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Application of the Advanced Distillation Curve Method to the Development of Unleaded Aviation Gasoline

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The primary fuel used within the general aviation industry is a petroleum-based gasoline blended with small amounts of tetraethyl lead (a lead-based additive used to increase the octane number of gasoline without affecting its performance) called 100LL aviation gasoline. Lately, concern has mounted regarding the health effects of leaded aviation gasoline (typically called avgas). This concern, in addition to the increasing price of 100LL, has led to research involved with developing an unleaded avgas with the ability to meet performance regulations and safely operate the entire general aviation fleet without engine modifications. In this paper, we assess the vapor liquid equilibrium of two newly developed unleaded avgas fluids. For complex fluids, such as gasoline, the distillation curve provides the most practical approximation of this property. The distillation curves of these two fluids were measured by use of the advanced distillation curve method. The advanced distillation curve method uses temperature, volume, and pressure measurements of low uncertainty, providing true thermodynamic state points that can be modeled with an equation of state, greatly aiding in the design of new fuels. In addition, the advanced distillation curve method incorporates a composition-explicit data channel, allowing for precise qualitative identification as well as quantitative analyses of each distillate fraction. In this paper, we present the distillation curves and track the composite enthalpy of combustion of the two unleaded aviation gasolines throughout their distillation. The results from this study are compared to previous vapor liquid equilibrium and composite enthalpy of combustion measurements performed on 100LL aviation gasoline.

Introduction

The high-compression reciprocating and rotary engines used in ~30% of the general aviation fleet require an appropriate fuel to meet the standards and safety regulations set by the engine manufactures and the Federal Aviation Administration (FAA). These aircrafts operate on the same basic principles as spark-ignition engines in automobiles but have much higher performance and reliability requirements. The high compression ratios and extreme operating conditions encountered by these aircraft engines require a fuel with a high octane number and one that is regulated to meet performance requirements (i.e., volatility, octane number, and energy content) over a wide range of operating conditions.[1,2] The primary aviation gasoline (avgas) used today, which meets these two important requirements is 100LL, a hydrocarbon mixture blended with small amounts of tetraethyl lead (TEL; an organometallic additive used to increase the octane number of gasoline). Avgas 100LL performs with a lean/rich octane number of 100/130. The current standard and specification of 100LL requires that the lead content be below 0.56 g/L.[3]

Following the U.S. Clean Air Act of 1996, lead-based additives were banned in automobile gasoline, while an exemption was given for leaded avgas.[4] Since then, avgas consumption has become one of the main contributors to environmental lead pollution, estimated as emitting ~565 000 kg of lead in 2002.[5] Recently, the potential health hazards of lead (decreased child brain development, reduced adolescent IQ,[6] and its link to cancer[7]) have been of much concern. In 2008, the U.S. Environmental Protection Agency (EPA), concerned with the health effects of lead exposure, altered a 30 year standard and reduced the limit of allowable lead in air by 90% to $0.15 \mu g/m^3$. This mandate requires all lead-emitting industries (including general aviation) to begin reducing their lead emissions by 2011 and meeting the new allowable limit by 2017.[8]

In addition to the aforementioned health concerns, leaded aviation gasoline can result in metallic lead deposits on the spark plugs and buildup in the engine, leading to spark plug

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fouling, valve and piston ring sticking, and cylinder wall glazing.[9] Also, 100LL avgas is expensive (currently ~$4−5/gallon), resulting in high operational costs for the pilot, especially when used in high-performing aircrafts that consume large amounts of fuel (10−40 gallons/h depending upon flight conditions). Indeed, although only 30% of the general aviation aircrafts require 100LL, the fuel usage by these aircrafts account for 70% of the avgas that is used.

There are a number of factors influencing the price of 100LL, including the lack of production of TEL (only one manufacturer is producing TEL since the leaded automotive fuel ban), the relatively small quantity of 100LL produced in comparison to automobile gasoline (on the basis of the demand), the separate storage and transportation needed for TEL-blended aviation gasoline, and the extra care and safety preparations needed to handle TEL-blended fuels. These factors have prompted some operators of the low-compression engine aircraft (comprising ~70% of the entire aviation fleet) to acquire supplemental-type certificates (STCs) allowing engine modifications to run on unleaded automobile gasoline.[10] Unfortunately, automobile gasoline is not subject to the quality control desired by many pilots for safe operation. In addition, most automobile gas now contains oxygenates (e.g., ethanol) that can be detrimental to general aviation aircraft engines. Also, the high-compression engines that burn considerably more fuel are unable to operate on lower octane automotive gasoline. Another potential issue is vapor lock, which usually occurs upon engine start-up but which can also occur in flight. This problem is far more common when automotive gasoline is used in general aviation aircrafts. As a result of these issues, it is rare for STCs to be granted. For these reasons, much effort has been expended to produce an unleaded drop-in replacement for 100LL avgas.[11,12]

Two potential fluids recently developed as possible replacements for 100LL include UL94 (94 lean octane number, unleaded) and UL102 (104 lean octane number, unleaded, bioderived). We note that the designation UL102 signifies that this fluid has a lean octane number target of 102, although current formulations have been measured somewhat higher at 104. The UL94 avgas, produced from conventional blending stocks, provides a lower octane than 100LL; however, it is an improvement compared to the non-oxygenated automobile gas (with lean octane numbers ranging from ~82−87) used in aircrafts that carry an STC. UL102 avgas was produced from cellulosic biomass, including switch grass and agricultural waste, and provides a lean octane number higher than that of 100LL; thus, it has the potential to operate the entire general aviation fleet.[13]

Knowledge of the vapor liquid equilibrium (VLE) properties of gasoline is vital in understanding its performance and limitations, and such information can greatly assist in the design of new energy-efficient and less polluting replacements. For complex fluids, such as gasoline, the distillation curve provides the most practical approximation of this property.

For example, a distillation curve has a significant value in describing the performance of a petrochemical, including engine starting ability, fuel system icing and vapor lock, fuel injection timing, and fuel autoignition.[14,15] For avgas, the distillation curve can provide valuable information pertaining to the volatility and VLE of the fuel during high engine temperatures (i.e., during a steep climb) as well as at reduced pressures (i.e., when the aircraft is cruising at high altitudes). Fundamentally, the distillation curve provides an avenue to the development of an equation of state (EOS) model for the fluid, which is an important step for the design of new fuels.

In earlier work, the method and apparatus for advanced distillation curves (ADCs) was described and has proven to be especially applicable to the characterization of fuels.[16−22] This method offers significant improvements over previous approaches, such as ASTM D-86, and can be applied to any complex fluid.[16−23] It features (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 EOS, (3) temperature, volume, and pressure measurements of low uncertainty suitable for EOS 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.[16−18,20−22,24]

A previously published study on 100LL avgas describes how the ADC method was used to assess the VLE of the fluid while measuring the energy content and tracking the TEL concentration as a function of the distillate volume fraction.[25] The current study describes the results of a similar analysis for the potential replacements, UL94 and UL102. Thermodynamically consistent distillation curves were measured for each fuel with the ADC protocol. The composition-explicit data channel of the ADC was applied to both samples. Analyses by gas chromatography (GC) coupled with mass spectrometry (MS) and flame ionization detection (FID) were performed for each distillate fraction. These compositional analyses were then used to derive a composite enthalpy of combustion for each of the distillate fractions, allowing for the change of the energy content of the fuel during distillation to be determined. This type of measurement is important because fuels typically undergo droplet combustion, in which vaporization and subsequent burning of the outside of the fuel droplet results in a shrinking volume that changes in composition and energy content similar to that of a fluid undergoing distillation. The measurements collected in this study, when

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compared to previous measurements performed on 100LL avgas, provide much needed information to aid in the development and implementation of an unleaded drop-in replacement avgas.

Experimental Section

Prior to any distillation measurements, the general composition of each sample of unleaded avgas was studied by a gas chromatographic method (30 m capillary column of 5% phenyl/ 95% dimethyl polysiloxane, with a thickness of 0.25 μm) with mass spectrometric detection. The GC analysis of both unleaded avgas mixtures was performed by passing a He carrier gas at 55.2 kPa (8 psi, gauge) through the column while undergoing sample-dependent temperature programming: the UL94 avgas (40 °C soak for 10 min) and the UL102 avgas (40 °C soak for 3 min, then increased to 60 °C at a rate of 2 °C/min, and followed by a 3 min soak).[26] After elution of all sample components, the column was subjected to ballistic temperature programming to 300 °C, ensuring complete removal of the solvent (*n*-tetradecane) and trace contaminates from the column prior to the next sample injection. MS was used with the aid of the National Institute of Standards and Technology/Environmental Protection Agency (NIST/EPA) mass spectral database,[27,28] following column separation to provide compositional information by identification of peaks in the resulting chromatogram.

The components of the two new unleaded avgas mixtures are presented along with the 100LL composition in Table 1.[25] These analytical results (compositions and relative quantities of components) are consistent with our knowledge of the nature of the feedstock and the processing used to obtain each fluid. We will note later in this paper that these analyses are also consistent with the results from the composition-explicit data channel of the ADC. No dye or taggent was found in any of the new unleaded avgas fluids.

ADC Measurements. The ADC apparatus and procedure has been described in much detail in previous papers;[16,17,21,22,24,29,30] thus, only a brief description (as it applies to this study) will be given here. For each measurement, 200 mL of avgas was placed in a boiling flask. The thermocouples were then inserted into the proper locations to monitor the kettle temperature (T_k), the temperature in the fluid, and the head temperature (T_h), the temperature at the bottom of the takeoff position in the distillation head. Enclosure heating was then commenced with a model-predictive temperature controller.[20] The heating profile was designed to be of similar shape to that of the distillation curve but leads the distillation curve by approximately 20 °C. As heating progressed, the volume of the distilled liquid was measured in a level-stabilized receiver. Measurements of the kettle and head temperatures were recorded at specific distillate volume fractions to construct the distillation curve. For distillate fraction sample analysis, ∼7 μL sample aliquots were collected at the receiver adapter hammock. Over the course of the work, four distillation curves were measured for each avgas sample. The temperatures for each distillate fraction were averaged across the four measurements, and the standard deviations were also determined.

Because the measurements of the distillation curves were performed at an elevation of ∼1655 m above sea level at local ambient atmospheric pressure (typically 83 kPa, measured with

Table 1. Listing of Major Components Found in Neat Samples of UL94, UL102, and 100LL Avgas

compound	CAS number	area percentage
(a) UL94		
2-methyl propane (isobutane)	75-28-5	0.2
butane	106-97-8	1.9
2-methyl butane	78-78-4	6.7
2,3-dimethyl butane	79-29-8	1.0
3-methyl pentane	96-14-0	0.2
2,4-dimethyl pentane	108-08-7	2.0
2,3-dimethyl pentane	565-59-3	3.8
2,2,4-trimethyl pentane	540-84-1	52.4
2,4-dimethyl hexane	589-43-5	3.0
2,3,4-trimethyl pentane	565-75-3	2.5
2,3,3-trimethyl pentane	560-21-4	3.0
2,3-dimethyl hexane	584-94-1	1.0
toluene	108-88-3	20.7
2,2,5-trimethyl hexane	3522-94-9	1.6
2,4,4-trimethyl hexane	16747-30-1	0.0
2,3,5-trimethyl hexane	1069-53-0	0.1
(b) UL102		
2-methyl propane (isobutane)	75-28-5	tr[a]
2,2-dimethyl propane	463-82-1	0.1
2-methyl butane	78-78-4	18.7
1-ethyl-3-methyl benzene	620-14-4	tr[a]
1,3,5-trimethyl benzene[b]	108-67-8	81.2
(c) 100LL		
hexane	110-54-3	0.2
2,4-dimethyl pentane	108-08-7	5.1
2,2,3-trimethyl butane	464-06-2	1.1
2,3-dimethyl pentane	565-59-3	9.7
2,2,4-trimethyl pentane	540-84-1	12.1
2,4-dimethyl hexane	589-43-5	13.9
2,3,4-trimethyl pentane	565-75-3	14.4
x,y,z-trimethyl pentane[c]	NA	8.1
x,y,z-trimethyl pentane[c]	NA	3.1
2,3-dimethyl hexane	584-94-1	3.5
toluene	108-88-3	4.7
2,2,5-trimethyl hexane	3522-94-9	5.0
2,3,5-trimethyl hexane	1069-53-0	1.3
2,2,6-trimethyl decane	62237-97-2	1.4
x,y,z-trimethyl heptane[c]	NA	1.4
x,y,z-trimethyl heptane[c]	NA	2.3
2,2-dimethyl decane	17302-37-3	0.7
tetraethyl lead	78-00-2	0.7

[a] The area percentages labeled tr represent compounds that were detected at trace amounts. [b] The 1,3,5-trimethyl benzene peak had a shoulder comprised of 1,2,4-trimethyl benzene. [c] The isomerization of the compounds listed as *x,y,z*-trimethyl pentane and *x,y,z*-trimethyl heptane could not be ascertained on the basis of the mass spectra alone.

an electronic barometer with an uncertainty of 0.003 kPa), temperature readings were corrected for what should be obtained at standard atmospheric pressure. The pressure corrections were performed with the modified Sydney Young equation, in which the constant term was assigned a value of 0.000 119.[30−33] This value corresponds to a *n*-alkane carbon chain of 8, which is a reasonable approximation for aviation gasoline.

Results and Discussion

Table 1 shows that the two unleaded avgas mixtures vary widely in their composition. The UL94 avgas is primarily composed of branched alkanes, whereas the GC analysis of the UL102 avgas provided detection of only three major

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Table 2. Initial Boiling Behavior of UL94, UL102, and 100LL Avgas

	UL94 avgas (°C) (83.5 kPa)	UL102 avgas (°C) (83.2 kPa)	100LL avgas (°C) (83.3 kPa)
onset	47.8	47.9	57.9
sustained	65.5	NA	64.3
vapor rising	69.3	54.7	68.1

compounds: 2-methyl butane (18.7% area) and 1,3,5-trimethyl benzene with a shoulder composed of 1,2,4-trimethyl benzene (81.2% total area). Resolution of the 1,2,4- and 1,3,5-trimethyl benzenes could not be accomplished with the column used in this analysis. The use of a liquid crystalline stationary phase (or mesophase) might provide baseline resolution, but such a separation was not required for our purpose.[26]

Both of the new unleaded fuels have significant compositional differences when compared to the 100LL avgas. For example, there are fewer heavier branched alkane components (i.e., *x,y,z*-trimethyl hexane and larger) in the UL94 and UL102 avgas than in the 100LL mixture. Another difference is the much higher concentration of aromatics found in the unleaded avgas (i.e., toluene in the UL94 avgas and 1,3,5-trimethyl benzene in the UL102 avgas), which have high octane numbers and can act as a replacement to TEL to increase the octane number of the fuel and reduce its engine knocking tendencies.

Initial Boiling Temperatures (IBTs). During the initial heating of each sample in the distillation flask, the fluid behavior was observed. Direct observation through the bore scope ports allowed for the measurement of the onset of the boiling behavior for each fluid. Typically, during the earlier stages of measurements, the first bubbles will appear intermittently and are rather small. These bubbles cease if the stirrer is stopped momentarily. The temperature at which this is observed is called the onset temperature. Sustained bubbling, which occurs subsequent to onset, is characterized by larger, more vigorous bubbles and is still observed when the stirring is briefly stopped. Finally, vapor is observed to rise into the distillation head, causing an immediate response on the T_h thermocouple. This temperature, called the vapor rise temperature, has been shown to be the IBT of the fluid. Furthermore, this temperature is of low uncertainty and thermodynamically consistent and can be modeled theoretically with an EOS.[34,35]

The initial temperature observations of each unleaded avgas are summarized in Table 2. These values are the average of four separate measurements. The uncertainty (with a coverage factor $k = 2$) of these measurements has been discussed in detail in previous papers and is approximately 2 °C in the onset and sustained bubbling temperatures and approximately 0.2 °C in the vapor rise temperature.[21] For comparison, the initial temperature observations previously made on 100LL avgas are also included in Table 2.[25]

It is interesting to note the lower onset temperatures of the two unleaded avgas mixtures compared to that of the 100LL avgas. As indicated in Table 1, the two unleaded fuels have higher concentrations of more volatile components than the 100LL avgas. This explains the lower onset temperatures that were observed in the unleaded mixtures. The sustained boiling temperatures were similar for the UL94 and 100LL fuels; however, the sustained boiling temperature of UL102

Table 3. Distillation Curve Data for UL94, UL102, and 100LL Avgas

distillate volume fraction (%)	UL94 avgas (83.5 kPa)		UL102 avgas (83.2 kPa)		100LL avgas (83.5 kPa)	
	T_k (°C)	T_h (°C)	T_k (°C)	T_h (°C)	T_k (°C)	T_h (°C)
5.0	88.1	81.5	77.3	60.8	82.3	68.3
10.0	93.2	89.0	86.7	66.7	87.8	76.6
15.0	96.7	93.9	106.1	80.1	91.6	82.7
20.0	99.0	96.5	140.4	102.4	94.7	87.1
25.0	100.3	98.0	162.6	161.2	96.7	90.9
30.0	101.2	99.2	165.0	163.9	98.7	93.4
35.0	101.8	100.0	165.2	164.3	100.1	95.2
40.0	102.3	100.7	165.3	164.5	101.9	96.5
45.0	102.8	101.2	165.1	164.5	103.2	98.6
50.0	103.2	101.7	165.0	164.6	104.3	99.7
55.0	103.5	101.8	164.9	165.9	105.3	102.1
60.0	103.8	102.1	165.0	166.2	106.1	103.7
65.0	104.3	102.8	165.1	165.5	106.8	104.5
70.0	104.8	103.6	165.1	165.2	107.9	105.5
75.0	105.4	104.7	165.1	165.2	109.0	106.6
80.0	106.2	106.5	165.2	165.1	110.6	108.7
85.0	107.5	108.6	165.1	166.1	114.0	111.2
90.0	113.8	108.2	165.9	167.6		

could not be measured because of the fact that vapor rise and condensation occurred before boiling was sustained. This was due to the high concentration of 2-methyl butane in the UL102 avgas (which has a low boiling point of 27.8 °C) contributing to the initial vapor before consistent boiling was reached in the fluid. This is also indicated in Table 2 with the significantly lower vapor rise temperature of the UL102 avgas (54.7 °C) compared to that of the other two mixtures (68.7 °C average).

Distillation Curves. The distillation curve data, presented in both T_k and T_h, for all three aviation fuels are provided in Table 3. The T_k data are true thermodynamic state points, while the T_h data allow for a comparison to historical measurements. In this table, the data were found to be highly reproducible and comparable to the repeatability achieved in our previous work with the ADC. The average standard deviations for replicate temperatures of the UL94 and UL102 avgas were 0.30 and 0.23 °C, respectively. As previously reported, the average standard deviation of the temperatures of the 100LL measurements was 0.25 °C.[25] The uncertainty in the volume measurement that was used to obtain the distillate fraction was 0.05 mL in each case. These uncertainties were determined from replicate measurements. These low uncertainties, combined with the low uncertainty in the pressure measurement (0.003 kPa), provide VLE data that are true thermodynamic state points suitable for the development of an EOS.

Despite the low combined standard deviations in the measurements of the UL102 avgas (0.23 °C), replicate T_k measurements at 15 and 20% volume fractions resulted in somewhat larger deviations of 0.7 and 1.0 °C, respectively. These points occur as the composition is rapidly changing, causing the distillation temperatures to rapidly change. Any slight alteration in the 2-methyl butane concentration could cause significant alteration in the temperature measurements along this region of rapid temperature growth, accounting for the increased scatter.

A graphical comparison of the VLE, represented by the T_k distillation curve, for all three of the avgas mixtures is presented in Figure 1. Comparing the data in Table 3 and the distillation (T_k) curves in Figure 1, one can see similarities in the VLE between the UL94 and 100LL avgas mixtures.

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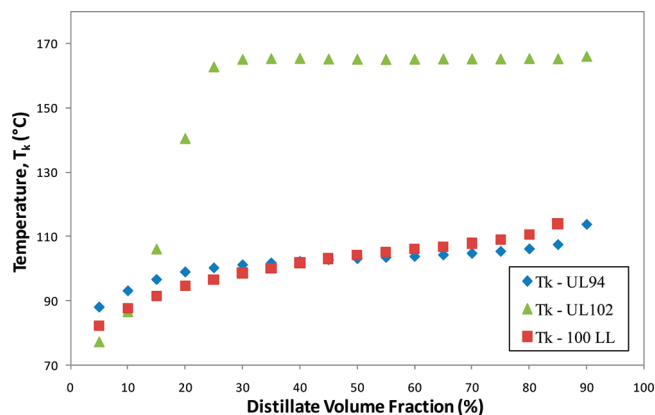
Figure 1. T_k distillation curve for the two unleaded avgas mixtures and the 100LL avgas previously reported by Lovestead et al.[25] The uncertainties are discussed in the text.

The boiling temperatures are very similar in magnitude and follow similar trends in curvature and slope. The UL102 avgas has a strikingly different distillation curve from those of the other fluids. Early in the curve, this fluid has lower boiling temperatures that rise steeply to a higher final boiling temperature. This is due to the high concentration of the uniquely different components. The second half of the UL102 distillation curve shows T_k leveling out as the boiling fluid is progressing into 1,2,4 and 1,3,5-trimethyl benzene, two very close isomers with similar thermophysical properties. This trend is expected and was noticed in previous studies analyzing binary mixtures when the concentration of the two components was varied.[16,36]

Distillate Composition. While the gross examination of the distillation curves is instructive and valuable for many design purposes, the composition channel of the advanced approach can provide an even greater understanding and information content. One can sample and examine the individual fractions as they emerge from the condenser. Sampling was performed by withdrawing ∼7 µL aliquots of distillate (at various distillate volume fractions) and diluting the aliquot in a known mass (∼1 mL) of *n*-tetradecane as a solvent. This fluid was chosen as a solvent because it had a long retention time and did not interfere with any of the GC peaks of the distillate fractions. Each of these fractions was analyzed by GC with a FID method using the same column and oven temperature program as described for the neat sample analysis.

To quantify the compositional mole fractions in the distillate cuts, calibration was performed with two standards. For the UL94 sample, the FID response of hexane was used to calibrate the instrument for all of the alkanes, while toluene was used in calibration to determine the concentration of toluene. For the UL102 sample, 2-methyl butane was used for calibration of the branched alkanes and 1,2,4-trimethyl benzene was used for the branched aromatics.

The bulk VLE properties of a complex fluid are directly related to the individual properties of the components that make up the fluid. Hence, the distillation curve, when used in concert with the composition-explicit data channel, can provide valuable information regarding the identification and interaction of the components that make up the complex fluid. For example, azeotropic activity can be detected
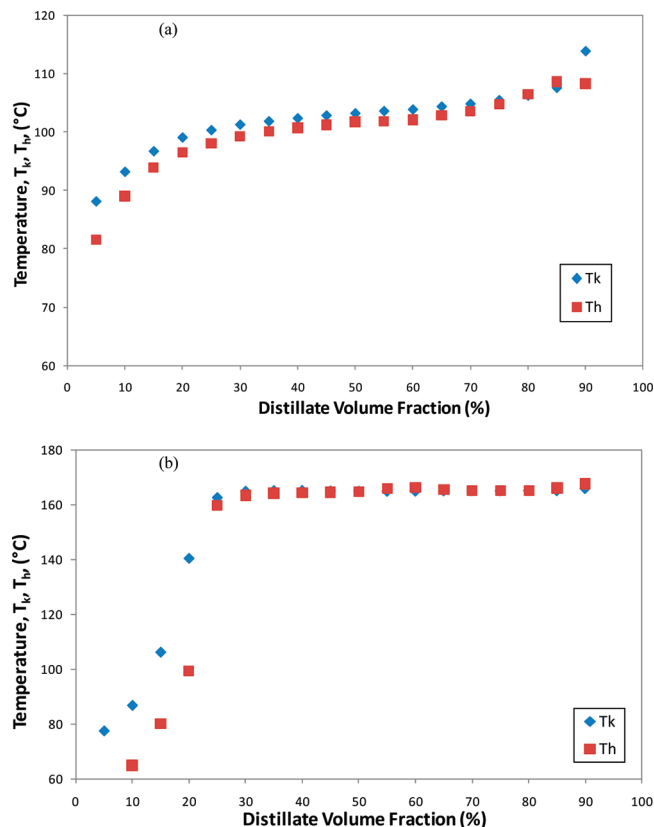

Figure 2. Distillation curve, T_k and T_h, for the (a) UL94 and (b) UL102 avgas. The uncertainties are discussed in the text.

through analysis of the distillation curve.[37] When azeotropes are present, T_k and T_h approach one another (called azeotropic convergence), because the mixture will then act as a pure fluid.[21,36] The T_k and T_h distillation curves for the UL94 and UL102 avgas are presented in panels a and b of Figure 2, respectively. As seen in Figure 2a, T_k and T_h for UL94 avgas converge between 45 and 70% distillate volume fractions. The composition channel analysis confirmed that the fluid at this volume fraction was not a single component but was comprised of multiple components, suggesting azeotropic activity as a probable explanation for the convergence of T_k and T_h in this region. In fact, an azeotrope has been reported in binary mixtures of toluene and 2,3,4-trimethyl pentane, two components present in the mixture at these volume fractions.[38,39] This behavior differed from that of the 100LL avgas in the previous study; no such convergence of T_k and T_h was observed, and no known azeotropic components were present.[25] Figure 2b shows that, for the UL102 avgas, T_h and T_k are the same following the 25% volume fraction. In this case, however, the composition channel analysis showed the presence of two components with nearly identical VLE properties (1,3,5 and 1,2,4-trimethyl benzene), thus behaving as a single component following the 25% volume fraction.

To help in visualizing the compositional progression during the distillation, a series of distillate chromatograms for both unleaded avgas mixtures are presented in Figure 3.

(36) Hadler, A. B.; Ott, L. S.; Bruno, T. J. *Fluid Phase Equilib.* **2009**, *281*, 49–59.

(37) Ott, L. S.; Bruno, T. J., *J. Chem. Educ.*, manuscript in preparation.
(38) Marschner, R. F.; Cropper, W. P. *Ind. Eng. Chem.* **1949**, *41*, 1357–1362.
(39) Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, K. *Azeotropic Data*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2004.
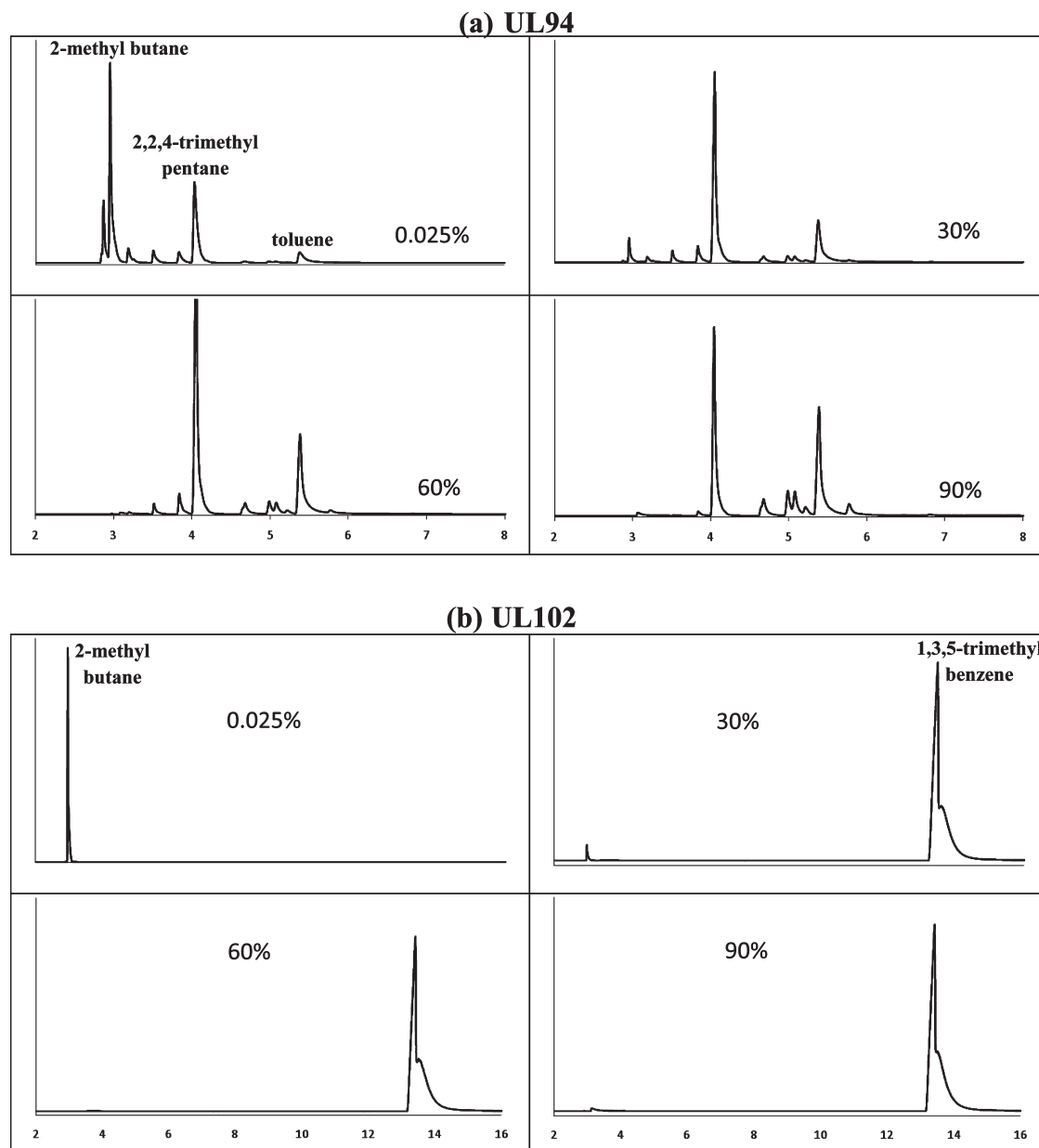
(a) UL94

(b) UL102

Figure 3. Chromatograms of the 0.25, 30, 60, and 90% distillate fractions of the (a) UL94 and (b) UL102 avgas.

For each chromatogram, the *x* axis represents the retention time in minutes and the *y* axis indicates the abundance presented in arbitrary units of area counts (voltage slices). It should be noted that the solvent (*n*-tetradecane) peak appeared at the end of each chromatogram, not interfering with the rest of the peaks, and was not included in Figure 3. In each series of chromatograms, one can see the gradual decrease of the lighter, more volatile components and the growth of the heavier, less volatile components as the distillation progressed. Concentrations of many of the major components in each unleaded avgas can be tracked in the series of chromatograms, including 2-methyl butane, 2,2,4-trimethyl pentane, and toluene in the UL94 sample and 2-methyl butane and 1,3,5-trimethyl benzene in the UL102 sample. As previously noted, the shoulder present on the 1,3,5-trimethyl benzene peak in the UL102 chromatograms was identified as 1,2,4-trimethyl benzene. Although baseline resolution for the 1,2,4-trimethyl benzene peak was not achieved, careful examination of the series of chromatograms

indicated an increase in peak size and, thus, an increase in the 1,2,4-trimethyl benzene concentration as the distillation progressed. Figure 3 illustrates just one fraction-by-fraction analysis strategy that can be applied to the composition-explicit data channel. It is possible to use any analytical technique that is applicable.

Hydrocarbon Classification. Another analytical technique that complements the above analyses examines the avgas samples for hydrocarbon types by use of a mass spectrometric classification method similar to that summarized in ASTM D-2789.[40] In this method, one uses MS (or GC−MS) to characterize hydrocarbon samples into six types. The six types or families include the following: paraffins, monocyclopar-affins, dicycloparaffins, alkylbenzenes (arenes or aromatics), indanes and tetralins (grouped as one classification), and

(40) 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.
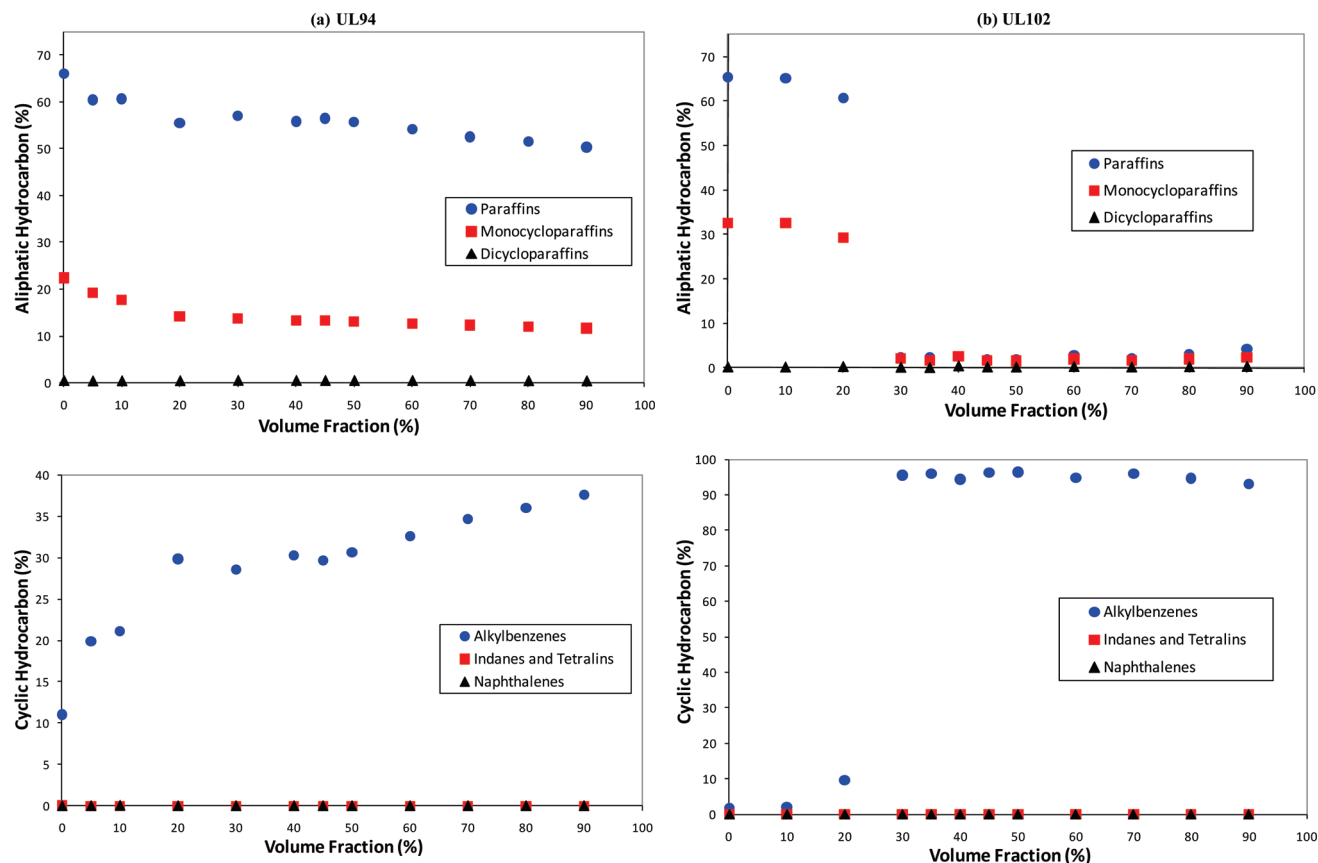
Figure 4. Plot of the aliphatic hydrocarbon family types resulting from the ASTM D-2789 analysis performed on the (a) UL94 and (b) UL102 avgas as a function of the distillate volume fraction.

naphthalenes. Although the method is specified only for application to low olefinic gasoline and 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.[41] The uncertainty of this method and the potential pitfalls were discussed earlier.[21] Once again, the sample solutions were prepared from ~7 μL aliquots of emergent distillate that were withdrawn from the sampling adapter at specified volume fractions and added to a vial containing a known mass of solvent (*n*-tetradecane). For the hydrocarbon-type analysis of the distillate fraction samples, 1 μL injections of these solutions were made into the GC−MS. Because of this consistent injection volume, no corrections were needed for sample volume.

The results of the hydrocarbon classification for the UL94 and UL102 avgas are presented in panels a and b of Figure 4. In both avgas mixtures, there is a clear change in the composition with the concentration of the aliphatic hydrocarbons decreasing and the cyclic hydrocarbons increasing. The trends represented in panels a and b of Figure 4 are both consistent with the trends shown in the series of chromatograms. In the UL94 avgas, the toluene concentration increases during distillation and this component is never completely removed. The normal boiling temperature of toluene (110.6 °C) is greater than the temperature measured at the 85% volume fraction (107.5 °C) in the distillation curve. Therefore, the later fractions become more concentrated with toluene as the

lighter components vaporize, as shown by the increasing percentage of the alkylbenzenes in Figure 4a. This trend of increasing alkylbenzenes is typical for gasoline, whereas the opposite has been measured for diesel fuels and kerosene.[21,22]

In Figure 4b, one can observe a dramatic change in the UL102 avgas hydrocarbons during distillation. The first drop up to 20% distillate volume fraction contains all aliphatic hydrocarbons (behaving like pure 2-methyl butane). The 30−90% distillate volume fraction contains nearly all aromatic hydrocarbons, with the fluid entirely composed of 1,2,4 and 1,3,5-trimethyl benzene.

The changes in composition with the distillate volume fraction of the two unleaded avgas mixtures are very different from the changes observed for 100LL avgas. This fluid has a constant hydrocarbon classification throughout the distillation, comprised primarily of paraffins (~75%) and monocycloparaffins (~23%).[25]

Distillate Fraction Energy Content. As we have demonstrated previously, it is possible to add thermochemical information to the distillation curve when the composition channel of data is used on specific distillate fractions.[21,22,29] This is performed by calculating a composite enthalpy of combustion based on the enthalpy of combustion of individual components of a distillate fraction and the mole fractions of those components. The enthalpy of combustion of the individual (pure) components is taken from a reliable database compilation.[42] Table 4 shows this type of analysis

(41) Shafer, L. M.; Striebich, R. C.; Gomach, J.; Edwards, T. Chemical Class Composition of Commercial Jet Fuels and Other Specialty Kerosene Fuels. Proceedings of the 14th AIAA/AHI Space Planes and Hypersonic Systems and Technologies Conference, Reno, NV, 2006.

(42) Rowley, R. L.; Wilding, W. V.; Oscarson, J. L.; Zundel, N. A.; Marshall, T. L.; Daubert, T. E.; Danner, R. P. *DIPPR Data Compilation of Pure Compound Properties*; Design Institute for Physical Properties (DIPPR): New York, Sept 2008.

Table 4. Summary of the Energy Content, Presented as the Composite Enthalpy of Combustion, $-\Delta H_c$, of the Neat Fraction for UL94 and UL102 Avgas[a]

compound name	enthalpy of combustion, $-\Delta H$ (kJ/mol)	percent molar composition	fractional enthalpy of combustion (kJ/mol)
		UL94	
2-methyl propane (isobutane)	2648.1	0.18	4.70 (0.23)
butane	2657.3	1.92	50.90 (2.55)
2-methyl butane	3239.5	6.75	218.68 (10.93)
2,3-dimethyl butane	3847.6	1.02	39.18 (1.96)
3-methyl pentane	3851.4	0.24	9.19 (0.46)
2,4-dimethyl pentane	4455.0	1.99	88.83 (4.44)
2,3-dimethyl pentane	4460.8	3.82	170.45 (8.52)
2,2,4-trimethyl pentane	5065.3	53.17	2693.16 (134.66)
2,4-dimethyl hexane	5067.3	3.04	153.98 (7.70)
2,3,4-trimethyl pentane	5069.4	2.55	129.36 (6.47)
2,3,3-trimethyl pentane	5068.8	2.99	151.70 (7.59)
2,3-dimethyl hexane	5071.9	1.02	51.64 (2.58)
toluene	3734.0	19.59	731.41 (36.57)
2,2,5-trimethyl hexane	5666.4	1.62	91.90 (4.59)
2,4,4-trimethyl hexane	5679.6	0.02	1.27 (0.06)
2,3,5-trimethyl hexane	5679.6	0.08	4.67 (0.23)
		total	4591.07 (229.55)
		UL102	
2-methyl propane (isobutane)	2648.1	0.01	0.13 (0.01)
2,2-dimethyl propane	3250.4	0.08	2.47 (0.12)
2 methyl butane	3239.5	25.28	818.89 (40.94)
1-ethyl 3-methyl benzene	4943.8	0.00	0.09 (0.004)
1,3,5-trimethyl benzene	4929.1	74.64	3679.00 (183.95)
		total	4500.58 (225.03)

[a] The uncertainties are discussed in the text and are provided in parentheses.

with the calculation of the combustion enthalpies (kJ/mol) for the neat samples of the UL94 and UL102 avgas. Uncertainty in this calculation has been attributed to a number of sources[21,22] including (1) the neglect of the enthalpy of mixing, (2) the uncertainty in the individual (pure component) enthalpy of combustion as tabulated in the database, (3) the uncertainty in the measured mole fraction, (4) the uncertainty posed by very closely related isomers that cannot be resolved by the analytical protocol, (5) the uncertainty introduced by neglecting components present at very low concentrations (that is, uncertainty associated with the chosen area cutoff), (6) the uncertainty introduced by a complete mis-identification of a component, (7) the uncertainty in quantitation introduced by eluting peaks that are poorly resolved, and (8) the uncertainty introduced when experimental data for the pure component enthalpy of combustion are unavailable (and the Cardozo equivalent chain model must be used).[43] On the basis of the uncertainty sources listed above and the samples being investigated, a 5% uncertainty was ascribed to the calculations.

Figure 5 shows the molar enthalpy of combustion as a function of the distillate fraction for each of the unleaded fuels (the raw data with the uncertainties can be seen in Table 5). The UL94 avgas quickly increases in molar energy content as 2,2,4-trimethyl pentane, which has a relatively high enthalpy of combustion (-5065.3 kJ/mol), becomes the most concentrated component. As distillation continues, the 2,2,4-trimethyl pentane vaporizes (T_{boil} = 99.2 °C) and toluene (T_{boil} = 110.6 °C) becomes the more prevalent component. Because toluene has a lower enthalpy of combustion (-3743.0 kJ/mol) than 2,2,4-trimethyl pentane, the curve levels off and eventually begins to fall as the molar ratio of 2,2,4-trimethyl pentane over toluene decreases.

The UL102 avgas follows a similar shape as the cyclic hydrocarbon plot in Figure 4b. The enthalpy of combustion
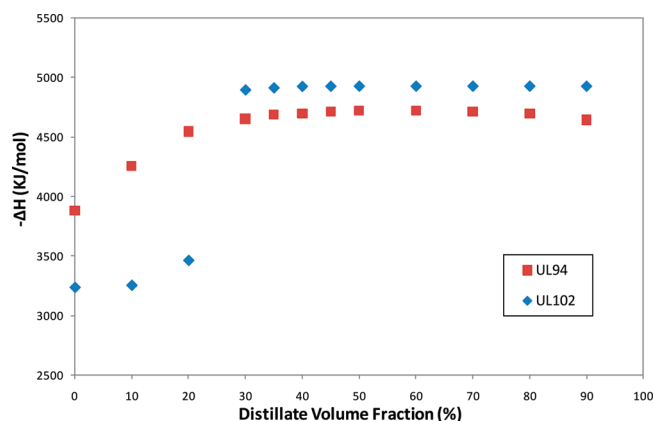
(43) Cardozo, R. L. *AIChE J.* **1986**, *32*, 844–848.

Figure 5. Energy content, presented as the composite enthalpy of combustion, $-\Delta H_c$, as a function of the distillate volume fraction for the UL94 and UL102 avgas. The uncertainties are discussed in the text.

initially follows that of 2-methyl butane (-3239.54 kJ/mol) until it is completely vaporized at approximately the 30% volume fraction. After the complete vaporization of 2-methyl butane, the boiling fluid is then primarily comprised of 1,3,5-trimethyl benzene (-4929.1 kJ/mol) and 1,2,4-trimethyl benzene (-4930.1 kJ/mol). Because the energy content, atomic mass, and density of 1,2,4- and 1,3,5-trimethyl benzene are essentially the same, the final enthalpy of combustion calculations were made by assuming that the entire feature (peak and shoulder) was comprised of 1,3,5-trimethyl benzene. The uncertainty caused by this assumption is negligible and resulted in a constant enthalpy of combustion for the remaining distillate fractions (30–100%).

As shown in Table 5, the lower concentration of the longer *n*-alkanes in both unleaded avgas mixtures significantly reduces the calculated molar combustion energy compared to that of the 100LL aviation fuel. In both unleaded mixtures, aromatic

Table 5. Energy Content, Presented as the Composite Enthalpy of Combustion, $-\Delta H_c$ (kJ/mol), as a Function of the Distillate Fraction for UL94, UL102, and 100LL Avgas[a]

distillate volume fraction (%)	composite enthalpy of combustion (kJ/mol)		
	UL94	UL102	100LL
0.025	3882 (194.1)	3240 (162.0)	4870 (243.5)
10	4254 (212.7)	3257 (162.9)	4902 (245.1)
20	4545 (227.2)	3466 (173.3)	4919 (246.0)
30	4651 (232.5)	4898 (244.9)	4925 (246.2)
35	4687 (234.3)	4914 (245.7)	4940 (247.0)
40	4699 (234.9)	4927 (246.3)	4935 (246.7)
45	4710 (235.5)	4928 (246.4)	4954 (247.7)
50	4718 (235.9)	4929 (246.4)	4966 (248.3)
60	4722 (236.1)	4929 (246.5)	4993 (249.7)
70	4714 (235.7)	4929 (246.5)	5020 (251.0)
80	4697 (234.9)	4929 (246.5)	5054 (252.7)
90	4644 (232.2)	4928 (246.4)	5084 (254.2)
neat	4591 (229.6)	4501 (225.0)	4988 (249.4)

[a] The uncertainties are discussed in the text and are provided in parentheses.

Table 6. Energy Content on a Mass Basis, Presented as the Composite Enthalpy of Combustion, $-\Delta H_c$ (kJ/g), as a Function of the Distillate Fraction for UL94, UL102, and 100LL Avgas[a]

distillate volume fraction (%)	composite enthalpy of combustion (kJ/g)		
	UL94	UL102	100LL
0.025	44.6 (2.2)	44.9 (2.2)	44.4 (2.2)
10	44.1 (2.1)	44.9 (2.2)	44.4 (2.2)
20	43.9 (2.2)	44.4 (2.2)	44.4 (2.2)
30	43.6 (2.2)	41.1 (2.1)	44.4 (2.2)
35	43.6 (2.2)	41.0 (2.1)	44.4 (2.2)
40	43.6 (2.2)	41.0 (2.1)	44.4 (2.2)
45	43.5 (2.2)	41.0 (2.1)	44.4 (2.2)
50	43.5 (2.2)	41.0 (2.1)	44.4 (2.2)
60	43.5 (2.2)	41.0 (2.1)	44.4 (2.2)
70	43.4 (2.2)	41.0 (2.1)	44.3 (2.2)
80	43.3 (2.2)	41.0 (2.1)	44.3 (2.2)
90	43.1 (2.2)	41.0 (2.1)	44.2 (2.2)
neat	43.7 (2.2)	42.0 (2.1)	44.4 (2.2)

[a] The uncertainties are discussed in the text and are provided in parentheses.

hydrocarbons, toluene in the UL94 avgas and 1,3,5-trimethyl benzene in the UL102 avgas, replace TEL to increase the octane number. High concentrations of aromatics are needed to have the same effect on the octane number as small concentrations of TEL.[44]

As shown in Table 6, the energy content on a mass basis slightly decreases with the distillate volume fraction in the UL102 avgas, while it remains constant (within the experimental uncertainty) for the 100LL and UL94 samples. The UL102 avgas has a slightly lower energy content per mass than that of the other fluids because of the fact that it contains significantly more aromatics, which have low enthalpies of combustion on a mass basis compared to those of branched alkanes. We can compare the enthalpy of combustion determined in this way with an experimental value obtained by bomb calorimetry. Atwood measured the energy content for the neat UL102 avgas and obtained 42.0 kJ/g, which is the same (within experimental uncertainty) as the value obtained here.[13] Because of the higher density of the aromatics, the unleaded avgas mixtures have a slightly higher enthalpy per volume than that of 100LL, with

(44) *Kirk−Othmer Encyclopedia of Chemical Technology*, 4th ed.; John Wiley and Sons, Inc.: New York, 1994; Vol. 12, p 24.

Table 7. Energy Content on a Volume Basis, Presented as the Composite Enthalpy of Combustion, $-\Delta H_c$ (kJ/mL), as a Function of the Distillate Fraction for UL94, UL102, and 100LL Avgas[a]

distillate volume fraction (%)	composite enthalpy of combustion (kJ/mL)		
	UL94	UL102	100LL
0.025	29.3 (1.5)	27.9 (1.4)	30.5 (1.5)
10	30.4 (1.5)	28.0 (1.4)	30.6 (1.5)
20	31.1 (1.6)	28.9 (1.4)	30.6 (1.5)
30	31.5 (1.6)	35.4 (1.8)	30.6 (1.5)
35	31.7 (1.6)	35.4 (1.8)	30.7 (1.5)
40	31.7 (1.6)	35.5 (1.8)	30.7 (1.5)
45	31.8 (1.6)	35.5 (1.8)	30.7 (1.5)
50	31.8 (1.6)	35.5 (1.8)	30.7 (1.5)
60	31.9 (1.6)	35.5 (1.8)	30.4 (1.5)
70	32.0 (1.6)	35.5 (1.8)	30.9 (1.5)
80	32.1 (1.6)	35.5 (1.8)	30.4 (1.5)
90	32.5 (1.6)	35.5 (1.8)	30.3 (1.5)
neat	31.4 (1.6)	33.6 (1.7)	30.7 (1.5)

[a] The uncertainties are discussed in the text and are provided in parentheses.

the UL102 mixture having the highest. Shown in Table 7, both unleaded avgas samples have an increasing enthalpy of combustion per volume as the distillation progresses because of the increasing concentration in aromatics. The 100LL distillate fractions show an essentially constant energy per volume.

Conclusion

The considerable public interest concerning the potential health risks of lead derived from TEL additives in aviation gasoline has sparked numerous research initiatives to replace 100LL avgas with a drop-in unleaded replacement. Two potential fluids were examined via the advanced distillation curve method, and the results were compared to those from a similar study performed on 100LL avgas. Distillation curves were measured for each of the unleaded fuels. The UL94 avgas was relatively similar to the 100LL avgas but differed by showing slight azeotropic activity indicated by the convergence of T_h and T_k around the 45% distillate volume fraction. The difference between the 100LL and UL102 avgas was more significant mainly because of the unique composition of UL102. Compositional analysis of the neat fluid and the distillate fractions for the two unleaded avgas mixtures was carried out with GC to trace the compositional alterations during distillation. Similar to the 100LL avgas, the neat composition of the UL94 avgas mostly consisted of alkanes; however, this fluid contained a much higher concentration of toluene and a lower concentration of longer alkanes. The UL102 avgas was mostly composed of three components: 2-methyl butane, 1,3,5-trimethyl benzene, and 1,2,4-trimethyl benzene. Hydrocarbon classification revealed for both unleaded avgas mixtures a reduction in aliphatic hydrocarbon concentration and an increase in cyclic hydrocarbon concentration during the distillation. The energy content in the neat samples of the unleaded fuels was less than that in the 100LL avgas on a molar basis. The neat energy contents for all three samples on a mass basis were all very similar, with UL102 containing a slightly lower value but still within the experimental uncertainty of the other fluids. The 100LL and UL94 avgas produced similar values in energy content on a volume basis, whereas UL102 contained a slightly higher energy content per volume because of its high concentration of aromatics, which are denser than equal carbon containing

alkanes. Independent of manufacturing and refining costs, the investigated fuels may be promising replacements to the TEL containing 100LL avgas; however, additional testing (such as materials compatibility, engine testing, etc.) would be needed. The practical applications of this work stem from the importance of the distillation curve in engine fuel schedule design and optimization. Power output, pollutant emission, and performance are all tied to volatility. Moreover, with the ADC, one can also develop an EOS for the fuel. This is important in formulation, because all process simulations used to model and operate industrial separations use EOSs to calculate the vapor liquid equilibrium.