Numerical Modeling of Vapor-Liquid Equilibrium by Using the Edmister -Okamoto Model

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The methods for calculating the liquid-vapor equilibrium for crude oil and for the oil products are divided into two categories. The first category uses the concept of the pseudo component and the calculus of the liquid-vapor equilibrium is based on their physical properties. The second category uses the Edmister-Okamoto method, based on experimental graphic correlations. The paper presents the achievements of the authors in order to develop a numeric algorithm for the calculation of the liquid-vapor equilibrium for the oil distillated fractions, algorithm based on the graphic correlations of the Edmister-Okamoto model. The authors have developed the relations to transpose into a numerical algorithm all the mathematical operations that were performed manually, transforming the graphic correlations into continuous functions and using numerical methods for solving the nonlinear equations. Based on the proposed algorithm, the authors have elaborated a computer programme system which estimates the liquid-vapor equilibrium associated to the petroleum fractions. The results obtained with the numerical algorithm allowed the validation of the numerical model proposed by the authors.

Keywords: liquid-vapor equilibrium, modelling, oil fractions, numerical solving

The model atmospheric distillation process is based on models of the liquid-vapor equilibrium adapted for the complex systems of hydrocarbons that are present in the crude oil. Worldwide there are available two categories of the liquid-vapor equilibrium models: first category is based on the Edmister-Okamoto correlation curves [1, 2] and the second one uses the decomposition of the complex mixture into pseudo-components and the estimation of physical properties [3, 4, 5].

The authors studied the possibility of the shaping numerical of the liquid-vapor equilibrium for the complex systems of hydrocarbons in the crude oil by using the Edmister-Okamoto model based on graphic correlations. The authors have developed a numerical algorithm and a calculation programme which allows the liquid-vapor equilibrium evaluation for both crude oil and petroleum fractions.

The numerical algorithm

The distilled oil fractions are characterized by the following distillation curves:
- the real boiling point curve, TBP, used as a reference curve in the product characterization;
- the vaporization curve in equilibrium, EFV, used for the calculations associated to the liquid-vapor equilibrium;
- the standard curve, ASTM, used to characterize the quality of the product.

The input data for the model are:
- the TBP curve of the crude oil, expressed by the discrete function;
- the final temperature on the curve ASTM of the oil fraction,
- the gap between two adjacent fractions expressed as a difference between the corresponding temperatures on the ASTM curve at 95% distillate for the light fraction and 5% distillate for the heavy fraction,
- the ASTM curve of the oil fraction,
- the gap temperature between two adjacent fractions, expressed as a difference between
- the products specification on the TBP curve;
- the white product potential;
- the distillation TBP, EFV and ASTM curves of the fractions.

Oil products specifications on the TBP crude oil curve

The products specifications on the TBP curve are represented by the initial and final temperatures on the TBP curve of the crude oil. The calculation stages of the products specifications on the TBP curve are:
- the calculation of the temperature 100% on the TBP curve;
- the calculation of the overlap temperature on the TBP curve between two adjacent fractions;
- the calculation of the initial temperature of the oil fractions on the TBP curve.

The input data needed for the calculation of the specifications on the TBP curve are:
- the final temperature on the ASTM curve of each fraction;
- the gap temperature between two adjacent fractions, expressed as a difference between

The calculation of the temperature 100% on the TBP curve
to determine the temperature on the TBP curve, corresponding to 100% distillate, there is used the approximation function, based on graphic correlation [7, 8]

The calculation of the overlap temperatures on the TBP curve between two adjacent fractions
The input data needed for the calculation on the temperatures overlap on the TBP curve between two adjacent fractions are:

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- the final temperature on the ASTM curve of the adjacent fractions,
  \( T_A \) - the final ASTM curve of fraction A;
  \( T_B \) - the final ASTM curve of fraction B.
- the gap between two adjacent fractions,
  \( t_{\text{StAS}}^{g} - t_{\text{StAS}}^{*} \).

The calculation methodology is based on graphic correlations \([6, 8]\) and was transformed into the next numerical algorithm:

- if \( T_A < 149^\circ\text{C} \) and \( 149 < T_B \leq 204^\circ\text{C} \)
  \[ dp = 85.3699 - 2.212585 \cdot \text{ds} - 0.6477465 \cdot 10^{-2} \cdot \text{ds}^{2}; \] \( (2) \)
- if \( 149 < T_A \leq 204^\circ\text{C} \) and \( 204 < T_B \leq 302^\circ\text{C} \)
  \[ dp = 67.76606 - 1.463848 \cdot \text{ds} - 0.1761701 \cdot 10^{-1} \cdot \text{ds}^{2}; \] \( (3) \)
- if \( 302 < T_A \leq 317^\circ\text{C} \) and \( 302 < T_B \leq 317^\circ\text{C} \)
  \[ dp = 60.2042 - 1.06864 \cdot \text{ds} - 0.244666 \cdot 10^{-1} \cdot \text{ds}^{2}; \] \( (4) \)
where \( dp = T_{\text{100PRF}}^{w} - T_{\text{0PRF}}^{w} \) is the overlap on the TBP curve [\(^{\circ}\text{C}\)].

The calculation of the initial temperature of the \( k \) fraction on the TBP curve

The initial temperatures of the fractions on the TBP curve are calculated using relation

\[ T_{\text{0PRF}, k+1} = T_{\text{100PRF}, k} - dp_k, \quad k = 1, \ldots, n_{\text{frac}} - 1. \] \( (5) \)

### The white oil products potential

The white oil products potential represents the percentage of products of a certain quality that is obtained from a crude oil distillation. The elements of the white oil products potential are:

- the calculation of the cutting temperature of the oil fractions;
- the calculation of the cumulated volume on the TBP curve of crude oil for each fraction;
- the calculation of white products potential.

The input data needed for the calculation of the white oil products potential are:

- the TBP curve of crude oil, expressed by the discrete function 
  \( T_{\text{PRF}0}, \text{vol}_c, T_{\text{PRF}} \), \( i = 1, \ldots, n_{\text{prf}} \) function that represents the TBP curve of crude oil.
- the temperatures on the TBP curve at 0% and 100% for each fraction.

Calculation of the cutting temperature

The input data for calculating the cutting temperature are:

- \( T_{\text{100PRF}}^{w} \) - the final temperature on the TBP curve of the fraction;
- \( T_{\text{0PRF}}^{w} \) - the initial temperature on the TBP curve of the next fraction.

The calculating relation used is:

\[ T_{\text{-PrF}k} = \frac{T_{\text{100PRF}, k} + T_{\text{0PRF}, k+1}}{2}, \quad k = 1, \ldots, n_{\text{frac}} - 1. \] \( (6) \)

The cutting temperature of the last fraction is considered being as final temperature of that fraction on the TBP curve of crude oil

\[ T_{\text{-PrF}n_{\text{frac}}} = T_{\text{-PrF}n_{\text{frac}}} \] \( (7) \)

Calculation of the cutted volume on the TBP curve of crude oil associated to \( k \) fraction

The cumulated volume, related to the cutting temperature of \( k \) oil fraction, \( T_{\text{PrF}i} \), is determined by polynomial interpolation of the discrete function \( (T_{\text{PRF}0}, \text{vol}_c, T_{\text{PRF}}), i = 1, \ldots, n_{\text{prf}} \) function that represents the TBP curve of crude oil. For polynomial interpolation the numerical methods presented in literature are used. This technical applies to all separated fraction.

The calculation for the white products potential

The potential for the first distilled fraction is equal to the cumulated volume on the TBP curve of this fraction

\[ \text{pot}_1 = \text{vol}_c \cdot _{\text{fr}1}. \] \( (8) \)

The white products potential of \( k \) fraction, \( k = 2, \ldots, n_{\text{frac}} - 1 \), is determined by subtracting the volume cumulated on the TBP curve of the previous fraction, \( k-1 \), out of the cumulated volume of that fraction on the TBP curve

\[ \text{pot}_k = \text{vol}_c \cdot _{\text{frac} k} - \text{vol}_c \cdot _{\text{frac} k-1}, \quad k = 2, \ldots, n_{\text{frac}} \] \( (9) \)

The calculation of the TBP curves of the oil fractions

The input data are:

- \( T_{\text{PrF}0}, \text{vol}_c, T_{\text{PrF}} \) - the TBP curve of crude oil;
- \( T_{\text{PrF}i} \) - the initial temperature of each oil fraction;
- \( T_{\text{-PrF}i} \) - the final temperature of each oil fraction;
- \( \text{pot} \) - the white products potential.

The distillated volumes associated to each fraction, in relation to that fraction, are ranged between 0 and 100%. In order to operate an unitary numerical treatment there is considered an equidistant of the points in the field mentioned at an 10% interval of volume, thus achieving 11 points:

\[ \text{vol}_{\text{frac} i} = 0.0001; \] \( (10) \)

\[ \text{vol}_{\text{frac} i} = 10 \cdot (i - 1), \quad i = 2, \ldots, 11. \] \( (11) \)

Knowing the initial and final temperatures of each fraction, \( T_{\text{-PrF}i} \) and \( T_{\text{PrF}i} \), they are fixed in the matrix of the temperatures on the TBP curve of fractions, points associated to the volume of 0 and 100%:

\[ T_{\text{-PrF}i} = T_{\text{-PrF}i}, \] \( (12) \)

\[ T_{\text{PrF}i} = T_{\text{PrF}i}. \] \( (13) \)

The volumes on the TBP curve of oil, corresponding to the percentages of distillate 20, 30, ..., 80% are determined with the relation \([9]\):

\[ v_j = \frac{\text{pot}_k \cdot \text{vol}_{\text{frac} j}}{100}, \quad j = 3, \ldots, 9; \quad i = 1, \ldots, n_{\text{frac}} \] \( (14) \)

For each \( i \) fraction, the temperatures corresponding to 20, 30, ..., 80% distillate, \( (T_{\text{fr-PrF}j}, \text{vol}_c, T_{\text{fr-PrF}j}) \), \( j = 3, \ldots, 9 \), are determined by polynomial interpolation on the TBP curve, \( (\text{vol}_c, T_{\text{PrF}0}), i = 1, \ldots, n_{\text{prf}} \).

The temperatures corresponding to 10 and 90% distillate, \( T_{\text{fr-PrF}1} \) and \( T_{\text{fr-PrF}n_{\text{frac}}} \), are determined by polynomial interpolation on the calculated curve of the fraction, curve containing 9 points, corresponding to the distilled volumes of 0, 20, 30, ..., 70, 80, 100%. 

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The calculation of the EFV curves of the oil fractions

To calculate the EFV curves of the distilled fractions there is used the Edmister-Okamoto method [1, 6-8]. The algorithm developed by the authors used of input data the TBP curves of the fractions, expressed as discrete function

\( T_{fr \text{ FRF}_{ij}} i=1,...,n_{frac}, j=1,...,11 \).

The algorithm is:
- the reference curve is divided into six segments: 0-10%, 10-30%, 30-50%, 50-70%, 70-90%, 90-100% and there are determined the differences in temperature at the ends of these segments:

\[
\begin{align*}
\Delta T_{10-0} &= T_{fr \text{ FRF}_{1,2}} - T_{fr \text{ FRF}_{1,1}}, \\
\Delta T_{30-10} &= T_{fr \text{ FRF}_{1,4}} - T_{fr \text{ FRF}_{1,2}}, \\
\Delta T_{50-30} &= T_{fr \text{ FRF}_{1,6}} - T_{fr \text{ FRF}_{1,4}}, \\
\Delta T_{70-50} &= T_{fr \text{ FRF}_{1,8}} - T_{fr \text{ FRF}_{1,6}}, \\
\Delta T_{90-70} &= T_{fr \text{ FRF}_{1,10}} - T_{fr \text{ FRF}_{1,8}} \\
\Delta T_{100-90} &= T_{fr \text{ FRF}_{1,11}} - T_{fr \text{ FRF}_{1,10}}
\end{align*}
\]

(15)

- with the proper temperature at 50% distillate on the TBP curve of the oil fraction, \( T_{fr \text{ PRF}_{i,6}} \), and the temperature difference \( \Delta T_{50-10} \) there is determined the temperature difference between the EFV and TBP curves, corresponding to 50% distillate, \( \Delta T_{50VE \text{ PRF}} \). For this purpose there is used the bi-dimensional interpolation [10]. The discrete function

\[
\Delta T_{50VE \text{ PRF}} = f(t_{50PRF}, t_{30-10PRF}), \quad i=1,...,11, \quad j=1,...,15
\]

(16)

has the values presented [10].
- the temperature at 50% distillate on the EFV curve is calculated with the relation

\[
T_{fr \text{ PRF}_{i,6}} = T_{fr \text{ PRF}_{i,6}} + \Delta T_{50VE \text{ PRF}}
\]

(17)

- the differences of temperature corresponding to the ends of the segments of the EFV curve \( t_{50PRF}, t_{30-10PRF} \) etc.) are calculated using the Edmister method. The differences of temperature at the ends of the curve segments on the TBP curve \( g(t_{50TBP}, t_{30-10TBP}) \) etc.) were calculated above and the differences \( (t_{50VEPRF}, t_{30-10VEPRF}) \) etc.) are calculated with the approximation functions shown in table 1;
- the appropriate temperatures at 0, 10, 30, 70, 90, 100% distillate on the EFV curve are calculated with the relations:

\[
\begin{align*}
T_{fr \text{ VE}_{1,6}} &= T_{fr \text{ VE}_{1,6}} - \Delta T_{VE}(per 50-30) \\
T_{fr \text{ VE}_{1,2}} &= T_{fr \text{ VE}_{1,2}} - \Delta T_{VE}(per 30-10) \\
T_{fr \text{ VE}_{1,1}} &= T_{fr \text{ VE}_{1,6}} - \Delta T_{VE}(per 10-0) \\
T_{fr \text{ VE}_{1,8}} &= T_{fr \text{ VE}_{1,6}} - \Delta T_{VE}(per 70-50) \\
T_{fr \text{ VE}_{1,10}} &= T_{fr \text{ VE}_{1,6}} - \Delta T_{VE}(per 90-70) \\
T_{fr \text{ VE}_{1,11}} &= T_{fr \text{ VE}_{1,6}} - \Delta T_{VE}(per 100-90)
\end{align*}
\]

(24)

- the appropriate temperature at 20, 40, 60 and 80% distillate are calculated by the interpolation of the discrete function \( (vol_k, temp_k), k=1,...,7 \), a function built from the results obtained at the above points.

The calculation of the ASTM curves of the oil fractions

To calculate the ASTM curves of the oil fractions there is also used the method Edmister-Okamoto. The numerical algorithm, proposed by the authors, has the following stages:

- the EFV curve is divided into six reference segments: 0-10%, 10-30%, 30-50%, 50-70%, 70-90%, 90-100% and there are determined the differences in temperature at the ends of these segments:

\[
\begin{align*}
\Delta T_{50VE \text{ PRF}} &= f(t_{50PRF}, t_{30-10PRF}), \quad i=1,...,11, \quad j=1,...,15
\end{align*}
\]

(16)

- the temperature corresponding to 50% distillate on the ASTM curve of the oil fraction, \( T_{fr \text{ STAS}_{i,6}} \), represents a solution of the non-linear equation [9]

\[
f(T_{fr \text{ STAS}_{i,6}}) = 0,
\]

(26)

where the function \( f \) has the expression

\[
f = T_{fr \text{ STAS}_{i,6}} - T_{fr \text{ VE}_{1,6}} + g(T_{50STAS_{30-10}}, T_{fr \text{ STAS}_{i,6}}).
\]

(27)

The discrete function \( g(T_{50STAS_{30-10}}, T_{fr \text{ STAS}_{i,6}}) \) belongs to the Edmister method and the numerical values associated to discrete correlation are presented in [10]

\[
\Delta T_{50STAS_{VE}} = g(T_{50STAS_{i,6}}, T_{fr \text{ STAS}_{30-10}}), \quad i=1,...,11, \quad j=1,...,15.
\]

(28)

<table>
<thead>
<tr>
<th>Cod</th>
<th>( \Delta T_{prf} )</th>
<th>Relation</th>
<th>The relation for calculation ( \Delta T_{ve} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10-0</td>
<td>(18)</td>
<td>( 4.361 \times 10^{-3} \times dprf^2 + 7.3696 \times 10^{-2} \times dprf - 0.14895 )</td>
</tr>
<tr>
<td>2</td>
<td>30-10</td>
<td>(19)</td>
<td>( -5.62259 \times 10^{-5} \times dprf^3 + 1.4330 \times 10^{-2} \times dprf^2 - 0.17524 \times dprf + 3.4177 )</td>
</tr>
<tr>
<td>3</td>
<td>50-30</td>
<td>(20)</td>
<td>( -7.04665 \times 10^{-5} \times dprf^3 + 1.493601 \times 10^{-2} \times dprf^2 - 0.124168 \times dprf + 2.50948 )</td>
</tr>
<tr>
<td>4</td>
<td>70-50</td>
<td>(21)</td>
<td>( -1.013204 \times 10^{-4} \times dprf^3 + 1.8654 \times 10^{-2} \times dprf^2 - 0.24421 \times dprf + 4.19721 )</td>
</tr>
<tr>
<td>5</td>
<td>90-70</td>
<td>(22)</td>
<td>( -8.2090 \times 10^{-5} \times dprf^3 + 1.4457 \times 10^{-2} \times dprf^2 - 5.5898 \times 10^{-3} \times dprf + 1.34288 )</td>
</tr>
<tr>
<td>6</td>
<td>100-90</td>
<td>(23)</td>
<td>( 1.6667 \times 10^{-3} \times dprf^2 + 3.7348 \times 10^{-4} \times dprf - 3.32727 )</td>
</tr>
</tbody>
</table>
FUNCTIONS OF APPROXIMATION OF $\Delta T_{ASM} = f(\Delta T_{EFV})$

**CORRELATION OF THE EDMISTER METHOD**

<table>
<thead>
<tr>
<th>Cod</th>
<th>$\Delta T_{EFV}$</th>
<th>Relation</th>
<th>Calculation relation for $\Delta T_{STAS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10-0</td>
<td>(29)</td>
<td>$-1.501463136 \times 10^{-02} \times d\nu e^2 + 2.1185439370 \times d\nu e + 5.4437538538$</td>
</tr>
<tr>
<td>2</td>
<td>30-10</td>
<td>(30)</td>
<td>$8.7842992495 \times 10^{-05} \times d\nu e^3 - 1.4732970742 \times 10^{-02} \times d\nu e^2 + 1.8919551798 \times d\nu e - 8.7458795762 \times 10^{-02}$</td>
</tr>
<tr>
<td>3</td>
<td>50-30</td>
<td>(31)</td>
<td>$1.2613267669 \times 10^{-04} \times d\nu e^3 - 1.633523094 \times 10^{-02} \times d\nu e^2 + 1.85900459984 \times d\nu e + 1.7318639283$</td>
</tr>
<tr>
<td>4</td>
<td>70-50</td>
<td>(32)</td>
<td>$1.1039325063 \times 10^{-04} \times d\nu e^3 - 1.3136512476 \times 10^{-02} \times d\nu e^2 + 1.7632471064 \times d\nu e + 3.229125733$</td>
</tr>
<tr>
<td>5</td>
<td>90-70</td>
<td>(33)</td>
<td>$2.1868847818 \times 10^{-04} \times d\nu e^3 - 2.4571700000 \times 10^{-02} \times d\nu e^2 + 2.1315053733 \times d\nu e + 1.9435741122$</td>
</tr>
<tr>
<td>6</td>
<td>100-90</td>
<td>(34)</td>
<td>$-2.2770468692 \times 10^{-02} \times d\nu e^2 + 2.5453268457 \times d\nu e + 2.7203392006$</td>
</tr>
</tbody>
</table>

The value of the function $g$ is determined by a bi-dimensional interpolation algorithm. The difference of temperature on the ASTM curve corresponding to points 30 and 10%, $\Delta T_{STAS,EFV}$, is calculated with the approximation function presented in table 2, number 2:

- by using the Edmister method there are determined the differences of temperature at the ends of the ASTM curve segments. The differences of temperature at the ends of the curve segments EFV were calculated above and for the correlations using graphical features of polynomial approximation functions, table 2.
- knowing the temperature at 50% on the ASTM curve, $T_{fr_{STAS}}$, and the differences at the ends of the segments of the ASTM curve, the temperatures are calculated at 0%, 10%, ..., 90%, 100% distillate on the ASTM curve:

$$
T_{fr_{STAS,1k}} = T_{fr_{STAS,1k}} - \Delta T_{STAS} (d\nu e \_ 53)
$$

$$
T_{fr_{STAS,12}} = T_{fr_{STAS,12}} - \Delta T_{STAS} (d\nu e \_ 51)
$$

$$
T_{fr_{STAS,13}} = T_{fr_{STAS,13}} - \Delta T_{STAS} (d\nu e \_ 10)
$$

$$
T_{fr_{STAS,14}} = T_{fr_{STAS,14}} + \Delta T_{STAS} (d\nu e \_ 75)
$$

$$
T_{fr_{STAS,15}} = T_{fr_{STAS,15}} + \Delta T_{STAS} (d\nu e \_ 97)
$$

- the temperatures at 20, 40, 60 and 80% are determined by the interpolation of the discrete function $(vol_k, temp_k)$, $k=1,\ldots,7$, function built from the results obtained above. The 7 decks of the discrete correlation are obtained with the relations:

$$
\begin{align*}
vol_1 &= 0.001 \\
vol_2 &= 10 \\
vol_3 &= 30 \\
vol_4 &= 50 \quad ; \quad (36) \\
vol_5 &= 70 \\
vol_6 &= 90 \\
vol_7 &= 100
\end{align*}
$$

The software system for calculating the liquid - vapor equilibrium

The programme for calculating the liquid - vapor equilibrium has the following structure:

- main program;
- procedures and mathematical functions;
- procedures for processing files;
- procedures and specific functions of calculating the liquid-vapor equilibrium for the distilled fractions;
- files for input data;
- files for output data;
- files contained the discrete functions.

Procedures and functions

For the software system, the authors have adapted and developed a set of PASCAL functions and procedures presented in table 3 [10]. They cover mathematical functions, procedures for solving the main types of mathematical problems, the procedures specific to the input data file format and functions associated to the algorithm presented in Chapter 1.

Files for input-output data

Files for input data are classified in files containing experimental data and files containing the specifications of the products to be obtained. In the first category there is the PRF0.dat file, that contains the TBP curve of the crude oil. The structure of this data is:

- first column contains the limit of the distillation intervals and the last record contains the upper limit of the last distillation interval;
- the second column contains the 0.0001 value followed by the distilled volume values for each distillation period;
- the third column contains the value of 0.0001 and then the density values for each distillation period.

The STAS.dat file is part of the second category of input files and contains specifications on the ASTM curve associated to the fractions distilled. The data structure is as follows:

- the final temperature on the ASTM curve of each distillated fraction;
- the gap temperature between two adjacent fractions on the ASTM curve, except for last fraction.

The files contained the discrete functions are destined to charge the discrete function associated Edmister-Okamoto method into the program. The programme system uses two discrete function files. File T50VPdat contains discrete correlation.
Table 3
FUNCTIONS AND PROCEDURES USED IN THE SOFTWARE SYSTEM

<table>
<thead>
<tr>
<th>Model Name</th>
<th>Type of sub-algorithm</th>
<th>The function performed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pow</td>
<td>function</td>
<td>Power lifting ( x^2 )</td>
</tr>
<tr>
<td>Gauss</td>
<td>procedure</td>
<td>Solves the linear equation system by using the Gauss method</td>
</tr>
<tr>
<td>Intbid</td>
<td>function</td>
<td>Approximates the function by using the bidimensional linear interpolation</td>
</tr>
<tr>
<td>Interpol</td>
<td>function</td>
<td>Approximates the function by using the polynomial interpolation</td>
</tr>
<tr>
<td>Incbis</td>
<td>procedure</td>
<td>Solves the nonlinear equation by using try-error method combined with successive bisection method</td>
</tr>
<tr>
<td>Citfis5</td>
<td>procedure</td>
<td>Reads the numerical data from a file organized like max 5 columns table</td>
</tr>
<tr>
<td>Citfis5t</td>
<td>procedure</td>
<td>Reads the data from a file organized like a table containing a first text ASCII column and maximum 5 numerical columns</td>
</tr>
<tr>
<td>Citfmat</td>
<td>procedure</td>
<td>Reads the numeric data from a file organized as matrix with ( m ) lines and ( n ) columns</td>
</tr>
<tr>
<td>Fdtve</td>
<td>function</td>
<td>Calculates the differences of temperatures on the EFV curve, using the differences of temperature on the TBP curve</td>
</tr>
<tr>
<td>Fdtve_stas</td>
<td>function</td>
<td>Calculates the differences of temperature on the EFV curve based on the temperature differences on the ASTM curve</td>
</tr>
<tr>
<td>Dtp</td>
<td>function</td>
<td>Calculates the overlap of temperature on the TBP curve by using the gap in temperature on the ASTM curve</td>
</tr>
<tr>
<td>F50</td>
<td>function</td>
<td>Function implementation (26)</td>
</tr>
</tbody>
</table>

\[ \Delta T_{50\text{SFPRF}} = f(t_{50\text{SFPRF}}, t_{30\text{-10\%PRF}}), \quad i = 1, \ldots, 11, \quad j = 1, \ldots, 15 \]

and the file STAS50_VE.dat contains the discrete correlation

\[ \Delta T_{90\text{STAS}_{\text{VE}}} = f(t_{90\text{STAS}_{\text{VE}}}, \Delta T_{\text{STAS} \text{30-10}}), \quad i = 1, \ldots, 11, \quad j = 1, \ldots, 15 \]

The output data file is named FIS_PRF1.dat and it contains all the experimental data, explicative messages and all the results obtained from the program. The file is an ASCII format and can be consulted by the user.

**Example of calculation**

*The input data*

The programme for the mass balance and the liquid-vapor equilibrium associated to the petroleum fractions was run on a control sample. The crude oil processed in crude distillation column is a Romanian crude oil from Baicoi reservoir, characterized by the TBP curve presented in table 4 [11].

The number, the type and the specifications of the distillate fractions are shown in table 5, under which there are created the STAS.dat file.

**Comparative study between the calculation algorithm and the graphical method of calculation**

By running the programme for calculating the input data presented above there were calculated the following sizes:

- temperature corresponding to 100% TBP curve of each oil fraction;
- overlap of temperature on the TBP curve between two adjacent oil fractions;
- initial temperatures of the oil fractions on the TBP curve;
- cutting temperature between two oil fractions on the crude oil TBP curve;
- cumulated volume of each oil fraction on the crude oil TBP curve;
- potential of white oil products;

---

Table 4

<table>
<thead>
<tr>
<th>No.</th>
<th>Temperatures range of the distillation</th>
<th>Distilled volume [%]</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>60</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>95</td>
<td>1.4</td>
</tr>
<tr>
<td>3</td>
<td>95</td>
<td>120</td>
<td>4.3</td>
</tr>
<tr>
<td>4</td>
<td>120</td>
<td>150</td>
<td>7.4</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>200</td>
<td>11.6</td>
</tr>
<tr>
<td>6</td>
<td>200</td>
<td>250</td>
<td>8.5</td>
</tr>
<tr>
<td>7</td>
<td>250</td>
<td>300</td>
<td>10.6</td>
</tr>
<tr>
<td>8</td>
<td>300</td>
<td>350</td>
<td>10.7</td>
</tr>
<tr>
<td>9</td>
<td>350</td>
<td>400</td>
<td>11.0</td>
</tr>
<tr>
<td>10</td>
<td>400</td>
<td>450</td>
<td>8.8</td>
</tr>
<tr>
<td>11</td>
<td>450</td>
<td>500</td>
<td>8.1</td>
</tr>
</tbody>
</table>

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Table 6

<table>
<thead>
<tr>
<th>No.</th>
<th>Fraction name</th>
<th>Final temperature on STAS curve (°C)</th>
<th>Gap temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Naptha</td>
<td>120</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>Gasoline</td>
<td>200</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>Petrol</td>
<td>300</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>Diesel</td>
<td>360</td>
<td>0.01</td>
</tr>
</tbody>
</table>

- TBP curve, the ASTM curve and the EFV curve of each oil fractions.

In table 6 there are presented the comparative results of temperatures associated to the EFV curve, calculated by the two methods. The conclusions are the following:
- misconduct is found between the two calculation methods in the range 3...10°C;
- results of the numerical algorithm proposed respect the trend imposed by the graphic method of calculation;
- the deviations between the results obtained by the two methods are relatively evenly scattered for all the petroleum fractions.

The validation of the numerical algorithm proposed by the authors is done by comparing the numerical results obtained by using the Edmister - Okamoto graphic method and running the programme developed by the authors. In table 7 there are presented results of statistical comparison of the two methods of calculation. These results lead to the following conclusions:
- there is an acceptable correspondence between the results obtained with the graphic method and the results of the numerical algorithm proposed by authors;
- the consistency of the data entry is particularly important for the numerical algorithm. The data on the TBP curve must come from experimental determinations. The oil products specifications must also reflect the achievement of real products. The authors tested the influence of this data and found significant variations of errors in relation to the input data specified in table 5;
- the differences between the results obtained have four major causes. The first is the source of data used to calculate the approximation functions (source graphics). The second issue is caused by the numerical errors introduced by the polynomial regression algorithm used to

Table 5

<table>
<thead>
<tr>
<th>% volume</th>
<th>Naptha</th>
<th>Gasoline</th>
<th>Petrol</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>73.9</td>
<td>68</td>
<td>132.4</td>
<td>125</td>
</tr>
<tr>
<td>10.0</td>
<td>76.6</td>
<td>70</td>
<td>137.7</td>
<td>128</td>
</tr>
<tr>
<td>20.0</td>
<td>80.2</td>
<td>72</td>
<td>142.2</td>
<td>131</td>
</tr>
<tr>
<td>30.0</td>
<td>83.3</td>
<td>74</td>
<td>145.8</td>
<td>134</td>
</tr>
<tr>
<td>40.0</td>
<td>85.6</td>
<td>76</td>
<td>147.9</td>
<td>137</td>
</tr>
<tr>
<td>50.0</td>
<td>87.7</td>
<td>77</td>
<td>150.2</td>
<td>140</td>
</tr>
<tr>
<td>60.0</td>
<td>89.3</td>
<td>80</td>
<td>152.1</td>
<td>143</td>
</tr>
<tr>
<td>70.0</td>
<td>91.1</td>
<td>82</td>
<td>154.9</td>
<td>146</td>
</tr>
<tr>
<td>80.0</td>
<td>91.9</td>
<td>84</td>
<td>158.9</td>
<td>149</td>
</tr>
<tr>
<td>90.0</td>
<td>94.6</td>
<td>85</td>
<td>163.1</td>
<td>153</td>
</tr>
<tr>
<td>100.0</td>
<td>99.1</td>
<td>88</td>
<td>167.6</td>
<td>155</td>
</tr>
</tbody>
</table>

Table 7

<table>
<thead>
<tr>
<th>The objective of calculation</th>
<th>Calculated parameter</th>
<th>Minimal deviation</th>
<th>Maximal deviation</th>
<th>Units of measure</th>
</tr>
</thead>
<tbody>
<tr>
<td>The TBP curve of the crude oil</td>
<td>The overlap on the TBP curve</td>
<td>1.14</td>
<td>3.80</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>The initial temperature of oil fractions on TBP curve</td>
<td>0.00</td>
<td>2.07</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>The final temperature of oil fractions on TBP curve</td>
<td>0.00</td>
<td>1.15</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>The cutting temperature</td>
<td>0.00</td>
<td>1.18</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>The volume of oil fraction</td>
<td>0.28</td>
<td>2.46</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>The potential of the white products</td>
<td>0.28</td>
<td>5.10</td>
<td>%</td>
</tr>
<tr>
<td>The TBP curve of oil products</td>
<td>10% distillate</td>
<td>1.4</td>
<td>7.1</td>
<td>°C</td>
</tr>
<tr>
<td></td>
<td>50% distillate</td>
<td>1.6</td>
<td>5.6</td>
<td>°C</td>
</tr>
<tr>
<td></td>
<td>90% distillate</td>
<td>1.8</td>
<td>4.5</td>
<td>°C</td>
</tr>
<tr>
<td>The EFV curve of oil products</td>
<td>10% distillate</td>
<td>4.4</td>
<td>9.7</td>
<td>°C</td>
</tr>
<tr>
<td></td>
<td>50% distillate</td>
<td>1.7</td>
<td>10.7</td>
<td>°C</td>
</tr>
<tr>
<td></td>
<td>90% distillate</td>
<td>4.0</td>
<td>10.1</td>
<td>°C</td>
</tr>
<tr>
<td>The ASTM curve of oil products</td>
<td>10% distillate</td>
<td>1.8</td>
<td>29.2</td>
<td>°C</td>
</tr>
<tr>
<td></td>
<td>50% distillate</td>
<td>1.9</td>
<td>36.5</td>
<td>°C</td>
</tr>
<tr>
<td></td>
<td>90% distillate</td>
<td>3.5</td>
<td>47.8</td>
<td>°C</td>
</tr>
</tbody>
</table>
calculate the mono-variable approximation functions. The third is introduced by using an algorithm of bi-dimensional linear interpolation functions for approximation of the bi-dimensional nonlinear interpolation. The last cause is introduced by the subjective determinations of the function approximation values used in the graphic method;

- the calculation errors are cumulated with the increasing molar mass of oil fractions. The small errors are found in the naphtha and gasoline petroleum fractions and the bigger errors are found in the diesel oil;
- the calculation errors are cumulated and they increase in the order: TBP curve, EFV and ASTM curve.

Given the results of statistical comparison of the two methods of calculation and the analysis of sources of numerical errors, the authors consider that the algorithm is properly developed and the goal is achieved through numerical algorithm validation.

**Conclusion**

In the paper there is developed a numerical algorithm for calculating the vapor-liquid equilibrium for oil distilled fractions. The algorithm is based on the Edmister-Okamoto graphical model. The mono-variable graphic correlations were approximated by continuous functions determined by non-linear regression and the bi-dimensional graphical correlations were approximated by linear bi-dimensional interpolation functions. The authors have developed calculation relationships to transpose into a numerical algorithm all operations that were done manually and used numerical methods for solving the original nonlinear equations.

Based on the proposed algorithm, the authors have developed a computer programme that estimates the liquid-vapor equilibrium associated to petroleum factions, the TBP, EFV and ASTM curves. The results obtained with the numerical algorithm were compared with results obtained by computer graphics. They identified the sources of errors, the propagation of their level of errors. Based on these results, the numerical algorithm proposed by the authors was validated. This algorithm can be used in the future as a checking instrument of the quality specifications imposed to the oil products and as a method of initialization of the other crude oil simulation programme (ex. the algorithms characterized by using the pseudo components of crude oil and petroleum products).

The list of variables

\( T_{PRF}, \text{vol c PRF}_i, i = 1, \ldots, n \text{ prf} \) - the discrete function which contains the crude oil TBP curve;

\( T_{0PRF} \) - the initial temperature on the TBP curve of petroleum fraction;

\( T_{-t PRF}, k = 1, \ldots, n \text{ frac} - 1 \) - the cutting temperature on the TBP curve for each petroleum fraction;

\( p_{oil}, k = 1, \ldots, n \text{ frac} \) - the potential for each petroleum fraction;

\( v_j, j = 1, \ldots, 11 \) - the distillate combined volumes of the 11 points equidistance, located in the range \([0...100]\%) for each petroleum fraction;

\( T_{fr PRF}, i = 1, \ldots, 11; j = 1, \ldots, n \text{ frac} \) - the matrix of points containing the temperature of points on the TBP curve of each oil fraction;

\( \Delta T_{50VE PRF} \) - the temperature difference between the distillate temperatures corresponding to percentages distillate of 30 and 10% on a TBP curve of petroleum fractions;

\( \Delta T_{50VE PRF} \) - the temperature difference between the EFV and TBP curve at 50% distillate;

\( T_{fr VE PRF}, i = 1, \ldots, 11; k = 1, \ldots, n \text{ frac} \) - the matrix of points containing the temperatures on the EFV curve of each oil fraction;

\( \Delta T_{ASTM PRF} \) - the difference between distillate temperatures corresponding to the distillate percentages of 30 and 10% on ASTM curve of oil fractions;

\( T_{fr ASTM PRF}, i = 1, \ldots, 11; k = 1, \ldots, n \text{ frac} \) - the matrix of points containing the temperature of points on the ASTM curve of each fraction.

**References**

5. **PRO II 5.0 User’s Guide, Simulation Sciences Inc., CA, USA, 1997**
11. RÂDULESCU, G., A., Proprietățile țieiurilor românești, Editura Tehnică, București, 1982

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