

Composition-Explicit Distillation Curves of Aviation Fuel JP-8 and a Coal-Based Jet Fuel

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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) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis); (2) temperature measurements that are true thermodynamic state points; (3) temperature, volume, and pressure measurements of low uncertainty suitable for an equation of state development; (4) consistency with a century of historical data; (5) an assessment of the energy content of each distillate fraction; (6) a trace chemical analysis of each distillate fraction; and (7) a corrosivity assessment of each distillate fraction. The most significant 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 military aviation fuel JP-8, and also to a coal-derived fuel developed as a potential substitute. We present not only the distillation curves but also a chemical characterization of each fraction and discuss the contrasts between the two fluids.

Introduction

The major gas turbine fuel that is currently the most commonly used by the United States military is JP-8 (MIL-DTL-83133), a kerosene fraction that has a higher flash point than the main military predecessor, JP-4.¹ 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 than JP-8 (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 typically contains an icing inhibitor, a corrosion inhibitor/lubricity enhancer, and an antistatic additive.² 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 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.

The gas turbine engine is more forgiving in operation than are internal combustion engines that burn gasoline. Indeed, the developer of the first gas turbine engine, Sir Frank Whittle, reportedly once remarked that his engine could run on anything from whiskey to peanut butter. While the reality might not be

so generous, it is clear that the gas turbine can utilize a wide variety of liquid fuels, especially in an emergency. A major consideration with alternatives to fuels such as Jet-A and JP-8 is how to derate the engines in terms of service life. The necessity to derate an engine designed for JP-8 after operating it on an alternative fuel stems mainly from the carbon deposits in the fuel system and fuel nozzles. This can typically require engine teardown and maintenance at more frequent intervals than if the engine were fueled only with the optimal fuel grade kerosene. It is therefore clear that the properties of alternative fuels must be well understood to permit substitutions to be made as needed.

In response to concerns of supply disruptions and environmental considerations, several alternative fuels to JP-8 have been developed that are based on alternative feed stocks. This includes synthetic fluids made from natural gas (designated as S-8, made by the Fischer–Tropsch process) and a blended fluid made from a significant fraction of coal liquids (designated in this paper as coal-derived fuel, CDF).^{3–10} This fluid is also referred to as a prototype JP-900.

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In earlier work, we described a method and apparatus for advanced distillation curve measurement that is especially applicable to the characterization of fuels.^{10–18} This method is a significant improvement over current approaches, featuring (1) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis); (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state; (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development; (4) consistency with a century of historical data; (5) an assessment of the energy content of each distillate fraction; (6) a trace chemical analysis of each distillate fraction; and (7) a corrosivity assessment of each distillate fraction. This approach also provides important advantages over other methods such as the simulated distillation method embodied in procedures such as ASTM D2887. In that method, for example, one uses the gas chromatographic behavior of a suite of compounds as a frame of comparison with a fuel. The very significant advantage offered by the approach discussed in this paper is the ability to model the distillation curve resulting from our metrology with an equation of state.

In this work, we have applied the new metrology to develop a comparison between JP-8 and CDF. Clearly, it is not always needed or desirable to apply all aspects of the advanced distillation curve metrology in every application. For highly finished fuels such as JP-8, for example, it is usually unnecessary to assess corrosivity as a function of the distillate fraction. The CDF fluid is a mixture of coal-derived liquid (a derivative of bituminous coal tar) and light cycle oil, a byproduct of catalytic cracking units in petroleum refining. The resulting mixture is treated to increase the number of carbon–hydrogen bonds by hydroprocessing at a high temperature and pressure. The fluid is intended for high chemical stability up to 480 °C (900 °F, hence the alternative name of the prototype, JP-900).

Experimental Section

The JP-8 used in this work was obtained from the Fuels Branch of the Air Force Research Laboratory (AFRL; Wright Patterson Air Force Base, Dayton, OH). This sample, designated as POSF-3773, is a real fuel taken directly from the flight line. The sample of CDF was also obtained from AFRL and was designated POSF-4765. The ultimate source of the fluid was the Pennsylvania State University Energy Institute's Coal Utilization Laboratory. The trailing numbers assigned have no significance beyond identifica-

tion. 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.

Each of the fuel samples was analyzed by gas chromatography (30 m capillary column of 5% phenyl/95% dimethyl polysiloxane having a thickness of 1 μ m, temperature program from 90 to 275 °C, at 9 °C per minute) using flame ionization detection and mass spectrometric detection (GC-MS).^{19,20} 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 prior to analysis. The composition of JP-8 and similar fluids has been reported in numerous sources.^{1,21} Our analyses, summarized in Table 1a, revealed a similar composition to those compositions that have been reported. Note that in some cases substituent positions are ambiguous on the basis of our analyses; in such cases, we designate the position with variables *x*, *y*, etc. The composition of the sample of CDF is significantly different from that of JP-8, as one would expect from the very different feedstock. The major constituents found in this sample, along with the uncalibrated area counts (obtained from an integration of the total ion chromatogram of GC-MS), are listed in Table 1b. We have presented the constituents of nearly 50% of the total area integrated. While we have focused on the largest chromatographic peaks for identification, we have also included a selection of very light and very heavy constituents as well, despite the fact that these constituents make up very little of the bulk. This is done to facilitate our future efforts in modeling the fluid with an equation of state.

It is clear from the components listed in Table 1 that the composition of the sample of CDF is very different from that of fuels that are based solely on a petroleum feedstock. There is an abundance of aliphatic ring compounds, and many compounds with two aliphatic rings. A dominant constituent of this fluid is *trans*-decahydronaphthalene.

In addition to this chemical analysis, the two fluids were characterized and compared by the measurement of some basic thermophysical properties. The density, viscosity, speed of sound, and refractive index of the samples of JP-8 and CDF are provided in Table 2 for 20, 25, and 30 °C, all at atmospheric pressure. These data were measured with a commercial vibrating tube densimeter, a commercial viscodensimeter, a commercial pulse echo speed of sound analyzer, and a commercial Abbe refractometer, respectively. These data show distinct property differences in the two fluids. CDF has, for example, a uniformly higher density (by approximately 8%), which is consistent with the large number of cyclic compounds present in the mixture. Even more striking is the difference in viscosity, with CDF having more than a 40% higher viscosity than JP-8 (under the experimental conditions listed). The uncertainties provided for each of these measurements were determined from three replicate measurements in which a different aliquot of sample was placed into the measurement cell. The coverage factor associated with these uncertainties is *k* = 2. We also provide in Figure 1 the infrared spectra of the samples we have measured. These spectra show that both fluids are hydrocarbons that have very few double bonds.^{19,20}

The *n*-hexane used as a solvent in this work was obtained from a commercial supplier and was analyzed by gas chromatography

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Table 1. Listing of the Major Components Found in the Samples of (a) JP-8 and (b) CDF^a

compound	CAS no.	area %	compound	CAS no.	area %
(a) JP-8					
<i>n</i> -heptane	142-82-5	0.125	2,3-dimethyl decane	17312-44-6	0.681
methyl cyclohexane	108-87-2	0.198	1-ethyl-2,2,6-trimethyl cyclohexane	71186-27-1	0.364
2-methylheptane	592-27-8	0.202	1-methyl-3-propyl benzene	1074-43-7	0.569
toluene	108-88-3	0.320	aromatic unknown	NA	0.625
<i>cis</i> -1,3-dimethyl cyclohexane	638-04-0	0.161	5-methyldecane	13151-35-4	0.795
<i>n</i> -octane	111-65-9	0.386	2-methyldecane	6975-98-0	0.686
1,2,4-trimethyl cyclohexane	2234-75-5	0.189	3-methyldecane	13151-34-3	0.969
4-methyl octane	2216-34-4	0.318	aromatic unknown	NA	0.540
1,2-dimethyl benzene	95-47-6	0.575	aromatic unknown	NA	0.599
<i>n</i> -nonane	111-84-2	1.030	1-methyl-(4-methylethyl) benzene	99-87-6	0.650
<i>x</i> -methylnonane	NA	0.597	<i>n</i> -undecane	1120-21-4	2.560
4-methylnonane	17301-94-9	0.754	<i>x</i> -methyl undecane	NA	1.086
1-ethyl-3-methyl benzene	620-14-4	1.296	1-ethyl-2,3-dimethyl benzene	933-98-2	1.694
2,6-dimethyl octane	2051-30-1	0.749	<i>n</i> -dodecane	112-40-3	3.336
1-methyl-3-(2-methylpropyl) cyclopentane	29053-04-1	0.285	2,6-dimethyl undecane	17301-23-4	1.257
1-ethyl-4-methyl benzene	622-96-8	0.359	<i>n</i> -tridecane	629-50-5	3.998
1-methyl-2-propyl cyclohexane	4291-79-6	0.370	1,2,3,4-tetrahydro-2,7-dimethyl naphthalene	13065-07-1	0.850
1,2,4-trimethyl benzene	95-63-6	1.115	2,3-dimethyl dodecane	6117-98-2	0.657
<i>n</i> -decane	124-18-5	1.67	2,6,10-trimethyl dodecane	3891-98-3	0.821
1-methyl-2-propyl benzene	1074-17-5	0.367	<i>x</i> -methyl tridecane	NA	0.919
4-methyl decane	2847-72-5	0.657	<i>x</i> -methyl tridecane	NA	0.756
1,3,5-trimethyl benzene	108-67-8	0.949	<i>n</i> -tetradecane	629-59-4	1.905
<i>x</i> -methyl decane	NA	0.613	<i>n</i> -pentadecane	629-62-9	1.345
(b) CDF					
cyclohexane	110-82-7	0.059	decahydro-2,3-dimethyl naphthalene	1008-80-6	3.700
methyl cyclohexane	108-87-2	0.070	decahydro-2,6-dimethyl naphthalene	1618-22-0	1.327
<i>cis</i> -1,3-dimethyl cyclohexane	638-04-0	0.074	decahydro- <i>x</i> , <i>y</i> -dimethyl naphthalene	NA	1.147
ethyl cyclohexane	1678-91-7	0.201	<i>cis,trans</i> -2-ethylbicyclo[4.4.0]decane	66660-38-6	1.448
<i>cis,trans</i> -1-ethyl-3-methyl cyclohexane	3728-55-0	0.254	dodecahydro acenaphthalene	2146-36-3	0.952
propyl cyclohexane	1678-92-8	0.362	<i>trans-anti-trans</i> -tricyclo[7.3.0.0]- (2,6)-dodecane	30159-17-2	1.386
<i>trans</i> -octahydro-1H-indene	3296-50-2	0.777	(cyclopentylmethyl)cyclohexane	4431-89-4	1.296
<i>cis</i> -octahydro-1H-indene	4551-50-3	1.147	(2-ethyl-1-methylbutylidene)cyclohexane	74810-41-6	1.209
(1-methylpropyl)-cyclohexane	7058-01-7	0.777	1,1'-bicyclohexyl	40250-64-4	1.999
octahydro-5-methyl-1H-indene	19744-64-0	1.170	perhydrophenylene	40250-64-4	1.670
<i>trans</i> -decahydro naphthalene	493-02-7	10.372	tetradecahydro anthracene	6596-35-6	0.813
<i>cis</i> -decahydro naphthalene	493-01-6	3.770	perhydrophenanthrene	2108-89-6	1.044
decahydro-2-methyl naphthalene	2958-76-1	3.082	<i>n</i> -hexadecane	544-76-3	0.432
decahydro-1-methyl naphthalene	2958-75-0	1.696	<i>n</i> -nonadecane	629-92-5	0.016
decahydro- <i>x</i> -methyl naphthalene	NA	1.097	<i>n</i> -eicosane	122-95-8	0.045
decahydro- <i>x</i> -methyl naphthalene	NA	0.991			

^a The area percentages provided are from raw uncorrected areas resulting from the integration of the GC-MS total ion chromatogram. Peaks were selected for identification on the basis of criteria described in the text.

Table 2. The Density, Sound Speed, Refractive Index, and Viscosity of the Samples of JP-8 and CDF Used in this Work^a

fuel	temperature, °C	density, g/mL	sound speed, m/s	refractive index, Na ^d	viscosity, mPa·s
JP-8	20	0.7938	1305	1.4447	1.3204
		(0.0001)	(1)	(0.0003)	(0.0003)
		0.7901	1285	1.4432	1.2172
	30	(0.0001)	(1)	(0.0003)	(0.0003)
		0.7865	1266	1.4404	1.1057
		(0.0001)	(1)	(0.0002)	(0.0002)
CDF	20	0.8652	1385	1.4700	2.3075
		(0.0001)	(2)	(0.0003)	(0.0009)
		0.8616	1365	1.4675	2.1001
	25	(0.0001)	(2)	(0.0001)	(0.0007)
		0.8581	1349	1.4658	1.9209
		(0.0001)	(2)	(0.0003)	(0.0005)

^a The uncertainty of each measurement determined from three replicate measurements (with coverage factor $k = 2$) is provided in parentheses.

(30 m capillary column of 5% phenyl/95% dimethyl polysiloxane having a thickness of 1 μ m, temperature program from 50 to 170 °C, at 5 °C per minute) using flame ionization detection and mass spectrometric detection. These analyses revealed the purity to be approximately 99.95%, and the fluid was used without further purification.

The method and apparatus for the distillation curve measurement have been reviewed in a number of sources, so additional general description will not be provided here.^{11–17} For each distillation curve measurement, two temperature channels are measured: T_h , the temperature measured in the distillation head, and T_k , the temperature measured directly in the fluid (kettle). The required amount of fluid for the distillation curve measurement (in each case, 200 mL) was placed into the boiling flask with a 200 mL volumetric pipet. The thermocouples were then inserted into the proper locations to monitor T_k , the temperature in the fluid, and T_h , the temperature at the bottom of the takeoff position in the distillation head. Enclosure heating was then commenced with a four-step program based upon a previously measured distillation curve. 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 two fluid 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. This value corresponds to a carbon chain of 12. In the chemical analyses of the JP-8 samples (see above), as well as in previous work on related fluids, it was

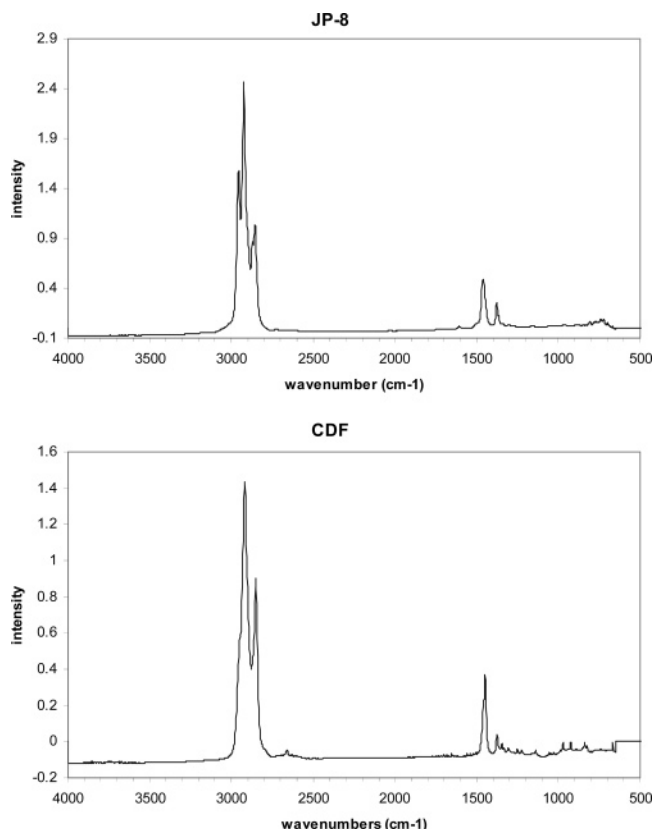


Figure 1. The infrared spectra of the JP-8 and CDF used for the measurements presented in this paper.

found that *n*-dodecane can indeed represent petroleum-based aviation fuels as a very rough surrogate. The very large number of ring compounds in the CDF makes the constant term more difficult to assign; however, since the CDF is intended as a fluid similar in operation to JP-8, we assigned the same constant value as for JP-8. The magnitude of the correction is of course dependent upon the extent of deviation from standard atmospheric pressure. The location of the laboratory in which the measurements reported herein were performed is approximately 1650 m above sea level, resulting in a typical temperature correction of 7 °C. The actual measured temperatures are easily recovered from the Sidney Young equation at each measured atmospheric pressure.^{12,22,23}

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,

Table 3. A Summary of the Initial Behavior of the JP-8 and CDF^a

observed temperature	Jet-A 4658: °C	JP-8 3773: °C	CDF 4765: °C
Onset	139.9	131.1	180.2
sustained	185.6	177.6	195.6
vapor rising	190.5	182.7	199.0

^a For reference, the behavior of a composite sample of Jet-A (prepared as a mixture of several batches of Jet-A from different sources) 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 Sidney Young equation. The uncertainties are discussed in the text.

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 3. For example, for the JP-8, the temperature for the appearance of the first vapor bubble was 131.1 °C, measured in the liquid. Bubbling was observed to be sustained when the temperature of the fluid reached 177.6 °C. Vapor was observed rising into the head when the temperature reached 182.7 °C, which is considered to be the IBT for the mixture. 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; the actual temperatures measured can be recovered from the Sidney Young equation. For reference, we have also included the initial temperature observations previously made on a fluid very similar to JP-8, namely, a composite of individual samples of Jet-A designated as -4658).¹⁵ The experimental atmospheric pressures were 83.5, 83.8, and 83.7 kPa, respectively, for Jet-A, JP-8, and CDF. The uncertainty in the pressure measurement was 0.001 kPa in each case.

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, 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 approximately 2 °C. The uncertainty in the vapor rise temperature is actually much lower, at approximately 0.2 °C.

As we have noted for all other fluids measured with the advanced approach, the IBT values we have presented are very different from those that would be obtained with the classical method, in which the first drop of distillate to arrive at the receiver triggers the reading of the IBT. We have shown those values measured with the classical approach to be between 7 and 13 °C in systematic error.

Distillation Curves. Representative distillation curve data for the samples of JP-8 and CDF, presented in both T_k (measured directly in the fluid) and T_h (measured in the distillation head), are provided in Table 4. For reference, representative data are also provided for the composite sample of Jet-A. The T_k data are true thermodynamic state points, while the T_h data allow comparison with historical 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 than that of T_h , but as a conservative position, we use the higher value for both temperatures. The uncertainty in the volume measurement that is used to obtain the distillate volume fraction is 0.05 mL in each case. These

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Table 4. Representative Distillation Curve Data for the Samples of JP-8 and CDF^a

distillate volume fraction, %	Jet-A 4658		JP-8 3773		CDF 4765	
	T_k , °C	T_h , °C	T_k , °C	T_h , °C	T_k , °C	T_h , °C
5	195.4	174.7	185.6	174.7	200.4	190.7
10	198.5	183.3	187.9	179.2	201.5	194.4
15	201.5	187.0	190.3	182.2	202.5	196.5
20	204.7	189.1	192.7	184.8	204.0	197.8
25	208.1	190.6	195.1	186.7	205.1	199.2
30	211.3	192.8	197.6	185.1	206.8	198.8
35	214.3	194.6	200.4	188.7	208.0	199.9
40	217.6	199.1	203.3	194.1	209.6	201.0
45	220.7	202.6	206.1	196.2	211.4	203.9
50	224.2	205.4	209.3	199.9	213.5	205.9
55	227.6	208.6	213.5	201.2	216.0	208.4
60	231.2	212.4	216.4	203.8	218.5	210.8
65	234.7	214.9	220.6	209.4	221.8	213.6
70	239.4	216.6	224.8	212.1	225.6	217.2
75	243.3	218.7	229.4	215.8	230.1	221.4
80	247.9	220.8	234.6	219.3	235.8	227.9
85	253.6	224.1	240.3	225.5	242.3	235.5

^a For reference, data are also provided for a composite sample of Jet-A. These data are plotted in Figure 1. The uncertainties are discussed in the text. These temperatures have been corrected to 1 atm with the Sidney Young equation. The experimental pressures for these measurements were 83.5, 83.8 and 83.7 kPa, respectively, for Jet-A, JP-8, and CDF.

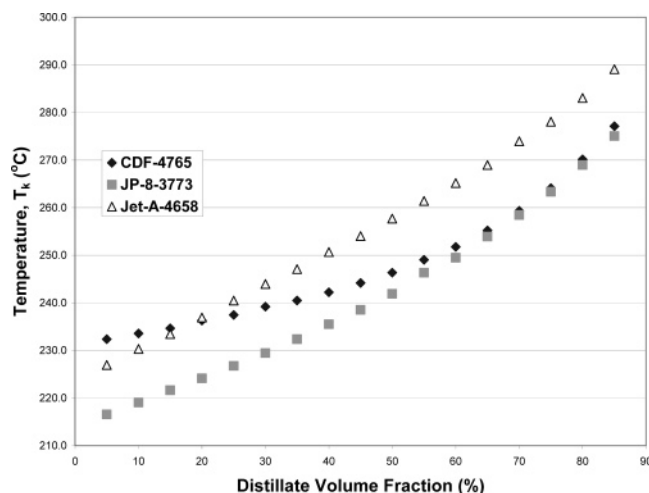


Figure 2. Distillation curves, presented in T_k , for JP-8 and CDF. For reference, a curve for a composite Jet-A is also included. The uncertainties of the measurements are discussed in the text.

uncertainties were determined from replicate measurements. The uncertainty in the pressure measurement (assessed by logging a pressure measurement every 15 s for 2 h, the duration of a typical distillation) is 0.001 kPa. These uncertainties make the measurements suitable for the development of equations of state. The data in Table 4 are provided graphically in Figure 2. 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.

The plotted curves are particularly instructive since the difference presented by the three samples is made clear. Consistent with the initial boiling behavior presented in Table 3, the distillation curves of Figure 2 show that JP-8 is the most volatile of the three fluids examined here. The composite Jet-A sample is a relatively low-volatility fluid, as shown in a previous study that was done on several Jet-A samples.¹⁵ The CDF shows an initial behavior that is less volatile than either the JP-8 or the composite Jet-A. As the distillation curves show, however, by the 60% volume fraction, the curve of CDF closely approaches the curve of JP-8. It might be tempting to conclude

from this observation that the heavier fractions of CDF are indeed similar in chemical composition to JP-8. We will show later that the composition-explicit data channel of the advanced distillation curve shows a very different character, consistent with the different feedstock.

Another interesting observation concerns the shape of the curve for CDF, the slope of which is far less pronounced than those of the JP-8 or Jet-A samples. As we have seen in previous work, a curve that flattens in this way is similar in behavior to that of either a pure fluid or an azeotrope.¹⁴ If the fluid were showing azeotropic characteristics, one would observe the azeotropic convergence of T_k and T_h , and this is not seen in Table 4. Another explanation of this behavior is that the distillation curve is being dominated to some extent by the presence of a constituent that is present in a large concentration, whereas the distribution of components of JP-8 and Jet-A is more disperse in terms of individual boiling temperatures. We will show later that this observation is consistent with the information provided by the composition channel.

Composition Channel Information: 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. This was done by withdrawing 7 μ L aliquots of distillate (as a function of the distillate volume fraction) and diluting this in a known mass (approximately 1 mL) of *n*-hexane. Each of these fractions thus prepared was analyzed by a gas chromatographic mass spectrometric method (30 m capillary column of 5% phenyl/95% dimethyl polysiloxane having a thickness of 1 μ m, temperature program from 90 to 275 °C, at 9 °C per minute, mass spectrometer set to record an ion mass range of 15–550).

Representative chromatograms for each fraction of CDF are shown in Figure 3. We do not present a similar figure for JP-8 because of its similarity to Jet-A, which was presented previously.¹⁵ The time axis is from 0 to 22 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, 60–80 minor peaks, and numerous trace peaks), these chromatograms are much simpler than that of the neat fluid, which showed 300–400 peaks. The distillation process in effect provides a preliminary separation on the basis of volatility. At the very start of each chromatogram is the solvent front (*n*-hexane), which does not interfere with the sample. This peak has been removed digitally.

One can follow the progression of the chromatograms in Figure 3 as the distillate fraction becomes richer in the heavier components, yet the major component that dominates each fraction is *trans*-decahydronaphthalene. This persists up to the 80% fraction. The identification of this peak is shown in Figure 4, in which the mass spectrum for this compound is shown superimposed on the total ion chromatogram for the 0.025% distillate volume fraction. The observation that this compound is present to a very significant amount in each distillate fraction provides the explanation of the observation of the distillation curve shape. As we noted earlier, the curve for CDF is notably flattened as compared with those for JP-8 and Jet-A. This is consistent with the presence of a dominating constituent compound in the fluid, and while the relative concentration of this compound changes through the distillation, it is always present. In more disperse fluids such as Jet-A, even the most

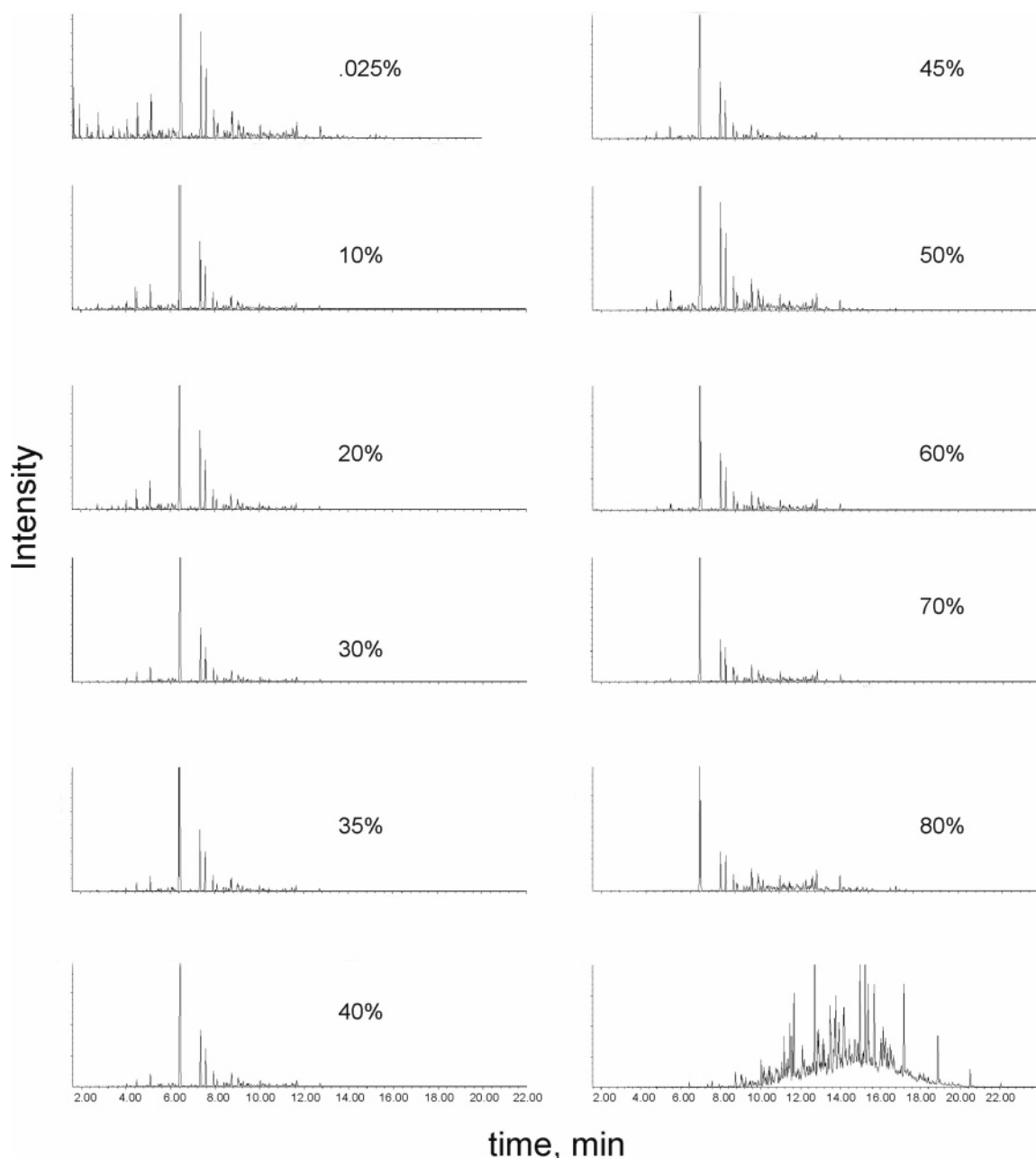


Figure 3. Chromatograms of distillate fractions of the CDF sample, presented in arbitrary units of intensity (from a flame ionization detector), plotted against time. The chromatogram on the lower-right side is the residue left behind in the distillation flask. The details of the chromatography are discussed in the text.

abundant components will grow in and gradually diminish to an undetectable level as the distillation proceeds.

Figures 3 and 4 illustrate just one chemical analysis strategy that can be applied to the distillate fractions. 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. The distillate fractions of the JP-8 and CDF samples were examined for hydrocarbon types by use of a mass spectrometric classification method summarized in ASTM method D-2789.²⁴ In this method, one uses mass spectrometry (or gas chromatography–mass spectrometry) to characterize hydrocarbon samples into six types. The six types or families are paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (arenes or aromatics), indanes

and tetralins (grouped as one classification), and naphthalenes. Although the method is specified only for application to low olefinic gasolines, and it has significant limitations, it is of practical relevance to many complex fluid analyses and is often applied to gas turbine fuels, rocket propellants, and missile fuels.⁵ The uncertainty of this method and the potential pitfalls were discussed earlier.¹⁴ As discussed above, the solutions were prepared from withdrawn 7 μL samples of a 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 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 these hydrocarbon type analyses are presented in Table 5 and plotted in Figure 5. All of the distillate fractions presented in the table were measured in the same way (*m/z* range

(24) Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, ASTM Standard D2789-02. *ASTM Annual Book of Standards*, 2004; ASTM: West Conshohocken, PA, 2004.

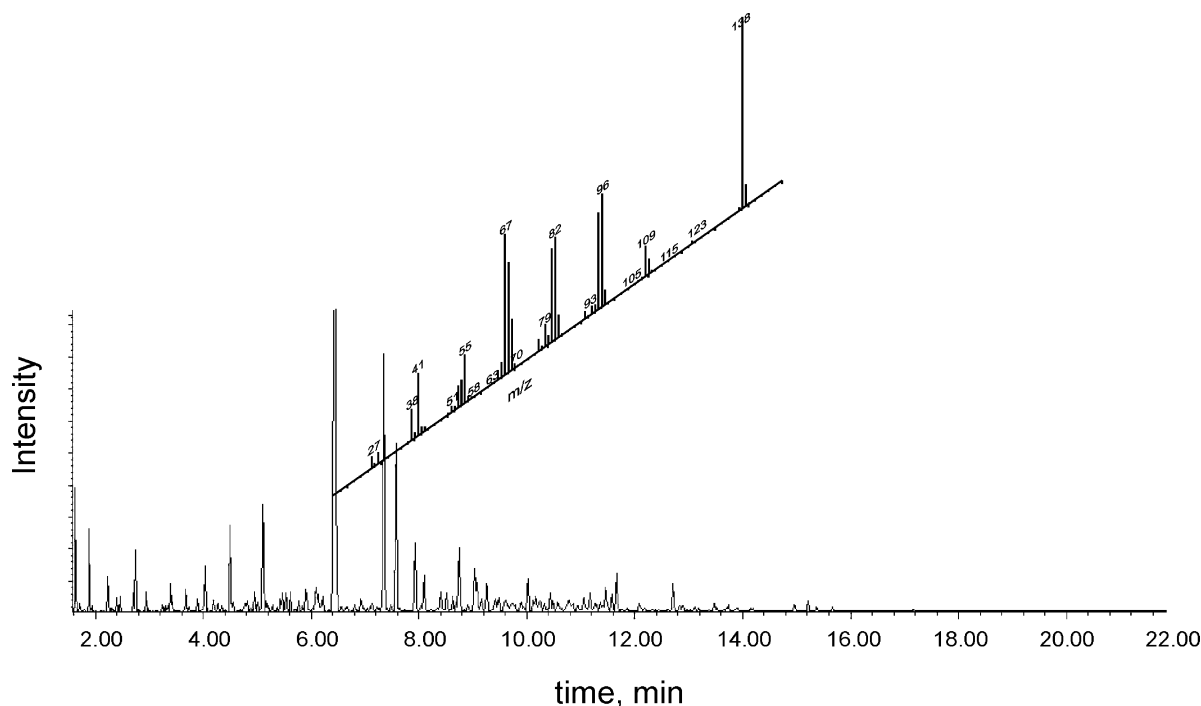


Figure 4. An example of how the composition explicit data channel can be used to identify chromatographic peaks of analyses performed on individual distillate fractions. Here, a mass spectrum consistent with *trans*-decahydronaphthalene is shown for the major peak in the chromatogram for the 0.025% distillate fraction.

Table 5. Summary of the Results of Hydrocarbon Family Calculations Based on the Method of ASTM D-2789: (a) JP-8 3773 and (b) CDF 4765

distillate volume fraction, %	paraffins vol %	monocycloparaffins vol %	dicycloparaffins vol %	alkyl aromatics vol %	indanes and tetralins vol %	naphthalenes vol %
(a) JP-8 3773						
0.025	40.8	30.3	11.4	16.8	0.5	0.3
10	49.0	27.0	2.3	20.7	0.7	0.3
20	45.9	28.1	4.7	18.0	1.9	1.3
30	47.4	27.4	3.6	19.2	1.5	1.0
35	48.6	26.8	3.1	19.4	1.3	0.7
40	52.1	24.8	2.1	18.8	1.2	0.9
45	57.6	21.8	1.0	18.4	0.2	1.0
50	56.1	23.5	1.6	17.0	0.8	1.1
60	57.2	23.5	1.7	14.9	1.0	1.8
70	61.4	22.2	1.0	11.0	1.7	2.6
80	56.3	26.6	2.5	8.0	2.5	4.0
residue	56.0	30.9	4.0	1.2	0.5	7.3
(b) CDF 4765						
0.025	1.3	32.2	63.1	3.3	0.1	0.0
10	0.5	27.5	68.6	3.4	0.1	0.0
20	0.5	27.2	68.7	3.4	0.1	0.0
30	0.4	25.5	70.7	3.3	0.1	0.0
35	0.4	25.1	71.0	3.4	0.1	0.0
40	0.4	25.3	70.9	3.4	0.1	0.0
45	0.5	26.0	69.8	3.4	0.2	0.0
50	0.8	28.0	67.4	3.6	0.2	0.0
60	0.5	26.1	69.9	3.3	0.1	0.0
70	0.6	26.6	69.7	3.0	0.1	0.0
80	1.2	30.4	65.1	3.3	0.1	0.0
residue	1.0	28.8	66.4	3.5	0.2	0.0

from 15 to 550 relative molecular mass units gathered in scanning mode, each spectrum corrected by subtracting trace air and water peaks).

The plots for JP-8 are similar in character to those that have been previously reported for the commercial aviation fuel Jet-A. Indeed, JP-8 differs from Jet-A mainly in the additive package, which represents less than 0.1% (vol/vol) of the total fluid. Figure 5a and b (for JP-8) show that, as a function of the distillate fraction, the paraffinic content increases modestly (from 40–60%); the monocyclic aliphatics decrease slightly; and the

dicyclo aliphatics, the indanes and tetralins, and the naphthalenes are at a constant very low level. The aromatics on the other hand decrease sharply. This is consistent with a kerosene-like fuel derived from petroleum. Figure 5c and d show a very different behavior for the CDF. In this fluid, the dominant family as a function of the distillate fraction is the dicyclo aliphatics (at a relatively constant 60–70%). The monocyclo aliphatics and the aromatics are also constant at approximately 30% and 3.5%, respectively. The indanes and tetralins and the naphthalenes are difficult to detect in this fluid. The hydrocarbon type

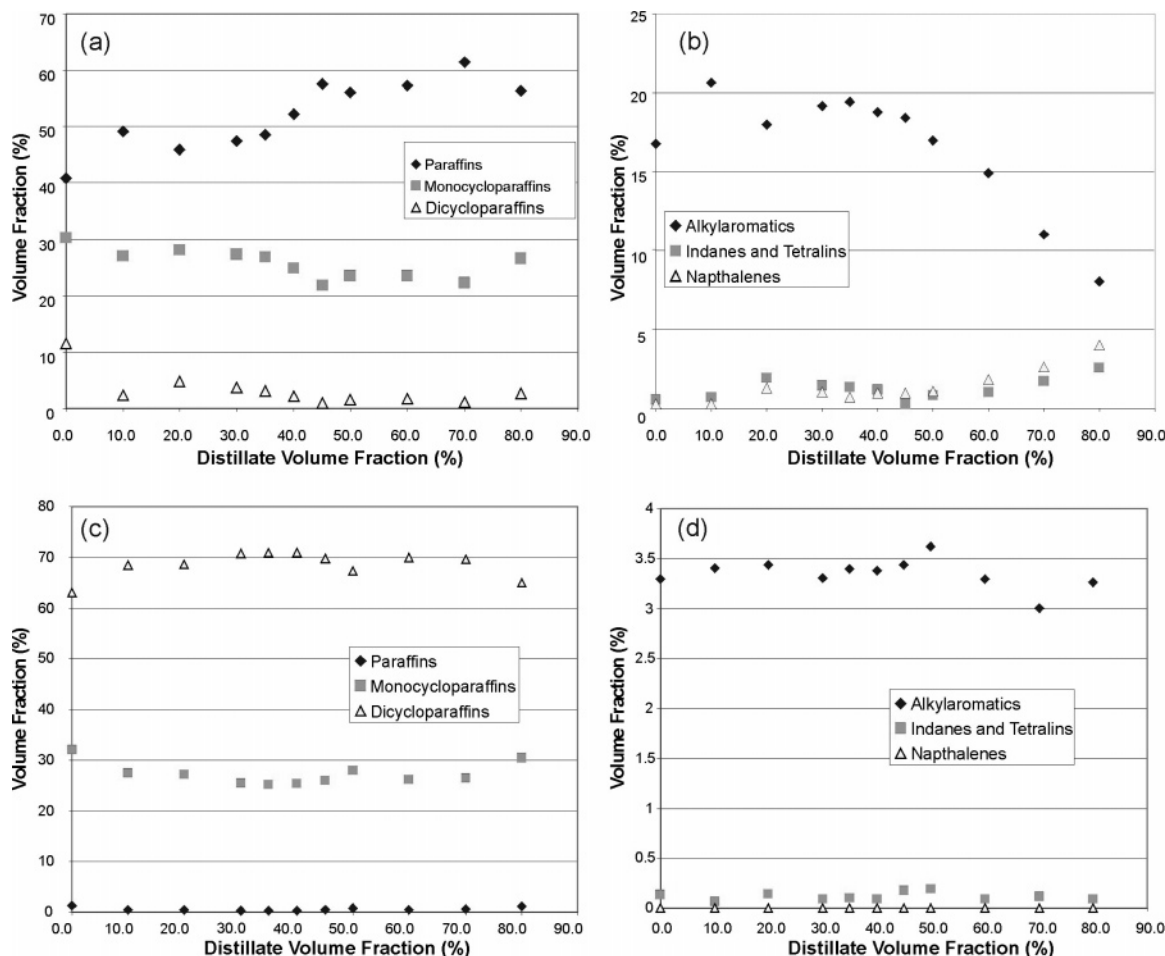


Figure 5. A plot of the aliphatic hydrocarbon family types resulting from the ASTM D-2789 analysis performed on JP-8 (a and b) and CDF (c and d) as a function of the distillate fraction. The uncertainties are discussed in the text.

classification is consistent with the identification of the major components of the fluid, provided in Table 1.

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.^{14,15,17} 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. The enthalpy of combustion of the individual components is taken from a reliable database compilation. The mole fraction is measured by a gas 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, but reference to the distillation curves of JP-8 and CDF shows a convergence at approximately the 70% distillate fraction; the curves start out at very different temperatures at the earlier stages of the distillation but then merge after this fraction. Such thermochemical information would be especially instructive and useful for this merge point.

We have previously presented a very detailed discussion of the uncertainty of composite enthalpy of combustion derived from this procedure.¹⁵ 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 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 misidentification 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 used²⁵).

In this work, we encountered still another source of uncertainty. Many of the compounds of CDF are not readily obtainable as pure components (only *trans*-decahydronaphthalene and 1,1'-bicyclohexyl were available); thus, a typical response factor standardization done by injecting mixtures of pure components is not currently possible (components are unavailable as pure standards). For the two available components (*trans*-decahydronaphthalene and 1,1'-bicyclohexyl), the pure components were obtained and used as standards. These two compounds represent approximately 45% (mol/mol) of the 70% distillate fraction. The chromatographic responses of the isomers of the decahydronaphthalenes were standardized with *trans*-decahydronaphthalene prepared in *n*-hexane, and the responses

(25) Rowley, R. L.; Wilding, W. V.; Oscarson, J. L.; Zundel, N. A.; Marshall, T. L.; Daubert, T. E.; Danner, R. P. *DIPPR(R) Data Compilation of Pure Compound Properties*; Design Institute for Physical Properties: New York, 2004.

Table 6. A Summary of the Energy Content, Presented as the Composite Enthalpy of Combustion, $-\Delta H_c$, of the 70% Distillate Fraction, for JP-8 and CDF^a

compound name	enthalpy of combustion, $-\Delta H_c$, kJ/mol	% molar composition	fractional enthalpy of combustion, kJ/mol
(a) JP-8			
<i>n</i> -decane	6294.2	6.02	379.0
2,3,6-trimethyloctane	6940.4*	1.59	110.4
(4-methylpentyl)cyclohexane	7376.5*	1.34	99.1
5-methyldecane	6952.7*	1.43	99.5
<i>x</i> -methyldecane	6952.7*	2.74	190.2
2-methyldecane	6952.7*	2.20	152.8
<i>x</i> -methyldecane	6952.7*	2.69	187.0
1-methyl-4-(1-methylethyl)benzene	5549.8	1.43	79.5
<i>n</i> -undecane	6903.6	15.77	1089.0
5-methyl undecane	7567.8	1.82	137.7
<i>t</i> -butyl benzene	5557.1	1.53	85.2
3,7-dimethyl decane	5549.8	1.40	78.0
1-methyl-2-(1-methylethyl)benzene	5554.8*	4.50	249.9
<i>n</i> -dodecane	7513.7	18.18	1366.0
2,6-dimethyl undecane	8182.9*	3.79	310.3
4-methyldodecane	8182.9*	1.38	113.2
2-methyldodecane	8182.9*	2.45	200.7
3-methyldodecane	8182.9*	2.50	204.7
6,6-dimethylundecane	8182.9*	2.02	165.3
<i>n</i> -tridecane	8122.9	14.54	1181.2
2-methylnaphthalene	5582.9	1.83	102.4
6-ethyl-2-methyl decane	8170.6	1.16	94.7
<i>n</i> -tetradecane	8732.8	6.31	551.3
5-propyltridecane	10028	1.44	144.8
(b) CDF			
<i>trans</i> -decahydro naphthalene	5880.9	41.98	2468.5
<i>cis</i> -decahydro naphthalene	5892.1	10.22	602.4
<i>trans</i> -2-methyldecalin	6773.7	7.77	526.6
<i>trans</i> -4a-methyl decahydronaphthalene	6786.6*	3.33	225.8
decahydro-2-methyl naphthalene	6786.6*	3.88	263.6
decahydro-2,6-dimethyl naphthalene	7376.5*	4.64	342.4
decahydro-2,3-dimethyl naphthalene	7376.5*	6.42	473.4
decahydro-1,5-dimethyl naphthalene	7376.5*	2.04	150.5
<i>cis,cis</i> -1,6-dimethylspiro[4.5]decane	7388.8*	1.24	91.3
<i>trans,trans</i> -1,6-dimethylspiro[4.5]decane	7388.8*	1.35	99.7
<i>cis,cis</i> -3-ethylbicyclo[4.4.0]decane	7388.8*	2.56	189.3
<i>cis,trans</i> -3-ethylbicyclo[4.4.0]decane	7388.8*	1.26	93.0
dodecahydroacenaphthalene	7409.7*	1.31	97.3
(cyclopentylmethyl)cyclohexane	7833.5*	1.43	111.7
(2-ethyl-1-methylbutylidene)cyclohexane	7865.5*	1.56	122.7
<i>trans-anti-trans</i> -tricyclo[7.3.0.0(2,6)]dodecane	7239.3*	2.45	177.3
<i>cis-anti-trans</i> -tricyclo[7.3.0.0(2,6)]dodecane	7239.3*	1.41	102.2
1,1'-bicyclohexyl	7053	3.21	226.4
perhydrophenalene	8003.9*	1.93	154.8

^a The uncertainties are discussed in the text. The enthalpy of combustion values determined by the Cardozo method, instead of being experimentally measured, are denoted by an asterisk. Composite enthalpy of combustion, $-\Delta H_c$: 7371.8 (811) and 37.9 (4.2) kJ/g (part a); 6518 (717) and 43.4 (4.8) kJ/g (part b).

of the compounds that contain at least one nonfused cyclohexyl ring were standardized with the $m/z = 83$ (the $(CH_2)_5CH^+$ ion) selected ion from methyl cyclohexane prepared in cyclohexane.¹⁹ In cases in which the cyclohexyl ring shares a carbon with another ring, the $m/z = 83$ ion is absent, and the $m/z = 55$ (the $CH_2=CHCH^+-CH_3$ ion) was used.¹⁹ While this method of standardization is less than satisfactory, it provides an approximate mole fraction required for the energy calculations. Fortunately, all of the components present in the 70% distillate fraction of the JP-8 were available for use in a standardization protocol, prepared as multicomponent mixtures in *n*-hexane.

Moreover, very few of the compounds of CDF have measured values of the enthalpy of combustion; thus, most required the application of the Cardozo method.²⁶ This method functions by developing an "equivalent chain" for an unknown compound,

then applying a correlation specific for a gas, a liquid, or a solid. Since there were experimental data for three of the compounds identified in the 70% distillate fraction (*trans*-decahydro naphthalene, *cis*-decahydronaphthalene, and 1,1'-bicyclohexyl), we were able to approximate the uncertainty introduced by calculating the enthalpy of combustion for these types of compounds. We note in passing that, fortuitously, the three compounds for which experimental data exist comprise more than 55% (mol/mol) of the composition of this fraction. To determine the typical uncertainty that might be introduced by the application of the Cardozo method for these aliphatic ring compounds, the calculated values for the three known compounds were compared with the experimental values. This comparison showed that the results from the Cardozo method were uniformly higher than the experimental values by approximately 3.5%. It is this uncertainty that was used in further propagation of uncertainty. This is a higher degree of uncertainty than the approximately 0.84% that was found previ-

(26) Cardozo, R. L. Prediction of the Enthalpy of Combustion of Organic Compounds. *AIChE J.* **1986**, *32*, 844–848.

ously for the predictions of enthalpies of combustion of the branched aliphatics in Jet-A fluids. It is possible that, in the future, as coal-based fuels become more important, the necessary thermophysical and thermochemical properties will be experimentally determined.

The composite enthalpies of combustion, $-\Delta H_c$, for the 70% fractions of JP-8 and CDF are listed at the bottom of Table 6 along with the estimated uncertainty (approximately 11%, with coverage factor $k = 2$). It is interesting to note that, on a molar basis, JP-8 appears to have a somewhat higher energy content than does CDF, although the relatively high uncertainty in these calculations precludes a definitive statement in this regard. When one converts to a mass basis, we note that this relationship is reversed. While this might initially seem inconsistent, it is not surprising considering that the ring compounds that predominate in the CDF fraction are expected to have a significantly higher density than the straight and branched chain aliphatics in JP-8. Certainly, that proved to be the case in our examination of the density of the bulk samples of JP-8 and CDF, shown in Table 2. It would be instructive to present the calculation in terms of volume also; however, the density of most of the individual compounds in the CDF list has not yet been measured.

Conclusions

We have presented the distillation curves of JP-8 and CDF, including the composition-explicit data channel. We have also demonstrated how it is possible to estimate the energy content of distillate fractions of these two very different fluids. The distillation curves show that the properties that control the volatility of the fluid (component vapor pressures and vapor liquid equilibrium) differ in a predictable and consistent way, as is expected from the different chemical compositions.

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