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General method for prediction of thermal conductivity for well-characterized hydrocarbon mixtures and fuels up to extreme conditions using entropy scaling

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Abstract

A general and efficient technique is developed to predict the thermal conductivity of well-characterized hydrocarbon mixtures, rocket propellant (RP) fuels, and jet fuels up to high temperatures and high pressures (HTHP). The technique is based upon entropy scaling using the group contribution method coupled with the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state. The mixture number averaged molecular weight and hydrogen to carbon ratio are used to define a single pseudo-component to represent the compounds in a well-characterized hydrocarbon mixture or fuel. With these two input parameters, thermal conductivity predictions are less accurate when the mixture contains significant amounts of iso-alkanes, but the predictions improve when a single thermal conductivity data point at a reference condition is used to fit one model parameter. For eleven binary mixtures and three ternary mixtures at conditions from 288 to 360 K and up to 4,500 bar, thermal conductivities are predicted with mean absolute percent deviations (MAPDs) of 16.0 and 3.0% using the two-parameter and three-parameter models, respectively. Thermal conductivities are predicted for three RP fuels and three jet fuels at conditions from 293 to 598 K and up to 700 bar with MAPDs of 14.3 and 2.0% using the two-parameter and three-parameter models, respectively.

Introduction

Advanced computational fluid dynamics (CFD) approaches have been utilized to simulate the performance of fuel injection equipment systems and to investigate phenomena, such as cavitation and fuel atomization [1-7]. The outcomes of CFD simulation at conditions up to high pressures are dependent on accurate representation of fluid physical properties. For extreme conditions, limited experimental thermal conductivity data are available for well-characterized hydrocarbon mixtures, and there is a greater lack of thermal conductivity data available for complex mixtures, such as rocket propellant (RP), jet, and diesel fuels. Various correlations and

theories have been developed for the prediction of thermal conductivity for pure hydrocarbons [8-32] and their mixtures [13, 21-23, 30, 33-37] including structure-based group-contribution methods [38-44].

A few pseudo-component based methodologies have been developed to model the thermal conductivity of complex mixtures, such as crude oil and its fractions. These methodologies include an expanded fluid-based (EFB) model [37, 45] and a corresponding-states approach defined by an effective carbon number (ECN) [21]. Yarranton and co-workers [37] used EFB to model the thermal conductivity of several crude oils up to 100 bar and 398 K. They fit four EFB pseudo-component parameters for the crude oils to available experimental data and predicted the thermal conductivity within 1% mean absolute percent deviation (MAPD) compared to experimental data [37]. They extended this work by developing structure independent correlations to calculate the EFB parameters and obtained predictions within 3% MAPD [45]. Teja and Tarlneu [21] used the ECN-based approach to predict the thermal conductivity of different cuts of three crude oils at temperatures from 308 to 528 K and atmospheric pressure within 7% MAPD. Their ECN-based model required as inputs the average molecular weight (MW) and critical properties of the pseudo-components, which were calculated using the reported boiling temperature and specific gravity of the pseudo-components [46] through the correlations developed by Kesler and Lee [47].

The two-abovementioned pseudo-component based techniques capture the effect of composition only through the mixture average MW and are limited in predictive capability by the need for multiple pseudo-components or for fitting to experimental data. Hence, a technique is needed that considers the effects of both the molecular structure and MW of compounds present in mixtures while only requiring a minimum number of parameters fit to experimental data.

In this study, a single pseudo-component technique is developed using the residual entropy scaling based thermal conductivity correlation of Hopp and Gross [26] and the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) [48] equation of state (EoS). Thermal conductivities of well-characterized hydrocarbon mixtures and fuels are predicted up to high temperature and high pressure (HTHP) conditions using two mixture properties: the number averaged MW and hydrogen to carbon (HN/CN) ratio. Less accurate predictions are obtained using the two-parameter model for the mixtures containing high amounts of iso-alkanes, but the predictions are improved when a single thermal conductivity data point at a reference condition is used to fix the value of one model parameter. The technique described here accurately predicts thermal conductivity up to HTHP conditions for fourteen well-characterized hydrocarbon mixtures and six fuels.

Technique Development

PC-SAFT pseudo-component technique

For pure compounds which do not exhibit association, the PC-SAFT EoS of Gross and Sadowski [48] requires three input parameters: m , the number of segments; σ , the segment diameter; and ε/k , the depth of the potential well. The reduced, residual Helmholtz free energy, \tilde{a}^{res} , of a pure compound is then expressed as:

$$\tilde{a}^{\text{res}} = \tilde{a}^{\text{hc}} + \tilde{a}^{\text{disp}} \quad (1)$$

where \tilde{a}^{hc} and \tilde{a}^{disp} are the reduced, Helmholtz free energies for the hard-chain reference fluid and dispersion interactions, respectively. Pure compound PC-SAFT parameters are determined by directly fitting to properties (*e.g.*, saturated liquid density and vapor pressure data) or using group contribution (GC) methods [49-51]. In this study, the PC-SAFT parameters are determined using the GC parameters of Sauer et al. [49] to be consistent with our earlier reported technique to predict

viscosity [52]. However, in general, other PC-SAFT GC parameters could be used, such as those reported by Tihic et al. [53] or Burgess et al. [54]. PC-SAFT parameters are fit as a function of molecular weight (MW) for a given chemical family. Table 1 presents the correlations for m , $m\sigma$, and ε/k for n-alkanes and poly-nuclear aromatics (PNAs), which provide numerical bounds for the m , σ , and ε/k values of other chemical families [55].

Equations 2-4 use a Z parameter to average the contributions from the two bounds. Z varies from zero for n-alkanes to one for PNAs, and is used to normalize the degree of unsaturation (DoU), as shown in Eq. 5. Equations 6 and 7 are used to calculate the pseudo-component DoU knowing the mixture number averaged MW and HN/CN ratio. Here we note that phenanthrene (MW = 178 g/mol, DoU = 10) is the largest PNA in the hydrocarbon mixtures and fuels [55]. Hence, the upper bound value for DoU is fixed at 10 in Eq. 5 when the mixture number averaged MW is greater than 178 g/mol. The DoU correlation for PNAs as a function of MW is provided in the Supplemental Information (SI). More details on the calculation of the PC-SAFT pseudo-component parameters can be found in our previous study [55]. A commercial software (VLXE/Blend [56]) is used to calculate the reduced residual entropy, \tilde{s}^{res} , shown in Eq. 8, where \bar{s}^{res} is equal to the molar residual entropy divided by the gas constant, R . The next section describes the steps needed for the calculation of the thermal conductivity knowing \tilde{s}^{res} .

Table 1. Correlations [52] for PC-SAFT parameters as a function of MW (g/mol) for n-alkanes and PNAs based on the GC parameters of Sauer et al. [49].

	n-alkanes	PNAs
m	$0.0325MW + 0.2463$	$0.0231MW + 0.7392$
$m\sigma$ (Å)	$0.1265MW + 0.7564$	$0.0874MW + 2.6366$
ε/k (K)	$\exp(5.4762 - 1.3302/MW)$	$\exp(5.8137 - 15.5490/MW)$

$$m_{\text{pseudo-component}} = (1 - Z)m_{\text{n-alkane}} + Zm_{\text{PNA}} \quad (2)$$

$$(m\sigma)_{\text{pseudo-component}} = (1 - Z)(m\sigma)_{\text{n-alkane}} + Z(m\sigma)_{\text{PNA}} \quad (3)$$

$$\left(\frac{\varepsilon}{k}\right)_{\text{pseudo-component}} = (1 - Z)\left(\frac{\varepsilon}{k}\right)_{\text{n-alkane}} + Z\left(\frac{\varepsilon}{k}\right)_{\text{PNA}} \quad (4)$$

$$Z = \begin{cases} \frac{\text{DoU}_{\text{pseudo-component}}}{\text{DoU}_{\text{PNA}}}, & \text{MW}_{\text{pseudo-component}} < 178 \text{ g/mol} \\ \frac{\text{DoU}_{\text{pseudo-component}}}{10}, & \text{MW}_{\text{pseudo-component}} \geq 178 \text{ g/mol} \end{cases} \quad (5)$$

$$\text{CN} = \frac{\text{MW}_{\text{pseudo-component}}}{12.01 + 1.01(\text{HN/CN})_{\text{pseudo-component}}} \quad (6)$$

$$\text{DoU} = \frac{1}{2}(2 \times \text{CN} + 2 - \text{HN}) \quad (7)$$

$$\tilde{s}^{\text{res}}(V, T) = -\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial T}\right)_V \quad (8)$$

Entropy scaling based pseudo-component technique

As observed by Rosenfeld [57], the reduced thermal conductivity, λ^* , (Eq. 9) of a pure compound scales with the residual entropy. Hopp and Gross [26] investigated several choices of a reference thermal conductivity including Chapman Enskog (CE), CE with Eucken correction, and the reference proposed by Liang and Tsai [58] based on the work of Stiel and Thodos [59]. None of these references was completely successful in describing the nonlinear entropy scaling behavior for the complete fluid space from low-density gas to dense liquid. Hopp and Gross [26] proposed a new, empirically-based reference that did correlate the complete fluid space and allowed for a mono-variable dependence on reduced residual entropy. Hopp and Gross [26] showed that the CE reference thermal conductivity (Eq. 10) can adequately reproduce λ^* in the dense fluid region,

which is the region of interest in the present study. Hence, the CE reference term is used as the reference thermal conductivity in the present study.

$$\lambda^* = \frac{\lambda}{\lambda_{\text{reference}}} \quad (9)$$

$$\lambda_{\text{reference}} = \lambda_{\text{CE}} = \frac{5}{16} \frac{\sqrt{MWkT/(mN_A\pi)}}{\sigma^2 \Omega^{(2,2)*}} \quad (10)$$

where, k , T , N_A , and $\Omega^{(2,2)*}$ are Boltzmann's constant, temperature, Avogadro's number, and the reduced collision integral, respectively. In Eq. 10, m and σ are the PC-SAFT parameters of a pure compound when calculating thermal conductivity for a pure compound or are those of a pseudo-component when calculating thermal conductivity of a pseudo-component. Hopp and Gross [26] modified the third-order polynomial reported by Lötgering-Lin and Gross [60] for viscosity and proposed Eq. 11 to correlate λ^* to the reduced, dimensionless residual, entropy, s^* (Eq. 12).

$$\ln(\lambda^*) = A + Bs^* + C(1.0 - \exp(s^*)) + Ds^{*2} \quad (11)$$

$$s^* = \left(\frac{\tilde{s}^{\text{res}}(V, T)}{m} \right) \quad (12)$$

where A , B , C , and D are the thermal conductivity coefficients. In the present study, instead of using Eq. 11 to calculate λ^* , the simpler expression in Eq. 13 is used since it adequately describes liquid-phase thermal conductivities.

$$\ln(\lambda^*) = A + Bs^* + Cs^{*2} + Ds^{*3} \quad (13)$$

where the thermal conductivity coefficients of a pure compound are used when calculating thermal conductivity of a pure compound or those of a pseudo-component are used when calculating the thermal conductivity of a pseudo-component.

Hopp and Gross [26] used Eq. 11 to fit thermal conductivity coefficients for 148 pure compounds that included normal and iso-alkanes, alkenes, aldehydes, ethers, esters, ketones, alcohols, acids, and benzenes. However, they did not report parameters for some compounds from chemical classes present in petro-fuels including cyclohexanes, decalins, tetralins, indanes, naphthalenes, and phenanthrenes due to the limited amount of thermal conductivity data available in the literature. In the pseudo-component approach, n-alkanes and PNAs are the two bounds for values of the thermal conductivity coefficients. Since Hopp and Gross [26] did not report coefficients for n-alkanes and PNAs using only the CE reference term, new pure compound liquid phase thermal conductivity coefficients (*i.e.*, A, B, C, D) are fit in the present study.

For many n-alkanes and PNAs, experimental thermal conductivity data at HTHP conditions are not reported in the literature. Thus, experimental thermal conductivities at atmospheric pressure are utilized here to fit the n-alkane parameters. Experimental data is lacking for PNAs even at atmospheric pressure, with the exception of benzene. Briggs [61] reported a thermal conductivity correlation as a function of temperature at atmospheric pressure for some PNAs (*i.e.*, benzene, naphthalene, and phenanthrene). However, thermal conductivities of benzene using the Briggs correlation deviate by up to 8% compared to data reported in the Dortmund Data Bank (DDB) [62] containing data of Rastorguev and Pugach [63]. Here we use the model of Gharagheizi et al. [38] for benzene at atmospheric pressure to predict thermal conductivity within 4% of the DDB. Furthermore, since no other experimental data for heavier PNAs are available to assess the accuracy of the Briggs correlation [61], the model of Gharagheizi et al. [38] is also used

to calculate the thermal conductivities of naphthalene and phenanthrene (PNAs) at atmospheric pressure. More information on the differences between the thermal conductivities of benzene, naphthalene, and phenanthrene using these two approaches is reported in the SI. Table 2 lists coefficients A , B , C and D fit to Eq. 13 for selected n-alkanes and PNAs. For n-alkanes, A does not vary monotonically with MW. B decreases with MW, whereas C and D appear constant for n-alkanes. For PNAs, A , B , and C monotonically increase with MW, whereas D is a constant. Figure 1 shows these coefficients plotted versus MW for n-alkanes and PNAs, and the correlations are listed in Table 3.

Table 2. Thermal conductivity coefficients fit to atmospheric pressure data using Eq. 13 for selected n-alkanes and PNAs.

Compounds	A	B	C	D	$T_{\text{range}} / \text{K}$	$\lambda_{\text{range}} / \text{Wm}^{-1}\text{K}^{-1}$	Reference
n-octane	0.482	-0.972	-0.001	0.013	298-348	0.127-0.112	Kashiwagi et al. [64]
n-decane	0.482	-0.990	-0.001	0.013	303-373	0.130-0.110	Kashiwagi et al. [64]
n-undecane	0.482	-1.002	-0.001	0.013	292-364	0.135-0.120	Wada et al. [65]
n-dodecane	0.482	-1.008	-0.001	0.013	298-373	0.136-0.119	Kashiwagi et al. [64]
n-tetradecane	0.506	-1.009	-0.001	0.013	284-363	0.143-0.126	Wada et al. [65]
n-hexadecane	0.506	-1.024	-0.001	0.013	296-362	0.144-0.132	Wada et al. [65]
benzene	0.303	-1.362	-0.217	-0.013	279-413	0.145-0.118	Gharagheizi et al. [38]
naphthalene	0.367	-1.307	-0.195	-0.013	354-545	0.126-0.088	Gharagheizi et al. [38]
phenanthrene	0.415	-1.293	-0.183	-0.013	375-483	0.129-0.107	Gharagheizi et al. [38]

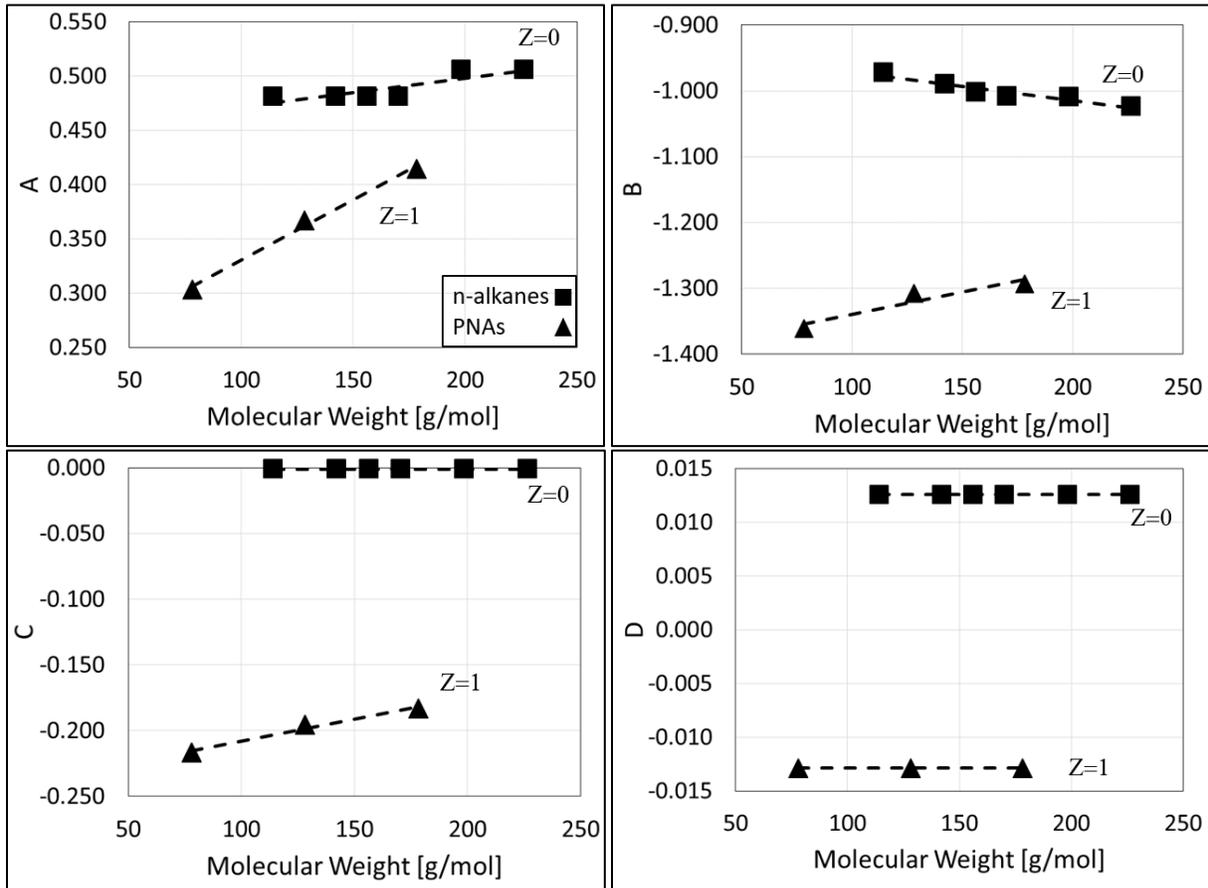


Figure 1. Effect of molecular weight (g/mol) on thermal conductivity coefficients for selected compounds from n-alkanes and PNAs. Note that the y-axis scale is different in each figure.

Table 3. Thermal conductivity coefficient correlations as a function of MW (g/mol) fit to selected compounds from n-alkanes and PNAs.

Coefficient	n-alkanes	PNAs
<i>A</i>	$2.6702 \times 10^{-4}MW + 4.4472 \times 10^{-1}$	$1.1140 \times 10^{-3}MW + 2.1893 \times 10^{-1}$
<i>B</i>	$-4.2810 \times 10^{-4}MW - 9.2891 \times 10^{-1}$	$6.8258 \times 10^{-4}MW - 1.4083 \times 10^0$
<i>C</i>	-1.0012×10^{-3}	$3.3215 \times 10^{-4}MW - 2.4099 \times 10^{-1}$
<i>D</i>	1.2568×10^{-2}	-1.2867×10^{-2}

In our previous study [52], the viscosity coefficients for chemical classes present in fuel were scaled with PC-SAFT parameter m , so that parameter values for n-alkanes and PNAs bounded parameter values for all other chemical families. Due to the lack of thermal conductivity data available in the literature for the pure compounds from different chemical classes found in fuels, only the thermal conductivity coefficients for n-alkanes and PNAs are considered here and the coefficients for the two groups are assumed to be the two bounds for the pseudo-component thermal conductivity coefficients in Eq. 13. The Z value, calculated using Eq. 5, is used in Eqs. 14-17 to calculate the pseudo-component thermal conductivity coefficients needed for the calculation of the reduced thermal conductivity using Eq. 13.

$$A_{\text{pseudo - component}} = (1 - Z)A_{\text{n - alkane}} + ZA_{\text{PNA}} \quad (14)$$

$$B_{\text{pseudo - component}} = (1 - Z)B_{\text{n - alkane}} + ZB_{\text{PNA}} \quad (15)$$

$$C_{\text{pseudo - component}} = (1 - Z)C_{\text{n - alkane}} + ZC_{\text{PNA}} \quad (16)$$

$$D_{\text{pseudo - component}} = (1 - Z)D_{\text{n - alkane}} + ZD_{\text{PNA}} \quad (17)$$

When applying this approach to well-characterized hydrocarbon mixtures and fuels, thermal conductivity predictions improve by fitting B to a single reference state data point. In this study, the reference state is chosen as the experimental data point at the lowest reported temperature and pressure for the samples of interest. Coefficient B is fit to reproduce the thermal conductivity at the reference state, while A , C , and D are determined from Eqs. 14, 16, and 17. The results for the two-parameter and three-parameter models are described in the following sections for well-characterized hydrocarbon mixtures and fuels.

The thermal conductivity predictions are compared with 655 data points for well-characterized hydrocarbon mixtures, rocket propellant fuels, and jet fuels. The performance of our approach is characterized by the percent deviation, maximum (Max) deviation, standard deviation (SD), MAPD, and bias, in Eqs. 18-22.

$$Deviation (\%) = 100 \times \frac{(\lambda_{\text{predict}} - \lambda_{\text{exp}})}{\lambda_{\text{exp}}} \quad (18)$$

$$Max\ Deviation (\%) = Max \left(100 \times \frac{|\lambda_{\text{predict}} - \lambda_{\text{exp}}|}{\lambda_{\text{exp}}} \right) \quad (19)$$

$$SD (\%) = \sqrt{\frac{\sum(\lambda - \bar{\lambda})^2}{N - 1}} \quad (20)$$

$$MAPD (\%) = \frac{1}{N} \sum 100 \times \frac{|\lambda_{\text{predict}} - \lambda_{\text{exp}}|}{\lambda_{\text{exp}}} \quad (21)$$

$$Bias (\%) = \frac{1}{N} \sum 100 \times \frac{(\lambda_{\text{predict}} - \lambda_{\text{exp}})}{\lambda_{\text{exp}}} \quad (22)$$

where, λ_{predict} , λ_{exp} , $\bar{\lambda}$, and N are the experimental thermal conductivity, the predicted thermal conductivity, the mean of the thermal conductivity, and the number of data points, respectively.

Well-characterized hydrocarbon mixtures

The pseudo-component technique is applied to several binary and ternary hydrocarbon mixtures [65-67]. Wakeham et al. [66] measured the thermal conductivity for binary mixtures containing benzene and tri-methyl-pentane (TMP) (referred to as M1) for two different compositions at temperatures from 313 to 345 K and pressures up to 3,500 bar. Fareleira et al. [67] and Wakeham et al. [66] reported thermal conductivity data for binary mixtures containing n-heptane (C7) and TMP (referred to as M2) for three different compositions at temperatures from 308 to 360 K and pressures up to 4,500 bar. Wada et al. [65] reported the thermal conductivity data for binary mixtures containing C7 and n-undecane (C11), C7 and n-hexadecane (C16), and

C11 and C16 (referred to as M3, M4, and M5, respectively) for three different compositions for each mixture at atmospheric pressure and a range of temperatures from 295 to 345 K. Wada et al. [65] also reported the thermal conductivity for ternary mixtures (referred to as M6) including C7, C11, and C16 for three compositions at temperatures from 295 to 345 K and 1 bar. Table 4 lists the molar composition of these mixtures. For brevity, only central compositions of mixtures M3-M6 (referred to as M3-2, M4-2, M5-2, and M6-2, respectively) are shown in the figures. However, all mixture compositions of mixtures M3-M6 are included in the reported statistical metrics.

Table 4. Molar composition (mol%) of the well-characterized hydrocarbon mixtures studied in this work. Data from ref. [65-67]

Compound	Chemical Family	M1	M2 ^a	M3	M4	M5	M6
n-heptane	n-alkanes	-	48.9	25.0	-	25.0	10.0
			74.4	50.0		50.0	33.4
			75.1	75.0		75.0	59.9
n-undecane	n-alkanes	-	-	balance	25.0	-	29.9
					50.0		33.3
n-hexadecane	n-alkanes	-	-	-	75.0	balance	30.0
					balance		balance
tri-methyl-pentane (TMP)	iso-alkanes	25.0	balance	-	-	-	-
		75.0					
benzene	benzenes	balance	-	-	-	-	-

^a The composition of mixture M2 containing 74.4 mol% C7 and 25.6 mol% TMP measured by Fareleira et al. [67] is close to that of the mixture containing 75.1 mol% C7 and 24.9 mol% TMP measured by Wakeham et al. [66], and the two data sets agree within 0.05%. Both sets of data are included in the reported statistics in Table 5, but only the data reported by Wakeham et al. [66], which have a greater temperature range, are shown in Figures 2 and 4.

Figures 2 and 3 present the thermal conductivity predictions for the investigated hydrocarbon mixtures at different temperatures and pressures. Figures 4 and 5 show the thermal conductivity prediction deviations for these mixtures. The SI provides information on the calculated MW, HN/CN ratio, Z parameter, thermal conductivity experimental data point (λ_0) at the lowest reported temperature and pressure used to fit B in the three parameter model, the PC-SAFT parameters, and the thermal conductivity coefficients for the pseudo-components for all of the well-characterized hydrocarbon mixtures considered in this study. Table 5 summarizes the statistical metrics of the thermal conductivity predictions for these mixtures.

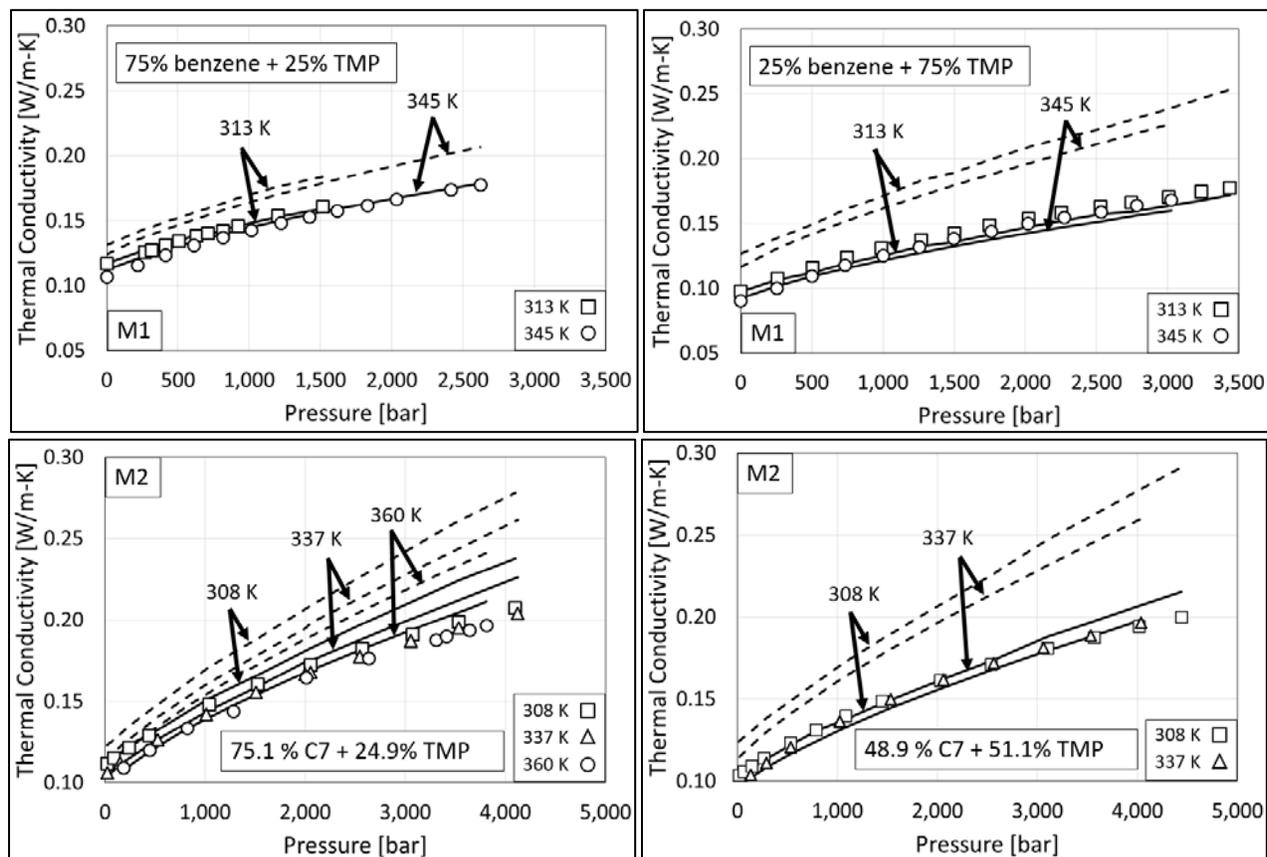


Figure 2. Pseudo-component thermal conductivity predictions compared to experimental data [66, 67] (symbols) for mixtures M1 and M2. Dashed lines show the two-parameter calculations and solid lines show the three-parameter calculations.

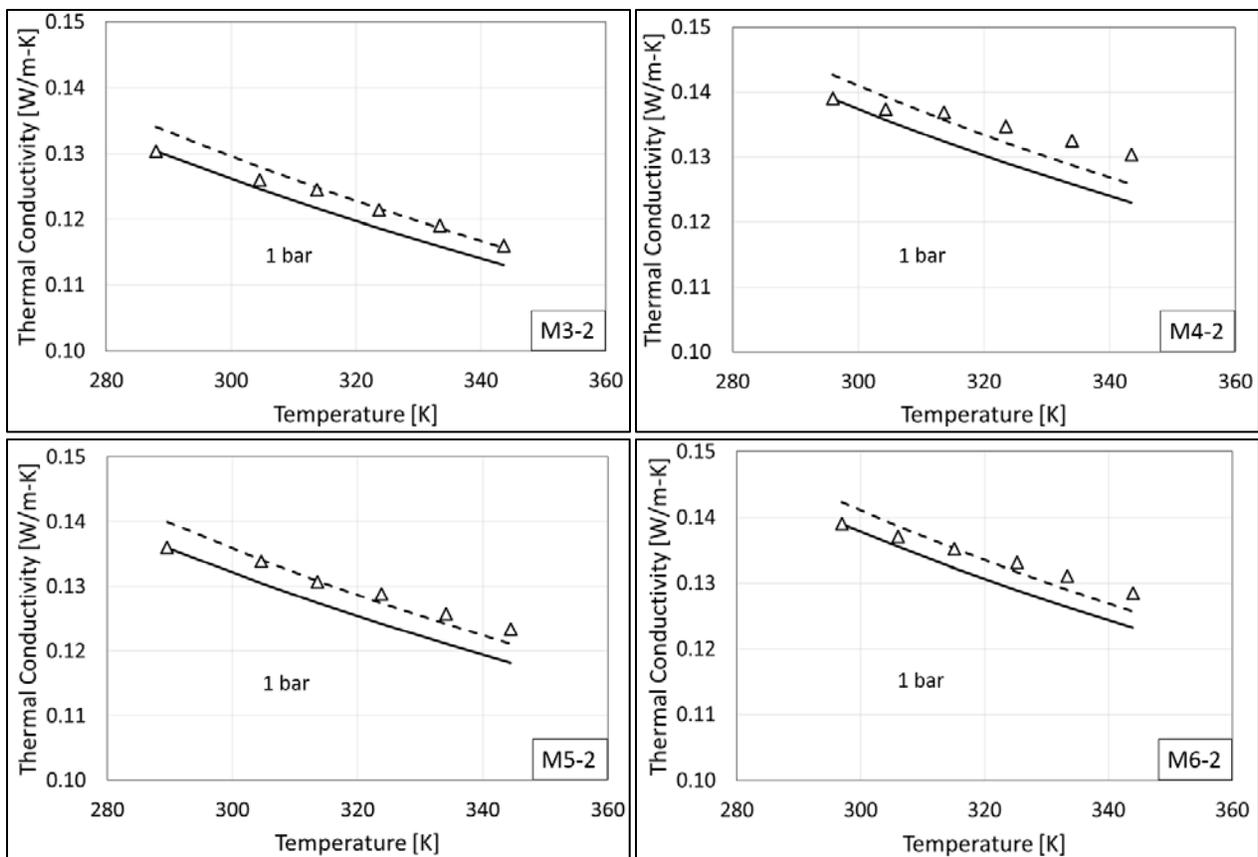


Figure 3. Pseudo-component thermal conductivity predictions compared to experimental data [65] (symbols) for mixtures M3-2 to M6-2. Dashed lines show the two-parameter calculations and solid lines show the three-parameter calculations.

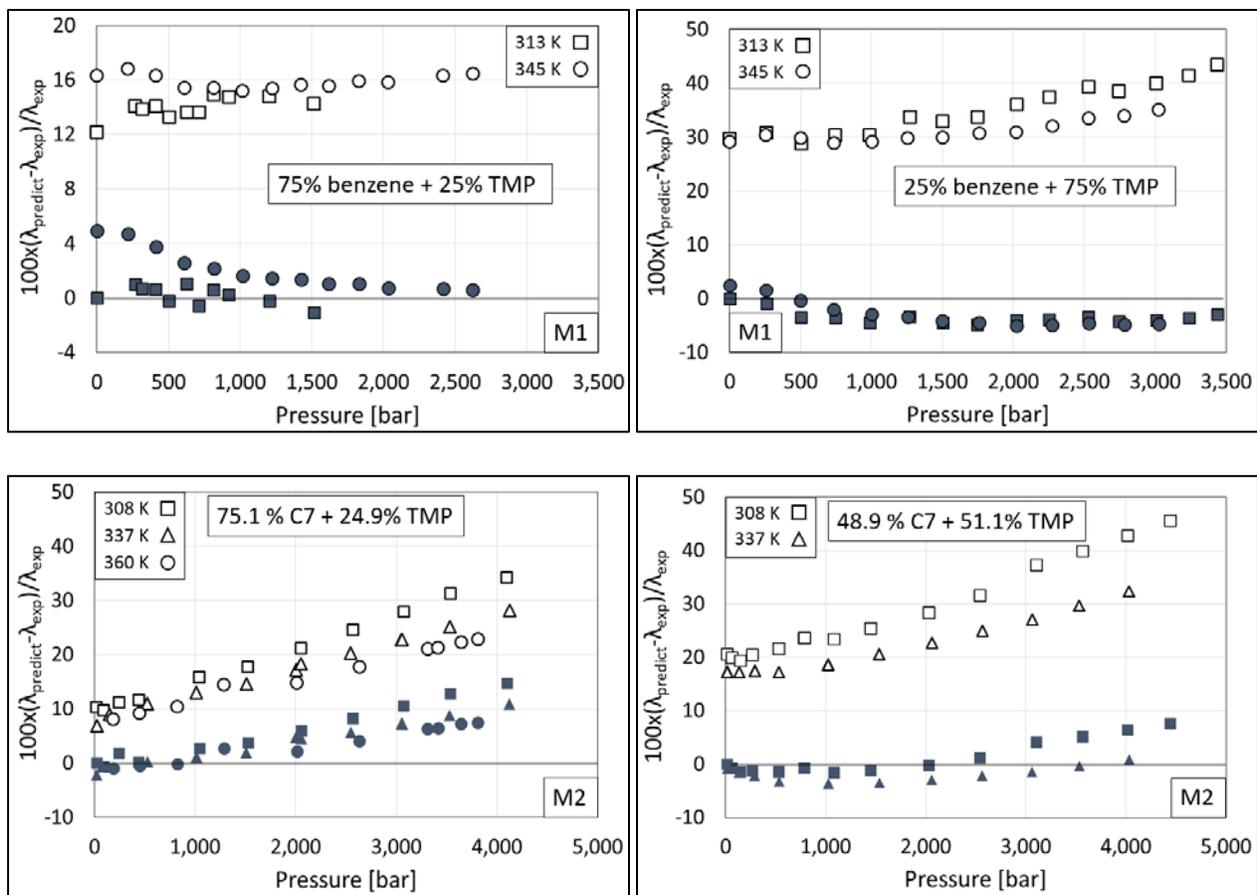


Figure 4. Pseudo-component thermal conductivity prediction deviations compared to experimental data [66, 67] for mixtures M1 and M2: two-parameter (open symbols) and three-parameter (filled symbols) models.

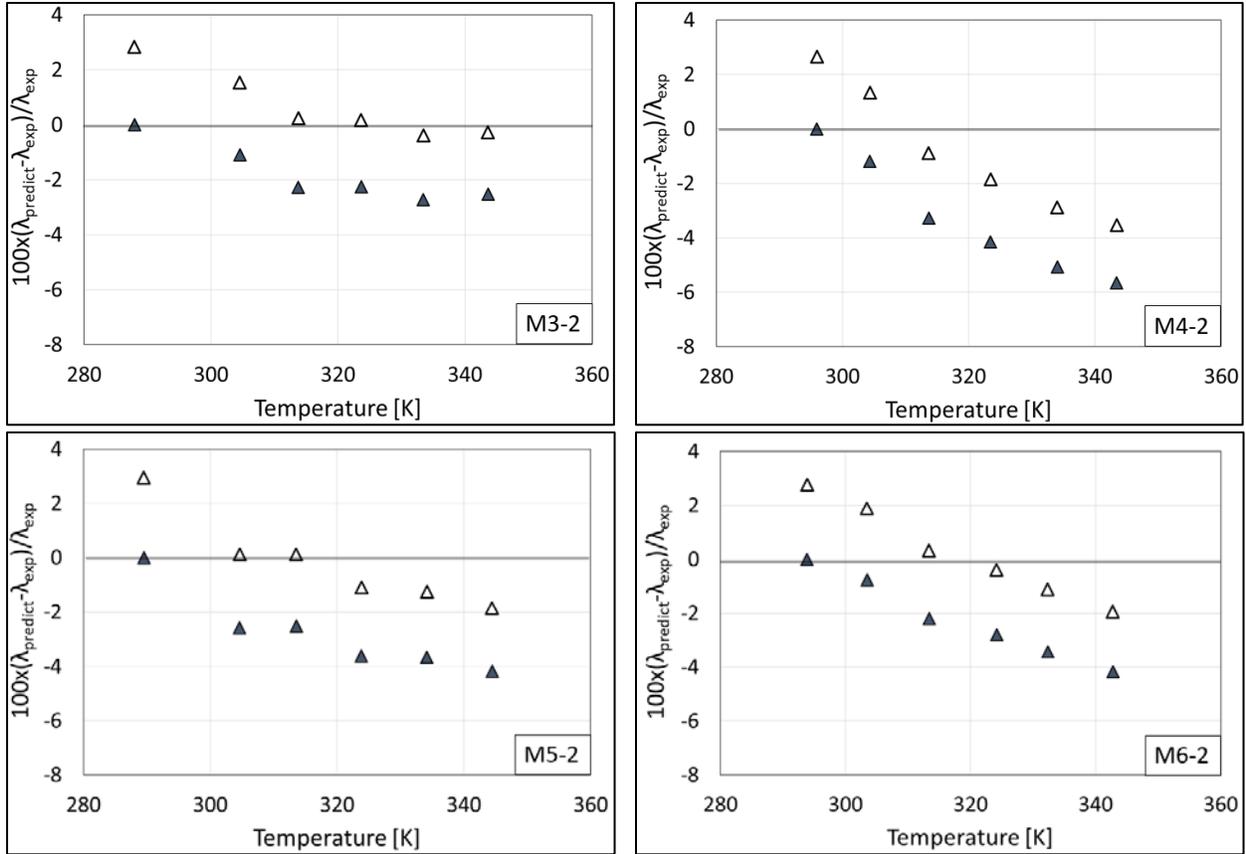


Figure 5. Pseudo-component thermal conductivity prediction deviations compared to experimental data [65-67] for mixtures M3-2 to M6-2 at 1 bar: two-parameter (open symbols) and three-parameter (filled symbols) models.

Table 5. The MAPD (%), bias (%), SD (%), and Max D (%) for the pseudo-component thermal conductivity of well-characterized hydrocarbon mixtures compared to the literature [65-67].

	Two-parameter				Three-parameter			
	MAPD	Bias	SD	Max Deviation	MAPD	Bias	SD	Max Deviation
M1	20.0	20.0	7.9	45.6	3.7	2.6	3.7	15.2
M2	24.6	24.6	9.8	43.4	2.4	-1.3	1.7	5.1
M3	1.2	0.5	0.9	2.8	1.9	-1.9	1.3	4.1
M4	2.0	-0.8	1.0	3.5	2.9	-2.9	2.0	5.6
M5	1.3	0.1	0.9	2.9	2.3	-2.3	1.4	4.2
M6	1.3	0.2	0.9	2.8	2.2	-2.2	1.4	4.2

The pseudo-component technique developed in this study captures the effects of temperature and pressure for all samples. Pseudo-component thermal conductivities are predicted for mixtures M1 and M2 with MAPDs of 20 and 25%, respectively, using the two-parameter model. The MAPDs for thermal conductivity predictions for all compositions of mixtures M1 and M2, shown in the SI, increase as the concentration of TMP, an iso-alkane, increases. More accurate thermal conductivities with MAPDs less than 2% are predicted at atmospheric pressure and a range of temperatures using the two-parameter model for mixtures M3-M6, composed of only n-alkanes. Their better predictions could be due the fact that the correlations in the technique were fit to ambient pressure data. Furthermore, since $Z = 0$ for n-alkane mixtures, the thermal conductivity coefficients in Eqs. 14-17 reduce to the correlations for n-alkanes, leading to reduced error, as there is no mixing with the PNA correlations.

It should be noted that the compounds present in mixtures M1 and M2 (C7 with MW = 100.21 g/mol, benzene with MW = 78.11 g/mol, and TMP with MW = 114.23 g/mol) are at the extreme lower MW bounds of the fitted PC-SAFT parameter and thermal conductivity coefficient correlations. The two-parameter pseudo-component model may not accurately represent the PC-SAFT parameters and thermal conductivity coefficients for mixtures with such low MW compounds. Note that the definition of DoU (Eq. 7) does not distinguish between normal and iso-alkanes, which could be an additional reason for thermal conductivity prediction deviations for mixtures containing significant amounts of iso-alkanes. Inclusion of a single thermal conductivity data point at a chosen reference state to fit B improves the predictions for mixtures M1 and M2 containing large amounts of iso-alkanes. Thermal conductivity is predicted for hydrocarbon mixtures using the three-parameter model with an MAPD of 3.0% for all compositions of all

investigated mixtures. This MAPD is comparable to thermal conductivity predictions for all 148 pure compounds studied by Hopp and Gross [26], who reported a 4.2% MAPD.

Fuels

Gasoline, kerosene, jet, and diesel fuel fractions distilled from crude oil are complex mixtures of hydrocarbon compounds with properties and composition that vary due to quality specifications [68, 69]. Table 6 lists the limited HTHP thermal conductivity literature data found only for rocket propellant (RP) and jet fuels. Akhmedova-Azizova et al. [70] measured the thermal conductivity of RP1 fuel at temperatures between 293 and 598 K and pressures up to 600 bar. Bruno [71] measured the thermal conductivity of RP2 fuel over a wide range of temperatures from 300 to 550 K and pressures up to 600 bar. Xu et al. [72] reported thermal conductivity measurements of RP3 fuel at temperatures from 285 to 513 K and pressures up to 50 bar. Jia et al. [73] reported thermal conductivity of RP3 fuel at temperatures from 311 to 399 K and a single isobar at 30 bar. Bruno [74] also measured the thermal conductivity of three different jet fuels including S-8 4734 (referred to as S-8), JP-8 3773 (referred to as JP-8), and Jet A 4658 (referred to as Jet A) at high temperatures from 270 to 470 K and pressures up to 400 bar. Table 7 lists the calculated MW, HN/CN ratio, Z parameter, thermal conductivity reference experimental data point (λ_0) at the lowest reported temperature and pressure used to fit B in the three parameter model, the PC-SAFT parameters, and the thermal conductivity coefficients for the pseudo-components for the fuels.

Table 6. Summary of HTHP thermal conductivity data available in the literature for rocket propellant (RP) and jet fuels.

Reference	Fuel	T _{range} /K	P _{max} /bar	Uncertainty (%)
Akhmedova-Azizova et al. [70]	RP1 ^a	293-598	600	2
Bruno [71]	RP2 ^b	300-550	600	-
Xu et al. [72], Jia et al. [73]	RP3 ^c	285-513	50	3
Bruno [74]	S-8 ^d	304-504	700	3
Bruno [74]	JP-8 ^d	303-407	600	3
Bruno [74]	Jet A ^d	303-501	400	3

^a The number averaged MW and the HN/CN ratio of the sample are calculated from the molecular formula of a typical RP1 fuel reported by Edwards [75].

^b The number averaged MW and the HN/CN ratio of the sample are calculated from the molecular formula of a typical RP2 fuel reported by Xu et al. [76].

^c The number averaged MW and the HN/CN ratio of the sample are calculated from the detailed composition of the RP3 fuel reported by Deng et al. [77]. The 30 bar thermal conductivities reported by Xu et al. [72], which are measured using a double transient hot-wire method, are on average 9% different compared to data reported by Jia et al. [73] at the single pressure of 30 bar, which are measured using a steady and kinetic method, an experimental technique proposed in the article [73]. We note that all three studies [72, 73, 77] are from the same research group.

^d The number averaged MW and the HN/CN ratio of the samples are reported by Won et al. [78] and Chickos and Zhao [79].

Table 7. The pseudo-component properties and parameters for fuels modeled in this study [70-74]. λ_0 (W/m-K) is the thermal conductivity at the lowest reported temperature and pressure used to fit B , here termed B^{fit} , in the three-parameter model. The lowest temperatures and pressures for the fuels are: RP1 at 293 K and 1 bar, RP2 at 300 K and 2 bar, RP3 at 299 K and 1 bar, S-8 at 304 K and 3 bar, JP-8 at 303 K and 8 bar, and Jet A at 302 K and 2 bar.

Fuel	MW	HN/CN	Z	λ_0	m	σ (Å)	ε/k (K)	A	B	C	D	B^{fit}
RP1	167.7	1.95	0.139	0.113	5.546	3.844	246.5	0.478	-1.041	-0.027	0.009	-0.926
RP2	177.0	2.03	0.082	0.108	5.903	3.851	242.8	0.486	-1.028	-0.016	0.010	-0.893
RP3	153.0	1.93	0.163	0.126	5.065	3.839	247.6	0.470	-1.045	-0.032	0.008	-0.989
JP-8	160.0	1.95	0.144	0.116	5.300	3.842	246.6	0.474	-1.041	-0.028	0.009	-0.948
S-8	154.5	2.14	0.028	0.117	5.241	3.851	238.7	0.483	-1.004	-0.006	0.012	-0.934
Jet A	157.5	1.96	0.140	0.112	5.227	3.842	246.2	0.474	-1.039	-0.027	0.009	-0.933

Figures 6 and 7 present the thermal conductivity predictions for the RP and jet fuels at different temperatures and pressures, respectively. Figures 8 and 9 show the thermal conductivity prediction deviations for these fuels. Table 8 summarizes the statistical metrics of the thermal conductivity predictions for the six fuels. The pseudo-component technique captures the effects of both temperature and pressure on thermal conductivity with an MAPD of 14.3% using the two-parameter model across all temperatures and pressures for all fuels. Two sets of experimental data are reported in the literature for the thermal conductivity of RP3 at 30 bar [72, 73]. Using the two-parameter model, thermal conductivity is predicted with 1% MAPD compared to the data reported by Jia et al. [73] and 9% MAPD compared to data reported by Xu et al. [72]. There is a 9% difference between these two sets of experimental measurements, which were obtained using two different techniques (double transient hot wire and steady and kinetic methods). It should be noted that Jia et al. [73] proposed the steady and kinetic method in the same article as the RP3

measurements at 30 bar. Typical RP and jet fuels contain between 10 to 40 weight percent iso-alkanes [75, 76, 80-82] and also contain amounts of alkylated compounds [72, 76, 81, 82] including alkylated cyclohexanes and alkylated benzenes. The pseudo-component technique does not distinguish the differences between normal and iso-alkanes. Since $Z = 0$ for both normal and iso-alkanes, the effect of the iso-alkanes and alkylated compounds (branching) in the fuel on the thermal conductivity may not be accurately captured using the two-parameter pseudo-component model for the fuels investigated in this study. By including a single thermal conductivity data point as a third input, predictions are significantly improved with an MAPD of 2.0%, which is within the experimental uncertainty of 3% reported in the literature [70-74]. RP3 thermal conductivities at 30 bar are predicted less accurately using the three-parameter model when comparing to the Jia et al. [73] data (8.3 % MAPD) than the Xu et al. [72] data (2.3 % MAPD) .

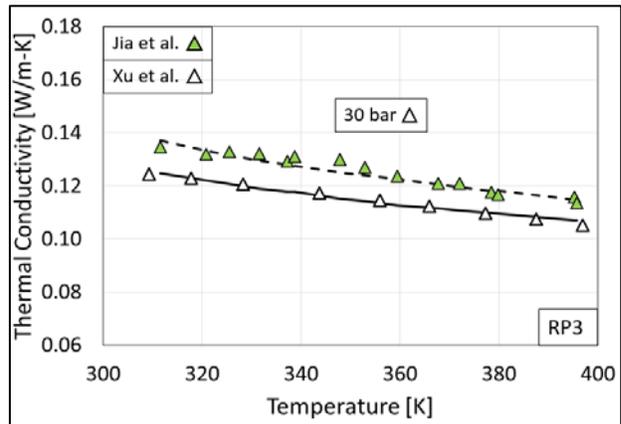
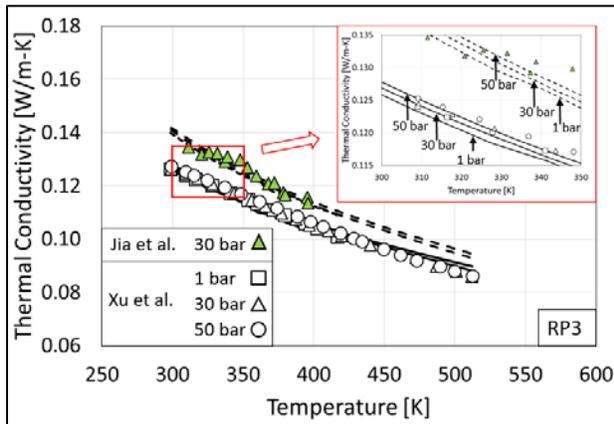
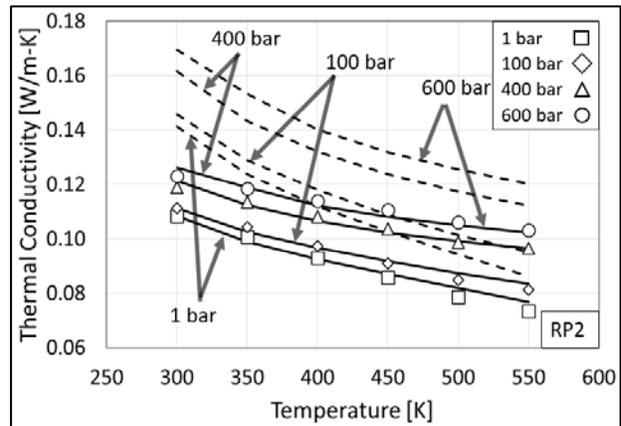
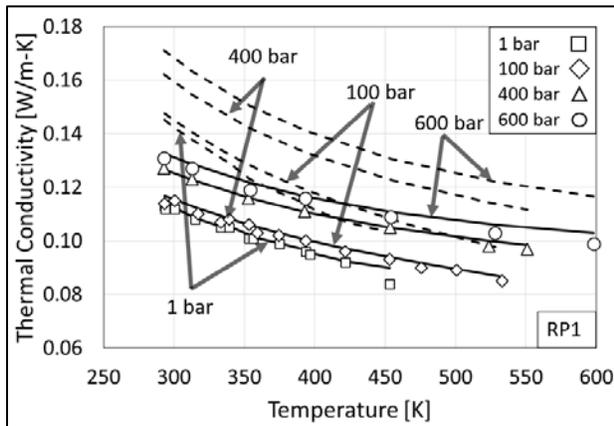


Figure 6. Pseudo-component thermal conductivity predictions compared to experimental data [70-73] (symbols) for rocket propellant (RP) fuels listed in Table 7. Dashed lines show the two-parameter calculations, and solid lines show the three-parameter calculations. A separate figure is shown for the RP3 thermal conductivities at 30 bar, since two data sets [72, 73] were reported in the literature. Note that the x-axis scale is different in the figure for RP3 at 30 bar.

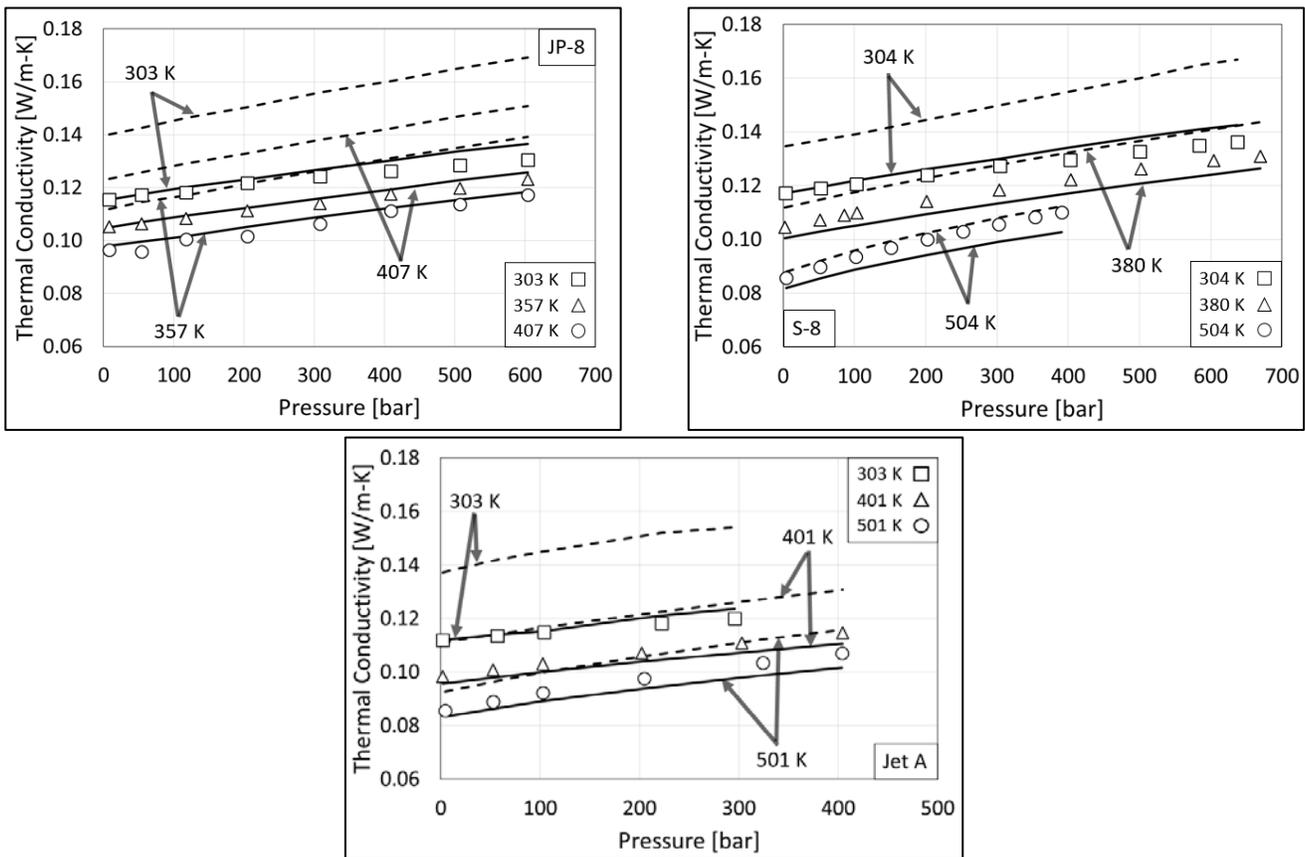


Figure 7. Pseudo-component thermal conductivity predictions compared to experimental data [74] (symbols) for jet fuels listed in Table 7. Dashed lines show the two-parameter calculations, and solid lines show the three-parameter calculations. Note that the x-axis scale is different in the figure for Jet A.

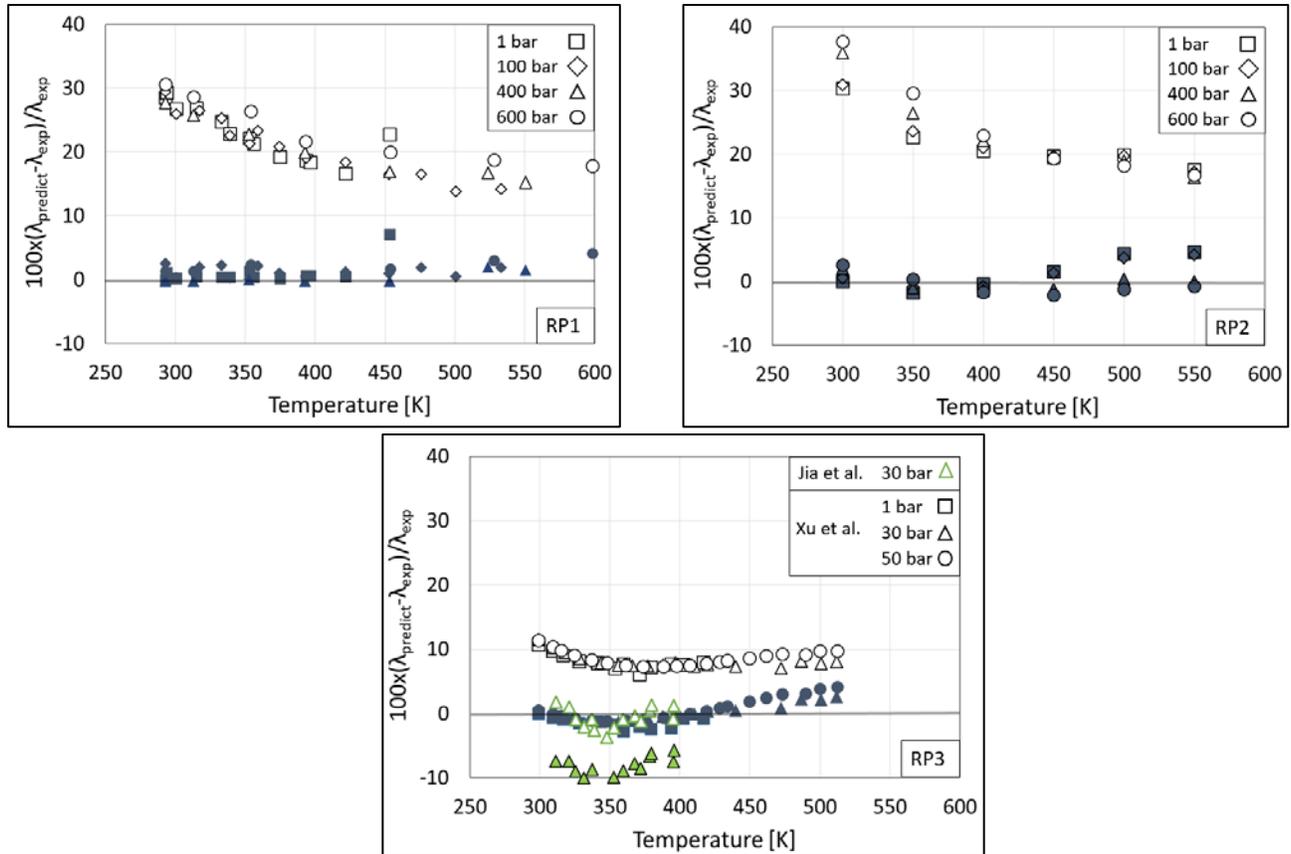


Figure 8. Pseudo-component thermal conductivity predictions deviations compared to experimental data [70-73] for rocket propellant (RP) fuels listed in Table 7: two-parameter (open symbols) and three-parameter (filled symbols) models.

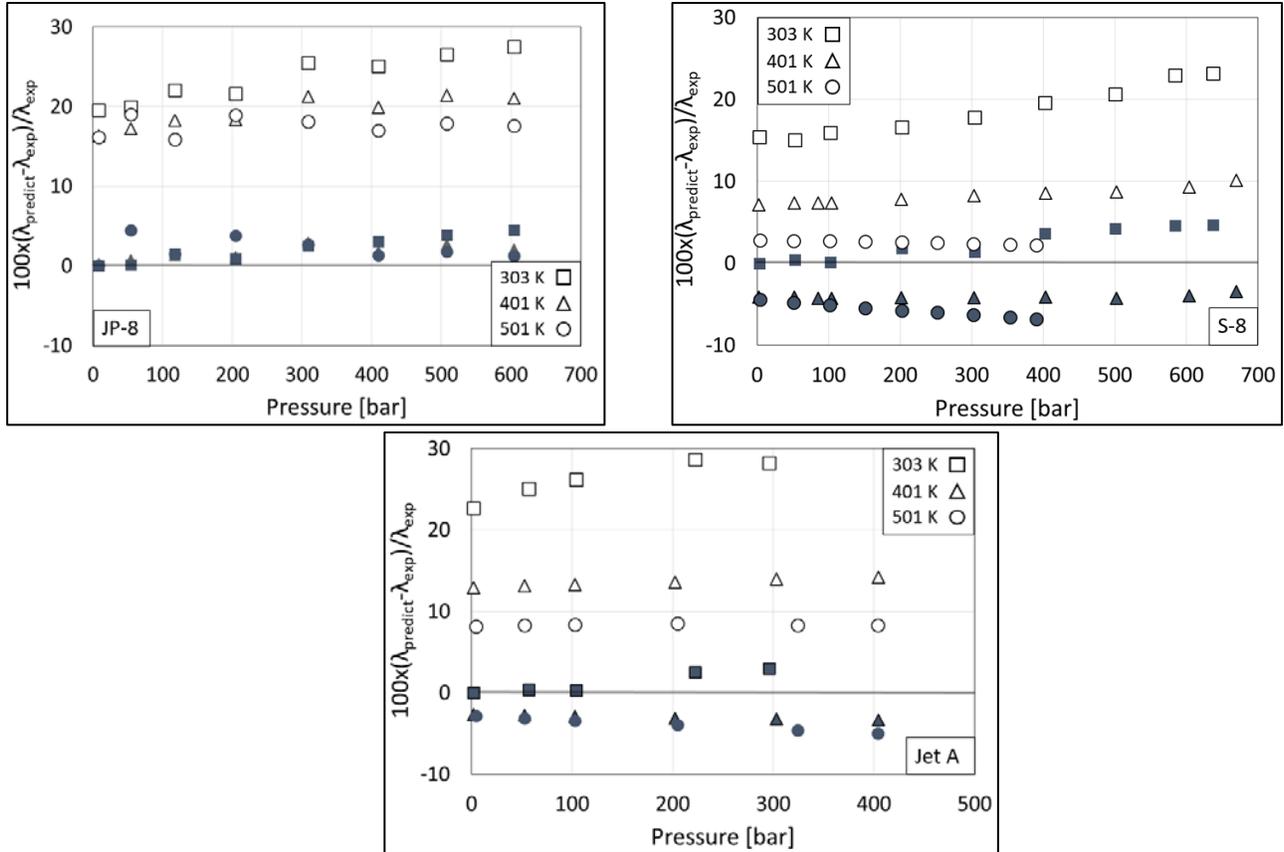


Figure 9. Pseudo-component thermal conductivity predictions deviations compared to experimental data [74] for jet fuels listed in Table 7: two-parameter (open symbols) and three-parameter (filled symbols) models. Note that the x-axis scale is different in the figure for Jet A.

Table 8. The MAPD (%), bias (%), SD (%), and Max D (%) for pseudo-component thermal conductivity predictions of rocket propellant (RP) and jet fuels listed in Table 7 [70-74] at temperatures from 293 to 598 K and pressures up to 700 bar.

	Two-parameter				Three-parameter			
	MAPD	Bias	SD	Max Deviation	MAPD	Bias	SD	Max Deviation
RP1	22.3	22.3	5.4	33.8	1.1	0.5	1.2	6.2
RP2	23.6	23.6	6.7	40.1	1.4	0.0	0.9	3.5
RP3	7.3	7.0	3.5	11.6	2.3	-1.2	2.8	11.2
S-8	13.3	13.3	4.1	22.5	2.2	-0.9	1.4	4.6
JP-8	21.2	21.2	3.6	29.7	1.8	1.8	1.3	4.7
Jet A	15.4	15.4	5.9	30.3	3.1	-2.8	1.5	5.6

Conclusion

A PC-SAFT, pseudo-component technique based on entropy scaling was presented to predict the thermal conductivity of well-characterized hydrocarbon mixtures, rocket propellant fuels, and jet fuels up to high temperature and high pressure (HTHP) conditions. The two experimental mixture properties required to predict thermal conductivity were the number average molecular weight and the hydrogen-to-carbon ratio. Correlations for the model parameters were developed from pure component thermal conductivity coefficients fit at atmospheric pressure. However, the predicted thermal conductivities deviated from the experimental data for mixtures containing significant amounts of iso-alkanes. A third input, the thermal conductivity at a single low-temperature, low-pressure reference state was incorporated in the model to improve the predictions for the mixtures of interest. Although the model was developed from atmospheric pressure data, accurate predictions were obtained when the technique was applied to well-characterized hydrocarbon mixtures and fuels up to HTHP conditions. The method was predictive

and did not require measurement of or fitting to HTHP thermal conductivity data. Thermal conductivities were predicted for fuels at conditions from 285 to 598 K and up to 700 bar using the three-parameter pseudo-component technique with a mean absolute percent deviation of 2.0%, which is within 3%, the reported uncertainty of the experimental measurements.

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Nomenclature

English symbols

\tilde{a}	reduced Helmholtz free energy
\AA	Angstrom
$A, B, C, \text{ and } D$	thermal conductivity coefficients
CN	carbon number
HN	hydrogen number
k	Boltzmann constant
K	Kelvin
m	number of segments
N	number of data points
N_A	Avogadro's number
\bar{s}	molar entropy
\tilde{s}	reduced entropy
s^*	reduced dimensionless residual entropy
T	temperature
V	volume
X	mole fraction
Z	averaging parameter, Eq. 5

Greek symbols

σ	segment diameter
$\Omega(2,2)^*$	reduced collision integral
ε/k	depth of the potential well

λ	thermal conductivity
λ_0	thermal conductivity experimental data at the lowest reported temperature and pressure
λ	thermal conductivity
λ^*	reduced thermal conductivity
$\bar{\lambda}$	thermal conductivity mean

Superscripts/Subscripts

CE	Chapman-Enskog
disp	dispersion
exp	experimental data
hc	hard-chain
predict	prediction
res	residual

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