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A Comparison of the Hypersonic Vehicle Fuel JP-7 to the Rocket Propellants RP-1 and RP-2 with the Advanced Distillation Curve Method

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Received February 3, 2009. Revised Manuscript Received May 4, 2009

JP-7 is a hydrocarbon-based kerosene fraction with a low volatility and high thermal stability. JP-7 was developed in the 1950s to meet the more stringent requirements necessary for the development of high-altitude reconnaissance aircraft that fly at speeds exceeding Mach 3. The extreme temperatures encountered due to the heat transmitted from compressed air on the aircraft, and air resistance, required the development of fuels with improved thermal stability and higher flash points. Although JP-7 also meets the operational demands for hypersonic aircraft (Mach 5+), this fluid is no longer produced. Currently, there is a desire in the hypersonic vehicle community to replace JP-7 with the rocket propellant RP-2; however, research and testing is necessary to determine whether this substitution will be possible. In this paper, we apply the advanced distillation curve method to a representative sample of the hypersonic vehicle fuel JP-7. Specifically, we present the thermodynamically consistent distillation curve and use the composition channel to characterize the curve in terms of composition and available energy content. We then compare the results with previous measurements performed on the rocket propellants RP-1 and RP-2. This work provides a basis of comparison among these fuels in terms of the fundamental thermophysical properties. This comparison will be critical in determining the applicability of substitute fuels and the refinement of future fuels for hypersonic vehicles.

Introduction

Hypersonic Vehicle Fuels. The development of high-altitude reconnaissance aircraft that fly at speeds exceeding Mach 3 led to more stringent fuel requirements than were necessary for conventional aircraft. The extreme temperatures encountered from the heating due to compressed air on the aircraft, and skin friction, required the development of fuels with improved thermal stability and higher flash points.^{1,2} JP-7 (MIL-DTL-38219),³ a highly processed hydrocarbon-based kerosene fraction, was developed in the 1950s to meet these more stringent requirements.^{1,2} JP-7 has a low volatility and is stable up to 287 °C (550 °F). The high temperatures encountered in Mach 3 flight made JP-7 a good endothermic fuel. Cracking reactions generated relatively small molecules when the fluid was used as a coolant prior to being burned in the engines. It is also interesting to note that in the SR-71 (the long-range, Mach 3 strategic reconnaissance aircraft of the United States Air Force), JP-7 was also used as a hydraulic fluid prior to being burned in the engines.⁴

While JP-7 meets the operational demands for supersonic and even hypersonic aircraft (Mach 5+), this fluid is no longer produced. There was a posting on the Federal Business Opportunities Web site from the Defense Logistics Agency on June 17, 2008 seeking potential sources in North America that

have the capability to supply JP-7; however, only 110 000 gallons were requested for experimentation.³ Currently, the hypersonic vehicle community is considering the use of various formulations of rocket grade kerosene, including an ultralow sulfur version of Rocket Propellant 1 (RP-1, MIL-DTL-25576D), as a replacement for JP-7.^{5,6}

RP-1 is a hydrocarbon fuel that is widely used in rocket propulsion systems. RP-1 has a much tighter allowable density and volatility range, and a much lower sulfur, olefin, and aromatic content than those of the common turbine aviation fuels. The desire to use rocket motors many times, rather than a single time, led to reformulations of the kerosene component of liquid rocket propellants. The resulting fuels demonstrated lower metal corrosion effects and are thus more amenable to multiple use rocket motors. This work led to the development of RP-2, an ultralow sulfur rocket kerosene. There has also been some research aimed at developing additives to blend with the jet propellant JP-8 and the missile propellant JP-10 to meet the requirements of hypersonic flight and therefore to potentially replace JP-7.^{1,7}

Advanced Distillation Curve Metrology. One of the most important and informative properties that is measured for complex fluid mixtures is the distillation (or boiling) curve.^{8–11} Simply stated, the distillation curve is a graphical depiction of

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the boiling temperature of a fluid or fluid mixture plotted against the volume fraction distilled.^{8–10} The most common presentation of the distillation curve is a plot of the boiling temperature (at ambient pressure) against volume fraction. The standard test method, ASTM D-86, provides the usual approach to measurement, yielding the initial boiling point, the temperature at predetermined distillate volume fractions, and the final boiling point.¹¹ The ASTM D-86 test suffers from several drawbacks, including large uncertainties in temperature measurements and little theoretical significance.¹²

The advanced distillation curve (ADC) approach addresses many of the shortcomings of the standard distillation method described above. First, we incorporate a composition explicit data channel for each distillate fraction (for both qualitative, quantitative, and trace analysis). Sampling very small distillate volumes (5–25 μL) yields a composition-explicit data channel with nearly instantaneous composition measurements. Chemical analysis of the distillate fractions allows for determination of how the composition of the fluid varies with volume fraction and distillation temperature, even for complex fluids. These data can be used to approximate vapor liquid equilibrium of complex mixtures and presents a more complete picture of the fluid under study. The ADC approach 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. Suitable analytical techniques include gas chromatography with either flame ionization detection (GC-FID) or mass spectral detection (GC-MS), element specific detection (such as gas chromatography with sulfur or nitrogen chemiluminescence detection, GC-SCD or GC-NCD), and Fourier transform infrared spectrophotometry (FTIR).

Another advantage of the ADC approach is that it provides temperature, volume, and pressure measurements of low uncertainty, and the temperatures obtained are true thermodynamic state points that can be modeled with an equation of state. In fact, we have used the ADC method to develop chemically authentic surrogate mixture models for the thermophysical properties of both a coal-derived liquid fuel and the synthetic aviation fuel S-8.^{13,14} This model development would not be possible with the ASTM D-86 approach, because this method does not have a theoretical link to the equation of state for complex mixtures.

In this paper, we apply the ADC method to a representative sample of the hypersonic vehicle fuel JP-7. Specifically, we present the thermodynamically consistent distillation curve and use the composition-explicit data channel to characterize the curve in terms of composition and available energy content. We then compare the results with previous measurements performed on the rocket propellants RP-1 and RP-2.¹⁵ The goal of this work is to provide a basis of comparison among these fuels in terms of the fundamental thermophysical properties. This comparison will be critical in determining the applicability of substitute fuels and the refinement of future fuels for hypersonic vehicles.

Theory—Enthalpy of Combustion. The composition-explicit data channel allows the addition of thermochemical data to the distillation curve.^{16–18} The enthalpy of combustion is the heat released when a given amount of a combustible pure substance is burned (in oxygen) to form incombustible products (e.g., water and carbon dioxide). Equation 1 presents the combustion reaction of *n*-octane,



which results in an enthalpy of combustion of -5074 kJ/mol .¹⁹ Enthalpies of combustion of pure substances are also used in comparing the stabilities of chemical compounds. Enthalpies of combustion are routinely used as a basis for comparing the heating value of fuels, since the fuel that produces the greater amount of heat for a given cost is often the more economical. The enthalpy of combustion can be specified in terms of either $\text{H}_2\text{O}_{(\text{g})}$ or $\text{H}_2\text{O}_{(\text{l})}$.¹⁶ We use the net enthalpy (or net heat) of combustion, in which the product specification is for $\text{H}_2\text{O}_{(\text{g})}$ because this quantity is used in the specification of JP-7 and rocket propellants.

The composite molar enthalpy of combustion (which we represent as $-\Delta H_c$) can be found by multiplying the enthalpy of combustion of each of the pure (or individual) components by the mole fraction of that component and, then, adding the contributions of the individual components to obtain the composite result:^{16–18}

$$-\Delta H_c = \sum x_i(-\Delta H_i) \quad (2)$$

where *i* refers to the individual components that have been identified or selected, and the enthalpy of mixing is ignored.^{16–18}

In this work, the enthalpy of combustion is examined because of the importance of this quantity to any finished fuel. In fact, any enthalpy can be calculated as a function of distillate cut. These quantities are also important because they are amenable to theoretical modeling.

Experimental Section

The *n*-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 μm , temperature program from 50 to 170 $^\circ\text{C}$ at a heating rate of 5 $^\circ\text{C}$ per minute) with flame ionization and mass spectrometric detection. These analyses revealed the purity to be approximately 99%, and the fluid was used without further purification.

The JP-7 that was measured in this work was obtained from the United States Air Force, Air Force Research Laboratory, Propulsion Directorate, and was used without treatment or purification. Care was taken to minimize exposure to the atmosphere to minimize oxidation, evaporation of the more volatile components, and uptake of moisture. The sample is considered to be representative in that the properties of JP-7 are typically more tightly controlled than are aviation or motor fuels. Despite this, there can be minor lot-to-lot differences among different batches of fluid.

The sample of JP-7 was subjected to a chemical analysis before the measurement of the distillation curve. It was analyzed by use

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of GC-MS detection (30 m capillary column of 5% phenyl/95%-dimethyl polysiloxane having a thickness of 0.25 μm , temperature program from 50 to 90 $^{\circ}\text{C}$, 3 $^{\circ}\text{C}$ per minute and from 90 to 170 $^{\circ}\text{C}$, 6 $^{\circ}\text{C}$ per minute) and a search of the NIST-EPA mass spectral database.^{20,21} Mass spectra were collected for each peak from 32 to 550 RMM (relative molecular mass) units. The assignment of major components having an area percent in excess of 1% are presented in Table 1. This fluid is primarily composed of linear and branched paraffins and mono- and dicycloparaffins. A proprietary fluorocarbon-based lubricity additive was present at a concentration of 250 ppm (mass/mass), which is an insufficient concentration to affect the distillation curve or most other thermophysical properties, or the modeling thereof. It is important to note that a small amount of alkylbenzenes was detected, but at area percents less than 1%. For comparison, the same type of analysis is included for RP-1 and RP-2 in Table 1.

The method and apparatus for ADC measurements has been reviewed in detail elsewhere;^{12,17,18,22,23} thus, no additional general description will be provided here. In brief, 200 mL of JP-7 for the distillation curve measurement was placed into the boiling flask with a 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, between four and six complete distillation curve measurements were performed. The uncertainty (with a coverage factor $k = 2$) of these measurements has been discussed in detail in previous papers and is approximately 2 $^{\circ}\text{C}$ in the onset and sustained bubbling temperatures and is approximately 0.2 $^{\circ}\text{C}$ in the vapor rise temperature.¹⁵ 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.

Because the measurements of the distillation curves were performed at ambient atmospheric pressure (typically 83 kPa, measured with an electronic barometer), temperature readings were adjusted for what should be obtained at standard atmospheric pressure. The average experimental atmospheric pressure for these initial temperature observations was 83.4 kPa. The uncertainty in the pressure measurement is 0.003 kPa. The adjustments to the pressure measurements were done with the modified Sydney Young equation, in which the constant term was assigned a value of 0.000109.^{24–26} This value corresponds to an n -alkane carbon chain of 12, which is a reasonable representative for JP-7. The magnitude of this correction depends on the extent of deviation from standard atmospheric pressure.²⁷ 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 adjustment of ~ 7 $^{\circ}\text{C}$.

To provide the composition channel to accompany the temperature information on the distillation curves, sample aliquots were withdrawn for 12 selected distillate volume fractions. To accomplish this, aliquots of ~ 7 μL of emergent fluid were withdrawn from the

sampling hammock in the receiver adapter with a blunt-tipped chromatographic syringe and added to a crimp-sealed vial containing a known mass (approximately 1 mL) of n -hexane solvent. A sample was withdrawn at the first drop of fluid from the condenser and then at each of 11 additional predetermined volume fractions of distillate, for 12 total sample aliquots. Each distillate volume aliquot was analyzed by GC-MS (30 m capillary column of 5% phenyl/95% dimethyl polysiloxane having a thickness of 0.25 μm , temperature program from 50 to 90 $^{\circ}\text{C}$, 3 $^{\circ}\text{C}$ per minute and from 90 to 170 $^{\circ}\text{C}$, 6 $^{\circ}\text{C}$ per minute, mass spectrometer set to scan a m/z range from 32 to 400 RMM units gathered in scanning mode) and a search of the NIST-EPA mass spectral database.^{20,21}

Compounds with a total area of greater than or equal to 2% on the raw total ion chromatogram (TIC) were standardized on the GC with external standards. Smaller peaks with uncalibrated area counts less than 2% of the total uncalibrated area were omitted. In past work, we determined that neglecting peaks with total uncalibrated area percentages of up to 4% increased the uncertainty of the calculated enthalpy by only 1.5%.¹⁶ Therefore, neglecting minor components in the JP-7 distillate fractions does not significantly affect the uncertainty of the composite enthalpy of combustion.

Analytical standardization was done on the basis of extracted ions (sometimes called single ion monitoring or selected ion monitoring, SIM).²⁸ The compounds used for standardization were purchased from a commercial supplier. Four concentrations of each standard solution were prepared by diluting the compound of interest in n -hexane. Each standard solution was subjected to seven replicate analyses. The JP-7 distillate samples were complex but were primarily composed of paraffins, monocycloparaffins, and dicycloparaffins. The lengths of the paraffin chains ranged from C_9 to C_{15} ; therefore, the paraffins were standardized with C_{12} (with the $m/z = 57$ ion dwelled on during SIM). The monocyclic paraffins present in the JP-7 samples were mostly cyclohexane compounds with varied hydrocarbon substituents. Hence, cyclohexane was used to standardize for the monocycloparaffins (with the $m/z = 83$ ion dwelled on during SIM). The dicyclic paraffins integrated in the chromatograms were all decahydronaphthalene (decalin) compounds or hydrocarbon-substituted decalins; these compounds were standardized with *trans*-decalin (with the $m/z = 81$ ion dwelled on during SIM).

After standardization, enthalpy of combustion analysis was performed for the JP-7s on distillate fractions corresponding to 0.025, 10, 50, and 90% of the distillate volume.

Results and Discussion

Initial Boiling Behavior. During the initial heating of the JP-7, the behavior of the fluid was carefully observed. For the ADC method, the temperatures at which bubbling is first observed, at which sustained bubbling was observed, and at which vapor was observed to rise into the distillation head (the vapor rise temperature) were recorded. The vapor rise temperature has been shown to be the initial boiling temperature (IBT) of the mixture and is highlighted in bold print in Table 2. The average temperature for the appearance of the first vapor bubble was 171.8 $^{\circ}\text{C}$, measured in the liquid. Bubbling was observed to be sustained when the temperature of the fluid reached 207.5 $^{\circ}\text{C}$. Vapor was observed rising into the head when the temperature reached 211.2 $^{\circ}\text{C}$, and this temperature, measured using T_k , is considered to be the IBT and can be modeled theoretically in an equation of state as the bubble point of the starting mixture. These temperatures have been corrected to standard atmospheric pressure with the Sidney Young equation as described above; the experimental pressures are provided so that the actual temperatures measured can be recovered. For comparison, the initial temperature observations previously made

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Table 1. Components of Tested Fuels Identified by GC-MS^a

RT (min)	compound	CAS No.	RMM	area %
JP-7				
5.250	<i>n</i> -decane	124-18-5	142.28	2.5
5.871	butylcyclohexane	1678-93-9	140.27	1.1
6.374	4-methyldecane	2847-72-5	156.31	1.7
6.451	2-methyldecane	6975-98-0	156.31	1.3
6.587	3-methyldecane	13151-34-3	156.31	1.8
7.267	<i>n</i> -undecane	1120-21-4	156.31	9.2
7.575	2-methyldecalin	2958-76-1	152.28	2.2
7.805	3,7-dimethyldecane	17312-54-8	170.33	1.3
7.924	1-methyldecalin	2958-75-0	152.28	1.8
8.024	pentylcyclohexane	4292-92-6	154.29	1.0
8.101	cyclododecane	294-62-2	168.32	1.1
8.456	5-methylundecane	1632-70-8	170.34	2.2
8.562	4-methylundecane	2980-69-0	170.34	1.8
8.675	2-methylundecane	7045-71-8	170.34	2.1
8.834	3-methylundecane	1002-43-3	170.34	2.4
9.668	<i>n</i> -dodecane	112-40-3	170.34	11.7
9.970	2,6-dimethylundecane	17301-23-4	184.36	2.9
10.632	hexylcyclohexane	4292-75-5	168.32	1.3
11.147	4-methyldodecane	6117-97-1	184.36	1.4
11.283	2-methyldodecane	1560-97-0	184.36	2.7
11.466	3-methyldodecane	17312-57-1	184.36	1.2
11.543	2,6-dimethyloctane	2051-30-1	142.28	1.6
12.389	<i>n</i> -tridecane	629-50-5	184.36	9.9
12.791	6-methyltridecane	13287-21-3	198.39	1.4
13.944	4-methyltridecane	26730-12-1	198.39	1.2
14.098	2-methyltridecane	1560-96-9	198.39	1.4
14.293	3-methyltridecane	6418-41-3	198.39	1.2
14.476	2,6,10-trimethyldodecane	3891-98-3	212.41	1.7
15.215	<i>n</i> -tetradecane	629-59-4	198.39	5.8
18.101	<i>n</i> -pentadecane	629-62-9	212.41	1.5
RP-1				
8.268	2,6-dimethyl nonane	17302-28-2	156.19	1.8
8.759	<i>x,y</i> -dipropyl cyclopentane	NA	154.17	1.1
9.286	trans-decahydro naphthalene	493-02-7	138.14	1.5
9.598	2-methyl decane	6975-98-0	156.19	1.6
9.813	3-methyl decane	13151-34-3	156.19	1.3
10.824	<i>n</i> -undecane	1120-21-4	156.19	2.6
11.128	2-methyl- <i>trans</i> -decalin	1000152-47-3	152.16	1.4
11.373	2,6-dimethyl decane	13150-81-7	170.2	1.2
11.671	2- <i>syn</i> -methyl decalin	1000155-85-6	152.16	2.0
11.931	1,3-dimethylbutyl cyclohexane	61142-19-6	168.19	1.4
12.703	5-methyl undecane	1632-70-8	170.2	1.7
13.00	2-methyl undecane	7045-71-8	170.2	2.3
13.223	5-ethyl decane	17302-36-2	170.2	1.4
13.714	1-methyl-1,2-pentyl cyclohexane	54411-01-7	168.19	1.1
14.278	<i>n</i> -dodecane	112-40-3	170.2	2.4
14.754	2,6-dimethyl undecane	17301-23-4	184.22	2.0
16.262	4-methyl dodecane	6117-97-1	184.22	1.5
16.447	2-methyl dodecane	1560-97-0	184.22	1.8
16.782	7-methyl tridecane	26730-14-3	198.24	1.7
17.710	<i>n</i> -tridecane	629-50-5	184.22	2.6
17.978	1-methyl naphthalene	90-12-0	142.08	1.2
18.253	6-methyl tridecane	13287-21-3	198.24	1.0
19.790	2-methyl tridecane	1560-96-9	198.24	1.1
RP-2 ^b				
5.528	2,6-dimethyl nonane	17302-28-2	156.31	1.48%
5.855	3,7-dimethyl nonane	17302-32-8	156.1	1.1%
6.279	<i>trans</i> -decalin	493-02-7	138.25	2.8%
6.37	2-methyl decane	6975-98-0	156.31	1.9%
7.425	2-methyl decalin	295-87-61	152.28	1.8%
7.48	2,6-dimethyl decane	13150-81-7	170.33	1.5%
7.771	1-methyl decalin	2958-75-0	152.28	1.8%
7.892	pentylcyclohexane	4292-92-6	154.29	1.1%
8.292	5-methyl undecane	1632-70-8	170.33	2.2%
8.389	4-methyl undecane	2980-69-0	170.33	1.5%
8.48	2-methyl undecane	7045-71-8	170.33	2.1%
8.62	3-methyl undecane	1002-43-3	170.33	2.4%
9.087	1-methyl 2-pentyl cyclohexane	54411-01-7	168.32	1.3%
9.547	<i>x,y</i> -dimethyl undecane	N/A	184.36	2.3%
9.857	2-ethyl decalin	66660-42-2	166.30	1.0%
10.087	hexylcyclohexane	4292-75-5	168.32	1.1%
10.384	<i>x,y</i> -dimethyl undecane	N/A	184.36	1.4%
10.481	4-methyl dodecane	6117-97-1	184.36	1.1%
10.584	2-methyl dodecane	1560-97-0	184.36	2.3%

Table 1. Continued

RT (min)	compound	CAS No.	RMM	area %
10.718	3-methyl dodecane	17312-57-1	184.36	1.1%
10.772	4,6-dimethyl dodecane	61141-72-8	168.15	2.3%
11.688	6-methyl tridecane	13287-21-3	198.39	1.3%
12.221	heptylcyclohexane	5617-41-4	182.35	1.2%
12.506	4-methyl tridecane	26730-12-1	198.39	1.2%
12.603	2-methyl tridecane	1560-96-9	198.39	1.6%
12.737	3-methyl tridecane	6418-41-3	198.39	1.1%
12.864	2,6,10-trimethyl dodecane	3891-98-3	212.41	2.1%
14.501	hexadecane	544-76-3	226.44	1.1%

^a Reported peaks have chromatographic peak area counts in excess of 1%. The area counts are uncalibrated and are intended only as a rough guide to the relative composition of the sample. ^b In addition to the components listed here, there was one additional component in excess of 1% in area counts that could not be assigned by mass spectra.

Table 2. A Comparison of the Initial Boiling Temperatures of JP-7 with the Rocket Propellants, RP-1 and RP-2^a

Sample (pressure)	onset (°C)	sustained (°C)	vapor rise (°C)
JP-7 (83.4 kPa)	171.8	207.5	211.2
RP-1 (83.1 kPa)	195.0	201.0	201.6
RP-2 (83.4 kPa)	197.6	202.2	203.3

^a These temperatures have been corrected to 1 atm with the Sydney Young equation. The pressures at which the measurements were made are provided in the first column to permit recovery of the actual measured temperature. The uncertainty (with a coverage factor $k = 2$) in the onset and sustained bubbling temperatures is ~ 2 °C. The uncertainty in the vapor rise temperature is actually much lower, at ~ 0.2 °C.¹⁵

Table 3. Representative Distillation Curve Data for a JP-7 Sample^a

distillate volume fraction, %	JP-7	
	T_k , °C	T_h , °C
5	212.2	207.0
10	213.1	208.4
15	214.2	210.2
20	215.1	210.8
25	216.1	212.2
30	217.2	213.1
35	218.6	214.5
40	219.6	215.3
45	221.0	216.5
50	222.4	218.0
55	223.9	219.7
60	225.7	221.3
65	227.6	223.4
70	229.4	225.6
75	231.6	228.0
80	233.9	231.6
85	238.1	234.4
90	241.0	238.6

^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 pressure for these measurements was 83.5 kPa.

on RP-1 and RP-2 are included in Table 2.¹⁵ Interestingly, the onset of bubble formation for JP-7 is ~ 25 °C lower than for the rocket propellants; yet the vapor rise temperature is 7 °C higher than for the rocket propellants. The significantly lower onset of bubble formation for JP-7 is due to the relatively higher concentration of light components in JP-7 compared to that of RP-1.

Distillation Curves. Representative distillation curve data for a JP-7 sample, presented in both T_k (measured directly in the fluid) and T_h (measured in the distillation head), are provided in Table 3. The T_k data are true thermodynamic state points whereas 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. We also note that there is no convergence of T_k and T_h , indicating that

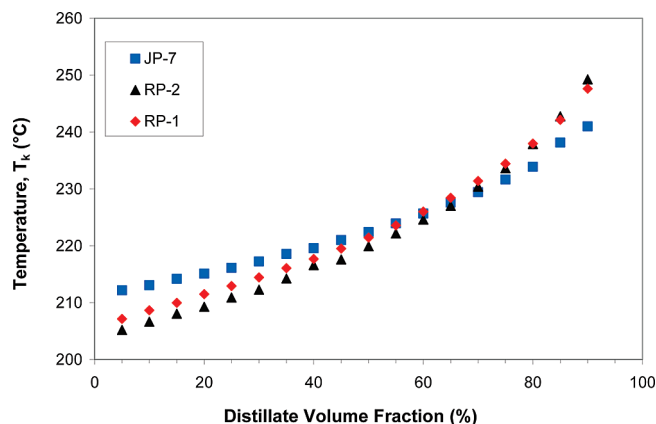


Figure 1. A representative distillation curve of JP-7 is presented in T_k (the temperature in the boiling kettle). For comparison, representative distillation curves of the two rocket propellants, RP-1 and RP-2, measured previously are presented.¹⁵ Only one curve for each fluid is shown, even though each curve was repeated four to six times. The error bars on the temperature measurements are smaller than the symbols used.

there appears to be no azeotropy among any of the components of the mixture.

A graphical depiction of the representative distillation curve data for JP-7 is provided in Figure 1 as T_k , the temperatures measured in the boiling kettle. For comparison, the distillation curves for RP-1 and RP-2 are also presented in Figure 1 (also as T_k).¹⁵ The distillation curves of JP-7 and the rocket propellants have the same shape without inflection points or other obvious features; however, the temperature range from 5 to 90% distillate fraction for the rocket propellants is from 205 to 255 °C, whereas for JP-7 this range is from 210 to 240 °C. Interestingly, the chemical components of JP-7 presented in Table 1 are strikingly similar to the components that make up both RP-1 and RP-2.¹⁵ At low distillation temperatures, the curve difference is observed because JP-7 is significantly richer in heavier components; specifically, it has a much larger concentration of tetradecane than either RP-1 or RP-2. At high distillation temperatures, the curve difference is likely due to the persistence of hexadecane (RMM = 226.44) throughout the rocket propellant distillation, as larger molecular mass molecules tend to distill at higher temperatures. The largest paraffin found in JP-7 is pentadecane (RMM = 212.41).

Composition Channel Information. 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. Representative chromatograms for each fraction of JP-7 are shown in Figure 2. The time axis is from 0 to 25 min for each chromatogram,

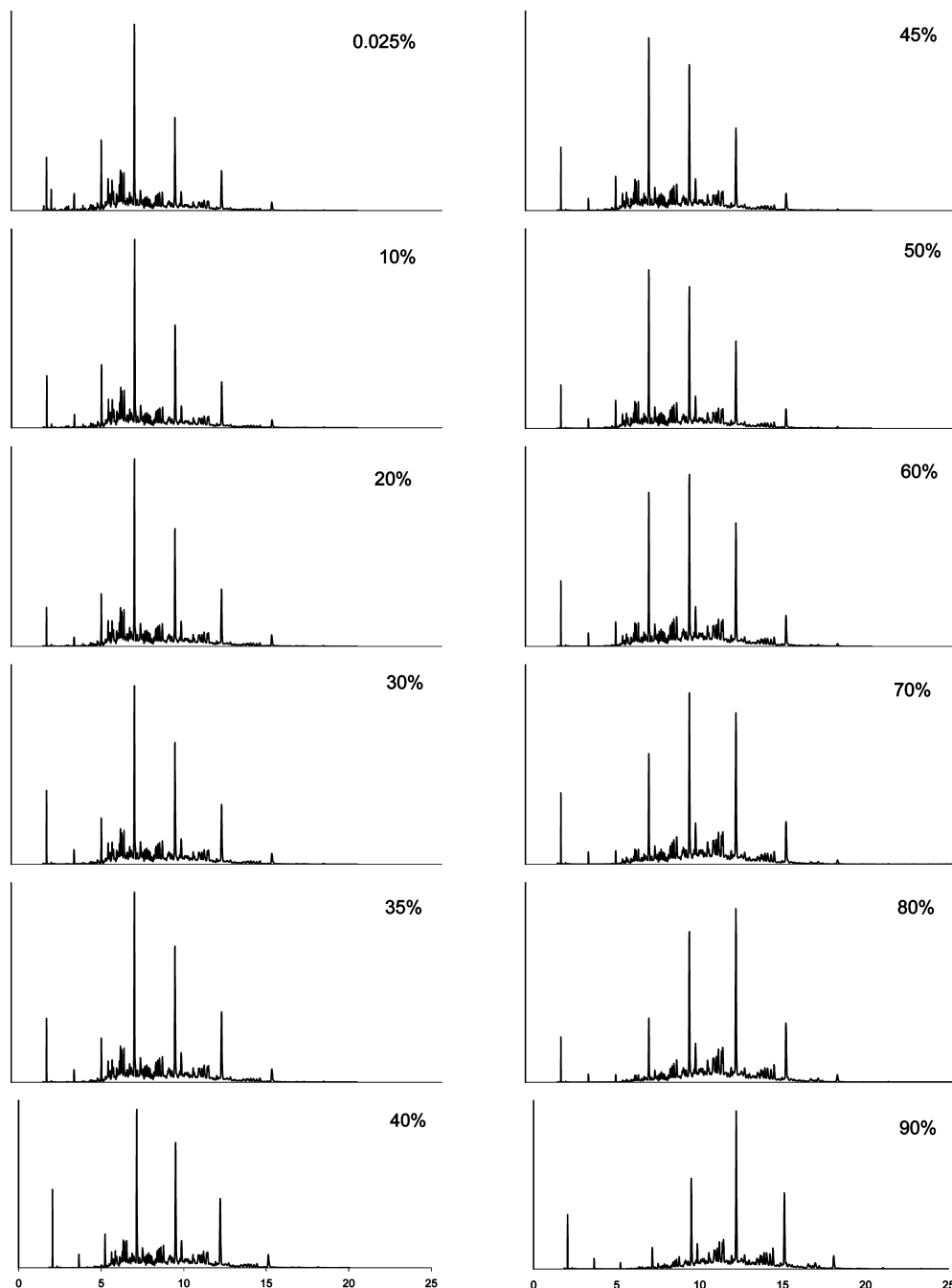


Figure 2. Representative chromatograms of the distillate volume fractions of JP-7 are presented. The y-axes are arbitrary units of intensity, and the x-axis is time (0–25 min). The details of the chromatography are discussed in the text.

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, 10–20 minor, and numerous trace peaks), these chromatograms are much simpler than those of both the neat and the residue fluids, 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*-hexane) appears at the front of each chromatogram. Its peak does not interfere with the sample peak 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. However, we note that most of the peaks persist throughout the distillation, albeit at concentrations that change with temperature.

Figure 2 illustrates a fraction by fraction analysis, which is just one chemical 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.

Another analytical technique that complements the above analyses examines the JP-7 samples for hydrocarbon types by use of a mass spectrometric classification method summarized in ASTM D-2789.²⁹ In this method, one uses mass spectrometry (or GC-MS) to characterize hydrocarbon samples into six types. The six types are paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (arenes or aromatics), indanes and tetralins

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

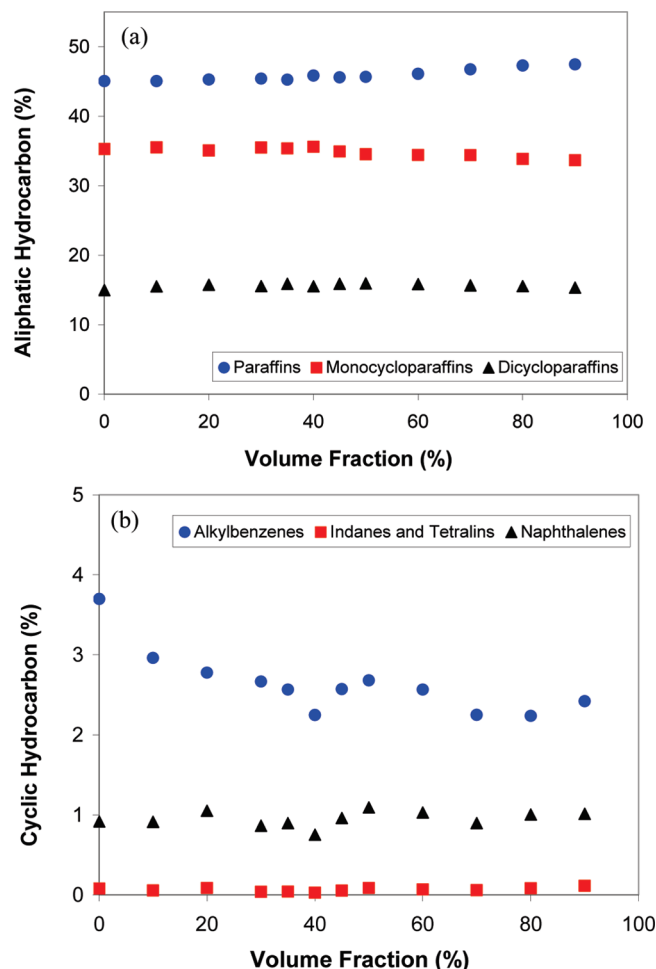


Figure 3. Plots of the aliphatic hydrocarbon family types resulting from the ASTM D-2789 analysis performed on JP-7 as a function of distillate volume fraction. Note that both axes on the graphs are in volume fractions; the y-axes are in volume fractions of each moiety, and the x-axes are in distillate volume fractions from the measurements. The uncertainties are discussed in the text.

(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.³⁰ The uncertainty of this method, and the potential pitfalls, were discussed earlier.¹⁷ The solutions were prepared from $\sim 7 \mu\text{L}$ aliquots of emergent distillate that were withdrawn at specified volume fractions and added to a crimp-sealed vial containing a known mass of solvent (*n*-hexane). For the hydrocarbon type analysis of the distillate fraction samples, $1 \mu\text{L}$ volumes of these solutions were injected into the GC-MS. Because of this consistent injection volume, no corrections were needed for sample volume.

The results of these hydrocarbon type analyses for JP-7 are plotted in Figures 3, panels a and b. All distillate fractions presented were measured in the same way (*m/z* range from 32 to 550 RMM gathered in scanning mode).

Figure 3 shows that there is no significant change throughout the distillation in the volume percent of any of the hydrocarbon type families. The volume percent of paraffins ($\sim 45\%$) is always

Table 4. Composite Enthalpy of Combustion, Presented in $-\text{kJ/mol}$, of Four Distillate Volume Fractions of JP-7, along with the Two Rocket Propellants^a

distillate volume fraction, %	JP-7	RP-1	RP-2
0.025	7228 (361)	6615 (331)	6425 (321)
10	7335 (367)	6700 (335)	6572 (329)
50	7471 (374)	7075 (356)	7098 (355)
90	8037 (402)	8322 (416)	8123 (406)

^a Values for RP-1 and RP-2 were investigated in a previous paper.¹⁵ The uncertainties are presented in parentheses.

greater than the volume percent of monocycloparaffins and dicycloparaffins (~ 35 and $\sim 15\%$, respectively). A very small and relatively constant volume percent of alkylbenzenes and naphthalenes was observed through the distillation (~ 3 and $\sim 1\%$, respectively), and very little of each fraction was composed of indanes or tetralins. 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 most peaks throughout the distillation.

The 2789 analyses show that JP-7, RP-1, and RP-2 have nearly identical composition profiles, that is, ~ 35 to 45% each of paraffins and monocycloparaffins, and ~ 15 to 20% of dicycloparaffins. However, the rocket propellants showed an increase in the paraffins and a decrease in the monocycloparaffins (although, these changes were very slight), whereas JP-7 exhibited a nearly constant composition throughout the distillation. Additionally, the RP-1 sample showed a decrease in the volume percent of alkylbenzenes from 8.9% in the first drop to approximately 5% throughout the remainder of the distillation. This result is consistent because benzene and toluene were the most abundant alkylbenzenes observed, and these low molecular mass molecules are very volatile and thus distill at low temperatures, that is, in the first drop. All three fuels showed relatively low levels of indanes and tetralins (grouped together in one classification) and naphthalenes, with the RP-1 having, in general, a slightly higher percentage of each.

Enthalpy of Combustion of JP-7. The composite enthalpy of combustion of JP-7 was calculated at four distillate volume fractions: 0.025, 10, 50, and 90%. We have discussed the contributions to the overall uncertainty of the composite enthalpy of combustion at great length elsewhere.^{16–18} There is uncertainty in neglecting the enthalpy of mixing and using the individual enthalpy of combustion values as tabulated in the databases. Additionally, there is uncertainty in the measured mole fraction, in the resolution of very closely related isomers via the analytical protocol, in neglecting components present at very low concentrations, and in the complete misidentification of a component. Last, we take into account the uncertainty attributable to our inability to resolve overlapping peaks in the chromatogram and the uncertainty arising from the absence of experimental enthalpy of combustion values for some components with the subsequent use of calculated enthalpies determined with the Cardozo method.³¹ In view of these sources of uncertainty, the overall combined uncertainty in our earlier composite enthalpy of combustion calculations (with a coverage factor $k = 2$) was $4\text{--}5\%$.¹⁶ The uncertainty is dominated by the analytical measurement and determination of the component mole fraction. In the present case, the sources and magnitudes of the uncertainties are very similar to those in our earlier work; therefore, we conservatively assign an uncertainty of 5% to the calculated enthalpies herein.

Table 4 presents the calculated enthalpies of combustion, in $-\text{kJ/mol}$, for the listed distillate volume fractions of JP-7. For

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

Table 5. Composite Enthalpy of Combustion, Presented in –kJ/g, of Four Distillate Fractions of JP-7, along with the Two Rocket Propellants^a

distillate volume fraction, %	JP-7	RP-1	RP-2
0.025	44 (2)	45 (2)	44 (2)
10	44 (2)	45 (2)	44 (2)
50	44 (2)	44 (2)	43 (2)
90	44 (2)	44 (2)	44 (2)

^a Values for RP-1 and RP-2 were investigated in a previous paper.¹⁵ The uncertainties are presented in parentheses.

comparison, the previously determined enthalpies of combustion for the rocket propellants, RP-1 and RP-2, are included.¹⁵ At each distillate volume fraction measured, the composite enthalpies of combustion (on a per-mole basis) of the JP-7 and the two rocket propellants are equivalent within the uncertainty of the measurements.¹⁵ As expected, given that the concentration of paraffins dominates the composition of each fuel, we observe gradually increasing enthalpies of combustions with increasing percent distillate fractions because the higher boiling compounds have larger molecular weights and contain more C–H bonds. Additionally, Table 4 shows that the enthalpy of combustion on a molar basis is greater for JP-7 than for RP-2 at the 0.025% volume distillate fraction. This result is in agreement with the result from Figure 1, which shows that JP-7 is less volatile at lower temperatures than at higher temperatures. Higher and lower volatility corresponds to higher and lower enthalpy of combustion, respectively.

The presentation of the thermochemical information in units of kJ/mol is useful for design and modeling studies, because 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 mass or volume, expressed in units of kJ/g or kJ/L, respectively. This conversion is simple to compute, requiring only the molar mass and density of each identified compound at a temperature of interest. The uncertainty on this calculation remains at 5%. Table 5 shows that the distillate fractions presented for each fuel have an equivalent mass-basis enthalpy.

Presenting the enthalpies of combustion on a volume-basis is more difficult, since the densities of every compound present in each of the propellants have not been measured. In cases where measured densities were not available, the density of the compound was predicted using interpolation/extrapolation.³² Although the uncertainty is low for the densities of the compounds that have been measured,³² assigning an uncertainty to the predicted densities is more difficult. In a previously published paper, an estimate of the uncertainty of the predicted densities was made with 10 compounds that are present in three rocket propellants (RP-1, RP-2, and TS-5) by use of an

Table 6. Composite Enthalpy of Combustion, Presented in –kJ/L, of Four Distillate Fractions of Each of JP-7 and the Two Rocket Propellants^a

distillate volume fraction, %	JP-7	RP-1	RP-2
0.025	33640	35504	34903
10	33667	35391	34756
50	33631	34541	34727
90	33312	33576	34800

^a The values for RP-1 and RP-2 were investigated in a previous paper.¹⁵

experimental density that can be compared to a predicted value.³³ The 10 compounds were determined to have an average error of 9.1%; yet, since such a low number of constituent fluids were used for the comparison, a reliable assessment of the uncertainties is not possible. Consequently, uncertainties on the volume-basis enthalpy are not given in Table 6.

As with the molar- and mass-basis comparisons, the volume-basis enthalpy is also the same for each fluid, within experimental uncertainty. However, lack of a concrete uncertainty assessment precludes arriving at any definitive conclusion on the part of the volume-based enthalpies.

Conclusions

The propellant, JP-7, utilized by the hypersonic community, was measured using the advanced distillation curve (ADC) metrology, and the results were compared to the previously measured rocket propellants, RP-1 and RP-2. The distillation curves of the three fluids exhibit similar shapes; however, the JP-7 fuel is less volatile at lower fractions and more volatile at higher fractions. The temperatures measured are true thermodynamic state points that can be used to model each fluid with an equation of state. The ADC metrology allowed for a detailed, fraction-by-fraction chemical analysis of JP-7, including calculation of the composite enthalpies of combustion of each distillate fraction. The enthalpies of combustion for the 0.025, 10, 50, and 90% distillate fractions are presented for JP-7, RP-1, and RP-2 and were determined to be equivalent when compared on a mass- or volume-basis. When compared on a mole-basis, all three fuels exhibit increasing enthalpy of combustions with increasing percent distillate fraction. Although the measurements presented here are a start, it is clear that additional measurements of other thermophysical properties (such as density, speed of sound, and transport properties) and operational parameters (such as flame properties) will be needed to develop a JP-7 replacement.

Acknowledgment. T.M.L. acknowledges a Professional Research Experiences Program (PREP) postdoctoral fellowship at NIST. We acknowledge the Air Force Research Laboratory, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, for providing the sample of JP-7 and RP-1. We acknowledge the Air Force Research Laboratory, Combustion Devices Group, Edwards Air Force Base, for providing the sample of RP-2.

EF900096Q

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