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Comparison and Evaluation of Transport Property Prediction Performance of Supercritical Hydrocarbon Aviation Fuels and Their Pyrolyzed Products via Endothermic Reactions

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Abstract: This study presents results of predicting the transport properties of hydrocarbon aviation fuels and their decomposed products after pyrolysis. Twenty-seven pure substances and two types of mixture, including both low and high molecular weight hydrocarbons as well as hydrogen, are considered. The specified temperature and pressure ranges, 300 to 1000 K and 0.1 to 5.0 MPa, respectively, correspond to representative operating conditions of a hydrocarbon aviation fuel that circulates as a coolant in the regenerative cooling system of a hypersonic vehicle and include the critical temperatures and pressures of most of the hydrocarbon fuels of interest. Four methods are adopted for the prediction of viscosity and thermal conductivity; the Brule-Starling method is used to predict viscosity, the Modified Propane TRAPP method for thermal conductivity, and the Methane TRAPP, Propane TRAPP, and Chung et al. methods are used for both transport properties. A comparison of the total average values concludes that the Chung et al. and Brule-Starling methods perform best in predicting the viscosity of all substances ranging from hydrogen to high molecular weight hydrocarbons in the temperature and pressure ranges specified in the current study. The quantified comparison by the total average also confirms that the Modified Propane TRAPP method best predicts the thermal conductivity of all of the 29 substances over the set temperature and pressure ranges, although the Propane TRAPP and Chung et al. methods offer a similar level of accuracy.

Keywords: hypersonic flight vehicle; regenerative cooling; thermophysical property; viscosity; thermal conductivity



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1. Introduction

The aviation industry has recently focused on developing low-emission propulsion systems as well as air vehicles capable of efficient mobility [1–4], and hypersonic cruise vehicles are considered viable candidates for efficient long-range flight [4]. A hypersonic cruise vehicle can fly over Mach 5 in the atmosphere, and it uses scramjet engines that can operate in a wide range of flight conditions. As a result, it can be used as hypersonic cruise missiles or hypersonic airliners [4,5]. In developing a practical hypersonic cruise vehicle, however, various complex phenomena occur during the flight at very high speeds, and among them, the issue of aerothermodynamic heating and supersonic combustion must be resolved [6].

Hydrocarbon aviation fuels have excellent cooling capacities through heat-absorbing chemical reactions such as thermal cracking or pyrolysis [7–9], and therefore, regenerative heat sink cooling systems have been studied worldwide. In such systems, hydrocarbon fuels are used as coolants in order to deal with aero-thermodynamic heating and to realize efficient supersonic combustion in scramjet-powered hypersonic flight vehicles [7–12]. Passing through a regenerative cooling system, however, the fuel is not only heated up to as high as 1000 K [12] but it must also be pressurized sufficiently inside cooling channels to prevent phase change at such high temperatures [13]. At these high temperatures and pressures, the circulating fuel may not only reach supercritical conditions but may

also be cracked into a variety of low molecular weight hydrocarbons via endothermic reactions [8,13,14].

When hydrocarbon fuel is heated to above its critical point and pyrolyzed into multiple components in a regenerative cooling system, its thermophysical properties change drastically, which subsequently influences the overall flow and heat transfer characteristics inside the cooling channels [11,13–16]. Furthermore, the injection and atomization characteristics of the supercritical and/or cracked fuel become different from those of the original liquid fuel, and this greatly affects its mixing, ignition, and combustion performance when it is supplied to the downstream supersonic combustor [17–19]. In order to assess precisely the performance characteristics of a regenerative cooling system and a scramjet combustor, therefore, it is essential to know as accurately as possible the thermodynamic and transport properties of the fuels and their decomposed product mixtures, over a wide range of temperature and pressure conditions.

NIST has developed extensive thermophysical property databases, such as REFPROP and SUPERTRAPP, based on theoretical models. They have been verified by comparison with a considerable amount of experimental data [20,21] and thus have been used in a variety of previous studies focusing specifically on the development of regenerative cooling technologies for hypersonic flight vehicles [14,16,18,22–24]. It has been reported, however, that they do not ensure accuracy in the supercritical region or near the critical point, and they do not offer properties for all hydrocarbons and their mixtures that are generated during the endothermic reactions [20,21].

In order to make accurate predictions of the thermophysical properties of circulating hydrocarbon aviation fuels and the mixtures of their products from thermal cracking, therefore, a variety of studies have been carried out [12,13,25–27]. For predicting the P - v - T behaviors, thermodynamic properties, and fluid phase equilibria of many fluids and mixtures, a rich diversity of equations of state (EoS) has been developed, with differing degrees of empiricism, predictive capability, and mathematical form [28]. Van der Waals proposed the first EoS capable of predicting both gaseous and liquid phases, reflecting real fluid properties, by considering the volume of gas particles and intermolecular forces [29]. The predictions are found to be qualitatively correct but quantitatively rather poor [28]. The majority of EoS models in use today are empirical modifications that retain Van der Waals' basic formulation [28]. Well-known examples are the Redlich–Kwong (RK), Soave–Redlich–Kwong (SRK), and Peng–Robinson (PR) EoSs, which were developed to handle the phase equilibria of complex multicomponent mixtures [28]. These are cubic equations whose parameters are determined for a pure fluid from the critical constants (P_c , T_c , Z_c) and Pitzer's acentric factor (ω) while, for a mixture, combining rules are used to express the parameters in terms of pure-component values [28]. The combination of relatively simple form with reasonably reliable prediction performance means that modified cubic EoSs are the most widely used in a variety of engineering problems [12,13,26,30–33]. More accurate results, on the other hand, generally depend on much more complicated EoSs, such as generalizations of the Benedict–Webb–Rubin (BWR) equation, with parameters fitted to accurate experimental data covering a wide range of conditions [25,28]. These are more difficult to implement than the cubic EoSs, and, thus, are less appropriate for general applications.

Both the SRK and PR EoSs are two-parameter EoSs (2P-EoS), which have limits as to the range of applicable critical compressibility factors. In predicting the thermodynamic properties of hydrocarbons, particularly, it is known that the SRK EoS is suitable for the prediction of low molecular weight hydrocarbons with large critical compressibility factor (Z_c), and the PR EoS for high molecular weight hydrocarbons with small Z_c [29,30]. By introducing additional parameters to combine the SRK and PR EoSs, Cismondi and Mollerup [34] proposed a three-parameter cubic EoS, the RK–PR (Redlich–Kwong–Peng–Robinson) EoS, in order to overcome the intrinsic limitations of these 2P-EoSs [30]. The RK–PR EoS has been confirmed to show similar or better performance in predicting P - v - T behaviors than the SRK and PR EoSs over a wide range of Z_c [30,34], and thus it became one

of the most promising candidates for predicting thermodynamic properties of hydrocarbons in the field of CFD, with a relatively convenient algorithm and low computational cost [29]. Furthermore, Seo et al. [29] recently developed an improved RK–PR EoS (eRK–PR EoS) by introducing a new δ parameter constraint condition, extending the applicable range of the maximum experimental critical compressibility factor from 0.29 of the RK–PR EoS to 0.375. The RK–PR EoS is, therefore, widely considered to be an efficient engineering modeling tool for developing regenerative cooling systems of a hypersonic flight vehicle [13,26,32,35], and Hwang and Lee [35], for example, have shown that the RK–PR EoS can predict the density and the constant-pressure specific heat of representative hydrocarbon aviation fuels and some of their pyrolyzed products with average relative differences of within 5%, compared with the NIST databases, over a wide range of temperature and pressure conditions, including both subcritical and supercritical regions.

Unlike thermodynamic properties, however, transport properties are fairly difficult to predict accurately. Hwang et al. [27], for example, tried predictions of the thermal conductivity as well as the viscosity of high molecular weight hydrocarbons and some of their expected products via pyrolysis using TRAPP methods, which adopt methane (CH_4) and propane (C_3H_8), respectively, as the reference fluids. They showed that even though the TRAPP methods can predict the transport properties of both light and heavy hydrocarbons and their mixtures over a broad range of liquid, gas, and supercritical regions, the relative differences become quite large for the higher molecular weight hydrocarbons in a liquid state. For viscosity, as a result, the methane-based TRAPP method was found to be more accurate, with an average relative difference of within 22%, while the propane-based TRAPP method is superior for prediction of thermal conductivity, with an average relative difference of within 14%. The performance of the TRAPP methods, however, is not satisfactory, and improved methods are required for predicting accurately the transport properties of aviation fuels and the light hydrocarbons produced by the fuels' endothermic reactions.

Many researchers studying regenerative cooling technologies for hypersonic flight vehicles have adopted one (or two) of the TRAPP, Chung, et al., and Brule-Starling methods, which will be discussed in detail below, to predict the transport properties of a variety of hydrocarbons and their mixtures [12,13,16,25,31,33,36,37]. Most of them, however, gave no real explanation for their selection, and few have investigated the accuracy of those methods in predicting the transport properties of hydrocarbon fuels and their products in the typical operating ranges of a regenerative cooling system. This paper, therefore, presents several methodologies that have been developed to improve the prediction accuracy of transport properties and compares their prediction performances in terms of relative difference from the values of the NIST database.

2. Prediction Methods

Transport properties determine the rate at which processes such as mass and heat transfer occur in a system that is not in equilibrium [28]. Transport properties are inherently difficult to measure accurately, and their theoretical treatments by the kinetic theory are complex. Nevertheless, several methodologies have been established to predict the transport properties of substances in the liquid, gas, and supercritical states [28,38].

The TRAPP (TRANsport Property Prediction) method predicts the transport property behaviors based on an extended corresponding states principle and the conformal solution of a one-fluid concept [28,38–43]. It is capable of predicting the viscosity and thermal conductivity of not only pure fluids but also their mixtures, over a wide range of thermodynamic states, from the dilute gas to the dense liquid, and in principle, the number of mixture components is unrestricted [39]. Two kinds of TRAPP methods—methane-based TRAPP (Methane TRAPP) and propane-based TRAPP (Propane TRAPP), using CH_4 and C_3H_8 as the reference fluids, respectively—are well established and thus available currently [27,28,38–44]. Even though their use requires very complicated procedures [28,38–40] and they were originally developed only for non-polar fluids and their mixtures [39], they have been extended for polar compounds as well [38].

As an alternative, Chung et al. [45] proposed empirically correlated density-dependent functions extending the kinetic theory for low-pressure (dilute) gas to include dense fluids. This method is relatively simple and can be applied in predicting both the viscosity and the thermal conductivity of nonpolar, polar, and associating fluids over wide ranges of P - v - T states, using Pitzer's acentric factor (ω), the dimensionless dipole moment (μ_r), and an empirically determined association parameter (κ), which characterize the molecular structure effect of polyatomic molecules, the polar effect, and the hydrogen-bonding effect, respectively [38,45].

In regard to obtaining the viscosity of a fluid specifically, Brule and Starling [46] emphasized that, for Newtonian fluids, the viscosity can characterize complex fluids and can have correlations with thermodynamic data, even though it is a transport (non-equilibrium) property. They developed a correlation between viscosity and density which is predicated on combining thermodynamic and transport analyses to obtain the characterization parameters most suitable for both types of estimations and thus enables the prediction of viscosity from temperature and the corresponding density information of a fluid. Polling et al. [38] suggested that the Brule-Starling method is preferable when complex hydrocarbons are of interest, and the Chung et al. method should be used at low reduced temperatures ($T_r < 0.5$) to retain the best accuracy.

For the thermal conductivity of hydrocarbon mixtures, Ely [43,47] found that the propane-based TRAPP method might be improved by modifying the translational correction factor for thermal conductivity X_λ as follows.

$$X_{\lambda, mix} = \frac{1 + 2.186634(\omega_{mix} - 0.152)}{1 - 0.5050059(\omega_{mix} - 0.152)} \quad (1)$$

Note that all the other parameters, as well as the formulation itself, are identical to the original Propane TRAPP method. Therefore, the Propane TRAPP method adopting X_λ as given in Equation (1) is designated as the modified propane-based TRAPP (Modified Propane TRAPP) method for thermal conductivity [43].

It is, therefore, noted that the present study considers viscosity as predicted using the Methane TRAPP, Propane TRAPP, Chung, et al., and Brule-Starling methods, and thermal conductivity as predicted using the Methane TRAPP, Propane TRAPP, Modified Propane TRAPP, and Chung et al. methods. Note also that the specific procedures, as well as the formulation itself for calculating the transport properties of pure fluids and mixtures using these methodologies, are described in detail in Refs. [28,39,40,44] For the Methane TRAPP method, Refs. [27,38,43] For the Propane TRAPP method, Refs. [38,45] for Chung et al. method, and Refs. [38,46] for the Brule-Starling method.

3. Prediction Condition and Hydrocarbon Fuels

3.1. Prediction Condition and Comparison Method

The transport properties of pure hydrocarbons and mixtures were predicted and compared in the ranges of temperatures between 300 and 1000 K and pressures between 0.1 and 5.0 MPa [35,44]. The range includes most hydrocarbons' critical points, as presented in Section 3.2, as well as the most states considered in several thermal cracking studies [12–14,48].

The values of estimated transport properties using the various methods have been compared with those from the NIST database by calculating a relative difference (RD), defined as follows [27,35,44].

$$\%RD = \left| \frac{\text{Prediction} - \text{NIST}}{\text{NIST}} \right| \times 100(\%) \quad (2)$$

where "NIST" indicates properties obtained from REFPROP or SUPERTRAPP. It is noted that only values for substances not included in REFPROP were acquired from SUPERTRAPP, as NIST has stated officially that REFPROP precedes SUPERTRAPP [20,21].

3.2. Hydrocarbon Fuels

Hydrocarbon substances, including components of several aviation fuels considered in the current study, are listed in Table 1. Among them, n-dodecane (C₁₂H₂₆) and exo-THDCPD (C₁₀H₁₆) are the main constituents of the JP-7 and JP-10 fuels, respectively, and JP-8 surrogate is a mixture of multiple hydrocarbons used as a simulant of the JP-8 fuel, of which components are combined by following Cooke et al. [49] and Hwang et al. [27]. Also included in Table 1 is a simple mixture of 25% methane (CH₄) and 75% ethylene (C₂H₄) in mass fraction, pure hydrogen, and 24 hydrocarbons which are produced via the endothermic reactions of representative aviation fuels and thus included in the PPD (Proportional Product Distribution) models of n-decane [14,31,50], n-dodecane [51], exo-THDCPD [52], and RP-3 or similar aviation kerosene [17,37].

Table 1. Hydrocarbon substances are used for the comparison of transport property prediction capabilities.

Name	Formula	M (kg/kmol)	P_c (MPa)	T_c (K)
hydrogen	H ₂	2.016	1.29	32.98
methane	CH ₄	16.04	4.60	190.6
ethylene	C ₂ H ₄	28.05	5.04	282.3
ethane	C ₂ H ₆	30.07	4.87	305.3
propene	C ₃ H ₆	42.08	4.60	364.9
propane	C ₃ H ₈	44.10	4.25	369.8
1,3-butadiene	1,3-C ₄ H ₆	54.09	4.32	425.0
butene	C ₄ H ₈	56.11	4.02	419.5
trans-2-butene	trans-C ₄ H ₈	56.11	4.10	428.6
cis-2-butene	cis-C ₄ H ₈	56.11	4.21	435.5
butane	C ₄ H ₁₀	58.12	3.80	425.1
1-pentene	C ₅ H ₁₀	70.13	3.56	464.8
pentane	C ₅ H ₁₂	72.15	3.37	469.7
benzene	C ₆ H ₆	78.11	4.90	562.1
1-hexene	C ₆ H ₁₂	84.16	3.14	504.0
hexane	C ₆ H ₁₄	86.18	3.03	507.6
toluene	C ₇ H ₈	92.14	4.11	591.8
1-heptene	C ₇ H ₁₄	98.19	2.92	537.3
heptane	C ₇ H ₁₆	100.2	2.74	540.2
ethylbenzene	C ₈ H ₁₀	106.2	3.61	617.2
1-octene	C ₈ H ₁₆	112.2	2.68	567.0
octane	C ₈ H ₁₈	114.2	2.49	568.7
1-nonene	C ₉ H ₁₈	126.2	2.33	594.0
nonane	C ₉ H ₂₀	128.3	2.29	594.6
decane	C ₁₀ H ₂₂	142.3	2.11	617.7
dodecane	C ₁₂ H ₂₆	170.3	1.82	658.0
exo-THDCPD	C ₁₀ H ₁₆	136.2	3.73	698.0
JP-8 surrogate	Mixture	144.6	2.19	628.4
methane + ethylene	Mixture	23.63	4.91	248.5

Table 1 lists the critical temperatures (T_c) and pressures (P_c) of each substance, too, in order to illustrate that the critical points of most of the hydrocarbons considered here are included in the prediction range. For mixtures, in addition, the pseudo-critical temperature and pressure (T_{pc} and P_{pc}) are listed in the T_c and P_c columns, assuming the mixtures as hypothetical pure fluids [39,40].

4. Results and Discussion

4.1. Viscosity

The predictions of viscosity are carried out using the Methane TRAPP, Propane TRAPP, Chung et al., and Brule-Starling methods for each of the substances listed in Table 1. As an example, Figures 1 and 2 present the distributions of the viscosity and its relative difference, respectively, of exo-THDCPD predicted by the four methods. Note that the white lines drawn in Figure 2 are the saturation line and the critical temperature and pressure lines. It

is, furthermore, noted that each figure presented in Figure 2 is drawn by using different color schemes scaled with the maximum relative difference for each method. The viscosity of exo-THDCPD over the entire temperature and pressure ranges considered here, as shown in Figure 1, is predicted nicely by both the Chung et al. and Brule-Starling methods—both methods describe well the higher viscosity in the liquid state as well as the lower viscosity in the gaseous or supercritical states of higher temperature conditions. This is confirmed by the distribution of the relative difference in Figure 2, which presents that the overall difference is smaller with the Chung et al. and Brule-Starling methods than with either of the TRAPP methods. The prediction performance of the TRAPP methods is, in fact, rather poor for liquid exo-THDCPD, as has already been reported and discussed in detail in the author’s previous study [27].

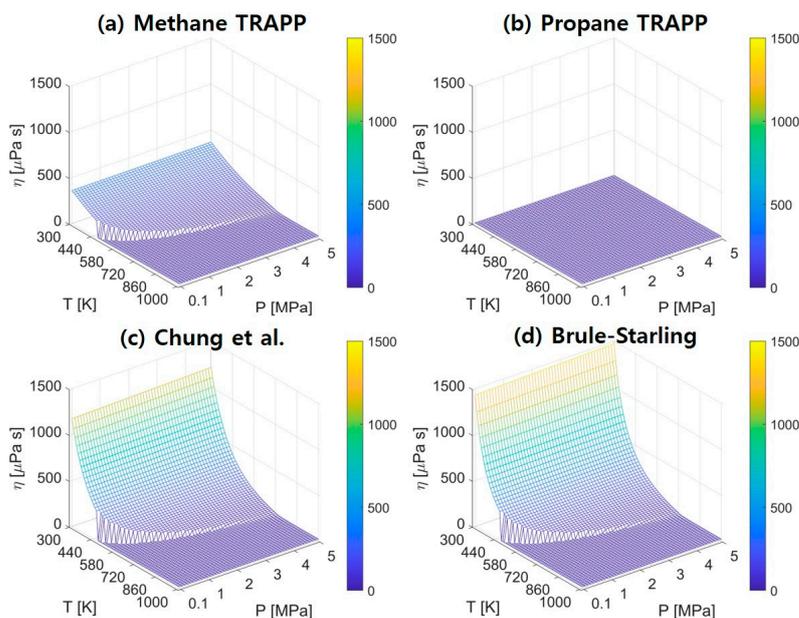


Figure 1. The viscosity of exo-THDCPD is predicted by (a) Methane TRAPP, (b) Propane TRAPP, (c) Chung et al., and (d) Brule-Starling methods.

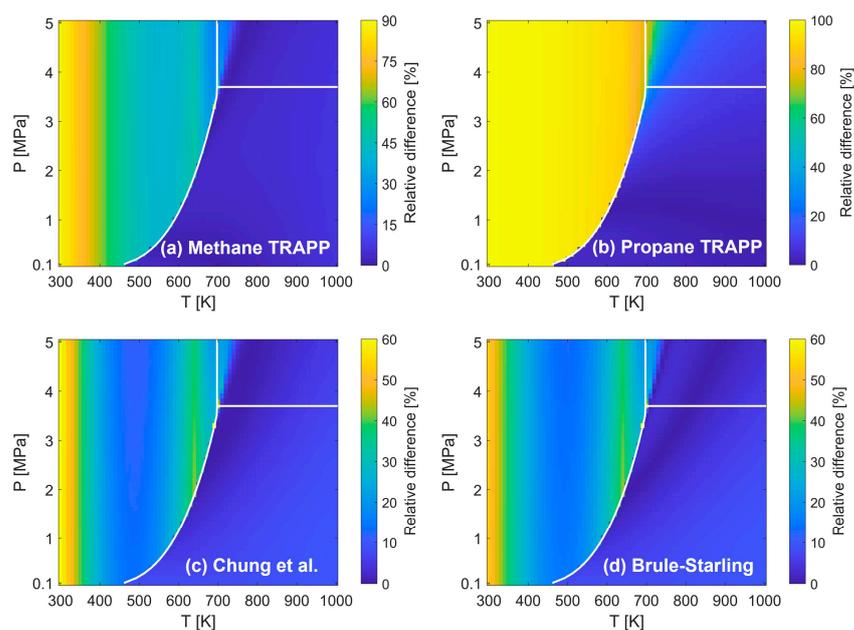


Figure 2. Relative difference from NIST values of the viscosity of exo-THDCPD predicted by (a) Methane TRAPP, (b) Propane TRAPP, (c) Chung et al., and (d) Brule-Starling methods.

The prediction results are compared with each other by the average of the relative difference over the entire temperature and pressure region for all of the 29 substances, as presented in Figure 3. Overall, the average relative difference appears to increase from the light hydrocarbons to heavier ones. Similar to the results for *exo*-THDCPD observed in Figures 1 and 2, furthermore, the Chung et al. and Brule-Starling methods show the best overall performance in predicting viscosity, as represented by the average relative difference for each substance, for the hydrocarbons of the current study in the specified temperature and pressure ranges, except for a few light-weight substances, such as hydrogen, methane, and ethylene.

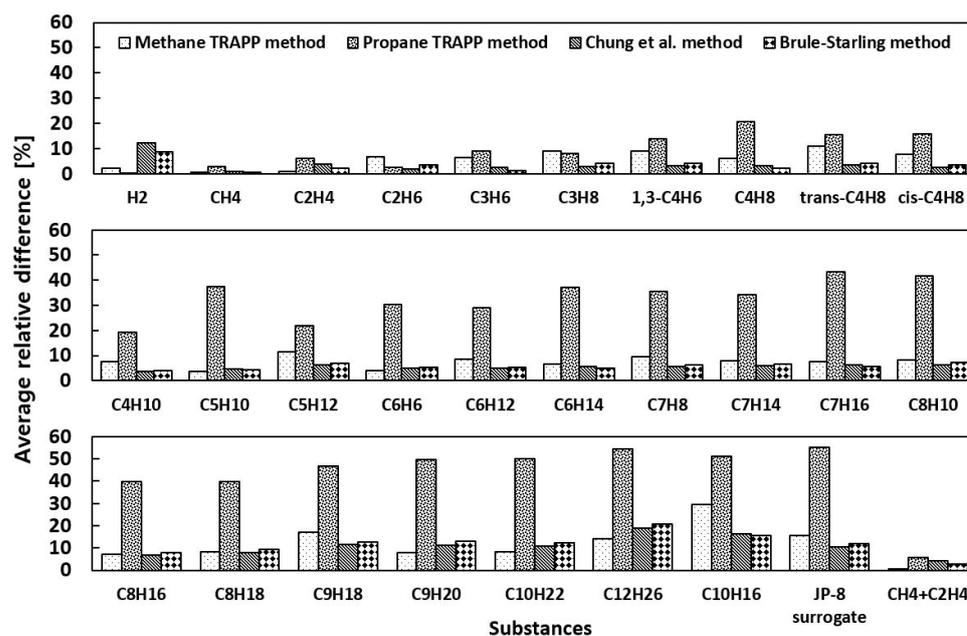


Figure 3. Average relative difference from NIST values of the predicted viscosity for each substance.

4.2. Thermal Conductivity

Thermal conductivity was predicted for each of the substances listed in Table 1 using the Methane TRAPP, Propane TRAPP, Modified Propane TRAPP, and Chung et al. methods, as discussed in Section 2. Figures 4 and 5 present, again as an example, the distributions of the predicted thermal conductivity and its relative difference of *exo*-THDCPD by the four methods. The typical behavior of thermal conductivity is clearly observed in Figure 4 for most of the methods except for Methane TRAPP; with the Propane TRAPP, Modified Propane TRAPP, and Chung et al. methods, the predicted thermal conductivity is very small at the saturation line and increases as the temperature either decreases or increases on both sides of the line [13,27]. Even though the three methods seem to predict the thermal conductivity nicely, however, the distribution of the relative difference in Figure 5 shows that the thermal conductivity of *exo*-THDCPD is predicted most accurately by the Modified Propane TRAPP and Chung et al. methods; most of the errors of those two methods are below 10% over the temperature and pressure ranges.

The predictions of the thermal conductivity for all of the 29 substances using the four methods are compared with each other by the average of the relative difference over the entire temperature and pressure region, as presented in Figure 6. Overall, the prediction performance of the three methods, excluding Methane TRAPP, is good for all substances, as observed for *exo*-THDCPD in Figures 4 and 5. For *exo*-THDCPD, specifically, the Chung et al. method is the best, followed closely by Modified Propane TRAPP. For most of the other substances, however, Figure 6 shows that the two Propane TRAPP methods also perform very nicely, and in fact, it is not easy to discern an overall superiority among the three methods for the prediction of thermal conductivity.

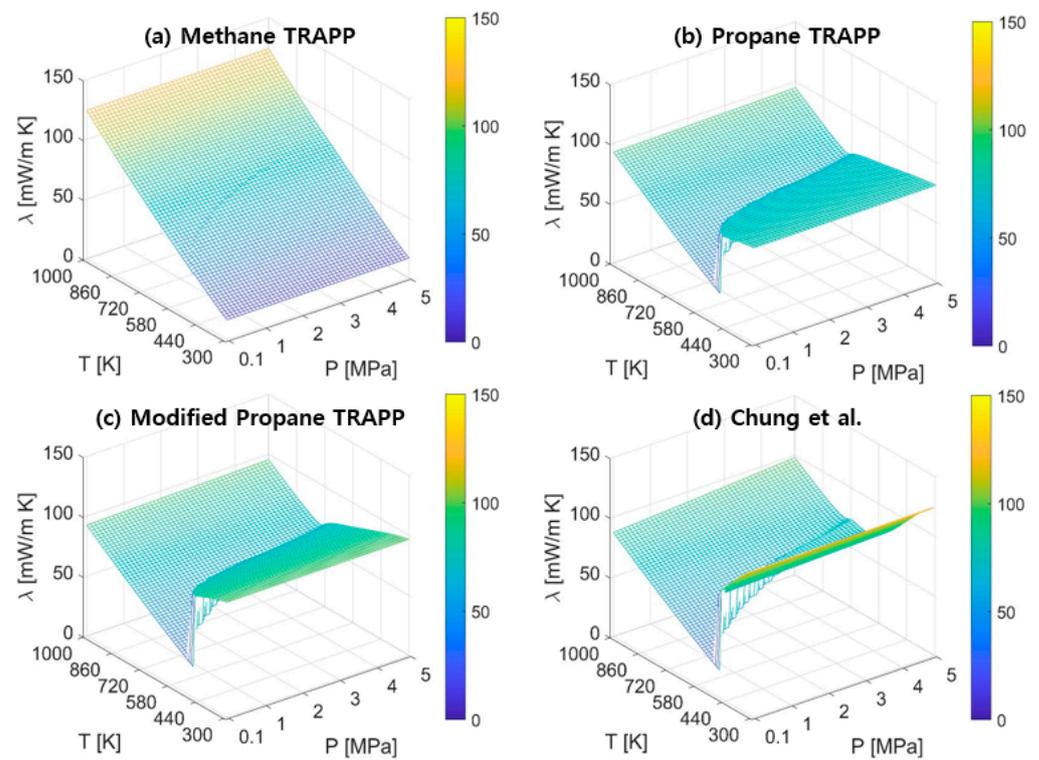


Figure 4. Thermal conductivity of exo-THDCPD predicted by (a) Methane TRAPP, (b) Propane TRAPP, (c) Modified Propane TRAPP, and (d) Chung et al. methods.

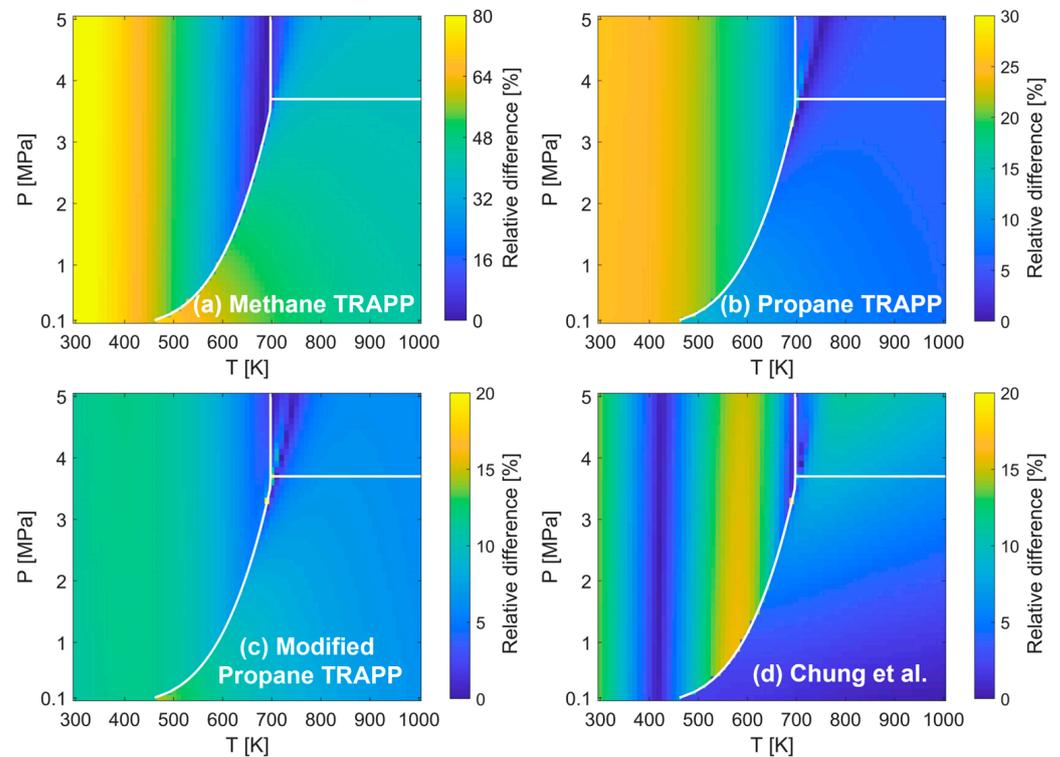


Figure 5. The relative difference of thermal conductivity of exo-THDCPD from NIST values, as predicted by (a) Methane TRAPP, (b) Propane TRAPP, (c) Modified Propane TRAPP, and (d) Chung et al. methods.

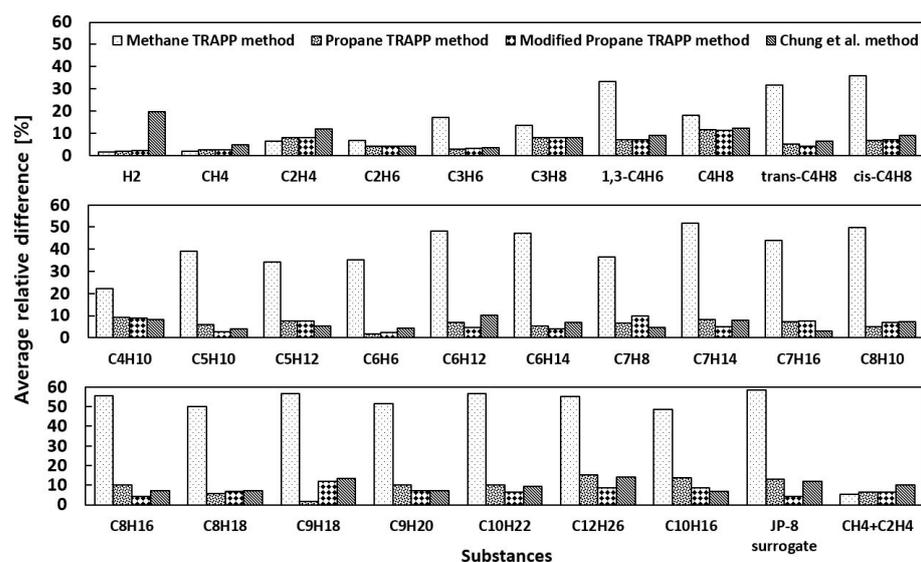


Figure 6. Average relative difference from NIST values of the predicted thermal conductivity for each substance.

4.3. Discussion

The results shown in Sections 4.1 and 4.2 confirm that several methods are capable of predicting the thermal conductivity as well as the viscosity of hydrocarbon fuels accurately over the temperature and pressure conditions ranging from the liquid to the gaseous and supercritical states. In predicting viscosity, the relative differences appear to increase for heavier hydrocarbons in the specified prediction ranges, and the prediction performance for the liquid state is generally inferior to that for the gaseous and supercritical states, although relative performance varies for each method. The example of the distributions of viscosity and its relative difference for exo-THDCPD, presented in Figures 1 and 2, confirm that the Chung et al. and Brule-Starling methods can predict viscosity quite nicely over the whole region, including the liquid, gas, and supercritical states, while the predictions from both the Methane and Propane TRAPP methods for the liquid state are much more inaccurate than for the gaseous and supercritical states. Similar differences in the prediction of viscosity for substances in the liquid state at low temperatures are observed for most of the other hydrocarbons explored here.

It is known that the fundamental theoretical background of the TRAPP methods is based on the gaseous state, even though the TRAPP procedure can be applied to all of the states, from dilute gas to dense liquid [38]. It is, as a result, reasonable that both the Methane and Propane TRAPP methods can predict transport properties in the gaseous and supercritical states much better than in the liquid state [27]. This results in relatively poor performance in predicting the viscosity of propane by using the Propane TRAPP method, as shown in Figure 3. On the other hand, the Chung et al. and Brule-Starling methods have no such limitations because they rely basically on empirical correlations between density and viscosity from low-pressure (dilute) gas to dense fluids [38,45,46]. It cannot, however, be simply concluded that the Chung et al. and Brule-Starling methods are superior to the TRAPP methods for all purposes; this is evident in the results of the average relative differences of the viscosity for all of the substances predicted by the four methods shown in Figure 3.

Table 2 lists the average relative difference data presented in Figure 3 in numerical values. It is obvious that the viscosity of low molecular weight substances, including hydrogen, methane, ethylene, and their mixture, is predicted much more accurately by the TRAPP methods, while that of most hydrocarbons with higher molecular weight is estimated with good accuracy by the Chung et al. and Brule-Starling methods. The reason for these results is as follows; as shown in Table 1, the critical points of the light-weight fuels

are located outside the ranges set for the current prediction, and as a result, the viscosity of those substances in the gaseous state over the entire prediction space is predicted more accurately by the TRAPP methods than by the Chung et al. and Brule-Starling methods. On the other hand, the heavy hydrocarbons, including exo-THDCPD, exist in the liquid state over a considerable fraction of the specified prediction range, as shown in Figure 2, and that is why the average relative differences of the TRAPP methods are generally higher than those of the Chung et al. and Brule-Starling methods. Figure 2, furthermore, shows that even the Chung et al. and Brule-Starling methods offer relatively poor prediction performance in the liquid state as compared with the gaseous and supercritical states, and this is why the accuracy of viscosity predictions for the light-weight substances is superior to that for heavier hydrocarbons for all of the prediction methods, as shown and listed in Figure 3 and Table 2, respectively.

Table 2. Average of the relative difference from NIST values of the predicted viscosity using four methods.

Substance	Methane TRAPP	Propane TRAPP	Chung et al.	Brule-Starling
H ₂	2.40	0.46	12.2	8.78
CH ₄	0.71	2.91	1.06	0.54
C ₂ H ₄	0.83	6.16	3.99	2.38
C ₂ H ₆	6.89	2.73	2.08	3.56
C ₃ H ₆	6.39	9.00	2.45	1.41
C ₃ H ₈	9.08	8.20	2.96	4.17
1,3-C ₄ H ₆	9.02	14.0	3.31	4.31
C ₄ H ₈	6.28	20.7	3.15	2.29
trans-C ₄ H ₈	10.9	15.4	3.66	4.08
cis-C ₄ H ₈	7.60	15.9	2.54	3.45
C ₄ H ₁₀	7.46	19.2	3.62	3.85
C ₅ H ₁₀	3.81	37.3	4.80	4.45
C ₅ H ₁₂	11.4	21.7	6.24	7.04
C ₆ H ₆	4.09	30.2	4.98	5.24
C ₆ H ₁₂	8.41	28.9	4.83	5.13
C ₆ H ₁₄	6.58	37.2	5.60	4.84
C ₇ H ₈	9.50	35.4	5.59	6.22
C ₇ H ₁₄	7.90	34.2	5.85	6.70
C ₇ H ₁₆	7.65	43.3	6.37	5.75
C ₈ H ₁₀	8.12	41.6	6.33	7.34
C ₈ H ₁₆	6.97	39.6	6.72	7.92
C ₈ H ₁₈	8.36	39.9	8.06	9.41
C ₉ H ₁₈	17.0	46.6	11.5	12.8
C ₉ H ₂₀	7.91	49.7	11.3	12.9
C ₁₀ H ₂₂	8.11	50.0	10.6	12.2
C ₁₂ H ₂₆	14.1	54.3	18.9	20.7
C ₁₀ H ₁₆	29.5	51.2	16.1	15.7
JP-8 surrogate	15.6	55.2	10.5	11.8
CH ₄ + C ₂ H ₄	0.39	5.54	4.25	2.70
Total average	8.38	28.2	6.54	6.82

Finally, also presented in Table 2 are the total average values, which are calculated by averaging all of the average relative differences for the 29 substances considered in the current study for each method. The total average of the Methane TRAPP, Propane TRAPP, Chung et al., and Brule-Starling methods are 8.38%, 28.2%, 6.54%, and 6.82%, respectively. A comparison of the total average values concludes that the Chung et al. and Brule-Starling methods best predict the viscosity of all of the subject substances, ranging from hydrogen to low and high molecular weight hydrocarbons, representing hydrocarbon aviation fuels and their possible decomposition products via thermal cracking, over the whole prediction ranges considered here.

Figure 6 shows that the Propane TRAPP, Modified Propane TRAPP, and Chung et al. methods all predict thermal conductivity very well, with the average relative differences

below 10% for most of the hydrocarbons in the present study. In order to take a closer look at the prediction performances of the three methods, the numerical values of the average relative difference data from Figure 6 are listed in Table 3. Even though each of these three methods is superior to the others in predicting the thermal conductivity for some substances, the overall performance represented by the total average value is found to be 34.9%, 7.19%, 6.28%, and 8.19% for the Methane TRAPP, Propane TRAPP, Modified Propane TRAPP, and Chung et al. methods, respectively. The quantified comparison confirms that Modified Propane TRAPP best predicts the thermal conductivity of all of the 29 substances over the present temperature and pressure ranges, but the Propane TRAPP and Chung et al. methods show very little difference.

Table 3. Average of the relative difference from NIST values of the predicted thermal conductivity using four methods.

Substance	Methane TRAPP	Propane TRAPP	Modified Propane TRAPP	Chung et al.
H ₂	1.74	1.99	2.23	19.6
CH ₄	1.92	2.68	2.57	4.84
C ₂ H ₄	6.33	8.07	8.12	12.0
C ₂ H ₆	6.88	4.33	4.24	4.35
C ₃ H ₆	17.2	3.04	3.06	3.67
C ₃ H ₈	13.7	8.17	8.17	8.11
1,3-C ₄ H ₆	33.3	7.04	7.06	9.06
C ₄ H ₈	18.2	11.6	11.4	12.4
trans-C ₄ H ₈	31.6	5.06	4.27	6.42
cis-C ₄ H ₈	35.9	6.74	7.23	8.95
C ₄ H ₁₀	22.3	9.34	8.72	8.33
C ₅ H ₁₀	39.0	5.87	2.76	3.84
C ₅ H ₁₂	34.3	7.60	7.62	5.26
C ₆ H ₆	35.3	1.63	2.45	4.18
C ₆ H ₁₂	48.1	7.05	4.68	10.1
C ₆ H ₁₄	47.2	5.29	4.11	7.07
C ₇ H ₈	36.6	6.56	9.88	4.57
C ₇ H ₁₄	51.9	8.18	5.05	7.80
C ₇ H ₁₆	44.0	7.27	7.44	3.07
C ₈ H ₁₀	50.0	4.94	6.82	7.18
C ₈ H ₁₆	55.3	10.1	4.10	7.20
C ₈ H ₁₈	50.0	5.71	6.64	7.20
C ₉ H ₁₈	56.6	1.55	12.0	13.5
C ₉ H ₂₀	51.6	10.1	7.05	7.07
C ₁₀ H ₂₂	56.5	10.1	6.49	9.22
C ₁₂ H ₂₆	55.0	15.3	8.52	14.0
C ₁₀ H ₁₆	48.4	13.8	8.61	6.93
JP-8 surrogate	58.5	12.9	4.28	11.8
CH ₄ + C ₂ H ₄	5.31	6.47	6.45	9.90
Total average	34.9	7.19	6.28	8.19

In summary, based on the current study, either the Chung et al. or Brule-Starling method is recommended for predicting the viscosity, and the Modified Propane TRAPP method for the thermal conductivity of hydrocarbon aviation fuels and their pyrolyzed products via endothermic reaction. Note, however, that even though a specific method may perform better than the others in predicting the transport properties of various hydrocarbons, performance generally depends on the specific substance and the temperature and pressure ranges, and therefore, it should not be asserted a given method is always absolutely superior to the others. This study also confirms that the transport property prediction methodologies investigated here can be employed for most engineering applications as useful approximation techniques, particularly when the NIST database is not available.

5. Summary and Conclusions

In order to optimize the prediction of transport properties of hydrocarbon aviation fuels and their pyrolyzed products via endothermic reaction, this paper compares the accuracy of several methods in predicting the viscosity and thermal conductivity of various pure hydrocarbon substances and some of their mixtures over temperature and pressure range corresponding to the representative operating conditions of a hydrocarbon aviation fuel which circulates as a coolant in the regenerative cooling system of a hypersonic vehicle.

Four methods were adopted for the prediction of viscosity and thermal conductivity in the current study: the Methane TRAPP, Propane TRAPP, and Chung et al. methods for both transport properties, and the Brule-Starling method for viscosity and the Modified Propane TRAPP method for thermal conductivity. The transport properties of 27 pure substances and two types of mixtures were predicted, including both low and high molecular weight hydrocarbons as well as hydrogen, which are the main constituents of typical aviation fuels and their decomposed products in regenerative cooling systems.

The prediction of the transport properties was performed in the range of temperatures between 300 and 1000 K and pressures between 0.1 and 5.0 MPa; these ranges include the critical points of most of the hydrocarbon fuels of interest. The values of thermal conductivity as well as viscosity estimated using the prescribed methods were compared in terms of relative difference from those acquired from the NIST database. The following major conclusions can be reached based on the comparison.

1. The viscosity of low molecular weight substances, including hydrogen, methane, ethylene, and their mixture, is predicted much more accurately by the TRAPP methods, while that of most high molecular weight hydrocarbons is estimated accurately by both the Chung et al. and Brule-Starling methods.
2. The comparison of the total average values concludes that the Chung et al. and Brule-Starling methods are best for the prediction of the viscosity of all substances, ranging from hydrogen to the low and high molecular weight hydrocarbons, in the temperature and pressure ranges specified in the present study.
3. The quantified comparison by total average difference from the NIST values confirms that Modified Propane TRAPP best predicts the thermal conductivity of all of the 29 substances over the temperature and pressure ranges, and the Propane TRAPP and Chung et al. methods show very little difference.

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Nomenclature

P	Pressure
P_c	Critical pressure
T	Temperature
T_c	Critical temperature
T_r	Reduced temperature

v	Specific volume
X_λ	Translational correction factor for thermal conductivity
Z_c	Critical compressibility factor
Greek symbols	
η	Viscosity
λ	Thermal conductivity
κ	Association parameter
μ_r	Dimensionless dipole moment
ω	Acentric factor

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