

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) 21-04-2010		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Assessment of the Compositional Variability of RP-1 and RP-2 with the Advanced Distillation Curve Approach				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Bret C. Windom, Tara M. Lovestead, Jennifer R. Riggs, Christopher Nickell, & Thomas J. Bruno (National Institute of Standards and Technology)				5d. PROJECT NUMBER	
				5f. WORK UNIT NUMBER 33SP0840	
				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-RZ-ED-TP-2010-202	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZSA 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				10. SPONSOR/MONITOR'S ACRONYM(S)	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZS 5 Pollux Drive Edwards AFB CA 93524-7048				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-RZ-ED-TP-2010-202	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited (PA #10187).					
13. SUPPLEMENTARY NOTES For presentation at the 57 th JANNAF Joint Subcommittee Meeting, Colorado Springs, CO, 3-7 May 2010.					
14. ABSTRACT RP-1 is a long-established hydrocarbon fuel that continues to be widely used as the kerosene component in rocket propulsion systems. The desire in recent years to use rocket motors many times, rather than a single time, has led to reformulations of RP-1. In terms of processing, increased hydro-treating of the component feedstock fluids used in the manufacture of RP-1 can lower the sulfur, olefin and aromatic content significantly. The resulting fuels have demonstrably lower metal corrosion effects, and are thus more amenable to multiple use rocket motors. In recent years, the reformulated RP-1 mixtures have been extensively studied in terms of thermophysical properties, combustion processes and kinetics, and performance. Still unknown is how compositional variability resulting from the various blending strategies affects the properties, and our ability to correctly predict the fluid behavior with mathematical models. To address this question, we have obtained eleven orthogonal batches of RP-1 that were prepared to represent the range of formulation recipes. For each of these representative formulations, we have assessed the compositional variability with the advanced distillation curve (ADC) metrology. This method is an improvement of classical boiling curve techniques. In this paper, we use the temperature grid of the ADC to conclude that the variability of RP-1 and RP-2 are significant, and perhaps higher than expected.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Mr. Matthew Billingsley
Unclassified	Unclassified	Unclassified	SAR	30	19b. TELEPHONE NUMBER <i>(include area code)</i> N/A

**Assessment of the Compositional Variability of RP-1 and RP-2 with the
Advanced Distillation Curve Approach***

**Bret C. Windom, Tara M. Lovestead, Jennifer R. Riggs, Christopher Nickell and
Thomas J. Bruno****
**Physical and Chemical Properties Division
National Institute of Standards and Technology
Boulder, CO**

*Contribution of the United States government; not subject to copyright in the United States.

** Author to whom correspondence should be addressed, bruno@boulder.nist.gov

Abstract:

RP-1 is a long-established hydrocarbon fuel that continues to be widely used as the kerosene component in rocket propulsion systems. The desire in recent years to use rocket motors many times, rather than a single time, has led to reformulations of RP-1. In terms of processing, increased hydro-treating of the component feedstock fluids used in the manufacture of RP-1 can lower the sulfur, olefin and aromatic content significantly. The resulting fuels have demonstrably lower metal corrosion effects, and are thus more amenable to multiple use rocket motors. In recent years, the reformulated RP-1 mixtures have been extensively studied in terms of thermophysical properties, combustion processes and kinetics, and performance. Still unknown is how compositional variability resulting from the various blending strategies affects the properties, and our ability to correctly predict the fluid behavior with mathematical models. To address this question, we have obtained eleven orthogonal batches of RP-1 that were prepared to represent the range of formulation recipes. For each of these representative formulations, we have assessed the compositional variability with the advanced distillation curve (ADC) metrology. This method is an improvement of classical boiling curve techniques. It features (1) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, (6) trace chemical analysis of each distillate fraction, and (7) corrosivity assessment of each distillate fraction. In this paper, we use the temperature grid of the ADC to conclude that the variability of RP-1 and RP-2 are significant, and perhaps higher than expected.

Keywords: Advanced distillation curve, compositional variability, RP-1, RP-2.

Introduction:

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, which include the complexity and cost of cryogen use (temperatures in the range of 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 (acronym for rocket propellant 1) in the mid 1950s. This fluid, produced as MIL-P-25576, has a much tighter allowable density and volatility range, and a much lower sulfur, olefin and aromatic content than the common turbine aviation fuels¹. 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.² Previous analysis of RP-1 has shown the fuel to be a complex mixture of compounds including paraffins, olefins, and aromatics³. 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). Historically, the formulation of RP-1 has been done by mixing separate blending stocks according to “recipes” that are known to produce fluids that are within specification. The recipes varied depending upon availability, economics and logistics. This is still the case with present formulations.

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 hydro-treating of fluids such as RP-1 can lower the sulfur, olefin and aromatic content 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 <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 RP-1, sometimes simply called ultra) 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 specification for RP-1 and RP-2 aromatic content are the same, however one commonly finds a lower aromatic content in RP-2.

As a result of the reformulations described above, it has been necessary to measure many of the chemical and thermophysical properties of both RP-1 and RP-2.³⁻⁷ These properties have included the volatility, density, viscosity, speed of sound, and thermal conductivity, much of which has been measured at NIST. From these data, we have developed surrogate mixture models to represent the thermophysical and transport properties. These surrogate models were implemented within the framework of the NIST Refprop computer program.⁸

A weakness of this body of work is that the measurements were performed on only one sample or batch, each, of RP-1 and RP-2. Only a single batch of RP-1 was used because of the two that were available for study at the time, one was known to be unusual and, in fact, out of specification^{9,10}. Only a single batch or formulation of RP-2 was used because at the time the measurements were made, the formulator had produced only one batch of this fluid. The limitations caused by these limited sample availabilities was clear even during the model development process, and was in fact discussed in detail upon release of the models.¹¹

We recognize that the specifications for RP-1 and RP-2 are stringent when compared to those of mass commodity fuels such as Jet-A or JP-8¹². Moreover, the potential for radical departures (within the specifications) may well be low, given the desire on the

part of formulators to deviate little from successful recipes. Despite this, there have been indications that some unexpected variability has been encountered by launch contractors¹¹. In an effort to evaluate what the range and effect of compositional variability might be, we have undertaken in this work an evaluation of the possible range of composition, derived from different recipes. We have obtained for this evaluation what we consider to be orthogonal batches (that is, independently prepared batches that are uncorrelated with one another) of rocket kerosene. These batches were intentionally prepared to reflect a significant range of possible variability, and are not necessarily to be construed as the typical range of variability that the user might encounter.¹³

In this paper, we report our initial findings as determined by the advanced distillation curve (ADC) approach. Additional evaluations with detailed chemical analyses, thermophysical property measurements (density, viscosity and speed of sound) and theoretical model implications will be presented in the future.

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. 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.¹⁴ 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.

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. Improvements to the traditional distillation apparatus include (1) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, (6) trace chemical analysis of each distillate fraction, and (7) corrosivity assessment of each distillate fraction¹⁵⁻²⁰. 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 to 25 μL) yields nearly instantaneous composition measurements to accompany the temperature data grid. 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-2887.²¹ 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^{8, 15-19, 22-24}. In addition, when designing a fuel surrogate, it is critical to know what components are actually present, with relation to the fuel volatility. This aspect 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). We have applied the advanced distillation curve method to a wide variety of mixtures, including gasoline, diesel fuel, and rocket and aviation kerosenes, and crude oils.²⁵⁻⁴⁹

Experimental:

For this work, eleven separate and orthogonal samples of RP-1 were obtained from the formulator, each prepared with a somewhat different recipe, yet all meeting the specification for the fluid. In addition to these samples, we also were in possession of the earlier sample of RP-1, upon which all of the thermophysical and transport property measurements were made pursuant to the development of the Refprop based model. The samples were all pink in color because of the presence of a dye, azobenzene-4-azo-2-naphthol. The samples were analyzed with a gas chromatography-mass spectrometry (GC-MS) method (30 m capillary column of 5% phenyl dimethyl polysiloxane, having a thickness of 1 μm , temperature program from 90 to 250 $^{\circ}\text{C}$, 10 $^{\circ}\text{C}/\text{min}$).^{50, 51} Mass spectra were collected for each peak from 15 to 550 RMM (relative molecular mass) units. The peaks having an area percentage in excess of 1 % were assigned with the assistance of the NIST mass spectral database.⁵² The fluids were primarily composed of linear and branched paraffins, cycloparaffins, alkenes, and some aromatics.

Two orthogonal samples of RP-2 were available for this evaluation. The samples were 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 μm , temperature program from 70 $^{\circ}\text{C}$ to 260 $^{\circ}\text{C}$, 7 $^{\circ}\text{C}/\text{min}$ and a ballistic heating step to 300 $^{\circ}\text{C}$). As with the

analysis of RP-1, the peaks having an area percentage in excess of 1 % were assigned with the assistance of the NIST mass spectral database.⁵² RP-2, like RP-1, is composed primarily of linear and branched paraffins with very few aromatics. Typical analyses have been reported elsewhere.¹⁶

The n-hexane used as a solvent in this work was obtained from a commercial supplier, and was analyzed by gas chromatography (30 m capillary column of 5 %-phenyl-95 %-dimethyl polysiloxane having a thickness of 1 μm , temperature program from 50 $^{\circ}\text{C}$ 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 method and apparatus for the distillation curve measurement have been reviewed in a number of sources (see the references cited above), so additional general description will not be provided here. 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 pipette. 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.

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, in which the constant term was assigned a value of 0.000109.⁵³⁻⁵⁶ The magnitude of the correction is of course dependent upon the extent of deviation from standard atmospheric pressure. The location of the laboratory in which the measurements reported herein were performed is approximately 1650 m above sea level, resulting in a typical temperature correction of 7 - 8 °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 µL 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 predetermined volume fractions of distillate. The detailed analyses, fraction by fraction, of the different blends are still being assessed; in this report we only present and discuss the temperature data grid.

Results and Discussion

Initial Boiling Behavior:

The initial boiling behaviors of each of the twelve samples of RP-1 and the two samples of RP-2 were measured. Typically, during the earlier stages of measurements, the first bubbles will appear intermittently and are rather small. These bubbles cease if the stirrer is stopped momentarily. The temperature at which this is observed is called the onset temperature, and typically corresponds to the departure of air and other dissolved light gases. Sustained bubbling, which occurs subsequent to onset, is characterized by larger, more vigorous bubbles, and is still observed when the stirring is briefly stopped. Finally, vapor is observed to rise into the distillation head, causing an immediate response on the T_h thermocouple. This temperature, called the vapor rise temperature, has been shown to be the initial boiling temperature (IBT) of the fluid. Furthermore, this temperature is of low uncertainty and thermodynamically consistent, and can be modeled theoretically with an equation of state.

The initial temperature observations for each of the 12 RP-1 samples are summarized in Table 1. These values are the average of two separate measurements done for each blend. The uncertainty (with a coverage factor $k=2$)⁵⁷ of these measurements has been discussed in detail in previous papers and is approximately 2 °C in the sustained bubbling temperatures and approximately 0.2 °C in the vapor rise temperature. We will confine our comments to the vapor rise temperature because of its significance to theory; the sustained bubbling temperature is merely used as a diagnostic. We note that the vapor

rise temperature for the twelve batches ranges from 203.9 to 214.0 °C, with a spread of 10.1 °C. It is somewhat difficult to interpret the significance of this spread, given the fact that the batches formulated for this work were intended to be variable. Moreover, no such study has been undertaken in the past to form the basis of a comparison.

Perhaps the most relevant comparison is with several samples of Jet-A/JP-8, a commodity aviation kerosene that is formulated according to a wide specification parameters to ensure an adequate supply for military and civilian aviation. In prior work, we performed extensive thermophysical property measurements on a series of these fluids. We can expect wide variability in Jet-A/JP-8, although the only comparison that has been done in prior work with the ADC considered only four separate samples.

Despite the relatively small sample number, we will use this study for comparison because the samples were in fact chosen to represent Jet-A/JP-8 variability. One of the samples considered in that earlier work was in fact a composite Jet-A fluid prepared by mixing approximately equal volumes of between ten and fifteen individual batches of Jet-A. This composite sample was prepared at the Air Force Research Laboratory, and was provided for many research projects in the aviation fuel community to represent what might be considered a typical Jet-A fluid⁵⁸. Another sample was known to be unusual in that it showed a remarkably high volatility, an unusually low aromatic content and density, while still meeting all of the specifications for Jet-A. While this fluid is acceptable for use in aviation, it is nevertheless understood to be unusual. The third sample was simply a typical Jet-A fuel chosen essentially at random among a collection of fuels, and the fourth sample was taken directly from the flight line at Wright Patterson

Air Force Base. Among those four samples of Jet-A, the range in the vapor rise temperature was 184.2 to 190.5 °C. This range of 6.3 °C is considerably less than what was measured for the RP-1 samples, discussed above.

The onset temperatures for the two samples of RP-2 that we have measured are provided in Table 2. We note that the variability is essentially the same as that for RP-1, with a range of 10.1 °C. It is not clear what conclusions can be drawn from these observations at this time, since there are only two orthogonal samples currently available for evaluation.

Distillation Curves:

The distillation curve data, presented in T_k , for all twelve RP-1 samples are provided in Table 3. These data include the eleven orthogonal blends studied, and also the earlier measurement upon which the Refprop model was formulated (RP-1-4572). The T_k data are true thermodynamic state points while T_h data allow for comparison with historical measurements. We do not list the T_h data in the table because it was mainly used as a diagnostic measurement in this work, and not for any intercomparison. The temperature data were found to be highly reproducible, comparable to repeatability achieved in our previous work with the ADC. The average standard deviation for replicate temperatures averaged over all twelve RP-1 samples was 0.26 °C. The uncertainty in the volume measurement that was used to obtain the distillate fraction was 0.05 mL in each case. The uncertainty in the measured atmospheric pressure was 0.003 kPa.

In Figure 1, we present the data of Table 3 graphically. In addition, we show on the plot a line that represents the mean temperature at each distillate volume fraction. The standard deviation of this mean value is indicated by the shaded region that surrounds the mean line. The variability among these samples is, at first glance, somewhat surprising, since RP-1 is a fluid whose specifications are relatively tightly controlled, especially compared with mass commodity fluids such as aviation turbine kerosene and diesel fuel. As mentioned earlier, however, the blends formulated for this work were intended to be variable, and cover the range that might reasonably be encountered.

We also present in Figure 1 the distillation curve data of the sample used for the Refprop model development, and the predictions generated from that model (the dashed line).⁸ Two problems are immediately apparent. First, we can see that the model lies below most of the temperatures measured in the present work. It is only in the latter stages of the distillation curves where the model merges with the curves measured here. The second problem is with the shape of the modeled curve. The slope of the modeled curve increases far too steeply in the late stages of the curve, compared with the curves measured in this work. We note that the model represents the behavior of RP-1-4572 (the fluid that was used in its development) very well. This is indicative of the precision with which we can target specific mixtures, but it is also indicative of the limitations encountered when the actual extent of compositional variability is unknown.

As a comparison, in Figure 2 we show the spread of aviation kerosene (Jet-A/JP-8) with the spread of RP-1 that we have measured in this work.^{16, 46} The range of Jet-A/JP-8 was determined in the research project on aviation kerosene that was discussed earlier. These data are presented on the same temperature scale, thus the shaded areas compare the variability of these two fluids. The variability of RP-1, as indicated on this figure, is striking despite being less than that of Jet-A.

The distillation curve data for the two currently available samples of RP-2 are provided in Table 4. These data are also presented graphically in Figure 3. We also show the prediction of the Refprop model for RP-2. This model was developed from measurements performed on the sample labeled EAFB. In Figure 4, we present the variability with the shading diagram similar to that provided for RP-1. Although it is difficult to draw conclusions based on only two samples, it appears that the variability of RP-2 can also be significant.

Conclusions:

In this paper, we have presented experimental work on twelve samples of RP-1 (eleven orthogonal blends specially prepared and a mixture used for model development earlier) and two of RP-2. The results were compared on the basis of temperature grid measurements with the advanced distillation curve approach. This series of

measurements is part of a larger study in which the distillation results will be augmented by measurements of density, viscosity and speed of sound, and a comparison with thermodynamic and transport model predictions. Moreover, the complete work will also include observations from the composition explicit data channel of the ADC. Thus, the presentation in this paper is very much a work in progress. The observations made on the basis of the distillation results are nevertheless of concern; it is clear that the model developed to represent “RP-1” may not in fact represent (1) all the variability that might be expected, and (2) the correct change in volatility at higher temperatures. This would not have been realized without these measurements on the 11 new blends. We will likely have to reconsider the model that has been developed, and potentially make revisions. We note that the work plan for a related project for AFOSR has recently been revised to develop a way to “tune” the models developed for Jet-A to reflect the variations in composition. This may, in fact, be required for RP-1 as well.

Acknowledgements:

B.C.W and T.M.L. acknowledge the National Academy of Science/National Research Council postdoctoral associateship program. J.R.R. and C.N. acknowledge Summer Undergraduate Research Fellowships at NIST. The financial support of the Air Force Research Laboratory (MIPR F4FBEX9205G001) is gratefully acknowledged.

Table 1: Initial boiling behavior for the 12 blends of RP-1. Measurements have been adjusted to standard atmospheric pressure with the Sydney Young equation. The pressures at which measurements were made are provided so the actual measured temperatures may be recovered.

Blend (pressure)	Sustained Boiling °C	Vapor Rise °C
1 (83.0 kPa)	208.0	211.2
2 (83.5 kPa)	207.6	210.3
3 (84.0 kPa)	204.5	207.3
4 (83.6 kPa)	206.5	208.6
5 (84.1 kPa)	210.2	212.8
6 (83.5 kPa)	205.5	207.7
7 (82.9 kPa)	212.1	214.0
8 (81.9 kPa)	206.1	208.9
9 (81.7 kPa)	209.3	211.0
10 (81.8 kPa)	211.1	213.6
11 (80.8 kPa)	206.3	208.9
4572 (83.7 kPa)	201.5	203.9

Table 2: Initial boiling behavior for the 2 blends of RP-2. Measurements in this table have been adjusted to standard atmospheric pressure with the Sydney Young equation. The pressures at which measurements were made are provided so the actual measured temperatures may be recovered.

Blend (P_{atm})	Sustained Boiling °C	Vapor Rise °C
EAFB (82.7 kPa)	202.9	206.4
5433 (83.1 kPa)	214.3	216.5

Table 3: Representative distillation curve data for the 12 blends of RP-1 measured in this work. The pressure has been adjusted to what would be obtained at standard atmospheric pressure with the Sydney Young equation.

Volume Fraction %	Blend 1 °C, 83.0 kPa	Blend 2 °C, 83.5 kPa	Blend 3 °C, 84.0 kPa	Blend 4 °C, 83.6 kPa	Blend 5 °C, 84.1 kPa	Blend 6 °C, 83.5 kPa	Blend 7 °C, 82.9 kPa	Blend 8 °C, 81.9 kPa	Blend 9 °C, 81.7 kPa	Blend 10 °C, 81.8 kPa	Blend 11 °C, 80.8 kPa	RP-1 4572 °C, 83.7 kPa
0.025	211.1	210.3	207.2	208.5	212.6	207.5	213.8	208.8	210.9	213.5	208.8	202.6
5	211.9	211.8	208.7	209.5	213.6	208.4	215.6	210.3	212.2	214.9	210.2	204.0
10	212.6	212.8	209.5	210.1	214.4	209.0	216.7	211.3	213.1	215.8	211.2	205.6
15	213.4	213.9	210.7	210.9	215.4	209.9	218.1	212.5	214.2	217.2	212.6	207.2
20	214.3	215.1	211.8	211.9	216.7	210.7	219.7	214.0	215.5	218.6	214.0	208.6
25	215.2	216.3	213.4	212.9	217.6	211.6	221.4	215.6	216.6	220.0	215.7	210.1
30	216.2	217.7	214.5	214.0	218.7	212.6	223.0	217.2	218.0	221.6	217.3	212.1
35	217.2	219.1	215.7	214.9	219.6	213.6	224.7	218.7	219.1	223.0	218.9	213.7
40	218.4	220.4	217.5	216.1	221.0	214.7	226.4	220.6	220.8	225.0	220.8	215.6
45	219.5	222.0	219.1	217.3	222.5	215.8	228.2	222.3	222.2	226.8	222.5	217.3
50	220.7	223.8	220.7	218.7	224.0	217.1	230.3	224.2	223.7	228.8	224.6	219.4
55	222.0	225.7	222.7	219.8	225.7	218.6	232.3	226.4	225.5	231.0	226.8	221.6
60	223.8	227.6	224.8	221.4	227.7	220.0	234.3	228.9	227.4	233.5	229.1	224.0
65	225.4	229.8	227.3	223.1	230.0	221.5	237.0	231.8	229.8	236.3	231.9	226.5
70	227.2	232.0	229.7	224.8	232.3	223.3	239.4	234.9	232.4	239.3	234.7	229.0
75	229.4	234.6	233.0	226.9	235.3	225.4	242.3	238.4	235.6	242.8	238.3	232.2
80	232.1	237.9	236.1	229.4	238.9	227.6	245.5	242.9	239.3	246.8	242.4	235.7
85	235.4	241.7	240.6	232.2	243.7	230.9	249.9	248.6	244.5	252.0	247.8	241.3
90	239.8	247.1	246.9	235.9	249.6	235.1	255.4	255.7	250.9	258.1	254.6	

Table 4: Representative distillation curve data for two orthogonal samples of RP-2. These are the only two samples of RP-2 currently available. The pressure has been adjusted to what would be obtained at standard atmospheric pressure with the Sydney Young equation.

Volume Fraction, %	EAFB °C (82.7 kPa)	5433 °C (83.1 kPa)
0.025	206.1	-
5	207.7	217.8
10	208.6	219.1
15	209.8	220.4
20	211.3	221.8
25	212.7	223.2
30	214.2	225.1
35	215.8	226.8
40	217.6	228.9
45	219.4	231.0
50	221.4	233.3
55	223.6	236.0
60	225.9	238.6
65	228.5	241.6
70	231.4	244.7
75	234.8	248.0
80	238.8	250.7
85	243.9	254.0
90	250.2	257.4

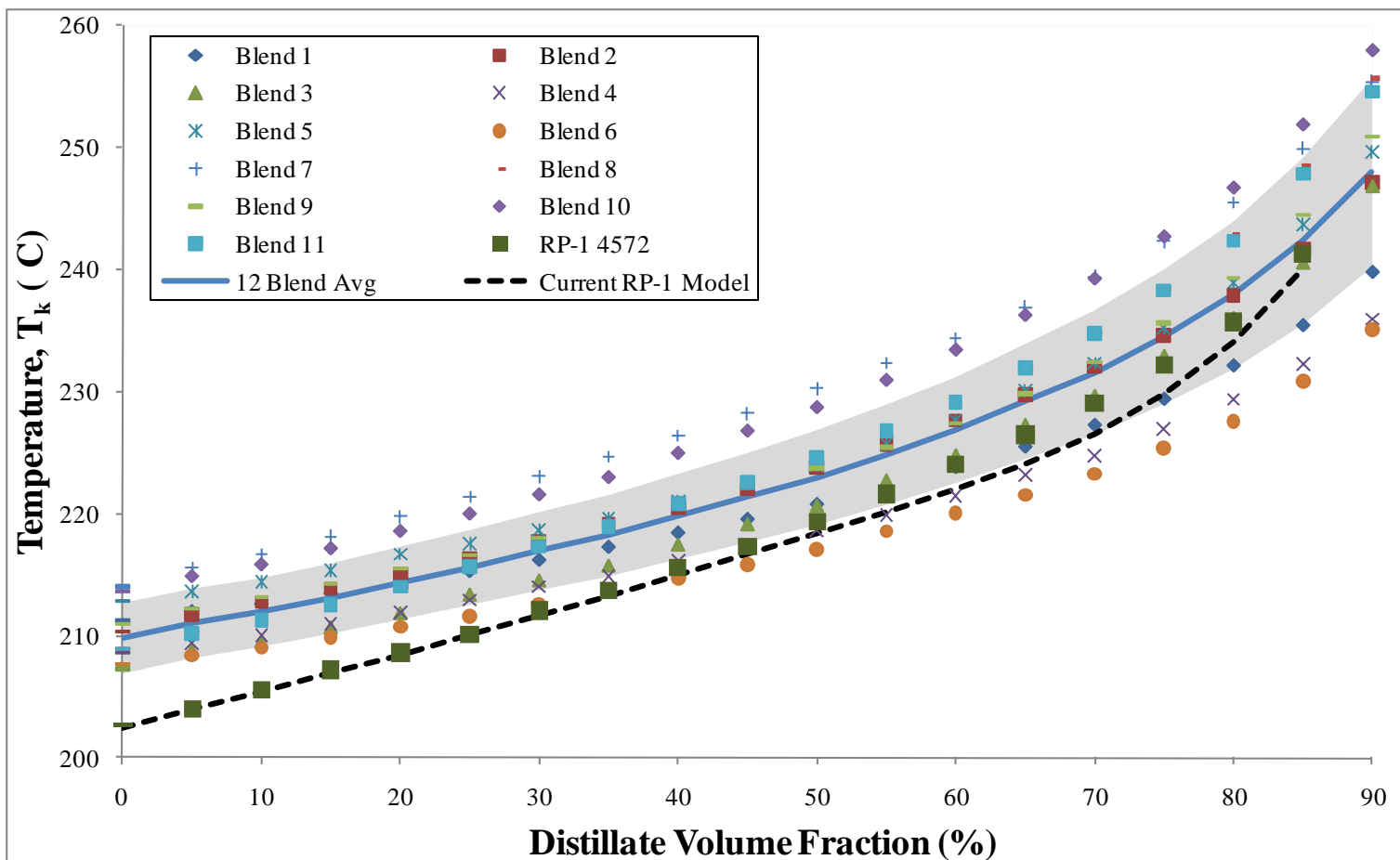


Figure 1: Graphical representation of the distillation curves of the eleven orthogonal samples of RP-1 measured in this work. In addition, we plot the measurements of RP-1 that were used to develop the Refprop model, and the predictions of the model itself as the dashed line. The solid line represents the mean temperature, and the shaded area represents the standard deviation of the mean, for all twelve measurements. The temperatures have been adjusted to what would be obtained at atmospheric pressure by use of the modified Sydney Young equation.

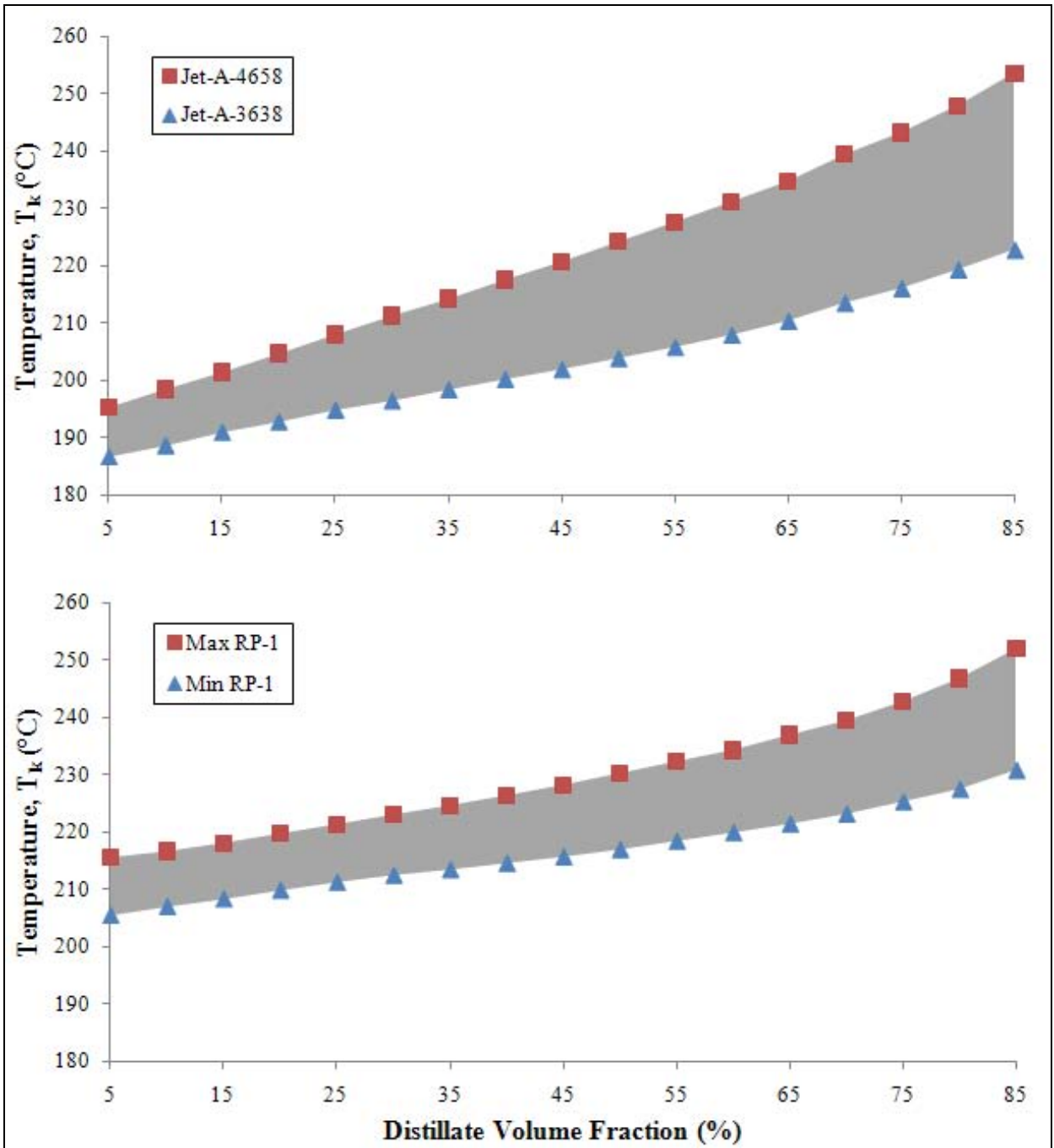


Figure 2: A graphical representation of the variability of the 12 samples of RP-1 measured in this work, and the 4 batches of Jet-A and JP-8 measured previously in other work on aviation kerosene. These data are presented on the same temperature scale, thus the shaded areas compare the variability of these two fluids. The temperatures have been adjusted to what would be obtained at atmospheric pressure by use of the modified Sydney Young equation.

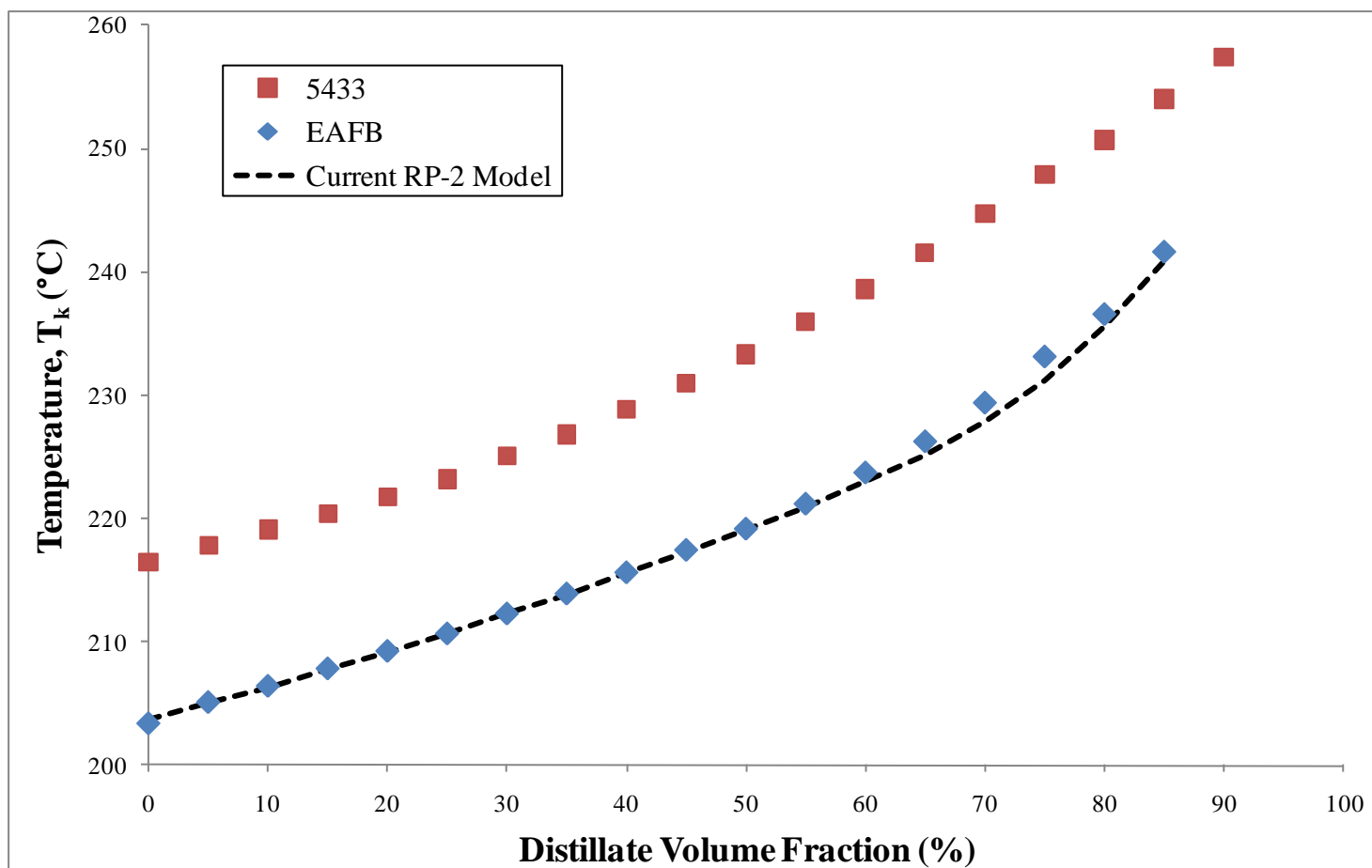


Figure 3: Representative distillation curves of RP-2, along with the predictions made with the Refprop model. The temperatures have been adjusted to what would be obtained at atmospheric pressure by use of the modified Sydney Young equation.

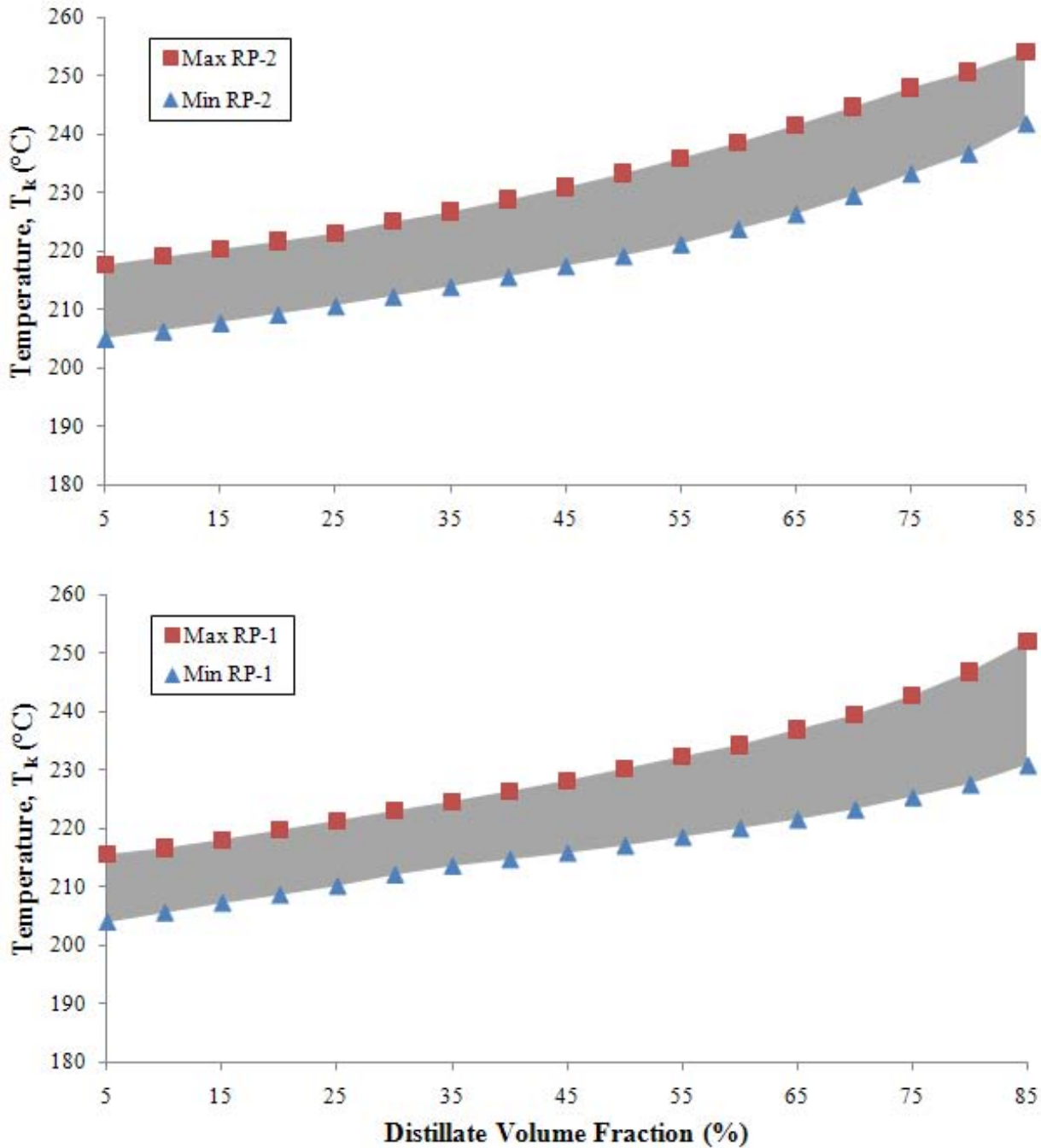


Figure 4: A graphical representation of the variability of the 2 samples of RP-2 measured in this work, and 12 samples of RP-1. These data are presented on the same temperature scale, thus the shaded areas compare the variability of these two fluids. The temperatures have been adjusted to what would be obtained at atmospheric pressure by use of the modified Sydney Young equation.

References:

1. Purchase Description, RP-1, Federal Business Opportunities, <http://fs2.eps.gov/EPSTData/DLA/Synopses/12671/SP0600-03-R-0322/rp-1sol.pdf>. In 2003.
2. Military Specification MIL-P-25576C, U. S. M., 1967.
3. Magee, J. W., Bruno, T.J., Friend, D. G., Huber, M.L., Laesecke, A., Lemmon, E.W., McLinden, M.O., Perkins, R.A., Baranski, J., Widegren, J.A. *Thermophysical Properties Measurements and Models for Rocket Propellant RP-1: Phase I, NIST- IR 6644, National Institute of Standards and Technology (U.S.);* 2006.
4. Andersen, P. C., Bruno, T.J., Thermal decomposition kinetics of RP-1 rocket propellant. *Ind. Eng. Chem. Res.* 2005, 44, (6), 1670-1676.
5. Widegren, J. A., Bruno, T.J., Thermal decomposition of RP-1 and RP-2, and mixtures of RP-2 with stabilizing additives, December, 2008. *Proc. 4th Liquid Propulsion Subcommittee, JANNAF 2008, December.*
6. Widegren, J. A., Bruno, T.J., Thermal decomposition kinetics of the kerosene based rocket propellants 2. RP-2 stabilized with three additives. *Energy & Fuels* 2009, 23, 5523-5528.
7. Widegren, J. A., Bruno, T.J., Thermal Decomposition Kinetics of Kerosene-Based Rocket Propellants. 1. Comparison of RP-1 and RP-2 *Energy & Fuels* 2009, 23, 5517-5522.
8. Huber, M. L., Lemmon, E., Ott, L.S., Bruno, T.J., Preliminary surrogate mixture models for rocket propellants RP-1 and RP-2. *Energy & Fuels* 2009, 23, 3083-3088.
9. Huber, M. L., Lemmon, E., Bruno, T.J., Effect of RP-1 compositional variability on thermophysical properties. *Energy & Fuels* 2009, 23, 5550-5555.
10. Akhmedova-Azizova, L. A., Abdulagatov, I.M., Bruno, T.J., Effect of RP-1 compositional variability on thermal conductivity at high temperatures and high pressures. *Energy & Fuels* 2009, 23, 4522-4528.
11. Bruno, T. J., Billingsley, M, Bates, R.D., Findings and recommendations from the joint NIST/AFRL workshop on rocket propellants and hypersonic vehicle fuels. In National Institute of Standards and Technology, September: 2008.
12. Detail Specification Turbine Fuel, Aviation, Kerosene Type JP-8 (NATO F-34), NATO F-35, and JP-8+100 (NATO F-37), MIL-DTL-83133F 11 April 2008, and references. In 2008.

13. Billingsley, M., Air Force Research Laboratory, Edwards Air Force Base, private communication. In 2010.
14. *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure, ASTM Standard D 86-04b, Book of Standards Volume: 05.01.* American Society for Testing and Materials: West Conshohocken, PA, 2004.
15. Bruno, T. J., Improvements in the measurement of distillation curves - part 1: a composition-explicit approach. *Ind. Eng. Chem. Res.* 2006, 45, 4371-4380.
16. Bruno, T. J., Smith, B.L., Improvements in the measurement of distillation curves - part 2: application to aerospace/aviation fuels RP-1 and S-8. *Ind. Eng. Chem. Res.* 2006, 45, 4381-4388.
17. Smith, B. L., Bruno, T.J., Advanced distillation curve measurement with a model predictive temperature controller. *Int. J. Thermophys.* 2006, 27, 1419-1434.
18. Smith, B. L., Bruno, T.J., Improvements in the measurement of distillation curves: part 3 - application to gasoline and gasoline + methanol mixtures. *Ind. Eng. Chem. Res.* 2007, 46, 297-309.
19. Smith, B. L., Bruno, T.J., Improvements in the measurement of distillation curves: part 4- application to the aviation turbine fuel Jet-A. *Ind. Eng. Chem. Res.* 2007, 46, 310-320.
20. Bruno, T. J., Method and apparatus for precision in-line sampling of distillate. *Sep. Sci. Technol.* 2006, 41, (2), 309-314.
21. *ASTM Standard D2887-02, Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography.* American Society for Testing Materials: West Conshohocken, PA, 2004.
22. 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.
23. Huber, M. L., Lemmon, E.W., Diky, V., Smith, B.L., Bruno, T.J., Chemically authentic surrogate mixture model for the thermophysical properties of a coal-derived-liquid fuel. *Energy and Fuels* 2008, 22, 3249-3257.
24. Huber, M. L., Lemmon, E.W., Bruno, T.J., Surrogate mixture models for the thermophysical properties of aviation fuel Jet-A. *Energy & Fuels* submitted.
25. Bruno, T. J., Thermodynamic, transport and chemical properties of "reference" JP-8. *Book of Abstracts, Army Research Office and Air Force Office of Scientific Research, 2006 Contractor's meeting in Chemical Propulsion* 2006, 15-18.

26. Bruno, T. J., The properties of S-8. In Final Report for MIPR F4FB EY6237G001, Air Force Research Laboratory: 2006.
27. 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, NIST-IR-6647*. 2007.
28. Bruno, T. J., Thermodynamic, transport and chemical properties of "reference" JP-8. *Book of Abstracts, Army Research Office and Air Force Office of Scientific Research, 2007 Contractor's meeting in Chemical Propulsion* 2007.
29. Bruno, T. J., Wolk, A., Naydich, A., Stabilization of biodiesel fuel at elevated Temperature with Hydrogen Donors: evaluation with the advanced distillation curve method. *Energy & Fuels* 2009, 23, 1015-1023.
30. Bruno, T. J., Wolk, A., Naydich, A., Composition-explicit distillation curves for mixtures of gasoline with four-carbon alcohols (butanols). *Energy & Fuels* 2009, 23, 2295-2306.
31. Bruno, T. J., Wolk, A., Naydich, A., Analysis of fuel ethanol plant liquor with the composition explicit distillation curve approach. *Energy & Fuels* 2009, 23, (6), 3277-3284.
32. Bruno, T. J., Wolk, A., Naydich, A., Huber, M.L., Composition explicit distillation curves for mixtures of diesel fuel with dimethyl carbonate and diethyl carbonate *Energy & Fuels* 2009, 23, (8), 3989-3997.
33. Bruno, T. J., Ott, L.S., Smith, B.L., Lovestead, T.M., Complex fluid analysis with the advanced distillation curve approach. *Anal. Chem.* 2010, 82, 777-783.
34. Bruno, T. J., Huber, M.L., Laesecke, A., Lemmon, E.W., McLinden, M.O., Outcalt, S.L., Perkins, R., Smith, B.L., Widegren, J.A., Thermodynamic, transport, and chemical properties of "reference" JP-8, NISTIR 6659, National Institute of Standards and Technology, Gaithersburg, MD
In 2010.
35. Bruno, T. J., Ott, L.S., Lovestead, T.M., Huber, M.L., The composition explicit distillation curve technique: relating chemical analysis and physical properties of complex fluids. *J. Chromatogr.* in press.
36. Bruno, T. J., Ott, L.S., Lovestead, T.M., Huber, M.L., Relating complex fluid composition and thermophysical properties with the advanced distillation curve approach. *Chemical Eng. Tech.* in press.
37. Bruno, T. J.; Smith, B. L., Enthalpy of combustion of fuels as a function of distillate cut: application of an advanced distillation curve method. *Energy & Fuels* 2006, 20, 2109-2116.

38. Lovestead, T. M., Bruno, T.J., Application of the advanced distillation curve method to aviation fuel avgas 100LL. *Energy & Fuels* 2009, 23, 2176-2183.
39. Lovestead, T. M., Bruno, T.J., 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, (7), 3637-3644.
40. Ott, L. S., Bruno, T.J., Corrosivity of fluids as a function of distillate cut: application of an advanced distillation curve method. *Energy and Fuels* 2007, 21, 2778 - 2784.
41. Ott, L. S., Smith, B.L., Bruno, T.J., Advanced distillation curve measurements for corrosive fluids: application to two crude oils. *Fuel* 2008, 87, 3055-3064.
42. Ott, L. S., Smith, B.L., Bruno, T.J., Advanced distillation curve measurement: application to a bio-derived crude oil prepared from swine manure. *Fuel* 2008, 87, 3379-3387.
43. Ott, L. S., Smith, B.L., Bruno, T.J., Composition-explicit distillation curves of mixtures of diesel fuel with biomass-derived glycol ester oxygenates: a fuel design tool for decreased particulate emissions. *Energy and Fuels* 2008, 22, 2518-2526.
44. Ott, L. S., Hadler, A., Bruno, T.J., Variability of the rocket propellants RP-1, RP-2, and TS-5: application of a composition- and enthalpy-explicit distillation curve method. *Ind. Eng. Chem. Res.* 2008, 47 (23), 9225-9233.
45. Ott, L. S., Bruno, T.J., Variability of biodiesel fuel and comparison to petroleum-derived diesel fuel: application of a composition and enthalpy explicit distillation curve method. *Energy & Fuels* 2008, 22, 2861-2868.
46. Smith, B. L., Bruno, T.J., Composition-explicit distillation curves of aviation fuel JP-8 and a coal based jet fuel. *Energy & Fuels* 2007, 21, 2853-2862.
47. Smith, B. L., Bruno, T.J., Application of a Composition-Explicit Distillation Curve Metrology to Mixtures of Jet-A + Synthetic Fischer-Tropsch S-8. *J. Propul. Power* 2008, 24, (3), 619 - 623.
48. Smith, B. L., Ott, L.S., Bruno, T.J., Composition-explicit distillation curves of diesel fuel with glycol ether and glycol ester oxygenates: a design tool for decreased particulate emissions. *Environ. Sci. Tech.* 2008, 42, (20), 7682-7689.
49. Smith, B. L., Ott, L.S., Bruno, T.J., Composition-explicit distillation curves of commercial biodiesel fuels: comparison of petroleum derived fuel with B20 and B100. *Ind. Eng. Chem. Res.* 2008, 47, (16), 5832-5840.
50. Bruno, T. J., Svoronos, P.D.N., *CRC Handbook of Basic Tables for Chemical Analysis, 2nd. ed.* Taylor and Francis CRC Press: Boca Raton, 2004.

51. Bruno, T. J., Svoronos, P.D.N., *CRC Handbook of Fundamental Spectroscopic Correlation Charts*. Taylor and Francis CRC Press: Boca Raton, 2006.
52. NIST/EPA/NIH Mass Spectral Database, S. R. D., 2005. SRD Program, National Institute of Standards and Technology, Gaithersburg, MD.
53. Ott, L. S., Smith, B.L., Bruno, T.J., Experimental test of the Sydney Young equation for the presentation of distillation curves. *J. Chem. Thermodynam.* 2008, 40, 1352-1357.
54. Young, S., Correction of boiling points of liquids from observed to normal pressures. *Proc. Chem. Soc.* 1902, 81, 777.
55. Young, S., *Fractional distillation*. Macmillan and Co., Ltd.: London, 1903.
56. Young, S., *Distillation principles and processes*. Macmillan and Co., Ltd.: London, 1922.
57. NIST/SEMATECH *e-Handbook of Statistical Methods*, <http://www.itl.nist.gov/div898/handbook/>, February 16, 2010.
58. Edwards, J. T., United States Air Force, Air Force Research Laboratory, Propulsion Directorate, personal communication. In 2006.