NON-TRADITIONAL CHARACTERIZATION OF PETROLEUM MIXTURES IN TERMS OF SELECTED COMPONENTS

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A non-traditional method of characterization of petroleum mixtures in terms of selected real components is described which stems from the results of the mixture analysis and from some of distillation curves – best of all, EFV curve. On the basis of mathematical modelling of the process of obtaining the EFV curve, it is possible to find the composition of a substitute mixture consisting of a lower number of real components of the original mixture. This substitute mixture exhibits very similar vapour–liquid equilibrium behaviour as the original multicomponent mixture, which makes it possible to simplify the calculation of, *e.g.*, a rectification column. At the same time, the need disappears of estimating the thermodynamic data of single mixture components on the basis of empirical relations subject usually to considerable errors so as it is with the commonly employed method of pseudocomponents.

Key words: Complex mixtures; Petroleum fractions; Characterization procedure; Mathematical modelling; Hydrocarbons; Rectification.

Petroleum fractions contain a great number of components of different groups – paraffins, olefins, naphthenes, aromates, *etc.* These components can be divided into three groups[1]:

a) Defined components from which a so-called light end is composed. In case of hydrocarbons, it is those ones whose length of chain is up to C_6. For them, all the needed thermodynamic parameters are known.

b) TBP (True Boiling Point) fractions, which are mixtures of hydrocarbons C_7 up to at most C_{30}, for which density and mean molecular weight can be measured.

c) TBP bottom products, which are mixtures consisting of components which are too heavy to be separated by the TBP distillation; for the whole it is possible to determine density and molecular weight but it is impossible to determine the boiling point distribution or molecular weights.

To calculate the technological lines which process the petroleum fractions, a number of modern simulation programs are employed, let us name, *e.g.*, ASPEN PLUS (ref.[2]), PRO II (ref.[3]), ChemCAD (ref.[4]). They make it possible to characterize a petroleum multicomponent mixture on the basis of knowledge of some of distillation curves differing in the way of their obtaining – *e.g.*, TBP, ASTM D 86, EFV (Equilibrium Flash Vapour), *etc.* (ref.[5]), by means of a substitute mixture consisting of a given number of pseudocomponent. A user of the program defines only the composition of a so-called light end, gives some of many possible distillation curves and determines the number of cuts – pseudocomponents along with the temperature intervals in which they are to be defined. The program itself calculates the composition of the substitute mixture of pseudocomponents and stores into the user database the thermodynamic data of these pseudocomponents which are necessary for calculating the vapour (gas)–liquid equilibrium behaviour or enthalpies of mixtures. The methodology of characterization of the mixture and of the formation of pseudocomponent is described, *e.g.*, in ref.[6]. In this way, the number of components considered for further calculations, *e.g.*, of distillation columns, is reduced to an acceptable value (as a rule, forty and less). A disadvantage of this procedure is the fact that for estimating the thermodynamic parameters of single pseudocomponents, it is necessary to employ empirical relations (*e.g.*, for estimating the molecular weight, critical properties, acentric factor, saturated vapour pressure, heat capacity, molar volume, *etc.*)[5]. These empirical relations have only limited range of validity and are not suitable for all mixtures equally well. In case of the mixtures containing mostly n-paraffins, their usual error is of the order of per cent up to tens per cent, in case of the mixtures with a high content of aromates, this error is still several times higher[7]. This finding holds also for the relations by Lee and Kesler[8,9] which are considered to be the best ones. On using these thermodynamic parameters in the subsequent enthalpy calculations and calculations of vapour– liquid equilibrium, which form the basis, *e.g.*, in computing rectification columns, the errors of the mentioned empirical relations are surprisingly not only propagated but probably are, from the greater part, even compensated. The calculations of rectification columns provide, as a rule, acceptable results which are subject to errors of only several per cent (*e.g.*, in case of boiling points of end products and distillation curves of products) up to tens per cent (in case of temperature profile along the column)[7]. This is apparently one of reasons why the methods of continuous thermodynamics (*e.g.* ref.[10]) are not widely used in practice for the characterization of petroleum mixtures, and the question remains to what extent other modern procedures (*e.g.* ref.[11]) will take off.

Even if it is possible to say that the introduction of pseudocomponent mixtures in mathematical modelling of diffusion separation equipments in the traditional conception – with equilibrium and/or in terms of efficiencies corrected stages – gives acceptable results, its use for modern concept of non-equilibrium plate is problematic. The reason consists in the fact that the calculations in terms of this concept require the possibility of estimating further thermodynamic and/or transport parameters of present components, such as, *e.g.*, diffusivity in the liquid and vapour phase. Common methods of their estimations in case of pseudocomponents may provide values still less accurate than it is in case of real components. As well, if we wish to calculate all the technological line processing the petroleum mixtures, problems in modelling arise if a device occurs in it in which chemical reactions take place (*e.g.*, a reforming line) in which it is not possible to assume the conservation of identity of single pseudocomponents.

The aim of this work is to show a simple way how to use, beside the knowledge of content of single groups of hydrocarbons, also the information provided by some of distillation curves to characterize a multicomponent petroleum mixture. On the basis of the procedure proposed, it is then possible to characterize the original multicomponent mixture in terms of a substitute mixture of real components present in the original mixture. In this way, it is possible to obviate the above-mentioned empirical relations for estimating thermodynamic parameters in all the following calculations because they are known for the real components.

MODEL

Characterization of Mixtures in Terms of Real Components

In practice, there exist a number of procedures for obtaining different distillation curves, *i.e.*, the dependences of a certain temperature T^{m} (*e.g.*, the temperature in the distillation flask neck) on the volume fraction of distilled-off fraction ϕ depending on the initial composition $\boldsymbol{x}_0^{\mathrm{m}}$

$$T^{\mathrm{m}} = T^{\mathrm{m}}(\boldsymbol{x}_0^{\mathrm{m}}, \phi) \; . \qquad (1)$$

The only, from the point of view of procedure and apparatus, standardized method of obtaining one of distillation curves, which can then serve for characterization of petroleum mixture, is the widespread ASTM D 86 (ref.[12]). Even though a great many authors describe it as a single-stage differential distillation, this process is probably not concerned. If it was really so, this distillation curve should exhibit the same initial point for $\phi = 0$ (corresponding to the boiling point of original mixture) with the EFV curve, which is not the case. As it is evident from the experimental assembly (*e.g.* ref.[12]), the thermally insufficiently insulated neck of used distillation flask functions evidently as a further separation part (partial condenser with a continual phase contact – running-down condensed liquid and vapour rising from the flask), and the equipment works as a differential rectification with more than one equilibrium stage. For this reason, this process cannot be simply mathematically modelled.

Analogous case is encountered with further popular distillation curve – TBP which is obtained by means of a multiplate batch rectification column (15–100 separation stages with reflux ratio 5 and more). The knowledge of true number of theoretical stages is here problematic, regardless of the questionable term "theoretical stage" in practical application.

The situation is not better even with oher methods used, and use of rigorous mathematical modelling of these methods has no great chances of good agreement with reality. The only exception in the whole number of distillation curves is represented by the EFV curve whose method of obtaining agrees with a general description of gradually repeated single-stage equilibrium distillation under constant pressure which will be presented.

The mass balances are represented by the relations

$$0 = x_{i,0} - \varphi y_i - (1 - \varphi)x_i \qquad i = 1, \ldots, I \,. \tag{2}$$

Here x_i, y_i are mole fractions of the i-th component in the liquid and vapour phase, respectively, φ is the molar portion of the vapour phase and I is the total number of component considered.

Further, the equilibrium between the vapour and liquid phase takes place

$$0 = y_i - K_i\,(T, P, \boldsymbol{x}, \boldsymbol{y})x_i \qquad i = 1, \ldots, I \,. \tag{3}$$

Here K_i is the vapour–liquid distribution coefficient of component i, $\boldsymbol{x}$, $\boldsymbol{y}$ are vectors of composition of the liquid and vapour phase, respectively, T is temperature and P is pressure. Since the mixture occurs at its boiling point,

$$0 = \sum_{i=1}^{I} K_i (T, P, \boldsymbol{x}, \boldsymbol{y}) x_i - 1 \tag{4}$$

holds. These relations are in addition completed with the relation between the molar portion distilled φ and the volume portion distilled ϕ which is, as a rule, measured:

$$0 = (\phi - 1) \sum_{i=1}^{I} \frac{x_{i,0}}{\rho_{i,0}} + (1 - \varphi) \sum_{i=1}^{I} \frac{x_i}{\rho_i} \, . \tag{5}$$

Here ρ_i and $\rho_{i,0}$ represent the density of the *i*-th component at the temperature T or at initial temperature, respectively. For a certain volume portion distilled ϕ, the given initial composition x_0 and operating pressure P, the system of equations $2I + 2$ generally non-linear equations (*2*)–(*5*) will give the solution for $2I + 2$ unknowns $\boldsymbol{x}$, $\boldsymbol{y}$, φ, T. If the initial composition x_0 or portion distilled ϕ are changed, even this solution is changed, *i.e.*, including the value of temperature T.

Let us show how it is possible to describe well a petroleum mixture, which is characterized by means of some of classical distillation curves (ASTM D 86, TBP, *etc.*), with a mixture of real components in terms of the mentioned mathematical model of obtaining the EFV distillation curve.

The first step will be the conversion of the measured curve to the EFV curve which is directly measured with difficulties and consequently rarely. Two ways are offered here. On the one hand, it is possible to use the modern simulation program and to simulate the single-stage equilibrium distillation of the feed for different molar portions distilled φ, through which we obtain the respective equilibrium temperatures T. For this way, we, however, must admit an automatic generation of sufficient number of pseudocomponents and shall obtain, in fact, an "untrue" EFV curve

$$T^{\mathrm{m}} = T^{\mathrm{m}} (\boldsymbol{x}_0^{\mathrm{m}}, \varphi) \, . \tag{6}$$

The second way is the use of converting relations[5,13] which were obtained by the regression processing of a great many experimental data. In this manner, we, however, introduce the error of these relations into the conversion, the error being often significant, especially in the case, when the conversion has to be carried out in two steps (TBP → D 86 → EFV). Therefore, the best way is to have the true experimentally obtained EFV curve.

Next step is the selection of real characterization components. An ideal case is when we may take a support, *e.g.*, of the analysis of the mixture considered and take into account the specificity of its composition (*e.g.*, the presence of polar components). On selecting the components, we must be respectful of the range of boiling points which had to be covered. Here we can, in case of wide- or high-boiling mixtures, meet with difficulties with thermodynamic parameters needed for calculating the vapour–liquid equilibrium of hydrocarbons with longer chains than C_{30} which are neither in the database of pure components nor in the literature[5]. But we do not make a great mistake when we select n-alkanes and, for them, we use group-contribution relations[5,14] for estimating the critical temperature T_c and critical pressure P_c. To estimate the acentric factor ω, the relation

$$\omega = \frac{3}{7}\left(T_b / T_c / \left(1 - T_b / T_c\right)\right)\log\left(P_c / 101\,325\right) - 1 \qquad (7)$$

is recommended[14], where T_b is normal boiling point. This relation yields wrong values for hydrocarbons with longer chain, and, therefore, it is better to use a suitable regression relation for extrapolating. On using the quadratic regression of values of acentric factor for aliphatic hydrocarbons C_1–C_{30} on the basis of data[5], we get, *e.g.*,

$$\omega = -0.0180675 + 0.0553812N - 0.000503263N^2\ , \qquad (8)$$

where N is the number of carbons in the chain. To estimate normal boiling point, the Stiel–Thodos method[15]

$$T_b = 10^3\left(1.209 - 1.163 / \left(1 + 0.0742N^{0.85}\right)\right) \qquad (9)$$

can be used. The molar liquid density at normal boiling point can be estimated from the very simple Schroeder relation[16]

$$\rho_b = 10^6 / \left(21N + 14\right)\ . \qquad (10)$$

Providing that we have selected the components for the characterization of the given petroleum mixture, for which we have at our disposal all the thermodynamic parameters needed for calculating vapour–liquid equilibrium, we found the composition $\boldsymbol{x}_0$ of the substitute mixture composed of these real components by minimizing the function

$$F(\boldsymbol{x}_0) = \sum_{j=1}^{J} \left(T_j(\boldsymbol{x}_0) - T_j^{\mathrm{m}} \right)^2 = \quad \min . \tag{11}$$

We sum here over all experimental points J for which we know EFV – the distillation curves T_j^{m} (ϕ_j). The calculated distillation curve $T_j(\boldsymbol{x}_0,\phi_j)$ is obtained at all the points ϕ_j as a repeated solution of system of equations (*2*)–(*5*) which represent the mathematical model of process of measuring the EFV curve. The composition $\boldsymbol{x}_0$ obtained in this way can be now used in all the subsequent calculations. In case we stem from the "untrue" EFV curve (*6*), we solve repeatedly only the system of equations (*2*)–(*4*) and minimize Eq. (*11*) at all the points φ_j for which the EFV curve was simulated.

Concept of Non-Equilibrium Stage

For a long time, the traditional concept of equilibrium stage in various forms was used for simulations of rectification. To correct the differences in behaviour between the real and equilibrium stage, the plate or evaporation efficiencies, introduced in different ways, were applied. Even if this pattern may be adequate in a great many binary mixtures, its disadvantages for multicomponent mixtures have been evident for a long time. Therefore, the concept of non-equilibrium stage (sometimes also designated as rate based approach), so as it was published by Krishnamurthy and Taylor[17,18], is applied more and more often in mathematical modelling of diffusion separation processes. The company Aspen Technology, Inc., engaged in the development of chemical-engineering software, has sold, already since 1988, as one of modules of its simulation program ASPEN PLUS, the module RATEFRAC for calculating the plate and packed columns, stemming from the non-equilibrium plate concept[19]. This module can be also used for calculating separation columns of processing petroleum mixtures which are characterized either traditionally in terms of psedocomponent or by means of the proposed procedure in the case when the formation of the second phase does not take place. Unfortunately, water vapour, which is in direct contact with petroleum mixture, is sometimes used in the columns for processing the petroleum mixtures. In this way, the coexistence of two liquid phases – aqueous and hydrocarbon – occurs in the column. The calculation of columns of this type is not made it possible by the RATEFRAC module. Lao and Taylor[20] as first proposed and verified several model concepts for the three-phase distillation using the rate based approach. Further elaboration of these procedures is the subject of continuing rersearch[21–23].

EXAMPLE[24]

Rectification column in the separation part of the hydrogen reforming.

Number of plates: 22 (including the total condenser and equilibrium boiler.

Pressure in head: 101 330 Pa.

Pressure drop over column (including the condenser): 36 800 Pa.

Reflux ratio: 1.6.

Feed: 1 000 t/day on the 7th plate from above, its temperature 20 °C.

Composition of feed: characterized by the TBP curve – see Fig. 1.

In the first part of characterization, the EFV curve for the feed was obtained by the simulation of equilibrium stage from the experimental TBF curve. From it, on using the mentioned procedure, the composition of the mixture consisting of real components, according to recommendation of authors[24], was obtained. The molar composition of mixtures substituting the real feed, as obtained by various methods (automatic generation of pseudocomponents by the simulation program ChemCAD II, by the proposed procedure or in terms of the volumes of single cuts[24]) is given in Table I. Whereas in case of 2-methylbutane or pseudocomponent NBP301 with identical boiling point, the mole fractions in the feed, calculated in

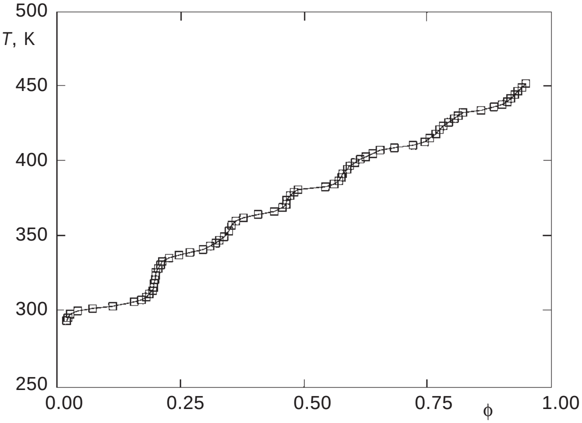

FIG. 1
TBP curve of feed

terms of the proposed method and the classical method of pseudocomponents, are close, with other components it is not so. Even it seems, that the composition of feed calculated in terms of volumes of single cuts and in terms of the pseudocomponent method are closer in comparison with the composition calculated by the proposed procedure. However, as it was found by the subsequent calculations of rectification column by means of all the variants of feed composition, the composition of feed calculated in terms of the volumes of cuts leads probably to wrong results.

Variants of Calculation

a) Seven pseudocomponents, normal boiling points of cuts correspond subsequently to 2-methylbutane, 3-methylpentane, 2-methylhexane, toluene, 1,4-xylene, 1,3,5-trimethylbenzene, 1,2-diethylbenzene (column 2 in Table I).

b) Seven real components (see above), composition of feed taken according to authors[24] (column 4 in Table I).

c) As at the preceding point, the composition of feed determined by the proposed method (column 3 in Table I).

d) Pseudocomponents as at point *a*), by means of RATEFRAC module. Further needed column parameters: diameter 2.5 m, height of weir 0.0508 m, length of weir 1.4 m, distance of plates 0.6 m, overflow area 0.49 m^2, active plate area 3.93 m^2.

TABLE I
Feed composition $\boldsymbol{x}_0$ obtained by different procedures: A method of pseudocomponents, B proposed method of real components, C method of volumes of cuts[24]

Real component or pseudocomponent *i*	A	B	C
2-Methylbutane (NBP301)	0.2846	0.2762	0.213
3-Methylpentane (NBP337)	0.1752	0.1029	0.144
2-Methylhexane (NBP363	0.1096	0.2204	0.108
Toluene (NBP383)	0.1134	0.0351	0.142
1,4-Xylene (NBP411)	0.1722	0.2523	0.192
1,3,5-Trimethylbenzene (NBP437)	0.0985	0.0406	0.141
1,2-Diethylbenzene (NBP454)	0.0464	0.0724	0.057

e) Real components as at point *c*), by means of the RATEFRAC module. The column parameters as at point *d*).

In all the cases, the Soave–Redlich–Kwong equation was used for the description of the vapour–liquid equilibrium behaviour. The used constants of this equation for the components are given in Table II.

DISCUSSION

The characteristic of products of the column for single variants of calculations by means of their boiling points or simulated EFV curves is given in Table III and illustrated in Figs 2 and 3. A very good agreement of the pro-

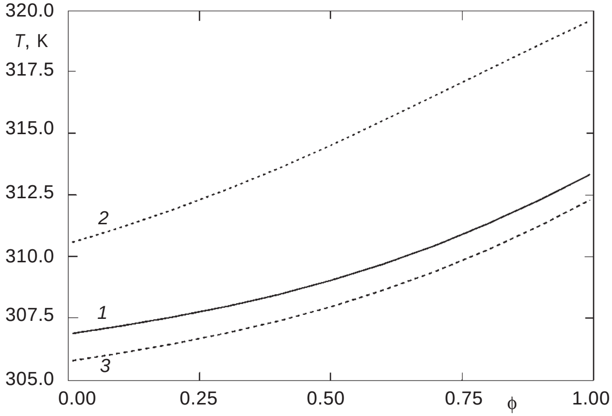

FIG. 2
Simulated EFV curves of distillate: *1* variant *a*), *2* variant *b*), *3* variant *c*)

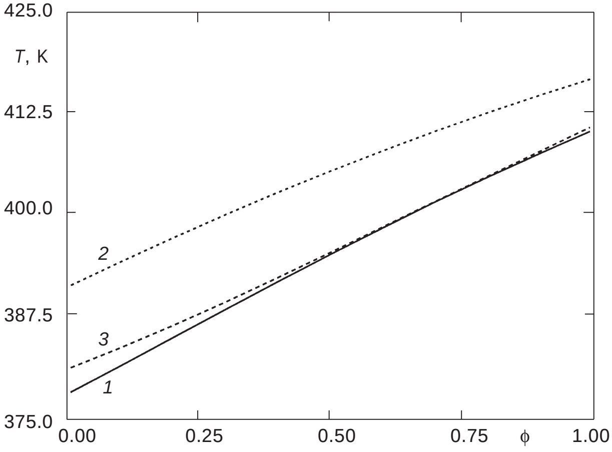

FIG. 3
Simulated EFV curves of bottom product: *1* variant *a*), *2* variant *b*), *3* variant *c*)

posed approach with the traditional method of pseudocomponents is apparent from the results. The difference in boiling points of both the products is about 1 or 3 K. The agreement of simulated EFV curves of bottom product for the comparable variants of calculation *a*) and *c*) is even surprising. The apparent disagreement between the simulated EFV curve of distillate in Fig. 2, having its beginning practically identical with the boiling point of distillate in Table III, follows from the fact that the distillate contains about 80 mole % 2-methylbutane (NBP301) and about 20 mole % 3-methylpentane (NBP337), whereas the portion of the other components is negligible. In this way, also the relatively small differences in boiling points of products are explained. The results obtained with the RATEFRAC module are interesting. If we compare variants *a*) and *d*), the boiling point

TABLE II
Constants of components for calculating vapour–liquid equilibrium

Component *i*	T_c	P_c	ω
2-Methylbutane	460.39	3.381E6	0.229
3-Methylpentane	504.35	3.124E6	0.274
2-Methylhexane	530.31	2.734E6	0.330
Toluene	591.79	4.109E6	0.263
1,4-Xylene	616.26	3.511E6	0.321
1,3,5-Trimethylbenzene	637.30	3.127E6	0.398
1,2-Diethylbenzene	668.00	2.880E6	0.3395

TABLE III
Boiling points of products of the column

Variant	B.p. of distillate, K	B.p. of bottom product, K
a	306.8	389.3
b	310.5	402.8
c	305.7	392.4
d	308.6	390.5
e	307.9	382.7

of distillate in variant *d*) is higher, which would correspond to really worse separation in a column with the same number of real plates. However, this consideration is at variance with the boiling point of bottom product which in variant *d*) is also higher than in variant *a*). A reason may be the above-mentioned problems of estimating the transport and thermodynamic parameters for pseudocomponents. On the contrary, the comparable variants *c*) and *e*) yield quite logical results. The results of variant *b*) show that judging of the composition from the volumes of single cuts, as do authors[24], leads to the results differing completely from the general practice.

CONCLUSIONS

The results obtained in terms of the proposed method show that it might serve as an alternative to the traditional procedure of the characterization of petroleum mixtures in terms of pseudocomponents, moreover, not only for the purpose of calculating the separation equipments. With the present possibilities of computational technique, it can be classified among the simpler procedures, which is also its advantage. As it has been said, it is possible to expect that the proposed method will yield the best results only in case that the true EFV curve and chemical analysis are available. The chemical analysis makes it possible to select well the characterization components not only with respect to the needed range of boiling points but also to the presence of components whose, if only small content may show a great effect on the equilibrium behaviour of mixture. As an example, let us say, polar components. Then it is necessary to put even the choice of suitable method for calculating vapour–liquid equilibrium under this choice of characterization components control. The necessity of obtaining the EFV distillation curve by some of the given replacing procedures may result in introducing significant, hardly quantifiable errors.

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SYMBOLS

I	number of components
i	component
J	number of measured points
j	measured point
K	liquid–vapour distribution coefficient
N	number of carbon atoms

P	pressure, Pa
T	temperature, K
x	mole fraction in the liquid phase
y	mole fraction in the vapour phase
ϕ	volume portion distilled
φ	molar portion distilled
ω	acentric factor
ρ	liquid molar density, mol m^{-3}

Subscripts

b	normal boiling point
c	critical value
0	original value

Superscripts

m	petroleum complex mixture value

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