Transport Properties of Petroleum Fractions

M. E. Baltatu, R. A. Chong, M. L. Huber, and A. Laesecke

A corresponding-states model for the transport properties of petroleum fractions is presented. The model requires only the API specific gravity and the mean average boiling point as input parameters. The extended corresponding-states model uses propane as a reference fluid, and new generalized shape factor expressions that are functions of the acentric factor and the reduced temperature are presented. Also presented are new correlating functions for the viscosity and thermal conductivity of the reference fluid that can be extrapolated well below the freezing point of propane. The performance of the model is demonstrated by comparing with experimental data for viscosity and thermal conductivity of petroleum fractions.

KEY WORDS: corresponding states; petroleum fractions; propane; viscosity, thermal conductivity.

1. INTRODUCTION

In the design of oil processing equipment and in reservoir simulation studies, it is important to be able to predict accurate values of the viscosity and thermal conductivity of petroleum fractions over a wide range of temperatures and pressures. In this work we modify the TRAPP extended corresponding states model [1, 2] for application to petroleum fractions. This type of model is valid over a wide range of thermodynamic states, from the dilute gas to the dense fluid state.

2 Fluor Daniel, Inc., Irvine, California 92730, U.S.A.
3 Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80303, U.S.A.
4 To whom correspondence should be addressed.

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2. EXTENDED CORRESPONDING STATES MODEL

Various forms of extended corresponding states models have been used to predict the transport properties of standard hydrocarbons [3] and their mixtures, petroleum fractions [4, 5], as well as refrigerants and their mixtures [6, 7]. Following the original TRAPP corresponding states model [1, 2], the viscosity of a fluid $\eta_i$ at density $\rho$ and temperature $T$ is related to the viscosity of a reference fluid $\eta_0$ at a corresponding state point using

$$\eta_i(\rho, T) = \eta_0(\rho_0, T_0) F_\eta$$

(1)

where

$$F_\eta = \sqrt{\frac{M_i}{M_0}} f_i^{1/2} h_i^{-2/3}$$

(2)

The subscript $0$ refers to the reference fluid, the subscript $i$ denotes the fluid of interest, $M$ is the molar mass, and $f_i$ and $h_i$ are functions called equivalent substance reducing ratios, that can depend upon both temperature and density.

The application of the model to thermal conductivity is very similar to that for the viscosity, except that we separate the thermal conductivity $\lambda_i$ into two contributions: $\lambda_i'$, arising from the transfer of energy from purely collisional or translational effects, and $\lambda_i''$, from the transfer of energy via internal degrees of freedom, such that $\lambda_i = \lambda_i' + \lambda_i''$. We apply the corresponding states assumption only to the translational contribution, such that

$$\lambda_i'(\rho, T) = \lambda_0'(\rho_0, T_0) F_\lambda X$$

(3)

where

$$F_\lambda = f_i^{1/2} h_i^{2/3} \sqrt{\frac{M_0}{M_i}}, \quad X = X_\omega = \frac{1 + 2.18664(\omega - \omega_0)}{1 - 0.505(\omega - \omega_0)}$$

(4)

The factor $X_\omega$ is a correction factor used successfully for predicting hydrocarbon thermal conductivity [8], and $\omega$ is the acentric factor. In this work we found improved results if we also permitted the $X$ correction factor to have density dependence, such that $X = X_p X_\omega$ with

$$X_p = 1 - 0.153 \rho_{r,0} + 0.177 \rho_{r,0}^2 - 0.04245 \rho_{r,0}^3$$

(5)
where \( \rho_{c,0} = \rho_0 / \rho_{c,0} \) is the reduced density of the reference fluid. We assume that \( \lambda^* \) is independent of density and is given by [2]

\[
\frac{\lambda^*_i M_i}{\eta_i^*} = 1.32 \left( \frac{C_i^g}{\rho_i} - \frac{5R}{2} \right)
\]  

(6)

where \( \eta_i^* \) is the dilute gas viscosity of fluid \( i \) (which can be estimated using the method given in Ref. 1), \( C_i^g \) is the ideal gas heat capacity, and \( R \) is the universal gas constant.

The state points \( T_0 \) and \( \rho_0 \) are defined by the relations \( T_0 = T / f_i \) and \( \rho_0 = \rho h_i \), where \( f_i \) and \( h_i \) are equivalent substance reducing ratios, defined by

\[
f_i = (T_{c,i} / T_{c,0}) \theta_i(T_{r,i}, \rho_{r,i}, \omega_i)
\]

(7)

\[
h_i = (\rho_{c,0} / \rho_{c,i}) \phi_i(T_{r,i}, \rho_{r,i}, \omega_i)
\]

(8)

and \( \theta_i \) and \( \phi_i \) are shape factors which are functions of the reduced temperature \( T_{r,i} = T / T_{c,i} \), reduced density of the fluid \( \rho_{r,i} = \rho_i / \rho_{c,i} \), and the acentric factor \( \omega_i \). The subscript \( c \) denotes the critical point.

Use of the model requires a very thorough representation of the PVT surface of the reference fluid and, also, an accurate method of determining the shape factors. For the reference fluid, we use a 32-term modified Benedict-Webb-Rubin (MBWR) equation of state for propane [10]. Propane was selected as a reference fluid because it has a very long saturation boundary, with a reduced triple point temperature of 0.24. The functional dependence of \( \theta_i \) and \( \phi_i \) in Eqs. (7) and (8), in contrast to constant factors, is a feature of “extended” corresponding states [11]. Various procedures have been used to determine shape factors [8, 11–13]. In this work, we use saturation boundary information about \( C_1 \) to \( C_{24} \) straight chain alkanes to obtain the following generalized expression for the shape factors:

\[
\Theta_i(T_{r,i}, \omega_i) = 1 + (\omega_i - \omega_0)[\alpha_1 + \alpha_2 \ln(T_{r,i})]
\]

(9)

\[
\Phi_i(T_{r,i}, \omega_i) = \left[ \frac{Z_{0,c}}{Z_{i,c}} \right] [1 + (\omega_i - \omega_0)(\beta_1 + \beta_2 \ln(T_{r,i}) + \beta_3 \ln(T_{r,i})^2)]
\]

(10)

where we obtained new coefficients \( \alpha_1 = 0.06354 \), \( \alpha_2 = -0.7256 \), \( \beta_1 = -0.2263 \), \( \beta_2 = 0.2831 \), and \( \beta_3 = 0.1184 \). In earlier work [4, 5] saturation boundary information was used to obtain the shape factors, but an iterative method was used that sometimes failed to converge.
Following the model given in Refs. 4 and 5, we use only the mean average boiling point [14] and the specific gravity as input to our procedure. The definition of the dimensionless quantity API gravity (°A.P.I.) relates it to the specific gravity (60°F/60°F) using the relationship °A.P.I. = (141.5/specific gravity) − 131.5. We calculate all other property information required for the extended corresponding states model. For the critical point and the molar mass, we use the Riazi [15] correlations. For ideal gas heat capacities, we use procedure 7D4.2 of the API Technical Data book [16]. We compute the acentric factor using its definition and the Lee–Kesler vapor pressure equation [17].

It is also necessary to have correlations for transport properties of the propane reference fluid. The reference fluid viscosity is expressed as the sum, \( \eta(p, T) = \eta^0(T) + \eta^1(T) \rho + \eta_{\text{high}}(p, T) \), where \( \eta^0 \) is the dilute gas contribution, \( \eta^1 \) is the first density correction, and \( \eta_{\text{high}} \) is the high-density contribution. In previous work [4, 5], the Younglove–Ely [10] correlation for viscosity was used for \( \eta_{\text{high}} \) and kinetic theory [9] was used for \( \eta^0 \). We wanted to use the very recent correlation for propane viscosity given by Vogel and Küchenmeister [18], which incorporates new experimental data. However, in extending the corresponding states model to heavy oil fractions, it sometimes is necessary to evaluate the reference fluid properties at temperatures as low as 50 K. The new viscosity fit of Vogel and Küchenmeister [18] is not appropriate for our purposes as its range is restricted to temperatures greater than the triple point; in particular, at very low temperatures and high densities a region of negative viscosities may be encountered. We therefore refit the propane viscosity data set recommended by Vogel to a new functional form for \( \eta_{\text{high}} \):

\[
\eta_{\text{high}} = \rho \beta_1 + \rho^2 \left( \frac{\beta_2}{T_c^2} + \frac{\beta_3}{T_c^3} + \frac{\beta_4}{T_c^{0.5}} \right) + \rho^3 \beta_5 + \beta_9 \left[ \exp \left( \frac{\beta_{10} p}{\rho_f} \right) - 1 \right]
\]

\[
T_H = \beta_4 T_c + \beta_7 T_c^2 + \beta_8 T_c^3, \quad T_c = T/T_e
\]

\[
\rho_f = \rho_{oo} - \rho, \quad \rho_{oo} = \beta_{14} E_{th}
\]

\[
E_{th} = 1 + \beta_{11} T_c^{0.5} + \beta_{12} T_c^{1.5} + \beta_{13} T_c^{3.5}
\]

The viscosity is obtained in mPa⋅s with the density in kg⋅m\(^{-3}\) the temperature in K, and the coefficients \( \beta_1 = -0.116097, \beta_2 = 0.790917 \times 10^{-4}, \beta_3 = -0.498527 \times 10^{-2}, \beta_4 = -0.831120 \times 10^{-2}, \beta_5 = 0.750653 \times 10^{-2}, \beta_6 = -1.687856, \beta_7 = 0.454393, \beta_8 = 0.210490, \beta_9 = 28.8119, \beta_{10} = -0.193272 \times 10^{-1}, \beta_{11} = -0.436061, \beta_{12} = 1.0, \beta_{13} = -0.293449, \) and \( \beta_{14} = 3.8. \) We compute the viscosity of propane using Eq. (11) for the high-density contribution, the Vogel and Küchenmeister expressions [18] for \( \eta^0 \).
and \( \eta_r \), and restrict \( \rho_f^{-1} \) to be greater than 0.1 kg \cdot m\(^{-3}\). Figure 1 shows the resulting percentage deviations (here defined as 100\*[(\( \eta_{\text{calc}} - \eta_{\text{exp}} \)/\( \eta_{\text{exp}} \)]) of the present correlation and the Vogel and Küchenmeister [18] correlation with the recommended data set of Vogel as a function of reduced density. Both correlations fit the data very well. The Vogel and Küchenmeister [18] fit is slightly better, with an average absolute deviation (AAD) of 0.83\%, a bias of \(-0.01\%\), and an RMS of 1.22\%, compared with an AAD of 1.32\%, a bias of \(-0.03\%\), and an RMS of 1.89\% for the present model. However, for our purposes we need the ability to extrapolate well to low temperatures and high densities, and the new fit gives us that capability.

We continue to work on finding a viscosity correlation function that can represent the experimental data to within experimental accuracy and that extrapolates well.

The reference fluid thermal conductivity is expressed as the sum \( \lambda = \lambda^0 + \lambda_{\text{high}} + \lambda_{\text{crit}} \), where the dilute gas contribution \( \lambda^0 \) and a critical enhancement \( \lambda_{\text{crit}} \) are described in Ref. 5. We refit the data in Refs. 19-24 along with a few points generated by extrapolating thermal conductivity data below 90 K and obtained

\[
\lambda_{\text{high}} = \frac{\rho}{\rho_c} \left[ a_1 + \left( a_2 + \frac{\rho}{\rho_c} \left( a_3 + a_4 \tau + \frac{\rho}{\rho_c} (a_5 + a_6 \tau) \right) \right) \left( \frac{\rho}{\rho_c} \right)^2 \right]
\]  

(12)
where \( \tau = T_c / T \), and new parameters \( a_1 = 20.53648, a_2 = -1.68353, a_3 = 2.34321, a_4 = -1.05427, a_5 = 6.92167 \times 10^{-2}, \) and \( a_6 = 0.252831 \), and with the thermal conductivity in mW \cdot m^{-1} \cdot K^{-1}. \) We computed the thermal conductivity of propane using Eq. (12) for \( \lambda_{high} \) and the method in Ref. 5 for \( \lambda_0 \) and \( \lambda_{crit} \). Figure 2 shows the resulting percentage deviations between our correlation and the data in Refs. 19–24; for these points, the AAD is 3.302\%, the bias is \(-0.112\%\), and the RMS is 6.69\%.

In earlier work \([4]\) we found that adding a correction factor for aromaticity and napthenicity improves the viscosity predictions. In this work we use a mass shape factor, \( g_i \), such that Eq. (2) becomes

\[
F_i = \frac{M_i}{\sqrt{M_0}} \int_{1/2}^{1/2} h_i^{-2/3} g_i^{1/2}
\]

Mass shape factors have been used for pure hydrocarbons \([3]\) as well as refrigerants \([6]\). Here, we obtain an expression specifically for petroleum fractions,

\[
g_i = b_1 + b_2 \exp \left[ -0.5 \left( \frac{(\Delta k_w - b_3)}{b_4} \right)^2 + \left( \frac{(\Delta \rho - b_5)}{b_6} \right)^2 \right] \right]^2
\]
where \( \Delta k_w = 13.9 - \text{UOP} \) and \( \Delta \rho = \rho_{0.2} - 2.9 \). We found the coefficients 
\[ b_1 = 1.191014, \quad b_2 = 157430.57, \quad b_3 = 3.5311755, \quad b_4 = 0.4906795, \quad b_5 = 1.2279506, \quad b_6 = 0.20108099. \]
The variable \( k_w \) is the Watson characterization factor or UOP, defined by \( k_w = \frac{T_b}{3} / \text{specific gravity} \), and \( T_b \) is the boiling point temperature in °R.

3. RESULTS

In Table I we compare the viscosity calculated with our model to the experimental data bank we used in Ref. 4 for a wide variety of petroleum fractions. The overall average absolute deviation (AAD) for 2060 points is 17.4% with a bias of −6.3%, compared with an AAD of 29.0% and a bias of −28.3% when Eq. (14) is not used. In Fig. 3 we show comparisons of experimental data and the model with and without the correction factor in Eq. (14), demonstrating the improvement with Eq. (14).

In Table II we give the results of comparisons of thermal conductivity with a large variety of crude oils, petroleum fraction cuts, and coal-derived liquids from the data bank in Ref. 5. The data cover a wide range of API
Fig. 3. Deviation plot for viscosity of petroleum fractions using the new model.

Fig. 4. Deviation plot for thermal conductivity of petroleum fractions using the new model.
specific gravity (−10.9 to 81.3) as well as a wide range of boiling points (337 to 858 K). The AAD for a total of 713 points is 6.8% and the bias is 1.2%, which is within the experimental accuracy of the data. Figure 4 shows the percentage deviations in thermal conductivity as a function of the reduced density of the reference fluid.

### Table II. Thermal Conductivity of Liquid Petroleum Fractions

<table>
<thead>
<tr>
<th>Description</th>
<th>Number of points</th>
<th>API gravity</th>
<th>BP (K)</th>
<th>AAD (%)</th>
<th>Bias (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil fraction</td>
<td>64</td>
<td>16.9–71.2</td>
<td>355–632</td>
<td>5.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Coal liquid</td>
<td>74</td>
<td>−10.9–52.2</td>
<td>372–750</td>
<td>4.2</td>
<td>−2.4</td>
</tr>
<tr>
<td>Alaska N. shore</td>
<td>8</td>
<td>18.4–43.3</td>
<td>469–755</td>
<td>4.2</td>
<td>3.7</td>
</tr>
<tr>
<td>San Joaquin Valley</td>
<td>24</td>
<td>11.8–34.3</td>
<td>469–755</td>
<td>3.4</td>
<td>−1.3</td>
</tr>
<tr>
<td>Altamont</td>
<td>8</td>
<td>36.8–53.5</td>
<td>469–755</td>
<td>12.2</td>
<td>−5.0</td>
</tr>
<tr>
<td>Undefined oils</td>
<td>172</td>
<td>16.7–50.2</td>
<td>388–766</td>
<td>9.6</td>
<td>5.5</td>
</tr>
<tr>
<td>SRC naphtha</td>
<td>26</td>
<td>49.7–49.7</td>
<td>387–396</td>
<td>6.5</td>
<td>5.1</td>
</tr>
<tr>
<td>Utah coed distillate</td>
<td>23</td>
<td>29.4–29.4</td>
<td>473–473</td>
<td>6.2</td>
<td>−6.2</td>
</tr>
<tr>
<td>Coolant and transformer oils</td>
<td>7</td>
<td>23.0–32.2</td>
<td>592–672</td>
<td>3.0</td>
<td>−3.0</td>
</tr>
<tr>
<td>Malgobek and Anastasevsk</td>
<td>30</td>
<td>20.0–70.5</td>
<td>338–811</td>
<td>6.1</td>
<td>2.8</td>
</tr>
<tr>
<td>Acid-refined napthenic oil</td>
<td>2</td>
<td>19.4–19.4</td>
<td>732–732</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Atmospheric residue</td>
<td>2</td>
<td>16.9</td>
<td>758</td>
<td>14.1</td>
<td>14.1</td>
</tr>
<tr>
<td>Paraffin oil</td>
<td>5</td>
<td>28.2–31.3</td>
<td>693–693</td>
<td>5.8</td>
<td>5.8</td>
</tr>
<tr>
<td>Cable oil</td>
<td>1</td>
<td>28.7–28.7</td>
<td>715–715</td>
<td>7.3</td>
<td>7.3</td>
</tr>
<tr>
<td>Diesel and fuel oils</td>
<td>20</td>
<td>27.1–41.7</td>
<td>505–689</td>
<td>4.4</td>
<td>−2.1</td>
</tr>
<tr>
<td>Dewaxed oil</td>
<td>3</td>
<td>26.2–26.2</td>
<td>694–753</td>
<td>8.3</td>
<td>4.8</td>
</tr>
<tr>
<td>Heat transfer oil</td>
<td>3</td>
<td>17.2–17.2</td>
<td>621–621</td>
<td>2.4</td>
<td>−0.1</td>
</tr>
<tr>
<td>Hydraulic oil</td>
<td>11</td>
<td>26.5–29.6</td>
<td>681–730</td>
<td>10.7</td>
<td>10.7</td>
</tr>
<tr>
<td>Kerosene</td>
<td>19</td>
<td>33.2–49.2</td>
<td>411–534</td>
<td>5.0</td>
<td>−2.0</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>35</td>
<td>9.3–38.5</td>
<td>622–794</td>
<td>9.7</td>
<td>8.3</td>
</tr>
<tr>
<td>Gasoline</td>
<td>14</td>
<td>33.2–49.2</td>
<td>411–534</td>
<td>4.1</td>
<td>−0.6</td>
</tr>
<tr>
<td>Residual</td>
<td>3</td>
<td>22.8–29.8</td>
<td>662–858</td>
<td>37.0</td>
<td>28.3</td>
</tr>
<tr>
<td>Solvent refined paraffinic oil</td>
<td>4</td>
<td>28.0–28.0</td>
<td>726–726</td>
<td>5.1</td>
<td>4.9</td>
</tr>
<tr>
<td>Misc. industrial</td>
<td>4</td>
<td>29.6–31.8</td>
<td>640–663</td>
<td>6.8</td>
<td>6.8</td>
</tr>
<tr>
<td>Waxy distillate</td>
<td>3</td>
<td>18.5–18.5</td>
<td>728–728</td>
<td>15.7</td>
<td>15.7</td>
</tr>
<tr>
<td>White spirit</td>
<td>2</td>
<td>53.8–53.8</td>
<td>434–434</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Russian distillate fractions</td>
<td>36</td>
<td>22.9–81.3</td>
<td>337–746</td>
<td>5.7</td>
<td>−5.4</td>
</tr>
<tr>
<td>Russian crude</td>
<td>29</td>
<td>15.9–45.0</td>
<td>439–686</td>
<td>10.4</td>
<td>−10.2</td>
</tr>
<tr>
<td>Misc. oils</td>
<td>7</td>
<td>24.9–33.5</td>
<td>626–763</td>
<td>7.1</td>
<td>7.1</td>
</tr>
<tr>
<td>Diphenyl mix</td>
<td>39</td>
<td>1.2–1.2</td>
<td>531–531</td>
<td>2.0</td>
<td>−2.0</td>
</tr>
<tr>
<td>Gazoil</td>
<td>15</td>
<td>34.0–34.0</td>
<td>507–507</td>
<td>6.0</td>
<td>−6.0</td>
</tr>
<tr>
<td>PAB</td>
<td>20</td>
<td>10.5–10.5</td>
<td>600–600</td>
<td>2.4</td>
<td>2.2</td>
</tr>
<tr>
<td>All points</td>
<td>713</td>
<td>−10.9–81.3</td>
<td>337–858</td>
<td>6.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

We have further modified the TRAPP extended corresponding states model [1, 2] to predict the transport properties of heavy crude oil fractions. The model requires only the specific gravity and mean average boiling point as input parameters. The model presents several new features including a noniterative scheme for calculating shape factors, new propane viscosity and thermal conductivity correlations that extrapolate well to low temperatures, and a new correction factor to improve the viscosity prediction for heavy crudes.

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REFERENCES

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