Heat Capacity Measurements of Conventional Aviation Fuels*

Tara J. Fortin[†] Thomas J. Bruno



National Institute of Standards and Technology

Material Measurement Laboratory Applied Chemicals and Materials Division 325 Broadway Boulder, CO 80305-3328, U.S.A.

> Phone: 1-303-497-3522 Fax: 1-303-497-6682 E-Mail: <u>tara.fortin@nist.gov</u>

Intended for submission to *Fuel Processing Technology*

Date of this version: April 28, 2022

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[†] Corresponding author.

Abstract

Isobaric specific heat capacities were measured for six conventional petroleum-derived aviation fuel samples: JP-10, JP-7, JP-4, JP-TS, TS-1, and Avgas. All measurements were made using modulated differential scanning calorimetry over the combined temperature range of (213 to 442) K. Experimental data, including an assessment of the associated expanded uncertainties, have been reported. Additionally, measurement results for the six fuels were compared with one another and with available literature data and existing surrogate mixture models.

Keywords

Aviation fuels; Differential scanning calorimetry; Isobaric specific heat capacity; Jet fuels; Temperature dependence

1. Introduction

A gas turbine, or jet engine, is simpler and can more directly convert thermal energy into mechanical energy than a piston engine [1]. Jet engines have the additional advantage of being able to produce much greater amounts of thrust horsepower at high altitudes and high speeds compared to piston engines [1]. While there were many pioneers in the field of turbine engines, the credit for their invention is often attributed to Sir Frank Whittle of England and Hans von Ohain of Germany, who both independently developed turbine engines in the 1930s [2]. Sir Frank Whittle was the first to patent his design for a gas turbine engine in 1930, but the first successful flight was executed in 1939 using Hans von Ohain's engine to power the HE178 aircraft [2]. Gasoline was used as the fuel for that first flight, primarily because it was readily available [3]. The first jet fuel in the United States (US) was aviation gasoline, or avgas, with the subsequent evolution of jet fuels largely being determined by a combination of the properties of avgas, the existing supply infrastructure, and the capabilities of the refining industry in the 1940s and 1950s [3].

Although gas turbine engines proved to be less constrained by fuel properties than piston engines, it was quickly realized that avgas would need to be altered to be suitable for jet aircraft. Avgas' high volatility resulted in vapor lock, and subsequent engine malfunction, at altitude. Additionally, the poor lubricity of the lighter components of gasoline and the antiknock additives caused wear and erosion of critical components [3]. In contrast, kerosene, which is obtained from the middle distillate fractions of petroleum between (423 and 548) K, is made up of clean burning, heavy paraffins that offer higher volumetric heating values (and, thus, more miles per gallon), making it well suited for use with jet engines [3].

Since the invention of flight, early advances in engine and aircraft technology were driven by military research; the same is true for the development of aviation fuels. The first fuel specified for gas turbine engines by the US Army Air Corps (predecessor to the US Air Force (USAF)) was 'Jet Propellant #1', or JP-1, in 1944 [3]. JP-1 was a kerosene fuel but the specified freezing point of < 213 K greatly restricted its availability since few refiners could meet such a strict freezing point requirement [3]. JP-1 was soon followed by JP-2 and JP-3, but both of these fuels also suffered from limited availability when refiners were unable to meet stringent specifications developed without the aid of input from fuel suppliers. Eventually, the USAF did enlist the help of fuel suppliers and, in 1951, a new specification was issued for JP-4 [3]. JP-4 was a mixture of gasoline and kerosene fractions of crude oil, with firm vapor pressure restrictions to reduce boiloff losses [3]. This new fuel remained the primary jet fuel for the USAF for four decades. Meanwhile, the US Navy (USN) adopted JP-5, which, unlike JP-4, was solely derived from the kerosene distillate fraction and had a higher flashpoint (> 333 K), making it more suitable for the safety concerns associated with operations aboard an aircraft carrier [4]. Additionally, since USN aircraft operations were normally carried out at lower altitudes, the freeze point specification was raised to < 233 K for JP-5 [3]. To date, JP-5 remains the primary jet fuel for use aboard aircraft carriers. The comparatively higher aircraft damage and losses attributed to the use of JP-4 during the Vietnam War (relative to losses attributed to the use of JP-5) ultimately led to the development of the less volatile and less explosive JP-8 [3]. By the mid-1990s, all USAF bases had been converted to JP-8, and it remains the primary fuel used by the US military to this day [3]. Several other specialty fuels have been developed to satisfy specific operational needs (e.g., JP-TS or JP-7), but these fuels are not readily available and tend to be very costly, by as much as a factor of three over JP-8 [3].

Today, the Department of Defense (DoD) is the largest single energy consumer in the United States, both within the federal government and compared to any single private-sector entity [5]. For example, in fiscal year 2018 (FY18), the DoD spent \$3.49 billion on installation energy, which is defined as the energy required to support the more than 500 fixed military installations located within the US and internationally [5]. Additionally, operational energy usage, or the "energy required for training, moving, and sustaining military forces and weapons platforms for military operations," exceeded 85 million barrels of fuel at a total cost of \$9.1 billion in FY18 [6]. These enormous energy requirements continue to drive fuel development efforts as the DoD seeks to minimize costs, maximize efficiency, and secure energy supplies. This last goal has helped spur research efforts in alternative fuel sources [7-9]. Effective and efficient fuel development requires knowledge of the physicochemical and thermophysical properties of both existing and candidate replacement fuels [10-13]. For more than a decade, our research efforts have included various property measurements and model development for several of these fuels [14-29]. In this work, we will focus on heat capacity measurements.

The specific heat capacity is defined as the amount of heat-energy required to produce a one unit change in temperature for one unit mass of a substance. In petroleum refinery operations and related processes, heat capacity data over a wide range of temperatures are instrumental to the design of plant equipment, as well as to process decisions related to issues such as prolonged storage or low temperature operability. In systems where fuels are used as a coolant, specific heat capacity data are required for heat transfer calculations. Furthermore, heat capacity can be used to evaluate other basic thermodynamic properties of a fuel. Despite this, there is limited availability of specific heat capacity data for jet fuels in the literature. Here, we report measurements of isobaric specific heat capacity over the combined temperature range (213 to 442) K for six

conventional petroleum-derived aviation fuel samples. Measurement results for nine additional turbine fuel samples, including some of the more common conventional, petroleum-derived fuels, as well as several synthetic and bio-derived fuels, can be found in the forthcoming paper of Fortin et al. [30].

2. Materials and Methods

2.1 Aviation Fuel Samples

Six samples of conventional, petroleum-derived aviation fuels were obtained from the Air Force Research Laboratory (AFRL) Propulsion Directorate at Wright Patterson Air Force Base. Specifically, the six samples were JP-10 (POSF 4795), JP-7 (POSF 3327), JP-4 (POSF 3121), JP-TS (POSF 4431), TS-1 (POSF 4893), and Avgas (POSF 5444). The number in parentheses is the AFRL identification number, which identifies specific fuel batches.

JP-10 is a unique specialty fuel that was developed for demanding applications, such as aircraft-launched missiles, which require fuels that are clean burning, with maximum volumetric energy content and good low-temperature performance [31]. These exacting properties are achieved by formulating a fuel with high-density naphthenes in essentially pure form [31]. According to its specification [32], JP-10 has a minimum volumetric energy content of approximately 39,321 MJ·m⁻³ and a freezing point of 194 K. In contrast, JP-8 has a minimum volumetric energy content of approximately 33,170 MJ·m⁻³ and a freezing point of 226 K [33]. As was previously mentioned, JP-7 and JP-TS are two specialty fuels developed in the 1950s to satisfy specific operational requirements. Specifically, JP-7 was developed for use with the SR-71 Blackbird, a high-altitude, supersonic (Mach 3+) reconnaissance aircraft, while JP-TS was developed for use with another high-altitude reconnaissance aircraft, the Lockheed U-2 spy plane

[3]. The extreme temperatures and stresses encountered during high-speed supersonic flight required that JP-7 have a high flash point (333 K) and good thermal stability [34]; while the low temperatures encountered at high altitude, and subsequently low fuel flow rates over hot engine surfaces, required that JP-TS have a low freezing point (220 K), relatively high viscosity (12 mm²·s⁻¹ at 233 K), and high thermal stability [35]. Since the SR-71 Blackbird was retired in the late 1990s, JP-7 is no longer produced; similarly, JP-TS has largely been replaced by a version of JP-8+100 that contains low temperature additives (the '100' indicates a 100 °F increase in thermal stability over standard JP-8). As was indicated earlier, JP-4 was a mixture of gasoline and kerosene that served as the primary jet fuel for the USAF from the early 1950s until the mid-1990s, when it was replaced by JP-8 [36]. Unlike the first four samples, the last two fuels were not developed for the US military. TS-1 is a kerosene fuel whose specifications meet the requirements of GOST 10227 [37]; it is the most commonly used civilian aircraft fuel in Russia and in several former Soviet republics that currently make up the Commonwealth of Independent States (CIS). TS-1 has slightly higher volatility (301 K flash point) and a lower freezing point (< 223 K) compared to Jet A-1 [37, 38], the most commonly used commercial jet fuel outside of the US. The final fuel sample, Avgas (100LL) [39], is the only sample that is not a gas turbine fuel, despite having been used in the early days of the jet engine. Rather, it is a highly flammable aviation gasoline used in spark-ignited piston-engine aircrafts, and it is the only remaining lead-containing transportation fuel in the US [40].

The chemical composition of each of the six fuel samples was determined by gas chromatography-mass spectrometry (GC-MS). JP-7 was analyzed as part of earlier research efforts and the corresponding experimental details can be found in the literature [21]. The remaining five samples (Avgas, JP-10, JP-4, JP-TS, and TS-1) were analyzed as part of this work using the same

methodology as was used for JP-7. Experimental details can be found in the Supporting Information, along with tables containing the major components identified for each of the five newly-analyzed fuel samples (see Tables S1–S5 in the Supporting Information). The previously reported [21] compositional analysis results for JP-7 are shown in Table S6 for reference. In each of these tables (Tables S1–S6), chemical names and corresponding CAS registry numbers are listed, sorted by the uncalibrated chromatographic peak area. Since JP-10 is essentially a pure fluid, there are only four components listed in Table S2, constituting approximately 100% of the measured chromatographic peak area. For the remaining samples, the listed components account for approximately 49% to 99% of the total measured chromatographic peak area. As Tables S1 through S6 show, all but JP-10 are composed primarily of linear and branched alkanes; JP-10 is composed primarily of *exo*-tetrahydrodicyclopentadiene (or *exo*-tricyclo[5.2.1.0(2.6)]decane), plus small amounts of three other cyclic compounds (Table S2).

Further comparison among the fuel samples is possible with the aid of a classification method based on ASTM Method D-2789 [41] where mass spectral fragments are used to classify hydrocarbon samples into six different types or families: paraffins (P), monocycloparaffins (MCP), dicycloparaffins (DCP), alkylbenzenes (AB), indanes and tetralins (I&T), and naphthalenes (N). It should be noted that ASTM Method D-2789 is specified for low olefinic gasoline and, therefore, suffers from significant limitations, but can still be effective for comparing related fluids [42]. Analysis results for JP-7 have previously been reported [21]; the remaining five fuels were analyzed as part of this work. The results for all six samples are represented schematically in Fig. 1. For all but JP-10, linear and branched paraffins dominate; together they account for approximately 35% to 62% (vol/vol) of the total composition for the other five fuels.



Fig. 1. Schematic representation of the hydrocarbon classification analysis of all measured fuel samples. Analysis is based on ASTM Method D-2789 [41], which classifies hydrocarbon samples into six families: paraffins (P), monocycloparaffins (MCP), dicycloparaffins (DCP), alkylbenzenes (AB), indanes and tetralins (I&T), and naphthalenes (N). Numbers shown represent the measured percent volume fraction for each of the six families. Analysis results for JP-7 have previously been reported [21]; the remaining five fuels were analyzed as part of this work.

In contrast, JP-10 contains no paraffins, and is instead predominantly cycloparaffins with approximately 64% and 12% (vol/vol) for dicycloparaffins and monocycloparaffins, respectively, despite the fact that the GC-MS results indicate it is actually approximately 95% *exo*-tetrahydrodicyclopentadiene (Table S2); this is a prime example of the aforementioned limitations of ASTM Method D-2789, which is discussed in more detail below. Cycloparaffins are also present in substantial quantities for the other five samples. With the exception of Avgas, both monocycloparaffins and dicycloparaffins are significant, accounting for approximately 27% to 34% (vol/vol) and 7% to 16% (vol/vol), respectively. For Avgas, only monocycloparaffins are present in an appreciable quantity, representing approximately 21% (vol/vol) of the total

composition. However, it is important to note that the apparent quantities of monocycloparaffins may be artificially high given that some mass spectral fragments, such as $CH_2=CHCH_2$ at m/z = 41, can be produced from paraffinic species but are only included in the summation of monocycloparaffins [43]. Finally, with the notable exception of JP-7, all of the fuel samples contain appreciable quantities of aromatics.

2.2 Experimental Methods

A commercial modulated differential scanning calorimeter (MDSC) was utilized to measure the isobaric specific heat capacity of the six jet fuel samples. MDSC allows for a simpler, more precise measurement of heat capacity relative to conventional DSC. The single most important advantage of MDSC is the ability to separate the total heat flow into its two components: the heat capacity, or "reversing" component, and the kinetic, or "nonreversing" component [44-47]. A detailed description of the experimental methods employed in this work can be found in Fortin et al. [30]; only a brief description is provided here.

Measurement runs were performed over a given temperature range using a linear heating rate of 3 K·min⁻¹ and modulating ± 1 K every 120 s. Each sample pan was initially held for 10 min at 183 K before being heated to a maximum temperature of 453 K; the two most volatile samples, JP-4 and Avgas, were heated to 423 K and 353 K, respectively. For all measurements, a continuous purge of 50 mL·min⁻¹ of dry nitrogen was employed.

Instrument temperature and heat flow were calibrated via measurements of pure materials with well-known transition temperatures and enthalpies. Specifically, indium SRM 2232, tin SRM 2220, and adamantane were utilized to calibrate temperature, while a single average calibration coefficient was determined for heat flow using only indium and tin; both calibrations were performed at a heating rate of 3 K \cdot min⁻¹. For indium and tin, the corresponding reference melting

temperatures and heats of fusion were obtained from their respective certificates [48, 49]. Highpurity adamantane purchased from a commercial supplier was used since adamantane is not currently available as a certified reference material (Sigma Aldrich, > 99%, lot # 02620MB and lot # MKCC2233). (In order to describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturers' names or labels. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.) The adamantane was used without further purification, and reference values were taken from Westrum [50] for the temperature and enthalpy of the first order solidsolid transition of interest. Measurements of sapphire (α -Al₂O₃) made under the identical experimental conditions as the jet fuel samples were used to calibrate instrument heat capacity. The heat capacity calibration coefficient (K_{cp}) is determined by dividing literature values [51, 52] by measured values, and was calculated and applied as a function of temperature during postprocessing of the measurement data.

All calibration and jet fuel samples were encapsulated in hermetically sealed aluminum pans, and an empty hermetically sealed pan served as the reference. Mass measurements employed a microbalance and a double-substitution weighing scheme [53], wherein air buoyancy effects are explicitly accounted for via the inclusion of the ambient air density [54]. For each sample, the empty pan was weighed and then filled with sample, sealed closed, and reweighted to determine sample weight. All pans were weighed again upon completion of the heat capacity measurements to check for mass loss. A change in mass of > 0.3% would require data be discarded [55]; in this work, no pans were discarded as a result of mass loss during measurement. Initially, four separate pans were prepared for each measured jet fuel sample. However, concerns that the enthalpy of vaporization could contribute significantly to the apparent heat capacity for low-mass samples, combined with some anomalous measurement results, led to the exclusion of all samples with masses < 7 mg, leaving two or three pans for each fuel. The masses of the remaining samples ranged from 7.00 mg to 15.38 mg.

Instrument verification checks, consisting of repeat baselines followed by a single indium measurement, were performed approximately every 24 h while the instrument was being run continuously over several days. For each jet fuel, a sample pan was placed in the measurement cell and three replicate runs were performed without moving the pan. Each jet fuel measurement was bracketed by a single sapphire calibration run. To better account for the observed random variability in heat capacity calibrations, the 109 separate sapphire measurements were combined to determine a single overall average calibration coefficient as a function of temperature, $\overline{K}_{cp}(T)$. It should be noted that, apart from JP-4, all measurements for the fuel samples reported in this work were made over the same several month period. For the JP-4 measurements, the same overall procedure was used; however, the instrument was calibrated anew at the start of these measurements and a separate average $\overline{K}_{cp}(T)$ was determined from the 14 bracketing sapphire calibrations. Finally, the instrument's performance and overall procedure were validated via measurements of high-purity hexadecane (Sigma Aldrich, anhydrous, ≥ 99%, lot # SHBG2582V). Hexadecane was chosen because its heat capacity is relatively well-known [56] and, as a longchain hydrocarbon, it is representative of the jet fuel samples. The agreement between hexadecane measurement results and values calculated using an equation of state [56] was within approximately 3%; this knowledge was also incorporated into the subsequent uncertainty analysis.

3. Results and Discussion

Averaged isobaric specific heat capacity measurement results (\bar{c}_p) for JP-10, JP-7, JP-4, JP-TS, TS-1, and Avgas are reported in Tables S7-S12 of the Supporting Information, respectively. As was previously discussed, for each fuel, two to three samples were each measured three times for a total of six to nine measurement runs per fuel. For a given fuel, first, replicate measurement results for each pan/mass were averaged (\bar{c}_p) , and then those mass averages were averaged together to produce a single overall average (\bar{c}_p) ; these overall averages are reported in Tables S7–S12. It should be noted that, although three replicate measurements were made for each sample pan, only the second and third replicates have been included in the final data analysis. The majority of pans measured showed systematically higher values for the first replicate relative to the other two replicates. The lack of observed mass loss for these pans seemed to rule out the loss of very volatile components upon initial heating as an explanation. Efforts were made to verify this conclusion via additional composition measurements, but it was not possible to extract sufficient sample from the sealed pans for testing. However, it should be noted that this phenomenon was also observed with the pure hexadecane samples for which loss of volatile components should not be an issue. Having eliminated compositional changes as an explanation, additional attempts were made to determine if thermal history effects could explain the observed behavior. Even though the thermal history test results were not conclusive, it was decided that the initial replicate measurement would be excluded from the analysis for all sample pans, thus ensuring all pans were treated identically.

Also included in Tables S7–S12 are the associated absolute expanded uncertainty estimates $(U(\bar{c}_n))$. These are calculated using the expression

$$U(\bar{c}_p) = t_{95} \left(df_{\bar{c}_p} \right) \cdot u(\bar{c}_p) \tag{1}$$

where the coverage factor, $t_{95} \left(df_{\bar{c}_p} \right)$, is taken from the *t*-distribution for $df_{\bar{c}_p}$ degrees of freedom and a 95% level of confidence, and $u(\bar{c}_p)$ is the combined standard uncertainty for the overall average heat capacity [57]. The reader is referred to the paper of Fortin et al. [30] for a detailed description of the determination of $u(\bar{c}_p)$. For clarity, the associated coverage factors have also been included in Tables S7–S12. Overall, expanded absolute uncertainties range between 0.034 J·g⁻¹·K⁻¹ and 0.078 J·g⁻¹·K⁻¹, corresponding to relative uncertainties of approximately 1.9% to 2.8%.

It should be noted that the data presented in Tables S7–S12 represent a subset of the collected measurement data. While measurements were made over larger temperature ranges than what is shown in the tables, only data for the liquid phase and from the stable portion of the heat flow curves are presented. Furthermore, even though data were collected at rate of > 1 point per second, the data have been reduced to a point every 1 K to make the amount of tabulated data more manageable.

To facilitate comparisons between the six samples, the averaged isobaric specific heat capacities shown in Tables S7–S12 are plotted as a function of temperature in Fig. 2. For clarity, the plotted data in Fig. 2 have been limited to a point every 5 K instead of every 1 K. For comparison, isobaric heat capacity values for Jet A, the most common commercial aviation fuel used within the US, are also shown in Fig. 2. These values were calculated using a surrogate mixture model [18, 22] that was developed at NIST and has been implemented within the framework of the Reference Fluid Thermodynamic and Transport Properties (REFPROP) program [56]. In the forthcoming paper of Fortin et al. [30], we report an absolute average deviation (AAD) of 0.4% for the surrogate mixture model relative to our experimental data for Jet A, with overall deviations ranging from -1.3% to 0.5%.



Fig. 2. Averaged isobaric specific heat capacities for six jet fuels plotted as a function of temperature. For clarity, data are only plotted every 5 K. Expanded absolute uncertainties for the six fuels are as follows: $0.036 - 0.065 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for JP-10, $0.050 - 0.073 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for JP-7, $0.034 - 0.052 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for JP-4, $0.050 - 0.076 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for JP-TS, $0.052 - 0.078 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for TS-1, and $0.041 - 0.052 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for Avgas. Heat capacities for the most commonly used commercial fuel in the US, Jet A, are shown for comparison; these values were derived from an existing surrogate mixture model [22].

Generally speaking, most of the fuels are relatively similar to one another and to Jet A; the two outliers being the two fuels that are most dissimilar in composition, JP-10 and Avgas. Specifically, the sole gasoline fuel among the measured samples, Avgas, exhibits the highest heat capacities, ranging from $1.879 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 213 K to $2.417 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 342 K. At the opposite extreme, the least compositionally complex fuel in the group, JP-10, exhibits heat capacities ranging from $1.282 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 233 K to $2.266 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 442 K. The relative difference between these two fuels is 48.4% at 223 K and 36.1% at 342 K. In contrast, the overall spread among the remaining four fuels ranges from 9.4% at 248 K to 8.4% at 412 K. Of these four fuels, TS-1

exhibits the highest heat capacities, ranging from $1.890 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 238 K to 2.753 J $\cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 442 K; while JP-7 exhibits the lowest, ranging from $1.752 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 248 K to 2.547 J $\cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 442 K. The final two fuels, JP-4 and JP-TS exhibit very similar heat capacities. JP-4 ranges from 1.757 J $\cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 233 K to 2.534 J $\cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 412 K; while JP-TS ranges from 1.841 J $\cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 238 K to 2.662 J $\cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 442 K. The relative difference between these two fuels is 3.8% at 223 K and - 0.6 % at 412 K; these differences are well within combined estimated experimental uncertainties. Unsurprisingly, heat capacity values for Jet A fall within this cluster of four fuels, ranging from 1.779 J $\cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 248 K to 2.555 J $\cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 442 K. Overall, JP-7 is most similar to Jet A, with relative differences that range from -1.5% at 248 K to -0.3% at 442 K, well within combined estimated experimental uncertainties. For the remaining five fuels, Avgas, TS-1, and JP-10 all show statistically relevant differences from Jet A over the full temperature range, with JP-10, showing the largest differences, ranging from -23.3% at 248 K to -11.3% at 442 K. In contrast, differences for both JP-4 and JP-TS relative to Jet A are statistically relevant at certain temperatures but otherwise fall within combined estimated experimental uncertainties.

In the most general terms, when energy is added to a system of complex molecules, there is an increase, not only in the translational motion of the molecules, but also in their rotational, vibrational, and bending motions. Ultimately, the amount of energy required to raise the temperature of a particular amount of a given substance (i.e., the heat capacity) depends upon the molecular structure, as well as the intramolecular and intermolecular interactions. Thus, when considering an unbranched paraffin and its branched counterpart, such as *n*-octane and isooctane, branching effectively lowers the number of possible rotational and vibrational degrees of freedom, which means less energy is required to raise the kinetic energy (i.e., temperature) since more of the energy goes directly to increasing translational motions; this results in a lower heat capacity for isooctane relative to *n*-octane [58]. Similar arguments can be made for cyclic and aromatic compounds in terms of decreasing rotational degrees of freedom, and thus decreasing heat capacity, moving from unbranched to branched to cyclic to aromatic (e.g., *n*-hexane > 3-methylpentane > cyclohexane > benzene) [58]. In light of these considerations, it is not surprising that Avgas exhibits the highest heat capacities given its comparatively large paraffinic content. Similarly, the low heat capacities observed for JP-10 can be explained by the fact that it is entirely composed of cyclic compounds (Table S2). For the remaining four fuels, we would expect their heat capacities to be similar, but given the relatively lower aromatic content of JP-7, we would perhaps expect it to have slightly higher heat capacities, but instead it exhibits heat capacities that are slightly lower than the others.

The final thing to notice in Fig. 2 is that the measured heat capacity values for Avgas appear to exhibit a noticeably different temperature dependence than the other five fuels. Given that Avgas is significantly more volatile than the other samples, a likely explanation for this behavior is an increasing contribution from the enthalpy of vaporization [59]. Since no clear evidence of significant vaporization was actually observed in the measured heat capacity curves for any of the fuel samples, and given that the actual internal volume of the sample pans is not known, no attempt was made to correct any of the measured data reported herein for enthalpy of vaporization contributions.

There are very limited data available in the literature to which we can compare our heat capacity measurement results. The *Handbook of Aviation Fuel Properties* [60] contains isobaric heat capacity data for JP-10, JP-7, JP-4, JP-TS, and Avgas, and is the sole source of comparison data for the last two. The bulk of reported data from this source were derived from a correlation published by Maxwell [61], which combines averaged fuel gravity (i.e., density) and distillation

data, rather than from experimental heat capacity data. Since the data are only presented graphically, we first had to digitize the graphs and then fit the resulting data points to a straight line to facilitate the calculation of heat capacity values at experimental temperatures for comparison. Additional isobaric heat capacity data for JP-7 and JP-4 are reported by Callanan [62]. Here, conventional DSC measurement results were correlated and the resulting cubic polynomial parameters reported; those parameters were used to calculate heat capacities at our experimental temperatures for the comparisons presented here. For TS-1, the only comparison data that could be located are reported by Hadaller and Johnson [63]. In general, they present the results of MDSC measurements for 57 jet fuel samples sourced from 18 countries as part of the World Fuel Sampling Program; for TS-1 the reported data are derived from measurements of a single fuel sample which is reported as a slope and intercept to facilitate the calculation of isobaric heat capacity as a function of temperature. Finally, in addition to the literature data discussed above, our measurement results for JP-10 can be compared to the predictions of an equation of state that was developed at NIST and has been implemented within the framework of the Reference Fluid Thermodynamic and Transport Properties (REFPROP) program [56].

The data comparison results, plotted as percent deviation as a function of temperature, are summarized in Fig. 3 for all six fuel samples. For each comparison data source, the same markers have been used throughout to facilitate comparisons between fuels. Additionally, dashed lines have been included to represent the maximum estimated experimental uncertainty limits for each fuel.



Fig. 3. Comparisons of available isobaric heat capacity data with measurement results from this work, plotted as percent deviation as a function of temperature. Deviation plots are shown for (A) JP-10, (B) JP-7, (C) JP-4, (D) JP-TS, (E) TS-1, and (F) Avgas. Values derived from an existing equation of state [56] (\approx) are included for JP-10. Literature data from the *Handbook of Aviation Fuel Properties* [60] (\bigcirc), Hadaller and Johnson [63] (\square), and Callanan [62] (+) are included where available. The dashed lines represent the maximum estimated experimental uncertainty limits for each fuel.

The first thing that is readily apparent when looking at Fig. 3 is that there is some variability observed among the comparison results, with some fuels showing good agreement, while others do not. For both JP-10 and JP-TS, good agreement is observed between values from the *Handbook*

of Aviation Fuel Properties [60] and experimental results from this work. Specifically, the AAD for JP-10 (Fig. 3A) is 1.2% with an overall range of -1.5% to 2.3%; for JP-TS (Fig. 3D) the AAD is 1.4%, and the deviations range from 0.4% to 1.9%, respectively. Similarly, relatively good agreement is also observed between model predictions [56] and experimental results for JP-10 (Fig. 3A), with deviations ranging from -4.8% to -0.1% and an AAD of 2.1%. Relatively good agreement is also observed for Avgas (Fig. 3F) between values from the Handbook of Aviation Fuel Properties [60] and experimental results, particularly at higher temperatures. In this case, deviations range from 0.3% to 3.4%, with an AAD of 2.1%. However, the situation gets progressively worse for JP-4 and JP-7; here, with limited exceptions, the values from the Handbook of Aviation Fuel Properties [60] do not agree with our results within experimental uncertainties. For JP-4 (Fig. 3C), deviations range from 1.1% to 3.9%, with an AAD of 2.9%. For JP-7 (Fig. 3B), the deviations are even greater, ranging from 4.2% to 6.1%, with an AAD of 5.7%. Similar behavior is observed for both of these fuels for the data reported by Callanan [62], with AADs of 3.5% and 4.9% for JP-4 (Fig. 3C) and JP-7 (Fig. 3B), respectively. The deviations for these fuels range from 1.2% to 4.2% for JP-4, and from 2.2% to 5.9% for JP-7. Finally, for TS-1 (Fig. 3E), the results from the World Fuel Sampling Program reported by Hadaller and Johnson [63] are significantly lower than the experimental results reported herein. Specifically, deviations range from -25.1% to -21.3%, with an AAD of 22.1%.

Fuel standards are primarily performance specifications rather than strict compositional specifications since differences in crude oil sources and manufacturing processes are expected to introduce a significant degree of variability among resulting fuel products [38]; past research has demonstrated that the variability extends to certain fuel properties as well [26, 28, 64]. Consequently, it would be reasonable to assume that at least some of the differences in heat

capacities observed in Fig. 3 can be attributed to variability among fuel batches. Unfortunately, specific batch information was not provided in any of the source references. In the case of the World Fuel Sampling Program data reported by Hadaller and Johnson [63], significant differences in measurement protocols seem the most likely explanation for the large observed deviations. As was the case with the results reported in this work, the data reported by Hadaller and Johnson were derived from MDSC measurements [63]. Differences in key experimental parameters such as purge gas, modulation conditions, and underlying heating rate will inevitably result in a reasonable degree of variability among measurement results. For the World Fuel Sampling Program data [63], the underlying heating rate employed was 20 K·min⁻¹; which is significantly higher than the 3 K·min⁻¹ employed in this work. This is important because MDSC assumes that the temperature as measured at the cell platform is representative of the encapsulated sample temperature and that temperature gradients within the sample are minimal. The higher the heating rate, the greater the chance that these assumptions no longer hold, which would manifest as negatively biased results, assuming heat capacity increases with increasing temperature. In fact, Hadaller and Johnson [63] report additional data from subsequent measurements that appear to support this hypothesis. For example, the authors discuss a single synthetic fuel sample that was measured both during the initial phase of the project and then again at a later date following an altered measurement protocol, the largest difference being the use of a much slower underlying heating rate of 5 K \cdot min⁻¹ [63]. These later, slower, measurements produced results that were approximately 15.0% to 18.2% higher than the initial results [63], thus bringing the World Fuel Sampling Program data for this particular sample closer in line with other available data [30, 65].

Table 1. Coefficients (α_i) and Associated Standard Uncertainties ($u(\alpha_i)$) from the Fit of Eq. 2 to Experimental Isobaric Heat Capacity Data for Six Aviation Fuels

Fuel	$lpha_0$	$u(\alpha_0)$	α_{l}	$u(\alpha_1)$	α_2	$u(\alpha_2)$	0 (3)	$u(\alpha_3)$	AAD ^a
	$(\mathbf{J} \cdot \mathbf{g}^{-1} \cdot \mathbf{K}^{-1})$	$(\mathbf{J} \cdot \mathbf{g}^{-1} \cdot \mathbf{K}^{-1})$	$(J \cdot g^{-1} \cdot K^{-2})$	$(J \cdot g^{-1} \cdot K^{-2})$	$(J \cdot g^{-1} \cdot K^{-3})$	$(J \cdot g^{-1} \cdot K^{-3})$	$(J \cdot g^{-1} \cdot K^{-4})$	$(\mathbf{J} \cdot \mathbf{g}^{-1} \cdot \mathbf{K}^{-4})$	(%)
JP-10	1.3095	0.0167	-4.5284E-03	1.5635E-04	2.4347E-05	4.7815E-07	-2.0878E-08	4.7838E-10	0.074
JP-7	1.5666	0.0421	-2.1878E-03	3.7630E-04	1.4078E-05	1.1040E-06	-9.3999E-09	1.0650E-09	0.078
JP-4	1.4227	0.0157	-1.0013E-03	1.4970E-04	1.2284E-05	4.6968E-07	-8.0191E-09	4.8469E-10	0.028
JP-TS	2.0659	0.0274	-5.3842E-03	2.4912E-04	2.2486E-05	7.4287E-07	-1.6417E-08	7.2704E-10	0.068
TS-1	2.1341	0.0301	-5.7562E-03	2.7338E-04	2.4072E-05	8.1524E-07	-1.7881E-08	7.9787E-10	0.069
Avgas	2.4830	0.0754	-9.2651E-03	8.2981E-04	3.6110E-05	3.0145E-06	-2.8003E-08	3.6163E-09	0.065

^aThe average absolute deviation (AAD) between experimental data and fit results.

Finally, to facilitate their use, the experimental data reported herein have been correlated as function of temperature using the expression

$$\bar{c}_p = \alpha_0 + (\alpha_1 \cdot T) + (\alpha_2 \cdot T^2) + (\alpha_3 \cdot T^3).$$
(2)

The resulting coefficients and the associated standard uncertainties are shown in Table 1 for all six fuel samples. Also shown in Table 1 are the observed AADs for calculated isobaric heat capacities relative to experimental values. Additionally, the relative deviations between calculated and experimental values are plotted as a function of temperature in Fig. 4 for all six fuels. In all cases, these deviations are approximately an order of magnitude smaller than estimated experimental uncertainties. The overall best fit is observed for JP-4 with deviations ranging from approximately -0.12% to approximately 0.08%; the overall worst fit is observed for JP-7 with deviations ranging from approximately -0.30% to approximately 0.23%.



Fig. 4. Relative deviations for the correlation of experimental isobaric heat capacity data with Eq. 2.

4. Conclusions

In this work, isobaric heat capacity measurements for six conventional, petroleum-derived fuel samples have been presented. Five of the samples were aviation turbine fuels, including several specialty fuels developed for the US military and one commercial fuel commonly used in Russia and in several former Soviet republics. The sixth sample was an aviation gasoline. All measurements were made using MDSC over the combined temperature range of (213 to 442) K. Significant variability was observed among the six samples; the overall spread in isobaric heat capacity ranged from 48.4% at 223 K to 36.1% at 342 K. However, these very large differences were between the two most compositionally distinct samples, the aviation gasoline, Avgas, and

the nearly pure fuel, JP-10. The variability observed among the remaining, more compositionally similar fuels was much less; the overall spread in isobaric heat capacity for these four fuels ranged from 9.4% at 248 K to 8.4% at 412 K. In addition to the fuel-to-fuel comparisons, measurement results for the six fuels were compared with available literature data and, in the case of JP-10, with predictions from an existing equation of state. In some instances, the calculated deviations were within estimated experimental uncertainties; while in others, deviations exceeded uncertainties by approximately a factor of two at worst. The most glaring exception was for the data from the World Fuel Sampling Program [63], which were approximately 22% lower than the experimental results reported in this work for TS-1. Evidence suggests that a significantly faster heating rate is largely to blame for such large observed differences. As was previously mentioned, for aviation engines where fuel is being used as a coolant, specific heat capacity data are required for heat transfer calculations. Additionally, heat capacity data can be used to evaluate other basic thermodynamic properties of a fuel; a particularly important consideration when exploring alternative fuel sources. It is our hope that the data reported here, combined with the data reported within the forthcoming paper of Fortin et al. [30], will aid the community in its ongoing search for sustainable aviation fuels.

Acknowledgments

We acknowledge the Propulsion Directorate of the Air Force Research Laboratory at Wright Patterson Air Force Base for providing the fuel samples measured in this work. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

CRediT Authorship Contribution Statement

Tara J. Fortin: Conceptualization, Methodology, Investigation, Writing – original draft. Thomas J. Bruno: Supervision, Writing – review & editing.

Supplementary Data

Supporting information this article be found online to can at https://doi.org/10.1016/j.fuproc.2022.107341. Additionally, data from Tables S7-S12 of Supporting digital Information are available online in format at https://doi.org/10.18434/mds2-2686.

References

[1] *Airplane Flying Handbook*, FAA-H-8083-3A; Federal Aviation Administration, Airman Testing Standards Branch: Oklahoma City, OK, USA, 2016.

[2] Crouch, T. D.; Bilstein, R. E.; Boyne, W. J.; Curley, R.; Dixon, L.; Gregersen, E.; Bhutia, T. K.; Hosch, W. L.; Lewis, R.; Lotha, G.; Murray, L.; Tikkanen, A. History of Flight, <u>https://www.britannica.com/technology/history-of-flight</u> (accessed April 28, 2020).

[3] Maurice, L. Q.; Lander, H.; Edwards, T.; Harrison, W. E. Advanced Aviation Fuels: A Look Ahead via a Historical Perspective. *Fuel* **2001**, *80*, 747-756.

[4] Botteri, B. P.; Cretcher, R. E.; Fultz, J. R.; Lander, H. R. *A Review and Analysis of the Safety of Jet Fuel*, AFAPL-TR-66-9; Air Force Aero Propulsion Laboratory, Research and Technology Division: Wright-Patterson Air Force Base, OH, USA, 1966.

[5] Department of Defense Annual Energy Management and Resilience Report (AEMRR) Fiscal Year 2018; U.S. Department of Defense: Washington, D.C., USA, 2019.

[6] *Fiscal Year 2018 Operational Energy Annual Report*; U.S. Department of Defense: Washington, D.C., USA, 2019.

[7] Striebich, R.; Shafer, L.; DeWitt, M. J.; West, Z.; Edwards, T.; Harrison III, W. *Dependence* of Fuel Properties During Blending of Iso-Paraffinic Kerosene and Petroleum-Derived Jet Fuel: Interim Report, AFRL-RZ-WP-TR-2009-2034; Air Force Research Laboratory: Wright-Patterson Air Force Base, OH, USA, 2009.

[8] Bartis, J. T.; Van Bibber, L. *Alternative Fuels for Military Applications*; RAND Corporation: Santa Monica, CA, USA, 2011.

[9] Edwards, J. T.; Shafer, L. M.; Klein, J. K. U.S. Air Force Hydroprocessed Renewable Jet (HRJ) Fuel Research: Interim Report, AFRL-RQ-WP-TR-2013-0108; Air Force Research Laboratory: Wright-Patterson Air Force Base, OH, USA, 2013.

[10] Corporan, E.; Casselberry, R. Q.; DeWitt, M. J. Gas-Phase Pyrolysis Characteristics of Hydrocarbon Fuels and Their Potential Impacts on Combustion Operational Performance. *Energy Fuels* **2020**, *34*, 14843-14852.

[11] Alsulami, R.; Windom, B. Liquid Jet Fuel Property Impacts on Combustion Performance. *J. Propuls. Power* **2021**, *37*, 276-282.

[12] Burton, J. L.; Martin, J. A.; Fioroni, G. M.; Alleman, T. L.; Hays, C. K.; Ratcliff, M. A.; Thorson, M. R.; Schmidt, A. J.; Hallen, R. T.; Hart, T. R.; Billing, J. M.; Fox, S.; Gaspar, D. J.; Zhu, J.; Kima, C.; Pfefferle, L. D.; McEnally, C. S.; McCormick, R. L. *Fuel Property Effects of a Broad Range of Potential Biofuels on Mixing Control Compression Ignition Engine Performance*

and Emissions, SAE Technical Paper 2021-01-0505; Society of Automotive Engineers (SAE): Warrendale, PA, USA, 2021.

[13] Woodroffe, J.-D.; Lupton, D.; Garrison, M.; Nagel, E.; Siirila, M.; Harvey, B. Synthesis and Fuel Properties of High-Energy Density Cyclopropanated Monoterpenes. *Fuel Process. Technol.* **2021**, *222*, 106952.

[14] Bruno, T. J.; Huber, M. L.; Laesecke, A.; Lemmon, E. W.; Perkins, R. A. *Thermochemical and Thermophysical Properties of JP-10*, NISTIR 6640; National Institute for Standards and Technology: Boulder, CO, USA, 2006.

[15] Bruno, T. J.; Smith, B. L. Improvements in the Measurement of Distillation Curves. 2. Application to Aerospace/Aviation Fuels RP-1 and S-8. *Ind. Eng. Chem. Res.* **2006**, *45*, 4381-4388.

[16] Smith, B. L.; Bruno, T. J. Improvements in the Measurement of Distillation Curves. 4. Application to the Aviation Turbine Fuel Jet-A. *Ind. Eng. Chem. Res.* **2007**, *46*, 310-320.

[17] Bruno, T. J.; Laesecke, A.; Outcalt, S. L.; Seelig, H. D.; Smith, B. L. *Properties of a 50/50 Mixture of Jet-A* + *S-8*, NISTIR 6647; National Institute of Standards and Technology: Boulder, CO, USA, 2007.

[18] Huber, M. L.; Smith, B. L.; Ott, L. S.; Bruno, T. J. Surrogate Mixture Model for the Thermophysical Properties of Synthetic Aviation Fuel S-8: Explicit Application of the Advanced Distillation Curve. *Energy Fuels* **2008**, *22*, 1104-1114.

[19] Widegren, J. A.; Bruno, T. J. Thermal Decomposition Kinetics of the Aviation Turbine Fuel Jet A. *Ind. Eng. Chem. Res.* **2008**, *47*, 4342-4348.

[20] Outcalt, S. L.; Laesecke, A.; Freund, M. B. Density and Speed of Sound Measurements of Jet A and S-8 Aviation Turbine Fuels. *Energy Fuels* **2009**, *23*, 1626-1633.

[21] Lovestead, T. M.; Bruno, T. J. A Comparison of the Hypersonic Vehicle Fuel JP-7 to the Rocket Propellants RP-1 and RP-2 with the Advanced Distillation Curve Method. *Energy Fuels* **2009**, *23*, 3637-3644.

[22] Huber, M. L.; Lemmon, E. W.; Bruno, T. J. Surrogate Mixture Models for the Thermophysical Properties of Aviation Fuel Jet-A. *Energy Fuels* **2010**, *24*, 3565-3571.

[23] Bruno, T. J.; Baibourine, E.; Lovestead, T. M. Comparison of Synthetic Isoparaffinic Kerosene Turbine Fuels with the Composition-Explicit Distillation Curve Method. *Energy Fuels* **2010**, *24*, 3049-3059.

[24] Bruno, T. J.; Baibourine, E. Comparison of Biomass-Derived Turbine Fuels with the Composition-Explicit Distillation Curve Method. *Energy Fuels* **2011**, *25*, 1847-1858.

[25] Outcalt, S. L.; Fortin, T. J. Density and Speed of Sound Measurements of Two Synthetic Aviation Turbine Fuels. *J. Chem. Eng. Data* **2011**, *56*, 3201-3207.

[26] Burger, J. L.; Bruno, T. J. Application of the Advanced Distillation Curve Method to the Variability of Jet Fuels. *Energy Fuels* **2012**, *26*, 3661-3671.

[27] Outcalt, S. L.; Fortin, T. J. Density and Speed of Sound Measurements of Four Bioderived Aviation Fuels. *J. Chem. Eng. Data* **2012**, *57*, 2869-2877.

[28] Fortin, T. J.; Laesecke, A. Viscosity Measurements of Aviation Turbine Fuels. *Energy Fuels* **2015**, *29*, 5495-5506.

[29] Lovestead, T. M.; Burger, J. L.; Schneider, N.; Bruno, T. J. Comprehensive Assessment of Composition and Thermochemical Variability by High Resolution GC/QToF-MS and the Advanced Distillation Curve Method as a Basis for Comparison for Reference Fuel Development. *Energy Fuels* **2016**, *30*, 10029-10044.

[30] Fortin, T. J.; Bruno, T. J.; Lovestead, T. M. Comparison of heat capacity measurements of alternative and conventional aviation fuels. *Int. J. Thermophys.* **2023**, *44*, 5.

[31] Aviation Fuels: Technical Review; Chevron U.S.A. Inc.: San Ramon, CA, USA, 2007.

[32] Detail Specification Propellant, High Density Synthetic Hydrocarbon Type, Grade JP-10, MIL-DTL-87107E; Air Force Petroleum Office: Wright-Patterson Air Force Base, OH, USA, 2012.

[33] Detail Specification Turbine Fuel, Aviation, Kerosene Type, JP-8 (NATO F-34), NATO F-35, and JP-8+100 (NATO F-37), MIL-DTL-83133J; Air Force Petroleum Office: Wright-Patterson Air Force Base, OH, USA, 2015.

[34] *Detail Specification Turbine Fuel, Low Volatility, JP-7*, MIL-DTL-38219D(USAF); Air Force Petroleum Office: Wright-Patterson Air Force Base, OH, USA, 1998.

[35] Detail Specification Turbine Fuel, Aviation, Thermally Stable (JPTS), MIL-DTL-25524F(USAF) w/ Amendment 1; Air Force Petroleum Office: Wright-Patterson Air Force Base, OH, USA, 2016.

[36] *Detail Specification Turbine Fuel, Aviation, Grades JP-4 and JP5*, MIL-DTL-5624W; Air Force Petroleum Office: Wright-Patterson Air Force Base, OH, USA, 2016.

[37] *Jet Fuels Specifications*, GOST 10227-2013; Euro-Asian Council for Standardization, Metrology and Certification (EASC): Minsk, Belarus, 2013.

[38] *Standard Specification for Aviation Turbine Fuels*, ASTM D1655-19a; ASTM International: West Conshohocken, PA, USA, 2019.

[39] *Standard Specification for Leaded Aviation Gasolines*, ASTM D910-10; ASTM International: West Conshohocken, PA, USA, 2019.

[40] *Fact Sheet - Leaded Aviation Fuel and the Environment*; Federal Aviation Administration: Washington, D.C., USA, 2019.

[41] Standard Test Method for Hydrocarbon Types in Low Olefinic Gasoline by Mass Spectrometry, ASTM D2789-95(2016); ASTM International: West Conshohocken, PA, USA, 2016.

[42] Smith, B. L.; Bruno, T. J. Improvements in the Measurement of Distillation Curves. 3. Application to Gasoline and Gasoline + Methanol Mixtures. *Ind. Eng. Chem. Res.* **2007**, *46*, 297-309.

[43] Bruno, T. J.; Svoronos, P. D. N. CRC Handbook of Basic Tables for Chemical Analysis - Data Driven Methods and Interpretation; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2021.

[44] Boerio-Goates, J.; Callanan, J. E. Differential Thermal Methods. In *Physical Methods of Chemistry, Volume VI: Determination of Thermodynamic Properties*; Rossiter, B. W.; Baetzold, R. C., Eds.; John Wiley & Sons: New York, NY, USA, 1992; pp 621-717.

[45] Reading, M.; Luget, A.; Wilson, R. Modulated Differential Scanning Calorimetry. *Thermochim. Acta* **1994**, *238*, 295-307.

[46] Wunderlich, B.; Jin, Y.; Boller, A. Mathematical Description of Differential Scanning Calorimetry Based on Periodic Temperature Modulation. *Thermochim. Acta* **1994**, *238*, 277-293.

[47] Höhne, G. W. H.; Hemminger, W.; Flammersheim, H. J. *Differential Scanning Calorimetry: An Introduction for Practitioners*; Springer-Verlag: Berlin, Germany, 1996.

[48] Rosasco, G. J.; Whetstone, J. R.; Watters, R. L. *Certificate of Analysis - Standard Reference Material 2232*; National Institute of Standards and Technology: Gaithersburg, MD, USA, 2003.

[49] Rasberry, S. D. *Certificate of Analysis - Standard Reference Material 2220*; National Institute of Standards and Technology: Gaithersburg, MD, USA, 1989.

[50] Westrum, E. F. The Thermophysical Properties of Three Globular Molecules. *J. Phys. Chem. Solids* **1961**, *18*, 83-85.

[51] Della Gatta, G.; Richardson, M. J.; Sarge, S. M.; Stølen, S. Standards, Calibration, and Guidelines in Microcalorimetry Part 2. Calibration Standards for Differential Scanning Calorimetry. *Pure Appl. Chem.* **2006**, *78*, 1455-1476.

[52] Archer, D. G. Thermodynamic Properties of Synthetic Sapphire (α -Al₂O₃), Standard Reference Material 720 and the Effect of Temperature-Scale Differences on Thermodynamic Properties. *J. Phys. Chem. Ref. Data* **1993**, *22*, 1441-1453.

[53] Harris, G. L.; Torres, J. A. *Selected Laboratory and Measurement Practices and Procedures to Support Basic Mass Calibrations*, NISTIR 6969; National Institute of Standards and Technology: Gaithersburg, MD, USA, 2003.

[54] Picard, A.; Davis, R. S.; Gläser, M.; Fujii, K. Revised Formula for the Density of Moist Air (CIPM-2007). *Metrologia* **2008**, *45*, 149-155.

[55] Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry, ASTM E1269-11; ASTM International: West Conshohocken, PA, USA, 2011.

[56] Lemmon, E. W.; Bell, I. H.; Huber, M. L.; McLinden, M. O. *NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties (REFPROP)*, 10.0; National Institute of Standards and Technology: Gaithersburg, MD, USA, 2018.

[57] *Guide to the Expression of Uncertainty in Measurement*; International Organization for Standardization: Geneva, Switzerland, 1995.

[58] Naef, R. Calculation of the Isobaric Heat Capacities of the Liquid and Solid Phase of Organic Compounds at and around 298.15 K Based on Their "True" Molecular Volume. *Molecules* **2019**, *24*, 1626.

[59] Hoge, H. J. Heat Capacity of a Two-Phase System, with Applications to Vapor Corrections in Calorimetry. *J. Res. Natl. Bur. Stand.* **1946**, *36*, 111-118.

[60] *Handbook of Aviation Fuel Properties*, CRC Report 635; Coordinating Research Council, Inc.: Alpharetta, GA, USA, 2004.

[61] Maxwell, J. B. *Data Book on Hydrocarbons: Application to Process Engineering*; Van Nostrand Co.: Princeton, NJ, USA, 1957.

[62] Callanan, J. E. Development of Standard Measurement Techniques and Standard Reference Materials for Heat Capacity and Heat of Vaporization of Jet Fuels, NBSIR 88-3093; National Bureau of Standards: Boulder, CO, USA, 2988.

[63] Hadaller, O. J.; Johnson, J. M. *World Fuel Sampling Program*, CRC Report 647; Coordinating Research Council, Inc.: Alpharetta, GA, USA, 2006.

[64] Fortin, T. J. Assessment of Variability in the Thermophysical Properties of Rocket Propellant RP-1. *Energy Fuels* **2012**, *26*, 4383-4394.

[65] Bessee, G. B.; Hutzler, S. A.; Wilson, G. R. *Analysis of Synthetic Aviation Fuels: Interim Report*, AFRL-RZ-WP-TR-2011-2084; Air Force Research Laboratory: Wright-Patterson Air Force Base, OH, USA, 2011.

Figure Captions

Fig. 1. Schematic representation of the hydrocarbon classification analysis of all measured fuel samples. Analysis is based on ASTM Method D-2789 [41], which classifies hydrocarbon samples into six families: paraffins (P), monocycloparaffins (MCP), dicycloparaffins (DCP), alkylbenzenes (AB), indanes and tetralins (I&T), and naphthalenes (N). Numbers shown represent the measured percent volume fraction for each of the six families. Analysis results for JP-7 have previously been reported [21]; the remaining five fuels were analyzed as part of this work.

Fig. 2. Averaged isobaric specific heat capacities for six jet fuels plotted as a function of temperature. For clarity, data are only plotted every 5 K. Expanded absolute uncertainties for the six fuels are as follows: $0.036 - 0.065 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for JP-10, $0.050 - 0.073 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for JP-7, $0.034 - 0.052 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for JP-4, $0.050 - 0.076 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for JP-TS, $0.052 - 0.078 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for TS-1, and $0.041 - 0.052 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ for Avgas. Heat capacities for the most commonly used commercial fuel in the US, Jet A, are shown for comparison; these values were derived from an existing surrogate mixture model [22].

Fig. 3. Comparisons of available isobaric heat capacity data with measurement results from this work, plotted as percent deviation as a function of temperature. Deviation plots are shown for (A) JP-10, (B) JP-7, (C) JP-4, (D) JP-TS, (E) TS-1, and (F) Avgas. Values derived from an existing equation of state [56] (*) are included for JP-10. Literature data from the *Handbook of Aviation Fuel Properties* [60] (O), Hadaller and Johnson [63] (\Box), and Callanan [62] (+) are included where available. The dashed lines represent the maximum estimated experimental uncertainty limits for each fuel.

Fig. 4. Relative deviations for the correlation of experimental isobaric heat capacity data with Eq. 2.