

# Application of the Advanced Distillation Curve Method to the Aviation Fuel Avgas 100LL

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We have recently introduced several important improvements in the measurement of distillation curves for complex fluids. First, we incorporate a composition explicit data channel for each distillate fraction (for qualitative, quantitative, and trace analysis). Moreover, the temperature, volume, and pressure measurements are of low uncertainty, and the temperatures are true thermodynamic state points that can be modeled with an equation of state. These two features make the measurements suitable for equation of state development. The approach also provides consistency with a century of historical data, an assessment of the energy content of each distillate fraction, and, where needed, a corrosivity assessment of each distillate fraction. The most significant modification is achieved with a new on-the-fly sampling approach that allows precise qualitative identification as well as quantitative analyses of each fraction. We have applied this new method, the advanced distillation curve method, to the measurement of rocket propellant, diesel fuels, gasoline, and jet fuels. In this paper, we apply this method to low-lead aviation gasoline, avgas 100LL, and compare the results with those for 91 AI (antiknock index) motor gasoline. We present the distillation curves and track the composite enthalpy of combustion and the molar concentration of tetraethyl lead throughout the distillation.

## Introduction

One of the most important and informative properties that is measured for complex fluid mixtures is the distillation (or boiling) curve.<sup>1–4</sup> Simply stated, the distillation curve is a graphical depiction of the boiling temperature of a fluid mixture plotted against the volume fraction distilled. Distillation curves are typically associated with petrochemicals and petroleum refining.<sup>4</sup> Such curves are of great value in assessing the properties of any complex fluid mixture; indeed, the distillation curve (representative of fluid volatility) is one of the few properties that can be used to characterize a complex fluid. Thus, distillation curves are used commonly in the design, operation and specification of liquid fuels such as gasoline, diesel fuel, rocket propellant, and gas turbine fuel.

In earlier work, we described a method and apparatus for advanced distillation curves (ADCs) that is especially applicable to the characterization of fuels.<sup>5–11</sup> This method is a significant improvement over current approaches such as ASTM D-86.<sup>4</sup> First, we incorporate a composition-explicit data channel for

each distillate fraction (for qualitative, quantitative, and trace analysis). The temperature, volume, and pressure measurements are of low uncertainty, and the temperatures are true thermodynamic state points that can be modeled with an equation of state (EOS). These two features make the measurements suitable for EOS development. The approach also provides consistency with a century of historical data, an assessment of the energy content of each distillate fraction, and, where needed, a corrosivity assessment of each distillate fraction.

This new approach also provides important advantages over other methods such as the simulated distillation method embodied in procedures such as ASTM D-2887.<sup>12</sup> In that method, for example, one uses the gas chromatographic behavior of a suite of compounds as a frame of comparison with a fuel. A significant advantage offered by the metrology discussed in this paper is the ability to develop a thermodynamic model of the distillation curve with an EOS.<sup>13,14</sup> Approaches such as ASTM D-86 and ASTM D-2887 do not have a theoretical link to the EOS for complex mixtures. Since the ADC provides thermodynamically consistent temperature measurements, the link to theory is possible. We have, in fact, used the ADC to develop chemically authentic surrogate mixture models for the thermophysical properties of both a coal-derived liquid fuel and of the synthetic aviation fuel S-8.<sup>13</sup>

In this paper, we apply the ADC to an aviation gasoline (avgas) used in aircraft that are equipped with piston engines. In the past, avgas grades were differentiated by the two numbers following the name avgas (e.g., avgas 80/87, avgas 115/145,

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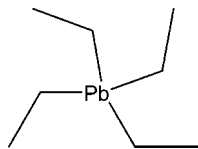
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**Table 1. Information on Tetraethyl Lead<sup>16,18,22</sup>**

CAS No. 78-00-2

InChI=1s/4C2H5.Pb/c4\*1-2;/h4\*1H2,2H3

RMM = 323.44

 $T_{\text{boil}} = 182.55 \text{ } ^\circ\text{C}$  $T_{\text{fus}} = -130.21 \text{ } ^\circ\text{C}$ 

density = 1.6485 g/mL (25 °C)

refractive index,  $n_D^{20} = 1.5202$  (20 °C)

synonyms: lead tetraethyl; tetraethylplumbane; TEL; (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Pb; Cz-terotylek olowiu; NCI-C54988; Tel-tml, reacted; tetra(methylethyl)-lead; NA 1649; Piombo tetra-etile; RCRA waste number P110; tetraethylolovo; Tetraethylplumbium; UN 1649

safety information: highly toxic; dangerous for the environment; may cause harm to the unborn child; very toxic by inhalation, in contact with skin and if swallowed; danger of cumulative effects; toxic to aquatic organisms; possible risks of impaired fertility; target organs: blood and central nervous system; possible carcinogen.

and avgas 100/130). The different fuels were differentiated in the field by a dye that colored the fluid. Thus, avgas 80/87 (phased out in the early 1990s) was colored red, avgas 115/145 (primarily used earlier in the military) was colored purple, avgas 100/130 (now available mainly in Australia and New Zealand) was colored green, and avgas 100LL is colored blue. The first number indicated how the fuel behaves under load and is the aviation lean octane rating, which is very close to the more familiar motor octane number (MON) commonly specified for automotive applications.<sup>15</sup> The second number indicated how the fuel behaves at takeoff and is the aviation rich octane rating.<sup>15</sup> Currently, only the aviation lean octane rating is used to specify different avgas grades (e.g., avgas 100LL and avgas 82UL). Here, LL and UL refer to low-lead and unleaded, respectively. Lead compounds (primarily, tetraethyl lead, TEL, CAS No. 78-00-2) are additives used to improve the MON.<sup>16</sup> Additives are the only way to achieve economical production of an avgas with a lean octane rating equal to or greater than 100.<sup>17</sup> Some representative properties of TEL are provided in Table 1.<sup>16,18</sup> For avgas 100LL, the lead concentration is specified as an upper limit of 0.56 g of TEL per liter of fuel.

Significant efforts have been made to develop a low-cost, lead-free alternative fuel to replace avgas 100LL for aircraft that use piston engines.<sup>19,20</sup> Ideally, this alternative should be a drop-in replacement. Since organic lead was banned from motor gasoline (but not general aviation gasoline), avgas is now one of the largest contributors of lead in the atmosphere in the United States and other developed countries.<sup>19</sup> Additionally, TEL is a possible carcinogen, leading to the potential exposure of operations personnel and general aviation pilots.<sup>21,22</sup>

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The examination of avgas 100LL in detail with the ADC method provides the opportunity to ultimately develop an EOS for avgas and to track the presence of the lead compound through the full range of the distillation curve. While we apply a detailed treatment to avgas in this paper, clearly it is not necessary or desirable to always apply all of the ADC capabilities for all fluids. For example, for highly finished fuels such as avgas 100LL, it is unnecessary to assess corrosivity as a function of distillate fraction, as it might be for a crude oil. Such fluids are of low corrosivity. Nevertheless, a significant benefit offered by the ADC is the ability to calculate both the composite enthalpy of combustion and the trace analysis of TEL throughout the distillation of the most common aviation gasoline, avgas 100LL. In the case of fuels, adding thermodynamic data to the chemical information obtained via the ADC approach provides yet another piece of valuable information for development and reformulation of fuels to meet evolving and emerging commercial and military requirements.

### Experimental Section

*N*-tetradecane, obtained from a commercial supplier, was used as a solvent in this work and was analyzed by gas chromatography (30 m capillary column of 5% phenyl/95%-dimethyl polysiloxane having a thickness of 0.25  $\mu\text{m}$ , temperature program from 50 to 90 °C at 3 °C/min and from 90 to 170 °C at 6 °C/min) using mass spectrometric detection.<sup>23</sup> These analyses revealed the purity to be approximately 99.5% (mass/mass), and the fluid was used without further purification.

Avgas 100LL, obtained from a commercial supplier, was analyzed by gas chromatography (30 m capillary column of 5% phenyl/95%-dimethyl polysiloxane having a thickness of 0.25  $\mu\text{m}$ , temperature program from 50 to 90 °C at 3 °C/min and from 90 to 170 °C at 6 °C/min) using mass spectrometric detection and a search of the NIST-EPA mass spectral database.<sup>24,25</sup> The purpose of these analyses was to obtain a general overview of the fluid composition. Our analyses, summarized in Table 2, reveal a similar composition to the composition that had been reported by the supplier.<sup>26</sup> The area percentages provided are from raw uncorrected areas resulting from the integration of the GC-MS total ion chromatogram. It is interesting to note the very low aromatics in the avgas 100LL in contrast with the large number of aromatics in the 91 AI motor gasoline, where AI is the antiknock index (the average of the research octane number and the motor octane number).<sup>7</sup>

The method and apparatus for ADC measurements have been reviewed in detail in a number of previously published papers;<sup>3-8,27-29</sup> thus, no additional general description will be provided here. In brief, 200 mL of avgas 100LL for the distillation curve measurement was placed into the boiling flask with a 250 mL graduated cylinder. 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 upon a previously measured distillation curve. Volume measurements

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**Table 2. Listing of the Major Components Found in the Samples of Avgas 100LL**

compound	CAS No.	area %
n-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
2,5-dimethyl hexane	592-13-2	13.9
2,3,4-trimethyl pentane	565-75-3	14.4
<i>x,y,z</i> -trimethyl pentane <sup>a</sup>	NA	8.1
<i>x,y,z</i> -trimethyl pentane <sup>a</sup>	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
<i>x,y,z</i> -trimethyl heptane <sup>a</sup>	NA	1.4
<i>x,y,z</i> -trimethyl heptane <sup>a</sup>	NA	2.3
2,2-dimethyl decane	17302-37-3	0.7
TEL	78-00-2	0.7

<sup>a</sup> 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.

were made in the level-stabilized receiver, and sample aliquots were collected at the receiver adapter hammock. In the course of this work, six complete distillation curve measurements were performed.

Since the measurements of the distillation curves were performed at local ambient atmospheric pressure (typically 83 kPa, measured with an electronic barometer), temperature readings were corrected for what should be obtained at standard atmospheric pressure. The average experimental atmospheric pressure for these initial temperature observations was 83.3 kPa. The uncertainty in the pressure measurement is 0.003 kPa. The pressure corrections were done with the modified Sydney Young equation, in which the constant term was assigned a value of 0.000119.<sup>30-33</sup> This value corresponds to an *n*-alkane carbon chain of 8, which is a reasonable representative for aviation gasoline.<sup>7</sup>

## Results and Discussion

**Initial Boiling Temperatures:** During the initial heating of each sample in the distillation flask, the fluid behavior was observed. For the ADC method, the temperatures at which bubbling is first observed, bubbling is sustained, and vapor is first observed to rise into the distillation head (the vapor rise temperature) are observed and recorded. This final temperature, the vapor rise temperature, has been shown to be the initial boiling temperature (IBT) of the mixture. The initial temperature observations for the average of three distillations are summarized in Table 3. The average temperature for the appearance of the first vapor bubble was 57.9 °C, measured in the liquid. Bubbling was observed to be sustained when the temperature of the fluid reached 64.3 °C. Vapor was observed rising into the head when the temperature reached 68.1 °C, and this temperature, measured using  $T_k$ , is considered to be the IBT and can be modeled theoretically (as the bubble point of the starting liquid), for example, in an EOS. These temperatures have been corrected to standard atmospheric pressure with the Sydney Young equation as described above; the experimental pressures are provided so that the actual temperatures measured can be

**Table 3. A Summary of the Initial Behavior of Avgas 100LL<sup>a</sup>**

observed temperature	avgas 100LL: °C (83.3 kPa)	91 AI gasoline: °C (81.9 kPa)
onset	57.9	35.4
sustained	64.3	43.4
<b>vapor rising</b>	<b>68.1</b>	<b>44.4</b>

<sup>a</sup> For reference, the behavior of 91 AI gasoline is also provided. 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 print). These temperatures have been corrected to 1 atm with the Sydney Young equation. The uncertainties are discussed in the text.

**Table 4. Representative Distillation Curve Data for an Avgas 100LL Sample<sup>a</sup>**

distillate volume fraction, %	avgas 100LL	
	$T_k$ , °C	$T_h$ , °C
5	82.3	68.3
10	87.8	76.6
15	91.6	82.7
20	94.7	87.1
25	96.7	90.9
30	98.7	93.4
35	100.1	95.2
40	101.9	96.5
45	103.2	98.6
50	104.3	99.7
55	105.3	102.1
60	106.1	103.7
65	106.8	104.5
70	107.9	105.5
75	109.0	106.6
80	110.6	108.7
85	114.0	111.2

<sup>a</sup> These data are plotted in Figure 1. The uncertainties are discussed in the text. These temperatures have been corrected to 1 atm with the Sydney Young equation. The experimental pressure for these measurements was 83.5 kPa.

recovered. The uncertainty (with a coverage factor  $k = 2$ )<sup>34</sup> of these measurements has been discussed in detail in previous papers and is approximately 2 °C in the onset and sustained bubbling temperatures and is approximately 0.2 °C in the vapor rise temperature.<sup>6</sup> For comparison, the initial temperature observations previously made on 91 AI winter quarter motor gasoline are included in Table 3.<sup>7</sup>

**Distillation Curves.** Measurement of the initial temperatures and the examination of the distillation curves can serve as methods to evaluate the operational parameters of fuels, such as engine starting ability, fuel system icing, vapor lock, etc.<sup>35,36</sup> Representative distillation curve data for an avgas 100LL sample, presented in both  $T_k$  (measured directly in the fluid) and  $T_h$  (measured in the distillation head), are provided in Table 4. The  $T_k$  data are true thermodynamic state points, and the  $T_h$  data allow for comparison with historical measurements. In this table, the estimated uncertainty (with a coverage factor  $k = 2$ ) in the temperatures is 0.5 °C. Note that the experimental uncertainty of  $T_k$  is 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 fraction is 0.05 mL in each case.

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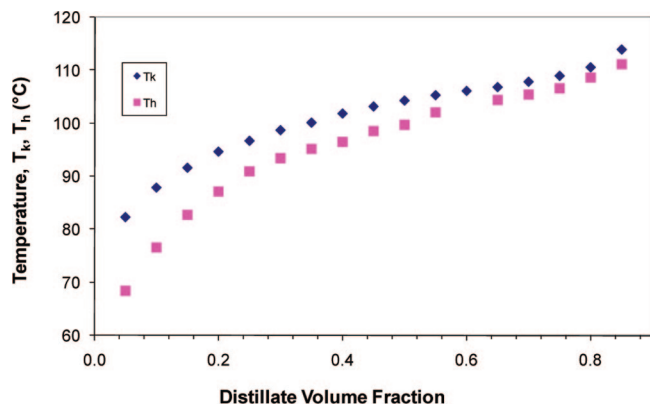
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**Figure 1.** Distillation curves, presented in the fluid temperature ( $T_k$ ) and the head temperature ( $T_h$ ), for avgas 100LL. The uncertainties of the measurements are discussed in the text. The error bars on the temperature measurement are smaller than the symbols used.

These uncertainties were determined from replicate measurements. The uncertainty in the pressure measurement is 0.003 kPa. These uncertainties make the measurements suitable for the development of an EOS.

A graphical depiction of the representative distillation curve data for avgas 100LL is provided in Figure 1. The shapes of the curves are of the subtle sigmoid or growth curve type proceeding from 65 to 115 °C. Figure 1 shows that the fluid temperature,  $T_k$ , always leads the head temperature,  $T_h$ . As we have demonstrated previously, the lack of convergence midcurve of these two temperatures is indicative of the absence of azeotropy among the major components of the fluid.<sup>7</sup> Additionally, the avgas 100LL distillation occurs over a much narrower temperature range than that of 91 AI winter quarter motor gasoline. The 5 and 80% distillate volume fractions of 91 AI gasoline distill at 58.2 and 177.4 °C, respectively, compared with 80.6 and 109.0 °C, respectively, for the 5 and 80% distillate volume fractions of avgas 100LL. Thus, the low fractions of 91 AI gasoline are more volatile than those of avgas 100LL, and the opposite trend is true for the high fractions. These results provide insight into both the cold and hot weather performance characteristics of the fuels (not taking into account the addition of TEL to the avgas 100LL). This result is a good example of how examining distillation curves can provide information on the operational parameters of complex fluids.

**Composition Channel Information.** *Analysis of Distillate Fractions.* Although the gross examination of the distillation curves is instructive and valuable for many design purposes, the composition channel of the advanced approach can provide even greater understanding and information content. One can sample and examine the individual fractions as they emerge from the condenser. Sampling was done by withdrawing  $\sim 7$   $\mu\text{L}$  aliquots of distillate (as a function of distillate volume fraction) and diluting the aliquot in a known mass ( $\sim 1$  mL) of *n*-tetradecane. Each of these fractions thus prepared was analyzed by a gas chromatographic–mass spectrometric (GC-MS) method (30 m capillary column of 5%-phenyl/95%-dimethyl polysiloxane having a thickness of 0.25  $\mu\text{m}$ , temperature program from 50 to 90 °C at 3 °C/min and from 90 to 170 °C at 6 °C/min, mass spectrometer set to record a  $m/z$  range from 40 to 400 relative molecular mass units gathered in scanning mode).

Representative chromatograms for each fraction of avgas 100LL are shown in Figure 2. The time axis is from 0 to 9.5 min for each chromatogram, and the abundance axis is presented in arbitrary units of area counts (voltage slices). Although there are many peaks for each distillate fraction chromatogram (5–10

major, 5–10 minor, and numerous trace peaks) these chromatograms are much simpler than those of both the neat and residue fluid, which show 50–100 major peaks and numerous trace peaks. This behavior is observed because the distillation process, in effect, provides a preliminary separation on the basis of volatility. Additionally, it is important to note that the solvent (*n*-tetradecane) appears at the very end of each chromatogram. This peak does not interfere with the sample and was removed digitally.

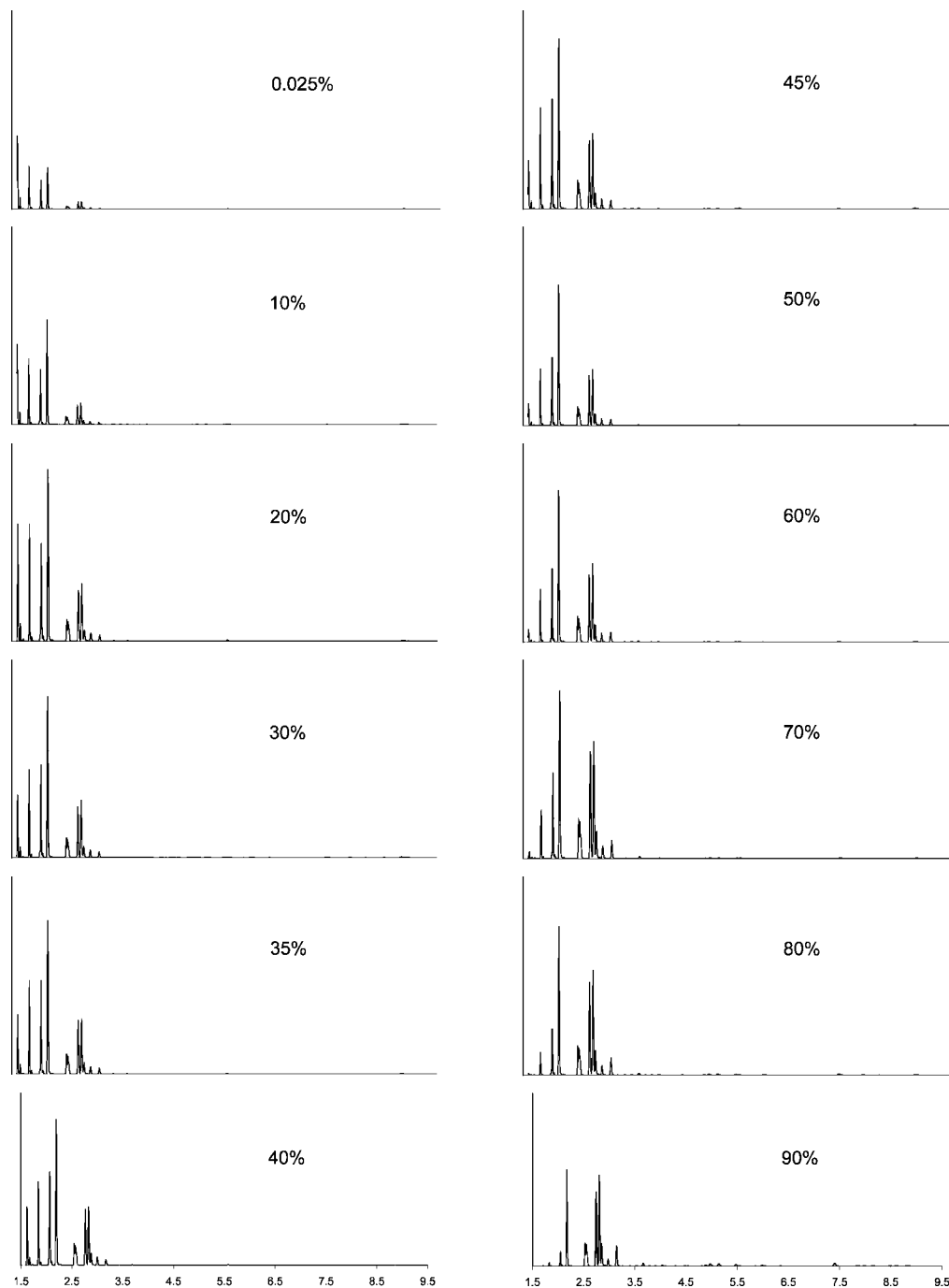
One can follow the progression of the chromatograms in Figure 2 as the distillate fraction becomes richer in the heavier components. We note that several major components dominate each fraction: 2,2,4-trimethyl pentane, 2,3,3-trimethyl pentane, and 2,5-dimethyl hexane. These peaks persist throughout the distillation, although at concentrations that change with temperature. Figure 2 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 to solvent-borne liquid samples that might be desirable for a given application.

*Hydrocarbon Type Classification.* Another analytical technique that complements the above analyses examines the avgas 100LL samples for hydrocarbon types by use of a mass spectrometric classification method summarized in ASTM D-2789.<sup>37</sup> In this method, one uses mass spectrometry (or GC-MS) to characterize hydrocarbon samples into six types. The six types or families include the following: paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (arenes or aromatics), indanes and tetralins (grouped as one classification), and naphthalenes. Although the method is specified only for application to low olefinic gasolines, and it has significant limitations, it is of practical relevance to many complex fluid analyses and is often applied to gas turbine fuels, rocket propellants, and missile fuels.<sup>38</sup> The uncertainty of this method, and the potential pitfalls, were discussed earlier.<sup>7</sup> As discussed above, the solutions were prepared from  $\sim 7$   $\mu\text{L}$  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  $\mu\text{L}$  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 these hydrocarbon type analyses are presented in Figure 3. All of the distillate fractions presented in the table were measured in the same way (a  $m/z$  range from 40 to 400 relative molecular mass units gathered in scanning mode, each spectrum corrected by subtracting trace air and water peaks).

Figure 3 shows that there is no significant change throughout the distillation in the volume percent of any of the hydrocarbon type families. At first glance, it appears that the alkylbenzene values show a great deal of scatter, but the changes (1.3–1.9%) are actually very small (less than 1%). The results of the hydrocarbon type classification are consistent with the aforementioned GC-MS analysis of distillate fractions (see Figure 2), which shows the persistence of major peaks (e.g., 2,2,4-trimethyl pentane, 2,3,3-trimethyl pentane, and 2,5-dimethyl

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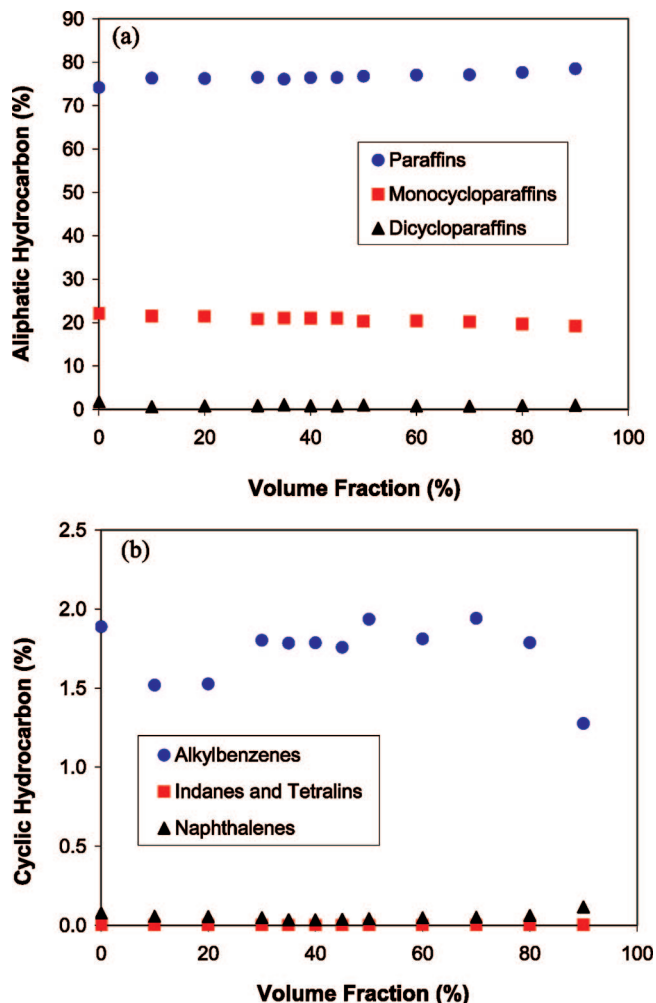
**Figure 2.** Chromatograms of distillate fractions of avgas 100LL, presented in arbitrary units of intensity plotted against time. The details of the chromatography are discussed in the text.

hexane) throughout the distillation. Thus, two independent analyses both indicate that the constituents of each distillate fraction of avgas 100LL are virtually unchanged throughout the distillation. Of course, the relative concentrations change through the distillation.

The 91 AI motor gasoline measured previously exhibits a very different behavior, that is, significant compositional change throughout the distillation.<sup>7</sup> The paraffins and monocycloparaffins were found to decrease sharply from 46.7 to 1.1% and from 26.7 to 0.2%, respectively; the alkylbenzenes were found to increase significantly from 26.2 to 92.0%; and the indanes and tetralins were found to increase from 0.0 to 6.7%. A similarity between the two fluids is that both the avgas 100LL and 91 AI gasoline samples exhibit very low constant levels of dicycloparaffins and naphthalenes.

*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.<sup>7,8,28</sup> This addition is done 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.<sup>39</sup>

We have presented previously a very detailed discussion of the uncertainty of the composite enthalpy of combustion derived from this procedure.<sup>7,8</sup> The major sources of uncertainty that were considered were: (1) the neglect of the enthalpy of mixing, (2) the uncertainty in the individual (pure component) enthalpy



**Figure 3.** (a-b) A plot of the aliphatic hydrocarbon family types resulting from the ASTM D-2789 analysis performed on avgas 100LL as a function of distillate volume fraction. The uncertainties are discussed in the text.

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).<sup>40</sup>

We assign an uncertainty of 1% to the pure component enthalpies of combustion because each value that has been used in this work is an experimental value rather than a prediction. We note that this uncertainty might be artificially high, since some of the experimental measurements have claimed uncertainties of approximately 0.2%. We choose to use the estimate provided in the database (1%) as a more conservative measure of uncertainty. The mole fraction is measured by a gas

**Table 5.** A Summary of the Energy Content, Presented As the Composite Enthalpy of Combustion,  $-\Delta H_c$ , of the 50% distillate fraction for avgas 100LL<sup>a</sup>

compound name	enthalpy of combustion, $-\Delta H$ , kJ/mol	% molar composition	fractional enthalpy of combustion, kJ/mol
2,4-dimethyl pentane	4455	10.17	453.2 (22.7)
2,3-dimethyl pentane	4461	9.34	416.6 (20.8)
2,2,4-trimethyl pentane	5065	52.89	2679 (134.0)
2,5-dimethyl hexane	5064	13.62	689.5 (34.5)
2,3,4-trimethyl pentane	5069	3.46	175.2 (8.8)
2,3,3-trimethyl pentane	5069	6.34	321.1 (16.1)
toluene	3734	0.30	11.1 (0.6)
2,2,5-trimethyl hexane	5666	3.89	220.6 (11.0)
tetraethyllead	5900	0.00045	0.03 (0.0013)

<sup>a</sup> The uncertainties are discussed in the text, and are provided in parentheses. Composite enthalpy of combustion,  $-\Delta H_c$ : 4966.4 (248.3) kJ/mol.

chromatographic method in which response factors are applied to the raw area counts obtained from either a flame ionization detector or from selected (or extracted) ion monitoring from a mass spectrometer. It is possible to perform this kind of energy analysis for each of the distillate fractions.

Gas chromatographic and mass spectrometric analyses identified that the avgas 100LL samples are composed of various branched and linear alkanes, a small amount of toluene, and a very small amount of TEL (see Table 2). To simplify the calibration process, each alkane was standardized by use of the characteristic ion peak at an  $m/z$  value of 57. Additionally, toluene has a characteristic ion peak at  $m/z$  value of 91, and TEL exhibits characteristic peaks at the  $m/z$  values 208, 237, and 295. Selected ion monitoring (SIM) was performed on the distillate fractions and on calibration standards for hexane, toluene, and TEL on only the above five  $m/z$  values. Since we do not standardize for each component, we assign an uncertainty in our measured composition of each component in the individual distillate fractions to be 10%. The overall combined uncertainty in our composite enthalpy of combustion is 5.0% (with a coverage factor  $k = 2$ ) for the avgas 100LL samples. As has been shown in previous papers, the uncertainty is dominated by the analytical measurement, and subsequently, determination of the mole fraction.

For each distillate fraction of avgas 100LL, the composite enthalpy of combustion was determined. Table 5 displays an example of the enthalpy calculation for the 50% distillate fractions of avgas 100LL. As described above, calculating the mole fraction of each component gives the fractional enthalpy of combustion for each component, and the summation of the fractional enthalpies gives the composite enthalpy of combustion for each distillate fraction. Thus, in the case of the 50% distillate fractions of avgas 100LL, the composite enthalpy of combustion,  $-\Delta H_c$ , is 4966 kJ/mol. The uncertainties of these values are listed in parentheses in both Tables 5 and 6. Table 6 shows that  $-\Delta H_c$  increases throughout the distillation from 4870 to 5129 kJ/mol. A graphical depiction of the enthalpy of combustion throughout the distillation is provided in Figure 4. In most cases, the error bars on the composite enthalpy of combustion calculation are smaller than the symbols used. This observed trend is consistent with heavier components distilling at higher temperatures (i.e., later in the distillation). The increase in  $-\Delta H_c$  throughout the distillation is small when compared to that of 91 AI gasoline (i.e., 259.3 vs 1229 kJ/mol), however.<sup>7</sup> Once again, the observations show that the constituents of each distillate fraction of avgas 100LL remain virtually constant throughout the distillation, whereas the relative concentrations are changing.

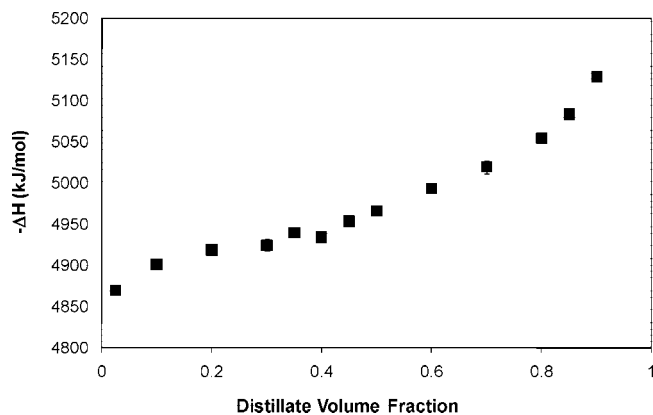
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(40) Cardozo, R. L. *AIChE J.* **1986**, *32* (5), 844–848.

**Table 6. The Energy Content, Presented As the Composite Enthalpy of Combustion,  $-\Delta H_c$ , as a Function of Distillate Fraction for Avgas 100LL<sup>a</sup>**

distillate volume fraction, %	composite enthalpy of combustion, kJ/mol
0.025	4870 (243.5)
10	4902 (245.1)
20	4919 (246.0)
30	4925 (246.2)
35	4940 (247.0)
40	4935 (246.7)
45	4954 (247.7)
50	4966 (248.3)
60	4993 (249.7)
70	5020 (251.0)
80	5054 (252.7)
90	5084 (254.2)

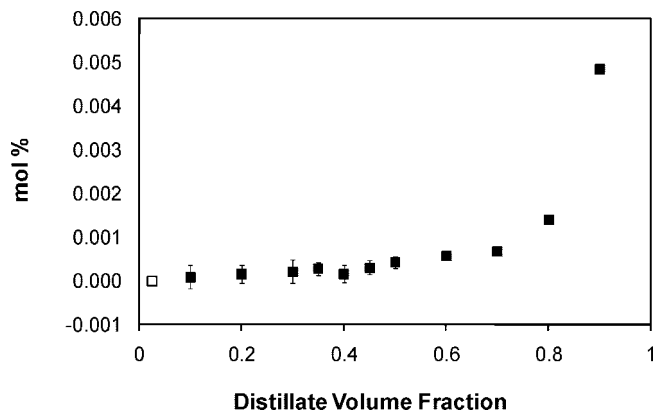
<sup>a</sup>The uncertainties are discussed in the text, and are provided in parentheses.



**Figure 4.** The energy content, presented as the composite enthalpy of combustion,  $-\Delta H_c$ , as a function of distillate volume fraction for avgas 100LL. The uncertainties are discussed in the text. Most of the error bars on the composite enthalpy of combustion calculation are smaller than the symbols used.

The presentation of the thermochemical information in units of kJ/mol is especially useful for design and modeling studies, since thermochemical information presented in this way represents fundamental values easily applied to the individual component mole fractions. A practical engineering alternative would be to present  $-\Delta H_c$  in terms of volume, expressed in kJ/L. This conversion is simple to compute, requiring only the density of each identified compound at a temperature of interest. Taking into account the liquid molar volumes (i.e., densities) of each component at 25 °C and at local ambient pressure, the composite enthalpy of combustion for the 50% volume fraction of avgas 100LL,  $-\Delta H_c$ , is 30 690 kJ/L. On a per volume basis, the composite enthalpy of combustion changes less (i.e.,  $-\Delta H_c$  increases 1.5% vs 5% on a per molar basis). The change in the composite enthalpy of combustion throughout the distillation will also change when computed on a per mass basis.

**Molar Percent of Tetraethyl Lead.** In addition to thermochemical information, it is also possible to add trace analysis to the distillation curve when the composition channel of data is used to analyze the distillate fractions. The uncertainty in evaluating the mole fraction of trace components in distillate fractions is two-fold; there is uncertainty in the area quantification and in the calibration. In this work we applied the trace analysis protocol to quantify the molar percent of TEL as a function of distillate fraction. Area quantification was done using selected ion monitoring as described above. A minimum of five injections from each sample were made



**Figure 5.** The molar percent of TEL is presented as a function of distillate volume fraction for avgas 100LL. The first point ( $\square$ ) is the first drop of the distillation (0.025 volume %); no tetraethyl lead was observed in this drop. The y-axis is displaced slightly to present the full range of the error bars. The uncertainties are discussed in the text. Some of the error bars on the mole percent calculation are smaller than the symbols used.

into the GC-MS. We assign an uncertainty in the area quantification of TEL in the individual distillate fractions to be 13%. This value is 3% higher than that assigned to the major (area greater than 1% of the total area) components found above. The increase is attributed to difficulties in determining the trace quantities of TEL found in these samples. Additionally, there is uncertainty in the calibration; however, this uncertainty is estimated to be <1%. Thus, the overall uncertainty for the calculation of the mole fraction of TEL is 13%.

We found 0.038 mol % TEL in the neat avgas 100LL sample (prior to distillation). This value corresponds to approximately 6.43 mL of TEL per liter (1.7 mL TEL per gallon) of avgas 100LL assuming a density of 0.7 g/mL for avgas 100LL. Our measured value is in good agreement with specifications reported by industrial suppliers: 4.98–7.56 mL/L (1.2–2 mL TEL/gallon avgas 100LL).<sup>26</sup> Figure 5 shows that the molar percent of TEL in the first drop is zero. From the 10–90% distillate fractions we found the mol % of TEL increased from 0.0001 to 0.0048 mol %. The majority of this increase occurs after the 60% distillate fraction is collected. In some cases, the error bars on the mole percent calculation are smaller than the symbols used.

## Conclusions

The ADC method was applied to low-lead aviation gasoline, avgas 100LL. We present the initial boiling point and the distillation curves measuring the temperature in both the fluid and the head of the distillation flask. The shapes of the curves are of the subtle sigmoid or growth curve type, and the fluid temperature always leads the head temperature, indicative of a lack of azeotropy among the major components of the fluid. Additionally, we tracked the chemical composition, the composite enthalpy of combustion, and the molar concentration of TEL throughout the distillation. Distillate fractions became slightly richer in the heavier components; however, most of the major constituents of each fraction persist throughout the distillation (e.g., 2,2,4-trimethyl pentane, 2,3,3-trimethyl pentane, and 2,5-dimethyl hexane appear in each distillate fraction). The hydrocarbon type classification results show that chemical families do not change significantly throughout the distillation, although the relative

concentrations change. The thermochemical information on the distillate fractions shows that the enthalpy of combustion slightly increases throughout the distillation, although the change in these values is an order of magnitude less than that of 91 AI motor gasoline. Last, we observed that the molar percent of TEL increases throughout the distillation, with the majority of TEL distilling off at higher temperatures. This information will be critical in developing an equation of state

for avgas, and ultimately, the development of a more environmentally friendly avgas alternative (drop-in) fuel.

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