Automated Prediction of the Liquid Paraffins Viscosity

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Abstract. The article deals with an approach to the construction of self-adjusting automatic control systems, in which parametric adaptation occurs when the properties of technological raw materials change during its processing due to changes in the parameters of state. A new algorithm for predicting the viscosity of hydrocarbon liquids is proposed, which can be used as part of the control systems software. The main dependences are obtained on the basis of reliable experimental data on the viscosity of normal C₈–C₂₀ alkanes, which are similar in properties to commodity petroleum products. The data of physicochemical analysis are used as the initial data for the computation. Based on the theory of corresponding states, a new approach to scaling the viscosity using a set of characteristic parameters is developed and technique for their determination is proposed. The method is tested in the temperature range (0.4–0.7)Tₑ at pressures up to 10 MPa. It is shown that the deviation of the predicted values from the experimental data is comparable to the error of the viscosity measurement.

1. Introduction

A scientifically based synthesis of automated control systems that are optimal from the point of view of efficiency is impossible without reliable information about the physicochemical and thermophysical properties of raw materials and products of its processing. This is especially important in the manufacture of commodity products, when the indicators of economic efficiency of production are directly related to the quality of technological parameters control.

When processing technological raw materials, its properties change with changes in temperature and pressure, and the control of the technological process ceases to be optimal. Therefore, it is important to make extensive use of self-adjusting systems, which include a controller parameter adjustment unit. Its purpose is to measure the current parameters of state, compute the values of thermal properties corresponding to these parameters, and change the controller settings. To ensure automatic adjustment of control devices, the prediction of the substances properties should also be performed automatically. Reliable predictive algorithms should be included in the control systems software.

Since the main way to regulate technological parameters is to change the flow rates of the corresponding flows, one of the most important properties is viscosity. Its value strongly depends on temperature and pressure, so the development of a reliable algorithm for predicting viscosity is relevant.

In the modern petrochemical industry, one of the main places is given to paraffins (normal alkanes). They are an important raw material in the processes of obtaining intermediates for the manu-
facturing of plastics, rubbers, synthetic fibers, detergents and many other substances. The viscosity of liquid alkanes has been studied sufficiently, but information about it is presented mainly in the table form. This makes its use in functioning control systems problematic.

The target of the study is to develop a computational scheme for automated prediction of the liquid paraffins viscosity, suitable for use as part of self-adjusting automatic control systems.

To obtain the dependence of the viscosity on the parameters of state, data on the properties of liquid normal alkanes C_8–C_{20} [1-2], close to commodity petroleum products, were used. The error of the experimental data is 1.2 %, which gives reason to consider them reliable. All the data were obtained on the same equipment according to a single method and have the same error, so the involvement of additional experimental material was considered superfluous. The samples viscosity was investigated at pressures up to 10 MPa in a fairly wide temperature range (0.4 – 0.7)\( T_c \), in which it varies by more than an order. Therefore, the selected experimental data can be reasonably used to form general conclusions. The values of the physicochemical properties of the samples, their critical parameters and the acentric factor \( \omega \) are taken from [3].

![Figure 1. Plots of the reduced viscosity on the reduced density dependence](image)

**Figure 1.** Plots of the reduced viscosity on the reduced density dependence: (a) old scaling; (b) new scaling.

2. The viscosity prediction method choosing

Detailed review of methods for prediction the hydrocarbon liquids viscosity based on the structural group components contribution is given in [3-4]. The recommended methods estimate the viscosity with an error of 10-15 %. They do not use integral indicators (such as molar mass, relative density or boiling point), which makes them unsuitable for practical use. Models based on the theory of free volume [5-6], the theory of friction [7] or the theory of expanded fluid [8-9] usually estimate the viscosity with an error of 6-30 % and cannot be considered reliable. Methods based on the use of equations of state [10-11] have limited application.

Empirical predictive methods in the temperature range of 20-300 °C at pressures up to 10 MPa usually provide an average viscosity estimation error of 3-9 % [12-14]. More accurate methods have been tested in a narrow temperature range up to 100 °C [15-17] or at atmospheric pressure only [18], which does not allow them to be considered universal.
The methods based on the corresponding states theory, with the correct choice of the generalized dependence $\eta(P,T)$ forms and the scaling variables methods, are quite reliable [19]. The viscosity estimation algorithm is developed on this basis. The critical isobar is used as a reference curve. This reduces the pressure effect, since the data for all products are taken in the corresponding state. In addition, the need to take into account phase transitions is eliminated.

Theoretically based viscosity scaling using the Kamerling-Onnes complex $\xi$ [3, 19] leads to a strong isobar stratification (Fig. 1, a), so it was decided to abandon it. To scale the viscosity, the complex is used

$$
\xi_x = \alpha_1 M^{\alpha_2} T_x^{\alpha_3} P_x^{\alpha_4}.
$$

The way to determining the parameters $T_x$ and $P_x$ is considered further. The coefficients $\alpha_1...\alpha_4$ were selected so as to ensure the closest isobars location in the new reduced coordinates. The graph (Fig. 1, b) shows that the data for all samples fall satisfactorily on the generalized curve.

3. Model development
The prediction method is based on the correlation of the viscosity and density of substances. At the first step, the viscosity value is determined at the critical pressure $P_c$ and the required temperature $T$

$$
\eta(P_c,T) = \xi_c \left[ C_1 \exp \left( C_2 \frac{\rho(P_c,T)}{\rho_c} \right) + C_3 \exp \left( C_4 \frac{\rho(P_c,T)}{\rho_c} \right) \right].
$$

At the second step, the viscosity is found at the required parameters of state $P$ and $T$

$$
\ln \frac{\eta(P,T)}{\eta(P_c,T)} = \exp(\beta_1 + \beta_2 (\frac{P}{P_c} - 1)).
$$

The coefficients of equations (1)-(3) were determined by the least square method. The residual function was minimized by the conjugate direction procedure using linear interpolation search [20]. The values of the coefficients are in Table 1.

| $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $\alpha_4$ |
| --- | --- | --- | --- |
| 0.158087 | 0.666258 | -0.415845 | 0.448612 |

| $C_1$ | $C_2$ | $C_3$ | $C_4$ | $\beta_1$ | $\beta_2$ |
| --- | --- | --- | --- | --- | --- |
| 5.699759 | 1.765027 | 3.834658·10⁻⁹ | 8.588425 | -2.893327 | -1.414989 |

The SP-QSPR model [21] was used to determine the density at critical pressure

$$
\ln \frac{\rho(P_c;\Omega)}{\rho_c} = \frac{\Omega^{F(\Omega)}}{T^{f(\tau)}} \ln \frac{\rho(P_c;293.15)}{\rho_c},
$$

$$
F(\Omega) = 0.325 \left[ 1 - 1.113 \left( \frac{\Omega^{0.4}}{\ln \Omega} \right) \right],
$$

$$
\tau = \ln \frac{T_c}{293.15}, \quad \Omega = \ln \frac{T_c}{T}.
$$
The \( \rho(P_c;293.15) \) value is obtained using \( \rho_x^{20} \) [22].

The values of the \( T_c \) and \( P_x \) are found as parameters of a point on the saturation line that satisfy the condition [23]

\[
T_x \rho_x = k P_x M ,
\]

where \( P_x \) is the saturated vapor pressure at \( T_x \); \( \rho_x = \rho(P_x; T_x) \) is the liquid phase density. For hydrocarbon liquids, the value of \( k = 0.01 \) is recommended [19]. The value \( \rho_x \) is found using the modified SP-QSPR model

\[
\ln \frac{\rho(P_x; T_x)}{\rho_c} = \frac{\Omega_x^{f(\Omega_x)}}{\tau^{f(\tau)}} \ln \frac{\rho_x^{20}}{\rho_c}. \tag{8}
\]

The value \( P_x \) is found by the equation [24]

\[
\ln \frac{P_x(\Omega_x)}{P_c} = -\alpha_R \Omega_x - b \Omega_x^{2.64} , \tag{9}
\]

\[
b = \left( \ln \frac{P_c}{P_a} - \alpha_R \Omega_b \right) \Omega_b^{2.64} , \tag{10}
\]

where \( P_a = 1 \text{ atm} ; \Omega_b \) is the reduced boiling point; \( \alpha_R \) is the Riedel's criterion [3].

4. The algorithm of automated viscosity prediction

May be defined the following algorithm for computing the dynamic viscosity coefficient for the specified parameters of state. Steps 4-6 implement the procedure for solving the nonlinear equation (7) with respect to the parameter \( \Omega_x \).

Step 1. Setting the initial data: molar mass \( M \); relative density \( \rho_x^{20} \); boiling point \( T_b \); critical parameters \( T_c, P_c \); and \( \rho_c \); acentric factor \( \omega \). Setting the temperature \( T \) and pressure \( P \).

Step 2. Calculation of the Riedel criterion by the formula [3]. Initial data: \( T_b, K; T_c, K; P_a = 1 \text{ atm}; P_c, \text{ atm} \). Result: \( \alpha_R \).

Step 3. Setting the initial value \( \Omega_x \in [0.1, 1.0] \).

Step 4. Calculation of density \( \rho_x \) by formulas (8), (5) and (6). Initial data: \( \Omega_x; T_c, K; \rho_x^{20}; \rho_c; \) g/cm\(^3\). Result: \( \rho_x \), g/cm\(^3\).

Step 5. Calculation of pressure \( P_x \) by formulas (9) and (10). Initial data: \( \Omega_x; T_c, K; T_b, K; P_c, \) atm; \( P_a = 1 \text{ atm} \). Result: \( P_x, \text{ atm} \).

Step 6. Testing the end of iterations condition. If \( \left| T_c \exp(-\Omega_x)\rho_x - k P_x M \right| > \varepsilon \), then change \( \Omega_x \) and go to step 4. Initial data: \( \Omega_x; T_c, K; T_b, K; \rho_x, \) g/cm\(^3\); \( P_x, \) mm Hg; \( M, \) g/mole; \( k = 0.01; \varepsilon \approx 10^{-6} \).

Step 7. Calculation of temperature \( T_x \) by formula (6). Initial data: \( \Omega_x; T_c, K \). Result: \( T_x, K \).

Step 8. Calculation of the complex \( \xi_x \) by formula (1). Initial data: \( \omega; M, \) g/mole; \( T_x, K; P_x, \) MPa. Result: \( \xi_x \).

Step 9. Calculation of density at critical pressure and temperature \( T \) by formulas (4)-(6). Initial data: \( T, K; T_c, K; \rho_x^{20}; \rho(P_c;293.15), \) g/cm\(^3\); \( \rho_c, \) g/cm\(^3\). Result: \( \rho(P_c; T), \) g/cm\(^3\).
Step 10. Calculation of viscosity at critical pressure and temperature $T$ by formula (2). Initial data: $\xi_c; \rho(P_c; T), \text{kg/m}^3; \rho_c, \text{kg/m}^3$. Result: $\eta(P_c; T), \text{MPa} \cdot \text{s}$.

Step 11. Calculation of viscosity at temperature $T$ and pressure $P$ by formula (3). Initial data: $\eta(P_c; T), \text{MPa} \cdot \text{s}; \omega; P, \text{MPa}; P_c, \text{MPa}$. Результат: $\eta(P; T), \text{MPa} \cdot \text{s}$.

5. Results and discussion
The developed method has been tested in the temperature range $(0.4-0.7)T_c$ at pressures up to 10 MPa, which meets the practical requirements. Integrated indicators are used as quality criteria: average absolute deviation (AAD), linear error probable (LEP), bias and maximum deviation (MAX). The quality indicators are in table 2.

Table 2. Comparison results between experimental and predicted viscosities.

| Sample | AAD, % | LEP, % | BIAS, % | MAX, % | Sample | AAD, % | LEP, % | BIAS, % | MAX, % |
|--------|--------|--------|---------|--------|--------|--------|--------|---------|--------|
| C_8    | 1.61   | 1.42   | -0.30   | 4.21   | C_15   | 1.61   | 1.14   | 1.23    | 4.85   |
| C_9    | 1.86   | 1.54   | 0.31    | 3.98   | C_16   | 1.01   | 1.02   | 0.58    | 4.19   |
| C_10   | 1.95   | 1.01   | 1.75    | 3.55   | C_17   | 1.24   | 0.86   | -0.68   | -2.75  |
| C_11   | 1.22   | 1.03   | -0.78   | -4.98  | C_18   | 1.45   | 1.10   | -0.62   | -3.26  |
| C_12   | 0.80   | 0.74   | -0.12   | -2.31  | C_19   | 2.08   | 1.72   | 0.37    | -4.16  |
| C_13   | 1.43   | 1.09   | -0.92   | -3.80  | C_20   | 1.27   | 1.06   | 0.40    | -3.02  |
| C_14   | 1.80   | 1.48   | 0.21    | -4.75  |        |        |        |         |        |

All types of error are quite acceptable from a practical point of view. In most cases, the maximum error was observed at pressures of 10 MPa. This is not critical, since pressures exceeding 4.0-6.0 MPa are relatively rare in technological processes. All this suggests that the quality of viscosity prediction is quite high

6. Conclusions
A new method for predicting the liquid paraffins viscosity for use in the temperature range $(0.4-0.7)T_c$ at pressures up to 10 MPa has been developed. The initial data for the computation are the parameters of state and the physicochemical properties of the hydrocarbon. Control testing confirmed the validity of the method. It can be concluded that the formulated target of the study has been achieved.

7. References
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