2120 J. Chem. Eng. Data **2008,** *53,* 2120–2127

Measurement and Correlation of the Thermal Conductivity of Methylcyclohexane and Propylcyclohexane from (300 to 600) K at Pressures to 60 MPa

Richard A. Perkins,* Ulf Hammerschmidt,[†] and Marcia L. Huber

Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, Colorado 80305-3328

New experimental data on the thermal conductivity of methylcyclohexane and propylcyclohexane are reported that allow the development of wide-range correlations. These new experimental data, covering a temperature range of (300 to 600) K and a pressure range of (0.1 to 60) MPa, are used to develop correlations for the thermal conductivity. The experimental data reported here have an uncertainty of less than 1 % for measurements removed from the critical point and for gas at pressures above 1 MPa, increasing to 3 % in the critical region and for gas at low pressures (less than 1 MPa). On the basis of the uncertainty of and comparisons with the present data, the thermal conductivity correlations for methylcyclohexane and propylcyclohexane are estimated to have a relative uncertainty of about 4 % at a 95 % confidence level. The present data include a contribution due to thermal radiation that increases in proportion to temperature cubed up to an estimated value from 2 % to 3 % near 600 K.

Introduction

Liquid fuels are mixtures of many components, and it is often desirable to model the thermodynamic and transport properties of such complex fuels by use of a surrogate mixture. Surrogate models contain a variety of pure components, depending on which particular fuel or propellant is the target material and on the specific purpose for which the surrogate is developed. Methylcyclohexane and propylcyclohexane are important components in surrogate mixtures for many jet fuels that have however very limited data available for their thermal conductivity. Recently, reliable equations of state (EOS) have been developed for the thermodynamic properties of both methylcyclohexane and propylcyclohexane over the entire fluid region.[1] In this manuscript, extensive measurements are reported for the thermal conductivity of methylcyclohexane and propylcyclohexane in their liquid and vapor phases at temperatures from 300 K to their critical temperature (572.2 K for methylcyclohexane[1]) or 600 K (onset of cracking for propylcyclohexane[2]). The thermal conductivity of supercritical methylcyclohexane near 593 K is also reported. On the basis of these accurate experimental data, correlations for the thermal conductivity of both fluids are developed that cover the entire fluid region.

Experimental Method

The methylcyclohexane and propylcyclohexane samples that were studied in this work had purities of 97.4 % and 96.9 %, respectively, based on analysis at NIST.[2−4] The purity of these samples was determined by gas chromatography (GC) with a mass spectrometer detector with details provided by Widegrin and Bruno.[2] Identification of the impurities was considered reliable with all compositions and purities reported as area fractions from the GC-mass spectrometer peaks. The reported area fractions provide an approximate indication of the mass fraction purity in the absence of calibration with each component. The most significant impurities in the methylcyclohexane were dimethylcyclohexane isomers at 1 %, 2-hydroxymethyl-2-methylcyclopentanol at 0.3 %, 3-methylcyclohexene at 0.3 %, methylcycloheptane at 0.2 %, and *cis*-1-ethyl-2-methylcyclopentane at 0.2 %. The most significant impurities in the propylcyclohexane were α-ethylcyclohexanemethanol at 2.1 % and methylcyclohexane at 0.5 %. The samples were degassed under vacuum prior to measurements and after liquid/supercritical measurements at the highest temperatures to remove any trace decomposition gases that may have accumulated. The maximum temperature studied was limited to 600 K for both fluids, based on knowledge of the decomposition kinetics.[2,5] All reported uncertainties are for a coverage factor of $k = 2$, approximately a 95 % confidence interval.

Transient Measurements. The measurements of thermal conductivity were obtained with a transient hot-wire instrument that has previously been described in detail.[6] During an experiment, the hot wires functioned as both electrical heat sources and resistance thermometers to measure the temperature rise. Each measurement cell consisted of a pair of hot wires of differing length operating in a differential arrangement to eliminate errors due to axial conduction. The outer cavity around the hot wires was stainless steel with a diameter of 9 mm. The transient hot wires were enclosed by a stainless-steel pressure vessel that is capable of operation from (250 to 750) K at pressures to 70 MPa in the liquid, vapor, and supercritical gas phases. Initial cell temperatures, T_i, were determined with a reference platinum resistance thermometer with an uncertainty of 0.005 K, and pressures, P_e, are determined with a pressure transducer with an uncertainty of 7 kPa. The first measurements on liquid methylcyclohexane were made with anodized tantalum hot wires with a diameter of 25 μm [(300 to 400) K]. This tantalum hot-wire cell failed due to lead grounding at 400 K. All other measurements on methylcyclohexane and propylcyclohexane were made with bare platinum hot wires with a diameter of 12.7 μm.

The basic theory that describes the operation of the transient hot-wire instrument is given by Healy et al.[7] The hot-wire cell

---

* Corresponding author. E-mail: richard.perkins@nist.gov.

[†] Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, Germany.

10.1021/je800255r CCC: $40.75

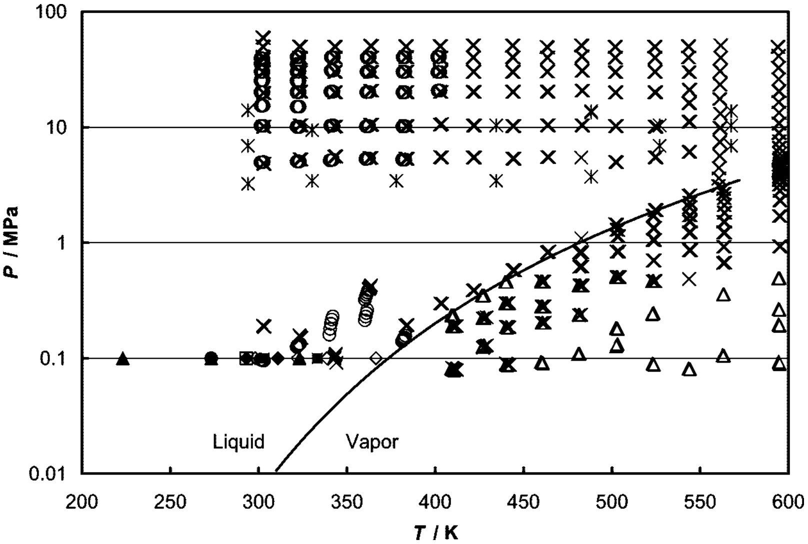

Figure 1. Distribution of the data for the thermal conductivity of methylcyclohexane: ×, transient (Pt); ○, transient (Ta); △, steady state (Pt); *, Perkins;[14] ◇, Mallan et al.;[15] ▲, Jamieson and Cartwright;[16] ●, Parkinson;[17] ◆, Sakiadis and Coates;[18] □, Briggs;[19] ■, Smith.[20] The solid line shows the vapor−liquid saturation boundary and terminates at the critical point[1] (572.2 K and 3.47 MPa).

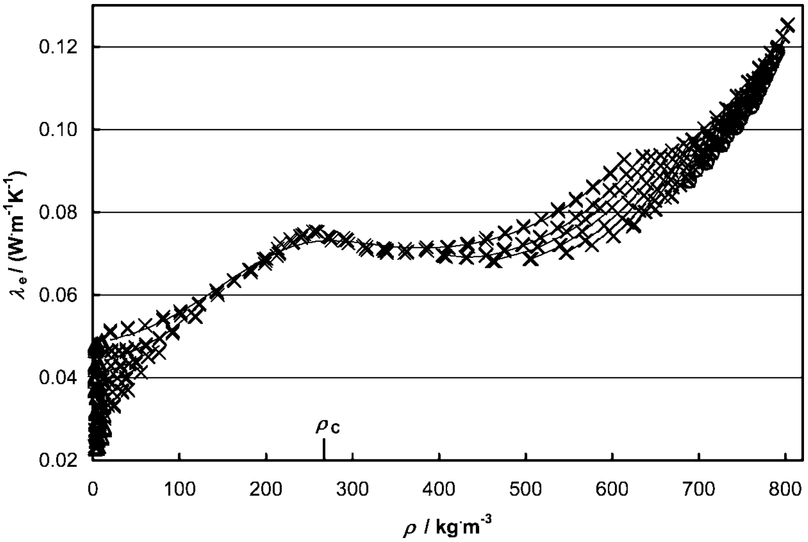

Figure 2. Thermal conductivity of methylcyclohexane as a function of the density calculated at the measured temperature and pressure: ×, transient (Pt); ○, transient (Ta); △, steady state (Pt); solid lines given by the correlation developed in this work.

was designed to approximate a transient line source as closely as possible, and deviations from this model are treated as corrections to the experimental temperature rise. The ideal temperature rise ΔT_{id} is given by

$$\Delta T_{\mathrm{id}} = \frac{q}{4\pi\lambda}\left[\ln(t) + \ln\left(\frac{4a}{r_0^{\,2}C}\right)\right] = \Delta T_{\mathrm{w}} + \sum_{i=1}^{10} \delta T_i \qquad (1)$$

where q is the power applied per unit length; λ is the thermal conductivity of the fluid; t is the elapsed time; $a = \lambda/(\rho C_p)$ is the thermal diffusivity of the fluid; ρ is the density of the fluid; C_p is the isobaric specific heat capacity of the fluid; r_0 is the radius of the hot wire; $C = 1.781$ is the exponential of Euler's constant; ΔT_{w} is the measured temperature rise of the wire; and δT_i are corrections[7] to account for deviations from ideal line-source conduction. During analysis, a line is fit to a linear section of the ΔT_{id} versus ln(t) data, and the thermal conductivity is obtained from the slope of this line. Both thermal conductivity and thermal diffusivity can be determined with the transient hot-wire technique as shown in eq 1, but only the thermal conductivity results are considered here. The experiment temperature, T_{e}, associated with the thermal conductivity is the average temperature at the wire's surface over the period that was fit to obtain the thermal conductivity.

For gas-phase measurements, two corrections[7−11] must be carefully considered. First, since the thermal diffusivity of the gas is much different from that of the wire, the correction for the wire's finite radius becomes very significant. Second, the thermal diffusivity of the dilute gas varies inversely with the pressure, so it is possible for the transient thermal wave to penetrate to the outer boundary of the gas region during an experiment at low pressures.[7−11] The preferred method to deal with such corrections is to minimize them by proper design. For instance, the correction for the finite wire radius can be minimized with wires of extremely small diameter, (4 to 7) μm, and penetration of the thermal wave to the outer boundary can be eliminated by use of a cell with an outer boundary of large diameter. However, such designs are often not optimal for a general-purpose instrument, where such extremely fine wires may be too fragile, and large outer dimensions may require too much of a scarce sample, particularly in the liquid phase.

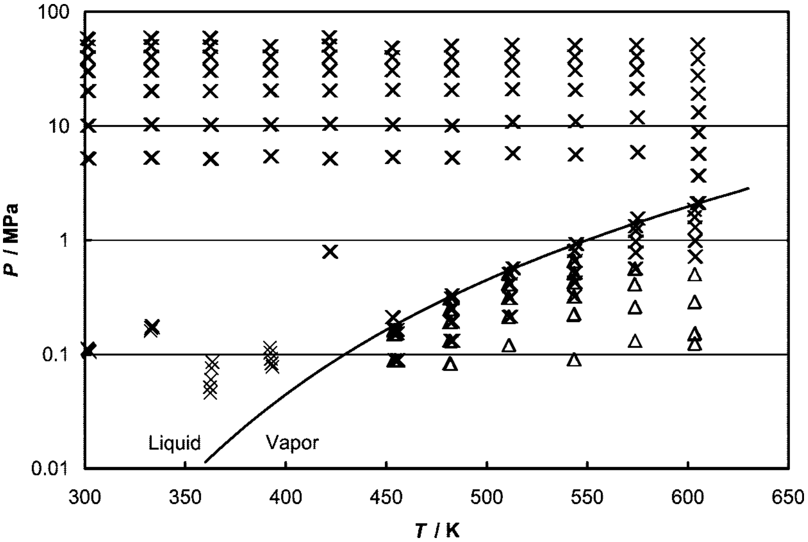

Figure 3. Distribution of the data for the thermal conductivity of propylcyclohexane: ×, transient (Pt); △, steady state (Pt). The solid line shows the vapor−liquid saturation boundary and terminates at the critical point[1] (630.8 K and 2.86 MPa).

The present transient hot-wire wires require careful correction for the wire's finite radius during such dilute-gas measurements. However, measurement times must be selected to minimize the correction for penetration to the outer boundary due to the relatively small diameter of the concentric fluid region around each hot wire. For the measurements reported here, only application of the full correction[7] for the finite wire dimensions was considered adequate. For a few of the measurements at the lowest pressures, the outer boundary was encountered during the one-second duration of the experiment, so the experiment time was reduced to minimize the magnitude of this correction. Experiments are generally limited to 1 s in duration, with 250 measurements of temperature rise as a function of elapsed time relative to the onset of wire heating. Fluid convection is normally not a problem, except in the critical region.

Thermal radiative heat transfer between media at two different temperatures T_1 and T_2 increases in proportion to absolute temperature cubed since it is proportional to $(T_1^4 - T_2^4) \approx T^3(T_1 - T_2)$ for small temperature differences. However, correction for thermal radiation during transient hot-wire measurements is generally limited to three cases: (1) transparent fluid (TF), (2) opaque fluid (OF), and (3) dominated by emission from fluid (EF).[6] For hydrocarbons such as toluene, methylcyclohexane, and propylcyclohexane, the radiative heat transfer ranges from transparent in the gas phase to being dominated by emission in the liquid phase. On the basis of our studies of liquid toluene at temperatures up to 550 K, the contribution of thermal radiation from fluid emission to the measured apparent thermal conductivity in the liquid phase should range from less than 1 % near 360 K to 3 % near 550 K.[6,12] Although it is possible to apply the transparent radiation correction to the vapor phase and the correction for fluid emission of radiation to the liquid phase, this would lead to a discontinuity along supercritical isotherms that span the entire range of density. In the present measurements, we have treated the fluid as transparent to thermal radiation. Errors due to absorption and emission of thermal radiation by the fluid at higher densities should be less than 3 % at the highest temperatures from (550 to 600) K based on differences between transparent fluid (TF) correction and emission from fluid (EF) corrections for thermal radiation.

Steady-State Measurements. At very low pressures, the steady-state hot-wire technique has the advantage of not requiring significant corrections.[13] The working equation for the steady-state mode is based on a different solution of Fourier's law, but the geometry is still that of concentric cylinders. This equation can be solved for the thermal conductivity of the fluid, λ,

$$\lambda = \frac{q \ln\left(\frac{r_2}{r_1}\right)}{2\pi(T_1 - T_2)} \tag{2}$$

where q is the applied power per unit length; r_2 is the internal radius of the outer cylinder; r_1 is the external radius of the inner cylinder (hot wire); and $\Delta T = (T_1 - T_2)$ is the measured temperature difference between the hot wire and its surrounding cavity.

For the concentric-cylinder geometry described above, the total radial heat flow per unit length, q, remains constant and is not a function of the radial position. Assuming that the thermal conductivity is a linear function of temperature, such that $\lambda = \lambda_0(1 + b_\lambda T)$, it can be shown that the measured thermal conductivity is given by $\lambda = \lambda_0(1 + b_\lambda(T_1 + T_2)/2)$. Thus, the measured thermal conductivity corresponds to the value at the mean temperature of the inner and outer cylinders

$$\bar{T} = (T_1 + T_2)/2 \tag{3}$$

This assumption of linear temperature dependence for the thermal conductivity is valid only for experiments with small temperature differences. The density assigned to the measured thermal conductivity is calculated from an equation of state with the temperature from eq 3 and the experimentally measured pressure. An assessment of corrections during steady-state hot-wire measurements is available.[13]

Experimental Results

The results of the transient and steady-state measurements of the thermal conductivities of methylcyclohexane and propylcyclohexane are tabulated in the Supporting Information. Transient experiments were analyzed over the time range from (0.1 to 1) s. The reproducibility of the thermal conductivity from relative uncertainty of the slope of the corrected transient-temperature-rise data over this time range is given in the tables of transient data in the Supporting Information. This uncertainty ($k = 2$) depends on both temperature-rise noise and systematic curvature and is less than 0.2 % for the transient measurements

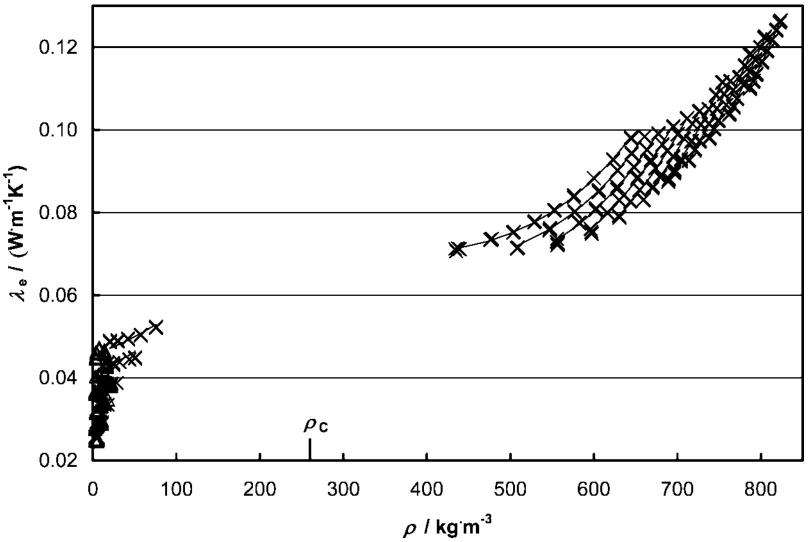

Figure 4. Thermal conductivity of propylcyclohexane as a function of the density calculated at the measured temperature and pressure: ×, transient (Pt); △, steady state (Pt); solid lines given by the correlation developed in this work.

in the liquid phase and less than 2 % for the transient measurements in the vapor phase that are reported from these samples. The tables of steady-state data in the Supporting Information provide the start time and the end time for evaluation of the temperature rise and the Rayleigh number during the experiment that characterizes the level of convection during the experiment. The Rayleigh numbers during the steady-state measurements were generally less than 17 000, corresponding to a 1 % correction to the measured thermal conductivity. Consistency between measurements at five different applied power levels for each initial temperature and pressure confirms that convection was not a problem during both transient and steady-state measurements.

Methylcylohexane. The range of state points covered by the present measurements is shown in Figure 1 relative to the vapor pressure curve of methylcyclohexane, along with the data sets from the literature.[14−20] Measurements are generally reported for five different applied powers at each initial fluid state point to verify the absence of convection during the measurements. There are 199 transient measurements of the liquid phase at temperatures from (300 to 400) K reported in the Supporting Information from the anodized-tantalum hot-wire cell. There are 133 steady-state measurements of the vapor phase at temperatures from (410 to 564) K, 172 transient measurements of the vapor phase at temperatures from (410 to 564) K, 537 transient measurements of the liquid phase at temperatures from (300 to 562) K, and 149 transient measurements that are supercritical at temperatures near 594 K reported in the Supporting Information from the platinum hot-wire cell. The liquid and supercritical measurements reach pressures up to 60 MPa. The uncertainty of the measured temperature (ITS-90) is 0.005 K, while the uncertainty of the measured pressure is 7 kPa. The thermal conductivity data have an expanded uncertainty (i.e., a coverage factor $k = 2$ and thus a two-standard deviation estimate) of less than 1 % for measurements removed from the critical point and for gas at pressures above 1 MPa, increasing to 3 % at the highest temperatures and for gas at low pressures (less than 1 MPa). There is an offset that is less than 0.7 % between the liquid measurements made with the tantalum hot-wire cell at temperatures from (300 to 400) K and those made with the platinum hot-wire cell. In this region, the data from the tantalum hot-wire cell are considered more reliable since the newly installed platinum hot wires were observed to be annealing significantly during these measurements. Reported densities, and other fluid property data required for corrections to the measured temperature rise during data analysis, are calculated with a short-form Helmholtz equation of state[1] for each experimental temperature and pressure associated with the measured thermal conductivity. These measurements are shown in Figure 2 as a function of calculated density.

Table 1. Parameters for the Dilute-Gas Thermal Conductivity of Methylcyclohexane, Equation 5

A_0/(W·m^{-1}·K^{-1})	2.89968·10^{-3}
A_1/(W·m^{-1}·K^{-1})	−1.80666·10^{-2}
A_2/(W·m^{-1}·K^{-1})	7.27576·10^{-2}
A_3/(W·m^{-1}·K^{-1})	−1.29778·10^{-2}

Table 2. Parameters for the Residual Thermal Conductivity Contribution of Methylcyclohexane, Equations 6 to 10

i	j	B_{ij}/W·m^{-1}·K^{-1}
1	1	9.19149·10^{-2}
1	2	−7.90408·10^{-2}
2	1	−8.17088·10^{-2}
2	2	9.23911·10^{-2}
3	1	2.96449·10^{-2}
3	2	−4.28498·10^{-2}
4	1	−2.99834·10^{-3}
4	2	7.27860·10^{-3}
q_d/m^{-1}		1.6026·10^{9}

Propylcyclohexane. The range of state points covered by the present measurements is shown in Figure 3 relative to the vapor pressure curve of propylcyclohexane. No literature data were found for the thermal conductivity of propylcyclohexane. Measurements are generally reported for five different applied powers at each initial fluid state point to verify the absence of convection during the measurements. There are 133 steady-state measurements of the vapor phase at temperatures from (453 to 604) K, 129 transient measurements of the vapor phase at temperatures from (454 to 604) K, and 406 transient measurements of the liquid phase at temperatures from (300 to 605) K reported in the Supporting Information from the platinum hot-wire cell. The liquid measurements reach pressures up to 60 MPa. The uncertainty of the measured temperature (ITS-90) is 0.005 K, and the uncertainty of the measured pressure is 7 kPa. The thermal conductivity data have an expanded uncertainty (i.e., a coverage factor $k = 2$ and thus a two-standard deviation estimate) of less than 1 % for measurements removed from the critical point and for gas at pressures above 1 MPa, increasing to 3 % at the highest temperatures and for gas at low pressures (less than 1 MPa). Reported densities, and other fluid property

Table 3. Parameters for the Dilute-Gas Thermal Conductivity of Propylcyclohexane, Equation 5

$A_0/(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$	$1.07402 \cdot 10^{-2}$
$A_1/(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$	$-6.09829 \cdot 10^{-2}$
$A_2/(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$	$1.38204 \cdot 10^{-1}$
$A_3/(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$	$-3.81213 \cdot 10^{-2}$

Table 4. Parameters for the Residual Thermal Conductivity Contribution of Propylcyclohexane, Equations 6 to 10

i	j	$B_{ij}/(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$
1	1	$1.16524 \cdot 10^{-1}$
1	2	$-1.02821 \cdot 10^{-1}$
2	1	$-1.13871 \cdot 10^{-1}$
2	2	$1.26431 \cdot 10^{-1}$
3	1	$4.45827 \cdot 10^{-2}$
3	2	$-5.94600 \cdot 10^{-2}$
4	1	$-5.45736 \cdot 10^{-3}$
4	2	$9.89360 \cdot 10^{-3}$
q_d/m^{-1}		$1.6026 \cdot 10^{9}$

data required for corrections to the measured temperature rise during data analysis, are calculated with a short-form Helmholtz equation of state[1] for each experimental temperature and pressure associated with the measured thermal conductivity. These measurements are shown in Figure 4 as a function of calculated density.

Thermal Conductivity Correlation

We represent the thermal conductivity λ of a pure fluid as a sum of three contributions

$$\lambda(\rho, T) = \lambda_0(T) + \Delta\lambda_r(\rho, T) + \Delta\lambda_c(\rho, T) \tag{4}$$

where λ_0 is the dilute-gas thermal conductivity, which depends only on temperature; $\Delta\lambda_r$ is the residual thermal conductivity; and $\Delta\lambda_c$ is the enhancement of the thermal conductivity in the critical region. Both $\Delta\lambda_r$ and $\Delta\lambda_c$ are functions of temperature, T, and density, ρ, with ρ calculated with an equation of state for each given T and P. In this work, we use the short-form Helmholtz equations of state[1] for each fluid that have temperature and pressure limits of 500 K and 50 MPa, which correspond to density limits of 9.1 $\mathrm{mol \cdot L^{-1}}$ for methylcyclohexane and 7.0 $\mathrm{mol \cdot L^{-1}}$ for propylcyclohexane. Some of the thermal conductivity data were measured at temperatures and pressures that exceed these limits, and extrapolation of the equation of state and present thermal conductivity model beyond these limits should be viewed with caution.

Dilute-Gas Thermal Conductivity. We represent the dilute-gas thermal conductivity as a polynomial in reduced temperature

$$\lambda_0(T)/(\mathrm{W \cdot m^{-1} \cdot K^{-1}}) = \sum_{k=0}^{3} \mathrm{A}_k (T/T_c)^k \tag{5}$$

with coefficients A_k, where T is the temperature and T_c is the critical temperature. The critical parameters for methylcyclohexane[1] are $T_c = 572.2$ K, $P_c = 3.47$ MPa, and $\rho_c = 267.07$ $\mathrm{kg \cdot m^{-3}}$ and for propylcyclohexane[1] are $T_c = 630.8$ K, $P_c = 2.86$ MPa, and $\rho_c = 260.05$ $\mathrm{kg \cdot m^{-3}}$.

Residual Thermal Conductivity. We used a polynomial in temperature and density to represent the excess, or residual, contribution to the thermal conductivity

$$\Delta\lambda_r(\rho, T)/(\mathrm{W \cdot m^{-1} \cdot K^{-1}}) = \sum_{i=1}^{4} \left(B_{i,1} + B_{i,2}\left(\frac{T}{T_c}\right)\right)\left(\frac{\rho}{\rho_c}\right)^i \tag{6}$$

with coefficients $B_{i,j}$, where ρ is the density and ρ_c is the critical density. This form has recently been shown to accurately represent other hydrocarbon fluids such as isobutane,[21] butane,[22] and propane,[23] and, most recently, dodecane.[24]

Critical Enhancement. Olchowy and Sengers[25] developed a theoretically based, but complex, model for the thermal conductivity enhancement in the critical region. We use a simplified version of their crossover model[26]

$$\Delta\lambda_c(T, \rho)/(\mathrm{W \cdot m^{-1} \cdot K^{-1}}) = \frac{\rho C_p R_0 k_B T}{6\pi\eta\xi}(\Omega - \Omega_0) \tag{7}$$

where the heat capacity at constant pressure, $C_p(T,\rho)$, is obtained from the equation of state; k_B is Boltzman's constant; $R_0 = 1.01$ is a universal constant;[26] and the viscosity, $\eta(T,\rho)$, is obtained from a separate correlation.[1]

The crossover functions Ω and Ω_0 are determined by

$$\Omega = \frac{2}{\pi}\left[\left(\frac{C_p - C_V}{C_p}\right)\arctan(q_d\xi) + \frac{C_V}{C_p}(q_d\xi)\right] \tag{8}$$

$$\Omega_0 = \frac{2}{\pi}\left[1 - \exp\left(\frac{-1}{(q_d\xi)^{-1} + \frac{1}{3}\left(\frac{(q_d\xi)\rho_c}{\rho}\right)^2}\right)\right] \tag{9}$$

The heat capacity at constant volume, $C_V(T,\rho)$, is obtained from the equation of state, and the correlation length ξ is given by

$$\xi = \xi_0\left[\frac{P_c\rho}{\Gamma\rho_c^2}\right]^{\nu/\gamma}\left[\frac{\partial\rho(T,\rho)}{\partial P} - \left(\frac{T_R}{T}\right)\frac{\partial\rho(T_R,\rho)}{\partial P}\right]^{\nu/\gamma} \tag{10}$$

where the critical amplitudes Γ and ξ_0 are system dependent and are determined by the asymptotic behavior of the equation of state in the critical region. The partial derivative $\partial\rho/\partial P$ is evaluated with the equation of state at the system temperature T and a reference temperature, T_R. For the reference temperature, we select a value where the critical enhancement is assumed to be negligible: $T_R = 1.5T_c$. The exponents $\gamma = 1.2415$ and $\nu = 0.63$ are universal constants.[26] We have chosen to use values of the critical amplitudes reported for carbon dioxide[26] that we consider reasonable for this family of fluids, $\Gamma = 0.052$ and $\xi_0 = 1.5 \cdot 10^{-10}$ m. The only parameter left to be determined is the cutoff wavenumber q_d (or, alternatively, its inverse, $q_d{}^{-1}$).

Correlation Results

To obtain the coefficients for the thermal conductivity of the dilute gas in the limit of zero density, eq 5, one can extrapolate the thermal conductivity at constant temperature to zero density, provided that there are data over a sufficient range of densities along an isotherm. An alternative method is to simultaneously fit the dilute-gas thermal conductivity, the excess contribution, and the critical enhancement, eqs 4 to 10, to obtain the dilute-gas coefficients A_i, the excess coefficients B_{ij}, and the cutoff wavenumber q_d. We chose the latter method, with equilibrium properties from the equation of state.[1] We used the fitting program ODRPACK[27] to fit the present experimental data to determine the coefficients in eqs 4 to 10, given in Tables 1 and 2 for methylcyclohexane and in Tables 3 and 4 for propylcyclohexane. There were sufficient data available for methylcyclohexane to determine an optimum value for the cutoff wavenumber q_d. This same value was used for propylcyclohexane where there were no supercritical data. Table 5 provides thermal conductivity values calculated for each fluid that allows verification of computer coding of the correlations. The state conditions of some of the data points exceeded the limits of the EOS. Their results are still included in the statistical analysis, but we recommend caution when extrapolating outside the limits of the EOS.

Table 5. Values of Thermal Conductivity Calculated with the Correlation Equations 4 to 10 at Specified T and ρ, with the Coefficients in Tables 1 and 2 for Methylcyclohexane or Tables 3 and 4 for Propylcyclohexane

		methylcyclohexane		propylcyclohexane	
T/K	P/MPa (calcd[1])	$\rho/(\mathrm{kg \cdot m^{-3}})$	$\lambda/(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$	$\rho/(\mathrm{kg \cdot m^{-3}})$	$\lambda/(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$
300.00	0.100	763.527 638	0.106 327 779	788.480 445	0.110 772 385
450.00	0.100	2.684 451 55	0.027 678 7553	3.527 271 23	0.024 318 5705
450.00	50.000	701.680 049	0.099 506 6894	729.367 278	0.105 375 558
600.00	0.100	1.984 341 55	0.049 060 1410	2.568 853 56	0.045 153 7166
600.00	4.744	267.000 153	0.070 854 7641	501.697 589	0.074 315 5503
600.00	50.000	610.749 122	0.093 158 9650	644.863 706	0.097 680 9646

Methylcyclohexane Deviations. The two most extensive data sets for methylcyclohexane are the present study, comprising 1389 points in the liquid, vapor, and supercritical regions at pressures to 60 MPa, and the set of Perkins[14] that contains 48 points obtained with a transient hot-wire apparatus at temperatures from (293 to 568) K and at pressures to 14 MPa with an estimated uncertainty of 1.5 % near 300 K, increasing to 3 % near 550 K. The data of Perkins[14] were corrected for thermal radiation (absorbing-emitting fluid), while the present results treat the fluid as transparent to thermal radiation. Mallan et al.[15] reported five liquid phase points at temperatures from (298 to 366) K with an estimated uncertainty of 3 %. Jamieson and Cartwright[16] reported three liquid phase points at temperatures from (223 to 323) K with an estimated uncertainty of 3 %. Parkinson[17] reported a liquid value at 273.15 K with an estimated uncertainty of 3 %. Sakiadis and Coates[18] reported two liquid values at temperatures of (293.15 and 310.93) K with an estimated uncertainty of 3 %. Briggs[19] reported a value at

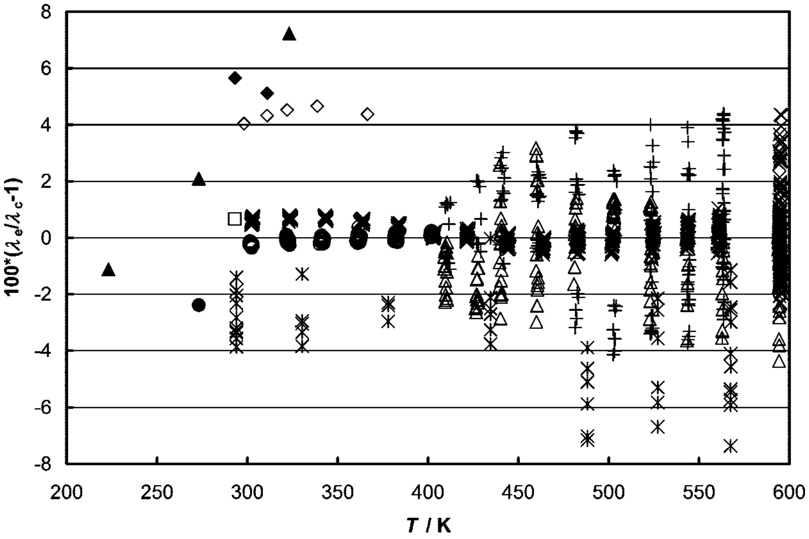

Figure 5. Relative deviations between the data (λ_e) and the correlation (λ_c) for the thermal conductivity of methylcyclohexane as a function of temperature: ×, transient liquid (Pt); ○, transient (Ta); △, steady state (Pt); *, Perkins;[14] ◇, Mallan et al.;[15] ▲, Jamieson and Cartwright.;[16] ●, Parkinson;[17] ◆, Sakiadis and Coates;[18] □, Briggs.[19]

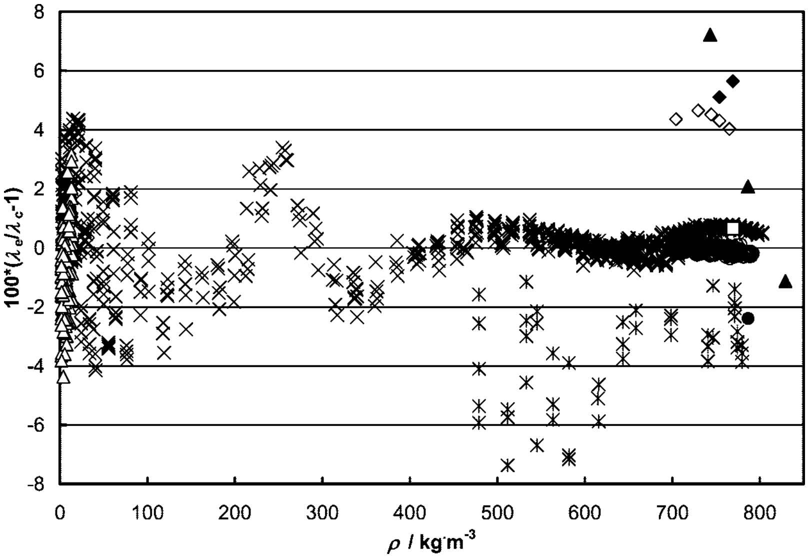

Figure 6. Relative deviations between the data (λ_e) and the correlation (λ_c) for the thermal conductivity of methylcyclohexane as a function of the calculated density: ×, transient (Pt); ○, transient (Ta); △, steady state (Pt); *, Perkins;[14] ◇, Mallan et al.;[15] ▲, Jamieson and Cartwright.;[16] ●, Parkinson;[17] ◆, Sakiadis and Coates;[18] □, Briggs.[19]

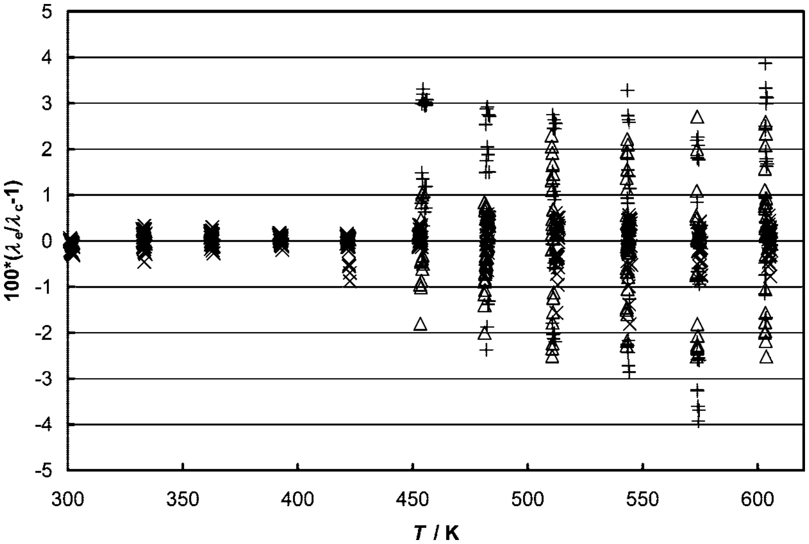

Figure 7. Relative deviations between the data (λ_e) and the correlation (λ_c) for the thermal conductivity of propylcyclohexane as a function of temperature: ×, transient liquid (Pt); △, steady state (Pt).

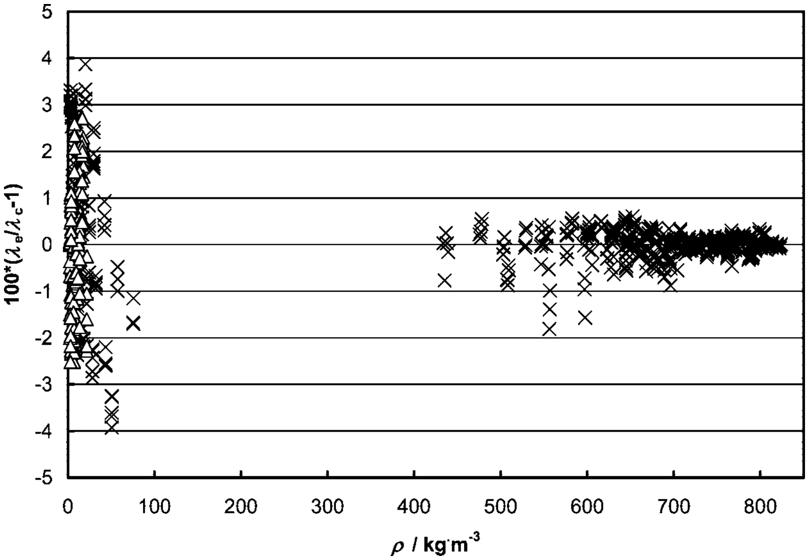

Figure 8. Relative deviations between the data (λ_e) and the correlation (λ_c) for the thermal conductivity of propylcyclohexane as a function of the calculated density: ×, transient (Pt); △, steady state (Pt).

293.15 K with an estimated uncertainty of 3 %. Finally, Smith[20] reported two liquid values at temperatures of (303.15 and 333.15) K that are 25 % larger than all other values, likely due to fluid convection during the measurements.

Figure 5 shows deviations between the data and the correlation as a function of measured temperature. The correlation placed a higher weight on the present results with the anodized tantalum hot-wire cell at temperatures from (300 to 400) K, so the results from the platinum hot-wire cell are up to 0.7 % higher near 300 K but still within the claimed uncertainty. Both hot-wire cells are in excellent agreement near 400 K after significant annealing of the new platinum hot wires had occurred. Good agreement, within 2 %, is found between the data of Jamieson and Cartwright,[16] Parkinson,[17] and Briggs[19] at temperatures below 300 K, even though these data sets were not used in development of the correlation. Thus, extrapolation to temperatures as low as 200 K is expected to give reasonable results. Figure 6 shows deviations between the data and the correlation as a function of density calculated from the measured temperature and pressure with the equation of state.[1] The data of Mallan et al.[15] and Sakiadis and Coates[18] and the highest temperature point of Jamieson and Cartwright[16] are 4 % to 7 % higher than the present work. The liquid data of Perkins[14] are lower than the present results by 1 % to 4 % near 300 K, but are up to 7 % lower at their highest temperature of 568 K where thermal radiation correction for absorbing-emitting liquids that was applied by Perkins[14] is significantly larger than the transparent fluid correction applied to the present data as discussed above. Since deviations for the data of Smith[20] are 25 % larger than all other values, they are not shown in either Figure 5 or 6.

The correlation accurately represents the present data over the temperature range from (300 to 594) K for the liquid, vapor, and supercritical fluid phases at pressures up to 60 MPa. All of the present data agree with the correlation to within ± 4 % at a 95 % confidence level. The trend of the present data being increasingly higher than the liquid data of Perkins[14] (a difference of about 2 % to 3 % near 600 K) is consistent with the differences between the radiation corrections that were applied to the data of Perkins[14] (EF correction) and the present data (TF correction), based on our earlier work with liquid toluene.[6,12] It is further expected that the correlation has significantly larger uncertainties at temperatures and densities that are closer to the critical point than are the present data.

Propylcyclohexane Deviations. The present study, comprising 668 points in the liquid and vapor regions at pressures to 60 MPa, is the only data set available for propylcyclohexane.

Figure 7 shows deviations between the present data and the correlation as a function of measured temperature. Figure 8 shows deviations between the present data and the correlation as a function of density calculated from the measured temperature and pressure with the equation of state.[1] The correlation accurately represents the present data over the temperature range from (300 to 604) K for the liquid and vapor phases at pressures up to 60 MPa. All of the data agree with the correlation to within ± 4 % at a 95 % confidence level. It is expected that the correlation has significantly larger uncertainties at temperatures and densities that are closer to the critical point than the primary data. The propylcyclohexane data likely include a contribution due to thermal radiation that is up to 2 % to 3 % at the highest temperatures near 600 K.

Conclusions

A total of 1389 points are reported for the thermal conductivity of methylcyclohexane in the liquid, vapor, and supercritical regions at pressures to 60 MPa. A total of 668 points are reported for the thermal conductivity of propylcyclohexane in the liquid and vapor regions at pressures to 60 MPa. The thermal conductivity data for these fluids have an uncertainty of less than 1 % for measurements removed from the critical point and for gas at pressures above 1 MPa, increasing to 3 % at the highest temperatures (near 600 K) and for gas at low pressures (less than 1 MPa) at a 95 % confidence level. A significant critical enhancement is observed in the thermal conductivity data near the critical point. There is an uncorrected contribution to the reported thermal conductivity values due to absorption and emission of thermal radiation by the fluid at higher densities that increases in proportion to temperature cubed up to 2 % to 3 % near 600 K, even though emission from the wires has been accounted for. Thus, the radiation-free thermal conductivity should be lower at elevated temperatures.

On the basis of these measurements, correlations are developed for the thermal conductivity of methylcyclohexane and propylcyclohexane. The data and correlations agree well with reliable data sets for methylcyclohexane from the literature. The correlations require thermodyamic property information that was obtained from a newly developed equation of state.[1] The correlations account for the critical enhancement with a crossover model and agree with the present data sets to within ± 4 % at a 95 % confidence level over the temperature range from (300 to 600) K. The correlations are expected to have increased uncertainty in the region near the critical point and at temperatures and pressures beyond the range of the underlying equation of state. Comparison with literature data for methylcyclohexane at temperatures below 300 K indicates reasonable extrapolation to temperatures between (200 and 300) K.

Supporting Information Available:

Tabulated experimental values (44 pages) are reported. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Bruno, T. J.; Huber, M. L.; Laesecke, A.; Lemmon, E. W.; Outcalt, S. L.; Ott, L. S.; Perkins, R. A.; Seelig, H. D.; Smith, B. L. *NISTIR 6648 The properties of S-8 Aviation Fuel*; Nat. Inst. Stand. Technol.: 2007.

(2) Widegrin, J. A.; Bruno, T. J. Thermal decomposition kinetics of propylcyclohexane. *Ind. Eng. Chem. Res.* **2008**, accepted.

(3) Bruno, T. J.; Svoronos, P. D. N. *CRC handbook of basic tables for chemical analysis*, 2nd ed.; CRC Press: Boca Raton, 1989.

(4) Bruno, T.; Svoronos, P. D. N. *CRC handbook of specific spectroscopic correlation charts*; Taylor and Francis CRC Press: Boca Raton, 2005.

(5) Lai, W. C.; Song, C. S. Pyrolysis of alkylcyclohexanes in or near the supercitical phase. Product distribution and reaction pathways. *Fuel Process. Technol.* **1996**, *48*, 1–27.

(6) Perkins, R. A.; Roder, H. M.; Nieto de Castro, C. A. A High-Temperature Transient Hot-Wire Thermal Conductivity Apparatus for Fluids. *J. Res. Natl. Inst. Stand. Technol.* **1991**, *96*, 247–269.

(7) Healy, J.; DeGroot, J. J.; Kestin, J. The Theory of the Transient Hot-Wire Method for Measuring the Thermal Conductivity. *Physica* **1976**, *C82*, 392–408.

(8) Assael, M. J.; Karagiannidis, L.; Richardson, S. M.; Wakeham, W. A. Compression Work using the Transient How-Wire Method. *Int. J. Thermophys.* **1992**, *13*, 223–235.

(9) Taxis, B.; Stephan, K. The Measurement of the Thermal Conductivity of Gases at Low Density by the Transient Hot-Wire Technique. *High Temp. High Press.* **1994**, *15*, 141–153.

(10) Li, S. F. Y.; Papadaki, M.; Wakeham, W. A. The measurement of the Thermal Conductivity of Gases at Low Density by the Transient Hot-Wire Technique. *High Temp. High Press.* **1993**, *25*, 451–458.

(11) Li, S. F. Y.; Papadaki, M.; Wakeham, W. A. Thermal Conductivity of Low-Density Polyatomic Gases. In *Thermal Conductivity 22*; Tong, T. W., Ed.; Technomic Publishing: Lancaster, PA, 1994; pp 531−542.

(12) Nieto de Castro, C. A.; Perkins, R. A.; Roder, H. M. Radiative heat transfer in transient hot-wire measurements of thermal conductivity. *Int. J. Thermophys.* **1991**, *12*, 985–997.

(13) Roder, H. M.; Perkins, R. A.; Laesecke, A.; Nieto de Castro, C. A. Absolute steady-state thermal conductivity measurements by use of a transient hot-wire system. *J. Res. Natl. Inst. Stand. Technol.* **2000**, *105*, 221–253.

(14) Perkins, R. A. Development of a transient hot wire instrument to measure the thermal conductivity of fluids at high temperatures and pressures, PhD, Colorado School of Mines, Golden, 1983.

(15) Mallan, G. M.; Michaelian, M. S.; Lockhart, F. J. Liquid thermal conductivities: Organic compounds and petroleum fractions. *J. Chem. Eng. Data* **1972**, *17*, 412–415.

(16) Jamieson, D. T.; Cartwright, G., Thermal conductivity of cycloaliphatic liquids. In *Thermal Conductivity 16*; Larsen, D. G., Ed.; Plenum: Chicago, IL, 1982; pp 435−438.

(17) Parkinson, W. Thermal conductivity of binary liquid mixtures, PhD, University of Southern California, Los Angeles, 1974.

(18) Sakiadis, B. C.; Coates, J. Studies of thermal conductivity of liquids, Part III. *AiChE J.* **1957**, *3*, 121–126.

(19) Briggs, D. K. H. Thermal conductivity of liquids. *Ind. Eng. Chem.* **1957**, *49*, 418–421.

(20) Smith, J. F. D. The thermal conductivity of liquids. *Trans. Am. Soc. Mech. Eng.* **1936**, *58*, 719–725.

(21) Perkins, R. A. Measurement and correlation of the thermal conductivity of isobutane from 114 to 600 K at pressures to 70 MPa. *J. Phys. Chem. Ref. Data* **2002**, *47*, 1272–1279.

(22) Perkins, R. A.; Ramires, M. L. V.; de Castro, C. A. N.; Cusco, L. Measurement and Correlation of the Thermal Conductivity of Butane from 135 to 600 K at Pressures to 70 MPa. *J. Chem. Eng. Data* **2002**, *47*, 1263–1271.

(23) Marsh, K. N.; Perkins, R. A.; Ramires, M. L. V. Measurement and Correlation of the Thermal Conductivity of Propane from 86 to 600 K at Pressures to 70 MPa. *J. Chem. Eng. Data* **2002**, *47*, 932–940.

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

(25) Olchowy, G. A.; Sengers, J. V. Crossover from Regular to Singular Behavior of the Transport Properties of Fluids in the Critical Region. *Phys. Rev. Lett.* **1988**, *61*, 15–18.

(26) Olchowy, G. A.; Sengers, J. V. A Simplified Representation for the Thermal Conductivity of Fluids in the Critical Region. *Int. J. Thermophys.* **1989**, *10*, 417–426.

(27) Boggs, P. T.; Byrd, R. H.; Rogers, J. E.; Schnabel, R. B. *ODRPACK, Software for Orthogonal Distance Regression*; NISTIR 4834; National Institute of Standards and Technology: Gaithersburg, MD, USA, 1992.

Received for review April 14, 2008. Accepted June 23, 2008. The authors also acknowledge support of the Air Force Research Laboratory for project MIPR F4FBEY6346G001.

JE800255R