# Improvements in the Measurement of Distillation Curves. 4. Application to the Aviation Turbine Fuel Jet-A

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We have recently introduced several important improvements in the measurement of distillation curves for complex fluids. The modifications to the classical measurement provide for (1) temperature and volume measurements of low uncertainty, (2) temperature control based upon fluid behavior, and, most important, (3) a composition-explicit data channel in addition to the usual temperature-volume relationship. This latter modification is achieved with a new sampling approach that allows precise qualitative as well as quantitative analyses of each fraction, on the fly. We have applied the new method to the measurement of rocket propellant, gasoline, and jet fuels. In this paper, we present the application of the technique to representative batches of the important aviation fuel Jet-A. The motivation behind the work is to provide a property database for the planned expansion of the use of military aviation fuel JP-8, which is nearly identical to Jet-A. JP-8 also contains an icing inhibitor, corrosion/lubricity enhancer, and antistatic additive. This fluid (JP-8) is currently the primary gas turbine fuel used by the United States Air Force and also naval shore-based aircraft. There is now interest in the United States Department of Defense to use this fuel for all military applications, including ground-based forces. This would mean use of JP-8 in tanks, armored personnel carriers, and other vehicles. This interest has renewed interest in the chemical and physical properties of JP-8, to facilitate adaptation and design. Since one of the most important design parameters for a fuel is the distillation curve, it is critical that the new approach be applied to the base fluid representative for JP-8, namely, Jet-A.

## Introduction

The first successful gas turbine engine used for aviation was attributable to Hans von Ohain in Germany; it powered an (Heinkel) He-178 on August 27, 1939. This engine utilized gasoline as a fuel, primarily because of the engineering community's familiarity with the physical and chemical properties of that fuel. Later, Sir Frank Whittle developed an aviation turbine engine that first flew in a Gloster E28/32 aircraft on May 14, 1941. Whittle's engine, which used illuminating kerosene as a fuel (since gasoline was in short supply because of World War II), became the forerunner of successful turbine engines in both the United States and Britain.<sup>1</sup> Indeed, kerosene-based fuels remain the primary jet fuel for commercial airlines and military fleets.<sup>2</sup>

The gas turbine engine is more forgiving in operation than are internal combustion engines that burn gasoline. Indeed, Whittle reportedly once remarked that his engine could run on anything from whiskey to peanut butter.<sup>1</sup> Despite this, fuels for these engines have been the topic of a great deal of research and development. The major gas turbine fuel that is currently the most common fuel used by the United States military is JP-8 (MIL-DTL-83133), a kerosene fraction that has a higher flash point than its main military predecessor, JP-4. JP-8 was first introduced at NATO bases in 1978; hence, it was also called NATO F-34 and is currently the U.S. Air Force's primary fuel and the primary fuel for U.S. Navy shore-based aviation. Aboard aircraft carriers, the major fuel is JP-5, which has an even higher flash point (desirable for safety considerations), although its higher cost restricts its use to the specialized fire control needs of aircraft carriers. JP-8 is very similar to Jet A-1, the most common commercial gas turbine fuel, with the major differences being in the additive package. JP-8 contains an icing inhibitor, corrosion/lubricity enhancer, and antistatic additive.<sup>1</sup> There is a desire in the United States defense community to utilize JP-8 as the main battlefield fuel for all vehicles, not only for aviation applications but also for ground-based forces. For this reason, the physical and chemical properties of Jet-A and JP-8 are receiving renewed interest. Moreover, there is a desire to develop thermodynamic models (such as equations of state) to correlate these properties, in order to enhance design and operational specifications for further application of this fluid.

One of the most important and informative properties that is measured for complex fluid mixtures is the distillation (or boiling) curve.<sup>3-6</sup> Simply stated, the distillation curve is a graphical depiction of the boiling temperature of a fluid mixture plotted against the volume fraction distilled. One most often thinks of distillation curves in the context of petrochemicals and petroleum refining,<sup>6</sup> but such curves are of great value in assessing the properties of any complex fluid mixture. Thus, distillation curves are commonly used in the design, operation, and specification of liquid fuels such as gasoline, diesel fuel, rocket propellant, and gas turbine fuel.

In previous work, several significant improvements in the measurement of distillation curves for complex fluids were introduced. The modifications to the classical measurement (embodied in ASTM D-86<sup>6</sup>) provide for (1) temperature and volume measurements of low uncertainty, (2) temperature control based upon fluid behavior, and, most important, (3) a composition-explicit data channel in addition to the usual temperature–volume relationship.<sup>7–10</sup> We have applied this advanced approach to the distillation curve to a variety of mixtures that include simple *n*-alkanes, gas turbine fuels, gasoline, and rocket propellant. In addition, we have demonstrated how the composition channel of information can be used to augment the distillation curve with thermochemical information.<sup>11</sup> Thus, for individual fractions, we can calculate the

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### **Experimental Section**

Three samples of Jet-A, representing three separate processing lots, were obtained from the Fuels Branch of the Air Force Research Laboratory (AFRL, Wright Patterson Air Force Base). The samples provide a range of compositional difference that is consistent with the rather loose specifications that are possible with this fluid. Thus, the three samples can represent a wide range of compositional difference. For this reason, the results of the work presented here are considered representative of the properties of the fluids. Note that this was not the case with the work presented previously on gasoline, in which the results were more representative of the method, rather than of the fluid. The three Jet-A samples were designated numerically as 3638, 3602, and 4658, numbers which in the context of this paper only serve to identify an individual fluid. The sample labeled 4658 is actually a composite of numerous available batches (from multiple manufacturers) of Jet-A, which was mixed in approximately equal volume aliquots. It is, therefore, considered to be the most representative of the three smples.<sup>13</sup> The sample labeled 3638 was known to be unusual in that the aromatic content was lower than is typical for a Jet-A specimen.<sup>13</sup> The samples were maintained in sealed containers at 7 °C during storage to prevent the loss of high vapor pressure components. No solidification or phase separation was noted during storage.

In addition to these samples of Jet-A, we have included in this study additional measurements on the synthetic fluid S-8 (CAS No. 437986-20-4), which is produced as a substitute for JP-8 from natural gas by the Fischer Tropsch process.<sup>14,15</sup> This fluid, which is intended as a synthetic to replace or augment JP-8, is a hydrocarbon mixture rich in C7–C18 linear and branched alkanes. It has a flash-point range of between 37.8 and 51.8 °C, an autoignition temperature of 210 °C, and explosive limits in air between 0.7 and 5 (vol/vol). Initial measurements on this fluid were presented in Part 2 of this series.<sup>8</sup>

Each of the samples was analyzed by gas chromatography (30 m capillary column of 5% phenyl–95% dimethyl polysiloxane having a thickness of 1  $\mu$ m, temperature program from 90 to 275 °C, 9 °C per minute) using flame ionization detection and mass spectrometric detection.<sup>16,17</sup> The purpose of these analyses was to obtain a general overview of the fluid composition and to determine a very rough surrogate to use in the pressure correction to the distillation temperature (see below). Beyond storage at 7 °C, no treatment or purification was done on any of the fluids.

The hexane 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  $\mu$ m, temperature program from 50 to 170 °C, 5 °C per minute) using flame ionization detection and mass spectrometric detection. These analyses revealed the purity to be ~99.95%, and the fluid was used without further purification.

The required fluid for the distillation-curve measurement (in each case 200 mL) was placed into the boiling flask (of Figure 1 in Part 1 of this series<sup>7</sup>) with a 200 mL volumetric pipet. The thermocouples were then inserted into the proper locations to

Table 1. Summary of the Initial Behavior of the Three Individual Samples of Jet-A and the Sample of  $S-8^{a}$ .

observed temperature	Jet-A-3602, °C	Jet-A-3638, °C	Jet-A-4658, °C	S-8, °C
onset	150.9	148.4	139.9	163.0
sustained	183.6	176.9	185.6	168.6
vapor rising	191.0	184.2	190.5	181.9

<sup>*a*</sup> In keeping with our advanced distillation-curve protocol, the onset temperature is the temperature at which the first bubbles are observed. The sustained bubbling temperature is that at which the bubbling persists. 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 Sidney Young equation. The uncertainties are discussed in the text.

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.<sup>10</sup> Volume measurements were made in the level-stabilized receiver, and sample aliquots were collected at the receiver adapter hammock. In the course of this work, we performed between four and six complete distillation-curve measurements for each of the three samples.

Since the measurements of the distillation curve are performed at ambient atmospheric pressure (measured with an electronic barometer), temperature readings were corrected for what should be obtained at standard atmospheric pressure. This was done with the modified Sidney Young equation, in which the constant term was assigned a value of 0.000 109.<sup>18–20</sup> This value corresponds to a carbon chain of 12. In the chemical analyses of the samples (see above), as well as in previous work on these fluids, it was found that *n*-dodecane can indeed represent these fluids as a very rough surrogate.<sup>21,22</sup> The magnitude of the correction is, of course, dependent upon the extent of departure from standard atmospheric pressure. The location of the laboratory in which the measurements reported herein were performed is ~1650 m above sea level, resulting in a typical temperature correction of 7 °C.

#### **Results and Discussion**

Initial Boiling Temperatures. During the initial heating of each sample in the distillation flask, the behavior of the fluid was observed. Direct observation through the flask window or through the illuminated bore scope allowed measurement of the onset of boiling for each of the mixtures. Typically, during the early stages of a measurement, the first bubbles will appear intermittently, and this action will quell if the stirrer is stopped momentarily. Sustained vapor bubbling is then observed. In the context of the advanced distillation-curve measurement, sustained bubbling is also somewhat intermittent, but it 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 is termed the vapor-rise temperature. These observations are important because they are the initial boiling temperatures (IBTs) of each fluid. Moreover, these temperatures can be modeled theoretically, for example, with an equation of state.

The initial temperature observations for a representative measurement are summarized in Table 1. For example, for Jet-A-3602, the temperature for the appearance of the first vapor bubble was 150.9 °C, measured by TC1 in the liquid. Bubbling was observed to be sustained when the temperature of the fluid reached 183.6 °C. Vapor was observed rising into the head when

the temperature reached 191.0 °C, which is considered to be the initial boiling temperature for the mixture (IBT). It is at this temperature ( $T_k$ ) that the bubbling is continuous and is observed to occur with or without stirring. These temperatures have been corrected to standard atmospheric pressure with the Sidney Young equation, as described above.

As with all observations of these initial temperatures, there is an element of subjectivity. For example, it is often difficult to distinguish between initial bubbling and the entrainment of air bubbles by the action of the stirrer. Since we have several replicate observations for each sample of Jet-A, it is possible to assign an uncertainty to these temperatures (despite the subjectivity in the observation), since these observations are made for each distillation-curve measurement. The uncertainty (with a coverage factor k = 2) in the onset and sustained bubbling temperatures is ~2 °C. The uncertainty in the vaporrise temperature is actually much lower, at ~0.2 °C.

Examination of the observed temperatures reveals a significant difference with sample Jet-A-3638 as compared to samples Jet-A-3602 and Jet-A-4658. The onset temperatures for sample 3638 are significantly lower than those for the other two. A possible explanation would be that Jet-A-3638 is somewhat richer in higher vapor pressure constituents than are Jet-A-3602 and Jet-A-4658. To test this hypothesis, a gas chromatographic analysis of all four neat fluids was done (30 m capillary column of 5% phenyl-95% dimethyl polysiloxane having a thickness of 1 µm, temperature program from 90 to 275 °C, 9 °C per minute, using flame ionization detection). The integrated areas (uncalibrated) of all peaks that eluted between 1.3 and 3 min (where one would expect to find the most volatile constituents) were then calculated. The resulting area percentages for each of the Jet-A fluids were remarkably consistent: Jet-A-3638 (2.80%), Jet-A-3602 (2.98%), and Jet-A-4658 (3.60%). It appears, therefore, that the difference in the onset temperatures is due to the character of the entire sample, including the moiety or hydrocarbon group distribution. By this, we mean that the entire sample (Jet-A-3638) behaves as a more volatile mixture than either Jet-A-3602 or Jet-A-4658. As we will see in the next section, this conclusion is consistent with the behavior seen on the distillation curve.

Even more striking than the difference of Jet-A-3638 with Jet-A-3602 and Jet-A-4658 is the difference between the onset temperatures of the Jet-A fluids and the synthetic S-8. In this case, however, it does in fact appear to be the result of a larger quantity of more volatile constituents (that elute early from the chromatographic column). For S-8, chromatographic peaks comprising 8.01% of the total integrated area (uncalibrated) of the sample elute between 1.3 and 3 min. As we will see in the next section, this is also consistent with the distillation curves.

We note in passing that the initial temperatures we have presented are very different from the initial boiling temperatures that would be obtained from a commercial ASTM D-86 instrument, in which the IBT would be recorded as the first drop of distillate enters the receiver.<sup>23</sup> As we have shown previously, the usual ASTM D-86 approach yields an initial boiling temperature that is between 7 and 13 °C in (systematic) error.

**Distillation Curves.** Representative distillation-curve data for the three samples of Jet-A, presented in both  $T_k$  and  $T_h$ , are provided in Table 2. The reason for presenting both  $T_k$  and  $T_h$ has been discussed earlier; the  $T_h$  data allows comparison with earlier measurements. In this table, the estimated uncertainty (with a coverage factor k = 2) in the temperatures is 0.1 °C. Note that the experimental uncertainty of  $T_k$  is somewhat lower

Table 2. Representative Distillation-Curve Data for the Three Individual Samples of Jet-A and the Sample of S-8 Measured in This Work<sup>*a*</sup>.

	Jet-A	-3602	Jet-A	-3638	Jet-A	-4658	S	-8
distillate volume fraction, %	$T_{\rm k},$ °C	T <sub>h</sub> , °C	$T_{\rm k},$ °C	$T_{\rm h}, ^{\circ}{\rm C}$	$T_{\rm k},$ °C	$T_{\rm h}, ^{\circ}{\rm C}$	$T_{\rm k},$ °C	T <sub>h</sub> ,°C
5	194.8	179.3	186.8	179.9	195.4	174.7	183.6	169.2
10	197.7	186.7	188.7	184.2	198.5	183.3	185.0	173.9
15	200.7	189.9	191.1	187.0	201.5	187.0	187.7	179.1
20	203.5	194.7	192.9	185.8	204.7	189.1	190.2	173.6
25	206.4	196.9	194.9	189.5	208.1	190.6	193.0	175.5
30	209.7	198.7	196.6	191.6	211.3	192.8	196.2	181.9
35	212.1	199.2	198.5	193.9	214.3	194.6	199.5	187.7
40	214.8	201.5	200.3	196.0	217.6	199.1	202.9	192.0
45	217.3	204.5	202.1	197.9	220.7	202.6	207.1	196.2
50	220.1	206.4	204.0	199.8	224.2	205.4	211.0	200.3
55	222.5	208.8	205.9	202.4	227.6	208.6	215.3	205.2
60	225.1	213.6	208.0	204.0	231.2	212.4	219.6	209.3
65	227.9	213.7	210.5	205.1	234.7	214.9	224.2	213.6
70	230.7	218.4	213.6	207.6	239.4	216.6	229.4	219.1
75	233.9	223.2	216.2	210.6	243.3	218.7	235.2	224.3
80	237.9	226.4	219.4	210.2	247.9	220.8	240.1	231.4
85	242.7	225.6	222.9	215.3	253.6	224.1	246.8	236.8

 $^{a}$  These data are plotted in Figure 1. The uncertainties are discussed in the text.

than that of  $T_{\rm h}$ , 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 same data are provided graphically in Figure 1.

The shapes of all of the curves are of the subtle sigmoid type that one would expect for a highly complex fluid with many components, distributed over a large range of relative molecular mass. There is no indication of the presence of azeotropic constituents, since there is an absence of multiple inflections and curve flattening. As an example of typical repeatability of these curves, we show in Figure 2 six curves measured for Jet-A-4658. We note that, in the latter stages of the distillations, the repeatability suffers slightly. Curves showing the repeatability of measurements for S-8 have been presented earlier.<sup>8</sup>

The plotted curves are particularly instructive since the differences presented by Jet-A-3838 with respect to Jet-A-3602 and Jet-A-4658 are clearly shown. It is also clear from the curves that the differences are not merely in the early parts of the curves, but rather the differences persist throughout the curve and are in fact magnified at higher distillate volume fraction values. This behavior is indicative of fluids that differ in overall composition or chemical family throughout the entire composition range of the fluid. This is in contrast to differences that result from one fluid merely having somewhat more volatile constituents that boil off in the early stages of the distillationcurve measurement and is often caused by the presence of a different distribution of components within a chemical family. Indeed, this observation was found to be consistent with a gas chromatographic analysis of the three fuel samples (the procedure for which was described in the Experimental Section), since Jet-A-3602 and Jet-A-4658 appear to contain much higher concentrations of heavier components. This can be shown by examining the total area of chromatographic peaks that elute subsequent to the emergence of *n*-tetradecane, for each sample. For Jet-A-3638, this comprises 2.47% of the total peak areas, while for Jet-A-3602 and Jet-A-4658, this comprises 12.07 and 17.57%, respectively. Note that these peak areas are the raw, uncalibrated values and are used only for comparison among the three fluids. For additional details on the chromatograms



Figure 1. Representative distillation curves for each of the three samples of Jet-A and the sample of S-8 that have been measured as part of this work. The uncertainties of each point are discussed in the text.



Figure 2. Plot showing the repeatability of the distillation-curve measurement. Here, six measurements of the curve for Jet-A-4658 are provided. The uncertainty bars of the individual temperatures are of the same size as the plotting symbols.

and for a representative neat fluid chromatogram, the reader is referred to Part 2 of this series.<sup>8</sup>

The rather consistent difference in the distillation curves of Jet-A-3638 and the other two Jet-A fluids is not seen when one examines the behavior of S-8. With this fluid, the curve rises much more sharply than do the Jet-A curves. This is typically observed when a fluid has somewhat more volatile constituents that boil off in the early stages of the distillation-curve measurement. While the fluid initially begins to vaporize at a relatively lower temperature (especially when compared to Jet-A-3602 and Jet-A-4658), by a distillate volume fraction of 45%, the curve of this fluid is approaching those of Jet-A-3602 and Jet-A-4658. By a distillate volume fraction of 60%, the curve of S-8 and those of Jet-A-3602 and Jet-A-4658 have essentially merged. Note that this is consistent with the onset behaviors and chromatographic analyses presented in the discussion of

the initial temperatures. Recall that, for S-8, chromatographic peaks comprising 8.01% of the total integrated area (uncalibrated) of the sample elute between 1.3 and 3 min.

The relationship between  $T_k$  and  $T_h$  is presented in Figure 3, in which both temperatures are presented for the data shown in Table 2 and plotted in Figure 1. We note that  $T_k$  always leads  $T_h$ . This behavior is consistent with a complex mixture with a continually changing composition. Note that, when these two temperatures converge, it is evidence of either a single component being generated (by vaporization) in the kettle or the presence of an azeotrope that controls the composition of both phases. The absence of such a convergence can be interpreted as further evidence of the absence of azeotropic behavior. This is in contrast to what was observed for the gasoline oxygenates, in which the convergence of  $T_k$  and  $T_h$ (due to azeotrope formation) was observed.<sup>12</sup>



Figure 3. Relationship of  $T_k$  and  $T_h$  for the three Jet-A fluids measured in this work. The uncertainty is discussed in the text.

It is clear that an examination of the initial temperatures and the detailed structures of the distillation curves (presented in  $T_k$  and  $T_h$ ) can serve as methods to evaluate the loose specifications that can sometimes characterize gas turbine fuels.

Composition Channel Information. (a) Analysis of Distillate Fractions. 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 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, samples were collected and prepared for analysis. Chemical analyses of each fraction were done by gas chromatography with flame ionization detection and mass spectrometric detection. Representative chromatograms (measured by flame ionization detection) for each fraction of Jet-A-4658 are shown in Figure 4. The time axis is from 0 to 12 min for each chromatogram, and the abundance axis is presented in arbitrary units of area counts (voltage slices). It is clear that, although there are many peaks on each chromatogram (30-40 major peaks and 60-80 minor and trace peaks), these chromatograms are much simpler than that of the neat fluids, which can contain 300-400 peaks. At the very start of each

chromatogram is the solvent front, which does not interfere with the sample. One can follow the progression of the chromatograms in Figure 4 as the distillate fraction becomes richer in the heavier components. This figure illustrates just one chemicalanalysis strategy that can be applied to the distillate fractions. It is possible to use any analytical technique that is applicable to solvent-born liquid samples that might be desirable for a given application.

(b) Hydrocarbon Type Classification. The distillate fractions of the three Jet-A samples and the S-8 sample were examined for hydrocarbon types by use of a mass spectrometric classification method summarized in ASTM Method D-2789,<sup>24</sup> In this method, one uses mass spectrometry (or gas chromatograph – mass spectrometry) to characterize hydrocarbon samples into six types.<sup>25</sup> The six types or families are paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (or aromatics), indanes and tetralins (grouped as one classification), and naphthalenes. Although the method is specified only for application to low-olefinic gasolines, it is of practical relevance to many complex fluid analyses and is often applied to gas turbine fuels, rocket propellants, and missile fuels.<sup>26,27</sup> The uncertainty of this method, and the potential pitfalls, were discussed in Part 3 of this series.<sup>12</sup> As discussed in the



Figure 4. Chromatograms of distillate fractions of a typical Jet-A sample, in this case Jet-A-4658, presented in arbitrary units of intensity (from a flame ionization detector) plotted against time. The details of the chromatography are discussed in the text.

Experimental Section, the solutions were prepared from withdrawn 7  $\mu$ 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  $\mu$ L injections were made into the GC–MS. Because of this consistent injection volume, no corrections were needed for sample volume. The details of the approach, including a detailed discussion on the uncertainty and nomenclature, were discussed in Part 3 of this series.

The results of these hydrocarbon type analyses are presented in parts a-d of Table 3 and plotted in Figure 5. The first line in each of the tables reports the results of the analysis as applied to the entire sample (called the composite) rather than to distillate fractions. This data listed in this line is actually an average of two separate determinations, one done with a neat sample of the fuel (that is, with no added solvent) and the other with the sample in *n*-hexane. The volume of the neat sample was 0.2  $\mu$ L, and only these mass spectra were corrected for sample volume. All of the distillate fractions presented in the table were measured in the same way as the composite (m/zrange from 15 to 550 relative molecular mass units gathered in scanning mode, each spectrum corrected by subtracting trace air and water peaks).

In general, the hydrocarbon type fractions for the composite (the first row in each table) are consistent with the compositions obtained for the distillate fractions (the remaining rows of each table). Thus, taking the S-8 fluid as an example, the paraffin fraction for the composite sample was found to be 80.0%, while that of the distillate fractions ranged from 79.1 to 87.8%. We have noted, however, that, with the composite samples (which naturally produce a much more complex total ion chromatogram), one obtains many more nonintegral m/z peaks on the mass spectrum. Thus, for a distillate fraction, one might obtain a peak at m/z = 43.0, while for the composite, one might obtain m/z = 43.0, 43.15, etc., despite the resolution of the instrument

Table 3. Summary of the Results of Hydrocarbon Family Calculations Based on the Method of ASTM D-2789<sup>a</sup>

distillate volume	paraffins,	monocycloparaffins,	dicycloparaffins,	alkylaromatics,	indanes and tetralins,	naphthalenes,
indection, /o	V01 /0	101 /0	() L : 1 2502	10170	101 /0	101 /0
•,	26.0	260	(a) Jet-A-3602	20.6		17
composite	30.0	20.9	4.5	20.0	0.9	1./
0.025	25.5	30.3	0.1	34.7	2.9	0.4
10	27.5	27.0	/.4	33.2	4.3	0.7
20	27.5	26.7	10.4	28.4	5.9	1.0
30	28.2	26.6	10.8	27.0	6.3	1.1
35	30.0	26.4	9.6	26.4	6.5	1.2
40	29.1	26.6	11.6	24.3	7.0	1.4
45	30.1	26.9	11.0	23.4	7.2	1.5
50	32.9	26.6	8.8	22.8	7.4	1.5
60	28.9	26.8	13.3	19.9	9.0	2.1
70	31.0	28.3	12.4	17.1	9.1	2.2
80	31.5	29.0	12.8	14.0	10.0	2.8
residue	34.3	32.5	13.9	6.8	7.9	4.5
			(b) Jet-A-3638			
composite	49.6	24.9	7.4	12.5	2.9	2.8
0.025	36.9	30.0	6.2	24.6	1.3	1.0
10	42.6	26.1	4.2	25.0	0.9	1.3
20	45.4	25.0	4.1	23.3	0.8	1.4
30	42.2	26.6	6.7	21.0	1.7	1.9
35	42.9	26.4	7.1	19.1	1.8	2.6
40	41.0	26.7	8.4	19.5	2.2	2.2
45	40.9	27.0	9.0	18.5	2.4	2.3
50	42.0	27.0	8.7	17.6	2.3	2.5
60	42.5	27.3	9.0	15.8	2.5	2.9
70	44.8	27.5	8.1	13.7	2.5	3.5
80	44.6	27.6	9.5	11.1	2.9	4.3
residue	43.2	27.7	12.0	3.9	3.1	10.1
			(-) I-+ A 4(50			
composito	16.5	22.5	(C) Jel-A-4038	19.4	4.5	2.4
o o25	40.3	22.5	3.4	10.4	4.5	2.4
0.025	40.4	27.5	5.4	27.5	1.2	0.3
10	39.0	23.1	4.3	21.2	2.0	0.8
20	41.2	24.0	4.4	25.0	3.1	1.1
30	40.9	25.2	5.8	22.1	4.3	1.0
33	43.2	24.5	4.5	21.9	4.2	1.8
40	45.5	25.3	4.8	20.0	4.0	2.0
45	41.7	25.9	6.4	18./	5.0	2.3
50	42.9	25.8	5.0	18.1	5.1	2.4
00 70	43.1	20.4	0./	15.0	5.9	2.9
70	45.8	27.1	7.4	11.8	0.3	3.0
00	40.7	29.9	7.0	0.5	4.0	5.5
residue	49.7	51.9	7.0	3.4	3.4	4.5
			(d) S-8			
composite	80.0	17.3	0.9	0.1	0	1.9
0.025	79.1	18.4	0.1	1.8	0.0	0.6
10	81.2	16.4	0.0	1.9	0.0	0.5
20	81.0	18.0	0.1	0.0	0.0	0.9
30	80.8	17.9	0.3	0.0	0.0	1.1
35	82.0	16.8	0.1	0.0	0.0	1.1
40	85.8	13.7	0.0	0.0	0.0	0.5
45	87.8	11.9	0.0	0.0	0.0	0.3
50	85.3	13.8	0.0	0.0	0.0	0.9
60	85.1	13.9	0.0	0.0	0.0	1.1
70	85.1	13.7	0.0	0.0	0.0	1.2
80	83.6	15.0	0.0	0.0	0.0	1.4
residue	84.8	14.7	0.0	0.0	0.0	0.5

<sup>a</sup> The first three parts (a-c) are for the individual lots of Jet-A, while the last is for the synthetic S-8.

being only 1 unit of mass. Our practice has been to round the fractional masses to the nearest integral mass, a practice that can sometimes cause bias. This is an unavoidable vagary of the instrument that can potentially be remedied with a higher resolution mass spectrometer. We maintain that the comparability among the distillate fractions is not affected by this characteristic, although the intercomparability between the distillate fractions and the composite should be approached with a bit more caution.

The distribution of hydrocarbon type as a function of distillate fraction is particularly instructive among the different Jet-A samples and with reference to Jet-A as compared to the synthetic S-8. We note from the data of parts a-d of Table 3 that Jet-A-3638 and Jet-A-4658 have very similar hydrocarbon family distributions. Moreover, the paraffin fractions of these fluids are significantly higher than that of Jet-A-3602. We also note that, for Jet-A-3638 and Jet-A-4658, the alkylaromatic content is relatively close, while for Jet-A-3602, it is much higher. This behavior is in striking contrast to the behavior apparent on the distillation curves, in which the curves of Jet-A-3602 and Jet-A-3638 was at a lower temperature. This observation illustrates the importance of the composition channel of our distillation-curve approach. Note also that this does not represent an



Figure 5. Plot of the hydrocarbon types resulting from the ASTM D-2789 analysis performed on Jet-A-3602, Jet-A-3638, Jet-A-4658, and S-8. The left side of the figure presents the aliphatic constituents, while the right side presents the cyclic constituents. The uncertainties are discussed in the text.

inconsistency, since it is clear that differing distributions of hydrocarbon types can give rise to different volatilities. Despite having very similar volatility characteristics, Jet-A-3602 and Jet-A-4658 are very different chemically, a fact that would not be noted without the composition channel.

As a function of distillate volume fraction, one can see from Figure 5 that, in general for the Jet-A fluids, the paraffin, monocycloparaffin, and dicycloparaffin contents remain essentially constant or increase very slightly. The alkylaromatic content decreases markedly, while the concentrations of the indanes and tetralins and the naphthalenic compounds increase. Note that the behavior of the alkylaromatic compounds in the turbine fuels are in sharp contrast to that in the gasoline studied earlier.<sup>12</sup> In gasoline, the alkylaromatic content increases with distillate cut fraction, while in turbine fuels, it decreases.

When one compares the Jet-A fluids with the synthetic S-8, the difference is very significant. Table 4d clearly shows that S-8 has a much higher paraffinic content than any of the Jet-A fluids. Moreover, the alkylaromatic content is very small. Indeed, the only aromatic constituents could be found in the very early

Table 4. Summary of the Energy Content, Presented as the Composite Enthalpy of Combustion,  $-\Delta H_c$ , of the 70% Distillate Fraction, for Each of the Fluids Studied<sup>*a*</sup>.

		ontholmy of	fractional
	mole	combustion	combustion
compound	fraction	-AH kI/mol	kI/mol
compound	maction	Δ11, KJ/III01	KJ/IIIOI
(a)	Jet-A-3602	2	
<i>n</i> -undecane	0.150	6903.6	1038.4
1-methyl-5-pentyl cyclohexane	0.053	$7329^{b}$	389.1
<i>n</i> -dodecane	0.212	7513.7	1594.4
2,6-dimethyl undecane	0.083	8104	668.8
n-hexyl cyclohexane	0.054	$7329^{b}$	392.8
2-methyl dodecane	0.059	8117	480.8
2,3,7-trimethyl decane	0.061	$8104^{b}$	453.4
2,6,7-trimethyl decane	0.056	8104	453.4
<i>n</i> -tetradecane	0.198	8732.8	1732.3
x,y,z-trimethyl dodecane	0.074	$9325^{b}$	689.7
total energy for fraction	on, $-\Delta H_c$ ,	kJ/mol: 7931 (32	25)
(b)	Iet_A_363	8	
<i>n</i> -decane	0.080	6294.2	502.0
2.6 dimethyl nonane	0.030	6884	220.4
n undecene	0.032	6002.6	1622.0
2 othyl popaga	0.233	6905.0	1023.0
1.4 dimethyl 2 athyl hangene(	0.024	5542h	1246
2. mathyl undegene	0.024	3343 <sup>8</sup> 7506h	154.0
2-methyl undecane	0.035	7506	202.0
5-metnyl undecane"	0.010	7506	121.4
5-etnyl decane"	0.010	/500	121.4
<i>n</i> -dodecane	0.216	/513./	1625.3
2,6-dimethyl undecane	0.062	8104 <sup>b</sup>	502.0
2-methyl dodecane	0.029	811/ <sup>b</sup> 750 <i>c</i> h	236.9
5-methyl undecane	0.044	/506	330.7
<i>n</i> -tetradecane	0.14/	8/32.8	1286.2
total energy for fraction	on, $-\Delta H_c$ ,	KJ/mol: 7013 (2)	88)
(c)	Jet-A-4658	5	
<i>n</i> -undecane	0.090	6903.6	621.5
<i>n</i> -dodecane	0.221	7513.7	1662.6
2,6-dimethyl undecane	0.060	8104 <sup>b</sup>	486.4
2,3-dimethyl undecane	0.068	8104 <sup>b</sup>	549.0
2-methyl dodecane	0.067	8117 <sup>b</sup>	541.5
<i>n</i> -tridecane	0.264	8122.9	2141.4
<i>n</i> -tetradecane	0.164	8732.8	1429.7
<i>n</i> -pentadecane	0.067	9342.4	624.7
total energy for fraction	on, $-\Delta H_{\rm c}$ ,	kJ/mol: 8057 (3	30)
	(d) S-8		
<i>n</i> -decane	0.040	6294.2	252.6
3-methyl decane	0.044	6896	304.0
<i>n</i> -undecane	0.110	6903.6	756.9
4,7-dimethyl undecane	0.056	7506 <sup>b</sup>	421.2
5-methyl undecane	0.053	7506 <sup>b</sup>	396.8
4-methyl undecane	0.048	$7506^{b}$	362.8
2-methyl undecane	0.049	$7506^{b}$	371.5
3-methyl undecane	0.057	7511	427.5
<i>n</i> -dodecane	0.137	7513.7	1031.9
4,6-dimethyl undecane	0.052	$8117^{b}$	421.8
6-methyl dodecane	0.041	$8117^{b}$	334.7
5-methyl dodecane	0.042	$8117^{b}$	344.7
4-methyl dodecane	0.044	8117 <sup>b</sup>	355.4
2-methyl dodecane	0.043	8117 <sup>b</sup>	345.6
3-methyl dodecane	0.049	8117 <sup>b</sup>	395.8
<i>n</i> -tridecane	0.092	8122.9	745 7
<i>n</i> -tetradecane	0.043	8732.8	371.1
	0.04J	1-1/	10)

total energy for fraction,  $-\Delta H_c$ , kJ/mol: 7640 (313)

<sup>*a*</sup> The uncertainties are discussed in the text and are provided in the table in parentheses. <sup>*b*</sup> The enthalpy of combustion values determined by the Cardozo method, instead of being experimentally measured. <sup>*c*</sup> .<sup>*d*</sup>Split peaks, baseline unresolved, taken as a 50/50 mol/mol fraction of a single chromatographic peak.

emerging distillate fractions. These two facts are consistent with the composition of the synthetic feed stock of this fluid, namely, natural gas.

(c) Distillate Fraction Energy Content. As we have previously demonstrated, it is possible to add thermochemical information to the distillation curve when the composition

channel of data is used to obtain an analysis of specific distillate fractions. This 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.<sup>11</sup> The enthalpy of combustion of the individual components was taken from a reliable database compilation.<sup>28</sup> The mole fraction was measured by a gas chromatographic method in which response factors were applied to the raw area counts obtained from either a flame ionization detector or from selected (or extracted) ion monitoring from a mass spectrometer. The differences in the distillation curves of the fluids measured in this work appear to be a maximum at a distillate fraction of 70%. Since this is one of the fractions that were sampled and analyzed as part of the composition channel of data, we present the composite enthalpy of combustion of this fraction for each of the fluids measured in this work.

We have previously discussed the contributions to the overall uncertainty of the composite enthalpy of combustion at great length.<sup>11</sup> The contributions included (1) the neglect of the enthalpy of mixing, (2) the uncertainty in the individual 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), and (6) the uncertainty introduced by a complete misidentification of a component. These contributions to the combined uncertainty of the composite enthalpy of combustion proved to be adequate in the treatment of simple mixtures and in considering the common components of gasoline that were presented in Part 3. In this work, we have found two additional sources of uncertainty that had to be considered.

First, we encountered two instances in which the analysis of the 70% fraction of one of the fluids produced closely eluting chromatographic peaks of appreciable area that could not be baseline resolved. Changes to the method (in terms of column temperature program or film thickness) were insufficient to resolve these peaks. In both of the cases in which this occurred, both components of the chromatographic peak appeared to be of approximately equal areas. This was different from the commonly encountered chromatographic situation of a leading or trailing shoulder, which introduces a relatively minor ambiguity. By examining the mass spectral purity on the leading and trailing edges of the two coeluting peaks that were encountered here, the identities of the two components could be ascertained. In both of these cases, the overall area of the two chromatographic peaks was measured (that is, the areas of both parts were taken as a single peak) and divided equally between the two components that were identified. We do not believe that this procedure has added markedly to the 10% uncertainty previously claimed for the mole fraction.<sup>11</sup>

Second, in this work, we encountered compounds for which experimental enthalpy of combustion data were not available. In these instances, we used the Cardozo method to predict the enthalpy of combustion.<sup>29</sup> This method functions by developing an "equivalent chain" for an unknown compound, then applying a correlation specific for a gas, liquid, or solid. In all cases of our application of this method, the correlation used was for the liquid. From this correlation, the enthalpy of combustion was obtained. In addition, for one component of Jet-A-3602, the isomerization could not be ascertained on the basis of the mass spectrum. This compound was, therefore, listed as *x*,*y*,*z*-trimethyl dodecane. The predicted values for the enthalpy of combustion



Figure 6. Column plot showing the composite enthalpy of combustion of the 70% distillate fraction for each of the fluids measured. In this figure, the fluids are presented in the order of increasing enthalpy of combustion of the 70% distillate fraction.

of all trimethyl dodecanes will be the same, however, so this ambiguity in isomerization adds no additional contribution to the uncertainty.

To evaluate the uncertainty of predictions made by the Cardozo method for the kinds of compounds we have considered in this work, a comparison was made with a set of compounds for which reliable experimental data are available. We found that, for a selection of straight-chain and branched hydrocarbons, the difference between the predictions and the experimental data was 0.84%. This value was, therefore, used as the contribution to overall uncertainty caused by the use of the Cardozo prediction in the absence of experimental data.

In view of the sources of uncertainty that have been discussed above, including those in the preceding two paragraphs, the overall combined uncertainty in our composite enthalpy of combustion is 4.1% (with a coverage factor k = 2). As usual, the uncertainty is dominated by the analytical measurement and determination of the component mole fraction. In Table 4, we have provided the components identified in the 70% fraction, along with the enthalpy of combustion for each compound, the approximate mole fraction for each, and the fractional contribution to the composite enthalpy of combustion. Below each of the individual tables is the composite enthalpy of combustion for that fluid. The uncertainty of this value is listed in parentheses. The data are presented in the form of a column plot in Figure 6 in order of increasing enthalpy.

The composite enthalpy of combustion for the 70% fraction ranges from a low of 7013 kJ/mol for Jet-A-3638 to a high of 8057 kJ/mol for Jet-A-4653. Thus, the difference in energy content represented by this difference in the composite enthalpy of combustion spans a range of 13%. The composite enthalpy of combustion of S-8 and Jet-A-3602 is essentially the same, within experimental uncertainty. It is interesting to note that the behavior of the two extreme fluids, Jet-A-3638 and Jet-A-4658, is reflected in the distillation-curve profile. The temperature at the 70% distillate fraction for Jet-A-4658 lies wellabove that for Jet-A-3638, a fact that is consistent with the presence of more heavy components (with more C–H bonds) in Jet-A-4658. This is another illustration of the advantage of the composition channel of data of the distillation curve: one can explain the shape and profile of the curve in terms of chemical composition and energy content as a function of distillate fraction.

As was the case with the gasoline mixtures, one can express the composite enthalpy on a volume or mass basis instead of on a molar basis. A practical alternative would be, for example, a presentation in units of kJ/L. This is a simple change, requiring only the density of each identified compound at a particular temperature of interest. While enthalpies of combustion presented in kJ/mol have very little temperature dependence, those presented in kJ/L may be expected to have significant temperature dependence.

### Conclusions

In this paper, we have reported the application of an improved method of distillation-curve measurement as applied to the aviation turbine fuel Jet-A and a synthetic made from natural gas. The measurements of the temperatures  $T_k$  and  $T_h$  provide a lower overall uncertainty and allow comments to be made about the fluid behavior. The composition channel of information provides access to more detailed insight into the fluid behavior. Finally, we have shown how the composition channel allows the combination of thermochemical data with the temperature data of the distillation curve. This provides an explicit measure of the energy content of each fraction.

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