

# Measurement and Correlation of the Thermal Conductivities of Biodiesel Constituent Fluids: Methyl Oleate and Methyl Linoleate

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**S** Supporting Information

**ABSTRACT:** New experimental data on the thermal conductivities of the methyl esters methyl oleate and methyl linoleate in the liquid phase are reported that allow for the development of correlations. These new experimental data, covering a temperature range of 302–508 K for methyl oleate and 302–505 K for methyl linoleate at a pressure range of 0.1–42 MPa, are used with estimated dilute gas values to develop correlations for the thermal conductivity. The experimental data reported here have an uncertainty of less than 1%. On the basis of the uncertainty of and comparisons to the present data, the thermal conductivity correlations for methyl oleate and methyl linoleate in the liquid phase are estimated to have a relative uncertainty of about 2.5% at a 95% confidence level.

## INTRODUCTION

Recently, there has been renewed interest in synthetic liquid fuels derived from natural gas, coal, or biomass feedstocks. Biodiesel fuel is composed primarily of fatty acid methyl esters (FAMEs) produced by a transesterification reaction between a triglyceride oil and methanol. The main components of biodiesel fuel derived from a soy feedstock are found to be the following five FAMEs: methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate. As biodiesel fuel continues to grow in popularity and use, the need for measurements of the physical properties of its constituent fluids also grows. Previously, equations of state for these fluids<sup>1</sup> based on available thermodynamic data<sup>2,3</sup> have been reported, but we are unaware of any previous measurements of the thermal conductivities of these fluids. This work provides new data for the thermal conductivities of two methyl esters and correlations that can be used to calculate their thermal conductivity surfaces as functions of the temperature and density. Knowledge of the thermal conductivity of these biodiesel components allows for the development of surrogate models for the thermal conductivity of complex mixtures that are needed for the optimal design of biodiesel production processes<sup>4,5</sup> and heated biodiesel injection systems for engines.<sup>6</sup>

## EXPERIMENTAL SECTION

**Materials.** The presence of double bonds in methyl oleate (CAS 112-62-9) and methyl linoleate (CAS 112-63-0) decreases their chemical stability, with the methyl linoleate oxidation rate about 41 times that of methyl oleate.<sup>7,8</sup> This chemical instability increases with an increasing temperature and includes oxidation and thermal decomposition reactions.<sup>8,9</sup> Oxidation typically occurs at lower temperatures, while thermal decomposition occurs at higher temperatures.<sup>9</sup> The samples of methyl oleate and methyl linoleate that were measured in this work were degassed to reduce the oxygen available for decomposition, and 0.1 wt % *tert*-butylhydroquinone (TBHQ; CAS 1948-33-0) was added to further stabilize each sample.<sup>8,10</sup> The maximum temperature studied was limited

to 500 K for both fluids. The samples of methyl oleate and methyl linoleate that were measured in this work were sealed and stored in a freezer until the addition of 0.1 wt % TBHQ with the introduction to the evacuated measurement cell several minutes after mixing. The purities of the samples were determined at NIST by gas chromatography with flame ionization detection before and after measurements.

The methyl oleate sample was found to have a purity of  $99.7 \pm 0.1\%$  as received from the supplier,  $99.6 \pm 0.1\%$  after the addition of TBHQ, and  $99.6 \pm 0.1\%$  after 5 sequential days of measurements at 302, 352, 404, 455, and 507 K. There was no measurable decomposition during the thermal conductivity measurements on this sample.

The methyl linoleate sample was found to have a purity of  $99.5 \pm 0.1\%$  after the addition of TBHQ and  $99.3 \pm 0.1\%$  after 3 days at 302 K and 1 day each at 352, 401, 453, and 504 K, indicating that there may have been very slight decomposition that would not be expected to alter the measured thermal conductivity.

**Transient Measurements.** The measurements of thermal conductivity were obtained with a transient hot-wire instrument that has previously been described in detail.<sup>11</sup> During an experiment, a single hot wire functioned both as an electrical heat source and a resistance thermometer to measure the temperature rise. The 8 mm cavity around the hot wire is formed by a stainless-steel pressure vessel that is capable of operation from 250 to 750 K at pressures up 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,  $P_e$ , were determined with a pressure transducer with an uncertainty of 7 kPa. The measurements on liquid methyl oleate and methyl linoleate were made with an anodized tantalum hot wire that was 10 cm long with a diameter of 25  $\mu\text{m}$ . All reported uncertainties are for a coverage factor<sup>12</sup> of  $k = 2$ , with a confidence interval of approximately 95%.

The basic theory that describes the operation of the transient hot-wire instrument is given by Healy et al.<sup>13</sup> The hot-wire cell was designed to approximate a transient line source as closely as possible, and deviations

**Received:** March 17, 2011

**Revised:** April 15, 2011

**Published:** April 26, 2011



from this model are treated as corrections to the experimental temperature rise. The ideal temperature rise  $\Delta T_{id}$  is given by

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

where  $q$  is the power applied per unit length,  $\lambda$  is the thermal conductivity of the fluid,  $t$  is the elapsed time,  $a = \lambda/(\rho C_p)$  is the thermal diffusivity of the fluid,  $\rho$  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,  $C = 1.781\dots$  is the exponential of Euler's constant,  $\Delta T_w$  is the measured temperature rise of the wire, and  $\delta T_i$  are corrections<sup>13</sup> to account for deviations from ideal line-source conduction. During analysis, a line is fitted to the linear section, from 0.2 to 2 s, of the  $\Delta T_{id}$  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,  $T_w$ , associated with the thermal conductivity is the average temperature of the wire over the period that was fitted to obtain the thermal conductivity.

Several corrections<sup>13–19</sup> that account for the finite dimensions of the wire and the concentric wall of the pressure vessel must be carefully considered. The temperature rise should always be corrected to account for the finite wire radius.<sup>13–17</sup> In the case of fluids with high thermal diffusivity, such as dilute gases, it is possible for the temperature rise to penetrate to the outer boundary of the fluid. The temperature rise must be corrected for the presence of the outer boundary in such cases.<sup>13–17</sup> A correction for axial conduction is also required for transient hot-wire cells with a single wire.<sup>18,19</sup> 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 (4–7  $\mu\text{m}$ ), 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. The correction for finite wire length could be eliminated with a more complex double-wire cell that requires about 50  $\text{cm}^3$  of sample.<sup>11,13</sup> However, such designs were not considered optimal for the present measurements, where such extremely fine wires are too fragile, and larger outer dimensions and double-wire geometries would require excessive amounts of scarce samples, particularly in the liquid phase.

The high-purity methyl oleate and methyl linoleate samples have normal boiling points above 600 K. Removal of all sample from the cell and pressure system was not possible by evacuation; therefore, it was decided to pressurize the samples with helium gas applied to the top of the hot-wire cell. A sufficient sample (7  $\text{cm}^3$ ) was injected into the bottom of the evacuated single-wire cell with a syringe to completely fill the hot-wire cell and connect tubing to a secondary 5  $\text{cm}^3$  vessel located above the hot-wire cell. It was necessary to clean the hot-wire cell after measurements with a suitable liquid solvent that was also injected and later removed from the bottom of the cell with a syringe.

Experiments were 1 or 2 s in duration, with 250 measurements of temperature rise as a function of elapsed time relative to the onset of wire heating. Consistency between measurements at five different applied power levels for each initial temperature and pressure confirms that convection was not a problem during the transient measurements. The parameter "STAT" reported in the Supporting Information provides a measure of repeatability of each thermal conductivity measurement from the uncertainty (coverage factor of  $k = 2$ ) in the slope of the line fit to ideal temperature rise versus the logarithm of elapsed time ("STAT" = 0.001 corresponds to 0.1%). The "STAT" parameter increases when the corrected temperature rise data are nonlinear because of either convection or thermal radiation. Fluid convection was normally not a problem, as indicated by consistency between measurements at different power levels and linearity over a wide range of experiment durations

("STAT" < 0.002). The corrections for the finite wire diameter and length<sup>18,19</sup> remained less than 0.25% for the measurements reported here.

Thermal radiative heat transfer between media at two different temperatures  $T_1$  and  $T_2$  increases in proportion to absolute temperature cubed because it is proportional to  $T_1^4 - T_2^4 \approx T^3(T_1 - T_2)$  for small temperature differences. Correction for thermal radiation during transient hot-wire measurements can be classified into three cases: (1) transparent fluid (TF), (2) opaque fluid (OF), and (3) dominated by emission from fluid (EF).<sup>11</sup> In the present measurements, we have treated the fluid as transparent to thermal radiation. Significant emission of thermal radiation from the fluid would add a linear-in-time correction term to the measured temperature rise that we have not taken into account. Thus, the presence of significant thermal radiation from fluid emission would be apparent as increasing nonlinearity in the temperature rise versus  $\ln(t)$  data as a function of the experiment temperature. This nonlinearity is reflected in the parameter "STAT" (described above and tabulated in the Supporting Information), which is not a function of the temperature and remains below 0.2% during these measurements. Errors because of absorption and emission of thermal radiation by the fluid remained less than 1% at the highest temperatures based on these considerations.

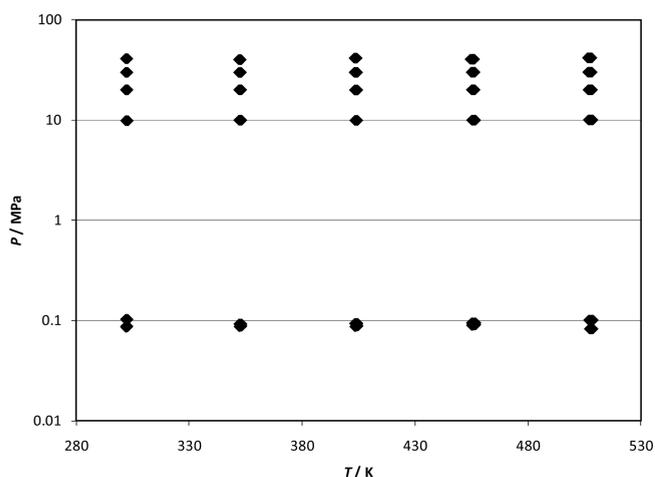
## EXPERIMENTAL RESULTS

The results of the transient measurements of the liquid thermal conductivity of methyl oleate and methyl linoleate are tabulated in the Supporting Information. Transient experiments with 1 and 2 s duration were analyzed over the time range from 0.2 to 1.5 s for methyl oleate and from 0.2 to 2 s for methyl linoleate. The measurements at each initial cell temperature were made over a single day. The cell temperature was then increased and equilibrated overnight. Measurements were made near 0.1 MPa prior to pressurization to the highest isotherm pressure near 42 MPa with helium. The pressure was then decreased in approximately 10 MPa increments to 0.1 MPa. No significant change in thermal conductivity was observed between the initial 0.1 MPa measurements and the final 0.1 MPa measurements at the end of the day. This indicates that the measured thermal conductivity was not significantly changed by dissolved pressurization helium in the sample or by thermal decomposition of the sample during the measurements for that isotherm.

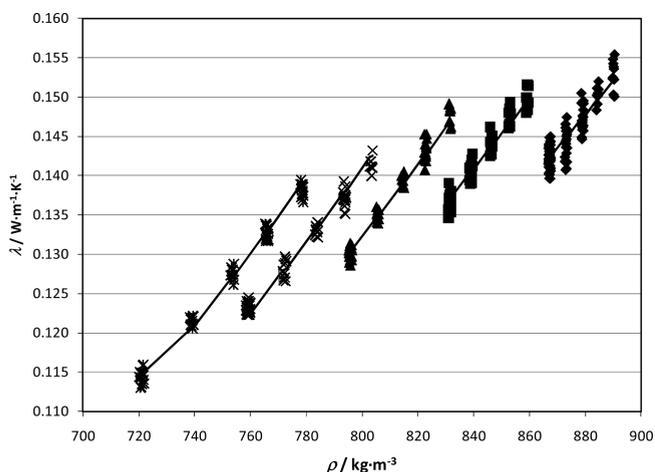
The vapor pressures of methyl oleate and methyl linoleate at the maximum temperature studied here are 0.0045 and 0.0039 MPa, respectively, significantly less than our lowest measured pressures near 0.1 MPa. Measurements of the liquid at pressures up to 42 MPa are generally reported for five different applied powers at each initial fluid state. 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 these liquid 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<sup>1</sup> for each experimental temperature and pressure associated with the measured thermal conductivity.

**Methyl Oleate.** The range of state points covered by the present measurements is shown in Figure 1 for methyl oleate. There are 395 transient hot-wire measurements of the liquid phase at temperatures from 302 to 508 K reported in the Supporting Information. These measured values are shown in Figure 2 as a function of the calculated density.

**Methyl Linoleate.** The range of state points covered by the present measurements is shown in Figure 3 for methyl linoleate. There are 350 transient hot-wire measurements of the liquid



**Figure 1.** Distribution of the data for the thermal conductivity of methyl oleate in the liquid phase. The vapor pressure is less than 0.01 MPa over this temperature range.



**Figure 2.** Thermal conductivity of methyl oleate along isotherms as a function of the density calculated at the measured temperature and pressure. Solid lines are given by the correlation developed in this work. The isotherms are identified as  $\blacklozenge$ , 302 K;  $\blacksquare$ , 352 K;  $\blacktriangle$ , 404 K;  $\times$ , 455 K; and  $*$ , 507 K.

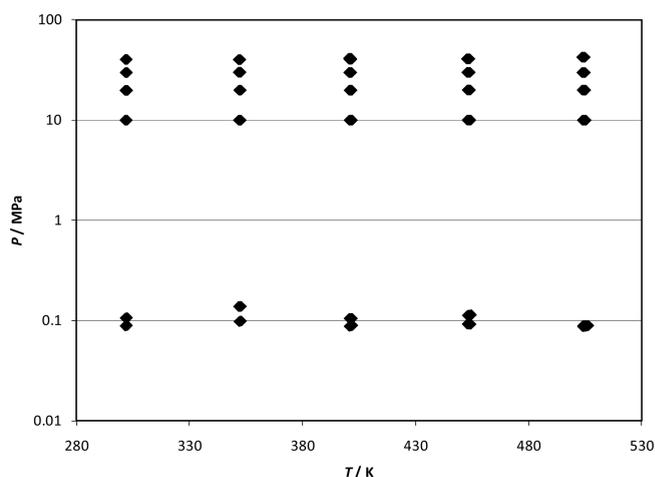
phase at temperatures from 302 to 505 K reported in the Supporting Information. These measured values are shown in Figure 4 as a function of the calculated density.

### ■ THERMAL CONDUCTIVITY CORRELATION

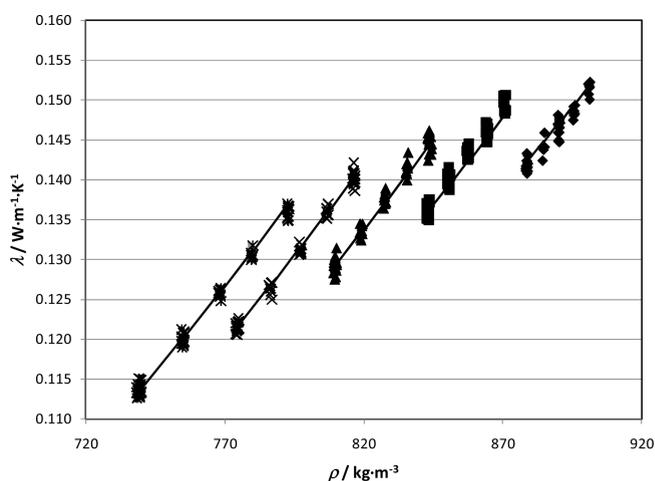
We represent the thermal conductivity  $\lambda$  of a pure fluid as a sum of three contributions

$$\lambda(\rho, T) = \lambda_0(T) + \Delta\lambda_r(\rho, T) + \Delta\lambda_c(\rho, T) \quad (2)$$

where  $\lambda_0$  is the dilute gas thermal conductivity, which only depends upon 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 the temperature,  $T$ , and density,  $\rho$ , with  $\rho$  calculated with an equation of state for each given  $T$  and  $P$ . In this work, for each fluid, we use recently developed short-form Helmholtz equations of state<sup>1</sup> that have temperature and pressure limits of 1000 K and 50 MPa.



**Figure 3.** Distribution of the data for the thermal conductivity of methyl linoleate in the liquid phase. The vapor pressure is less than 0.01 MPa over this temperature range.



**Figure 4.** Thermal conductivity of methyl linoleate along isotherms as a function of the density calculated at the measured temperature and pressure. Solid lines are given by the correlation developed in this work. The isotherms are identified as  $\blacklozenge$ , 302 K;  $\blacksquare$ , 352 K;  $\blacktriangle$ , 401 K;  $\times$ , 453 K; and  $*$ , 504 K.

The corresponding density limits for methyl oleate and methyl linoleate are 3.05 and 3.16 mol L<sup>-1</sup>, respectively. The critical parameters for methyl oleate<sup>1</sup> are  $T_c = 782.0$  K,  $P_c = 1.246$  MPa, and  $\rho_c = 241.0$  kg m<sup>-3</sup>, and the critical parameters for methyl linoleate<sup>1</sup> are  $T_c = 799.0$  K,  $P_c = 1.341$  MPa, and  $\rho_c = 238.05$  kg m<sup>-3</sup>.

**Dilute Gas Thermal Conductivity.** Because the experimental data set is very limited and restricted to the liquid phase, we supplemented the experimental data set with predicted values found by the method by Chung et al.<sup>20</sup> The method by Chung et al. was used to generate values in the limit of zero density at temperatures up to 1000 K, along the saturated vapor boundary above 500 K and for several points at 1500 K (to guide the extrapolation behavior at high temperatures). In addition to the critical parameters, the method by Chung et al. also requires the acentric factor. For the acentric factors of methyl oleate and methyl linoleate, we used 0.91 and 0.805, respectively, that were obtained from the equations of state in ref 1. We represent the

dilute gas thermal conductivity  $\lambda_0$  ( $\text{W m}^{-1} \text{K}^{-1}$ ) as a polynomial in reduced temperature

$$\lambda_0(T) = \sum_{k=0}^3 A_k (T/T_c)^k \quad (3)$$

with coefficients  $A_k$ , where  $T$  is the temperature and  $T_c$  is the critical temperature.

**Residual Thermal Conductivity.** We use a polynomial in the temperature and density to represent the background or residual contribution to the thermal conductivity

$$\Delta\lambda_r(\rho, T) = \sum_{i=1}^3 \left( B_{i,1} + B_{i,2} \left( \frac{T}{T_c} \right) \right) \left( \frac{\rho}{\rho_c} \right)^i \quad (4)$$

with coefficients  $B_{ij}$ , where  $\Delta\lambda_i$  is in  $\text{W m}^{-1} \text{K}^{-1}$ ,  $\rho$  is the density, and  $\rho_c$  is the critical density. This form has been shown to accurately represent alkane hydrocarbons.<sup>21–25</sup>

**Critical Enhancement.** Olchowy and Sengers<sup>26</sup> developed a theoretically based but complex model for the enhancement of thermal conductivity in the critical region. We use a simplified version of their crossover model<sup>27</sup>

$$\Delta\lambda_c(T, \rho) = \frac{\rho C_p R_0 k_B T}{6\pi\eta\xi} (\Omega - \Omega_0) \quad (5)$$

where the correlation length,  $\xi$ , and the heat capacity at constant pressure,  $C_p(T, \rho)$ , are obtained from the equation of state,  $k_B$  is Boltzmann's constant,  $R_0 = 1.03$  is a universal constant,<sup>27</sup> and the viscosity,  $\eta(T, \rho)$ , is obtained from an extended corresponding states estimation method.<sup>28</sup>

The crossover functions  $\Omega$  and  $\Omega_0$  are determined by

$$\Omega = \frac{2}{\pi} \left[ \left( \frac{C_p - C_v}{C_p} \right) \arctan(q_d \xi) + \frac{C_v}{C_p} (q_d \xi) \right] \quad (6)$$

$$\Omega_0 = \frac{2}{\pi} \left[ 1 - \exp \left( \frac{-1}{(q_d \xi)^{-1} + \frac{1}{3} \left( \frac{(q_d \xi) \rho_c}{\rho} \right)^2} \right) \right] \quad (7)$$

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

$$\xi = \xi_0 \left[ \frac{P_c \rho}{\Gamma \rho_c^2} \right]^{v/\gamma} \left[ \frac{\partial \rho(T, \rho)}{\partial P} \Big|_T - \frac{T_R \partial \rho(T_R, \rho)}{T \partial P} \Big|_T \right]^{v/\gamma} \quad (8)$$

where the critical amplitudes  $\Gamma$  and  $\xi_0$  are system-dependent and are determined by the asymptotic behavior of the equation of

state in the critical region. The partial derivative  $\partial \rho / \partial P|_T$  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  $\gamma = 1.239$  and  $\nu = 0.63$  are universal constants.<sup>27</sup> We have chosen to use values of the critical amplitudes reported for carbon dioxide<sup>27</sup> that we consider reasonable for this family of fluids,  $\Gamma = 0.0496$  and  $\xi_0 = 1.94 \times 10^{-10}$  m. The only parameter left to be determined is the cutoff wavenumber  $q_d$  (or, alternatively, its inverse,  $q_d^{-1}$ ). This parameter can be obtained by regression of data in the critical region; because we have no data in this region, we use a very rough estimate of  $q_d^{-1} = 0.875$  nm, which is similar to the value determined for butane.<sup>22</sup>

We include the critical enhancement term to represent the correct behavior near the critical point, but for calculations below 500 K, the enhancement may be neglected to provide a simpler form for the correlation.

## CORRELATION RESULTS

We used the fitting program ODRPACK<sup>29</sup> to fit the supplemented data sets for methyl oleate and methyl linoleate to determine the dilute gas coefficients for eq 3 and the residual coefficients for eq 4 that are tabulated in Tables 1 and 2, respectively. Table 3 provides thermal conductivity values calculated for each

**Table 1. Parameters for the Dilute Gas Thermal Conductivity (eq 3)**

coefficient	methyl oleate	methyl linoleate
$A_0$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	-0.000271250	-0.000109042
$A_1$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	0.00259365	0.00240543
$A_2$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	0.0350241	0.0407364
$A_3$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	-0.00902273	-0.0105928

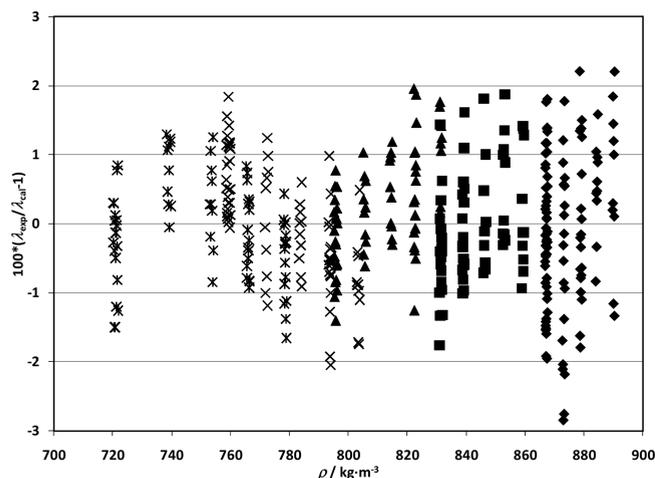
**Table 2. Parameters for the Residual Thermal Conductivity Contribution (eq 4)**

coefficient indices		methyl oleate	methyl linoleate
$i$	$j$	$B_{ij}$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	$B_{ij}$ ( $\text{W m}^{-1} \text{K}^{-1}$ )
1	1	-0.0410106	-0.0713126
1	2	0.0606657	0.0989415
2	1	0.0328443	0.0466421
2	2	-0.0498407	-0.0657850
3	1	-0.00418506	-0.00557406
3	2	0.0121752	0.0128922

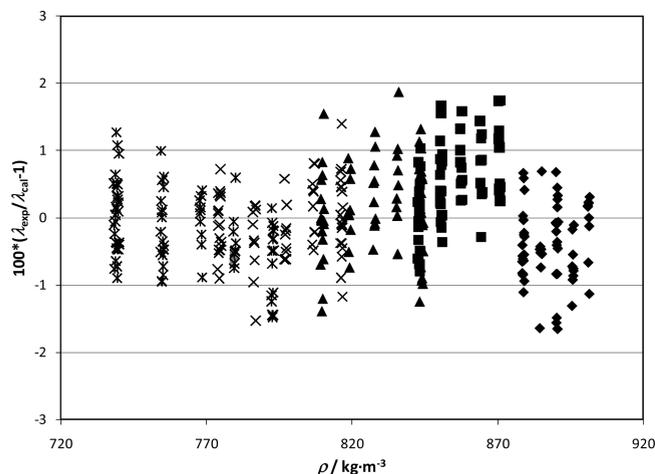
**Table 3. Values of Thermal Conductivity Calculated with the Correlation of eqs 2–8 at Specified  $T$  and  $\rho$ , with the Coefficients in Tables 1 and 2**

$T$ (K)	$P$ (MPa) <sup>a</sup>	methyl oleate		methyl linoleate	
		$\rho$ ( $\text{kg m}^{-3}$ )	$\lambda$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	$\rho$ ( $\text{kg m}^{-3}$ )	$\lambda$ ( $\text{W m}^{-1} \text{K}^{-1}$ )
450	0.0001	0.00792667	0.0110996	0.00787223	0.0122743
450	1	764.716	0.123794	778.176	0.122742
450	20	787.080	0.133856	799.160	0.131867

<sup>a</sup> Pressures calculated with the equation of state in ref 1.



**Figure 5.** Relative deviation between the experimental data and the correlation for the thermal conductivity of methyl oleate as a function of the density along isotherms  $\blacklozenge$ , 302 K;  $\blacksquare$ , 352 K;  $\blacktriangle$ , 404 K;  $\times$ , 455 K; and  $*$ , 507 K.



**Figure 6.** Relative deviation between the experimental data and the correlation for the thermal conductivity of methyl linoleate as a function of the density along isotherms  $\blacklozenge$ , 302 K;  $\blacksquare$ , 352 K;  $\blacktriangle$ , 401 K;  $\times$ , 453 K; and  $*$ , 504 K.

fluid that allow for verification of computer coding of the correlations (eqs 2–8).

**Deviations.** We are unaware of any measurements for the thermal conductivity of methyl oleate or methyl linoleate other than the present study. Measurements on methyl oleate comprise 395 points in the liquid region along five isotherms from 302 to 507 K at pressures up to 42 MPa, and the measurements for methyl linoleate contain 350 points in the liquid region along five isotherms from 302 to 504 K at pressures up to 42 MPa. Figure 5 shows deviations between the data for methyl oleate and the correlation as a function of the density calculated from the measured temperature and pressure with the equation of state.<sup>1</sup> The present experimental data agree with the correlation to within  $\pm 2.5\%$  at a 95% confidence level. Figure 6 shows deviations between the data for methyl linoleate and the correlation as a function of the density calculated from the measured temperature and pressure with the equation of state.<sup>1</sup> The

present experimental data agree with the correlation to within  $\pm 2.0\%$  at a 95% confidence level. It is expected that the correlation has significantly larger uncertainties in the vapor phase, because experimental data were not available; we estimate the uncertainty in this region to be 10–30%.

## CONCLUSION

A total of 395 points are reported for the thermal conductivity of liquid methyl oleate at pressures up to 42 MPa. A total of 350 points are reported for the thermal conductivity of liquid methyl linoleate at pressures up to 42 MPa. The thermal conductivity data for these fluids have an uncertainty of less than 1% at a 95% confidence level.

On the basis of these measurements, correlations are developed for the thermal conductivity of methyl oleate and methyl linoleate. We could not locate any other thermal conductivity data for either fluid. The correlations require thermodynamic property information that was obtained from newly developed equations of state.<sup>1</sup> The correlations agree with the present liquid phase data set to within  $\pm 2.5\%$  at a 95% confidence level.

## ASSOCIATED CONTENT

**Supporting Information.** Tabulated experimental values of thermal conductivity for methyl oleate and methyl linoleate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ACKNOWLEDGMENT

We thank Jason Widegren of NIST for sharing his experience on decomposition of methyl oleate during measurements of vapor pressure<sup>3</sup> and for recommendation of TBHQ as a stabilizer. We also thank Jason Widegren for his chemical analysis of the purity of these samples.

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