

Evaluation of the Physicochemical Authenticity of Aviation Kerosene Surrogate Mixtures. Part 1: Analysis of Volatility with the Advanced Distillation Curve

Thomas J. Bruno* and Beverly L. Smith

Thermophysical Properties Division, National Institute of Standards and Technology (NIST),
Boulder, Colorado 80305

Received April 20, 2010. Revised Manuscript Received June 24, 2010

Because of the complexities involved in measuring and modeling the performance and properties of finished fuels, the fuel science community must often use surrogate mixtures as substitutes, especially in the absence of consensus standard mixtures. While surrogate mixtures are often formulated on the basis of the ability of a particular mixture to reproduce a particular property, there is usually a desire to employ surrogate mixtures that are physicochemically authentic. This means that, provided that the primary purpose is satisfied, researchers are inclined to choose mixtures that have physical and chemical properties appropriate to the finished fuel. In this paper, we apply the advanced distillation curve method as a means to evaluate the physicochemical authenticity of surrogate mixtures. While the strategy outlined here can be used for any family of surrogates, we apply it to surrogate mixtures for Jet-A/JP-8. Mixtures were divided into two groups: (1) simple surrogate mixtures with up to three components and (2) complex surrogate mixtures with more than three components. We found that the modified Aachen surrogate (among the simple fluids) and the Schultz surrogate (among the complex fluids) had the best physicochemical authenticity.

Introduction

The study of finished fuels and their performance in practical engines is necessarily a nontrivial undertaking. Fuels can contain upward of 1000 components (that can be identified), some of which can interact with one another and, thus, affect the properties of the overall mixture.¹ In addition to this complexity, which can be ascribed to each individual batch of fuel, fuels made primarily from petroleum feed stocks by refineries or blenders exhibit a pronounced batch–batch variability in composition that adds to the complexity.² Despite this significant chemical ambiguity, the need to optimize the performance of machinery operating with practical finished fuels is not diminished. Current pressures for improving efficiency while minimizing environmental damage, the uncertainties in traditional supply sources, and introduction of non-traditional supply sources simply augment the need to deal with these issues. It is and will continue to be vital to measure and model such fundamental properties as the fluid thermophysics and kinetics, as well as engineering properties, such as threshold sooting index (TSI), ignitability, flame relight ability, flame propagation, etc.

For some fuels, such as gasoline, reference fluid mixtures have been developed as consensus standards upon which scientists and engineers can develop and perform such property measurements.³ The availability of such consensus standard mixtures ensures that all measurements are performed

on a well-understood or at least an accepted fuel. Aviation turbine kerosenes are a class of finished fuels for which no set of consensus standard fluids currently exist. This is partially because the requirements of testing protocols for turbine fuels are more diverse; consensus on a detailed set of specifications is simply more difficult to achieve. Moreover, the required knowledge base for some of the components of the real fuel (such as detailed kinetic mechanisms) is often absent. The resulting approach that has been adopted is to test and model surrogate fluids (simpler stand-in mixtures that are more easily characterized) instead of the finished fuel.^{4–16} An inherent limitation of this approach is that surrogate mixtures

(4) Agosta, A. Development of a chemical surrogate for JP-8 aviation fuel using a pressurized flow reactor. Ph.D. Dissertation, Drexel University, Philadelphia, PA, 2002.

(5) Colket, M.; Edwards, T.; Williams, S.; Ceranasky, N. P.; Miller, D.; Egolfopoulos, F.; Linstedt, P.; Seshadri, K.; Dryer, F. L.; Law, C. K.; Friend, D.; Lenhart, D. B.; Pitch, H.; Sarofim, A.; Smooke, M.; Tsang, W. Development of an experimental database and kinetic models for surrogate jet fuels, http://www.stanford.edu/group/pitsch/publication/ColketJet_Fuel_Surrogate_AIAA_2007.pdf (accessed in 2008).

(6) Colket, M.; Edwards, J. T.; Williams, S.; Cernansky, N. P.; Miller, D. L.; Egolfopoulos, F.; Dryer, F. L.; Bellan, J.; Linstedt, P.; Seshadri, K.; Pitch, H.; Sarofim, A.; Smooke, M.; Tsang, W. Identification of target validation data for development of surrogate jet fuels. *Proceedings of the 46th American Institute of Aeronautics and Astronautics (AIAA) Aerospace Sciences Meeting and Exhibit*; AIAA: Reno, NV, Jan 7–10, 2008; AIAA Paper 2008-972.

(7) Dagaut, P.; El Bakali, A.; Ristori, A. The combustion of kerosene: Experimental results and kinetic modeling using 1- to 3-component surrogate model fuels. *Fuel* **2006**, 85 (7–8), 944–956.

(8) Edwards, J. T.; Maurice, L. Q. Surrogate mixtures to represent aviation and rocket fuels. *J. Propul. Power* **2001**, 17 (2), 461–466.

(9) Heneghan, S. P.; Locklear, S. L.; Geiger, D. L.; Anderson, S. D.; Schulz, W. D. Static tests of jet fuel thermal and oxidative stability. *J. Propul. Power* **1993**, 9 (1), 5–9.

(10) Heneghan, S. P.; Zabarnick, S. Oxidation of jet fuels and the formation of deposits. *Fuel* **1994**, 73 (1), 35–43.

(11) Kanandawala, M. S. P.; DeWitt, M. J.; Corporan, E.; Sidhu, S. S. Ignition and emission characteristics of surrogate and practical jet fuels. *Energy Fuels* **2008**, 22, 3673–3679.

*To whom correspondence should be addressed. E-mail: bruno@boulder.nist.gov.

(1) Edwards, J. T. Advancements in gas turbine fuels from 1943 to 2005. *Trans. ASME* **2007**, 129 (1), 13–20.

(2) 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.

(3) Andersen, V. F.; Anderson, J. E.; Wallington, T. J.; Mueller, S. A.; Nielsen, O. J. Distillation curves for alcohol–gasoline blends. *Energy Fuels* **2010**, 24, 2683–2691.

often must be developed for specific purposes. Mixtures developed to represent kinetic parameters^{17–22} might not be the best to represent, for example, the TSI or other engineering parameters.^{12,21,23–28} We also note that the term “surrogate fluid” can have different meanings depending upon the specific faction of the fuel science community that is coining the term. Thus, for modeling thermophysical properties, the Helmholtz free-energy equation of state is often implemented

(12) Mensch, A.; Santoro, R. J.; Litzinger, T. A.; Lee, S.-Y. Sooting characteristics of surrogates for jet fuels. *Proceedings of the 47th American Institute for Aeronautics and Astronautics (AIAA) Aerospace Sciences Meeting*; AIAA: Orlando, FL, 2009; AIAA Paper 2009-1525.

(13) Natelson, R. H.; Kurman, M. S.; Cernansky, N. P.; Miller, D. L. Experimental investigation of surrogates for jet and diesel fuels. *Fuel* **2007**, *87* (10–11), 2339–2342.

(14) Ranzi, E. A wide-range kinetic modeling study of oxidation and combustion of transportation fuels and surrogate mixtures. *Energy Fuels* **2006**, *20* (3), 1024–1032.

(15) Selle, L. C.; Bellan, J. Characteristics of transitional multi-component gaseous and drop laden mixing layers from direct numerical simulation: Compositional effects. *Phys. Fluids* **2007**, *19*, 1–33.

(16) Shulz, W. D. Oxidation products of surrogate JP-8 fuel. *Symposium on the Structure of Jet Fuels III*; Division of Petroleum Chemistry, American Chemical Society: San Francisco, CA, 1991.

(17) Dagaut, P. Kinetics of kerosene combustion over extended conditions: Experimental and modeling. *Proceedings of the American Society of Mechanical Engineers (ASME) Turbo Expo 2006*; ASME: New York, 2006; Vol. 1, pp 1–9.

(18) Mawid, M. A.; Park, T. W.; Sekar, B.; Arana, C. Detailed chemical kinetic modeling of JP-8/JET-A ignition and combustion. *Proceedings of the American Society of Mechanical Engineers (ASME) Turbo Expo 2005*; ASME: New York, 2005; Vol. 2, pp 603–621.

(19) Mawid, M. A.; Sekar, B. Development of a detailed JP-8/Jet-A chemical kinetic mechanism for high pressure conditions in gas turbine combustors. *Proceedings of the American Society of Mechanical Engineers (ASME) Turbo Expo 2006*; ASME: New York, 2006; Vol. 1, pp 369–388.

(20) Strelkova, M. I.; Kirillov, I. A.; Potapkin, B. V.; Safonov, A. A.; Sukhanov, L. P.; Umanskiy, S. Y.; Deminsky, M. A.; Dean, A. J.; Varatharajan, B.; Tentner, A. M. Detailed and reduced mechanisms of Jet A combustion at high temperatures. *Combust. Sci. Technol.* **2008**, *180* (10–11), 1788–1802.

(21) Violi, A.; Yan, S.; Eddings, E. G.; Sarofim, F.; Granata, S.; Faravelli, T.; Ranzi, E. Experimental formulation and kinetic model for JP-8 surrogate mixtures. *Combust. Sci. Technol.* **2002**, *174* (11–2), 399–417.

(22) Humer, S.; Frassoldati, A.; Granata, S.; Faravelli, T.; Ranzi, E.; Seiser, R.; Seshadri, K. Experimental and kinetic modeling study of combustion of JP-8, its surrogates and reference components in laminar nonpremixed flows. *Proc. Combust. Inst.* **2007**, *31*, 393–400.

(23) Bufferand, H.; Tosatto, L.; La Mantia, B.; Smooke, M. D.; Gomez, A. Experimental and computational study of methane counterflow diffusion flames perturbed by trace amounts of either jet fuel or a 6-component surrogate under non-sooting conditions. *Combust. Flame* **2009**, *156* (8), 1594–1603.

(24) Dean, A. J.; Penyzkov, O. G.; Sevruck, K. L.; Varatharajan, B. Autoignition of surrogate fuels at elevated temperatures and pressures. *Proc. Combust. Inst.* **2007**, *31*, 2481–2488.

(25) Kahandawala, M. S. P.; DeWitt, M. J.; Corporan, E.; Sidhu, S. S. Ignition and emission characteristics of surrogate and practical jet fuels. *Energy Fuels* **2008**, *22* (6), 3673–3679.

(26) Tosatto, L.; La Mantia, B.; Bufferand, H.; Duchaine, P.; Gomez, A. Chemical structure of a methane counterflow diffusion flame perturbed with the addition of either JP-8 or a jet fuel surrogate. *Proc. Combust. Inst.* **2009**, *32*, 1319–1326.

(27) Vasu, S. S.; Davidson, D. F.; Hanson, R. K. Corrigendum to “Jet fuel ignition delay times: Shock tube experiments over wide conditions and surrogate model predictions” [*Combust. Flame* 152 (2008) 125–143]. *Combust. Flame* **2009**, *156* (4), 946–946.

(28) Yan, S. H.; Eddings, E. G.; Palotas, A. B.; Pugmire, R. J.; Sarofim, A. F. Prediction of sooting tendency for hydrocarbon liquids in diffusion flames. *Energy Fuels* **2005**, *19* (6), 2408–2415.

(29) 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.

(30) 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.

with a surrogate component slate that allows for the calculation of density, speed of sound, volatility, etc.^{29–33} Here, the surrogate mixture is built only to minimize deviations of a property-explicit objective function with the experimental values. Attention is paid to the availability of data on properties relevant to thermophysical model development.^{34–38} These surrogate mixtures are not typically prepared for a laboratory or test rig measurement and may not necessarily resemble the finished fuel being modeled. Moreover, the components of such a mixture may be lacking in some data critical to other research needs, such as detailed kinetic mechanisms.

While surrogate mixtures are formulated for specific purposes, there is a clear desire in the fuel research community at large to achieve physicochemical authenticity with the mixtures that are used. This desire is reflected in many of the above-cited publications, in which authors discuss the agreement of particular surrogate mixtures with at least some measured or modeled physical properties. A surrogate mixture developed to represent the TSI of Jet-A or JP-8 but which has thermophysical properties that are unrealistic, is far less desirable than a mixture that does in fact show reasonable thermophysical properties (density, speed of sound, volatility, etc.). One can, in principle, attempt to match any given thermophysical property in an effort to achieve physicochemical authenticity in surrogate mixtures. Indeed, some thermophysical properties might have more importance than others for such a purpose. For example, a measure of the speed of sound is incorporated into sensors that are used on aircrafts to measure fuel levels in tanks.³⁹ Thus, the speed of sound might be a desirable thermophysical property to match in a surrogate for some very specific gas turbine fuel property measurements. The difficulty with this *ad hoc* approach is that it is too specific and ignores the overarching goal. More to the point, the speed of sound shows only a modest variability over the known composition range of aviation kerosene.^{40,41} This means that, over the specified, allowed composition range of such fuel, the speed of sound may vary by less than a few

(31) Huber, M. L.; Lemmon, E.; Kazakov, A.; Ott, L. S.; Bruno, T. J. Model for the thermodynamic properties of a biodiesel fuel. *Energy Fuels* **2009**, *23*, 3790–3797.

(32) 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.

(33) 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.

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

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

(36) 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* (3), 1626–1633.

(37) Widegren, J. A.; Bruno, T. J. Thermal decomposition kinetics of the aviation fuel Jet-A. *Ind. Eng. Chem. Res.* **2008**, *47* (13), 4342–4348.

(38) Widegren, J. A.; Bruno, T. J. Thermal decomposition kinetics of propylcyclohexane. *Ind. Eng. Chem. Res.* **2009**, *48* (2), 654–659.

(39) Senibi, S. D.; Anderson, D. M.; Banks, D. L.; Childress, J. J.; Rasanian, M. Ultrasonic fuel gauging system. U.S. Patent 6,925,869, 2005.

(40) Bruno, T. J. Thermodynamic, transport and chemical properties of “reference” JP-8. *Book of Abstracts, 2007 Army Research Office and Air Force Office of Scientific Research Contractor’s Meeting in Chemical Propulsion*; Army Research Office and Air Force Office of Scientific Research: Boulder, CO, June 11–13, 2007.

(41) 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. *Final Report*; National Institute of Standards and Technology (NIST): Gaithersburg, MD, 2010; NISTIR 6659.

percent. The same is true of thermal conductivity, while density and heat capacity show even smaller changes. Viscosity shows a larger spread but one that decreases significantly with increasing temperature. An evaluation metric that is only modestly sensitive to the commonly encountered variations of Jet-A and JP-8 is less useful.

The only property that shows an appreciable change over the allowable (or customary) composition range is the volatility, as expressed by the distillation curve.⁴¹ Moreover, this property is directly related to composition, is sensitive to even subtle compositional variability, and has theoretical meaning provided that it is measured properly (see below). Thus, of the common thermophysical properties, the volatility is one with sufficient sensitivity and scope to assess physicochemical authenticity. Indeed, as will be demonstrated in part 2 (10.1021/ef1004978) of this work, it is possible for other properties (such as the densities) of two surrogate mixtures to be very close yet for the mixtures to have very different volatilities. Moreover, the volatility of a surrogate is actually of critical importance to many of the purposes for which surrogates are intended to serve. Very specific engineering properties, such as relight, combustion and flame characteristics, and fire simulations, require a surrogate with a close match in volatility with the real fuel.^{11,21,23–28}

Advanced Distillation Curve (ADC) Measurement. The most common presentation of the distillation curve is a plot of the boiling temperature (at ambient pressure) against volume fraction. The American Society for Testing and Materials (ASTM) D-86 standard test method provides the classical approach to the measurement, in which the data obtained are the initial boiling temperature (IBT), the temperature at volume fractions of 10, 20, 30, 40, 50, 60, 70, 80, and 90%, and then the final boiling temperature (FBT).⁴² The method historically suffers from major disadvantages, and we have developed several improvements to the metrology.^{2,43–49} These improvements are discussed in detail elsewhere; therefore, only a very brief summary will be provided here. Of particular importance is the ability to model the volatility with an equation of state, as we have discussed above. This precludes distillation curve determination with the classical methods that have little or no basis in theory. Our improved metrology is called the ADC approach and is especially applicable to the characterization of fuels. This method 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) a corrosivity assessment of each distillate fraction. The fuels that we have measured include rocket propellants, gasolines, turbine kerosene (jet) fuels, diesel fuels (including oxygenated diesel fuel and biodiesel fuels), and crude oils.^{41,50–71} Moreover, the measurements have facilitated the development of thermodynamic models

(50) Bruno, T. J.; Huber, M. L.; Laesecke, A.; Lemmon, E. W.; Perkins, R. A. Thermochemical and thermophysical properties of JP-10. *Final Report*; National Institute of Standards and Technology (NIST): Gaithersburg, MD, 2006; NIST-IR 6640.

(51) Bruno, T. J. The properties of S-8. *Final Report*; Air Force Research Laboratory: Wright-Patterson Air Force Base, OH, 2006; MIPR F4FBY6237G001.

(52) 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. *Final Report*; National Institute of Standards and Technology (NIST): Gaithersburg, MD, 2007; NIST-IR-6647.

(53) 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.

(54) 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.

(55) 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.

(56) 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.

(57) 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.

(58) 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., A* 2010, 1217, 2703–2715.

(59) 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.

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

(61) 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.

(62) Ott, L. S.; Bruno, T. J. Corrosivity of fluids as a function of distillate cut: Application of an advanced distillation curve method. *Energy Fuels* 2007, 21, 2778–2784.

(63) 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.

(64) 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.

(65) 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 Fuels* 2008, 22, 2518–2526.

(66) 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.

(67) 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.

(68) 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.

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

(43) 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. *Chem. Eng. Technol.* 2010, 33, 363–376.

(44) Bruno, T. J. Improvements in the measurement of distillation curves—Part 1: A composition-explicit approach. *Ind. Eng. Chem. Res.* 2006, 45, 4371–4380.

(45) 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.

(46) Bruno, T. J. Method and apparatus for precision in-line sampling of distillate. *Sep. Sci. Technol.* 2006, 41 (2), 309–314.

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

(48) 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.

(49) Ott, L. S.; Smith, B. L.; Bruno, T. J. Experimental test of the Sydney Young equation for the presentation of distillation curves. *J. Chem. Thermodyn.* 2008, 40, 1352–1357.

Table 1

(a) List of the Simple Surrogate Mixtures Studied in This Work along with Their Compositions	
surrogate A	60% <i>n</i> -decane + 20% methylcyclohexane + 20% toluene
surrogate B	60% <i>n</i> -decane + 20% methylcyclohexane + 20% <i>o</i> -xylene
surrogate C	60% <i>n</i> -dodecane + 20% methylcyclohexane + 20% <i>o</i> -xylene
surrogate F	60% <i>n</i> -decane + 20% butylcyclohexane + 20% butylbenzene
surrogate G	60% <i>n</i> -decane + 40% isooctane
Aachen	80% decane + 20% 1,2,4-trimethylbenzene
modified Aachen	80% dodecane + 20% 1,2,4-trimethylbenzene
(b) List of the More Complex Multicomponent Surrogate Mixtures and Their Compositions	
Utah surrogate	30% <i>n</i> -dodecane + 20% <i>n</i> -tetradecane + 20% methylcyclohexane + 15% <i>o</i> -xylene + 10% isooctane + 5% tetralin
Drexel surrogate 1	36% isocetane + 26% <i>n</i> -dodecane + 14% methylcyclohexane + 18% 1-methylnaphthalene + 6% decalin
Drexel surrogate 2	43% <i>n</i> -dodecane + 27% isocetane + 15% methylcyclohexane + 15% 1-methylnaphthalene
Schulz surrogate	21% dodecane + 16.2% decane + 15.6% tetradecane + 10.2% hexadecane + 5.7% isooctane + 5.1% methylcyclohexane + 4.7% cyclooctane + 4.6% butylbenzene + 4.5% <i>m</i> -xylene + 4.4% 1,2,4,5-tetramethylbenzene + 4.1% tetralin + 3.9% 1-methylnaphthalene
surrogate 1	30% dodecane + 20% tetradecane + 20% methylcyclohexane + 15% <i>m</i> -xylene + 10% isooctane + 5% tetralin
surrogate 3	73.5% <i>n</i> -dodecane + 10% methylcyclohexane + 10% toluene + 5.5% isooctane + 1% benzene
Violi surrogate	20% tetradecane + 25% dodecane + 25% decane + 20% toluene + 5% methylcyclohexane + 5% isooctane

(on the basis of equations of state) to describe complex fuels.^{29–33,72} In this paper, we report the application of the ADC to the evaluation of the physicochemical authenticity of aviation kerosene surrogate mixtures.

Evaluation of Physicochemical Authenticity of Surrogate Mixtures. Clearly, the most straightforward way to evaluate the physicochemical authenticity of surrogate mixtures is to compare them to the finished aviation kerosene fuels on the basis of one or more carefully selected metrics. The volatility of such fluids is very sensitive to compositional variability and was therefore chosen as the primary target property. The problem then becomes defining or selecting benchmark Jet-A or JP-8 behavior and developing an objective protocol for the comparison. We approached this problem with the ADC volatility data for two samples of Jet-A, designated Jet-A-4658 and Jet-A-3638. The sample designated 4658 is actually a composite Jet-A fluid prepared by mixing approximately equal volumes of five individual batches of Jet-A. This composite sample was prepared at the Air Force Research Laboratory and was provided for this work (as well as other research projects in the aviation fuel community) to represent what might be considered a typical Jet-A fluid.⁷³ The sample designated Jet-A-3638 was known to be unusual in that it showed a remarkably high volatility and an unusually low aromatic content and density while still meeting all of the specifications for Jet-A.⁷³ While this fluid is acceptable for use, it is nevertheless understood to be unusual. We also note here that, in terms of most thermophysical and engineering properties, there will be no practical difference between Jet-A and JP-8, because the difference between

these two fluids is the additive package.⁷⁴ JP-8 contains an icing inhibitor, corrosion/lubricity enhancer, and anti-static additive, often prepared by splash blending from base Jet-A stock at the end-user tank. Thus, a surrogate mixture prepared to represent the behavior of Jet-A will represent the behavior of JP-8 in almost all applications.⁶⁸

When one examines the surrogate fluid mixtures that have been used or proposed in the past to represent Jet-A or JP-8, it is possible to divide them into two classes. Some surrogates contain very few components (two or three, listed in Table 1a), while others have more components, upward of 10 (listed in Table 1b). In each case, the composition specified is on a volume basis, prepared at ambient temperature and pressure, reflecting the preparation and use in the engineering measurements that were discussed earlier in the Introduction. Simple mixtures often show a bimodal distillation curve behavior, in which the boiling temperatures of the small number of components act as anchor points for a highly sigmoidal shaped curve. We noted this kind of behavior in the early work with the ADC, in mixtures of *n*-decane and *n*-tetradecane.⁴⁴ The curves resulting from those simple mixtures were “anchored” at the boiling temperatures of the pure components, and the curve connecting these two points was a pronounced sigmoid. More complex mixtures usually show a less pronounced, subtle sigmoid shape, at least for some segment of the curve. It is possible, as shown below, for surrogate mixtures containing a component with a very low boiling temperature to produce an anchor point in one region of the curve, while a subtle sigmoid is observed over the remainder of the curve. This is called a combined bimodal curve. Departures from the subtle sigmoid of the finished fuel, of either the bimodal or combined bimodal variation, represent significant departures from physicochemical authenticity.

We point out that the list of surrogates that we have presented for study here is not exhaustive. Other mixtures have been suggested in the literature cited above and at various fuel conferences.⁴⁰ This should not be regarded as a disadvantage, because the present study outlines a generic strategy by which any surrogate mixture that has been considered in the past or is proposed in the future can be evaluated for physicochemical authenticity. We also point out that the surrogate mixture designations that we employ are not self consistent. Some are named; some have number designations; and some have letter designations. We have done this to be consistent with designations in the literature and at fuel conferences. Note also that there are apparent gaps (there is no surrogate 2 or surrogate D), also

(69) 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.

(70) 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. Technol.* **2008**, *42* (20), 7682–7689.

(71) 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.

(72) Huber, M. L.; Lemmon, E.; Bruno, T. J. Effect of RP-1 compositional variability on thermophysical properties. *Energy Fuels* **2009**, *23*, 5550–5555.

(73) Edwards, J. T. Personal communication. Propulsion Directorate, Air Force Research Laboratory, United States Air Force, 2006.

(74) Detail specification turbine fuel, aviation, kerosene type JP-8 (NATO F-34), NATO F-35, and JP-8 + 100 (NATO F-37), April 11, 2008; MIL-DTL-83133F.

consistent with the most common fluids presented in the past.^{75,76}

We also point out that, in this work, we have concentrated primarily on the thermophysical aspects of physicochemical authenticity. It is also possible to evaluate surrogate components for chemical moiety type and match primary, secondary, tertiary, and quaternary carbons, ring attachments, aromaticity, etc. While such an evaluation might be sensible for the multicomponent complex surrogate mixtures (Table 1b), it is not possible for the simple mixtures (Table 1a). There is simply too small a variety of bond moieties available for consideration. Continuation of this aspect will be a topic for future work on the more complex mixtures.

Experimental Section

The surrogate mixtures that are listed in parts a and b of Table 1 were prepared volumetrically from pure components that were obtained from commercial sources. For each component, we used fluids with purities of at least 99.9% (mass/mass). The purities of the starting components were verified by gas chromatography with mass spectrometric detection. All of the pure starting fluids were found to meet or exceed the purity specification of the manufacturer, and all were used as received. Enough of each mixture was prepared to provide a stock solution sufficient for three replicate measurements for each mixture. Once prepared, the mixtures were carefully sealed in inert containers at 7 °C, to minimize the loss of volatiles and the uptake of moisture.

The samples of Jet-A (designated 4658 and 3638) used for comparison were obtained from the Fuels Branch of the Air Force Research Laboratory (AFRL, Wright-Patterson Air Force Base, OH). The samples were maintained in sealed containers at 7 °C during storage to prevent the loss of high-vapor-pressure components. No solidification or phase separation was noted during storage. Both samples were analyzed by gas chromatography (30 m capillary column of 5% phenyl–95%–dimethyl polysiloxane having a thickness of 1 μ m and temperature program from 90 to 275 °C, at 9 °C/min) using flame ionization detection and mass spectrometric detection.^{77,78} The purpose of these analyses was to obtain a general overview of the fluid composition and to determine the value for the constant term to use in the pressure correction to the distillation temperature (with the Sydney Young equation; see below).

The required fluid for the distillation curve measurement (in each case, 200 mL) was placed in the boiling flask with a 200 mL volumetric pipet. The thermocouples were then inserted into the proper locations to monitor T_k (the temperature measured directly in the fluid) and T_h (the temperature measured at the bottom of the take-off position in the distillation head), as indicated in Figure 1. More details can be found in our prior work on the ADC method (see refs 44–48 cited above). Heating was then commenced with a multi-step program based on a previously measured distillation curve. The purpose of the

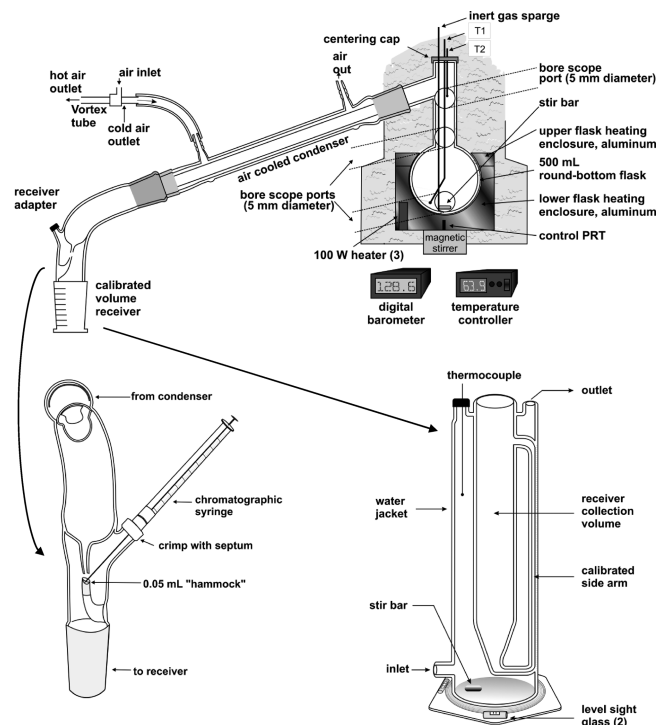


Figure 1. Schematic diagram of the ADC apparatus. Expanded views of the sampling adapter and the stabilized receiver are shown in the lower half of the figure.

program was to impose a heating profile similar in shape to the distillation curve but leading the curve by approximately 20 °C. This heating rate applied to the fluid provides a constant mass flow rate of vapor into the distillation head. Volume measurements were made in the level-stabilized receiver, and sample aliquots were collected at the receiver adapter hammock. In the course of this work, we performed at least six complete distillation curve measurements for the Jet-A samples and three for each of the surrogate mixtures.

Because the measurements of the distillation curve are performed at local ambient atmospheric pressure (measured with an electronic barometer at an elevation of 1655 m), temperature readings were corrected for what should be obtained at standard atmospheric pressure. This was performed with the modified Sydney Young equation, in which the constant term was assigned a value of 0.000 109.^{49,79–81} This value corresponds to a carbon chain of 12. We chose this constant term because it allows for the equation to represent the behavior of both Jet-A and JP-8.^{68,69} This may not be the optimal constant for each of the individual surrogate mixtures; however, we consider it better to hold this term constant (optimized for the finished fuel). The uncertainty introduced by this selection is expected to be far less than the experimental uncertainty of the temperatures. On balance, this approach is less ambiguous than allowing for the constant to “float” for each surrogate. Regardless of the choice of constant, the magnitude of the correction is dependent upon the extent of departure 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 adjustment of 8 °C.

(75) Bruno, T. J. Thermodynamic, transport and chemical properties of “reference” JP-8. *Book of Abstracts, 2006 Army Research Office and Air Force Office of Scientific Research Contractor’s Meeting in Chemical Propulsion*; Army Research Office and Air Force Office of Scientific Research: Arlington, VA, June 12–14, 2006; pp 15–18.

(76) Seshadri, K. Autoignition and combustion of diesel and JP-8. *Book of Abstracts, 2007 Army Research Office and Air Force Office of Scientific Research Contractor’s Meeting in Chemical Propulsion*; Army Research Office and Air Force Office of Scientific Research: Boulder, CO, June 11–13, 2007.

(77) 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, 2004.

(78) Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Fundamental Spectroscopic Correlation Charts*; Taylor and Francis CRC Press: Boca Raton, FL, 2006.

(79) Young, S. Correction of boiling points of liquids from observed to normal pressures. *Proc. Chem. Soc.* **1902**, 81, 777.

(80) Young, S. *Fractional Distillation*; Macmillan and Co., Ltd.: London, U.K., 1903.

(81) Young, S. *Distillation Principles and Processes*; Macmillan and Co., Ltd.: London, U.K., 1922.

Results and Discussion

Initial Boiling Temperatures. During the initial heating of each sample in the distillation flask, the behavior of the fluid was carefully observed. Direct observation through the flask window or through the bore scope allowed for measurement of the onset of boiling for each of the mixtures (measured with T_k). Typically, to ascertain the initial boiling behavior, we measure the onset of bubbling, the temperature at which bubbling is sustained, and the temperature at which the vapor rises into the distillation head. We have shown that the vapor rise temperature is actually the initial boiling temperature (the IBT, an approximation of the bubble point temperature at ambient pressure) of the initial fluid. This measurement is significant for a mixture because it is thermodynamically consistent and can be modeled with an equation of state. Measurement of these temperatures for simple mixtures (such as the surrogates studied in this work) can be complicated by rapid phase changes. As a result, we only report the onset and vapor rise temperatures here. The vapor rise is accompanied by a sharp increase in T_h and is therefore far less subjective to ascertain and, thus, is less uncertain than the onset of bubbling. Experience with previous mixtures, including *n*-alkane standard mixtures that were prepared gravimetrically, indicates that the uncertainty in the onset of the bubbling temperature is approximately 1 °C. The uncertainty in the vapor rise temperature is 0.3 °C. The repeatability in the pressure measurement (assessed by logging a pressure measurement every 15 s for the duration of a typical distillation) is 0.001 kPa. The transducer itself was calibrated against an air dead weight pressure balance traceable to a National Institute of Standards and Technology (NIST) primary pressure standard. In each case, a coverage factor $k = 2$ was applied to the uncertainty.

As a means of comparison between the surrogate mixtures and the finished Jet-A samples chosen for reference, the IBT is a relatively weak parameter. Even if the IBT of a surrogate closely matches that of Jet-A, the remainder of the distillation curve can be significantly divergent. This is especially true for mixtures whose full distillation curves exhibit bimodal or combined bimodal shape. We will discuss this aspect later in the paper, subsequent to the introduction of the distillation measurements. In Tables 2a, 3a, and 4a, we present the IBT (obtained as the vapor rise temperatures from the ADC) for the Jet-A samples, the simple surrogates, and the complex surrogates, respectively. As an objective measure of the departure of the surrogate mixture IBT from that of the Jet-A, we calculate the difference between the surrogate and Jet-A-4658 and Jet-A-3638 and average them while weighting Jet-A-4658 heavier than Jet-A-3638 by a factor of 2. These comparisons are provided in Table 5. Smaller values indicate an IBT closer to that of Jet-A, with the agreement to Jet-A-4658 (the composite sample) considered more important. Among the simple surrogates, the modified Aachen surrogate and surrogate F are closest to the Jet-A, and among the complex surrogates, the Drexel surrogates and the Schultz surrogate are closest. It is important not to overinterpret the absolute numbers, because as noted above, the IBT is merely the (one) point from which the distillation curves diverge. While this measure alone cannot be used to arrive at an overall rating for the surrogates, one can nevertheless use it to evaluate situations in which the IBT is of paramount importance.

Table 2

(a) Initial Boiling Behavior of the Two Samples of Jet-A Used as the Basis of Comparison to the Surrogate Formulations^a

observed temperature	Jet-A-3638 (°C, at 82.11 kPa)	Jet-A-4658 (°C, at 83.63 kPa)
onset	148.4	139.9
sustained	176.9	185.6
vapor rising	184.2	190.5

(b) Representative Distillation Curve Data of the Two Samples of Jet-A Used as the Basis of Comparison to the Surrogate Formulations^b

distillate volume fraction (%)	Jet-A-3638 (82.11 kPa)		Jet-A-4658 (83.63 kPa)	
	T_k (°C)	T_h (°C)	T_k (°C)	T_h (°C)
5	186.8	179.9	195.4	174.7
10	188.7	184.2	198.5	183.3
15	191.1	187.0	201.5	187.0
20	192.9	185.8	204.7	189.1
25	194.9	189.5	208.1	190.6
30	196.6	191.6	211.3	192.8
35	198.5	193.9	214.3	194.6
40	200.3	196.0	217.6	199.1
45	202.1	197.9	220.7	202.6
50	204.0	199.8	224.2	205.4
55	205.9	202.4	227.6	208.6
60	208.0	204.0	231.2	212.4
65	210.5	205.1	234.7	214.9
70	213.6	207.6	239.4	216.6
75	216.2	210.6	243.3	218.7
80	219.4	210.2	247.9	220.8
85	222.9	215.3	253.6	224.1

^a The vapor rise temperature is that at which vapor is observed to rise in the distillation head, considered to be the initial boiling temperature of the fluid. These temperatures have been corrected to standard atmospheric pressure with the modified Sydney Young equation; the experimental atmospheric pressures are provided to allow for recovery of the actual measured temperatures. The uncertainties are discussed in the text. ^b These temperatures have been corrected to standard atmospheric pressure with the modified Sydney Young equation; the experimental atmospheric pressures are provided in parentheses to allow for recovery of the actual measured temperatures.

ADC Measurement. Representative distillation curve data for the samples of Jet-A and the surrogate mixtures, presented in both T_k (measured directly in the fluid) and T_h (measured in the distillation head), are provided in Tables 2b, 3b, and 4b. The T_k data are true thermodynamic state points, while the T_h data allow for a comparison to measurements made with a classical apparatus. The estimated uncertainty (with a coverage factor $k = 2$) in the temperatures is 0.3 °C. Note that the experimental uncertainty of T_k is always somewhat lower than that of T_h , but as a conservative position, we use the higher uncertainty value for both temperatures. The uncertainty in the volume measurement that is used to obtain the distillate volume fraction is 0.05 mL in each case. The repeatability in the pressure measurement (assessed as described earlier) is 0.001 kPa. The relatively low uncertainties in the measured quantities facilitate modeling the results, for example, with an equation of state. The measurements for the simple and complex surrogates are presented in Figures 2 and 3, respectively. Distillation curves for Jet-A-4658 and Jet-A-3638 are also presented (along with best fit lines). Because of the choice of these two fluids, we consider the region subtended between these two curves as acceptable in terms of physicochemical authenticity.

While it is certainly possible to make coarse judgments about the physicochemical authenticity of the surrogates by

Table 3

(a) Initial Boiling Behavior of the Simple Surrogate Formulations Listed in Table 1a ^a														
observed temperature (°C)	surrogate A 83.35 kPa		surrogate B 83.70 kPa		surrogate C 83.40 kPa		surrogate F 83.99 kPa		surrogate G 83.53 kPa		Aachen 83.74 kPa		modified Aachen 83.23 kPa	
onset	86.8		77.5		64.8		127.9		76.9		135.6		184.1	
vapor rise	125.4		138.0		142.5		176.8		126.4		172.2		197.2	
(b) Representative Distillation Curve Data of the Simple Surrogate Formulations Listed in Table 1a ^b														
distillate volume fraction (%)	surrogate A 83.35 kPa		surrogate B 83.70 kPa		surrogate C 83.40 kPa		surrogate F 83.99 kPa		surrogate G 83.53 kPa		Aachen 83.74 kPa		modified Aachen 83.23 kPa	
	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)
5	127.0	113.1	140.2	134.8	146.6	130.8	176.7	176.0	129.4	118.5	172.2	171.7	198.2	193.0
10	128.6	116.9	142.3	133.6	150.4	126.8	176.7	176.2	131.6	122.6	172.2	171.6	199.2	195.2
15	130.7	121.9	144.5	136.8	155.3	137.5	176.7	176.2	134.1	126.6	172.2	171.6	200.7	197.1
20	132.8	125.3	146.9	141.4	160.6	144.8	176.7	176.1	137.5	131.3	172.3	171.6	202.0	198.9
25	136.4	130.6	149.8	145.6	167.0	153.1	176.8	176.1	140.5	134.7	172.3	171.6	203.5	199.5
30	140.0	134.6	151.9	148.1	174.0	161.2	176.9	176.2	144.4	138.7	172.4	171.6	205.1	196.9
35	143.8	138.8	154.4	151.3	181.4	168.3	176.8	176.1	148.3	142.8	172.4	171.7	206.6	201.1
40	148.0	143.1	156.7	153.9	189.1	177.9	176.8	176.2	152.5	145.2	172.5	171.7	208.2	204.7
45	153.6	149.0	159.3	156.8	196.8	187.0	176.9	176.3	157.9	152.5	172.6	171.7	209.9	206.8
50	158.9	154.6	161.2	158.9	204.0	196.2	176.9	176.2	162.8	157.3	172.7	171.8	211.4	208.6
55	163.7	160.3	163.3	161.4	208.7	203.7	177.0	176.3	166.4	163.0	172.8	171.7	212.9	210.2
60	168.0	165.8	165.1	163.4	212.0	209.7	177.2	176.4	169.1	166.5	172.9	171.8	213.8	211.8
65	170.9	169.6	167.2	165.3	213.9	212.8	177.4	176.4	171.6	169.5	173.1	171.9	214.9	212.9
70	172.8	171.6	168.6	166.9	215.1	214.3	177.6	176.5	173.0	171.3	173.4	171.9	215.5	213.4
75	173.8	172.9	169.9	168.3	215.8	215.1	177.7	176.5	174.1	172.1	173.4	172.0	216.4	213.9
80	174.3	173.3	171.3	169.7	216.2	215.5	177.7	176.6	174.8	173.1	173.5	172.1	216.6	214.9
85	174.8	173.6	172.9	171.3	216.6	215.7	177.9	176.7	175.5	173.4	173.5	172.2	216.7	215.3
90	174.9	173.9	173.9	172.6	216.6	215.6	177.8	176.7	175.5	173.5	173.6	172.3	216.6	215.6

^a The vapor rise temperature is that at which vapor is observed to rise in the distillation head, considered to be the initial boiling temperature of the fluid. These temperatures have been corrected to standard atmospheric pressure with the modified Sydney Young equation; the experimental atmospheric pressures are provided to allow for recovery of the actual measured temperatures. The uncertainties are discussed in the text. ^b These temperatures have been corrected to standard atmospheric pressure with the modified Sydney Young equation; the experimental atmospheric pressures are provided to allow for recovery of the actual measured temperatures. The uncertainties are discussed in the text.

examining Figures 2 and 3, more objective means of assessment are desirable. Two simple approaches to this are (1) an evaluation, point by point (that is, as a function of the distillate cut), of the displacements in the temperature of the surrogate mixtures from the Jet-A fluids and (2) an evaluation of the displacements in the overall shape and slope of the distillation curves.

For the point-by-point approach, we used three metrics for comparison. Metric 1 was simply the average of the absolute values of the temperature difference (in T_k) between Jet-A-4658 and the surrogate, for each distillate volume fraction

$$\text{metric 1} = \frac{1}{n} \sum_{i=1}^n |T_{\text{Jet-A-4658}}^i - T_{\text{surrogate}}^i| \quad (1)$$

where $T_{\text{Jet-A-4658}}$ is the distillation temperature of Jet-A-4658 at a particular distillate volume fraction, $T_{\text{surrogate}}$ is the corresponding distillation temperature of the surrogate mixture, i is an index corresponding to the distillate volume fraction, and n is the total number of temperature and volume pairs. As discussed earlier, we considered the comparison to Jet-A-4658 to be somewhat more important than the comparison to Jet-A-3638, because the former fluid is a composite mixture and the latter fluid is an individual batch of unusual composition and properties. The average of these temperature differences (for all distillate volume fractions) provides a single number upon which to evaluate the departure of the surrogate from a typical Jet-A fluid. A lower number for

this metric indicates less of a departure from the finished fuel.

For the second point-by-point metric, we begin with the average of the absolute values of the temperature difference (in T_k) between Jet-A-4658 and the surrogate, for each distillate volume fraction. We divide this by the absolute value of the difference in the temperature (again in T_k , for each distillate volume fraction) of the two Jet-A samples and calculate the average over all distillate volume fractions

$$\text{metric 2} = \frac{1}{n} \sum_{i=1}^n \frac{|T_{\text{Jet-A-4658}}^i - T_{\text{surrogate}}^i|}{|T_{\text{Jet-A-4658}}^i - T_{\text{Jet-A-3638}}^i|} \quad (2)$$

where $T_{\text{Jet-A-4658}}$ and $T_{\text{Jet-A-3638}}$ are the distillation temperatures of Jet-A-4658 and Jet-A-3638 at a particular distillate volume fraction. $T_{\text{surrogate}}$, i , and n are defined as in eq 1. The difference between this metric and metric 1 is that, as the Jet-A-4658 and Jet-A-3638 diverge later in the distillation, metric 2 typically decreases. Thus, this metric is more tolerant of the diverging volatility of (generic) Jet-A late in the distillation. As with metric 1, a smaller numerical value indicates less of a departure from the behavior of a “real” Jet-A fluid.

The third point-by-point metric takes more explicit account of a comparison to Jet-A-3638, recognizing that this fluid is indeed an acceptable Jet-A, which meets specifications, despite its unusual physicochemical behavior. Following this intent, metric 3 evaluates the absolute value of the difference in the temperature (again in T_k , for each distillate volume fraction) of the surrogate mixture with

Table 4

(a) Initial Boiling Behavior of the Complex Surrogate Formulations Listed in Table 1b ^d														
observed temperature (°C)	Utah 83.73 kPa		Drexel 1 83.98 kPa		Drexel 2 83.91 kPa		Schulz 83.62 kPa		surrogate 1 83.60 kPa		surrogate 3 83.53 kPa		Violi 84.15 kPa	
onset	91.2		85.9		94.3		71.6		98.0		71.9		118.9	
vapor rise	130.4		167.0		164.5		160.0		129.4		139.7		134.3	
(b) Representative Distillation Curve Data of the Complex Surrogate Formulations Listed in Table 1b ^b														
distillate volume fraction (%)	Utah 83.73 kPa		Drexel 1 83.98 kPa		Drexel 2 83.91 kPa		Schulz 83.62 kPa		surrogate 1 83.60 kPa		surrogate 3 83.53 kPa		Violi 84.15 kPa	
	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)
5	135.9	113.6	179.3	132.9	176.1	131.2	169.9	119.5	135.4	117.8	145.8	121.3	139.0	125.4
10	139.4	118.8	194.3	144.3	189.3	143.3	176.0	148.0	138.7	123.6	152.7	127.9	142.5	131.4
15	143.5	122.1	215.8	137.3	208.3	128.5	182.6	157.4	143.0	124.8	162.1	132.4	147.7	136.5
20	149.0	126.2	224.7	213.4	223.0	200.8	188.8	156.6	147.8	129.1	174.3	136.2	152.9	141.1
25	155.6	130.9	226.4	219.5	225.1	216.1	194.1	159.2	154.2	134.2	192.9	133.8	160.4	148.2
30	163.5	136.5	227.6	224.4	226.0	221.8	199.1	162.5	162.0	140.3	211.3	181.8	168.6	155.3
35	172.8	142.9	228.3	225.0	226.8	223.8	203.5	165.6	171.3	146.3	214.4	208.7	178.8	164.3
40	183.3	151.8	229.0	225.3	227.4	224.5	207.6	167.8	182.5	155.6	215.3	213.5	189.7	157.5
45	195.5	169.5	229.7	225.4	227.8	223.4	211.9	170.9	195.2	161.5	215.8	214.2	198.8	143.9
50	206.7	173.6	230.3	227.3	228.2	225.3	216.2	175.6	208.9	147.8	216.1	214.6	206.1	143.8
55	216.0	177.5	231.1	229.0	228.7	226.3	220.6	180.4	219.2	153.4	216.3	215.0	212.2	143.9
60	222.0	184.3	231.9	230.1	229.5	227.1	225.2	185.4	224.2	169.8	216.4	215.6	218.1	147.1
65	225.7	190.2	232.9	231.3	230.1	228.1	230.2	190.3	227.2	186.2	216.4	215.8	223.8	153.3
70	228.4	200.3	233.9	232.2	230.8	228.9	235.5	194.8	229.5	196.9	216.5	215.7	229.0	161.4
75	230.8	210.3	235.0	233.2	231.6	229.6	240.9	199.9	231.8	203.9	216.6	215.9	233.9	169.4
80	233.8	217.9	235.8	234.2	232.5	230.5	247.3	203.8	234.6	212.0	216.8	215.8	238.8	177.4
85	237.3	224.7	236.6	235.2	233.7	231.6	254.7	204.2	238.3	215.5	217.0	215.8	244.6	182.3
90	245.7	227.7	237.7	236.8	235.1	233.0	263.4	250.5	243.5	218.7	216.7	215.9	251.4	187.3

^aThe vapor rise temperature is that at which vapor is observed to rise in the distillation head, considered to be the initial boiling temperature of the fluid. These temperatures have been corrected to standard atmospheric pressure with the modified Sydney Young equation; the experimental atmospheric pressures are provided to allow for recovery of the actual measured temperatures. The uncertainties are discussed in the text. ^bThese temperatures have been corrected to standard atmospheric pressure with the modified Sydney Young equation; the experimental atmospheric pressures are provided to allow for recovery of the actual measured temperatures. The uncertainties are discussed in the text.

Table 5. Comparison of the IBT of the Surrogate Mixtures with Jet-A, Weighting Agreement with Jet-A-4658 by a Factor of 2

surrogate name	weighted average difference (°C)
surrogate A	63.0
surrogate B	50.4
surrogate C	45.9
surrogate F	11.6
surrogate G	62.0
Aachen surrogate	16.2
modified Aachen surrogate	8.8
Utah surrogate	58.0
Drexel 1 surrogate	21.4
Drexel 2 surrogate	23.9
Schultz surrogate	28.4
surrogate 1	59.0
surrogate 2	49.1
Violi surrogate	54.1

Jet-A-4658 and Jet-A-3638 and then chooses the smaller of the two

$$\text{metric 3} = \frac{1}{n} \sum_{i=1}^n \min(|T_{\text{Jet-A-4658}}^i - T_{\text{surrogate}}^i|, |T_{\text{Jet-A-3638}}^i - T_{\text{surrogate}}^i|) \quad (3)$$

where the temperatures and indices are defined as above. As with metrics 1 and 2, the average of all values for all distillate volume fractions provides a numerical evaluation criterion. A smaller numerical value indicates less of a departure from the behavior of a “real” Jet-A fluid.

A compilation of the point-by-point metrics for each of the surrogate mixtures is provided in parts a and b of Table 6. We note that for the simple surrogate mixtures, the modified

Aachen surrogate is physicochemically closest to Jet-A, followed by surrogate C. Following these two are surrogate F, the Aachen surrogate, and surrogates B, G, and A. For the complex surrogate mixtures, the Schulz surrogate is closest to Jet-A, followed by the two Drexel surrogates and then surrogate 3, followed by the Violi surrogate, the Utah surrogates, and surrogate 1.

We can also address physicochemical authenticity by comparing the overall shape and slope of the distillation curves of the surrogate mixtures to those of the Jet-A samples. For this criterion, we fit the distillation curve to a simple linear model ($y = mx + b$). Recall that finished fuels such as Jet-A contain many hundreds of components, and therefore, the distillation curves are subtle sigmoids in shape with no abrupt inflections. For this reason, evaluation of the shape and slope will be a two-step process. We must first determine if the shape is realistic (that is, subtle sigmoidal), and then we can evaluate the slope for agreement with the Jet-A distillation curves. It is not appropriate to use a simple linear model to fit curves with bimodal and combined bimodal shapes, because these represent too great of a departure in shape from the curve of the finished fuel. We also recognize that a distillation curve might have a very similar shape and slope to that of a Jet-A fluid but be far displaced in temperature from the locus subtended between the curves of Jet-A-4658 and Jet-A-3638.

Fitting the distillation curve to a simple linear model requires some comment. We acknowledge that the distillation curve, with its sigmoidal shape, is not in fact linear, and therefore, a simple linear model cannot account for all of the structure in the curve. Indeed, if one fits the distillation curve

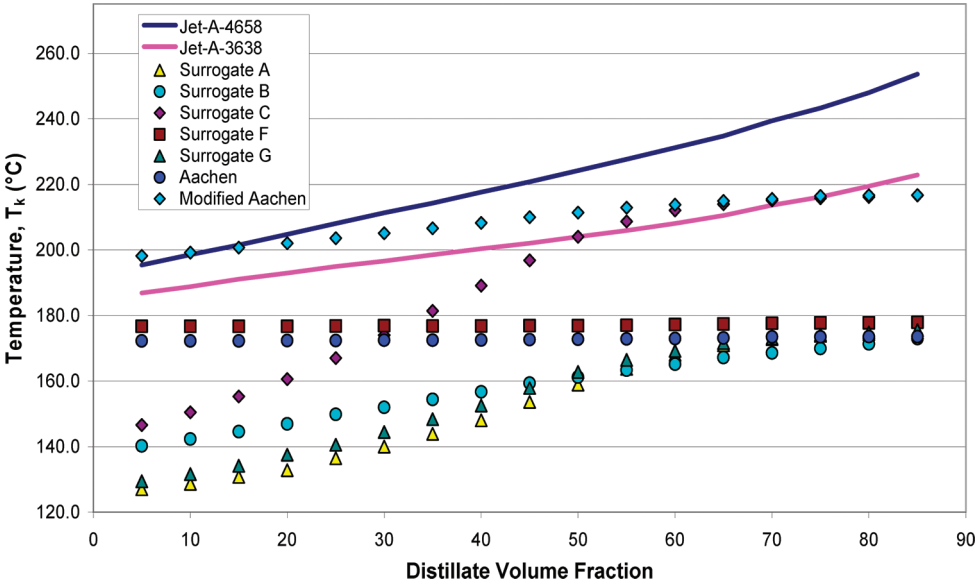


Figure 2. Distillation curves of Jet-A-4658, Jet-A-3638 (both presented as lines instead of plotting symbols), and the simple surrogate mixtures. The uncertainties in the temperature are smaller than the plotting symbols.

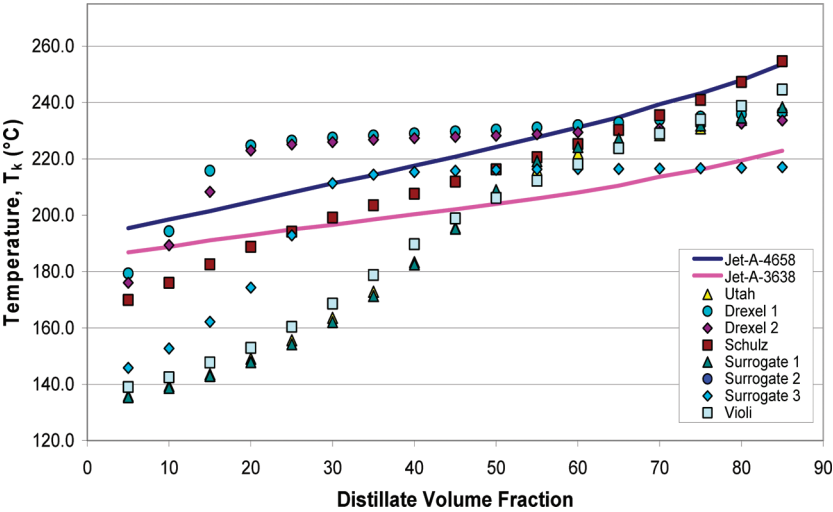


Figure 3. Distillation curves of Jet-A-4658, Jet-A-3638 (both presented as lines instead of plotting symbols), and the complex surrogate mixtures. The uncertainties in the temperature are smaller than the plotting symbols.

Table 6

(a) Evaluation of the Simple Surrogate Mixtures on the Basis of the Metrics Described in the Text							
criterion	surrogate A	surrogate B	surrogate C	surrogate F	surrogate G	Aachen	modified Aachen
metric 1	69.20	64.00	32.40	44.90	66.50	49.30	13.50
metric 2	4.25	3.77	2.20	2.36	4.06	2.63	0.60
metric 3	50.26	45.11	14.85	26.01	47.58	30.34	4.51
slope validity	poor	good	poor	invalid	poor	invalid	good
slope	0.70	0.42	0.99	NA	0.66	NA	0.25
(b) Evaluation of the Complex Surrogate Mixtures on the Basis of the Metrics Described in the Text							
criterion	Utah	Drexel 1	Drexel 2	Schulz	surrogate 1	surrogate 3	Violi
metric 1	31.50	10.50	10.70	10.10	31.20	21.00	28.90
metric 2	2.39	0.70	0.70	0.80	2.39	1.46	2.21
metric 3	23.33	9.82	9.02	5.90	23.51	10.51	20.06
slope validity	poor	invalid	invalid	fair	good	invalid	fair
slope	0.97	NA	NA	0.97	0.99	NA	0.99

of Jet-A-4658 or Jet-A-3638 to such a model, the residual plot is necessarily sinusoidal. Previous work with multiple

samples of Jet-A and JP-8 showed that such a residual plot has only two nodes. An example (for Jet-A-4658) is provided

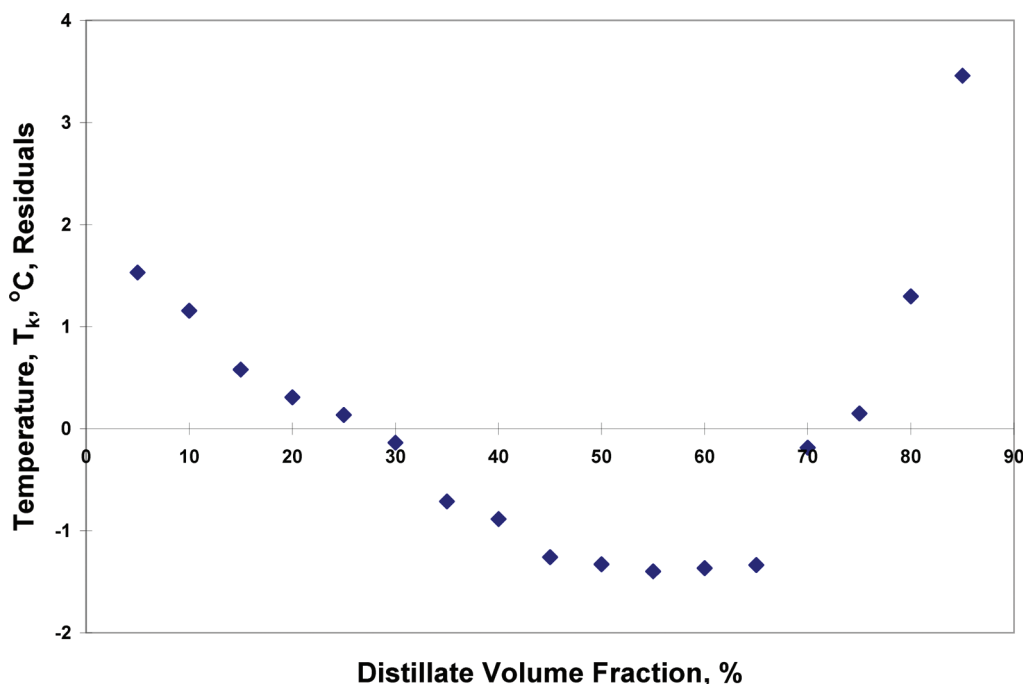


Figure 4. Residual plot resulting from the linear fit to the distillation curve data for Jet-A-4658, showing two nodes and the typical temperature departure, not exceeding approximately 1.5 °C.

in Figure 4. The plot begins with positive residuals decreasing to zero (and becoming negative) after the 30% (± 3) distillate volume fraction, reverting to positive residuals at a distillate volume fraction of 73% (± 3). The typical magnitude of the residuals (resulting from a linear fit as described earlier) for a finished fuel is typically less than 1.5 °C. Although the residual plots are sinusoidal, the normal probability plots are typically linear ($r^2 = 0.99$).⁸² An example of such a normal probability plot is shown in Figure 5a, for Jet-A-4658. Thus, these curve-fit diagnostics can be used as tools to evaluate the slope of surrogate fluid distillation curves.

We used the results of the distillation curve fits to the simple linear model as a means to rate the shape and slope as good, fair, or poor based on an evaluation of the number of nodes in the residual plot, the residual magnitude, and the linearity of the normal probability plot. A fit with a linear normal probability plot and a residual plot having two nodes with a maximum departure of 2 °C or less was given a “good” rating. Ratings of fair or poor were given if the fit met two or one of these criteria, respectively. When the curve was bimodal or combined bimodal, we simply rated the shape evaluation as being invalid and did no further comparison of the slope.

In terms of the actual calculated slope from the linear model, Jet-A-4658 showed a slope of 0.70 and Jet-A-3636 showed a slope of 0.43, a significant variation. Experience shows that approximating the distillation curve slope of a finished fuel containing hundreds of components with a surrogate composed of a relatively small number of components is very difficult. We therefore report the calculated slopes from a linear fit but emphasize that we primarily used the shape evaluation criteria discussed in the previous paragraph for the overall shape/slope evaluation of the surrogate mixtures. The slope evaluations are listed in parts a and b of

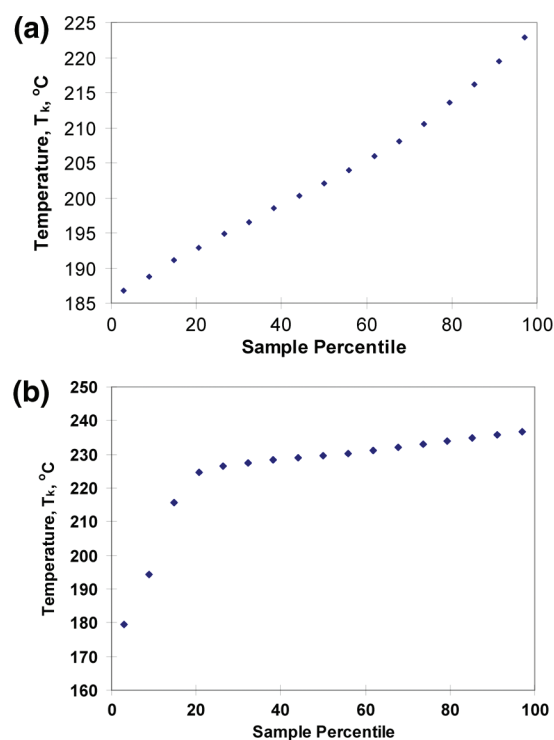


Figure 5. Normal probability plot for the simple linear model fit of the distillation curve of (a) Jet-A-4658 and (b) Drexel 1 surrogate.

Table 6, and in the discussion below, we will only consider the surrogates that performed well in the point-by-point metrics discussed earlier. On this basis, among the simple surrogate mixtures, those that were physicochemically closest to Jet-A were the modified Aachen surrogate and surrogate C. Between these two, the modified Aachen surrogate has a better shape/slope rating. Among the complex surrogates, the Schultz surrogate, followed by the Drexel surrogates and then surrogate 3, was physicochemically

(82) National Institute of Standards and Technology (NIST). *NIST/SEMATECH e-Handbook of Statistical Methods*; <http://www.itl.nist.gov/div898/handbook/> (accessed on Feb 16, 2010).

closest to Jet-A. We note, however, that the Drexel surrogates show an unfavorable shape/slope rating, and indeed, the reason for this can be seen in Figure 2, where combined bimodal shapes are apparent. Confirmation of the unfavorable shape/slope can be seen in the very nonlinear normal probability plot for the Drexel 1 surrogate mixture, provided in Figure 4b. Surrogate 3 is also unfavorable in its shape but for a different reason; the distillation curve shows a nearly straight line behavior. Thus, after the Schultz surrogate, the Violi surrogate is physicochemically closest to the behavior of Jet-A.

Conclusions

In this work, we have used the ADC method to evaluate the physicochemical authenticity of a number of Jet-A/JP-8 surrogate mixtures. The ADC method measures the volatility and approximates the vapor liquid equilibrium of a complex mixture; thus, the physicochemical authenticity is evaluated by analyzing the volatility difference between the finished fuel (Jet-A or JP-8) and the surrogate mixture. The volatility measurement is a sensitive method to evaluate the physicochemical authenticity, because even minor changes in composition can affect the volatility strongly, whereas such changes in composition may have a very modest effect on density,

speed of sound, heat capacity, and most other thermophysical properties. We divided the most common Jet-A/JP-8 surrogate mixtures into two categories: simple surrogate mixtures consisting of two or three components and more complex multicomponent surrogate mixtures. On the basis of volatility, we were able to rate the mixtures on the basis of similarity to the finished fuel, Jet-A/JP-8. We found that among the simple surrogate mixtures, the modified Aachen mixture was closest to Jet-A/JP-8, and among the complex surrogate mixtures, the Schulz surrogate was closest. The components that compose these two surrogate mixtures have properties that most closely approach a real Jet-A/JP-8 mixture. While we do not make any kind of a value judgment regarding the mixtures considered in this study, we recommend that, if physicochemical authenticity is a consideration in the application of a surrogate, an evaluation based on volatility be used in selection.

Acknowledgment. The financial support of the Air Force Office of Scientific Research (MIPR-F1ATA09114G004-000-000) is gratefully acknowledged. We acknowledge the Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, for providing the samples of Jet-A. B.L.S. acknowledges a Professional Research Experiences Program (PREP) and Summer Undergraduate Research Fellowship (SURF) at NIST.