

Procedures for the Selection of Real Components to Characterize Petroleum Mixtures*

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Received 10 April 2002

An alternative approach to the characterization of petroleum mixtures is shown. Traditional methods can be abandoned when real components instead of pseudo-components are selected to form the substitute mixture. Algorithms for the selection of real components and for the determination of the mixture composition are presented. Also questions concerning the requirements on a database of real components used for this purpose are discussed. Application of the proposed approach is illustrated on a practical example.

Calculations of thermodynamic and physical properties of pure components and mixtures are crucial for the modelling and simulation of industrial processes. In case of complex petroleum mixtures containing hundreds of partially identifiable components, it is necessary to use some substitute mixture, which possesses similar properties and behaves similarly as the original mixture. Complex mixtures are usually described using pseudo-components. Particularly, this is true in oil refining and petroleum processing, where crude oil, primary oil cuts, or petroleum mixtures are being processed. The use of pseudo-components has been accepted as a convenient approach as the identification of all components actually present in the mixture and the mixture composition is practically impossible to obtain. Even if we have some information about most of the components present in the mixture, their number would be too high for simulation calculations with respect to the dimension of the model, convergence, and availability of interaction coefficients in thermodynamic models, *etc.*

The use of pseudo-components, on the other hand, exhibits a number of drawbacks. Of course, the primary goal is to supply for pseudo-components the same set of parameters for thermodynamic models as for pure well-defined components. Starting from a minimum number of characteristic parameters (some temperature gained from characterization curves and the specific gravity), the remaining parameters needed

for the application of common thermodynamic models, molar masses, critical properties, acentric factors, *etc.* are calculated using traditional approximate procedures [1–3]. It has been shown that the accuracy of resulting estimates is often insufficient or even poor [4].

In order to achieve a more reliable characterization of complex mixtures a new approach has been suggested. The basic assumption is that a system of selected real components can better substitute the real mixture than any system of “mysterious” pseudo-components. Moreover, thermodynamic data of real components are readily available and no erroneous procedures to estimate these data are needed. The substitute mixture also exhibits very similar vapour-liquid equilibrium behaviour to that of the original multi-component mixture, thus simplifying the calculation of, *e.g.* their separation in a rectification column. The proposed procedure of establishing the substitute mixture has two distinct phases. First, we have to select a set of pure components to be included into the mixture. Here, the chosen strategy strongly affects the final result and beside the boiling points of pure components also other information about the original mixture can be utilized. In the second phase, a suitable optimization technique is used to fit the composition of the substitute mixture with respect to the TBP characterization curve, or to the mathematical model of some other characterization procedure.

*Presented at the 29th International Conference of the Slovak Society of Chemical Engineering, Tatranské Matliare, 27–31 May 2002.

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THEORETICAL

Traditional and Nontraditional Methods for the Characterization of Petroleum Mixtures

Crude oil and primary oil cuts are very complex mixtures of many hydrocarbons and other organic and inorganic compounds. The number of the carbon atoms in the compound could be one or as high as fifty or more. Accordingly, the components present in the mixture can exhibit normal boiling points ranging from -162°C up to 540°C [5]. In order to characterize the mixture globally, a number of parameters are measured and referred, *e.g.* mean molar mass, density and viscosity at a defined temperature, ASTM colour, iodine value, *etc.* For the modelling of operations in which these mixtures are processed, *e.g.* rectification, pyrolysis, *etc.*, the knowledge of a limited number of parameters mentioned above is generally insufficient. Therefore, it is desirable to find a substitute mixture and its composition in order to achieve an agreement with the behaviour of the original mixture in the modelled processes as close as possible.

The distillation behaviour of oil fractions is often characterized by laboratory distillation tests: ASTM D86 (the analogy of batch atmospheric distillation in a column with a low number of stages, ASTM is the American Society for Testing and Materials), ASTM D1160 (the analogy of batch vacuum distillation), EFV (Equilibrium Flash Vapour, the single stage flash distillation at various pressures), and TBP (True Boiling Point, vacuum or atmospheric batch distillation under a high value of reflux ratio in a column with many trays). Usually, the result is a curve plotting the dependence of a temperature measured at some place in the experimental equipment on the volume or mass fraction distilled. Using the chromatographic analysis it is also possible to get the so-called simulated TBP curve (by ASTM D3170 or ASTM D2887 method).

Only the ASTM D86 test appears to be standardized and, according to its simplicity and the possibility of the reproduction of its performance, it is often used despite the fact that resulting data have a small theoretical significance. Up to now, no reliable mathematical model of this complex process has been found. The last attempt by *Greenfield et al.* [6] appears not to be quite correct. Their model represented by a system of DAE (Differential-Algebraic Equations) exhibits the index two, so that its use for the theoretical description of the process is doubtful.

One of the most laborious tests is the EFV characterization procedure, which is therefore rarely used. In order to gain the complete EFV curve, it is necessary to perform series of experiments, each resulting in one point on the curve. The theoretical description of this process is possible [7], but the infrequent use of this procedure limits its applicability.

Data resulting from the TBP test give a good theo-

retical basis for characterization of complex mixtures. If the mixture comprises a small number of components with significant differences in boiling points, the TBP curve exhibits a "staircase" shape because the individual components appear overhead one by one according to the high separation ability of the column. On the contrary, when the mixture contains a large number of components with almost continuously increasing boiling points, the "staircase" shape vanishes. This is typical for oil fractions. Beside the pure TBP curve, we can often gain from the experiments also the curves for the molar mass, density or viscosity as functions of volume or mass fraction distilled.

As the characterization tests are mostly time-consuming, it is usual to perform only one of them and to calculate the other curves using empirical regression functions, which can be found in literature. The key type of a curve, to which all others are converted, is the TBP curve. However, we should be very precautionary when using these calculated characterization curves as the empirical conversion functions may generate errors. This is well documented by Fig. 1 where the experimental TBP curve is compared to two TBP curves resulting from the conversion of the D86 curve [8] for the same mixture but using two different commonly accepted methods – according to Riazi and Daubert [9].

For the modelling of processes dealing with petroleum mixtures the substitute mixture is usually build up starting from the light end where actual real components can be included (mostly up to C_5). The chromatographic analysis often gives also the informa-

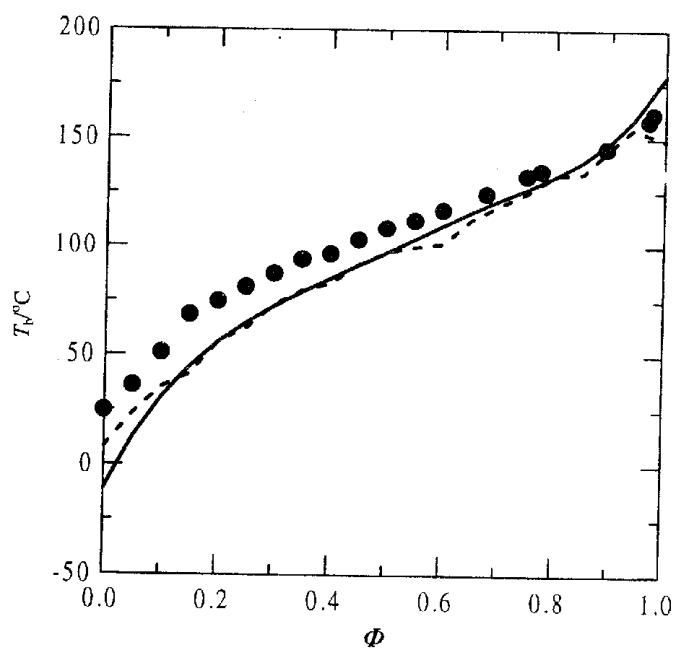


Fig. 1. Comparison of measured (\bullet) and from D86 calculated TBP curves – according to Daubert (—) and Riazi (---).

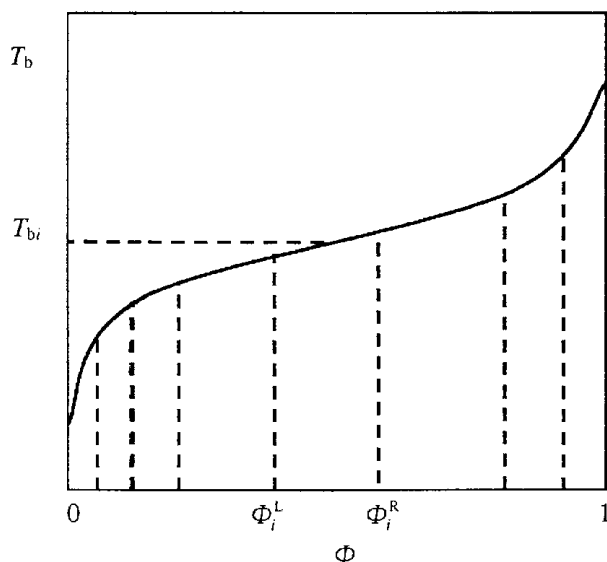


Fig. 2. Traditional definition of pseudo-components from a TBP curve.

tion about the presence of some components in higher boiling fractions but many components could not be identified. Thus, the pseudo-components have been used for characterization of the entire higher boiling fraction. The resulting substitute mixture is therefore composed of a small number of light-end real components and several tenths of pseudo-components. The pseudo-components are obtained from the experimental or calculated TBP curve by cutting the temperature range to equidistant or partially equidistant intervals with the step about 20 to 30 K. The number of pseudo-components should follow the modelling demands. The method how to assign volume or mass fractions to individual pseudo-components is depicted in Fig. 2. Each difference ($\Phi_i^R - \Phi_i^L$) corresponds to the volume or mass fractions of the i -th pseudo-component. The mean normal boiling point is then defined within the interval either as the arithmetical mean value

$$T_{bi} = \frac{T_b(\Phi_i^L) + T_b(\Phi_i^R)}{2} \quad i = LE + 1, \dots, I \quad (1)$$

or, more precisely, as the integral mean value

$$T_{bi} = \frac{1}{\Phi_i^R - \Phi_i^L} \int_{\Phi_i^L}^{\Phi_i^R} T_b(\Phi) d\Phi \quad i = LE + 1, \dots, I \quad (2)$$

Using the mean normal boiling point and the specific gravity of a pseudo-component it is possible to estimate its molar mass and some properties needed for the description of its phase equilibrium behaviour, *i.e.* critical temperature, critical pressure, and acentric factor. The estimation methods are empirical and among them the methods suggested by Kesler and Lee

[1], Riazi and Daubert [2] or Sim and Daubert [3] are mostly used.

The utilization of pseudo-components for the establishment of a substitute mixture has the following disadvantages:

- Empirical relations for the estimation of parameters used for the calculation of physical properties exhibit significant deviations [4].

- It is disabled to incorporate real components that could be important from several points of view (presence in chemical reactions, a strong impact on the behaviour of the mixture, *e.g.* polar components or prevailing paraffins or aromatics).

- It is not possible to combine real component with a pseudo-component when the boiling point of the real component falls into the range of boiling points represented by the pseudo-component, even if the concentration of the real component is known.

Then, why not to use real components instead of pseudo-components when building the substitute mixture? The thermodynamic and transport properties of real components are readily available with high accuracy and, consequently, all disadvantages adhered to the use of pseudo-components are eliminated. The successful application of such approach has been already shown for EFV and TBP characterization tests with intuitive selection of real components [7, 10, 11]. An analogous approach could be used for the ASTM D86 test if a reliable mathematical model were found. The summary of steps involved in the selection of a substitute mixture is presented in Fig. 3. Simultaneously, it is a comparison of the traditional approach using pseudo-components and the nontraditional approach based on real components.

Selection of Real Components for the Substitute Mixture

The chromatographic analysis of the mixture could be a good basis for the formation of a substitute mixture. Instead of incorporating unidentified components alternative real components can be used, *e.g.* according to the measured retention times. This method is sometimes used to represent groups of components with close boiling points by a selected single member component inheriting in the mixture the "weight" of the entire group (lumping).

If no chromatographic analysis is available but the TBP curve is known, the substitute mixture can be selected intuitively. The simplest idea is to choose series of *n*-alkanes as these are almost always prevailing in the mixture. If some other information is available, then we receive an enhanced possibility how to select representative real components. For example, we can exploit measured dependences of molar mass, liquid density or liquid viscosity (the latter two at specified reference temperature(s)) on the volume or mass fraction distilled. Alternatively, the phase portraits can be

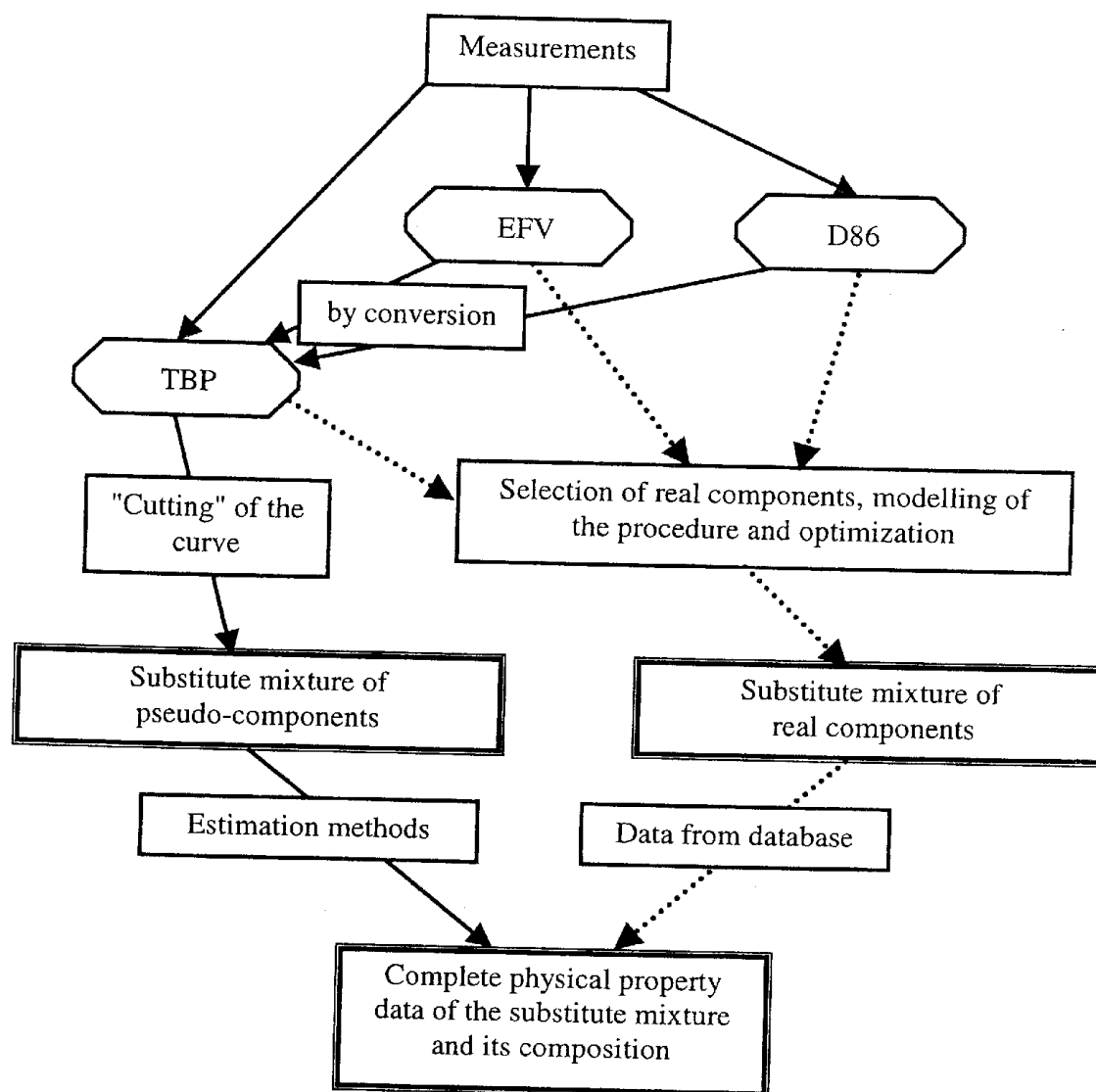


Fig. 3. The traditional (→) and nontraditional (···→) approaches to the derivation of a substitute mixture.

derived, *i.e.* the mappings of the appropriate characteristic temperature to these properties can be used

$$M_m = M_m(T_b) \quad (3)$$

$$\rho_m = \rho_m(T_b) \quad (4)$$

$$\eta_m = \eta_m(T_b) \quad (5)$$

The suggested algorithm for the selection of real components assumes that a database, containing sufficient number of components and their properties, is available. The database should contain the normal boiling points of components, (optionally) their molar masses, M , and densities, ρ , and/or viscosities, η , at the reference temperature(s). Each component in the database should be also provided with an indication of a family of components that expresses its chemical nature or category (*e.g.* general hydrocarbons, ketones, amines, or in more detail paraffins, aromatics, *etc.*). The algorithm comprises the following steps:

1. Specify temperature intervals (one real component will be chosen for each of them). The decision is

mostly based on the shape of the TBP curve. The intervals should not be overlapping but not necessarily interconnected.

2. Specify the desired component family in each interval (usually hydrocarbons only).

3. For each interval collect from the database all components belonging to the specified family and having their normal boiling points within the appropriate range of temperatures.

4. With respect to data available, choose one of the following possibilities:

4.1 Only the TBP curve is available: Select one component matching best some criterion – for instance the component having its normal boiling point as close as possible to the mean temperature of the interval.

4.2 TBP curve and some or all of curves stated as eqns (3–5) are available:

a) For each component, retrieve M_c if the curve (3) is available. When curves (4) or (5) are also available, retrieve or calculate ρ_c and η_c at reference temperature(s), respectively.

b) Compare all or selected properties of the compo-

nent in consideration with values retrieved from curves (3–5) at T_b . Select the component having the best match according to some criterion (see below).

The choice of temperature intervals in Step 1 of the algorithm is mostly a matter of an experience. For relatively smooth TBP curve the usual method is to consider an approximately equidistant grid of temperatures, more or less dense according to the desired number of components in the substitute mixture. In case of a TBP curve with a more “staircase” shape, the mixture probably contains a certain number of dominant components and the choice could take this into account. The algorithm presented here is formulated generally allowing the use of various criteria for the selection of a component from a group of candidate components. For the branch 4.2 in point b) a weighted sum of relative differences for all properties, considered or available, can be used

$$\sum_{k=1}^K w_k |\zeta_{c,k,i} - \zeta_{m,k,i}| / \zeta_{m,k,i} \rightarrow \min_i \quad (6)$$

where i is the index of candidate components. In eqn (6) ζ_m represents the measured value and ζ_c represents the retrieved or calculated value of a certain property of the candidate component and w is the weight assigned to this property, e.g. chosen according to the usual accuracy of measurements.

Composition of the Substitute Mixture

When the selection of the substitute mixture components is completed, the content of individual components in the mixture has also to be specified. We can use an analogy to the establishment of volume or mass fractions of pseudo-components. Then, each selected real component would represent an interval $\Phi_i^R - \Phi_i^L$ of fraction distilled and its boiling point $T_{b,i}$ should be the integral mean value according to eqn (2) for $i = LE + 1, \dots, I$. Alternatively, the arithmetic mean value, eqn (1), is often sufficient. At the same time, the entire range should be covered by these intervals as much as possible but in nonoverlapping mode. Mathematically this criterion can be formulated as follows

$$F(\Phi^L, \Phi^R) = \sum_{i=LE+1}^{I+1} (\Phi_{i-1}^R - \Phi_i^L)^2 \rightarrow \min \quad (7)$$

with respect to eqns (1) or (2), and assuming $\Phi_{LE}^R = \Phi_{LE+1}^L$, $\Phi_{I+1}^L = 1$ (see Fig. 4). Conversion of the resulting intervals into volume or mass fractions requires certain “normalization”, as the minimization algorithm not always generates a system of intervals, which fulfils the necessary condition

$$\sum_{i=LE+1}^I (\Phi_i^R - \Phi_i^L) = 1 - \Phi_{LE}^R \quad (8)$$

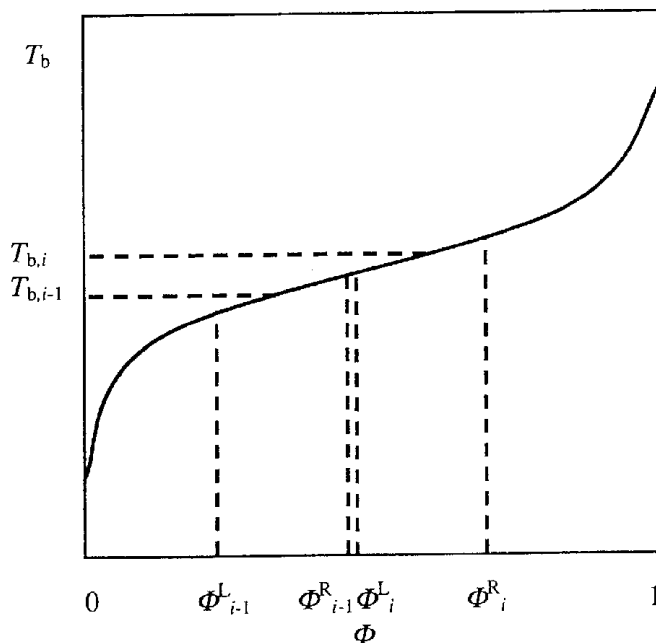


Fig. 4. Characterization of a mixture by real components using a TBP curve.

Nevertheless, defining the volume or mass fractions for selected real components by the equation

$$x_j = (\Phi_j^R - \Phi_j^L) (1 - \Phi_{LE}^R) / \sum_{i=LE+1}^I (\Phi_i^R - \Phi_i^L) \quad (9)$$

$j = LE + 1, \dots, I$

and preserving the fractions of light-end components leads to complete and consistent composition of the substitute mixture.

Database of Real Components

The quality of the substitute mixture is affected not only by the algorithm chosen and by the extent of available data, but also by the quality of the database of real components used for this purpose. The higher the number of components in the database, the higher the probability to find components matching closely the characterization data. Moreover, it is important to have in the database components covering a range of normal boiling temperatures, as wide as possible. Another point of view is the reliability of data contained in the database.

With respect to these recommendations, two databases were developed for this work and attached to the program providing the selection. First database is taken from the universal simulation program ChemCAD and contains about 950 components but only about 270 hydrocarbons. Second database taken from American Petroleum Institute (API) Data Book [12] was originally developed for employment in petroleum processing industry and incorporates about 480 components, exclusively hydrocarbons.

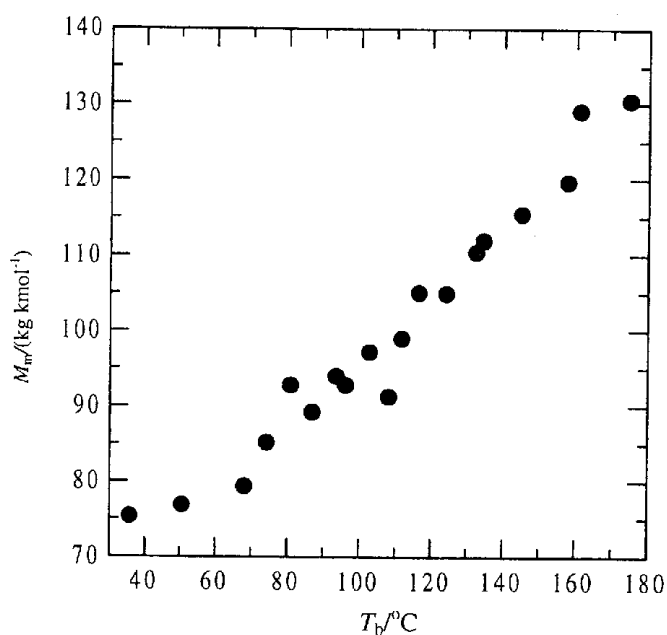


Fig. 5. Phase portrait $M_m = M_m(T_b)$ from the example.

RESULTS AND DISCUSSION

The suggested approach to the selection of real components was applied to data from literature [8]. The authors presented experimentally obtained ASTM D86 and ASTM D2892-73 (TBP) data for a gasoline blend. For 19 fractions consecutively collected by distillation the TBP, density, viscosity, both at 25°C, and molar mass had been measured. The TBP curve is depicted in Fig. 1 and the phase portrait, *i.e.* the dependence of molar mass of fractions on its TBP, is shown in Fig. 5. The temperature intervals for Step 1 of the algorithm were simply chosen to match

the temperature intervals used in the experiment.

The selection of real components has been performed using three types of assumptions. In the discussion of results we will refer to variants A, B, and C. First, we utilized only the experimental TBP curve, according to branch 4.1 of the selection algorithm as if no other additional curves were available. Consequently, the selection of components was based only on the comparison of component normal boiling points with the mean temperatures of the intervals. Second, we used the measured molar masses of fractions "as is" including possible deviations due to the measurement errors. In intermediate points of this phase portrait $M_m = M_m(T_b)$ an interpolation from 4 neighbour points was used to calculate the desired value of molar mass for a given boiling point temperature. Third, the phase portrait was smoothened by regression resulting in a polynomial of the degree 2 in T_b . This variant seems to be reasonable, but we will discuss further its partial unfeasibility. Other phase portraits, *i.e.* $\rho_m = \rho_m(T_b)$ and $\eta_m = \eta_m(T_b)$, were not utilized here because their implementation into the program providing the selection of components was not finished yet.

The results of the selection of components are summarized in Tables 1–3. In order to illustrate the principles of the algorithm presented above, the intermediate results for one of the temperature intervals are shown in Table 4. The subset of candidate components was determined in Step 3 of the algorithm with respect to their normal boiling points and, in addition to these data, also their molar masses were retrieved from the database. For variants B and C the expected values of molar masses were calculated using the phase portrait $M_m = M_m(T_b)$ for $T_b = T_{bi}$, *i.e.* for the nor-

Table 1. Components Selected into the Substitute Mixture for Variant A

No.	T_b range/ $^\circ\text{C}$	$T_b / ^\circ\text{C}$	Selected components	x_i
1	24.6–35.8	29.96	Pent-1-ene	0.09718
2	35.8–50.8	44.06	<i>cis</i> -Penta-1,3-diene	0.00912
3	50.8–68.2	59.46	Hexa-1,5-diene	0.08552
4	68.2–74.4	71.33	Hex-1-yne	0.01447
5	74.4–81.0	77.89	2,3,3-Trimethylbut-1-ene	0.08773
6	81.0–87.0	83.90	3-Methylhex-1-ene	0.00699
7	87.0–93.6	90.05	2-Methylhexane	0.08970
8	93.6–96.2	95.18	<i>trans</i> -3-Methylhex-2-ene	0.02036
9	96.2–102.8	99.53	<i>cis</i> -1,2-Dimethylcyclopentane	0.07358
10	102.8–108.2	105.43	<i>cis</i> -2,2-Dimethylhex-3-ene	0.02394
11	108.2–111.8	109.84	2,2,3-Trimethylpentane	0.07323
12	111.8–116.6	113.73	1,1,2-Trimethylcyclopentane	0.01840
13	116.6–124.2	120.09	<i>cis</i> -1,3-Dimethylcyclohexane	0.14097
14	124.2–132.5	128.05	<i>cis</i> -1-Methyl-2-ethylcyclopentane	0.00542
15	132.5–134.6	133.60	2,2,3-Trimethylhexane	0.06056
16	134.6–145.1	140.27	2,2,3,3-Tetramethylpentane	0.16220
17	145.1–158.0	151.14	Cyclooctane	1×10^{-6}
18	158.0–161.2	159.87	2,7-Dimethyloctane	0.01855
19	161.2–174.8	167.80	3-Methylnonane	0.01209

Table 2. Components Selected into the Substitute Mixture for Variant B

No.	T_b range/°C	T_b /°C	Selected components	x_i
1	24.6—35.8	31.16	2-Methylbut-1-ene	0.04495
2	35.8—50.8	36.06	Pentane	0.05784
3	50.8—68.2	68.00	Hexa-2,3-diene	0.08996
4	68.2—74.4	70.60	Ethylcyclobutane	0
5	74.4—81.0	76.74	<i>trans</i> -4,4-Dimethylpent-2-ene	0.09137
6	81.0—87.0	86.73	4-Methylhex-1-ene	0.03175
7	87.0—93.6	88.11	2-Methylhexa-1,5-diene	0.02038
8	93.6—96.2	96.01	3-Ethylpent-2-ene	0.10891
9	96.2—102.8	99.74	Hept-1-yne	0
10	102.8—108.2	106.33	1-Ethylcyclopentene	0.09875
11	108.2—111.8	110.29	1-Methylcyclohexene	0.00190
12	111.8—116.6	113.73	1,1,2-Trimethylcyclopentane	0.08247
13	116.6—124.2	123.30	<i>trans</i> -Oct-3-ene	0.12211
14	124.2—132.5	131.20	1-Propylcyclopentene	4×10^{-6}
15	132.5—134.6	133.83	2,2-Dimethyl-3-ethylpentane	0.02131
16	134.6—145.1	136.99	1-Ethylcyclohexene	0.13055
17	145.1—158.0	156.60	Butylcyclopentane	0.07907
18	158.0—161.2	161.11	3,7-Dimethylocta-1,6-diene	6×10^{-6}
19	161.2—174.8	169.85	Dicyclopentadiene	0.01867

Table 3. Components Selected into the Substitute Mixture for Variant C

No.	T_b range/°C	T_b /°C	Selected components	x_i
1	24.6—35.8	27.84	Isopentane	0.02529
2	35.8—50.8	36.06	Pentane	0.09771
3	50.8—68.2	67.87	<i>trans</i> -Hex-2-ene	0.06075
4	68.2—74.4	68.89	<i>cis</i> -Hex-2-ene	6×10^{-6}
5	74.4—81.0	80.74	Cyclohexane	0.13210
6	81.0—87.0	86.73	4-Methylhex-1-ene	0
7	87.0—93.6	93.54	<i>trans</i> -3-Methylhex-3-ene	0.09078
8	93.6—96.2	96.01	3-Ethylpent-2-ene	7×10^{-6}
9	96.2—102.8	99.74	Hept-1-yne	0.04492
10	102.8—108.2	103.46	Ethylcyclopentane	0.04854
11	108.2—111.8	110.29	1-Methylcyclohexene	0.05756
12	111.8—116.6	113.73	1,1,2-Trimethylcyclopentane	0.05639
13	116.6—124.2	123.30	<i>trans</i> -Oct-3-ene	0.13529
14	124.2—132.5	131.20	1-Propylcyclopentene	4×10^{-6}
15	132.5—134.6	133.83	2,2-Dimethyl-3-ethylpentane	0.02194
16	134.6—145.1	136.99	1-Ethylcyclohexene	0.13128
17	145.1—158.0	156.72	Propylcyclohexane	0.07502
18	158.0—161.2	159.24	Propylbenzene	0
19	161.2—174.8	172.79	Isobutylbenzene	0.02191

mal boiling point of the i -th candidate component. Of course, for variants B and C different approaches to the phase portrait were used. The resulting optimum selection for this interval is indicated in the last three columns.

For each of the three variants the composition of the substitute mixture was also calculated. The method used in this example took into account eqn (7) as an optimization problem with equality constraints represented by eqns (1) or (2) for each $i = LE + 1, \dots, I$, where the boiling points are for real components *a priori* given. In order to eliminate these constraints from the formulation of the optimization problem we treated each of eqns (1) or (2) as an implicit relation between Φ_i^L and the

corresponding Φ_i^R , $i = LE + 1, \dots, I$. Therefore, only Φ_i^L , $i = LE + 1, \dots, I$ or, alternatively, Φ_i^R , $i = LE + 1, \dots, I$ can be considered as independent optimization variables and the remaining subset of variables can be calculated from eqns (1) or (2). Actually, eqn (2) was not used in this example. The reason was that the integral in eqn (2) had to be evaluated using a numerical method and the grid of experimental points showed to be too sparse for maintaining numerical stability. Moreover, we have further simplified the calculation of Φ_i^R , $i = LE + 1, \dots, I$ by assuming that Φ_i (corresponding to the normal boiling point T_{bi} of i -th component) is always the mean value between Φ_i^L and Φ_i^R , $i = LE + 1, \dots, I$.

Table 4. Details about the Selection of Components in the Temperature Interval 68.2–74.4 °C for Variants A, B, and C; the Mean Temperature of the Interval Used in Variant A is 71.3 °C

Components retrieved from database	Normal boiling point °C	Molar mass			Selection for variants		
		Database	kg kmol ⁻¹		A	B	C
			Orig. curve	Smooth. curve			
Hexane	68.73	86.18	81.537	84.067			
2,3-Dimethylbuta-1,3-diene	68.78	82.15	81.604	84.082			
cis-Hex-2-ene	68.89	84.16	81.752	84.117			
3-Methylpenta-1,2-diene	70.00	82.15	83.304	84.465			X
trans-3-Methylpent-2-ene	70.44	84.16	83.941	84.605			
Ethylcyclobutane	70.60	84.16	84.174	84.656			
Hex-1-yne	71.33	82.15	85.292	84.889	X	X	
Methylcyclopentane	71.81	84.16	86.668	85.043			
4,4-Dimethylpent-1-ene	72.51	98.19	88.381	85.270			
2,3-Dimethylbut-2-ene	73.20	84.16	89.753	85.494			

For the solution of the optimization problem the optimization package MINOS [13] has been utilized. Certain additional constraints were introduced in order to preserve some obvious conditions, e.g. $0 \leq \Phi_i^L \leq \Phi_i$, $i = LE, \dots, I$ and $\Phi_{i+1}^L \geq \Phi_i^L$, $i = LE+1, \dots, I-1$. The resulting volume fractions were obtained from eqn (9) and they are presented in Tables 1 to 3 for variants A, B, and C, respectively.

The results of the example proved the ability of the suggested approach to find a substitute mixture. Obviously, the solution is not unique but depends on various selection criteria used and on the experimental data supplied. The problem is that it is not easy to compare the individual solutions unless an extensive testing within simulation calculations of a chemical engineering process would have been provided. A comparison with the traditionally built substitute mixture using pseudo-components would be also interesting. While this is the content of a future work, in the current paper we shall comment only some conclusions from results obtained for the example in consideration.

From Figs. 6 to 8 it is apparent that the inclusion of the phase portrait into the selection algorithm improves the overall match between the molar masses of selected real components and molar masses measured for appropriate fractions. For the variant A the summation of squares of differences between the molar masses of selected real components and measured molar masses of corresponding fractions is 1892 kg² kmol⁻² (see Fig. 6) but for variant B the same quantity is 770 kg² kmol⁻² and for C only 744 kg² kmol⁻². On the other hand, the utilization of a smoothed phase portrait in variant C can be inadequate for the description of the original complex mixture as the dependence of the molar mass on the mean boiling point of the fraction is not necessarily monotonous. Consequently, a fraction with a lower boiling point can exhibit higher molar mass than some other fraction with a higher boiling point.

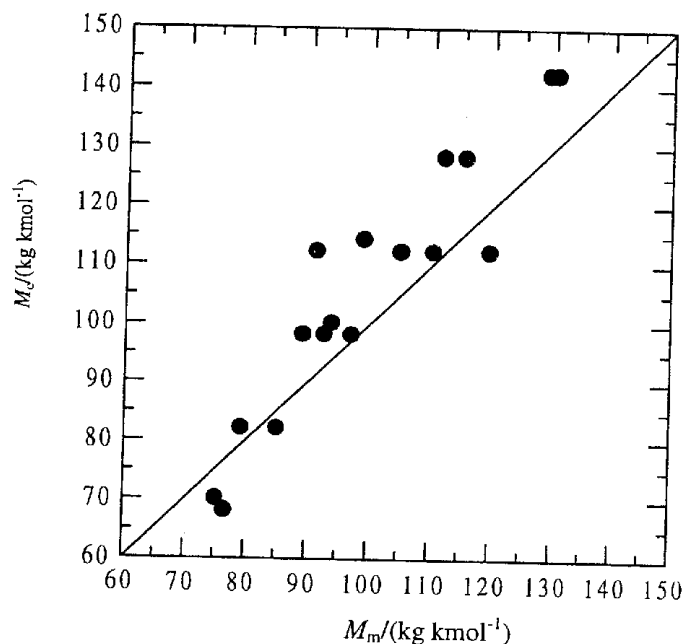


Fig. 6. Comparison of retrieved values of molar masses (M_c) and values obtained by interpolation from the original measured curve (M_m) for variant A.

The composition of the substitute mixture resulting from the optimization algorithm in the second part of the procedure also needs some comment. In Tables 2 and 3 it can be observed that for certain components the appropriate calculated volume fractions are zero. This seems to be a common feature implied by the algebraic properties of the objective function defined by eqn (7) where in the optimum some intervals can regularly degenerate to points, i.e. $\Phi_i^L = \Phi_i^R = \Phi_i$, or even it could be $\Phi_i^L \geq \Phi_i^R$. Such components are in fact excluded from the mixture and the question is if we can accept such types of a solution. One potential direction is to formulate some other objective function or to adjust the composition of the mixture later when the substitute mixture is used for simulation cal-

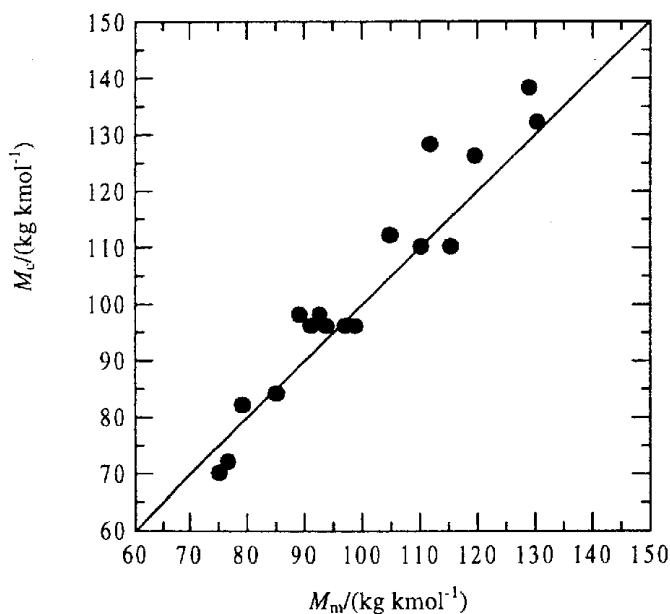


Fig. 7. Comparison of retrieved values of molar masses (M_c) and values obtained by interpolation from the original measured curve (M_m) for variant B.

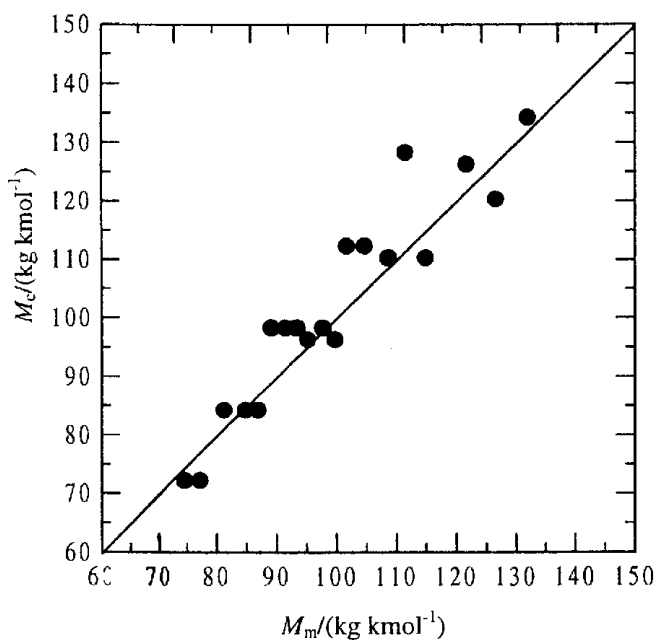


Fig. 8. Comparison of retrieved values of molar masses (M_c) and values obtained from the smoothed measured curve (M_m) for variant C.

culations and the simulation results could have been compared to measured process data. The reason why for variant A all components received nonzero volume fractions is probably very simple. The selection criterion used in variant A prefers components with normal boiling points, which are close to the middle of the temperature interval, and the corresponding grid of Φ_i is therefore more regular. For variants B and C certain pairs of neighbour components can have very

close boiling points and the optimization algorithm is not able to expand some of the intervals $\langle \Phi_i^L, \Phi_i^R \rangle$ without getting worse values of the objective function.

Acknowledgements. The authors appreciate the support of the fund MSM 223400007.

SYMBOLS

F	function	
I	total number of components	
K	number of measured properties	
LE	index of the last component of the "light end"	
M	molar mass	kg kmol ⁻¹
T	temperature	K
x	volume or mass fraction	
w	weight of measurement	
η	viscosity	Pa s
Φ	volume (mass) fraction distilled	
ρ	density	kg m ⁻³
ζ	general symbol for a physical property	

Subscripts

b	at boiling point
c	calculated or retrieved value
i, j	component i, j
k	k -th measured property
m	measured value or value obtained from a smoothed curve

Superscripts

L	left edge of an interval
R	right edge of an interval

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