Composition-Explicit Distillation Curves for Mixtures of Gasoline with Four-Carbon Alcohols (Butanols)

Thomas J. Bruno,* Arron Wolk, and Alexander Naydich

Thermophysical Properties Division, National Institute of Standards and Technology (NIST), Boulder, CO 80305

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Interest in the domestic production of bioderived fuels, sparked by the high cost of petroleum crude oil, has led to consideration of fluids to replace or extend conventional petroleum-derived fuels. While ethanol as a gasoline 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. For these and other reasons, the butanols have been studied as gasoline extenders. For any extender to be designed or adopted, a suitable knowledge base of thermophysical properties is a critical requirement. In this paper, we provide volatility measurements of mixtures of a typical gasoline with n-butanol, 2-butanol, isobutanol, and t-butanol, performed with the advanced distillation curve metrology. This recently introduced technique is an improvement of classical approaches, featuring (1) a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analyses), (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 have applied the new method to fundamental work with hydrocarbon mixtures and azeotropic mixtures and also to real fuels. The fuels that we have measured include rocket propellants, gasolines, jet fuels, diesel fuels (including oxygenated diesel fuel and biodiesel fuels), and crude oils.

Introduction

High motor fuel costs and the possibility of interruptions in supply have caused a great deal of interest in biofuels, renewable fuels that are produced by plant matter or algae.¹ 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.^{2,3} The primary motor biofuel in relatively widespread use for lightweight vehicles is ethanol. Indeed, ethanol has been used for many years as a gasoline oxygenate, added to gasoline to decrease certain pollutant emissions, primarily carbon monoxide.^{4,5} The typical oxygenate additive concentration of ethanol is approximately 10% (vol/vol). The addition of higher concentrations on a large scale has been problematic because of numerous technical problems.⁶ To

* To whom correspondence should be addressed. E-mail: bruno@ boulder.nist.gov.

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use ethanol concentrations in gasoline in excess of 10%, engine modifications are usually required.^{7,8} Higher concentrations of ethanol can be corrosive toward ferrous metals and cause swelling of common elastomers used as seals in fuel systems. In addition to the seals, many flexible transfer lines are degraded by high ethanol concentration gasoline mixtures. Ethanol mixtures can absorb water; phase separation will occur at some water concentrations (especially at lower operating temperatures); and such mixtures have a significantly lower energy content than typical gasoline.^{3,9} Moreover, high ethanol concentrations can cause problems with electric fuel pumps and also with capacitance-based fuel level gauges. Other problems with the large scale increase in ethanol-blended fuels include the effect on food costs worldwide and the inability to ship commodity ethanol in pipelines.¹⁰

In an effort to overcome some of the problems associated with the use of fuel ethanol, the adoption of higher alcohols has been suggested, primarily the butanols.^{5,6,11–13} The butanols are a family of four-carbon alcohols, representative properties

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1-butanol:

CAS No. 71-36-3 INChl=://C4H10O/c1-2-3-4-5/h5H, 2-4H2, 1H3 RMM = 74.1216 $T_{boil} = 119 \ ^{\circ}C$ $T_{fus} = -89 \ ^{\circ}C$ Density = 0.804 g/mL (20 \ ^{\circ}C) Refractive index, Na⁴ = 1.3971

Synonyms:

butyl alcohol; n-butan-1-ol; n-butanol; n-butyl alcohol; butyl hydroxide; CCS 203; hemostyp; methylolpropane: propylcarbinol; n-C₄H₉OH; butanol; butan-1-ol; 1hydroxybutane; n-butanolbutanolen; alcool butylique; butanolo; butylowy alkohol; butyric alcohol; propylmethanol; butanolen; 1-butyl alcohol.

isobutanol



CAS No. 78-83-1 InChI=1/C4H100/c1-4 (2) 3-5/h4-5H, 3H2, 1-2H3 RMM = 74.1216 T_{boil} = 108 °C T_{fus} = -108 °C Density = 0.798 g/mL (20 °C) Refractive Index, Na^d = 1.3938

Synonyms:

1-propanol, 2-methyl-; isobutyl alcohol; isopropylcarbinol; 2-methyl-1-propanol; iso-C₄H₅OH; fermentation butyl alcohol; 1-hydroxymethylpropane; 2-methylpropanol; 2methylpropan-1-ol; 2-methylpropanol-1; 2-methylpropyl alcohol; butanol-iso; alcool isobutylique; isobutylalkohol; RCRA waste number U140; UN 1212; i-butyl alcohol; IBA; isopropyl carbitol; propanol, 2-methyl-; 2-methyl-1-propanyl alcohol; 2methylpropanol; i-butanol; methyl-2 propanol-1.

of which are listed in Table 1.14 Because the butanols have more carbon-hydrogen bonds than ethanol, the energy content is higher, although still lower than straight gasoline.¹⁵ The butanols are significantly less volatile than ethanol, and they appear to lower sulfur and nitrogen oxide emissions in mixtures when compared to gasoline.¹¹ The material compatibility problems are also substantially less severe with the butanols as well, with little or no reported swelling of elastomers (in the limited testing that has been performed) and a lower corrosivity toward ferrous metals. Indeed, it is likely that distribution of butanol gasoline mixtures can be performed with the existing infrastructure, including pipeline transport. The phase-separation problems are far less serious with the butanols than with lower alcohols. Higher concentration butanol blends are possible in existing engines without requiring engine modifications, because the butanols affect gasoline properties to a lesser extent than the lower alcohols. For example, with carbureted spark-ignition engines, the addition of 20% (vol/vol) methanol to gasoline requires modification of carburetor jets to obtain acceptable 2-butanol: OH



CAS No. 78-92-2 InChI=1/C4H100/c1-3-4 (2) 5/h4-5H, 3H2, 1-2H3 RMM = 74.1216 $T_{boil} = 100 \ ^{\circ}C$ $T_{fus} = -115 \ ^{\circ}C$ Density = 0.802 g/mL (20 \ ^{\circ}C) Refractive Index, Na^d = 1.3949

Synonyms

sec-butyl alcohol; *sec*-butanol; CCS 301; ethyl methyl carbinol; methyl ethyl carbinol; 1methyl-1-propanol; 1-methylpropyl alcohol; 2-hydroxybutane; sec-C₄H₅OH; butane, 2hydroxy-; butanol-2; butan-2-ol; 2-butyl alcohol; *s*-butyl alcohol; butylene hydrate; Dsec-butanol; L-sec-butanol; alcool butylique secondaire; butanol secondaire; S.B.A.; sbutanol; 1-methyl propanol; UN 1120; n-butan-2-ol.

tert-butanol:



 $\begin{array}{l} {\rm CAS \ No.\ 75-65-0} \\ {\rm Inchl=1/C4H100/c1-4\ (2,3)\ 5/h5H, 1-3H3} \\ {\rm RMM} \ = \ 74.1216 \\ {\rm T}_{boil} \ = \ 82\ ^{\circ}{\rm C} \\ {\rm T}_{fus} \ = \ 26\ ^{\circ}{\rm C} \\ {\rm Density} \ = \ 0.782\ g/mL\ (20\ ^{\circ}{\rm C}) \\ {\rm Refractive\ Index,\ Na^{d}} \ = \ 1.3852 \end{array}$

Synonyms

ethanol, 1, 1-dimethyl-; 2-propanol, 2-methyl-; tert-butyl alcohol; trimethylcarbinol; trimethylmethanol; 1, 1-dimethylethanol; 2-methyl-2-propanol; tert-C₄H₉OII; *t*-butanol; tert-butyl hydroxide; 2-methylpropanol-2; *t*-butyl alcohol; 2-methylpropan-2-ol; alcool butylique tertiaire; butanol tertiaire; *t*-butyl hydroxide; methanol, trimethyl-; NCI-C55367; UN 1120; 2-methyl n-propan-2-ol; *tert*.-butyl alcohol; methyl-2 propanol-2.

performance, while a 20% (vol/vol) mixture of blended butanols requires no modifications.¹⁶

The renewable butanols produced for fuel use, generally referred to as biobutanol, can be made by a number of processes.^{6,17–20} Biobutanol can be produced from biomass with the ABE process, making use of the bacterium *Clostridium acetobutylicum*. This bacterium is also called Weitzmann's organism (named for Chiam Weitzmann, who used it for the production of acetone). Butanols can also be produced from algae and from a three-step thermal, catalysis, and reformulation process called the Centia process.^{21,22} There is currently far less experience and capacity for the production of butanols as

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⁽²²⁾ Green Car Congress. Centia biofuels process produces bio-gasoline similar to conventional unleaded gasoline, 2008 (http://www.greencarcon-gress.com/2008/01/centia-biofuels.html).

compared to that for the lower alcohols, such as methanol and ethanol, although increased demand could increase development in the near term.

The successful application of new finished fuels requires a substantial knowledge base of fluid properties and how those properties impact engine performance. Critical among these properties are the volatility characteristics of the fluids, usually described by the distillation curve.²³⁻²⁵ Indeed, it has been possible in recent years to relate the distillation curve to operational parameters of complex liquid fuels. For a sparkignition engine operating with gasoline as the fuel, these parameters include engine-starting ability, vehicle drivability, fuel system icing and vapor lock, the fuel injection schedule, fuel auto-ignition, etc.^{26,27} For example, it is possible to directly correlate the fuel system icing rate (which is a consequence of intake manifold rarefaction) with the distillation temperature of various fractions of gasoline. The front end (low-temperature region) of the distillation curve of gasoline (up to approximately 70 °C) is used to assess and optimize ease of starting and the potential for hot-weather vapor lock in engines. The mid range of the gasoline curve (up to a temperature of approximately 100 °C) is used to assess and optimize cold-weather performance, the operational readiness of a hot engine, and the acceleration behavior of a hot engine under load. The top range of the distillation curve is used to assess and optimize fuel economy in a hot engine. In addition to these applications to performance optimization and design, the distillation curve provides an avenue to long-term trend analysis of fuel performance, because changes in the distillation curve are related to changes in fuel performance. The distillation curve is therefore one of the parameters for which there is a relatively long historical record of results.28

Of particular importance is the ability to model the volatility with an equation of state that also describes the other fundamental properties. This precludes distillation curve determination with the classical methods that have little or no basis in theory.²⁹ In earlier work, however, we described a method and apparatus for an advanced distillation curve (ADC) measurement that is especially applicable to the characterization of fuels. 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 analyses), (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) a corrosivity assessment of each distillate fraction. The fuels that we have

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measured include rocket propellants, gasolines, jet fuels, diesel fuels (including oxygenated diesel fuel and biodiesel fuels), and crude oils.^{30–46} Moreover, the measurements have facilitated the development of thermodynamic models (on the basis of equations of state) to describe complex fuels.^{47,48} In this paper, we present the results of ADC measurements on mixtures of a typical premium-grade gasoline with 1-butanol, 2-butanol, isobutanol, and *t*-butanol.

Experimental Section

The gasoline used as the base fluid in this work was a 91 antiknock index (AI, the average of the motor and research octane numbers) summer-grade 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 μ m and temperature program from 50 to 170 °C, at 7 °C/min) separately with flame ionization detection

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and mass spectrometric detection.^{49,50} This analysis showed a large fraction of aromatic constituents, consistent with the relatively high AI number. Although no specific tests were performed 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 1-butanol, 2-butanol, 2-methyl-2-propanol (*t*-butanol), and 2-methyl-1-propanol (isobutanol) used in this work were obtained from a commercial source with stated purities of 99.5–99.8% (mass/mass). The purities were verified with the same gas chromatographic method used for the gasoline samples, discussed above. These analyses revealed that the purities were in fact higher than stated, but traces of disec-butyl ether (CAS registry number 6868-58-7) and 2-butyl formate (CAS registry number 589-40-2) were found in each, along with traces of the other butanols. Karl Fisher Coulombic titrimetry was performed to measure the moisture content of each sample. These analyses revealed the presence of water between 8 and 12 ppm (mass/mass). On the basis of these analyses, the fluids were used as received, although precautions were taken to prevent the uptake of moisture.

The dodecane used as a solvent 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 μ m and temperature program from 90 to 170, at 7 °C/min) using 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 butanols used were obtained from a commercial supplier and were also analyzed by gas chromatography (30 m capillary column of 5% phenyl/95% dimethyl polysiloxane, having a thickness of 1 μ m and temperature program from 90 to 170, at 7 °C/min) using flame ionization detection and mass spectrometric detection.

The method and apparatus for the distillation curve measurement has been reviewed in a number of sources; therefore, additional general description will not be provided here.^{30,32} 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 was then commenced with a four-step program based on a previously measured distillation curve.⁵¹ 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 between four and six complete distillation curve measurements on separate samples for each of the mixtures. To accomplish this, we prepared stock solutions of each mixture and maintained each in a sealed container at 7 °C to prevent evaporation or moisture uptake. Thus, each measurement was performed on a consistent starting fluid.

Because 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 performed with the modified Sidney Young equation, in which the constant term was assigned a value of $0.000 \ 119.^{52-54}$ This value corresponds to a hydrocarbon molecule of eight carbons. In the chemical analysis of the fuel samples (see above), as well as in previous work on gasoline blends, it was found

that *n*-octane can indeed represent the fluid as a very rough compositional surrogate.

Results and Discussion

Gasoline is a commodity fluid with many seasonal and regional varieties. The variability is reflected in the specifications, which are intentionally inclusive (or loose) in terms of thermophysical properties. The variation in the thermophysical properties is clearly reflected in the chemical properties and the composition. Thus, any study performed on a particular sample of a particular gasoline and mixtures thereof cannot be considered typical of the gasoline supply in general, because this cannot be strictly defined. Indeed, our earlier work on gasoline plus methanol mixtures used a 91 AI winter-quarter sample, which was (not surprisingly) found to be more volatile that the summer-quarter sample used here.⁴² This study must therefore be considered an example of an analytical or testing protocol that can be applied as needed to any sample (of any type) of gasoline.

We performed three complete distillation curve measurements of the 91 AI gasoline and between four and six measurements on gasoline mixtures with each of the four butanols at 10, 20, and 30% (vol/vol) butanol. The repeatability of the distillation curves has been discussed extensively elsewhere. For this reason, only representative data will be presented here, along with appropriate estimates of uncertainty.

Initial Boiling Temperatures. 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 for measurement of the onset of boiling for each of the mixtures. Typically, the first bubbles will appear intermittently and will quell if the stirrer is stopped momentarily. Sustained vapor bubbling is then observed. In the context of the ADC measurement, sustained bubbling is also somewhat intermittent but is observable even when the stirrer is momentarily stopped. Finally, the temperature at which vapor is first observed to rise into the distillation head is observed. This temperature is termed the vapor rise temperature, which we have shown is actually the initial boiling temperature of the mixture. These observations are important because they can be modeled theoretically, for example, with an equation of state. Clearly, there is an element of subjectivity in determining the initial temperatures, especially the onset and sustained bubbling temperatures. For example, it is often difficult to distinguish between initial bubbling and the entrainment of air bubbles by the action of the stirrer. 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. Experience with previous mixtures, including *n*-alkane standard mixtures that were prepared gravimetrically, indicates that the uncertainty in the onset and sustained bubbling temperatures is approximately 1 °C. The uncertainty in the vapor rise temperature is 0.3 °C.

In Table 2, we present the initial temperature observations for straight 91 AI summer gasoline and also for mixtures with 10, 20, and 30% each of 1-butanol, 2-butanol, 2-methyl-2-propanol (*t*-butanol), and 2-methyl-1-propanol (isobutanol). Before treating the initial boiling temperatures of the gasoline

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	observed temperature	91 AI SQ gasoline (°C) (83.74 kPa)			
	onset sustained vapor rise	51.5 52.1 54.2			
observed temperature	91 AI SQ gasoline plus 10% 1-butanol	91 AI SQ gasoline plus 20% 1-butanol	91 AI SQ gasoline plus 30% 1-butanol		
	(vol/vol) (°C) (83.59 kPa)	(vol/vol) (°C) (83.46 kPa)	(vol/vol) (°C) (83.81 kPa)		
onset	49.5	50.2	51.4		
sustained	52.1	55.5	60.0		
vapor rise	58.9	61.1	63.8		
observed temperature	91 AI SQ gasoline plus 10% 2-butanol	91 A SQ I gasoline plus 20% 2-butanol	91 AI SQ gasoline plus 30% 2-butanol		
	(vol/vol), °C (83.54 kPa)	(vol/vol), °C (83.46 kPa)	(vol/vol), °C (83.39 kPa)		
onset	48.4	46.3	49.7		
sustained	50.60	52.4	54.0		
vapor rise	58.3	59.8	62.0		
observed temperature	91 AI SQ gasoline plus 10% <i>t</i> -butanol	91 AI SQ gasoline plus 20% <i>t</i> -butanol	91 AI SQ gasoline plus 30% <i>t</i> -butanol		
	(vol/vol) (°C) (83.25 kPa)	(vol/vol) (°C) (83.80 kPa)	(vol/vol) (°C) (83.50 kPa)		
onset	40.9	41.1	44.8		
sustained	49.9	50.2	51.7		
vapor rise	56.3	57.9	59.4		
observed temperature	91 AI SQ gasoline plus 10% isobutanol	91 AI SQ gasoline plus 20% isobutanol	91 AI SQ gasoline plus 30% isobutanol		
	(vol/vol) (°C) (83.35 kPa)	(vol/vol) (°C) (83.62 kPa)	(vol/vol) (°C) (83.87 kPa)		
onset	46.6	48.7	54.9		
sustained	52.5	55.9	58.8		
vapor rise	58.2	59.7	63.3		

Table 2. Summary of the Initial Behavior of the 91 AI Summer Quarter (SQ) Gasoline Mixtures with the Butanols^a

^{*a*} The vapor rise temperature is that at which vapor is observed to rise into the distillation head, considered to be the initial boiling temperature of the fluid (highlighted in bold). These temperatures have been corrected to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided to allow for recovery of the actual measured temperatures. The uncertainties are discussed in the text.

plus butanol mixtures, it is instructive to examine those values for the straight gasoline vis a vis our previous measurements on a 91 AI winter-quarter gasoline. In that earlier work, we found that the initial boiling temperature of that typical premium winter fluid was 44.4 °C, while that of the summer fluid was observed to be 54.2 °C. This winter–summer difference of 10 °C is typical, reflecting the higher fraction of the so-called butane fraction of the winter fluid.⁵⁵

When we examine the initial boiling temperatures of the gasoline plus butanol mixtures, we note that the addition of any of the butanols will increase the initial boiling temperatures between 4 and 9%, as reflected in the column labeled "vapor rise". We also note that the initial boiling temperature increases as the concentration of the butanol increases from 10 to 30% (vol/vol). It is not surprising that the butanols with the highest normal boiling temperatures cause the most significant departures relative to the straight gasoline. As we have noted for all other fluids measured with the ADC approach, the IBT values that we have presented are very different from those that would be obtained with the classical method, which are systematically in error. Those values, being obtained as the first drop of distillate enters the receiver, are 7-13 °C too high.³⁰

Distillation Curves. Representative distillation curve data for the 91 AI summer gasoline and this gasoline with 10, 20, and 30% (vol/vol) of each of the four added butanols are presented in Tables 3 and 4, respectively. Distillation data presented in both T_k (measured directly in the fluid) and T_h (measured in the distillation head) are provided in Table 3. The T_k data are true thermodynamic state points, while the T_h data allow for a comparison to earlier measurements. In this respect, these data are comparable to the temperatures that might be obtained with ASTM D-86.²⁹ In this table, the estimated uncertainty (with a

(55) Howstuffworks. Why is summer fuel more expensive than winter fuel? 2008 (http://auto.howstuffworks.com/summer-fuel.htm/printable).

coverage factor k = 2)⁵⁶ in the temperatures is 0.4 °C. We note that the experimental uncertainty of T_k is always somewhat lower than that of T_h , but as a conservative position, we use the higher value for both temperatures. The uncertainty in the volume measurement that is used to obtain the distillate volume fraction is 0.05 mL in each case. The uncertainty in the pressure measurement (assessed by logging a pressure measurement every 15 s for the duration of a typical distillation) is 0.001 kPa. The relatively low uncertainties in the measured quantities facilitate modeling the results, for example, with an equation of state. The data in Table 3 show that T_k leads T_h by several degrees for all distillate volume fractions. The distillation data, in terms of T_k , are presented graphically in Figure 1.

A gross examination of the distillation curves for each of the butanols show that the early behavior of the curves (for distillate volume fractions up to 0.15) are consistent with the observed initial boiling points described earlier. The butanol mixtures start out less volatile than gasoline, and then a crossover point is observed, after which the mixtures are more volatile than gasoline. The crossover points are different for each of the butanols, and in addition, these points correlate with the butanol normal boiling temperature. We find that the crossover for 1-butanol occurs at a distillate volume fraction of approximately 0.3, the crossover for *i*-butanol and 2-butanol occurs at a distillate volume fraction of approximately 0.2, and the crossover for *t*-butanol occurs at a distillate volume fraction of approximately 0.15. Thus, the crossover is progressively later for the higher boiling butanols.

We also note that, as the concentration of the butanol increases, the distillation curves show a pronounced flattening, approximating the behavior of a pure fluid. While this behavior

⁽⁵⁶⁾ Taylor, B. N.; Kuyatt, C. E. Guidelines for evaluating and expressing the uncertainty of NIST measurement results. NIST Technical Note 1297, National Institute of Standards and Technology (NIST), Gaithersburg, MD, 1994; 20402.

(a) 91 AI SQ Gasoline							
dictillata voluma			91 AI SQ gasoline (83.74 kPa)			_	
fract	tion (%)		$T_{\rm k}$ (°C)		$T_{\rm h}$ (°C)	_	
	~						
	5		69.5 74.4		59.4		
	10		/4.4		00.0 76.2		
	15		82.0		/0.3		
	20		91.1		03.3		
	23		100.4		95.5		
	50 25		107.1		100.9		
	35		112.1		112.5		
	40		117.2		112.3		
	45		121.0		115.5		
	55		124.0		123.1		
	55		120.0		125.1		
	65		133.4		127.3		
	70		130.0		131.9		
	70		142.9		136.7		
	80		149.5		145.7		
	85		164.5		160.3		
	90		175.7		170.5		
	(b) Mixtures of	Gasoline and the Addi	tive 1-Butanol in 10,	20, and 30% (vol/vol)	Concentrations		
	91 AI SO gas	soline plus 10%	91 AI SO gas	oline plus 20%	91 AI SO gasol	ine plus 30%	
	(vol/vol) 1-but	anol (83.59 kPa)	(vol/vol) 1-buta	anol (83.46 kPa)	(vol/vol) 1-butan	ol (83.81 kPa)	
distillate volume	(((((((((((((((((((T (00)	(T (00)	(((((((((((((((((((T (0 C)	
fraction (%)	$T_{\rm k}$ (°C)	$T_{\rm h}$ (°C)	$I_{\rm k}$ (°C)	$T_{\rm h}$ (°C)	$T_{\rm k}$ (°C)	$T_{\rm h}$ (°C)	
5	76.3	69.6	80.1	71.0	83.7	72.6	
10	82.4	75.6	85.3	77.8	89.0	80.9	
15	88.0	82.4	91.3	84.9	95.0	88.3	
20	93.6	88.3	96.6	90.9	100.2	95.0	
25	98.4	93.0	101.0	96.1	104.1	99.8	
30	102.9	97.8	104.6	100.6	107.2	103.7	
35	106.1	101.2	107.2	103.7	109.2	106.0	
40	109.6	104.6	109.7	106.9	111.4	107.8	
45	112.4	107.5	111.9	107.6	113.0	109.5	
50	115.1	108.7	114.0	109.5	114.7	111.1	
55	118.7	112.9	116.2	110.9	116.3	112.5	
60	123.7	115.5	118.6	113.1	117.9	114.0	
65	129.6	121.4	121.8	114.6	119.3	115.3	
70	137.3	130.4	126.1	117.3	121.3	116.6	
75	146.9	140.2	135.1	123.6	123.6	118.0	
80	156.0	149.3	151.5	144.1	128.4	121.1	
85	167.3	162.2	166.9	160.8	150.6	135.6	
90	185.9	171.0	188.5	170.2	178.5	168.8	
	(c) Mixtures of	Gasoline and the Addit	tive 2-Butanol in 10,	20, and 30% (vol/vol)	Concentrations		
	91 AI SQ gas	soline plus 10%	91 AI SQ gas	oline plus 20%	91 AI SQ gasol	ine plus 30%	
distillate volume	(vol/vol) 2-but	anol (83.54 kPa)	(vol/vol) 2-buta	anol (83.46 kPa)	(vol/vol) 2-butanol (83.39 kPa)		
fraction (%)	$T_{\rm k}$ (°C)	$T_{\rm h}$ (°C)	<i>T</i> _k (°C)	$T_{\rm h}$ (°C)	$T_{\rm k}$ (°C)	$T_{\rm h}$ (°C)	
5	76.2	71.3	76.1	71.0	78.6	71.1	
10	80.1	75.7	80.3	75.2	82.9	77.1	
15	85.0	80.4	84.9	81.1	87.3	83.0	
20	89.8	85.6	89.3	85.3	91.2	87.8	
25	94.1	90.1	92.8	89.8	93.8	90.3	
30	98.3	94.6	95.8	93.7	96.2	93.7	
35	101.7	97.8	98.1	96.0	97.9	95.4	
40	106.2	101.9	100.6	98.4	99.6	97.2	
45	110.3	105.6	102.7	100.5	101.0	97.6	
50	115.2	110.1	105.1	101.4	102.4	98.5	
55	121.0	115.8	108.2	103.2	104.0	99.6	
60	126.8	121.9	112.6	105.6	105.9	100.9	
65	132.6	127.9	119.4	110.1	108.5	102.7	
70	139.4	135.0	130.3	124.1	112.8	105.7	
75	146.4	142.0	141.4	135.8	123.8	112.7	
80	155.1	150.4	151.1	145.7	143.9	134.7	
85	166.6	162.2	161.9	156.8	158.5	152.5	
90	184.3	170.1	178.5	170.3	174.1	168.2	

			Table 3. Continued				
(d) Mixtures of Gasoline and the Additive t-Butanol in 10, 20, and 30% (vol/vol) Concentrations							
distillate volume	91 AI SQ gasoline plus 10% (vol/vol) tert-butanol (83.25 kPa)		91 AI SQ gasoline plus 20% (vol/vol) tert-butanol (83.80 kPa)		91 AI SQ gasoline plus 30% (vol/vol) tert-butanol (83.50 kPa)		
fraction (%)	T_k (°C)	$T_{\rm h}$ (°C)	<i>T</i> _k (°C)	$T_{\rm h}$ (°C)	$T_{\rm k}$ (°C)	$T_{\rm h}~(^{\circ}{\rm C})$	
5	71.3	65.4	72.0	67.3	72.4	69.3	
10	74.9	69.8	75.0	71.1	75.2	72.7	
15	79.2	75.0	78.5	75.1	78.2	76.1	
20	83.7	79.4	81.6	78.4	80.8	79.4	
25	88.3	83.2	84.5	81.5	82.9	81.7	
30	93.5	87.9	87.2	84.6	84.9	83.8	
35	98.5	92.7	89.7	86.4	86.5	85.3	
40	106.0	99.6	93.3	89.3	88.5	87.2	
45	112.9	106.6	97.2	92.3	89.9	89.1	
50	112.9	112.7	102.8	96.3	02.3	91.0	
55	124.0	112.7	111.8	104.8	05.7	03.4	
55	124.0	110.0	111.0	104.0	101.2	95.4	
65	120.9	123.0	122.5	110.5	101.5	90.0	
05	134.0	128.8	129.9	125.9	115.0	102.9	
70	139.9	134.7	136./	131./	129.1	121.2	
75	147.4	142.0	144.1	138.6	138.6	132.8	
80	155.6	150.3	152.3	147.1	147.6	141.5	
85	167.9	162.8	165.2	159.5	160.9	154.8	
90	189.5	171.5	182.1	173.7	177.7	169.4	
	(e) Mixtures of	Gasoline and the Add	itive Isobutanol in 10,	20, and 30% (vol/vol)) Concentrations		
1' .''11 . 1	91 AI SQ gasoline plus 10% (vol/vol) isobutanol (83.35 kPa)		91 AI SQ gasoline plus 20% (vol/vol) isobutanol (83.62 kPa)		91 AI SQ gasoline plus 30% (vol/vol) isobutanol (83.87 kPa)		
fraction (%)	<i>T</i> _k (°C)	$T_{\rm h}~(^{\circ}{\rm C})$	<i>T</i> _k (°C)	$T_{\rm h}$ (°C)	<i>T</i> _k (°C)	$T_{\rm h}~(^{\circ}{\rm C})$	
5	76.3	69.7	77.3	71.4	80.8	75.3	
10	80.3	74.8	81.9	76.2	85.3	80.5	
15	85.6	80.2	87.0	82.1	90.9	86.5	
20	90.9	85.6	92.0	87.5	95.6	92.1	
25	95.3	90.4	95.9	92.2	98.8	95.5	
30	00.2	94.7	99.0	95.5	101.3	08 7	
35	102.6	07.0	101.4	08.0	101.5	101.0	
40	102.0	101.7	101.4	101.0	103.1	101.0	
40	100.2	101.7	105.7	101.0	104.9	103.2	
43	109.7	104.9	105.8	105.1	100.2	104.0	
50	115./	107.0	107.7	104.9	107.0	105.0	
33	118.9	112.0	109.8	100.7	109.0	100.1	
6U	125.2	11/./	112.4	108.9	110.4	107.5	
65	131.8	125.0	116.3	111./	111.9	108.7	
70	139.4	132.7	124.1	117.2	115.0	111.2	
75	146.7	142.6	138.6	131.9	119.5	115.6	
80	154.5	152.8	150.4	146.9	134.5	125.5	
85	164.7	163.0	162.4	158.9	159.5	154.4	
90	181.1	175.8	178.0	172.7	176.0	172.1	

^{*a*} The uncertainties are discussed in the text. These temperatures have been corrected to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided in parentheses to allow for recovery of the actual measured temperatures.

is observed whenever a single component dominates the mixture (as is the case with the mixtures presented here), it is especially pronounced when azeotropes are present. In earlier work, we demonstrated that a further effect is observed when one plots the distillation curves as T_k and T_h . In the region of the distillation curves where the azeotropic mixtures exist, there will be a convergence of T_k and T_h . In Figure 2, we plot T_k and T_h for a mixture of the gasoline with 20% 1-butanol and see such a convergence. The data of Tables 2 and 3 provide this quantitively. For the straight gasoline, between distillate volume fractions 0.2 and 0.6, the difference in T_k and T_h is on average 6.7 °C, while for the same region of the 20% 1-butanol mixture, it is 3.8 °C. This convergence is expected because 1-butanol will form azeotropes with a number of the components in the gasoline.^{42,57} This behavior is noted only for distillate volume fractions between 0.2 and 0.6 because it is in this region that the mixtures remaining in the distillation flask are reaching the azeotropic concentrations and the effect must disappear when the butanol additive has distilled out of the mixture.

It might at first be surprising that the azeotropic convergence is very subtle, because our observation of the convergence with gasoline plus methanol was very dramatic. In that case, in the azeotropic region, T_k and T_h converged to the extent that they overlaid on one another. The more subtle behavior here can be understood, however, by the respective phase diagrams of the butanols with the constituents of gasoline. The temperature of the azeotropic state point produced by the addition of methanol to a hydrocarbon is typically rather far from the boiling temperatures of the hydrocarbons themselves. For example, for cyclohexane, *n*-heptane, *n*-octane, and toluene, the temperature displacements are 53, 39, 63, and 47 °C, respectively. For 1-butanol with these same hydrocarbons, the displacements are 3, 7, 16, and 5 °C, respectively. Thus, the effect of 1-butanol

⁽⁵⁷⁾ Hadler, A. B.; Ott, L. S.; Bruno, T. J. Study of azeotropic mixtures with the advanced distillation curve approach. *J. Phys. Chem. B*, manuscript submitted.

Table 4. Summar	v of the Results of H	vdrocarbon Family	V Calculations Based on the	e Method of ASTM D-2789
	J of the flestites of fi	, al ocal soli i anni	Curculations Dubed on the	

distillate volume	naraffins	monocyclo paraffins	dicycloparaffins	alkyaromatics	indanes and	nontholonos
faction (%)	(vol %)	(vol %)	(vol %)	(vol %)	tetralins (vol %)	(vol %)
			(a) 10% 1-Butanol			
0.025	54.3	30.0	2.4	13.1	0.2	0.0
20	49.4	25.7	2.6	21.9	0.4	0.0
40	43.9	20.8	2.5	32.0	0.7	0.1
60	36.1	16.1	2.1	44.3	1.2	0.1
80	23.1	9.6	1.8	61.2	3.8	0.4
residue	20.9	8.2	1.5	57.4	9.3	2.7
			(b) 20% 1-Butanol	<i>.</i>		
0.025	57.5	33.5	2.1	6.8	0.0	0.0
20	48.7	26.4	2.7	21.8	0.3	0.0
40	42.8	20.9	2.3	33.2	0.7	0.0
60	33.8	17.4	2.0	45.6	1.2	0.1
80	19.1	9.3	1.5	65.8	4.1	0.2
residue	19.5	8.0	1.4	57.8	10.2	5.1
0.025	50 7	22.7	(c) 30% 1-Butanol	5 4	0.0	0.0
0.025	58.7 40.2	55.7 25.7	2.2	5.4 22.1	0.0	0.0
20	49.2	20.2	2.0	22.1	0.5	0.0
40 60	40.7	20.3	2.3	55.8 A7 7	0.8	0.1
80	20.8	12.0	1.5	47.7	2.4	0.1
residue	18.6	7.3	1.5	61.1	9.2	2.4
· · · · · · · · · · · · · · · · · · ·	10.0		(d) 10% 2 Butanol		>- -	
0.025	54 7	28.3	(u) 10 /0 2-Butanon 2 4	14.2	0.2	0.1
20	49.3	25.2	2.7	22.3	0.4	0.0
40	43.8	19.8	2.6	33.0	0.7	0.0
60	35.0	14.1	2.2	47.3	1.3	0.1
80	19.9	8.5	1.7	65.2	4.4	0.3
residue	19.8	7.5	1.4	58.2	10.0	3.1
			(e) 20% 2-Butanol			
0.025	55.8	31.1	1.8	11.3	0.0	0.0
20	50.2	26.7	2.7	20.1	0.3	0.0
40	44.8	20.8	2.6	31.3	0.5	0.0
60	37.2	16.2	2.3	43.2	1.0	0.1
80	21.7	9.3	1.8	63.0	4.0	0.2
residue	20.3	7.9	1.5	57.2	10.0	3.1
			(f) 30% 2-Butanol			
0.025	55.0	26.6	2.0	16.1	0.2	0.1
20	48.3	25.8	2.7	22.9	0.3	0.0
40	41.2	20.0	2.6	35.5	0.7	0.1
60	34.8	16.4	2.3	45.3	1.1	0.1
80	21.3	9.5	1.7	65.1	2.3	0.1
residue	17.0	0.8	1.5	02.3	9.5	2.5
0.025	541	21.0	(g) 10% tert-Butanol	11.0	0.2	0.1
0.025	50.2	31.2 26.4	2.5	20.4	0.2	0.1
20	30.5	20.4	2.5	20.4	0.5	0.0
40 60	34.7	14.1	2.0	16.8	1.0	0.1
80	19.4	8.2	1.6	65.6	47	0.2
residue	23.2	8.7	1.6	51.1	10.9	4.5
			(h) 20% tert-Butanol			
0.025	55.7	31.5	2.1	10.5	0.1	0.0
20	50.5	26.8	2.5	19.8	0.3	0.0
40	46.6	22.4	2.5	28.0	0.4	0.0
60	37.7	15.8	2.4	43.0	1.1	0.1
80	22.4	9.5	1.8	62.1	3.9	0.2
residue	20.5	8.0	1.5	57.2	9.9	3.1
			(i) 30% tert-Butanol			
0.025	55.3	30.6	2.2	11.7	0.2	0.0
20	49.0	26.6	2.5	21.5	0.3	0.0
40	44.1	21.9	2.5	30.9	0.6	0.1
60	40.8	19.3	2.3	37.0	0.7	0.0
80	22.5	9.5	1.9	62.3	3.6	0.2
residue	17.5	6.9	1.4	61.7	9.8	2.8
0.025	~	20.1	(j) 10% Isobutanol	10.0	0.0	0.1
0.025	54.1	30.1	2.4	13.2	0.2	0.1
20	49.1	25.5	2.5	22.4	0.4	0.0
40 60	44.1 24.9	20.0	2.5	32.1 47 2	0.0	0.0
80	34.0 10.2	14.J & A	2.1 1 7	47.3 66.1	1.5 A A	0.1
residue	19.2	7 4	1.7	57.9	10.4	33
	- / • /	/	4.1	01.9		0.0

distillate volume faction (%)	paraffins (vol %)	monocyclo paraffins (vol %)	dicycloparaffins (vol %)	alkyaromatics (vol %)	indanes and tetralins (vol %)	napthalenes (vol %)	
(k) 20% Isobutanol							
0.025	54.6	29.7	2.2	13.3	0.2	0.0	
20	50.3	26.2	2.5	20.6	0.3	0.0	
40	43.8	20.2	2.4	32.8	0.7	0.0	
60	37.3	16.8	2.0	42.8	1.1	0.1	
80	20.6	8.9	1.7	64.6	4.0	0.2	
residue	19.0	7.2	1.3	60.4	9.4	2.7	
(1) 30% Isobutanol							
0.025	53.5	29.5	2.1	14.6	0.3	0.0	
20	51.0	26.8	2.5	19.4	0.3	0.0	
40	43.1	20.7	2.2	33.2	0.7	0.0	
60	36.0	17.7	1.9	43.1	1.2	0.1	
80	24.0	11.7	1.5	60.4	2.2	0.1	
residue	18.5	7.1	1.3	61.4	9.2	2.5	

Table 4. Continued

on the mixture boiling points is clearly more subtle. We chose these four hydrocarbons for comparison because they are common to both methanol and 1-butanol among the known azeotropic binaries. No other measurements of azeotropic binary mixtures common to the butanols and the constituents of gasoline could be found in the literature.

At the last distillate volume fraction, we observe evidence of thermocouple lift-out. Here, the curves are seen to increase in temperature in response to the surrounding walls rather than in response to the fluid. This behavior signals the end of the ADC experiment, and these temperatures would not be used in any thermophysical property model development.

Composition Channel Information. Analysis of Distillate Fractions. While the gross examination of the distillation curves is instructive and valuable for many design purposes, the



Figure 1. Distillation curves of 91 AI SQ gasoline with mixtures of 1-butanol, *i*-butanol, 2-butanol, and *t*-butanol. Here, we present T_k , the temperature measured directly in the fluid. The uncertainties are discussed in the text.



Figure 2. Plot of the distillation curves of gasoline plus 20% (vol/vol) 1-butanol, presented as $T_{\rm k}$ and $T_{\rm h}$. Note that, between distillate volume fractions of 0.2 and 0.6, there is a slight azeotropic convergence in temperature. The uncertainties are discussed in the text.

composition channel of the ADC approach can provide even greater understanding and information content. One can sample and examine the individual fractions as they emerge from the condenser, as discussed in the Introduction. Following the analytical procedure described in the Experimental Section, samples were collected and prepared for analysis. Chemical analyses of each fraction were performed by gas chromatography with flame ionization detection and mass spectrometric detection.

The analysis of alcohols, such as the butanols, is less than facile by either method, especially when the concentrations are low (as they are when 7 μ L aliquots of distillate are withdrawn and dissolved in a solvent for subsequent analysis). The very weak parent ions in primary and secondary alcohols and the absence of parent ions in tertiary alcohols make the analysis by mass spectrometry difficult and uncertain.49,50 The analysis by flame ionization detection is also problematic. One can examine the relative flame ionization detection response factors (with respect to *n*-heptane) to understand the difficulty: 1-butanol, 0.66; 2-butanol, 0.63; *i*-butanol, 0.68; and *t*-butanol, 0.74.58 Clearly, the analysis for the butanols by either method is more uncertain at the concentration levels attempted in this work than for the hydrocarbon species that we have measured in previous work. When analyzing distillate fractions specifically for the butanols, we applied low split ratios (25:1) and larger injection volumes (4 μ L). The usual procedures for trace analysis by gas chromatography, such as splitless injection and solvent focusing, were not applicable to these mixtures because many peaks elute in the region of the butanol peaks and the solvent eluted after the gasoline components. These difficulties result in an uncertainty in the quantitative determination of the butanols of approximately 15%.

As an example of the quantitative analysis of a butanol and its relation to the distillation curve, we present in Figure 3 the results for 1-butanol at selected distillate cuts. We note that, at the first drop (representative of the 0.025 distillate fraction), we observe very little 1-butanol, and indeed, for the 10% starting mixture, it is nearly undetectable. The concentrations increase as expected for the 0.2 and 0.4 distillate fractions, in the expected ratio corresponding to the starting mixture concentration, with the 30% mixture showing more 1-butanol than the 10% mixture. Then, at the 0.8 distillate volume fraction, we note that for the 10 and 20% mixtures there is a decrease in the 1-butanol concentration, while there is a (continued) increase in the 30%





Figure 3. Histogram plot showing the results of the analysis for 1-butanol as a function of the distillate volume fraction for the three starting mixtures (10, 20, and 30% 1-butanol). There is no detectable 1-butanol in the residue left behind after the distillation. The uncertainty is discussed in the text.

mixture. This pattern in 1-butanol concentration is consistent with and, in fact, explains what is observed late in the distillation curve (at a distillate volume fraction of approximately 0.8). Here, we note that, for the 30% mixture, the departure from the straight gasoline is maximized. In contrast, for the 20% mixture, the curve has closely approached the gasoline curve, while for the 10% mixture, the convergence is nearly complete as the 1-butanol distills out of the mixture. Traces of the additive persist into the 0.9 distillate fraction, but none can be detected in the residue left behind after the distillation is complete. In this way, the composition-explicit data channel can provide insight into the structure of distillation curves.

Hydrocarbon-Type Classification. The distillate fractions of 91 AI summer gasoline with the butanols were examined for hydrocarbon types by use of a mass spectrometric classification method summarized in ASTM D-2789.59 In this method, one uses mass spectrometry [or gas chromatography-mass spectrometry (GC-MS)] 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 has significant limitations, it is of practical relevance to many complex fluid analyses and is often applied to gas turbine fuels, diesel fuels, rocket propellants, and missile fuels. The uncertainty of this method, and the potential pitfalls were treated earlier. As discussed above, the solutions were prepared from withdrawing 7 μ L samples of distillate fraction that were dissolved in a known mass of solvent (n-hexane). This solvent was chosen because it causes no interference with the sample constituents. For the hydrocarbon-type analysis of the distillate fraction samples, 1 μ L injections of these solutions were made into the GC-MS. Because of this consistent injection volume, no corrections were needed for the sample volume.

The results of these hydrocarbon-type analyses for mixtures of the 91 AI summer gasoline with the butanols are provided in Table 4, and a graphical example for the 20% mixtures of the four butanols is provided in Figure 4. All of the distillate fractions presented in the table were measured in the same way (m/z range from 15 to 550 relative molecular mass units

⁽⁵⁹⁾ American Society for Testing and Materials (ASTM). Standard test method for hydrocarbon types in low olefinic gasoline by mass spectrometry, ASTM Standard D 2789-04b. *Book of Standards*; ASTM: West Conshohocken, PA, 2005; Vol. 05.01.



Figure 4. Plots showing the hydrocarbon family distribution in mixtures of 91 AI summer gasoline with (a-d) 20% (vol/vol) 1-butanol, *i*-butanol, 2-butanol, and *t*-butanol. The uncertainty is discussed in the text.

gathered in scanning mode, with each spectrum corrected by subtracting trace air and water peaks). The figure showing the results for the 20% mixtures is representative of the behavior of gasoline plus butanol mixtures. We note that the volume fractions of the paraffins and monocycloparaffins decrease uniformly as the distillation proceeds, while the dicycloparaffins increase slightly from a low level to peak in the middle of the distillation, before decreasing again. The volume fractions of the alkylbenzenes increase sharply, while the indanes and tetralins increase slightly from a very low level. The naphthalenes are consistently at a low or trace level. This behavior is consistent with our earlier measurements on the 91 AI winter-quarter gasoline and mixtures of this fluid with methanol.

Conclusions

In this paper, we have presented measurements of the volatility of a typical gasoline with mixtures of four butanols. The significance of these mixtures is that they anticipate part of the thermophysical property knowledge that will be required if biobutanol were to be adopted as a component of motor fuel. These data have been developed by the application of the ADC metrology. The temperature data are thermodynamically con-

sistent and can therefore be used in the development of equations of state models for these complex fluids, as we have demonstrated for other mixtures. These temperature data are augmented by the compositional information provided by the ADC approach. We anticipate the development of thermodynamic models for such mixtures in the near future.

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