

# Variability of The Rocket Propellants RP-1, RP-2, and TS-5: Application of a Composition- and Enthalpy-Explicit Distillation Curve Method<sup>†</sup>

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We have recently introduced several important improvements in the measurement of distillation curves for complex fluids. This method is a significant improvement over current approaches, featuring a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis) and an assessment of the energy content of each distillate fraction, among other features. 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 a wide variety of fluids, including hydrocarbons, gasoline, jet fuel, diesel fuels (both petroleum-derived and biodiesel), and crude oils. In this paper, we present the application of the technique to representative batches of the rocket propellants RP-1, RP-2, and TS-5. We not only present the distillation curves but also utilize the composition-explicit information to characterize distillate cuts in terms of composition and available energy content. The measure we use for the fluid energy content is the composite enthalpy of combustion for each component selected for identification in each distillate fraction. Overall, the distillation curves and enthalpy data for all three fluids are remarkably similar.

## Introduction

**Rocket Propellants.** Modern rocket motors can operate on either a liquid or a solid fuel package, although the liquid fuel package is the more easily controlled and the more flexible of these two classifications. Indeed, Goddard's initial 1926 rocket flight tests used a liquid fuel package consisting of oxygen and gasoline. Since that time, the major practical liquid fuel packages have been those based either on oxygen + hydrogen or oxygen + kerosene. While the oxygen + hydrogen mixture is the highest performing practical propellant mixture commonly used in terms of specific impulse (actually hydrogen + fluorine is higher, but is not practical), it has significant limitations that include the complexity and cost of cryogen use (temperatures ~20 K), the hazards associated with liquid hydrogen, and very low density (when compared to a hydrocarbon mixture such as kerosene). The initial oxygen + kerosene propellant mixtures that were developed utilized turbine aviation fuels as the kerosene component, starting with the kerosene-like fluid JP-4. The aviation fuels were not produced with a sufficiently tight set of specifications (in terms of physical properties such as density, volatility, chemical components, enthalpy of combustion, etc.) to be effective rocket propellants, however.

This limitation led to the development of RP-1 (for rocket propellant 1) in the mid-1950s. This fluid, produced as MIL-P-25576, has a much tighter allowable density and volatility range, as well as much lower sulfur, olefin, and aromatic contents than the common turbine aviation fuels. RP-1 is now a long-established hydrocarbon fuel that continues to be widely used in propulsion systems. Distillates from crude oil that are high in naphthalene content are generally used for RP-1 production in order to meet the specifications for density, heat of combustion, and aromatic content.<sup>1</sup> Previous analysis of RP-1 has shown the fuel to be a complex mixture of compounds including paraffins, olefins, and aromatics.<sup>2</sup> Although the sulfur

concentration specification for RP-1 was set at 500 ppm (mass/mass), the typical as-delivered lot was much lower at 30 ppm (mass/mass).

The desire in recent years to use rocket motors many times, rather than a single time, has led to reformulations of the kerosene component of liquid rocket propellants. In terms of processing, increased hydrotreating of fluids such as RP-1 can lower the sulfur, olefin, and aromatic contents significantly. The resulting fuels have demonstrably lower metal corrosion effects and are, thus, more amenable to multiple-use rocket motors. Three grades of RP-1 were later specified with the ultimate goal of decreasing the sulfur concentration specification: TS-30 (with a total sulfur specification of <30 ppm, mass/mass, which was similar to typical as-delivered RP-1), TS-5 (total sulfur specification of <5 ppm, mass/mass), and UL (ultralow sulfur, <100 ppb, mass/mass). Testing showed that ultralow sulfur RP-1 provided significant performance benefits over TS-5 with only marginally greater costs, so this fluid (ultralow) was selected to become what is now called "RP-2". The RP-1 sulfur limit was lowered from 500 to 30 ppm (mass/mass), more closely reflecting the as-delivered material. We note that the specifications for RP-1 and RP-2 aromatic content are the same; however, one commonly finds a lower aromatic content in RP-2.

**Advanced Distillation Curve Metrology.** Simply stated, the distillation curve is a graphical depiction of the boiling temperature of a fluid or fluid mixture plotted against the volume fraction distilled.<sup>3–5</sup> 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.<sup>6</sup> The data obtained with ASTM D-86 are the initial boiling point, the temperature at predetermined distillate volume fractions, and the final boiling point. The ASTM D-86 test suffers from several drawbacks, including large uncertainties in temperature measurements and little theoretical significance.<sup>7</sup>

In an effort to remedy the shortcomings of the standard distillation method described above, we have recently reported in detail an improved distillation method and apparatus.<sup>7–10</sup>

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Improvements to the traditional distillation apparatus include (i) a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (ii) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (iii) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development, (iv) consistency with a century of historical data, (v) an assessment of the energy content of each distillate fraction, (vi) trace chemical analysis of each distillate fraction, and (viii) corrosivity assessment of each distillate fraction. Perhaps the most important advantage presented by the advanced distillation curve metrology is the ability to sample the fluid during the course of the distillation. Sampling very small volumes of the distillate (5–25  $\mu\text{L}$ ) yields a composition-explicit data channel with nearly instantaneous composition measurements. Chemical analysis of the distillate fractions allows for some understanding of how the composition of the fluid varies with volume fraction and distillation temperature, even for complex fluids. The fraction-by-fraction chemical analysis coupled with the distillation curve (which can be used to approximate vapor–liquid equilibrium of complex mixtures) presents a more complete picture of the fluid under study. All inflections and slopes of the distillation curve are the result of the changing composition, and this feature provides a measurement of this changing composition.

This improved distillation method also provides important advantages over other methods, such as the simulated distillation method embodied in procedures such as ASTM D-2887. In that method, for example, one uses the gas chromatographic behavior of a suite of compounds as a frame of comparison with a fuel. A significant advantage offered by the metrology discussed in this paper is the ability to develop a thermodynamic model of the distillation curve with an equation of state.<sup>11,12</sup> In addition, when designing a fuel surrogate, it is critical to know what components are actually present, with relation to the fuel volatility. This permits a physically authentic surrogate to be derived.

The composition-explicit data channel of the advanced distillation curve metrology allows for a detailed fraction-by-fraction chemical analysis of the composition of the fluid under study. Some 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), Fourier transform infrared spectrophotometry (FTIR), or nuclear magnetic resonance spectroscopy (NMR).

The composition-explicit data channel also allows us to add thermochemical data to the distillation curve.<sup>13–15</sup> In the case of fuels, it is clear that knowledge of the enthalpy of combustion of each fraction of the distillation curve would be invaluable. Fortunately, enthalpy of combustion is a well-known thermochemical quantity for a large number of compounds, tabulated in several reliable databases.<sup>16–18</sup> Thus, for a mixture, knowledge of the identities of the chemical components and their relative concentrations allows access to the composite enthalpy of combustion of the mixture. In this way, the composition-explicit data channel of the advanced distillation curve approach allows determination of the composite enthalpy of combustion of each distillate fraction.

### Theory—Enthalpy of Combustion

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). For example, the combustion reaction of *n*-octane is



which results in an enthalpy of combustion of  $-5074 \text{ kJ/mol}$ .<sup>16</sup> This thermochemical quantity is a characteristic of the substance. 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. Enthalpies of combustion of pure substances are also used in comparing the stabilities of chemical compounds. One must be explicit in terms of the definition of the enthalpy of combustion, since it is possible to define the water produced in terms of vapor or liquid.<sup>13</sup> If the enthalpy is specified in terms of  $\text{H}_2\text{O}_{(\text{g})}$ , then the enthalpy is called the net heat or net enthalpy of combustion. If the enthalpy is specified in terms of  $\text{H}_2\text{O}_{(\text{l})}$ , then the result is called the gross heat or gross enthalpy of combustion. The difference between the two values is the enthalpy of vaporization of water. Throughout this paper, we will use the net enthalpy of combustion, in which the product specification is for  $\text{H}_2\text{O}_{(\text{g})}$ . We note also that it is indeed the net heat of combustion, not the gross, that is used in the specification of rocket propellants.

In the case of mixtures, the situation is complicated slightly by the enthalpy of mixing, although in most practical situations this is not a concern.<sup>13</sup> The enthalpy of combustion is much larger than the enthalpy of mixing for hydrocarbon species. For example, a typical enthalpy of mixing of two hydrocarbons, that of *n*-hexane + toluene, is  $0.8\text{--}0.9 \text{ kJ/mol}$ .<sup>13</sup> Since this is in the range of 0.02% of the enthalpy of combustion and most tabulated enthalpies of combustion (for hydrocarbons, such as those found in petroleum-derived diesel fuel) report uncertainties between 0.2 and 3%, we will neglect this effect. Ignoring the enthalpy of mixing, the composite enthalpy of combustion, which we will 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,

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

where *i* refers to the individual components that have been identified or selected.

In this work, we have focused on the enthalpy of combustion because of the importance of this quantity to any finished fuel. In fact, any enthalpy can be calculated as a function of distillate cut. This is important because these quantities, in addition to being important to fuel design themselves, 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  $\mu\text{m}$ , temperature program from 50 to 170  $^\circ\text{C}$  at a heating rate of 5  $^\circ\text{C}$  per minute) with flame ionization detection and mass spectrometric detection. These analyses revealed the purity to be approximately 99%, and the fluid was used without further purification.

The fluids that were measured in this work, RP-1, RP-2, and TS-5, were obtained from the United States Air Force, Air Force Research Laboratory, and Propulsion Directorate, respectively, and were used without treatment or purification. Care was taken

**Table 1. Listing by Retention Time (R.T.) of the Components of RP-2 Identified by Gas Chromatography–Mass Spectrometry, Having Chromatographic Peak Area Counts in Excess of 1%<sup>a</sup>**

R. T. (min)	name	CAS no.	RMM	area %
5.528	2,6-dimethylnonane	17302-28-2	156.3083	1.388%
5.855	3,7-dimethylnonane	17302-32-8	156.3083	1.018%
6.279	<i>trans</i> -decalin	493-02-7	138.2499	2.846%
6.37	2-methyldecane	6975-98-0	156.3083	1.886%
7.425	2-methyl decalin	295-87-61	152.2765	1.705%
7.48	2,6-dimethyldecane	13150-81-7	170.3348	1.463%
7.771	1-methyl decalin	2958-75-0	152.2765	1.822%
7.892	pentylcyclohexane	4292-92-6	154.2924	1.108%
8.292	5-methylundecane	6132-70-8	170.3348	2.196%
8.389	4-methylundecane	2980-69-0	170.3348	1.487%
8.48	2-methylundecane	7045-71-8	170.3348	2.104%
8.62	3-methylundecane	1002-43-3	170.3348	2.396%
9.087	1-methyl-2-pentylcyclohexane	54411-01-7	168.319	1.283%
9.547	<i>x,y</i> -dimethylundecane	N/A	184.3614	2.285%
9.857	2-ethyl decalin	66660-42-2	166.3031	1.015%
10.087	hexylcyclohexane	4292-75-5	168.319	1.086%
10.384	<i>x,y</i> -dimethylundecane	N/A	184.3614	1.408%
10.481	4-methylundecane	6117-97-1	184.3614	1.103%
10.584	2-methylundecane	1560-97-0	184.3614	2.307%
10.718	3-methylundecane	17312-57-1	184.3614	1.128%
10.772	4,6-dimethylundecane	61141-72-8	168.1498	2.332%
11.688	6-methyltridecane	13287-21-3	198.388	1.328%
12.221	heptylcyclohexane	5617-41-4	182.3455	1.231%
12.506	4-methyltridecane	26730-12-1	198.388	1.172%
12.603	2-methyltridecane	1560-96-9	198.388	1.571%
12.737	3-methyltridecane	6418-41-3	198.388	1.092%
12.864	2,6,10-trimethylundecane	3891-98-3	212.4146	2.104%
14.501	hexadecane	544-76-3	226.4412	1.087%

<sup>a</sup> The area counts are uncalibrated and are intended only as a rough guide to the relative composition of the sample. 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.

to minimize exposure to the atmosphere to minimize oxidation, evaporation of the more volatile components, and uptake of moisture. The samples are considered to be representative in that the properties of rocket propellants are typically more tightly controlled than are aviation fuels or motor fuels. Despite this, there can be minor lot-to-lot differences among different batches of fluid.

The sample of RP-1 was pink in color because of the presence of a dye, azobenzene-4-azo-2-naphthol. This sample has been subjected to an extensive chemical analysis in previous work.<sup>9,19,20</sup> This work was done with a gas chromatography–mass spectrometry–infrared spectrophotometry method (30 m capillary column of 5% phenyl dimethyl polysiloxane, having a thickness of 1  $\mu\text{m}$ , temperature program from 90 to 250  $^{\circ}\text{C}$ , 10  $^{\circ}\text{C}/\text{min}$ ). Mass spectra were collected for each peak from 15 to 550 RMM (relative molecular mass) units, and infrared spectra were collected between 4000 and 600  $\text{cm}^{-1}$ . The assignment of major components (having an area percent in excess of 1%) was presented an earlier publication.<sup>9</sup> This fluid is primarily composed of linear and branched paraffins, cycloparaffins, alkenes, and some aromatics.

The sample of RP-2 was clear and colorless (no dye is added to this fuel). RP-2 was also analyzed by gas chromatography–mass spectrometry–infrared spectrophotometry (30 m capillary column of 5% phenyl dimethyl polysiloxane, having a thickness of 1  $\mu\text{m}$ , temperature program from 70 to 260  $^{\circ}\text{C}$ , 7  $^{\circ}\text{C}/\text{min}$  and a ballistic heating step to 300  $^{\circ}\text{C}$ ). The peaks having an area percentage in excess of 1% were assigned. RP-2, like RP-1, is composed primarily of linear and branched paraffins with some aromatics. The main components of RP-2 are shown in Table 1.

**Table 2. Listing by Retention Time (R.T.) of the Components of TS-5 Identified by Gas Chromatography–Mass Spectrometry, Having Chromatographic Peak Area Counts in Excess of 1%<sup>a</sup>**

R.T. (min)	name	CAS no.	RMM	area %
4.399	1-ethyl-2,3-dimethylcyclohexane	7058-05-1	120.107	1.06%
5.482	4-methyldecane	2847-72-5	156.3083	1.91%
5.721	butylcyclohexane	1678-93-9	140.2658	1.60%
5.807	1-methyl-2-propylcyclohexane	4291-79-6	140.2658	1.29%
6.219	<i>trans</i> -decalin	493-02-7	138.2499	2.45%
6.319	2-methyldecane	6975-98-0	156.3083	2.54%
6.455	3-methyldecane	13151-34-3	156.3083	2.30%
6.616	1,2-diethyl-3-methylcyclohexane	61141-80-8	154.2924	1.46%
7.060	undecane	1120-21-4	156.3083	2.65%
7.361	<i>trans</i> -2-methyl decalin	1000152-47-3	152.2765	2.13%
7.423	2,6-dimethyldecane	13150-81-7	170.3348	1.86%
7.637	3,7-dimethyldecane	17312-54-8	170.3348	1.11%
7.706	<i>cis</i> -2-methyl decalin	1000155-85-6	170.3348	2.33%
7.828	pentylcyclohexane	4292-92-6	154.2924	1.57%
8.003	2,3-dimethylundecane	17312-77-5	184.3614	1.14%
8.113	cyclododecane	294-62-2	168.3190	1.13%
8.226	dodecane	112-40-3	170.3348	2.61%
8.318	4-methylundecane	2980-69-0	170.3348	2.02%
8.409	2-methylundecane	7045-71-8	170.3348	2.68%
8.548	3-methylundecane	1002-43-3	170.3348	3.39%
9.180	tridecane	629-50-5	184.3614	3.53%
9.464	2,6-dimethylundecane	17301-23-4	184.3614	3.11%
10.017	4-methylpentylcyclohexane	61142-20-9	168.319	1.76%
10.306	2,7-dimethylundecane	17301-24-5	184.3614	2.83%
10.408	4-methylundecane	6117-97-1	184.3614	1.42%
10.503	2-methylundecane	1560-97-0	184.3614	2.99%
10.686	4,6-dimethylundecane	61141-72-8	168.1498	3.31%
11.056	1-methyl-2-pentylcyclohexane	54411-01-7	168.319	1.36%
11.259	tetradecane	629-59-4	198.3880	2.17%
11.421	1,1'-bicyclohexyl	92-51-3	166.3031	1.51%
11.612	<i>x,y</i> -dimethylundecane	N/A	168.1498	1.68%
12.151	heptylcyclohexane	5617-41-4	182.3455	1.47%
12.329	<i>x,y</i> -dimethylundecane	N/A	168.1498	1.00%
12.524	2-methyltridecane	1560-96-9	198.388	1.89%
12.66	3-methyltridecane	6418-41-3	198.388	1.33%
12.78	<i>x,y,z</i> -trimethylundecane	N/A	212.4146	2.24%
13.246	6-methyltridecane	13287-21-3	198.388	1.02%
14.19	octylcyclohexane	1795-15-9	196.3721	1.49%
14.422	pentadecane	629-62-9	212.4146	1.05%

<sup>a</sup> The area counts are uncalibrated and are intended only as a rough guide to the relative composition of the sample. In addition to the components listed here, there were two additional components in excess of 1% in area counts that could not be assigned by mass spectra.

The sample of TS-5 was also clear and colorless. The fluid was analyzed with a gas chromatography–mass spectrometry method on the same column and with the same temperature program as RP-2. Mass spectra were collected for each peak from 15 to 550 RMM (relative molecular mass) units. Each chromatographic peak was identified with the assistance of the NIST Mass Spectral Database.<sup>21</sup> Again, only peaks with a raw area percent in excess of 1% were assigned. The main components of TS-5 are shown in Table 2.

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.<sup>7–10,15</sup> For each distillation curve measurement, two temperature channels are measured:  $T_k$ , the temperature measured directly in the fluid (kettle), and  $T_h$ , the temperature measured in the distillation head. 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 3 and 6 complete distillation curve measurements on each of the three 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 Sydney Young equation,<sup>22–24</sup> in which the constant term was assigned a value of 0.000109. The magnitude of the correction is, of course, dependent upon the extent of deviation from standard atmospheric pressure.<sup>25</sup> 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.

To provide the composition channel to accompany the temperature information on the distillation curves, sample aliquots were withdrawn for 10 selected distillate volume fractions. To accomplish this, aliquots of ~7  $\mu$ L of emergent fluid were withdrawn from the sampling hammock in the receiver adapter with a blunt-tipped chromatographic syringe and added to a sealed autosampler 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 9 additional predetermined volume fractions of distillate, for 10 total sample aliquots. Each distillate volume aliquot was analyzed in scanning mode by gas chromatography with mass spectrometric detection and flame ionization detection with the same column and temperature program described earlier for the bulk samples of RP-2 and TS-5. Each chromatographic peak was identified with the assistance of the NIST Mass Spectral Database.<sup>21</sup>

After each peak was identified as discussed earlier, each peak was quantitated by standardization of the GC with external standards. Compounds with a total area of greater than or equal to 2% in raw total ion chromatogram (TIC) were standardized; small peaks with uncalibrated area counts comprising <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%.<sup>13</sup> We therefore expect the neglect of minor components in the rocket propellant distillate fractions to be an insignificant source of uncertainty that will not affect the uncertainty of the composite enthalpy in a significant way.

Analytical standardization was done on the basis of extracted ions (sometimes called single ion monitoring or selected ion monitoring, SIM).<sup>26</sup> 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 rocket propellant distillate samples were complex but were primarily composed of paraffins, monocycloparaffins, and dicycloparaffins. The length of the paraffin chains ranged from C<sub>9</sub> to C<sub>16</sub>; therefore, the paraffins were standardized with C<sub>12</sub> (with the *m/z* = 57 ion dwelled on during SIM). The monocyclic paraffins present in the three rocket propellant samples were all 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). Finally, the

**Table 3. Comparison of the Initial Boiling Temperatures of the Three Rocket Propellants<sup>15a</sup>**

sample (pressure)	onset (°C)	sustained (°C)	vapor rise (°C)
RP-1 (83.13 kPa)	195.0	201.0	<b>201.6</b>
RP-2 (83.38 kPa)	197.6	202.2	<b>203.3</b>
TS-5 (82.86 kPa)	199.2	203.9	<b>207.1</b>

<sup>a</sup> 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.

dicyclic paraffins integrated in the three 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 three rocket propellants on distillate fractions corresponding to 0.025, 10, 50, and 90 volume % of the distillate. Calculation of the composite enthalpies of combustion and their associated uncertainties will be discussed further later.

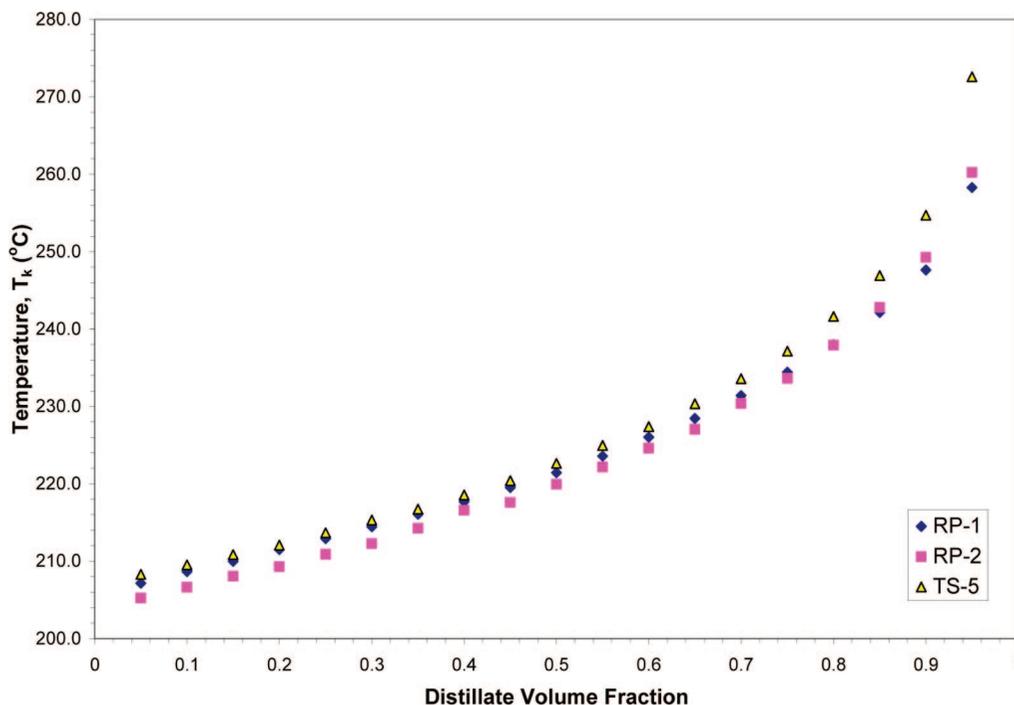
## Results and Discussion

**Initial Boiling Behavior.** The initial boiling behavior of each of the three fluids was measured. 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 in Table 3). 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.<sup>15</sup> Although the initial boiling measurements shown in Table 3 are similar, there is a trend in the values for all three of the rocket propellants: the temperatures for RP-1 are slightly lower than those for RP-2, which are in turn slightly lower than those for TS-5.

**Distillation Curves.** The distillation curves of the rocket propellants are presented in Figure 1 as *T<sub>k</sub>*, the temperatures measured in the boiling kettle. These data are true thermodynamic state points that can be used to model each fluid with an equation of state.<sup>11,12</sup> In this figure, the estimated uncertainty (with a coverage factor *k* = 2) in the temperatures is 0.1 °C. The uncertainty in the volume measurement that is used to obtain the distillate volume fraction is 0.05 mL in each case. The uncertainty in the pressure measurement (assessed by logging a pressure measurement every 15 s for the duration of a typical distillation) is 0.001 kPa. The distillation curves of all three rocket propellants have the same shape; each distillation proceeds between 205 and 275 °C without inflection points or other obvious features. As was the case with the initial boiling temperatures, the distillation temperatures for TS-5 are slightly higher than those for the other two samples.

**Chemical Analysis.** Each distillate fraction was examined by gas chromatography with flame ionization detection and mass spectrometric detection. Chromatograms of the 0.025, 10, 50, and 90% distillate volume fractions of all three rocket propellants are shown in Figure 2.

Each of the distillate fractions has a very complex chromatogram. The gross structures of the chromatograms illustrate that the component suite for the early fractions are rich in light components. As the distillation curve progresses to higher and



**Figure 1.** Representative distillation curves of the three rocket propellants, presented in  $T_k$  (the temperature in the boiling kettle). Only one curve for each fluid is shown, even though each curve was repeated 3–6 times. The error bars on the temperature measurements are smaller than the symbols used.

higher volume fractions, the chromatograms show that the components that make up the fraction shift to longer retention times. Having the data presented as on-the-fly chromatograms is advantageous in that one can relate the compound suite to the temperature on the distillation curve.

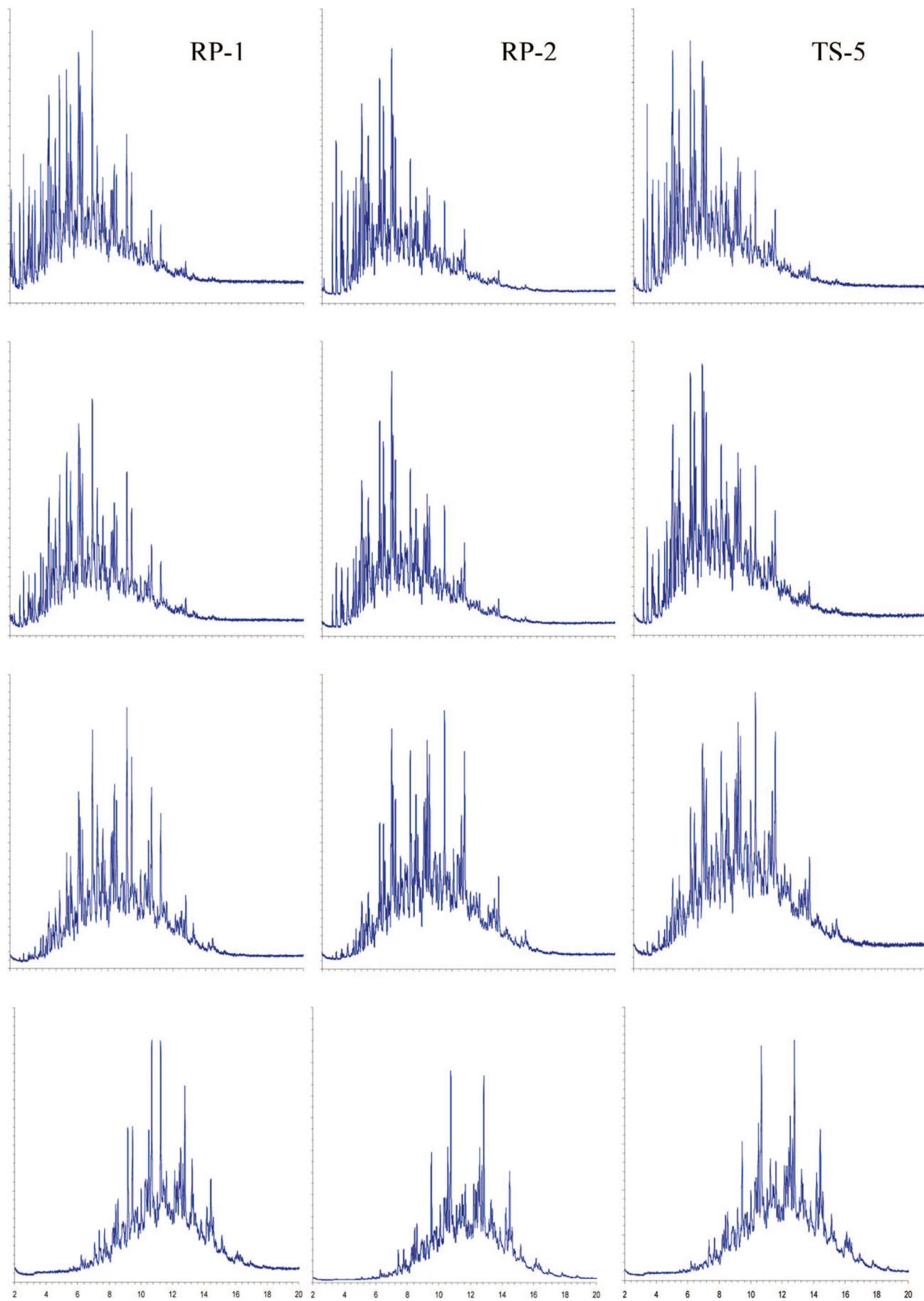
The composition of each fraction can also be examined on a moiety-by-moiety basis by use of a mass spectrometric classification method summarized in ASTM Method D-2789.<sup>27</sup> In this method, one uses mass spectrometry (or gas chromatography–mass spectrometry) to characterize hydrocarbon samples into six types. The six types or families are paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (or aromatics), indanes and tetralins (grouped as one classification), and naphthalenes. Although the method is specified only for application to low-olefinic gasolines and has significant limitations, it is of practical relevance to many complex fluid analyses and is often applied to gas turbine fuels, rocket propellants, and missile fuels.<sup>28</sup> The uncertainty of this method and some potential pitfalls (such as the overpredicting of alkylbenzene concentration) were addressed earlier.<sup>29</sup> The solutions were prepared from samples of distillate that were dissolved in a known mass of *n*-hexane solvent. This solvent was chosen because it causes no interference with the sample constituents. For the hydrocarbon-type analysis of the distillate fraction samples, 2  $\mu$ L injections of these solutions were made into the GC-MS. Because of this consistent injection volume, no corrections were needed for sample volume.

The results of these hydrocarbon type analyses are plotted in Figure 3 for RP-1, RP-2, and TS-5. All distillate fractions presented in the table were measured in the same way ( $m/z$  range from 15 to 550 relative molecular mass units gathered in scanning mode, each spectrum corrected by subtracting trace air and water peaks).

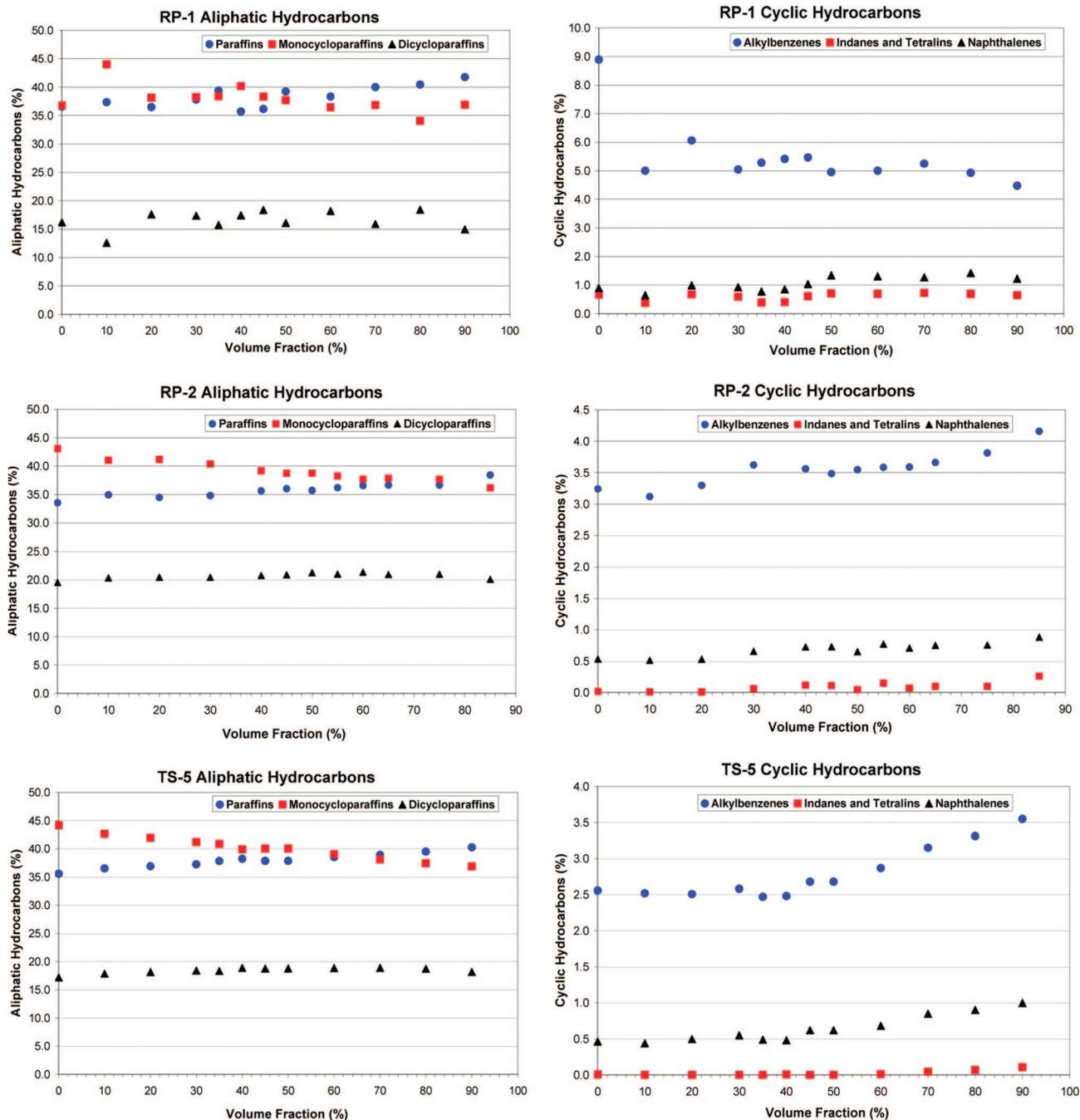
The 2789 analysis shows that each of the three fuels is composed of 35–45% each of paraffins and monocycloparaffins and also 15–20% dicycloparaffins. The paraffins decrease with increasing distillate fraction, while the monocycloparaffins

increase and the dicycloparaffins remain relatively constant. The RP-1 sample has a higher total percentage of alkylbenzenes than that of the other two fuels; it decreases from a value of 8.9% in the first drop to approximately 5% for the remainder of the distillation. The RP-2 and TS-5 samples both show an approximately 1% increase in alkylbenzenes throughout the course of the distillation, with total percentages ranging from 2.4% to 4.2%. The lower levels of alkylbenzenes in RP-2 and TS-5 are a result of the hydrotreating of these samples, as discussed earlier. All three fuels show 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 Three Rocket Propellants.** The composite enthalpy of combustion of each of the three rocket propellants was calculated at four distillate volume fractions: 0.025, 10, 50, and 90 volume percent. We have earlier discussed the contributions to the overall uncertainty of the composite enthalpy of combustion at great length.<sup>14,15</sup> The contributions include (i) the neglect of the enthalpy of mixing, (ii) the uncertainty in the individual enthalpy of combustion as tabulated in the databases, (iii) the uncertainty in the measured mole fraction, (iv) the uncertainty posed by very closely related isomers that cannot be resolved by the analytical protocol, (v) the uncertainty introduced by neglecting components present at very low concentrations (that is, uncertainty associated with the chosen area cutoff), (vi) the uncertainty introduced by a complete misidentification of a component, (vii) the uncertainty attributable to unresolvable overlapping peaks in the chromatogram, and (viii) 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.<sup>15,17</sup> 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 4–5%.<sup>13</sup> The uncertainty is dominated by the analytical measurement and determination of the component



**Figure 2.** Chromatograms of the 0.025, 10, 50, and 90% distillate volume fractions (presented top to bottom) of RP-1, RP-2, and TS-5 (presented left to right). The y-axes are arbitrary units of intensity, and the x-axis is time (min).



**Figure 3.** Moeity-by-moeity analysis using ASTM method D-2789 for the three rocket propellants. Note that both axes on the above graphs are in volume fractions; the y-axes are in volume fractions of each moeity, while the x-axes are in distillate volume fractions from the measurements.

**Table 4.** Composite Enthalpy of Combustion, Presented in  $-kJ/mol$ , of Four Distillate Volume Fractions of Each of the Three Rocket Propellants; The Uncertainties Are Presented in Parentheses

distillate volume fraction	RP-1	RP-2	TS-5
0.025%	6615 (331)	6425 (321)	6498 (325)
10%	6700 (335)	6572 (329)	6559 (328)
50%	7075 (356)	7098 (355)	7285 (364)
90%	8322 (416)	8123 (406)	8230 (412)

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  $-kJ/mol$ , for the listed distillate volume fractions of the three rocket propellants.

At each distillate volume fraction measured, the composite enthalpies of combustion on a per-mole basis of the three rocket

propellants are equivalent within the uncertainty of the measurement. Each rocket propellant has a gradually increasing enthalpy with increasing distillate volume fraction. Given that all three fuels are, in large part, paraffinic in nature, the enthalpy is expected to increase with distillate fraction because the higher boiling compounds have larger molecular weights and contain more C–H bonds. The presentation of these enthalpy measurements on a molar basis is useful for design and modeling studies, since thermochemical information presented in this way is a fundamental value.

Two other useful presentations of the same data, which may be of more practical interest, are on a mass or volume basis. These conversions require the molecular weight and/or density of all of the components in each distillate fraction of each fuel. The molecular masses of all of the compounds are readily

**Table 5. Composite Enthalpy of Combustion, Presented in  $-kJ/g$ , of four Distillate Fractions of Each of the Three Rocket Propellants; The Uncertainties are Presented in Parentheses**

distillate volume fraction	RP-1	RP-2	TS-5
0.025%	45 (2)	44 (2)	43 (2)
10%	45 (2)	44 (2)	44 (2)
50%	44 (2)	43 (2)	43 (2)
90%	44 (2)	44 (2)	43 (2)

**Table 6. Composite Enthalpy of Combustion, Presented in  $-kJ/L$ , of Four Distillate Fractions of Each of the Three Rocket Propellants**

distillate volume fraction	RP-1	RP-2	TS-5
0.025%	35504	34903	34721
10%	35391	34756	34756
50%	34541	34727	34397
90%	33576	34800	34031

available,<sup>16</sup> allowing for a fairly simple conversion. Since the molecular weights of the fluid constituents are well-known, the uncertainty on this calculation remains at 5%. From Table 5, it is plain that each distillate fraction of each rocket propellant has an equivalent mass-basis enthalpy.

Presenting the enthalpies of combustion in a volume basis is more difficult, since the density of every compound present in each of the three rocket propellants has not been measured. In cases where densities were not available, the density of the compound was predicted using interpolation/extrapolation.<sup>17</sup> While the uncertainty is low for the densities of the compounds that have been measured,<sup>17</sup> assigning an uncertainty to the predicted densities is more difficult. An estimation of the uncertainty of the predicted densities was made with 10 compounds that are present in all three rocket propellants where an experimental density can be compared a predicted value. These 10 compounds had an average error of 9.1%. Yet, with such a low number of constituent fluids to use for this comparison, we feel that we are not in a position to provide a reliable assessment of the uncertainties. Consequently, uncertainties on the volume-basis enthalpy are not given in Table 6.

Like the molar and mass basis comparisons, the volume basis enthalpy appears as if it is equivalent within the likely uncertainty of the measurement. Lacking the uncertainty assessment precludes arriving at any definitive conclusion on the part of the volume-based enthalpies.

## Conclusions

Three rocket propellants were measured with the advanced distillation curve metrology. The distillation curves of the three fluids were similar, with the TS-5 sample always having a slightly higher distillation temperature than those of the other two samples. The temperatures measured are true thermodynamic state points that can be used to model each fluid with an equation of state. The advanced distillation curve metrology also allowed for a detailed, fraction-by-fraction chemical analysis of each of the three fluids, including calculation of the composite enthalpies of combustion of each distillate fraction. The enthalpies of combustion for the four distillate fractions of the three rocket propellants are equivalent within the uncertainty of the measurement.

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