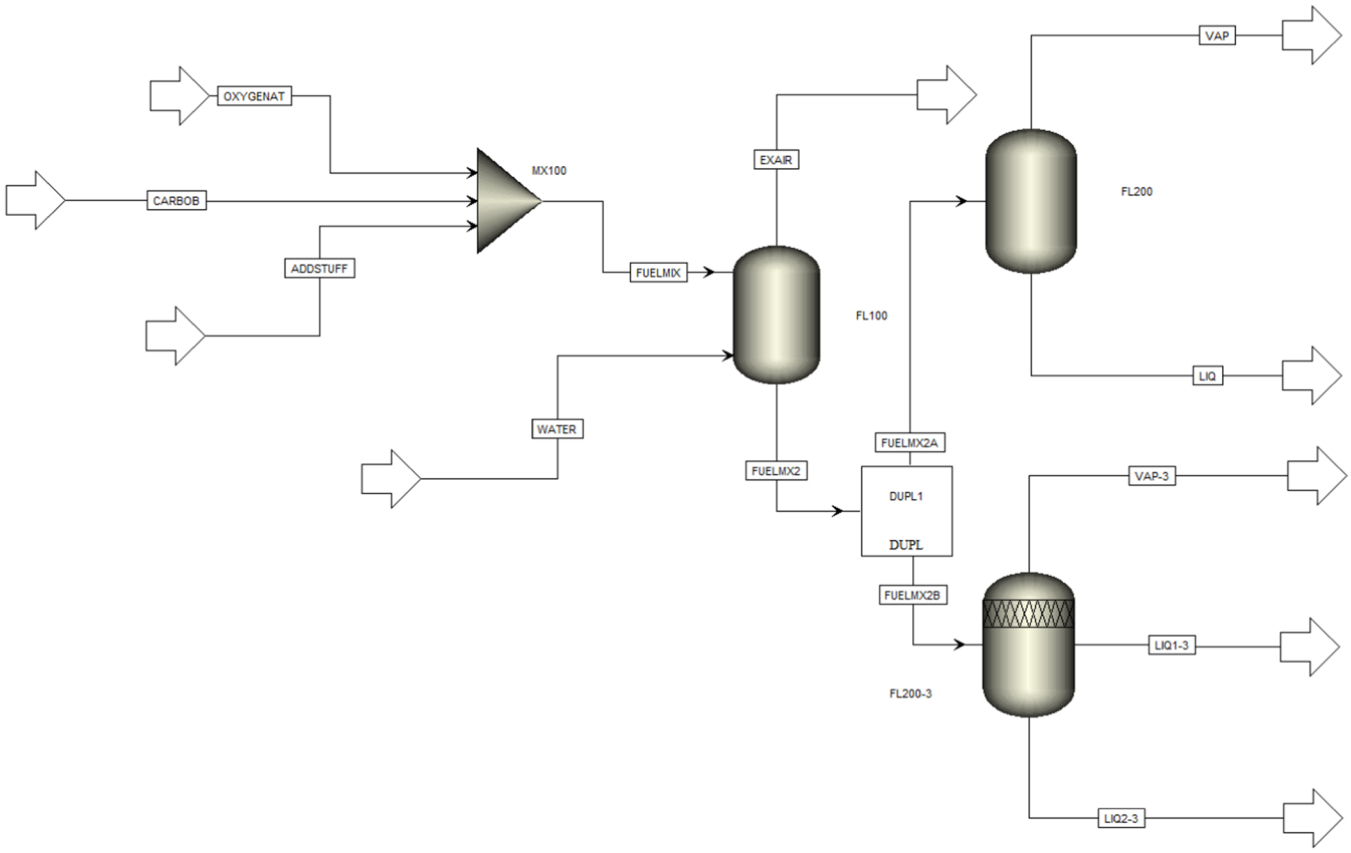


Fig. 4. ASPEN Plus process flowsheet used to estimate the RVP of an oxygenated hydrocarbon mixture.

information. The largest errors in NRTL model predictions occurred for the dioxolane-ethanol and ethanol-only blends. The Cubic Plus Association EOS model (CPA) was the only model able to estimate the RVP for all six oxygenate components present in the ASPEN Plus database. The CPA model is not included among the choices in the heuristic model selection method described in Section 5.1, but has been cited in literature as being a good model for estimating RVP [69,89,90]. The current results confirm that the CPA model works well with the tested oxygenates.

One benefit of having a computational model is the ability to use it to estimate the RVP for hypothetical blends, including co-blending ethanol and other oxygenates. As an example, four oxygenates (2-butanol, isobutanol, allyl acetate, and 2,5-dimethyltetrahydrofuran) that were not used in the current study were selected from the list of components in the ASPEN Plus database to be modeled as blended into a CARBOB/E10 mixture. The compounds selected have functional groups similar to those used in this study. The RVP was estimated for each oxygenate blended from 0 to 30 vol% into a CARBOB/E10 from this

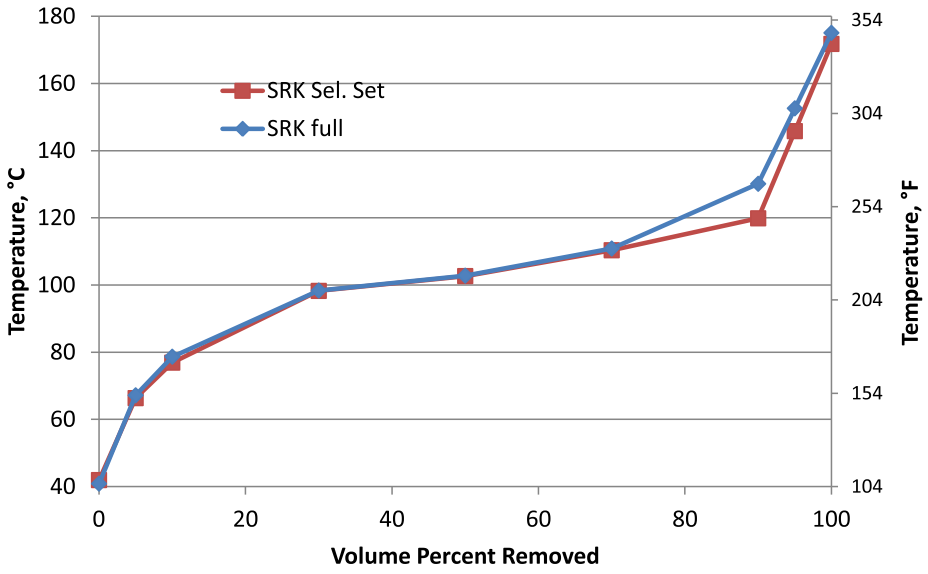


Fig. 5. Estimated ASTM D86 simulated distillation curves. The diamond symbols are estimates made using all 136 available components. Square symbols are estimates made using a slightly smaller subset of 122 component selected by removing the 14 components with the smallest mass fractions. A decrease in the high-boiling components is noted for the last 25 vol% removed.

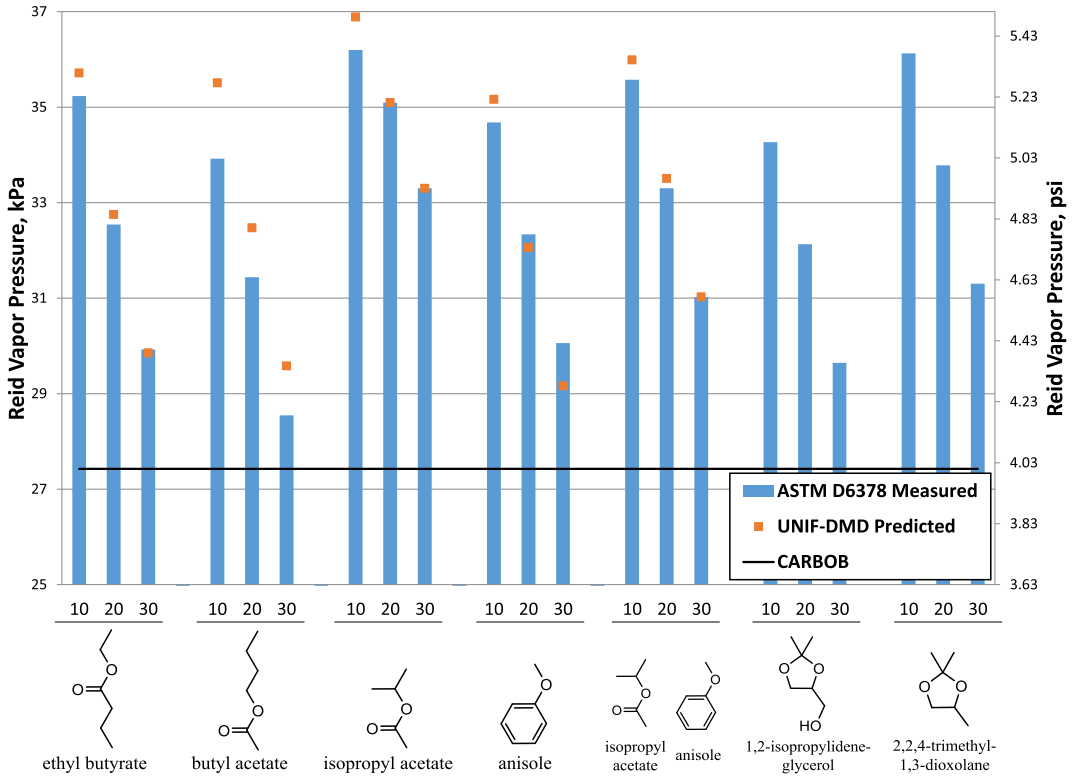


Fig. 6. Measured DVPE values measured using ASTM D6378 for 10%, 20%, and 30 vol% blend levels. The predicted values were determined using the UNIF-DMD method in Aspen Plus via the method detailed above. Note the mixture of isopropyl acetate and anisole consisted of an equivolume mixture of the two compounds to create each blending level (*e.g.*, 5 vol% isopropyl acetate plus 5 vol% anisole blended to produce the 10 vol% blend level), and the UNIF-DMD method was not applied to the dioxolane compounds as no BIPs were available in Aspen Plus.

work. The RVP was also estimated for a mixture comprised of all four components, each having an equal volume fraction in the mixture of the total oxygenate blend. The results of these estimates are shown in Fig. 8. The lines for each mixture in the graph converge at the estimated RVP for CARBOB/E10 at the left side of the graph and decreases as its volume fraction of the oxygenate increases in the mixture. The RVP for the four-component blend falls well below the RVP based on the linearly proportional contributions from each component shown as a dashed line in Fig. 8.

The RVP method used in this study showed good agreement with most of the tested oxygenates. The dioxolane-ethanol blends and the ethanol-only blend had the largest divergence from measured values.

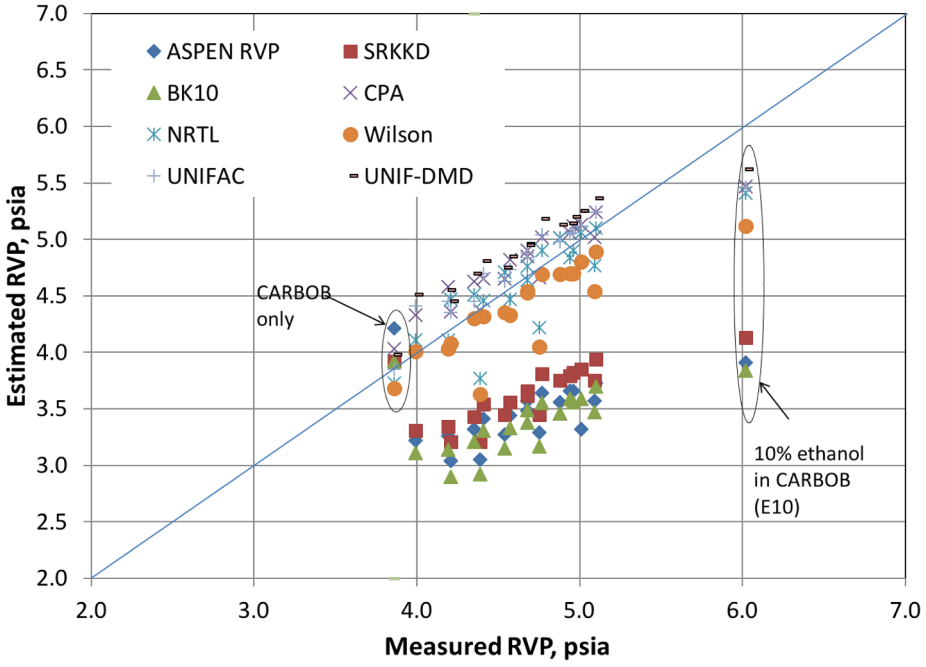


Fig. 7. RVPs calculated using various thermodynamic models available in ASPEN Plus are compared to experimental measurements. As expected, the equation-of-state models (excluding the CPA model) give outputs significantly lower than measured values. The estimates for the 10% ethanol/CARBOB (E10) were relatively lower than the blends of E10 with additional oxygenates.

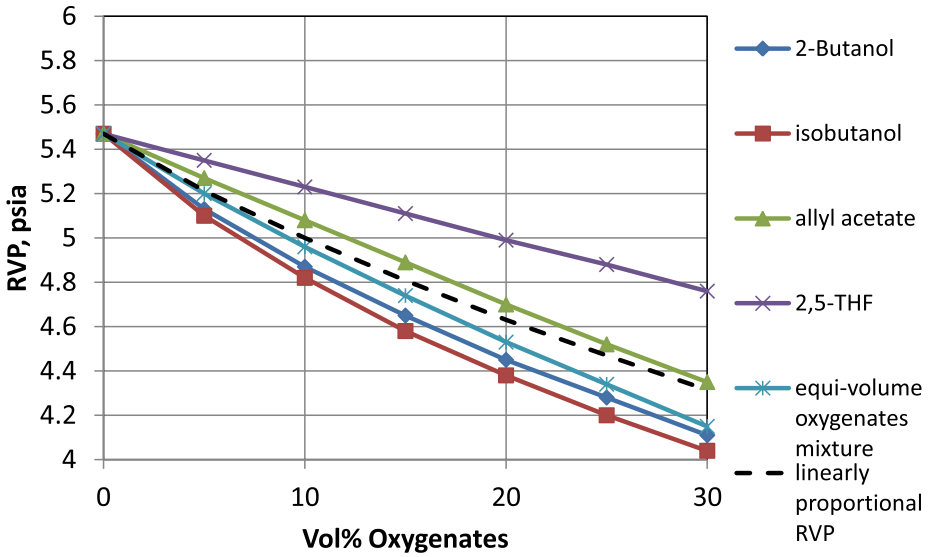


Fig. 8. RVP estimates made using the Cubic-Plus-Association EoS method (CPA) for a range of four oxygenate blends with the CARBOB/E10 base fuel used in this study. The estimated RVP for the equi-volume mixture falls below the value calculated by proportionally summing the RVP from each component.

The other blends reduced the RVP value relative to the ethanol-only mixture, a change the RVP estimation method accurately predicted.

6. Conclusions

As advanced biofuels containing more oxygen are considered for use in gasoline, the impact on critical fuel properties such as vapor pressure must be accurately measured. Accurately predicting the vapor pressure of new candidate materials, especially those which are available in very limited quantities, requires an understanding of the chemical nature of ideal and non-ideal behavior in vapor-liquid equilibria. As the examples demonstrate, we can accurately predict the vapor pressure of oxygenates within a few percent if an appropriate method is selected. The picture is complicated further by the potential for contamination by water or other unexpected components. It is essential, therefore, that researchers use an appropriate test method to measure vapor pressure, and that the appropriate characterization is performed prior to testing. If done properly, the combination of modeling and characterization has the potential to more rapidly assess the influence of oxygenates on critical fuel properties such as vapor pressure, leading to a more sustainable fuel supply.

Declarations of interest

None.

Acknowledgments

The authors gratefully acknowledge support from the Co-Optimization of Fuels & Engines (Co-Optima) project sponsored by the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE), Bioenergy Technologies and Vehicle Technologies Offices.

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