

Surrogate Mixture Models for the Thermophysical Properties of Aviation Fuel Jet-A

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We developed surrogate mixture models to represent the thermophysical properties of two samples of aviation turbine fuel Jet-A. One sample is a composite of numerous batches from multiple manufacturers and is considered to be a representative fuel. A second sample, while still meeting the fuel specifications, contained a lower than normal aromatic content and was selected to demonstrate some of the compositional variability seen among different batches of Jet-A fuel. A surrogate for each fuel was developed with a procedure that incorporated experimental data for the density, sound speed, viscosity, thermal conductivity, cetane number, and the volatility (as indicated by advanced distillation curves) for samples of the two fuels. The surrogates are simple mixtures containing eight or fewer components, yet they can represent with low uncertainty the thermophysical properties of actual real fluids that are very complex mixtures of hundreds of components.

Introduction

There has been a great deal of recent interest in fuels for gas turbine engines. This has included efforts to expand the scope of fuel feedstocks to include nonpetroleum sources such as coal, natural gas, and biomass. There are many reasons for this, the most important of which are guarding against potential supply disruptions, overcoming the dependence on foreign sources of petroleum, overcoming the vulnerability of large centralized refineries (to both weather events and terrorist acts), and mitigation of the rising costs of current fuel streams. The major gas turbine fuel most commonly used by the United States military is JP-8 (MIL-DTL-83133).¹ JP-8 is very similar to Jet-A, the most common commercial gas turbine fuel used in the United States, with the major differences being in the additive package. JP-8 contains an icing inhibitor, corrosion/lubricity enhancer, and antistatic additive.² Jet-A-1, the most common commercial aviation turbine fuel used in Europe, contains an additive package similar to that in JP-8. Apart from the factors mentioned above, there is a desire in the United States defense community to utilize JP-8 as the main battlefield fuel for most vehicles, not only for aviation applications but also for ground-based forces. For this reason, the physical and chemical properties of Jet-A and JP-8 are receiving renewed interest. Moreover, there is a desire to develop thermophysical property models to correlate these properties, in order to enhance design and operational specifications for further application of this fluid.

The focus of this work is modeling the thermophysical properties (density, sound speed, viscosity, thermal conductivity, and the volatility) of aviation jet fuel Jet-A. In this work we examined two samples of Jet-A, obtained from the Fuels

Branch of the Air Force Research Laboratory (AFRL, Wright Patterson Air Force Base). The samples are designated as Jet-A-3638 and Jet-A-4658, numbers which in the context of this paper only serve to identify an individual fluid. The sample labeled Jet-A-4658 is a composite of numerous available batches (from multiple manufacturers) of Jet-A, which was mixed in approximately equal volume aliquots. It is, therefore, considered to be representative of Jet-A.³ The sample labeled Jet-A-3638 is unusual in that, although it meets the fuel specifications, it is lower in aromatic content than is typical for Jet-A.^{3–6} We focus on Jet-A instead of JP-8 for several reasons. JP-8 is often prepared at the flight line by splash blending the additive package into a Jet-A or Jet-A-1 base stock. Thus, from the standpoint of thermophysical properties, there will be little or no discernible difference. Moreover, the availability of the composite Jet-A sample (Jet-A-4658) allows the work presented here to be more comprehensive.

Jet-A is a complex mixture of hundreds of components, and modeling each individual constituent and its interactions in the mixture is not feasible. Instead, we have been successful in the use of a surrogate mixture concept^{7–10} that incorporates advanced distillation curve measurements^{6,11–19} along with thermophysical property data measurements such as density,

(3) Edwards, J. T., USAF, AFRL, Propulsion Directorate, Wright Patterson AFB, OH, personal communication to T. J. Bruno.

(4) Bruno, T. J.; Huber, M. L.; Laesecke, A.; Lemmon, E. L.; McLinden, M. O.; Outcalt, S. L.; Perkins, R. A.; Smith, B. L.; Widgren, J. A. *Thermodynamic, Transport, and Chemical Properties of "Reference" JP-8*, NISTIR 6659; 2009.

(5) Bruno, T. J. *Thermodynamic, Transport, and Chemical Properties of "Reference" JP-8*; Final Report, Air Force Office of Scientific Research, MIPR-F1ATA06004G004; 2010.

(6) 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.

(7) Huber, M. L.; Lemmon, E. L.; Kazakov, A.; Ott, L. S.; Bruno, T. J. Model for the Thermodynamic Properties of a Biodiesel Fuel. *Energy Fuels* **2009**, *23*, 3790–3797.

(8) 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 Fuels* **2008**, *22*, 3249–3257.

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(1) *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, April 11, 2008 and references within.

(2) AirBP The history of jet fuel. <http://www.bp.com/sectiongenericarticle.do?categoryId=4503664&contentId=57733> (accessed January 26, 2010).

heat capacity, sound speed, viscosity, and thermal conductivity.^{20–23} The general principle is to use a mixture slate of a relatively small number of components (usually less than 15) to represent the behavior of the actual complex fuel. Edwards and Maurice²⁴ reviewed some of the surrogates available for aviation and rocket fuels and provided an overview of the general requirements and expectations of fuel surrogates.

Surrogate fuel mixtures vary in complexity, and most are intended for specific purposes. In this work, the goal is to provide a surrogate model to represent the volatility, density, sound speed, viscosity, thermal conductivity, and cetane number of the fuel. We also try to develop a model that is chemically authentic, meaning that although the exact fluids that constitute the surrogate may not be present in the actual fuel, they do in fact represent the chemical types present in the real fuel. For example, if a real fuel has a low aromatic content, then the surrogate should also have a low aromatic content. The desire is to provide a model that will be applicable to a wider range of applications, perhaps even those sensitive to sooting behavior.

Modeling

The procedure for developing the surrogate mixture can be summarized as follows. First, a chemical analysis is performed to identify the composition of the fuel sample. From this analysis, a list of representative fluids is constructed, including

(9) Huber, M. L.; Lemmon, E. W.; Ott, L. S.; Bruno, T. J. Preliminary Surrogate Mixture Models for the Thermophysical Properties of Rocket Propellants RP-1 and RP-2. *Energy Fuels* **2009**, *23*, 3083–3088.

(10) 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.

(11) Bruno, T. J. Improvements in the Measurement of Distillation Curves. 1. A Composition-Explicit Approach. *Ind. Eng. Chem. Res.* **2006**, *45*, 4371–4380.

(12) 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.

(13) Bruno, T. J. Method and apparatus for precision in-line sampling of distillate. *Sep. Sci. Technol.* **2006**, *41*, 309–314.

(14) Smith, B. L.; Bruno, T. J. Advanced distillation curve measurement with a model predictive temperature controller. *Int. J. Thermophys.* **2006**, *27*, 1419–1434.

(15) Smith, B. L.; Bruno, T. J. Improvements in the measurement of distillation curves. 3. Application to gasoline and gasoline plus methanol mixtures. *Ind. Eng. Chem. Res.* **2007**, *46*, 297–309.

(16) 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.

(17) Bruno, T. J.; Laesecke, A.; Outcalt, S. L.; Seelig, H. D.; Smith, B. L. *The properties of a 50/50 mixture of Jet-A and S-8*; NISTIR 6647; 2007.

(18) 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*, 618–624.

(19) 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*, 3637–3644.

(20) Outcalt, S.; Laesecke, A.; Brumback, K. Thermophysical Properties Measurements of Rocket Propellants RP-1 and RP-2. *J. Propul. Power* **2009**, *25*, 1626–1633.

(21) Outcalt, S. L.; Laesecke, A.; Freund, M. B. Density and Speed of Sound Measurements of Jet A and S-8 Aviation Fuels. *Energy Fuels* **2009**, *23*, 1626–1633.

(22) Bruno, T. J. *The Properties of S-8 and JP-10*; Report prepared for Wright Laboratory Aero Propulsion Power Directorate under MIPR F4FBY6346G001; 2007.

(23) Bruno, T. J.; Huber, M. L.; Laesecke, A.; Lemmon, E. W.; Ott, L. S.; Outcalt, S.; Perkins, R.; Seelig, H.-D.; Smith, B. L. *The Properties of S-8*, NISTIR 6648; National Institute of Standards and Technology: Boulder, CO, 2007.

(24) Edwards, T.; Maurice, L. Q. Surrogate mixtures to represent complex aviation and rocket fuels. *J. Propul. Power* **2001**, *17*, 461–466.

compounds representative of the various chemical families (branched or linear paraffins, alkenes, aromatics, mono or polycyclic paraffins, etc.) found in the sample. For each of these possible pure-fluid constituents, an equation of state, a viscosity surface, and a thermal conductivity surface are required. A mixture model is used that incorporates the pure fluid equations for both thermodynamic and transport properties. The fluids in the surrogate mixture and their compositions are then chosen by determining the surrogate composition that minimizes the difference between the predicted and experimental data for the targeted properties. In this work, we are interested in representing the volatility (that is, the distillation curve), density, sound speed, cetane number, viscosity, and thermal conductivity.

From the analysis by gas chromatography–mass spectrometry^{25,26} of the Jet-A samples, we compiled a list of potential candidate fluids for the surrogate model. These fluids are listed in Table 1 along with their normal boiling point and their boiling points at an atmospheric pressure of 83 kPa (the typical local pressure of our laboratory, located at 1655 m above sea level). The list contains fluids used in our earlier work^{9,10} on the modeling of RP-1, RP-2, and S-8 but in addition includes aromatic compounds such as toluene, *o*-xylene, and tetralin that were not used previously in modeling these fuels. For each monobranched alkane identified in the chemical analysis, a representative chemical species was selected as a candidate constituent fluid for the surrogates. Thus, for our purposes, all *x*-methylnonanes are represented as a single methylnonane. Similarly, we used a particular *x,y*-dimethylnonane to represent the dimethylnonane family. A major factor governing the specific choice of compound to represent a moiety was the availability of property data: priority was given to the selection of compounds for which the most abundant and reliable experimental measurements were available. For each possible constituent fluid, we searched the open literature as well as databases such as Landolt–Börnstein,²⁷ DIPPR,²⁸ and NIST-TDE²⁹ for experimental physical property data. (We use trade names to specify procedure adequately and do not imply endorsement by the National Institute of Standards and Technology. Similar products by other manufacturers may perform as well or better.) For some of the fluids, the data were sparse and were supplemented with predicted values from the NIST-TDE and DIPPR programs.

Because our modeling approach^{8,10} requires thermophysical property models for all pure constituent fluids, it was necessary to have available equations of state (for thermodynamic information) and surfaces for the viscosity and thermal conductivity (for the transport properties). These are needed for each of the potential constituent pure fluids.

(25) Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Basic Tables for Chemical Analysis*, 2nd ed; Taylor and Francis CRC Press: Boca Raton, FL, 2003.

(26) Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Fundamental Spectroscopic Correlation Charts*; Taylor and Francis CRC Press: Boca Raton, FL, 2005.

(27) Wohlfarth, C.; Wohlfarth, B. *Viscosity of Pure Organic Liquids and Binary Liquid Mixtures*. Landolt–Börnstein–Numerical Data and Function Relationships in Science and Technology, IV/18; Springer-Verlag: Berlin, Germany, 2001; Vol. subvolume B. Pure Organic Liquids.

(28) Rowley, J. R.; Wilding, W. V.; Oscarson, J. L.; Rowley, R. L. *DIADDEM, DIPPR Information and Data Evaluation Manager*, version 3.1.0; Brigham Young University: Provo, UT, 2008.

(29) Frenkel, M.; Chirico, R. D.; Diky, V.; Muzny, C.; Lemmon, E. W.; Yan, X.; Dong, Q. *NIST Standard Reference Database 103, NIST ThermoData Engine*, version 3.0; Standard Reference Data, National Institute of Standards and Technology: Gaithersburg, MD, 2008.

Table 1. Potential Constituent Fluids for the Surrogate Fuel Mixtures

| compound | CAS no. | class | no. of carbon atoms | boiling point at 83 kPa (K) | normal boiling point (K) |
|-----------------------------|------------|---------------------|---------------------|-----------------------------|--------------------------|
| <i>n</i> -heptane | 142-82-5 | linear paraffin | 7 | 364.90 | 371.53 |
| toluene | 108-88-3 | aromatic | 7 | 376.87 | 383.75 |
| <i>n</i> -octane | 111-65-9 | linear paraffin | 8 | 391.75 | 398.77 |
| <i>ortho</i> -xylene | 95-47-6 | aromatic | 8 | 410.16 | 417.54 |
| <i>n</i> -nonane | 111-84-2 | linear paraffin | 9 | 416.54 | 423.81 |
| <i>n</i> -propylcyclohexane | 1678-92-8 | monocyclic paraffin | 9 | 422.13 | 429.86 |
| 5-methylnonane | 15869-85-9 | branched paraffin | 10 | 430.7 | 438.3 |
| <i>n</i> -decane | 124-18-5 | linear paraffin | 10 | 439.6 | 447.3 |
| transdecalin | 493-02-7 | dicyclic paraffin | 10 | 452.0 | 460.4 |
| tetralin | 119-64-2 | aromatic | 10 | 472.31 | 480.75 |
| 2-methyldecane | 6975-98-0 | branched paraffin | 11 | 454.4 | 462.3 |
| 2,4-dimethylnonane | 17302-24-8 | branched paraffin | 11 | 437.6 | 445.4 |
| <i>n</i> -undecane | 1120-21-4 | linear paraffin | 11 | 461.1 | 469.0 |
| <i>n</i> -pentylcyclohexane | 4292-92-6 | monocyclic paraffin | 11 | 468.3 | 476.7 |
| 1-methyldecalin | 2958-75-0 | dicyclic paraffin | 11 | 469.6 | 478.2 |
| 3-methylundecane | 1002-43-3 | branched paraffin | 12 | 478.1 | 486.3 |
| <i>n</i> -dodecane | 112-40-3 | linear paraffin | 12 | 481.2 | 489.4 |
| <i>n</i> -hexylcyclohexane | 4292-75-5 | monocyclic paraffin | 12 | 489.7 | 498.4 |
| 5-methyldodecane | 17453-93-9 | branched paraffin | 13 | 494.7 | 503.2 |
| <i>n</i> -tridecane | 629-50-5 | linear paraffin | 13 | 500.2 | 508.7 |
| <i>n</i> -heptylcyclohexane | 5617-41-4 | monocyclic paraffin | 13 | 509.2 | 517.9 |
| 2-methyltridecane | 1560-96-9 | branched paraffin | 14 | 512.7 | 521.1 |
| <i>n</i> -tetradecane | 629-59-4 | linear paraffin | 14 | 518.1 | 526.7 |
| <i>n</i> -pentadecane | 629-62-9 | linear paraffin | 15 | 535.0 | 543.8 |
| <i>n</i> -hexadecane | 544-76-3 | linear paraffin | 16 | 551.0 | 560.1 |

Details of the modeling procedure are available in other work,^{8,10} so we provide only a brief summary here. With the available experimental data supplemented with predictions obtained from the TDE program, we developed Helmholtz-form equations of state (similar to the form developed by Span and Wagner³⁰) that can represent not only the vapor pressure and density but also other properties such as the speed of sound and heat capacity. For viscosity and thermal conductivity, we primarily used an extended corresponding-states model,^{31,32} with *n*-dodecane or propane as a reference fluid.^{33,34} When sufficient data were available, the representation of the viscosity or thermal conductivity was improved by fitting the data to correction functions for the shape factors.³² In the absence of experimental data, we used the predictive method of Van Velzen for viscosity and the method of Baroncini for thermal conductivity (as implemented in the DIPPR Diadem program²⁸). Additionally, we incorporated earlier work on the thermal conductivity of methyl and propylcyclohexane³⁵ to represent the alkyl cyclohexane family in terms of a scaled

form of the thermal conductivity correlation developed for propylcyclohexane.

For calculations of the thermodynamic properties of mixtures, we used the mixture model^{36–38} incorporated into the REFPROP program.³⁹ This model includes an algorithm for estimating binary interaction parameters when data are unavailable for a particular fluid pair. The model for calculating the transport properties of a mixture is an extended corresponding-states method.^{32,40–44} In addition, we used an algorithm developed in earlier work¹⁰ to compute the distillation curve; this procedure incorporates data from the advanced distillation curve metrology.^{6,11–16,45}

Cetane numbers for individual pure fluids were obtained from the work of Murphy et al.⁴⁶ or estimated using the work of Ghosh.⁴⁷ The cetane number for a mixture was estimated by a linear volume fraction mixing rule,^{46,48} as is common in

(30) Span, R.; Wagner, W. Equations of state for technical applications. I. Simultaneously optimized functional forms for nonpolar and polar fluids. *Int. J. Thermophys.* **2003**, *24*, 1–39.

(31) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001.

(32) Huber, M. L.; Laesecke, A.; Perkins, R. A. Model for the viscosity and thermal conductivity of refrigerants, including a new correlation for the viscosity of R134a. *Ind. Eng. Chem. Res.* **2003**, *42*, 3163–3178.

(33) Lemmon, E. W.; Huber, M. L. Thermodynamic properties of *n*-dodecane. *Energy Fuels* **2004**, *18*, 960–967.

(34) Huber, M. L.; Laesecke, A.; Perkins, R. A. Transport properties of *n*-dodecane. *Energy Fuels* **2004**, *18*, 968–975.

(35) Perkins, R. A.; Hammerschmidt, U.; Huber, M. L. Measurement and Correlation of the Thermal Conductivity of Methylcyclohexane and Propylcyclohexane from 300 to 600 K at Pressures to 60 MPa. *J. Chem. Eng. Data* **2008**, *53*, 2120–2127.

(36) Lemmon, E. W.; Jacobsen, R. T. Equations of State for Mixtures of R-32, R-125, R-134a, R-143a, and R-152a. *J. Phys. Chem. Ref. Data* **2004**, *33*, 593–620.

(37) Lemmon, E. W.; McLinden, M. O. In *Method for Estimating Mixture Equation of State Parameters*; Thermophysical Properties and Transfer Processes of New Refrigerants Conference, Paderborn Germany, 2001; International Institute of Refrigeration, Commission B1: Paderborn, Germany, 2001; pp 23–30.

(38) Kunz, O.; Klimeck, R.; Wagner, W.; Jaeschke, M. *The GERG-2004 Wide-Range Reference Equation of State for Natural Gases and Other Mixtures*; GERG Technical Monograph; Fortsch.-Ber. VDI, VDI-Verlag: Düsseldorf, Germany, 2007.

(39) Lemmon, E. W.; Huber, M. L.; McLinden, M. O. *NIST Standard Reference Database 23, NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP)*, version 8.0; Standard Reference Data, National Institute of Standards and Technology: Gaithersburg, MD, 2007.

(40) Chichester, J.; Huber, M. L. *Extended Corresponding States Model for Viscosity and Thermal Conductivity of Pure Fluids and Their Mixtures as Implemented in REFPROP*, version 8; NIST IR 6650; National Institute of Standards and Technology: Boulder, CO, 2008.

(41) McLinden, M. O.; Klein, S. A.; Perkins, R. A. An Extended Corresponding States Model for the Thermal Conductivity of Pure Refrigerants and Refrigerant Mixtures. *Int. J. Refrig.* **2000**, *23*, 43–63.

(42) Klein, S. A.; McLinden, M. O.; Laesecke, A. An Improved Extended Corresponding States Method for Estimation of Viscosity of Pure Refrigerants and Mixtures. *Int. J. Refrig.* **1997**, *20*, 208–217.

(43) Huber, M. L.; Ely, J. F. Prediction of the Thermal Conductivity of Refrigerants and Refrigerant Mixtures. *Fluid Phase Equilib.* **1992**, *80*, 249–261.

(44) Huber, M. L.; Ely, J. F. Prediction of the Viscosity of Refrigerants and Refrigerant Mixtures. *Fluid Phase Equilib.* **1992**, *80*, 239–248.

(45) 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.

(46) Murphy, M. J.; Taylor, J. D.; McCormick, R. L. *Compendium of Experimental Cetane Number Data*; NREL/SR-540-36805; National Renewable Energy Laboratory: Golden, CO, 2004.

the literature. While the cetane number is primarily of interest in the design and characterization of diesel fuels, it is often used as a parameter by which aviation kerosenes are evaluated as well.

The properties measurements discussed earlier formed the basis of the experimental data set used to obtain the surrogate models. We then used a multiproperty, nonlinear regression procedure to minimize the differences between the experimental data and the predictions of the model in order to determine the components and their relative abundances to define the surrogate fluid mixtures for each Jet-A sample. The objective function was the weighted sum of the squared percentage differences between the experimental data and the predicted values.

$$F = \sum_{i=1}^{N_{\text{dis}}} W_{i,\text{dis}} F_{i,\text{dis}}^2 + \sum_{i=1}^{N_{\rho}} W_{i,\rho} F_{i,\rho}^2 + \sum_{i=1}^{N_w} W_{i,w} F_{i,w}^2 + \sum_{i=1}^{N_{\lambda}} W_{i,\lambda} F_{i,\lambda}^2 + \sum_{i=1}^{N_{\eta}} W_{i,\eta} F_{i,\eta}^2 + W_{\text{CN}} F_{\text{CN}}^2 \quad (1)$$

In eq 1, the weights for each data point are denoted by W_i , the objective function is F , and the subscripts dis, ρ , w , λ , η , and CN refer to the data type (distillation, density, sound speed, thermal conductivity, viscosity, and cetane number). Other types of information, such as the C/H ratio, could also be easily added to eq 1 if desired. The objective function components are defined as the percent deviations between the calculated value and the experimental value for each type,

$$F_{\text{dis}} = 100 \times (T_{\text{calc}} - T_{\text{exp}})/T_{\text{exp}} \quad (2)$$

$$F_{\rho} = 100 \times (\rho_{\text{calc}} - \rho_{\text{exp}})/\rho_{\text{exp}} \quad (3)$$

$$F_w = 100 \times (w_{\text{calc}} - w_{\text{exp}})/w_{\text{exp}} \quad (4)$$

$$F_{\lambda} = 100 \times (\lambda_{\text{calc}} - \lambda_{\text{exp}})/\lambda_{\text{exp}} \quad (5)$$

$$F_{\eta} = 100 \times (\eta_{\text{calc}} - \eta_{\text{exp}})/\eta_{\text{exp}} \quad (6)$$

$$F_{\text{CN}} = 100 \times (\text{CN}_{\text{calc}} - \text{CN}_{\text{exp}})/\text{CN}_{\text{exp}} \quad (7)$$

where T is an absolute temperature on the distillation curve, in kelvins. The distillation curve contains the initial boiling point as its first point, and the summation in eq 1 is over all of the distillation points as measured by the advanced distillation curve. The weighting factors for each type of property data are found by trial and error based on the desired results. For example, in this work we place a major emphasis on the advanced distillation curve, so the weighting factors on the distillation points were increased until the distillation curve was matched to within about a half a percent, as described later.

The independent variables are the mole fraction compositions of the surrogate mixture components. Our initial guess included all of the components in Table 1. Successive calculations gave very small concentrations of some components, and these were removed from the mixture and the minimization process was repeated until further reductions in the number of components resulted in unacceptably large deviations from the

Table 2. Summary of Details from the Regression

| property | Jet-A-3638 | | Jet-A-4658 | |
|----------------------|---------------|---------------------|---------------|---------------------|
| | no. of points | weight factor W_i | no. of points | weight factor W_i |
| distillation curve | 18 | 1000 | 18 | 1000 |
| density | 233 | 1000 | 244 | 1000 |
| sound speed | 8 | 100 | 8 | 20 |
| thermal conductivity | 325 | 20 | 333 | 20 |
| viscosity | 115 | 20 | 115 | 20 |
| cetane number | 1 | 100 | 1 | 100 |

Table 3. Compositions of the Surrogate Mixtures

| fluid | Jet-A-4658 surrogate composition, mole fraction | Jet-A-3638 surrogate composition, mole fraction |
|-----------------------------|---|---|
| <i>n</i> -hexylcyclohexane | 0 | 0.268 |
| <i>n</i> -heptylcyclohexane | 0.279 | 0 |
| 1-methyldecalin | 0.013 | 0.064 |
| 5-methylnonane | 0.165 | 0.130 |
| 2-methyldecane | 0.154 | 0.284 |
| <i>n</i> -tetradecane | 0.057 | 0.035 |
| <i>n</i> -hexadecane | 0.033 | 0 |
| <i>ortho</i> -xylene | 0.071 | 0.094 |
| tetralin | 0.228 | 0.125 |

experimental data. The minimization algorithm proceeds until a minimum is located, and due to the complex nature of the search space, this may not be the absolute minimum. Runs from different starting points were tried to investigate alternative solutions. The values of the weights used in eq 1 and details on the numbers of points of the different types of data used are given in Table 2. The final value of the objective function for Jet-A-4658 was 2.87 and for Jet-A-3636 was 3.52.

The final compositions of the surrogate mixtures are summarized in Table 3. The surrogate for the composite Jet-A, Jet-A-4658, contains a heavier cycloalkane than the Jet-A-3638 sample and also contains hexadecane. The Jet-A-3638 sample contains more of the lighter components. This is not unexpected, since the distillation curves indicate that the Jet-A-4658 sample contains more of the higher-boiling components. The Jet-A-3638 surrogate also has a lower aromatic content than the Jet-A-4658 sample, which is consistent with the chemical analysis of the two fuels.

Table 4 presents selected calculated characteristics of the surrogate mixtures. (Detailed comparisons with experimental data will be presented later.) The net heat of combustion was computed by a mole-fraction average of the component molar enthalpies of combustion, ignoring the enthalpy of mixing.^{45,49,50} The constituent heats of combustion were obtained from the DIPPR database.²⁸ When available, experimental data were used; otherwise the Cardozo method of equivalent chains⁵¹ (as implemented in the DIPPR database) was utilized. The cetane number was calculated with a linear volume fraction model. The experimental values of the cetane numbers for the Jet-A-3638 and Jet-A-4658 fuel samples³ are 44.74 and 45.27, respectively.

(49) Ott, L. S.; Hadler, A. B.; 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*, 9225–9233.

(50) Lovestead, T. M.; Bruno, T. J. Application of the advanced distillation curve method to the aviation fuel avgas 100LL. *Energy Fuels* **2009**, *23*, 2176–2183.

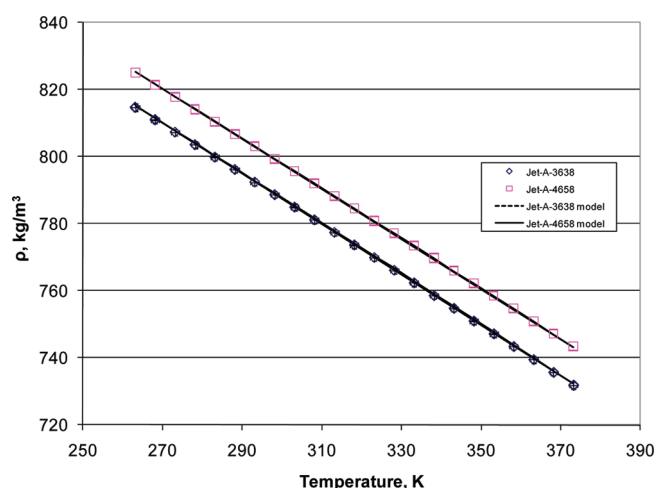
(51) Cardozo, R. L. Prediction of the Enthalpy of Combustion of Organic-Compounds. *AIChE J.* **1986**, *32*, 844–848.

(47) Ghosh, P. Predicting the Effect of Cetane Improvers on Diesel Fuels. *Energy Fuels* **2008**, *22*, 1073–1079.

(48) Ghosh, P.; Jaffe, S. B. Detailed Composition-Based Model for Predicting the Cetane Number of Diesel Fuels. *Ind. Eng. Chem. Res.* **2006**, *45*, 346–351.

Table 4. Selected Calculated Characteristics of the Surrogate Mixtures

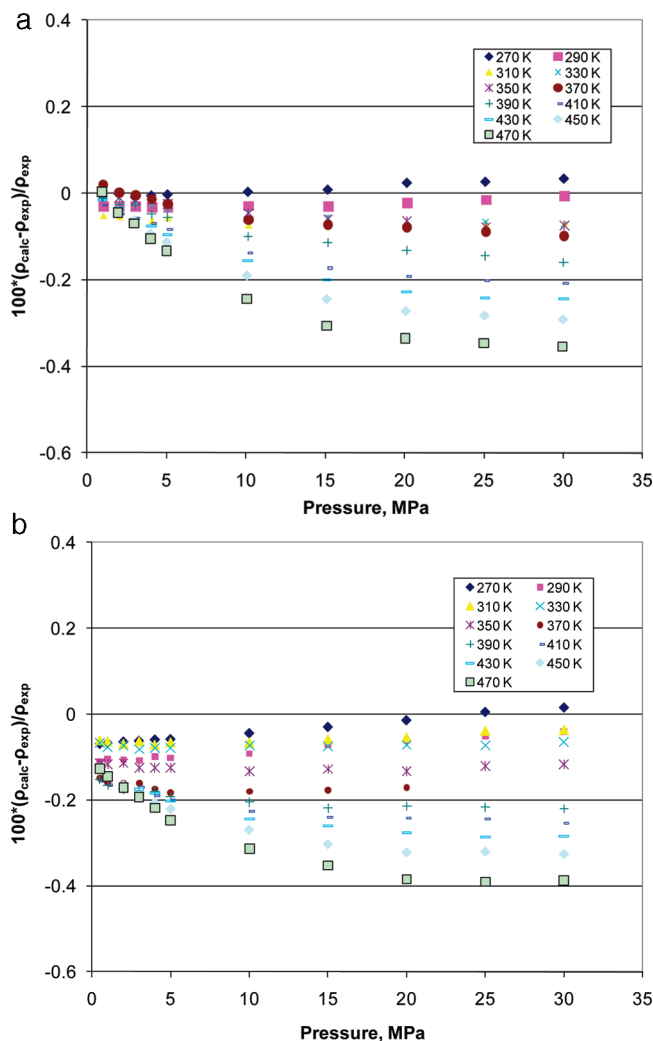
| | Jet-A-3638 surrogate model | Jet-A-4658 surrogate model |
|-------------------------------|-------------------------------------|-------------------------------------|
| relative molecular mass | 151.19 | 156.86 |
| formula | C _{10.8} H _{20.9} | C _{11.3} H _{21.1} |
| H/C | 1.93 | 1.87 |
| heat of combustion, J/mol | -6.55×10^6 | -6.76×10^6 |
| T_c (K) | 662.3 | 676.2 |
| p_c (kPa) | 2474 | 2399 |
| ρ_c (kg/m ³) | 249.4 | 250.5 |
| cetane number | 41.6 | 45.6 |
| volume fraction aromatics | 14 | 20 |

**Figure 1.** Plot of density as a function of temperature, at 83 kPa. The experimental error bars are smaller than the plot symbols on the figure.

This compares well with the calculated values of the surrogates, 41.6 and 45.6. According to Murphy et al.,⁴⁶ the repeatability of the pure fluid cetane numbers in their compendium varies from 7.9% to 8.6% so the estimated uncertainty of our results are comparable to those of the recommend values for pure fluids. The volume fractions of aromatics were calculated for each surrogate at 288.15 K, 0.1 MPa, assuming ideal mixing. The experimentally determined³ volume fractions of aromatics as determined by ASTM D1319⁵² were 12 and 19 for the Jet-A-3638 and Jet-A-4658 samples, respectively. This compares well with the calculated values of 14 and 20. Note the Jet-A-3638 sample has a lower aromatic content than the Jet-A-4658 sample. The surrogate models also show this behavior, demonstrating that the surrogate models can model the differences in aromatic content of the actual fuels.

In Figures 1–6, we present comparisons of our surrogate models with experimental data. Figure 1 shows the density as a function of temperature at atmospheric pressure²¹ (83 kPa). The data have an estimated uncertainty of 0.1%. The densities of the two different samples differ from each other by approximately 1.5%. Parts a and b of Figure 2 show the deviations in density between the experimental measurements²¹ as a function of pressure, over the temperature range 270–470 K for the Jet-A-3638 and the Jet-A-4658 samples. The models both show increasing deviations as the pressure increases, but they remain within 0.4% at pressures to 30 MPa.

(52) Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption, ASTM Standard D 1319-08; American Society for Testing and Materials: West Conshohocken, PA, 2008.

**Figure 2.** (a) Deviation plot for density as a function of pressure for sample Jet-A-3638 and (b) deviation plot for density as a function of pressure for sample Jet-A-4658.

The experimental values of the speed of sound²¹ and those calculated from the surrogate models are presented in Figure 3. All measurements were taken at local atmospheric pressure and have an estimated uncertainty of 0.1%. Neither of the models is able to represent the data to within their experimental uncertainty and they systematically overpredict the speed of sound; however, both of our models have deviations within 3.5%. We attribute this to the inability of the underlying pure-fluid equations of state to adequately represent sound speed due to the lack of data for this property for some of the constituent fluids.

Figure 4 is a plot of the calculated and experimental viscosity at atmospheric pressure as a function of temperature.⁵³ This property is very sensitive to changes in composition, as indicated by an approximately 20% difference in viscosity of the two samples at 270 K. The model was tuned so that the viscosity is represented by the model to within 3%, with the largest deviations occurring at the lowest temperatures.

Figure 5 demonstrates the performance of the surrogate models for the thermal conductivity.⁵⁴ The measurements

(53) Fortin, T.; Laesecke, A. Viscosity measurements of aviation turbine fuels. In preparation.

(54) Perkins, R. A. Thermal conductivity measurements of aviation turbine fuels. In preparation.

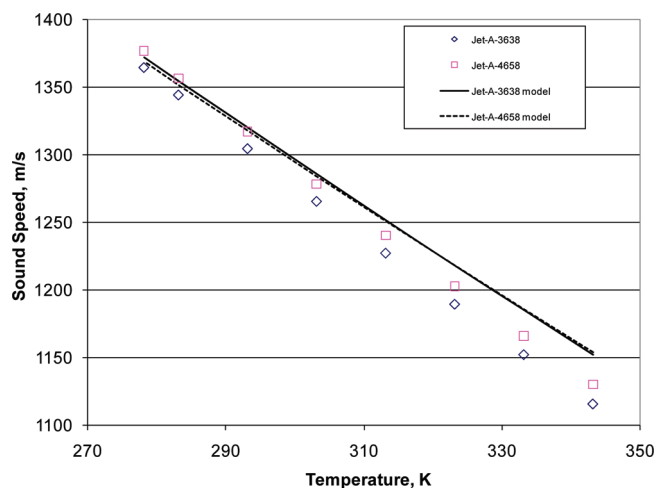


Figure 3. Plot of calculated and experimental speed of sound at 83 kPa. The experimental error bars are smaller than the plot symbols on the figure.

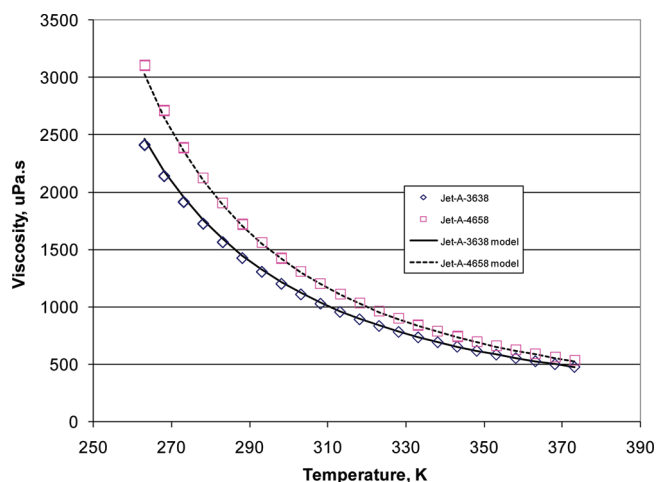


Figure 4. Plot of calculated and experimental viscosity at 83 kPa. The experimental error bars are smaller than the plot symbols on the figure.

covered temperatures from approximately 300 K to a maximum of 500 K, at pressures up to 40 MPa, and were obtained from a transient hot-wire apparatus with an estimated uncertainty of 1%. The present surrogate models represent the data to within 4% over the range of conditions studied.

Our final comparison with experimental data is presented in Figure 6, which shows the calculated and experimental advanced distillation curves.⁶ We note that the advanced distillation curve is not the same as that obtained from the ASTM D86 procedure.⁵⁵ A unique feature of the advanced distillation curve procedure is that it can be modeled by an equation of state approach, as demonstrated here, while the traditional ASTM D86 method cannot. The uncertainty of the experimental advanced distillation data is on average 0.3 K for both fluids. The distillation curves of the Jet-A-3638 and Jet-A-4658 sample differ significantly; at the end of the distillation they are 30 K apart. The surrogate models are able to capture

(55) *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure, ASTM Standard D 86-04b*; American Society for Testing and Materials: West Conshohocken, PA, 2004.

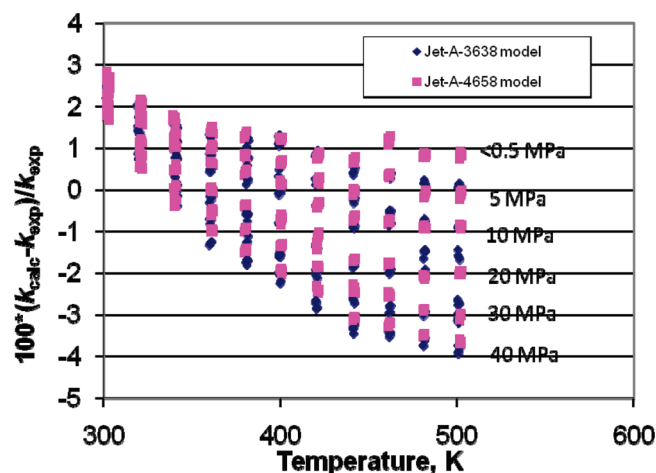


Figure 5. Deviation plot of calculated and experimental thermal conductivity at pressures to 40 MPa.

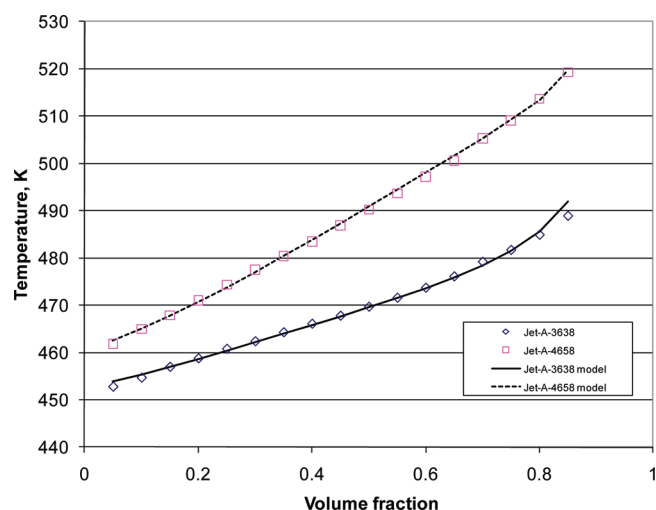


Figure 6. Advanced distillation curves of the two fuel samples, at 83 kPa. The experimental error bars are smaller than the plot symbols on the figure.

this behavior for each sample. The predicted value is within 1 K of the experimental value except for the highest volume fraction point for the Jet-A-3638 sample, where the deviation is 3 K. The volatility, as indicated by the advanced distillation curve, is very sensitive to changes in composition of the fuels.

The model for the Jet-A-4658 sample may be considered as a representative model for a typical Jet-A.^{56–58} The model for Jet-A-3638 demonstrates some of the changes in properties that may be observed due to significant (and intentional) compositional variability of the fuels. Future work will address in more detail the compositional variability of Jet-A fuels as we explore the properties of additional fuel samples.

(56) 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.

(57) 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, 2008 Contractor's meeting in Chemical Propulsion, 2008.

(58) 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, 2009 Contractor's meeting in Chemical Propulsion, 2009.

Work is in progress to develop a methodology to represent the Jet-A fuels as a single model that will characterize the fuels in terms of compositionally sensitive properties that can be used to “tune” the calculation. Such properties might include selected points on the distillation curve and viscosities. In addition, comparisons with existing surrogate models are in progress, as is further development of the equation of state models to improve the representation of the properties.

Conclusions

Determination of the best surrogate model depends upon the intended application. The surrogate models in this work were designed for the simultaneous representation of thermodynamic (density, sound speed, and volatility) and transport (viscosity and thermal conductivity) properties. In addition,

we also modeled the cetane number. The density, sound speed, viscosity, thermal conductivity, and cetane number of both fuels are represented to within 0.4%, 3.5%, 3%, 4%, and 7%, respectively (at a 95% confidence level). The volatility behavior, indicated by the temperatures obtained from the advanced distillation curves, is reproduced to within 0.7%.

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