## energy fuels

# **Composition-Explicit Distillation Curves for Mixtures of Gasoline and Diesel Fuel with** $\gamma$ -Valerolactone

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Interest in the domestic production of bioderived fuels, sparked by the high cost of petroleum crude oil, the potential of supply disruptions, and fears about climate change has led to consideration of fluids to replace or extend conventional petroleum derived fuels. While ethanol as a gasoline oxygenate and extender has received a great deal of attention, this fluid has numerous problems such as aggressive behavior toward engine components and a relatively low energy content. Many other fluids have been considered as oxygenates for gasoline, such as the butanols, ethers, and other alcohols. For diesel fuel, oxygenates have included glycol ethers, glycol esters, carbonates, acetates, and ethers. Some of these oxygenates and extenders can be made from biomass and are thus renewable and in some cases can decrease the overall carbon dioxide budget. One new renewable fluid being considered as both a gasoline and diesel fuel oxygenate is y-valerolactone. In this paper, we present a characterization of selected mixtures of  $\gamma$ -valerolactone in both gasoline (mixtures of 10, 20, and 30%, vol/vol) and diesel fuel (1 and 2.5%, vol/ vol), performed with the advanced distillation curve metrology. This method features: (1) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis); (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state; (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development; (4) consistency with a century of historical data; (5) an assessment of the energy content of each distillate fraction; (6) trace chemical analysis of each distillate fraction; and (7) corrosivity assessment of each distillate fraction. We discuss the effect of  $\gamma$ -valerolactone on the vapor-liquid equilibrium (volatility) of the mixtures.

#### Introduction

High motor fuel costs, the possibility of interruptions in supply, and concerns about climate change have caused a great deal of interest in biofuels for motor applications. Biofuels are renewable fuels that are produced by plant matter or algae. While it is unlikely that a fuel stream that is composed entirely of biofuels is practical, the widespread use of biofuels as extenders or enhancers is a strong possibility. The primary motor biofuel in relatively widespread use for lightweight vehicles that burn gasoline is ethanol.<sup>1-7</sup> Indeed,

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ethanol has been used for many years as a gasoline oxygenate, added to gasoline to decrease certain pollutant emissions, primarily carbon monoxide. The typical oxygenate additive concentration of ethanol is approximately 10% (v/v). The addition of higher concentrations on a large scale has been problematic because of numerous technical problems. In an effort to overcome some of the problems associated with the use of fuel ethanol, the adoption of higher alcohols (primarily the butanols) has been suggested for use as gasoline extenders.<sup>8</sup> These fluids mixed with gasoline are still in the early stages of development.

Bioderived extenders for diesel fuel have also received attention. Biodiesel fuel made primarily from soy can be used in mixtures with petroleum-based diesel fuel in fractions between 5 and 20% without violating many current engine performance specifications and voiding warranties.9,10 The resulting mixtures of these upper and lower concentration limits are named accordingly, B5 and B20. In some cases, with engine modifications, pure biodiesel fuel (B100) can be used as a drop-in replacement in compression ignition engines. Apart from the addition of biodiesel fuel to conventional diesel fuel, oxygenates (added to decrease particulate emissions) have

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also been studied.<sup>11–14</sup> The most well studied of these fluids are the lower organic carbonates, organic ethers, acetates, glycol ethers, and glycol esters.<sup>11–13,15–28</sup> Some bioderived glycol esters have also been proposed and studied.29

y-Valerolactone. Recently, another bioderived fluid has been suggested as an oxygenate and extender for petroleum

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Table 1. Data on the additive studied in this work

 $\gamma$ -valerolactone:

CAS No. 108-29-2 INChI = 1S/C5H8O2/c1-4-2-3-5(6)7-4/h4H, 2-3H2, 1H3

RMM = 100.116

 $T_{\text{boil}} = 207.6 \text{ °C}$  $T_{\text{fus}} = -31 \text{ °C}$ 

density = 1.0491 g/mL (25 °C)

refractive index,  $Na^d = 1.433 (20 \text{ °C})$ 

flash point: open cup: 96 °C

lower flammability limit: 1.7%

upper flammability limit: 10.6%

enthalpy of combustion: -2493 kJ/mol (predicted)

synonyms:

 $\gamma$ -methyl- $\gamma$ -butyrolactone;  $\gamma$ -pentalactone;  $\gamma$ -valerolactone; pentanoic acid, 4-hydroxy-,  $\gamma$ -lactone; valerolactone; 4-hydroxypentanoic acid lactone; 4-hydroxyvaleric acid lactone; 4-methyl-y-butyrolactone; 4-pentanolide; 4-valerolactone;  $\gamma$ -pentanolactone; 4-valerolacetone; γ-valerolakton; dihydro-5-methyl-2(3H)-furanone; 5-methyldihydro-2(3H)-furanone; valeric acid, 4-hydroxy-, gamma-lactone; gammavalerolactone; 5-methyldihydrofuran-2(3H)-one; 5-methyltetrahydrofuran-2-one; dihydro-5-methyl-2-furanone.

based fuel stocks:  $\gamma$ -valerolactone.<sup>30–32</sup> Moreover, it has been suggested that  $\gamma$ -valerolactone can be used in mixtures of both gasoline and diesel fuels, making it a more flexible additive, and thus potentially more economically acceptable. This natural product is found in many fruits and is used in perfumes and foods. It has been used in diet supplements for weight loss, prompting more in-depth studies on toxicity than would have been performed on a typical fluid being considered as a fuel extender. It has also been used in the dye industry as a fixant enhancer. The suggestion for use as an additive and extender for motor fuels was made after a study of relevant physical and chemical properties, several of which are especially attractive. $^{30-32}$  Unlike ethanol,  $\gamma$ -valerolactone will not form an azeotrope with water, thus eliminating the need for azeotropic distillation or molecular sieve methods in the final purification steps. It has a relatively high boiling temperature and flash point, it is stable in long-term storage, and it has a low hazard rating. Moreover, it has two oxygen atoms on a small five-membered ring (see Table 1), providing a relatively high oxygenating potential and a high density. The vapor pressure of this fluid is relatively low when compared with ethanol; thus the fluid, when mixed with gasoline, will result in lower VOC emissions in storage, since it serves as a "keeper".<sup>33</sup> Some representative properties of this fluid are provided in Table 1.<sup>34</sup>

Advanced Distillation Curve Measurement. One of the most important and informative parameters that is measured for complex fluid mixtures is the distillation (or boiling) curve.<sup>35</sup> It has been possible in recent years to relate the distillation curve to many operational parameters of complex liquid fuels. For gasoline-burning engines, these parameters include engine starting ability, vehicle drivability, fuel system icing and vapor lock, fuel injection schedule, fuel

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autoignition, etc.<sup>36–39</sup> In addition to these applications to performance optimization and design, the distillation curve provides an avenue to determine a long-term trend analysis of fuel performance, since changes in the distillation curve are related to changes in fuel performance. In diesel engines, it is possible to use the distillation curve in the same way as for gasoline combustion engines to design fuels for operability. Especially important with diesel fuels are the latter regions of the distillation curve, which describe the high relative molecular mass components of the fuel.<sup>10,40–43</sup> It is also possible to correlate the distillation curve of fuels with exhaust emissions, a fact that is especially important with diesel engines.<sup>44,45</sup>

In earlier work, we described a method and apparatus for an advanced distillation curve measurement (ADC) that is especially applicable to the characterization of fuels.<sup>46–48</sup> This method is a significant improvement over current approaches, featuring (1) a composition explicit data channel for each distillate fraction (for both qualitative and

quantitative analysis); (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state; (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development; (4) consistency with a century of historical data; (5) an assessment of the energy content of each distillate fraction; (6) trace chemical analysis of each distillate fraction; (7) a corrosivity assessment of each distillate fraction. This approach also provides important advantages over other methods such as the simulated

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We have applied this metrology to gasolines, aviation fuels, and rocket propellants.<sup>8,26,39,46,47,54–78</sup> Clearly, it is not always needed or desirable to apply all aspects of the advanced distillation curve metrology in every application. For highly finished fuels such as the low sulfur diesel fuels used today, for example, it is usually unnecessary to assess corrosivity as a function of distillate fraction. In this paper, we use the ADC metrology to analyze the properties of mixtures of  $\gamma$ -valerolactone with gasoline and diesel fuel. We have shown that these measurements are helpful in the application and adoption of oxygenated diesel fuels.

## **Experimental Section**

The gasoline used as the base fluid in this work was a 91 AI (antiknock index, the average of the motor and research octane numbers) summer quarter gasoline formulated with no oxygenate additive. It was obtained from a commercial source and used without purification. This fluid was analyzed by gas chromatography (30 m capillary column of 5% phenyl-95% dimethyl polysiloxane having a thickness of 1  $\mu$ m, temperature program from 50 to 170 °C, 7 °C per minute) separately with flame ionization detection and mass spectrometric detection.<sup>79,80</sup> This analysis showed a large fraction of aromatic constituents, consistent with the relatively high antiknock index number. Although no specific tests were done for olefin content, the GC-MS measurement mentioned above was consistent with a very low olefin content. We maintained the gasoline in a sealed container at 7 °C, to minimize moisture uptake and to ensure that no compositional changes would occur during the course of our measurements.

The diesel fuel used in this work was obtained from a commercial source. The fuel was a winter grade, low wax, ultra low sulfur diesel fuel that incorporated a red dye

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(80) Bruno, T. J.; Svoronos, P. D. N. CRC Handbook of Fundamental Spectroscopic Correlation Charts; Taylor Francis CRC Press: Boca Raton, FL, 2005. (specifying off-road use) and was refined locally from petroleum of the Denver–Julesburg field. This fluid was used without any purification or modification. The composition was studied with a gas chromatographic method (30 m capillary column of 5% phenyl–95% dimethyl polysiloxane having a thickness of 1  $\mu$ m, temperature program from 90 to 275 °C, 9 °C per minute) by use of flame ionization detection and mass spectrometric detection. We maintained the diesel fuel at 7 °C to preserve any volatile components. No phase separation was observed as a result of this storage procedure.

The  $\gamma$ -valerolactone used in this work was obtained from a commercial source with a stated purity of 99% (mass/mass). The purity was checked with gas chromatography (30 m capillary column of 5% phenyl–95% dimethyl polysiloxane having a thickness of 1  $\mu$ m, temperature program from 85 to 170 °C, 7 °C per minute) separately using flame ionization detection and mass spectrometric detection. This analysis revealed the presence of a small quantity of  $\delta$ -valerolactone (CAS No. 542-28-9), but the overall purity of the fluid was found to be better than stated by the manufacturer. The fluid was analyzed for water by Karl Fisher Coulombic titrimetry, revealing the presence of water at 50 ppm (mass/mass). On the basis of these analyses, the fluid was used as received, although precautions were taken to prevent the uptake of additional moisture.

The dodecane used as a solvent for gasoline in this work was obtained from a commercial supplier and was analyzed by gas chromatography (30 m capillary column of 5% phenyl-95% dimethyl polysiloxane having a thickness of 1  $\mu$ m, temperature program from 90 to 170 at 7 °C per minute) by use of flame ionization detection and mass spectrometric detection. These analyses revealed the purity to be higher than 99.9% (mass/mass), and the fluid was used without further purification. The *n*-hexane used as a solvent for diesel fuel in this work was obtained from a commercial supplier and was analyzed by gas chromatography (30 m capillary column of 5% phenyl-95% dimethyl polysiloxane having a thickness of 1  $\mu$ m, temperature program from 50 to 170 °C, 5 °C per minute) by use of flame ionization detection and mass spectrometric detection. These analyses revealed the purity to be approximately 99.9% (mass/mass), and the fluid was used without further purification.

The method and apparatus for the distillation curve measurement has been reviewed in a number of sources, so an additional general description will not be provided here. The required fluid for the distillation curve measurement (in each case 200 mL) was placed into the boiling flask with a 200 mL volumetric pipet. The thermocouples were then inserted into the proper locations to monitor  $T_k$ , the temperature in the fluid, and  $T_h$ , the temperature at the bottom of the takeoff position in the distillation head. Enclosure heating then commenced with a four-step program based upon a previously measured distillation curve.<sup>48</sup> Volume measurements were made in the level-stabilized receiver, and sample aliquots were collected at the receiver adapter hammock. In the course of this work, we performed four complete distillation curve measurements for each of the fluid samples.

Since the measurements of the distillation curves were performed at ambient atmospheric pressure (approximately 83 kPa, measured with an electronic barometer), temperature readings were corrected for what should be obtained at standard atmospheric pressure. This was done with the modified Sidney Young equation, in which the constant term was assigned a value appropriate for the fuel being measured.

<sup>(70)</sup> Ott, L. S.; Smith, B. L.; Bruno, T. J. Advanced distillation curve measurement: application to a bio-derived crude oil prepared from swine manure. *Fuel* **2008**, *87*, 3379–3387.

<sup>(71)</sup> Ott, L. S.; Smith, B. L.; Bruno, T. J. Composition-explicit distillation curves of mixtures of diesel fuel with biomass-derived glycol ester oxygenates: a fuel design tool for decreased particulate emissions. *Energy Fuels* **2008**, *22*, 2518–2526.

<sup>(72)</sup> Ott, L. S.; Smith, B. L.; Bruno, T. J. Experimental test of the Sydney Young equation for the presentation of distillation curves. *J. Chem. Thermodynam.* **2008**, *40*, 1352–1357.

In the case of the gasoline mixtures, this was assigned to be 0.000119.<sup>72,81-83</sup> This value corresponds to a hydrocarbon molecule of eight carbons. In the case of the diesel fuel mixtures, the constant term was assigned a value of 0.000109. This corresponds to a carbon chain of 12. In the chemical analyses of the gasoline and diesel fuel samples (see above), as well as in previous work on these fuels, it was found that *n*-octane and *n*-dodecane can indeed represent gasoline and diesel fuel, respectively, as very rough surrogates.

#### **Results and Discussion**

Both gasoline and diesel fuel are commodity fluids that can vary considerably in composition between regions and over the course of a year. This variability in composition is evident in any thermophysical property measurement or chemical analysis of these mixtures. This variability makes it difficult to consider any given sample of gasoline or diesel fuel as being representative, although individual samples can be used to further analytical or property measurement protocols used in the characterization of these fluids. The aim of this study falls into this category, thus our choice to characterize mixtures of  $\gamma$ -valerolactone with a 91 AI gasoline (summer quarter without oxygenate additives) and a winter-grade low sulfur diesel fuel.

We performed four complete distillation curve measurements for all of the mixtures presented in this paper. The repeatability of the distillation curves has been discussed extensively elsewhere and is typically 0.3 °C over all of the curves. For this reason, only averaged temperature data will be presented here, along with appropriate estimates of uncertainty. Two concentrations of  $\gamma$ -valerolactone in diesel fuel were measured: 1 and 2.5% (v/v). We did not prepare higher concentrations because we noted the onset of phase separation (liquid-liquid equilibrium) at concentrations above 2.5% (v/v) with diesel fuel at ambient temperature. At somewhat higher temperatures, we noted complete miscibility at concentrations in excess of 2.5% (v/v). Complete miscibility was found to occur (in mixtures with up to approximately 5%  $\gamma$ -valerolactone) with slight warming of the flask (by running warm water around the sides, or even with rubbing hand contact), but we chose not to pursue mixtures above 2.5% (v/v). Although we did not investigate this extensively, it is likely that significantly higher temperatures would be required to achieve complete miscibility in mixtures with high concentrations of  $\gamma$ -valerolactone. Three concentrations of  $\gamma$ -valerolactone in gasoline were measured: 10, 20, and 30% (v/v). We did not note issues of immiscibility with the gasoline mixtures.

Some discussion is warranted regarding our choice of mixture ratios. Mixtures that contain high concentrations of  $\gamma$ -valerolactone in either gasoline or diesel fuel might not be practical fuels for all circumstances, and the performance of an engine using such a mixture could potentially be poor. Our study of a particular mixture ratio does not imply that mixtures with very high oxygenate concentrations are practical formulations for fuel, nor do we advocate such mixtures for use as fuels. Rather, our mixtures were chosen to cover as large a range of composition as practical for the purpose of modeling the results with equations of state. Indeed, our

 Table 2. Summary of the Initial Behavior of the Diesel Fuel Mixtures

 with the γ-Valerolactone (GVL) Additive<sup>a</sup>

observed temperature	diesel fuel °C (83.5 kPa)	diesel fuel + 1% GVL (v/v) °C (83.13 kPa)	diesel fuel + 2.5% GVL (v/v) °C (82.93 kPa)
vapor rise	233.4	219.3	212.6

<sup>*a*</sup> The vapor rise temperature is that at which vapor is observed to rise into the distillation head and is the initial boiling temperature of the fluid. Due to the dark red color of the diesel fuel mixtures, it is not possible to accurately record the onset and sustained bubbling temperatures. These temperatures have been corrected to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided to allow recovery of the actual measured temperatures. The uncertainties are discussed in the text.

ultimate purpose is to predict the behavior (as expressed by the thermophysical properties) of such diverse mixtures.

**Diesel Fuel**  $+ \gamma$ -Valerolactone Mixtures. During the initial heating of each sample in the distillation flask, the behavior of the fluid was carefully observed. Direct observation through the flask window or through the bore scope allowed measurement of the onset of boiling for each of the mixtures (measured with  $T_k$ ). Typically, to ascertain the initial boiling behavior, we measure the onset of bubbling, the temperature at which bubbling is sustained, and the temperature at which the vapor rises into the distillation head. Additional details on how these observations are made have been presented earlier in this paper and in the references cited above. The vapor rise temperature can be noted visually and by noting the rapid increase in temperature of the thermocouple that monitors  $T_{\rm h}$ . We have shown that the vapor rise temperature is actually the initial boiling temperature (the IBT, an approximation of the bubble point temperature at ambient pressure) of the starting fluid mixture. This measurement is significant for a mixture because it can be modeled with an equation of state. Measurement of these temperatures with mixtures of commercial diesel fuel is complicated by the presence of the dye mentioned above. As a result, we only report the onset and vapor rise temperatures here. Vapor rise is accompanied by a sharp increase in  $T_{\rm h}$  and is therefore far less subjective to ascertain and thus is less uncertain than the onset of bubbling. Experience with previous mixtures, including *n*-alkane standard mixtures that were prepared gravimetrically, indicates that the uncertainty in the onset of bubbling and sustained bubbling temperatures is approximately 1 °C. The uncertainty in the vapor rise temperature is 0.3 °C. We also note that the IBT that is measured with the ADC approach is very different from what would be measured with the classical distillation curve measurement. The classical measurement produces a temperature that can be as much as 15 °C too high.46,54

In Table 2, we present the initial temperature observations for neat winter-grade diesel fuel, and also for mixtures with 1% and 2.5%  $\gamma$ -valerolactone. All temperatures are corrected to standard atmospheric temperature by use of the modified Sidney Young equation, discussed above. The vapor rise temperature for neat diesel fuel was measured at 233.4 °C; the addition of 1% of the  $\gamma$ -valerolactone additive lowered the boiling point of the diesel fuel to 219.3 °C, and the addition of 2.5% of the additive lowered it further to 212.6 °C. This drop in initial boiling temperature is consistent with the difference in boiling temperatures between the diesel fuel and the additive. The drop in IBT is significant; 2.5% (v/v) additive lowers the vapor rising temperature by 9%.

<sup>(81)</sup> Young, S. Correction of boiling points of liquids from observed to normal pressures. *Proc. Chem. Soc.* **1902**, *81*, 777.

<sup>(82)</sup> Young, S. Fractional distillation; Macmillan and Co., Ltd.: London, 1903.
(82) Young S. Distillation in the second seco

<sup>(83)</sup> Young, S. Distillation principles and processes; Macmillan and Co., Ltd.: London, 1922.

Table 3. Representative Distillation Curve Data (Given As the Average of Four Distillation Curves) for Mixtures of Diesel Fuel with  $\gamma$ -Valerolactone (GVL) Additive in 1 and 2.5% (v/v) Concentrations<sup>*a*</sup>

distillate volume	diesel fuel, °C (83.50 kPa)		$\begin{array}{c} \text{diesel fuel} + 1\% \\ \text{GVL } (v/v) \ ^{\circ}\text{C} \\ (83.13 \ \text{kPa}) \end{array}$		$\begin{array}{c} \text{diesel fuel} + 2.5\% \\ \text{GVL } (\text{v/v})  ^{\circ}\text{C} \\ (82.93  \text{kPa}) \end{array}$	
fraction, %	$T_{\rm k}$	$T_{\rm h}$	$T_{\rm k}$	$T_{\rm h}$	$T_{\rm k}$	$T_{\rm h}$
5	242.9	197.8	231.5	210.9	224.9	203.8
10	247.1	226.7	236.5	218.1	232.2	211.0
15	253.5	238.3	242.4	225.7	239.0	221.1
20	258.9	244.8	249.0	233.5	247.1	232.5
25	264.0	250.2	254.0	239.0	253.7	239.0
30	269.3	257.1	259.0	245.0	259.2	246.5
35	274.2	261.1	263.4	249.4	263.3	249.0
40	279.0	266.7	268.9	255.5	270.8	257.9
45	284.4	271.9	273.9	260.5	273.5	260.6
50	289.2	277.3	278.6	265.6	278.1	264.6
55	294.4	282.4	284.1	271.7	283.5	270.4
60	299.0	287.3	289.3	277.5	289.7	276.4
65	305.4	292.9	294.9	283.2	294.8	283.7
70	311.7	298.9	300.9	288.8	300.8	290.6
75	318.1	303.9	307.6	297.8	307.9	298.6
80	324.9	310.9	314.4	305.7	316.4	307.7
85	332.5	318.9	323.4	314.8	324.9	312.5

<sup>*a*</sup> Data for the neat diesel fuel are also provided. The uncertainties are discussed in the text. These temperatures have been corrected to 1 atm with the Sydney Young equation.

Representative distillation curve data for the winter-grade diesel fuel, and this fuel with 1 and 2.5% (v/v)  $\gamma$ -valerolactone additive are given in Table 3. The data are presented in both  $T_{\rm k}$  (fluid temperature measured directly) and  $T_{\rm h}$  (head temperature). The  $T_k$  values represent the true thermodynamic state point (the temperature of the mixture itself), while the  $T_{\rm h}$  values (the temperature of the vapor at the distillation head) can be used for comparison to earlier measurements. The uncertainty in the temperature measurements (expressed as the average standard deviation for each volume fraction, over four distillations) was 0.3 °C. The uncertainty in the volume measurements was 0.05 mL (expressed as the standard deviation among the replicate curves). The uncertainty in the pressure measurement (assessed by logging a pressure measurement every 15 s for the duration of a typical distillation) was 0.001 kPa. The relatively low uncertainties in the measured quantities facilitate modeling the results, for example with an equation of state.

The  $T_k$  data for the diesel fuel plus  $\gamma$ -valerolactone mixtures are presented graphically in Figure 1. The same trend in the lowering of the IBT can be identified in this figure. The 2.5% mixture temperatures trail those of straight diesel fuel by 15 °C at a 10% distillation volume fraction and by 7 °C at 85% completion. The 1% mixtures follow the same trend and trail the straight diesel fuel by 11 and 8 °C at the same respective distillate volume fractions. Though these temperature differences do indicate a slight nonuniform shift in the distillation curves over the course of the distillation, there is no evident change in the shape of the distillation curve. This indicates that there is no significant interaction between the additive and the components of the mixture at these relatively low additive concentrations, and the presence of the additive acts to increase the volatility of the fluid. A pronounced flattening of the curve, for example, might indicate the formation of azeotropic mixtures with  $\gamma$ -valerolactone and the components of diesel fuel.<sup>64</sup> We can further check for the possibility by examining the behavior of



**Figure 1.** Distillation curves of diesel fuel with 1 and 2.5% (v/v)  $\gamma$ -valerolactone. Here, we present  $T_k$ , the temperature measured directly in the fluid. The uncertainties are discussed in the text.



**Figure 2.** Histogram plot showing the results of the analysis for  $\gamma$ -valerolactone (GVL) as a function of distillate volume fraction for the two diesel fuel starting mixtures (1 and 2.5% GVL in diesel). There is no detectable GVL in either mixture after the 40% distillate cut.

 $T_{\rm k}$  relative to  $T_{\rm h}$ . As we have demonstrated in previous work, the convergence of  $T_{\rm k}$  and  $T_{\rm h}$  is indicative of azeotropy. We did not note azeotropic convergence with any mixture of diesel fuel with  $\gamma$ -valerolactone.

The composition-explicit data channel of the ADC is a functional means of explaining the appearance of distillation curves in terms of the chemical composition of the distillate over the course of a distillation. This was done by withdrawing 7  $\mu$ L samples of selected distillate fractions and dissolving this aliquot in a known mass of solvent (*n*-hexane). This solvent was chosen because it causes no chromatographic interference with the sample constituents. We can then apply any appropriate analytical method to the diluted sample. Thus, we can use this compositional data to make a detailed examination of each fraction, or to track specific components. The concentration of  $\gamma$ -valerolactone (expressed as ppm (mass/mass)) as a function of the distillate volume fraction is shown in Figure 2. The uncertainty in the concentration is approximately 3%. We note that more  $\gamma$ -valerolactone is found in the early distillate fractions of the 2.5% (v/v) mixture than in the 1% (v/v) mixture, as expected. We also note that, for both mixtures, the  $\gamma$ -valerolactone has been completely removed by 60% distillate volume fraction. At this point in the distillation curves of both mixtures, we can

Table 4. Summary of the Initial Behavior of the 91 AI Summer	· Quarter (SQ) Gasoline Mixtures with the $\gamma$ -Valerolactone (GVL) Additive"
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observed temperature	91 AI SQ gasoline, °C (83.74 kPa)	91 AI SQ gasoline + 10% GVL (v/v), °C (83.20 kPa)	91 AI SQ gasoline + 20% GVL (v/v), °C (83.40 kPa)	91 AI SQ gasoline + 30% GVL (v/v), °C (83.40 kPa)
onset	51.5	71.2	71.8	74.3
sustained	52.1	80.3	79.9	80.2
vapor rise	54.2	86.2	86.7	88.4

<sup>*a*</sup> The vapor rise temperature is that at which vapor is observed to rise into the distillation head and is the initial boiling temperature of the fluid (highlighted in bold print). These temperatures have been corrected to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided to allow recovery of the actual measured temperatures. The uncertainties are discussed in the text.

Table 5. Representative Distillation	Curve Data (Given As the	e Average of Three	Distillation (	Curves) for	Mixtures of C	Gasoline and t	the Additive
	γ-Valerolactone (GVL	a) in 10, 20, and 30 <sup>o</sup>	% (v/v) Conce	entrations <sup>a</sup>			

	91 A gasoli	I SQ ne, °C	91 AI SQ 10% GVL (v/	gasoline + v) (83.70 kPa)	a) $\begin{array}{c} 91 \text{ AI SQ gasoline} + 20\% & 91 \text{ AI} \\ \text{GVL } (v/v) (83.40 \text{ kPa}) & \text{GVI} \end{array}$		+ 20% 91 AI SQ gasoline + 30% 0 kPa) GVL (v/v) (83.42 kPa)	
distillate volume fraction, %	$T_{\mathbf{k}}, ^{\circ}\mathbf{C}$	$T_{\rm h}, {}^{\circ}{\rm C}$	$T_{\rm k}, ^{\circ}{\rm C}$	$T_{\rm h},^{\rm o}{\rm C}$	$T_{\rm k}$ , °C	$T_{\rm h},^{\rm o}{\rm C}$	$T_{\rm k}$ , °C	$T_{\rm h},{}^{\rm o}{\rm C}$
5	69.5	59.4	79.2	69.2	80.5	69.7	84.4	71.6
10	74.4	66.0	85.7	76.5	87.9	76.5	94.6	81.8
15	82.0	76.3	93.6	84.6	97.5	86.4	104.8	93.1
20	91.1	83.5	102.1	94.4	106.2	96.7	114.7	103.7
25	100.4	93.3	108.4	100.2	113.4	104.6	122.0	111.5
30	107.1	100.9	114.3	106.6	119.8	111.0	129.7	119.4
35	112.1	106.3	118.7	111.1	125.0	116.6	137.1	126.4
40	117.2	112.5	123.7	116.4	131.6	123.3	146.4	136.2
45	121.0	115.3	127.0	120.9	137.6	129.6	155.4	145.7
50	124.6	119.6	133.0	126.2	145.0	136.9	165.3	156.7
55	128.8	123.1	138.6	131.6	153.2	145.4	175.3	168.1
60	133.4	127.3	144.9	138.7	162.0	155.4	184.3	179.1
65	138.0	131.9	151.4	145.7	170.8	165.5	193.1	189.1
70	142.9	138.7	159.1	153.7	180.4	174.8	199.9	197.9
75	149.3	145.7	167.7	162.4	190.1	186.7	204.1	202.7
80	155.7	151.7	176.4	172.1	199.2	197.5	205.8	204.6
85	164.5	160.3	190.2	184.3	204.9	203.4	206.9	206.3
90	175.7	170.5	204.4	200.0	206.7	204.8	207.0	207.5

"The uncertainties are discussed in the text. These temperatures have been corrected to 1 atm with the Sydney Young equation.

see that the curves approach that of neat diesel fuel, but never overlap. Indeed, the distillation temperatures of the mixtures trail the neat diesel fuel by 10-11 °C in the late stages. We have observed this kind of behavior with many fuel additives that distill out early in the curves.<sup>39,60</sup> Early in the distillation, the applied energy is being used to preferentially vaporize the additive. Hydrocarbon constituents that are less volatile and that would otherwise begin to vaporize early in the distillation remain in the liquid phase. Their evaporation is delayed; thus the distillation curves of the 1 and 2.5% starting mixtures are seen to lie below that of diesel fuel, although the  $\gamma$ -valerolactone is no longer present in the liquid. The absence of the additive and the increased presence of the hydrocarbons can be observed experimentally with the composition explicit data channel and modeled with a Helmholtz free energy equation of state.60

We also examined the distillate fractions for moiety family types by use of a mass spectrometric classification method based on ASTM Method D-2789.<sup>84</sup> In this method, one uses mass spectrometry (or gas chromatography–mass spectrometry) to characterize hydrocarbon samples into six types. The six types or families are paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (arenes or aromatics), indanes and tetralins (grouped as one classification), and naphthalenes. Although the method is specified only for application to low olefinic gasolines, and it has significant limitations, it is of practical relevance to many complex fluid analyses and is often applied to gas turbine fuels, rocket propellants, and missile fuels. The uncertainty of this method and the potential pitfalls were treated earlier.<sup>39,54</sup> The result of this analysis for the two mixtures of  $\gamma$ -valerolactone with diesel fuel were not noticeably different from that of the neat diesel fuel, no doubt due to the relatively low concentrations of the additives in the mixtures that we measured. This aspect makes a direct comparison with our earlier work on glycol ethers, glycol esters, and carbonates (see above) difficult. This should not be viewed as a disadvantage of  $\gamma$ -valerolactone, but rather an indication that an in-depth investigation of the liquid—liquid equilibrium requires more study before additional work on diesel fuel mixtures can be done.

**Gasoline**  $\gamma$ -Valerolactone Mixtures. As noted above, we were able to measure higher concentrations of  $\gamma$ -valerolactone in gasoline (10, 20, and 30%, vol/vol) since we did not encounter the immiscibility issues that we encountered with diesel fuel. The initial boiling temperature results obtained for mixtures of  $\gamma$ -valerolactone are given in Table 4. With the addition of the additive to neat gasoline, both onset and sustained boiling temperatures increased by an average of 20.9 and 28.0 °C, respectively. The vapor rising temperatures showed more pronounced increases averaging 32.9 °C. These increases in boiling temperatures are expected since GVL has a higher boiling point than the initial boiling point of neat 91 AI summer quarter gasoline.

Representative distillation curve data for straight 91 AI summer quarter gasoline and its mixtures with 10, 20, and 30% vol/vol  $\gamma$ -valerolactone are given in Table 5. A plot of the distillation curves for the four fluids (each an average of the results from four separate runs) is given in Figure 3. As with the mixtures with diesel fuel, we did not note any

<sup>(84)</sup> ASTM Standard D 2789–04b, Standard test method for hydrocarbon types in low olefinic gasoline by mass spectrometry; ASTM International: West Conshohocken, PA, 2005; Vol. 05.01.

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azeotropic convergence of  $T_k$  and  $T_h$ . We note that this is in contrast to our previous measurements with methanol and 1-butanol, where we did observe convergence corresponding with the known azeotropic binaries.<sup>8,39</sup> From 5 to 35% distillate volume fraction, all three additive-containing mixtures closely mirror the temperature trend exhibited by neat gasoline. In this "early distillation" region, the vaporization temperatures of the 10% v/v mixture exceeds the unmodified gasoline in temperature by an average of 9.3 °C, the 20% mixture by an average of 13.4 °C, and the 30% mixture by an average of 21.5 °C.

In the middle and later stages of the distillation curve, the behavior of the gasoline +  $\gamma$ -valerolactone mixtures diverge. For the 10% mixture, we note that the vaporization temperatures exceed that of the neat gasoline by 15.0 °C (a 5.7 °C increase over the average temperature lead in the early distillation region). The divergence of the distillation curves of the 20 and 30% mixtures is more pronounced, exceeding the neat gasoline curve by an average temperature difference



**Figure 3.** Distillation curves of 91 AI summer quarter gasoline with 10, 20, and 30% (v/v)  $\gamma$ -valerolactone. Here, we present  $T_k$ , the temperature measured directly in the fluid. The uncertainties are discussed in the text.

of 30.0 and 44.8 °C, respectively. Using the composition channel of the ADC methodology, we can associate these changes in distillation behavior with the concentration of the  $\gamma$ -valerolactone in the distillate. The concentration of this fluid (expressed as %, mass/mass) as a function of the distillate volume fraction is shown in Figure 4. The additive is present at a low level in the first drop of the distillate, despite the fact that the mixture temperature at this point is more than 100 °C less than the normal boiling point of  $\gamma$ -valerolactone.

At a 20% distillate volume fraction for all three additive mixtures, the concentration of the additive approaches 1% v/v. It is at the 40% distillate fraction that the additive concentrations significantly diverge, which correlates with the behavior of the distillation curves visible in Figure 3. The concentration of GVL in the distillate for the 10% additive mixture lies significantly lower than that in the 20 and 30%



**Figure 4.** Histogram plot showing the results of the analysis for  $\gamma$ -valerolactone (GVL) as a function of distillate volume fraction for the three gasoline mixtures' starting mixtures (10, 20, and 30%; vol/ vol, GVL in 91 AI summer quarter gasoline).

Table 6. Summary of the Results of Hydrocarbon Family	V Calculations Based on the Method of A	ASTM D-2789 on $\gamma$ -Valerolacto	one (GVL)/Gasoline
	Mixtures		

distillate volume faction, %	paraffins, vol %	monocyclo paraffins, vol %	dicyclo paraffins, vol %	alky aromatics, vol %	indanes and tetralins, vol %	napthalenes, vol %
			(a) 10% GVL			
0.025	53.6	31.5	2.6	12.1	0.1	0.0
20	47.0	24.6	3.1	24.8	0.5	0.0
40	39.6	17.1	2.7	39.6	0.9	0.1
60	25.1	10.6	2.0	60.3	2.0	0.1
80	18.2	7.9	1.4	66.1	5.8	0.7
residue	67.7	31.5	0.6	0.2	0.0	0.1
			(b) 20% GVL			
0.025	55.5	23.7	2.3	18.0	0.4	0.1
20	51.8	21.9	2.7	23.1	0.5	0.1
40	40.7	15.8	2.4	39.9	1.1	0.1
60	22.9	9.7	1.8	61.3	3.9	0.3
80	30.9	13.7	1.2	47.8	5.6	0.9
residue	68.9	30.1	0.6	0.4	0.0	0.1
			(c) 30% GVL			
0.025	58.1	28.3	2.6	10.7	0.2	0.1
20	50.9	20.6	2.8	25.1	0.6	0.1
40	32.9	13.2	2.3	49.9	1.6	0.1
60	21.5	9.4	1.3	62.6	4.8	0.5
80	65.9	28.8	0.7	3.9	0.7	0.1
residue	69.4	30.1	0.4	0.1	0.0	0.0

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mixtures and can explain why its distillation behavior exhibits more of a constant temperature shift rather than a significant change in slope. By the 60% distillate volume fraction mark, however, the 20 and 30% additive mixture distillates contain 22.1 and 33.6% (mass/mass) additive, respectively, a significant fraction of  $\gamma$ -valerolactone that considerably alters the distillation behavior. Indeed, by the 80% distillate fraction mark, the distillation curves of both higher concentration additive mixtures have begun to level off.

This leveling off of the two curves in the last 20% of the distillation corresponds to the additive composing most of the distillate. At this point, the curves approach the normal boiling point of  $\gamma$ -valerolactone (207.6 °C), and the concentrations of the additive approach 100% (at the 80% distillate volume fraction, the concentration of GVL in the 20%

mixture has reached 65.6%, mass/mass, and in the 30% mixture it has reached 73.1%, mass/mass). By 90% distillate volume fraction, both the 20 and 30% curves exhibit a fluid  $(T_k)$  temperature within 1 °C of the boiling point of the additive, again confirming the dominating presence of  $\gamma$ -valerolactone at these later points in the distillation.

The behavior of the distillation curves can also be further explained and understood with the results of the moiety family analysis method described above for the diesel fuel mixtures. These results are provided in Table 6 and Figure 5. A general trend of decreasing aliphatic and increasing cyclic hydrocarbon content over the course of a distillation was reported previously for neat gasoline. In high AI gasoline samples, a high aliphatic hydrocarbon content generally corresponds to lower boiling temperatures, and a high cyclic hydrocarbon content to higher boiling temperatures.



**Figure 5.** Plots showing the hydrocarbon family distribution in mixtures of 91 AI summer quarter gasoline with (a–c) 10, 20, and 30%  $\gamma$ -valerolactone.

The shift from aliphatic to cyclic hydrocarbon content over the course of a simple distillation can explain the slope of the distillation curve. For the 10%  $\gamma$ -valerolactone mixture, the hydrocarbon moiety family trend that is typical for neat gasoline is still apparent; the distillation curve mirrors that of the 91 AI gasoline. For the 20 and 30%  $\gamma$ -valerolactone mixtures, we see a significant departure from this trend beginning approximately at the 65% distillate volume fraction. Here, the slope changes to reveal nearly pure fluid behavior. This results from the significant presence of  $\gamma$ -valerolactone at this point in the distillation; indeed, the additive dominates the fluid composition. This can be seen on the distillation curves, and the moiety family analysis explains the structure of the curves. We note at the 80% distillate volume fraction that the aliphatic hydrocarbon concentration has jumped significantly. This is because the ASTM 2789 methodology identifies some of the fragment ions of  $\gamma$ -valerolactone as characteristic of paraffins and monocycloparaffins (m/z = 41, 43, 57, 85). The characterization of  $\gamma$ -valerolactone as an aliphatic hydrocarbon is an artifact of the methodology, because those hydrocarbon fragments from  $\gamma$ -valerolactone produce the change in trend. This is not a major disadvantage, since we recognize the cause and can reinterpret the spectra accordingly. We also note an abrupt drop in the alkylbenzene (aromatic) content at this for these more concentrated mixtures. This result is in stark contrast to the neat gasoline, which typically shows an increasing aromatic content as the vaporization proceeds. The drop is due to the dominance of the mixture by the additive, and the resulting decrease in aromatic content.

#### Conclusions

We have used the Advanced Distillation Curve methodology to characterize mixtures of winter-grade, low wax, ultra low sulfur diesel fuel and mixtures of 91 AI summer quarter gasoline with the renewable, bioderivable additive  $\gamma$ -valerolactone. The additive shifts the distillation curve for diesel fuel to lower temperatures, with most of the additive removed from the mixture by the 40% distillate volume fraction. The presence of up to 2.5% (v/v) of  $\gamma$ -valerolactone in diesel fuel does not appear to affect the volatility to any great extent. We did not study mixtures of higher concentrations because of the onset of liquid-liquid phase separation at ambient temperature. We note that this issue may have more importance operationally than we have been able to ascribe to our volatility measurements alone. In this respect, the onset of phase separation at lower than ambient temperatures will require investigation. Conversely to the effect on diesel fuel, the additive shifts the distillation curve of gasoline to higher temperatures. The extent of these shifts is proportional to the amount of additive in the mixtures. Mixtures of up to 10%  $(v/v) \gamma$ -valerolactone in gasoline appear to have a relatively minor effect on the shape of the curve and the overall volatility, however. Further investigations underway will address the effect of additive concentration on the energy content of the distillate fractions. We also plan to apply our modeling methods to these mixtures.

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