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Preliminary Surrogate Mixture Models for the Thermophysical Properties of Rocket Propellants RP-1 and RP-2

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We have developed surrogate mixture models to represent the thermophysical properties of two kerosene rocket propellants, RP-1 and RP-2. The surrogates were developed with a procedure that incorporated experimental data for the density, sound speed, viscosity, thermal conductivity, and the advanced distillation curves for samples of the two fuels. The surrogate for RP-1 contains four components (α -methyldecalin, n-dodecane, 5-methylnonane, and heptylcyclohexane), and the surrogate for RP-2 contains five components (α -methyldecalin, n-dodecane, 5-methylnonane, 2,4-dimethylnonane, and heptylcyclohexane). Comparisons with experimental data demonstrate that the models are able to represent the density, sound speed, viscosity, and thermal conductivity of both fuels to within (at a 95% confidence level) 0.4, 2, 2, and 4%, respectively. The volatility behavior, as measured by the advanced distillation curves, is reproduced to within 0.5%.

Introduction

There has been a great deal of interest in recent years on the part of both NASA and the United States Air Force in developing new aerospace fuels, and in the reformulation of existing fuels. One such fuel is Rocket Propellant 1 (RP-1, MIL-P-25576C with amendment 2).¹ This fuel belongs to the general class of hydrocarbon fuels called “kerosenes,” and has been used with liquid oxygen as the oxidizer on vehicles such as the Saturn V launch vehicle (first-stage booster engine),² and more modern engines. Recent interest in developing the capability to reuse rocket motors multiple times (rather than a single time) has led to the reformulation of hydrocarbon fuels such as RP-1 to decrease the level of sulfur compounds, aromatics, and alkenes in the fuel. Three grades of RP-1 were specified with an eye toward decreasing the sulfur concentration specification: TS-30 (total sulfur less than 30 ppm, mass/mass, which was similar to typical as-delivered RP-1), TS-5 (total sulfur less than 5 ppm, mass/mass) and UL RP-1 (ultralow sulfur, less than 100 ppb, mass/mass). Experience showed that ultralow sulfur RP-1 showed significant performance benefits over TS-5 with only marginally greater costs, so this fluid (ultralow) was selected to become “RP-2” (and the RP-1 sulfur limit was lowered from 500 to 30 ppm, mass/mass). Thus, RP-1 and RP-2³ have emerged as the primary kerosene rocket propellants for use in United States rocket motors. We note that the specification for RP-1 and RP-2 aromatic content are the same, however one commonly finds a lower aromatic content in RP-2. Other specifications, including those related to the distillation behavior, viscosity, density, freezing point, and net heat of combustion are identical for RP-1 and RP-2.³

The focus of this work is the modeling of thermophysical properties of RP-1 and RP-2. These fuels are complex mixtures of hundreds of components, and modeling each individual constituent is not feasible. Instead, we use the concept of a surrogate mixture. The general principle is to use a mixture of a relatively small number of components (usually less than 20) to represent the behavior of the actual complex fuel. Edwards and Maurice⁴ reviewed some of the surrogates available for aviation and rocket fuels and provided an overview of the general requirements and expectations of fuel surrogates. There currently are active working groups for developing experimental databases and surrogate models for the kinetics of jet, diesel, and gasoline fuels,^{5–7} and various groups have proposed and studied surrogate fuel mixtures for gasoline, diesel fuel, and aviation turbine fuel.^{8–18} Only two published surrogate mixtures

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for RP-1 exist—the work of Farmer et al.¹⁹ and that of Huang and Sobel.²⁰ We are unaware of any thermophysical property surrogate models for RP-2. Alternative models, based on continuous thermodynamics, have been used for modeling the evaporation of droplets of RP-1.²¹

Surrogate fuel mixtures vary in complexity, and most are intended for specific purposes. Single-component surrogates may be adequate for simple applications such as assessing combustion efficiency.¹¹ However, more complex multicomponent surrogate mixtures are necessary for applications that are dependent upon fuel chemistry, such as soot formation, emissions, radiation loading, combustion staging, or applications involving lean premixed flames. Surrogate mixtures are also relevant to the study of physical properties. Specifically, the properties that describe fuel volatility (distillation properties, vapor pressures, etc.) are needed for the study of preferential vaporization phenomena and pool fire hazards. A surrogate mixture designed for one specific purpose may not be adequate for alternative tasks.

Previously, we used a surrogate model approach to model the thermophysical properties of a synthetic aviation fuel derived from natural gas (referred to as S-8),²² an aviation fuel derived from coal,²³ and RP-1.²⁴ Unfortunately, the sample of RP-1 used in our earlier work was atypical in terms of properties and is therefore of limited usefulness, since it is not representative of currently as-delivered RP-1. In this work, we implement a similar modeling procedure to develop a surrogate mixture for samples of rocket propellants RP-1 and RP-2 that are more typical of as-delivered fuels.

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 candidate fluids is constructed, including 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 developed, and 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 composition that minimizes the difference between the predicted and experimental data for the distillation curve, density, sound speed, viscosity, and thermal conductivity.

The fuel samples of RP-1 and RP-2 were both obtained from the United States Air Force, Air Force Research Laboratory, Propulsion Directorate, and were used without treatment or purification. In an earlier manuscript,²⁵ we reported the analysis of the RP-1 sample by gas chromatography and mass spectrometry and found 24 major constituents (peak area counts in excess of 1%) ranging from 11 carbon fluids such as 2,6-dimethylnonane to 15 carbon fluids such as 2-methyltridecane that represented about 40% of the total area counts. Overall, the sample showed approximately 350 peaks that could be easily distinguished from noise level and perhaps twice that number that were slightly above noise level. The predominant species were linear and branched paraffins, and one and two-ring cyclic paraffins of 11–14 carbon atoms. Aromatics and olefins were not found. The analysis of the sample of RP-2 is described elsewhere.²⁶ The analytical results for RP-2 were similar to the RP-1 sample; there were 28 major constituents (peak area counts in excess of 1%) ranging from 2,6-dimethylnonane to n-hexadecane. The major constituents were comprised of linear and branched paraffins, and one- and two-ring cyclic paraffins of 11–16 carbon atoms with no significant aromatic or olefin content.

From these analyses, we formulated a list of 18 representative compounds to be used for the development of the surrogate; these are provided 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). For each monobranched alkane identified in the chemical analysis, a representative species was selected as a candidate constituent fluid for the surrogates. In other words, 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 compounds for which the most abundant and reliable experimental measurements were available. Our intent was to match the thermophysical properties of a fuel, but the concept of using species representative of what is actually present in the fuel is also applicable to selection of components for studies of soot formation,²⁷ as well as extinction and autoignition.²⁸ We did not consider other factors that may be relevant to some applications, such as knowledge of the kinetic mechanisms of the component or the cost and availability. For each possible constituent fluid, we searched the open literature as well as databases such as NIST TDE,²⁹ DIPPR,³⁰ and

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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)
5-methylnonane	15869-85-9	branched paraffin	10	430.7	438.3
2,4-dimethylnonane	17302-24-8	branched paraffin	11	437.6	445.4
n-decane	124-18-5	linear paraffin	10	439.6	447.3
transdecalin	493-02-7	dicyclic paraffin	10	452.0	460.4
2-methyldecane	6975-98-0	branched paraffin	11	454.4	462.3
n-undecane	1120-21-4	linear paraffin	11	461.1	469.0
propylcyclohexane	4292-92-6	monocyclic paraffin	11	468.3	476.7
α -methyldecalin	2958-75-0	dicyclic paraffin	11	469.6	478.2
3-methylundecane	1002-43-3	branched paraffin	12	478.1	486.3
n-dodecane	112-40-3	linear paraffin	12	481.2	489.4
hexylcyclohexane	4292-75-5	monocyclic paraffin	12	489.7	498.4
5-methyldodecane	17453-93-9	branched paraffin	13	494.7	503.2
n-tridecane	629-50-5	linear paraffin	13	500.2	508.7
heptylcyclohexane	5617-41-4	monocyclic paraffin	13	509.2	517.9
2-methyltridecane	1560-96-9	branched paraffin	14	512.7	521.1
n-tetradecane	629-59-4	linear paraffin	14	518.1	526.7
n-pentadecane	629-62-9	linear paraffin	15	535.0	543.8
n-hexadecane	544-76-3	linear paraffin	16	551.0	560.1

Landolt-Börnstein³¹ for experimental physical property data. For some of the fluids, the data were sparse and were supplemented with predicted values from the TDE²⁹ and DIPPR³⁰ programs.

Since our modeling approach^{22,23} requires thermophysical property models for all pure constituent fluids, it was necessary to have available equations of state and surfaces for the viscosity and thermal conductivity for each of the potential constituent pure fluids. Details of this procedure are available in other work,^{22,23} so we provide only a brief summary here. In our previous work²³ we generated equations of state with the TDE computer program,²⁹ but as part of this project we developed a new regression algorithm that allows the use of very limited experimental data to develop Helmholtz-form equations of state similar to the form developed by Span and Wagner,³² which can represent not only the vapor pressure and density, but also other properties such as the speed of sound and heat capacity. Details on this procedure are presented elsewhere.³³ For viscosity and thermal conductivity, we primarily used an extended corresponding-states model,^{34,35} with n-dodecane as a reference fluid.^{36,37} 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.³⁵ 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 program³⁰). Additionally, we incorporated earlier work on the thermal conductivity of methyl- and propylcyclohexane³⁸ to represent the alkyl cyclohexane family in terms of a scaled form of the thermal conductivity correlation developed for propylcyclohexane. Individual fluid files for use with the REFPROP

software program³⁹ containing the appropriate parameters for a preliminary representation of the thermophysical properties can be obtained from the authors.

For calculations of the thermodynamic properties of mixtures, we used the mixture model⁴⁰⁻⁴² incorporated into the REFPROP computer 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.^{35,43-47} In addition, we used an algorithm developed in earlier work²² to compute the distillation curve; this procedure incorporates data from an improved advanced distillation curve metrology.^{25,48-54}

An extensive measurement program was undertaken to obtain experimental data for the thermophysical properties of RP-1 and RP-2.⁵⁵ Measurements were made of the advanced distillation

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Table 2. Composition of the Surrogate Mixtures

fluid	composition, mole fraction	
	RP-1 surrogate	RP-2 surrogate
α -methyldecalin	0.354	0.354
5-methylnonane	0.150	0.084
2,4-dimethylnonane	0.000	0.071
n-dodecane	0.183	0.158
heptylcyclohexane	0.313	0.333

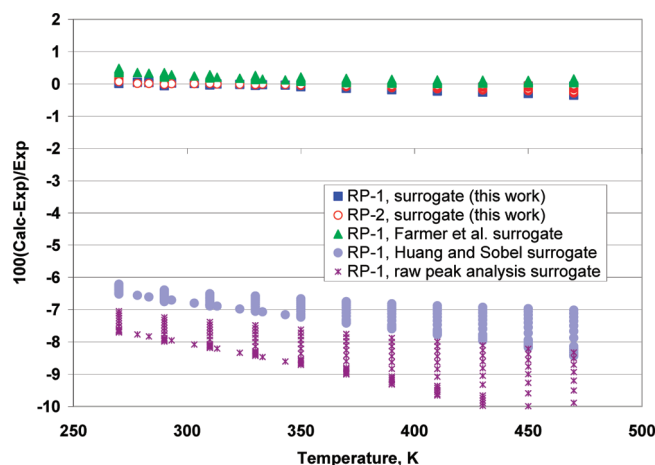
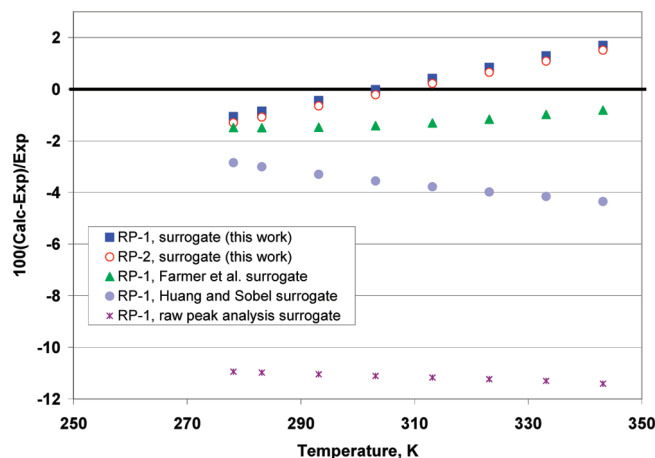
curves,²⁶ viscosity,⁵⁶ density,⁵⁶ speed of sound,⁵⁶ and thermal conductivity.^{55,57} Additional studies on the decomposition of these fuels^{58–61} were undertaken. The decomposition studies focus on measurement of global pseudofirst-order rate constants for the decomposition, and the measurement protocol includes a separate analysis of the vapor and liquid phases.⁶² The decomposition measurements aided in planning the properties experiments; they were not used directly in the determination of the surrogate model. The properties measurements formed the basis of the experimental data set used to develop the surrogate model. 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. The objective function was the sum of the squared percentage differences between the experimental data and the predicted value. The independent variables were the compositions of the fluid mixture. Our initial guess included all of the components in Table 1. Successive calculations gave very small concentrations of some components, and these were then removed from the mixture, and the minimization process was repeated until further reductions in the number of components resulted in unacceptably large deviations with the experimental data. The final surrogate mixtures contained only four components for RP-2 and five components for RP-1.

The final compositions of the surrogate mixtures are summarized in Table 2. The surrogate for RP-1 contains the four components: α -methyldecalin, 5-methylnonane, n-dodecane and heptylcyclohexane; and the surrogate for RP-2 contains one additional component: 2,4-dimethylnonane. Table 3 presents some calculated properties of the surrogates. The net heat of combustion was computed by a mole-fraction average of the component enthalpies, ignoring the enthalpy of mixing.²⁶ The constituent heats of combustion were obtained from the DIPPR database.³⁰ When available, experimental data for heat of combustion were used; otherwise, predictions from the DIPPR database³⁰ implementing the Cardozo method of equivalent chains were utilized. The calculated density; kinematic viscosity at 238.7 K (−30 °F); hydrogen, aromatic, and olefin content; and heat of combustion meet the military specifications for RP-1 and RP-2.³ The values of the critical point (T_c , p_c , and ρ_c) are obtained by calculation from the mixture model given the surrogate compositions of RP-1 and RP-2.

Table 3. Selected Calculated Characteristics of the Surrogate Mixtures

property	RP-1 surrogate	RP-2 surrogate
MW	163.5	164.6
formula	$C_{11.66}H_{23.32}$	$C_{11.74}H_{23.40}$
H/C	2.00	1.99
heat of combustion, J/mol	-7.18×10^6	-7.23×10^6
density ^a at 288.7 K (60 °F), kg/m ³	808.1	809.5
speed of sound ^a at 288.7 K, m/s	1330.9	1330.3
Thermal conductivity at 288.7 K, mW/m•K	112.76	111.34
Viscosity ^a at 288.7 K, mPa•s	1.90	1.98
initial boiling point (K)	475.6	476.7
kinematic viscosity ^a at 238.7 K (−30 °F) cm ² /s	0.098	0.106
T_c (K)	677	678
p_c (kPa)	2210	2204
ρ_c (kg/m ³)	235	240

^a At 101.325 kPa.

**Figure 1.** Deviation plot of calculated and experimental density.**Figure 2.** Deviation plot of calculated and experimental speed of sound.

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In Figures 1–5, we present comparisons of our surrogate models with experimental data. We also show results calculated with two surrogate models for RP-1 from the literature—the model of Farmer and co-workers¹⁹ and a surrogate developed by Huang and Sobel.²⁰ The calculations are done with our property models, but with the application of surrogate compositions provided in the Farmer¹⁹ and Huang²⁰ manuscripts. The RP-1 surrogate model presented by Farmer et al.¹⁹ contains 13 components. This model¹⁹ was developed primarily to provide thermodynamic and physical properties for use in computational fluid dynamic codes for the analysis of rocket propulsion system

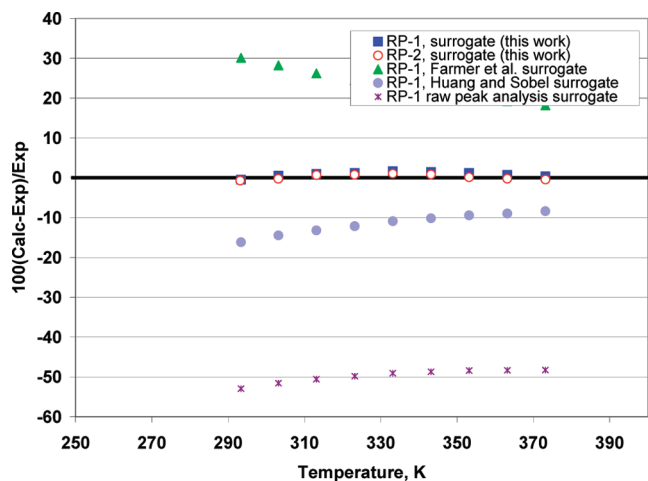


Figure 3. Deviation plot of calculated and experimental viscosity.

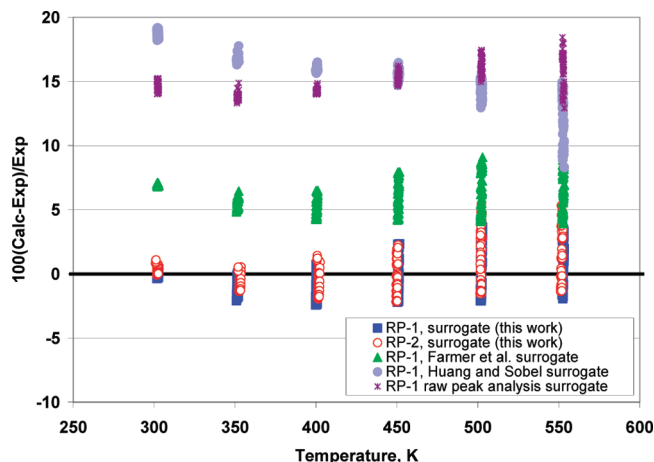


Figure 4. Deviation plot of calculated and experimental thermal conductivity.

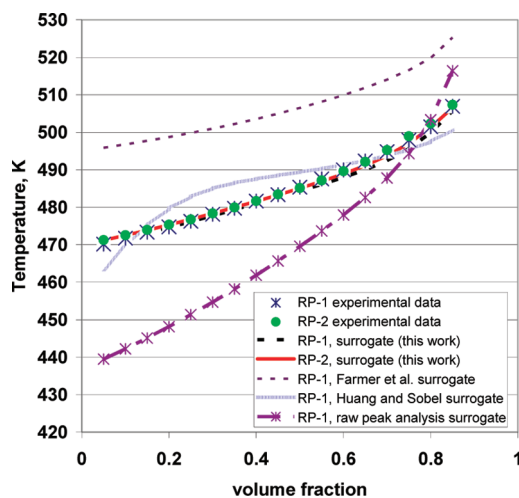


Figure 5. Distillation curves of RP-1 and RP-2. The points listed as experimental data were measured with the ADC method.

performance and operational characteristics. Among the 13 components are linear paraffins *n*-undecane through *n*-tetradecane; alkylcyclohexanes from *n*-hexyl to *n*-nonylcyclohexane; the aromatic compounds pentamethylbenzene, hexamethylbenzene, and dimethylnaphthalene; and two unspecified polycyclic paraffins with molecular formulas $C_{11}H_{20}$ and $C_{12}H_{22}$. This surrogate¹⁹ has the general formula $C_{12.39}H_{24.15}$, a H/C ratio of 1.9492, a general molecular mass of 173.1453, and a liquid density of 811.1 kg/m³. For our calculated comparisons with

this model, we used α -methyldecalin for $C_{11}H_{20}$ and bicyclohexyl for $C_{12}H_{22}$, and 2,6-dimethylnaphthalene for dimethylnaphthalene. An alternative surrogate for RP-1 was developed by Huang and Sobel²⁰ for modeling the physical and thermodynamic properties for endothermic fuel-cooled applications. This surrogate has six components: the linear alkanes from *n*-undecane to *n*-pentadecane and ethylcyclohexane.²⁰

Finally, we show calculations performed with a surrogate model that we call the “raw peak analysis surrogate”. This surrogate is obtained by simply taking all 24 major components (peak area counts in excess of 1%) found from the gas chromatography and mass spectrometry analysis mentioned earlier,²⁵ and normalizing the concentrations to 100%. This normalization procedure was necessary since the major peak analysis represented approximately 40% of the total area counts. Equations of state for compounds not present in Table 1 were generated by the TDE computer program,²⁹ with transport properties estimated by extended corresponding states.³⁵ These results are considered as predictive or estimates, due to the lack of experimental data for some of these fluids.

Figure 1 shows the deviations between the surrogate models and experimental density data of Outcalt et al.⁵⁶ Measurements were over the temperature range 270–470 K and at pressures up to 40 MPa with an estimated uncertainty of 0.1%. Our surrogate models and the Farmer¹⁹ surrogate have deviations within 0.5% over the entire range of conditions explored experimentally. The Huang and Sobel²⁰ surrogate contains roughly 80 mol % linear alkanes, and calculated densities from this model are less than the experimental measurements^{55,56} by about 6–8%. The raw peak analysis surrogate shows similar results as the Huang and Sobel²⁰ model, except it has somewhat greater negative deviations. At atmospheric pressure, the RP-1 and RP-2 models presented in this work have density deviations of 0.1%, which is at the level of uncertainty of the experimental data. The density of the RP-1 sample is not significantly different than the RP-2 sample, with the RP-1 sample having densities about 0.2% lower than RP-1 at atmospheric pressure. Additional details on the density measurements can be found in refs 55 and 56.

The deviations between the values of the speed of sound calculated from the surrogate models and the experimental data of Outcalt et al.⁵⁶ are shown in Figure 2. All measurements were taken at atmospheric pressure and have an estimated uncertainty of 0.1%. None of the models are able to represent the data to within its experimental uncertainty; however, all models except the raw peak analysis surrogate have deviations within about 4%. (The larger deviations seen for the raw peak analysis surrogate are presumed to be indicative of limitations in the EOSs for some of the constituent fluids that are based on predictions). The RP-1 and RP-2 models we have developed in this work show deviations within 2%. We also note that the compositional differences between RP-1 and RP-2 do not greatly affect the speed of sound; the differences in this property for the two samples were within 0.3%, with RP-1 having slightly lower sound speed.

Figure 3 shows the deviations of the surrogate models and the experimental viscosity data.⁵⁶ The RP-1 surrogate developed in this work is significantly better for viscosity than calculations made with compositions of the surrogate models in the literature.^{19,20} The Farmer model overpredicts the viscosity by approximately 18–30%, with the largest deviations occurring at the lowest temperatures, whereas the Huang and Sobel model underpredicts the viscosity with deviations approaching 20% at the lowest temperatures. The raw peak analysis surrogate has

even larger negative deviations. Our RP-1 and RP-2 surrogate models show deviations within 2%, while the experimental uncertainty is estimated to be 1.5%. Of the properties that we have examined, the viscosity is one of the most sensitive to the compositional differences between RP-1 and RP-2; the atmospheric pressure viscosity of RP-1 is lower than RP-2 by 3.3–4.9% over the temperature range 293.4–373.15 K, with the largest differences at the lowest temperatures.

Figure 4 demonstrates the performance of the surrogate models for the thermal conductivity. The measurements⁵⁵ covered temperatures from approximately 300 K to a maximum of 550 K, at pressures up to 60 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; the surrogate of Farmer and co-workers¹⁹ has slightly larger deviations, ranging from approximately 4 to 9%, showing a tendency to overpredict the thermal conductivity. The Huang and Sobel²⁰ surrogate and raw peak analysis surrogates have even larger positive deviations. The experimental measurements show that the thermal conductivity of RP-1 is slightly greater than the thermal conductivity of RP-2 at similar conditions; details on the experimental measurement are presented in ref 55.

Our final comparison with experimental data is presented in Figure 5, which shows the calculated and experimental advanced distillation curves.^{25,26} The distillation curve for RP-1 is almost identical to that of RP-2, and the surrogate models of this work represent the curves well, to within 0.5%. The Farmer surrogate model predicts much higher temperatures for the distillation and overpredicts the curve by more than 20 K. The shape of the distillation curve computed with the model of Huang and Sobel²⁰ is slightly different than the experimental curve, but the temperature values are within 1.5% of experiment. The raw peak analysis surrogate underpredicts the early part of the distillation curve by 30 K, and overpredicts the late end of the curve by almost 20 K.

The raw peak analysis surrogate contains fluids that were found to be present in the RP-1 fuel sample, but the analysis represented only 40% of the peaks in the sample. Even if one could use a more detailed analysis containing perhaps 350 compounds that would incorporate almost 100% of the peak counts, we do not think this would be a productive approach for several reasons. First of all, it is difficult to develop property models for all of these fluids since many lack experimental data,

and we lack information on mixture interactions for these fluids as well. Second, as the number of constituent fluids increases, the time required to calculate properties becomes excessive. We argue that the approach that we use, to develop a surrogate containing a limited number of constituent fluids that are either present, or chemically similar to, those found in the sample by gas chromatography/ mass spectrometry, is a more practical approach. The initial chemical analysis, although it cannot be used directly as a surrogate, is nevertheless extremely important as it allows one to include chemically relevant fluids in the slate of potential fluids for the surrogate.

Conclusions

Determination of the best surrogate model for a complex fluid depends upon the intended application. We have demonstrated that our surrogate model for RP-1 is superior to existing surrogate models in the literature for the simultaneous representation of thermodynamic (density, sound speed, and volatility) and transport (viscosity and thermal conductivity) properties. We also present a surrogate model for Rocket Propellant RP-2. The density, sound speed, viscosity, and thermal conductivity of both fuels are represented to within (at a 95% confidence level) 0.4, 2, 2, and 4%, respectively. The volatility behavior shown by the advanced distillation curves is reproduced to within 0.5%. The range of applicability of this model is determined mainly by the range of applicability of the constituent fluids and is estimated to be valid for temperatures to 800 K and pressures to 60 MPa.

Our surrogate models represent the thermophysical properties of the two samples studied. However, future work is needed to determine how much variability there is for different samples of the two rocket propellants; this may impact how well these surrogates represent an actual fuel sample.

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