Prediction of the Viscosity of Liquid Petroleum Products

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Abstract. The article deals with the new technique for predicting the viscosity of liquid petroleum products, which differ significantly in physicochemical properties and fractional composition, in a wide range of state parameters. No specific information is used to predict viscosity other than molar mass, average volume boiling point, and relative density at 20 °C. It is shown that the deviation of the predicted values from the experimental data is comparable to the error of the viscosity measurement. Methods for correcting the calculation results using limited experimental information are proposed. The application of the developed method is advisable in conditions of a lack of empirical information about the petroleum products viscosity. Keywords: viscosity prediction; petroleum products; petroleum fractions.

1. Introduction

The successful development of the oil refining and petrochemical industry involves constant improvement of technological equipment due to the instability of the raw material base, the need to produce new products with properties that meet the requirements of newly created devices. The solution of this problem is impossible without reliable information about the thermophysical properties of oil raw materials and products of its processing. One of the most important properties is viscosity. Knowledge of it is necessary for the science-based design of effective processes and devices for oil refining, petrochemistry and transportation of petroleum products.

At present, the theory of the liquid state cannot predict the viscosity of petroleum products with acceptable precision for practical purposes. The main source of information about the viscosity of substances remains the experiment. The serious disadvantages of this practice are obvious. When the nomenclature of industrially important substances is expanded, their complex research is impossible due to its difficulty and labor intensity. Therefore, it is important to create reliable methods for predicting viscosity.

Existing methods for prediction the viscosity of liquid petroleum products are not perfect. The methods which the authors are trying to give a theoretical basis, develop ideas generalized in [1]. Typically, modifications of the Andrade, Antoine, or Eyring equations are used. Without changing the form of the functions $\eta(T)$ or $\eta(V)$, the authors try to link the coefficients of the equations to the physical properties, such as Arrhenius activation energy or Gibbs energy, which makes the equations unusable for practical use. Models based on free volume theory or friction theory usually give a significant error in the viscosity estimation. The expanded fluid model, which gives an error of 20-
50% in the estimation of viscosity of oils and petroleum products, cannot be considered reliable. Structural modeling methods can only be used in a restricted range of state parameters.

Existing empirical predictive methods are usually based on data obtained for individual hydrocarbons and their mixtures [2, 3]. Their use for heavy products that currently dominate technological processes is unreasonable. Specialized techniques are focused on low-boiling products and distillates of a specific fractional composition [4, 5], which limits their use. Most prediction techniques have been tested in a restricted area of state parameter, where the viscosity does not change too much [6, 7]. This does not allow to consider them universal.

Of greatest practical interest are models derived from the theory of corresponding states [8, 9], and models based on the similarity between $P-V-T$ and $T-\eta-P$ relationships [10, 11]. The quality of the first ones strongly depends on the choice of reference fluids, which is a non-trivial task for petroleum products. The reliability of the second is determined by the quality of the selected equation of state and the ability to account for the fractional composition of petroleum products. These are the models chosen as the basis for the development of a methodology for predicting viscosity.

### 2. Experimental data

When developing the viscosity prediction method, an empirical approach was chosen. The main dependencies are obtained on the basis of reliable experimental material. Data on the physicochemical properties, density and viscosity of normal C₅-C₂₀ alkanes [12] and oil refining products [12–14, 21] is used. The error of the viscosity data in the temperature range of 20–300°C at pressures up to 10 MPa is 2%, the error of the density data is 0.05%. Information about the ranges of samples property changes and the Watson $K$ factor determined by the procedure [13] are in table 1.

| Samples                  | Num. of samples | $M$     | $\rho_a^{20}$ | $t_{BV}$ deg. C | $K$ | $\eta$ (mPa·s) |
|--------------------------|-----------------|---------|---------------|-----------------|-----|----------------|
| West Siberian oil vacuum | 10              | 195–455 | 0.88–0.93     | 335.6–499.4     | 11.5–12.0 | 0.28–59.6     |
| distillate fractions     |                 |         |               |                 |     |                |
| West Siberian oil       | 7               | 160–386 | 0.88–0.97     | 213.6–470.2     | 10.6–11.3 | 0.24–45.3     |
| catalyisate vacuum       |                 |         |               |                 |     |                |
| distillate fractions     |                 |         |               |                 |     |                |
| Pyrolysis products       | 6               | 94–155  | 0.85–0.93     | 96.3–224.4      | 10.2–10.7 | 0.17–3.47     |
| Catalytic cracking       | 4               | 190–565 | 0.83–0.99     | 206.0–547.0     | 11.4–12.0 | 0.42–67.9     |
| products                 |                 |         |               |                 |     |                |
| Straight-run Mangyshlak | 4               | 128–206 | 0.75–0.81     | 145.0–265.0     | 12.0–12.2 | 0.20–2.95     |
| oil fractions            |                 |         |               |                 |     |                |
| Alkanes C₅-C₂₀           | 13              | 114–283 | 0.70–0.79     | 125.7–342.7     | 12.6–13.0 | 0.21–2.59     |

For petroleum products, the values of pseudocritical parameters $T_{pc}$, $P_{pc}$ and $\rho_{pc}$ are estimated using the Riazi and Daubert formulas [15]; the values of the Pitzer acentric factor $\omega$ are estimated using the Lee and Kesler formula [1]. For normal alkanes, the values of the critical parameters and the acentric factor are taken from [1].

### 3. Model development

The viscosity estimation is carried out in two stages: first, viscosity is determined at pseudocritical pressure and the required temperature; then, based on this value, the viscosity is calculated over the entire range of state parameters. Using a pseudocritical isobar as a reference curve reduces the pressure effect, since the data for all products are taken in the corresponding state. It is important that at pseudocritical pressure in the researched temperature range, all samples are liquids.
The predictive model is based on the correlation of viscosity and density of substances. A modified SP-QSPR model [16] is used to determine density at pseudocritical pressure:

\[
\ln \left[ \frac{\rho(P_{pc}, \Omega)}{\rho_{pc}} \right] = \ln \left[ \frac{\rho(P_{pc}, 293.15)}{\rho_{pc}} \right] F^c(\Omega),
\]

\[
F^c(\Omega) = \beta \left( 1 - \frac{1}{1.113} \frac{\Omega^{0.4}}{\ln \Omega} \right),
\]

where \( \tau = \ln \left( \frac{T_{pc}}{293.15} \right) \) and \( \Omega = \ln \left( \frac{T_{pc}}{T} \right) \) — reduced temperatures; \( \beta = 0.325 \) [17]; \( \rho(P_{pc}, 293.15) \) is determined using the value of \( \rho_{pc} \) according to [18].

A modified equation [19] is used to determine the temperature dependence of the viscosity at pseudocritical pressure. The orthochor value is replaced by an empirical coefficient \( V_0 \):

\[
\eta(P_{pc}, T)^{-1} = A_\eta \left[ V(P_{pc}, T) - V_0 \right]^{B_\eta},
\]

where \( V(P_{pc}, T) \) — molar volume of liquid at pressure \( P_{pc} \).

The dependence of coefficients \( A_\eta \) and \( B_\eta \) on the acentric factor \( \omega \) is quite complex. Therefore, it is necessary to use an additional criterion that is not based on the critical point similarity. The parameters of the point on the saturation line are used, which satisfy the following condition [17]:

\[
T_x \rho_x = kP_x M,
\]

where \( T_x \) in Kelvin; \( \rho_x = \rho(P_x, T_x) \) — liquid phase density in grams per cubic centimeter; \( P_x \) — saturated vapor pressure at temperature \( T_x \) in millimeters of mercury; \( M \) in grams per mole. For hydrocarbon liquids, the recommended value is \( k = 0.01 \) [17].

The SP-QSPR model [16] is used for \( \rho_x \) calculation:

\[
\ln \left( \frac{\rho_x}{\rho_{pc}} \right) = \ln \left( \frac{\rho_{pc}^{0.325}}{\rho_{pc}} \right) \frac{\Omega_x^{F(\Omega_x)}}{\tau^{F(\tau)}},
\]

The \( P_x \) value is calculated using the equation [20]:

\[
P_x(\Omega_x) = P_{pc} \exp \left[ -\alpha_R \Omega_x - b \Omega_x^{2.64} \right],
\]

\[
b = \ln \left( \frac{P_{pc}}{P_x} \right) - \alpha_R \Omega_x^{0.564} \Omega_x^{2.64},
\]

where \( \alpha_R \) — the Riedel coefficient [1]; \( P_0 = 1 \) standard atmosphere. Formulas (4)-(6) form a system of equations, the numerical solution of which is the value of \( \Omega_x \) and, therefore, \( T_x \). Then \( \rho_x \) is estimated by equation (5).

The equations (8) and (9) are proposed for \( A_\eta \) and \( B_\eta \):

\[
A_\eta = A_\eta Z(C_A, M, T_x, \rho_x, K) \omega^{a_1} \exp(\alpha_2 + \alpha_3 \omega),
\]

\[
B_\eta = B_\eta Z(C_B, M, T_x, \rho_x, K) \omega^{b_1} \exp(\beta_2 + \beta_3 \omega).
\]
\[ Z(C, M, T_x, \rho_x, K) = M^C T_x^C \rho_x^C (K - 9)^C, \]
where \( M \) in grams per mole; \( T_x \) in Kelvin; \( \rho_x \) in grams per cubic centimeter.

The equation (11) is proposed for \( V_0 \):
\[ V_0 = \sigma_1 + \frac{V_{pc}}{K} (\sigma_2 K + \sigma_3), \]
(11)
where \( V_{pc} \) in cubic meters per kilomol.

At pressures up to 10 MPa, the viscosity of the samples changes by 15-25%, and with increasing temperature, the pressure effect changes slightly. Therefore, to determine the viscosity at the required pressure, a simplified equation is used:
\[ \eta(P, T) = \eta(P_{pc}, T) \exp \left( \gamma_1 + \gamma_2 \omega \right) \left( P - P_{pc} \right). \]
(12)

The coefficients of equations (8), (9), (11), (12) are in tables 2-4. The viscosity prediction results are in millipascals per second.

**Table 2.** The coefficients of the equation (8).

| Samples | \( \Lambda_i \) | 1 | 2 | 3 | 4 | \( \alpha_1 \) | \( \alpha_2 \) | \( \alpha_3 \) |
|---|---|---|---|---|---|---|---|---|
| \( M < 300 \) | 1.1194 \( \cdot 10^{-2} \) | 3.1636 | -0.6881 | -22.6255 | -4.4556 | 1.5375 | -0.3867 | -7.8644 |
| \( M \geq 300 \) | 9.0782 \( \cdot 10^{-6} \) | 1.7363 | 2.2847 | -63.8769 | -17.5104 | 2.6867 | -0.2300 | -11.2284 |

**Table 3.** The coefficients of the equation (9).

| Samples | \( B_0 \) | 1 | 2 | 3 | 4 | \( \beta_1 \) | \( \beta_2 \) | \( \beta_3 \) |
|---|---|---|---|---|---|---|---|---|
| \( M < 300 \) | 1.4250 \( \cdot 10^{-2} \) | 1.5077 | -0.5846 | -7.4547 | -1.5362 | 0.6335 | 1.0681 | -2.4282 |
| \( M \geq 300 \) | 9.7994 \( \cdot 10^{-2} \) | 1.3251 | -0.8207 | -13.9878 | -4.0871 | 1.3213 | 3.0716 | -3.1660 |

**Table 4.** The coefficients of the equations (11) and (12).

| Samples | \( \sigma_1 \) | \( \sigma_2 \) | \( \sigma_3 \) | \( \gamma_1 \) | \( \gamma_2 \) |
|---|---|---|---|---|---|
| \( M < 300 \) | 0.01925 | 0.3349 | -0.8250 | -4.8018 | 0.7403 |
| \( M \geq 300 \) | 0.01823 | 0.4017 | -1.6458 | -4.6196 | 0.4802 |

4. **Results and discussion**

The developed method was tested at pressures up to 10 MPa in the temperature range \( (0.4 – 0.7)T_{pc} \), which meets the practical requirements. Integrated indicators are used as quality criteria for predicting viscosity: average absolute deviation (AAD), linear error probable (LEP) and bias. The method was tested separately for products with \( M < 300 \) and \( M \geq 300 \). The quality indicators averaged through
the sample groups are in table 5. The predicted values for icosane \((C_{20})\) differ significantly from the experimental data due to the lack of reliable literature data on the critical parameters of the substance. They are excluded from further consideration.

It can be concluded that the quality of viscosity prediction is quite acceptable from a practical point of view, especially when there is a significant difference in the samples properties. It is noted that the viscosity estimating error becomes greater with an increase in the molar mass and the width of boiling interval of the samples (this is noticeable for heavy catalytic cracking products). The relative error in predicting viscosity is greater at high temperatures, where the absolute viscosity value is less.

If there is single experimental value of viscosity \(\eta^{\exp}(P, T)\) at pressure \(P^*\) and temperature \(T^*\), the calculated viscosity values can be corrected using the formula \((13)\):

\[
\eta^{corr}(P, T) = \frac{\eta^{exp}(P^*, T^*)}{\eta^{calc}(P^*, T^*)},
\]

\[
(13)
\]

\[
\eta^{corr}(P, T) = \frac{\eta^{exp}(P^*, T)}{\eta^{calc}(P^*, T)}.\]

\[
(14)
\]

The quality indicators of viscosity prediction results before and after correction are in table 6.

### Table 5. Comparison results between experimental and predicted viscosities.

| Samples                              | \(M < 300\) | \(M \geq 300\) |
|--------------------------------------|-------------|-----------------|
|                                      | Num. of    | AAD (%) | LEP (%) | BIAS (%) | Num. of    | AAD (%) | LEP (%) | BIAS (%) |
|                                      | samples    |         |         |          | samples    |         |         |          |
| WS oil vacuum distillate fractions   | 3          | 3.96    | 3.07    | −1.56    | 7          | 5.40    | 2.26    | −2.41    |
| WS oil catalysate vacuum distillate  | 6          | 5.69    | 1.94    | 3.50     | 1          | 4.32    | 3.28    | −1.87    |
| fractions                            |            |         |         |          |            |         |         |          |
| Pyrolysis products                   | 6          | 4.96    | 2.28    | 0.42     |             |         |         |          |
| Catalytic cracking products          | 1          | 9.52    | 2.48    | −9.52    | 3          | 7.97    | 3.85    | 2.26     |
| Mangyshlak oil fractions             | 4          | 4.79    | 0.96    | 3.52     |             |         |         |          |
| Alkanes \(C_8-C_{19}\)               | 12         | 2.54    | 1.16    | −0.13    |             |         |         |          |

### Table 6. Results of viscosity prediction correction.

| Samples                              | \(M < 300\) | \(M \geq 300\) |
|--------------------------------------|-------------|-----------------|
|                                      | Num. of    | AAD (%) | LEP (%) | BIAS (%) | Num. of    | AAD (%) | LEP (%) | BIAS (%) |
|                                      | samples    |         |         |          | samples    |         |         |          |
| Before correction                    | 32         | 4.21    | 1.71    | 0.69     | 11         | 6.01    | 2.79    | −1.09    |
| After correction by equation (13)    | 32         | 2.41    | 1.66    | 0.52     | 11         | 4.13    | 2.81    | −1.48    |
| After correction by equation (14)    | 32         | 0.59    | 0.57    | −0.19    | 11         | 0.82    | 0.77    | −0.26    |

5. Conclusions
A new technique for prediction the viscosity of liquid petroleum products has been developed for use in the temperature range \((0.4–0.7)\ T_{pc}\) at pressures up to 10 MPa. A set of necessary initial data is defined, which includes the molar mass, relative density at 20 °C and the average volume boiling point, and the sequence of their conversion to the final result is specified. The results of the control calculations for the normal alkanes and petroleum products, which are characterized by a variety of properties and a difference in the fractional composition, confirmed the reliability of the method. if there is limited information about the viscosity of the product at one experimental point and at one experimental isobar, then correcting the calculation results improves the quality of the viscosity prediction.

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