Extended Utilization of the Characterization of Petroleum Mixtures Based on Real Components*

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Received 1 April 2005

Recently, a novel approach to the characterization of petroleum mixtures based on substitute mixtures of real components has been described. This approach can replace the traditional approach based on pseudo-components. It can be shown that the approach based on real components is also well-suited for certain special tasks in the modelling of oil processing. Very often it is needed to blend petroleum fractions. It is shown how to modify the basic algorithm for assembling the substitute mixture of real components in order to cover also this problem. Second interesting area is incorporation of compounds containing sulphur, which is currently in the focus of refiners according to increasing environmental demands. The content of thiols and other compounds having impact on the environment is rather low but cannot be neglected for the simulation of separation processes if the results should be realistic and showing the way how to decrease the content of sulphur in gasoline mixtures. The adoption of the algorithm for the selection of real components into the substitute mixture for both cases is described and documented by examples.

The new approach of a complex mixture characterization can be used in many directions. It is not only substituting the traditional approach based on pseudo-components but also enables to solve special tasks as the problems of oil blending and characterization of mixtures containing sulphur. The superiority of the approach using real components becomes apparent when the information about well-defined components is needed for modelling, *i.e.* when reliable physical property data and/or chemical character of components should be known.

Characterization of complex mixtures is an important task, especially in oil processing industry. For the modelling, simulation, and other chemical engineering calculations, it is impossible to deal with thousands or even millions of components, which, moreover, cannot be properly identified. A common method is to find a substitute mixture comprising a relatively low number of components (usually 10—40) and having its behaviour close to the original mixture. For this purpose a novel approach to the characterization of petroleum mixtures based on substitute mixtures of real components has been described in several previous contributions [1—3]. Therefore, the traditional approach based on pseudo-components can be replaced by this new one exhibiting a number of advantageous features, *e.g.* direct availability of physical and chemical properties from the database or definition of the "chemical character" of the substitute mixture, which might be useful in certain situations.

Generally, properties of pseudo-components have to be estimated using various more or less unreliable empirical relations and no chemical character is defined for the substitute mixture of pseudo-components. Other possibilities for the characterization of complex mixtures, *i.e.* continuous thermodynamics [4] or wavelet models [5] are employing different mathematical background and will not be discussed here. Moreover, their practical applicability within simulation calculations is not easy since the models of unit operations must be formulated on a completely different basis. Therefore, in standard commercial simulation programs the principles of continuous thermodynamics mostly have not been implemented so far.

Up to now, the use of substitute mixtures of real components has been shown for modelling and simulation of common separation processes [2] as well as for complex columns in crude oil processing [6]. Generally, substitute mixtures of real components proved to behave at least as the alternative mixtures of pseudo-components. Another direction, which proved to be very promising, is the modelling of pyrolysis reactors by empirical artificial neural network models in com-

*Presented at the 32nd International Conference of the Slovak Society of Chemical Engineering, Tatranské Matliare, 23—27 May 2005.

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bination with substitute mixtures of real components [7]. Here, the advantage of defined chemical character of the substitute mixture can be fully exploited. However, the substitute mixture of real components was treated as the basis for the decomposition to molecular functional groups (increments), the amounts of which are part of the input to the artificial neural network. The output from the network represents predicted yields of pyrolysis products.

There are at least two other special tasks in oil processing where the approach can be found useful. Very often it is needed to blend petroleum fractions. It is shown how to modify the basic algorithm for assembling the substitute mixture of real components in order to cover also this problem. Second interesting area is incorporation of compounds containing nitrogen and/or sulphur, which is currently in the focus of refiners according to increasing environmental demands. The content of thiols and other compounds having impact on the environment is rather low but cannot be neglected in the simulation of separation processes. The goal is, of course, to decrease the content of sulphur in gasoline mixtures. Both problems will be discussed in this contribution and illustrated by examples.

THEORETICAL

Only a rough description of the procedure for establishing the substitute mixture is given here. There are several prerequisites needed, first of all some measured characterization curves. The TBP ("True Boiling Point") curve is mandatory

$$T_\mathrm{b} = T_\mathrm{b}(\Phi) \tag{1}$$

but at least some additional curves are desired

$$M = M(\Phi) \tag{2}$$
$$\rho = \rho(\Phi) \tag{3}$$
$$\eta = \eta(\Phi) \tag{4}$$

T_b being boiling temperature, Φ volume fraction, M molar mass, ρ density, and η viscosity.

Instead of using eqns (*2*—*4*) directly, it is better to convert them into "phase portraits" by eliminating the distilled-off mass or volume fraction and establishing direct relation between these properties and the boiling point temperature

$$M = M(T_\mathrm{b}) \tag{5}$$
$$\rho = \rho(T_\mathrm{b}) \tag{6}$$
$$\eta = \eta(T_\mathrm{b}) \tag{7}$$

Second assumption concerns the definition of a certain cutting of the overall temperature range into a system of nonoverlapping temperature intervals continuously covering the range. The number of intervals corresponds to the number of chosen real components. For this purpose, one needs a suitable database of physical properties with sufficiently large number of chemical compounds to choose from.

In the first phase of the algorithm one gets a list of real components forming the substitute mixture. For each temperature interval defined above, a subset of candidate components having their boiling points in this interval is chosen. Then, after comparing the candidate components properties taken from the database with "desired" values obtained from eqns (*5*—*7*), one can select the component with the best property match

$$\sum_{k=1}^{K} w_k \frac{|\zeta_{\mathrm{r},k,\mathrm{c}} - \zeta_{\mathrm{m},k,\mathrm{c}}|}{\zeta_{\mathrm{m},k,\mathrm{c}}} \rightarrow \min_\mathrm{c} \tag{8}$$

where w represents weight, ζ mixture property, k property index, K number of properties available, and c denotes candidate component.

The second phase of the algorithm is used for determination of the substitute mixture composition, assuming that mass or volume fractions are related to the mass or volume fraction distilled similarly as for pseudo-components. Details of this phase were described elsewhere [8].

EXPERIMENTAL

When using pseudo-components, description of complex mixtures obtained by blending of oil fractions is a serious problem. However, blending of crude oils from different resources is generally done before entering fractionation processes. In simulation programs it is possible to define pseudo-components only for the blend itself avoiding the definition of a system of pseudo-components separately for each crude oil involved. Usually, a weighted average is constructed from all TBP characterization curves and the same is done for other types of curves, which enables to build a unique substitute mixture of pseudo-components, *i.e.* the blend. This technique is implemented, for example, in HYSYS simulation program version 3.2. Apparently, it brings certain limitations in the modelling of petroleum refining processes.

Advantages of the characterization of complex mixtures using real components are apparent also for blending. There are three main possibilities how to provide the substitute mixture. First of all, the weighted average can also be used, but this brings nothing new. Second, the algorithm described in the previous paragraph could be applied to each mixture separately. This would probably lead to a relatively high total number of components in the system if different substitute mixtures would share none or only few components. The third possibility is applicable to mixtures having their phase portraits not too far from

each other. Then the system of real components forming the substitute mixture can be derived simultaneously, *e.g.* by modifying criterion (*8*) in order to take into account all mixtures and their relative contributions

$$\sum_{\mathrm{l}=1}^{L} u_{\mathrm{l}} \sum_{k=1}^{K} w_{k,\mathrm{l}} \frac{|\zeta_{\mathrm{r},k,\mathrm{l},\mathrm{c}} - \zeta_{\mathrm{m},k,\mathrm{l},\mathrm{c}}|}{\zeta_{\mathrm{m},k,\mathrm{l},\mathrm{c}}} \rightarrow \min_{\mathrm{c}} \qquad (9)$$

u being weights attached to individual mixtures, l index denoting individual blended mixture, and L is the number of blended mixtures.

It is reasonable to set relative weights to relative amounts or flow rates of each mixture. It should be noted that the relative differences between expected (measured) value of a physical property and the value retrieved from the database in (*9*) are for each complex mixture related to its particular TBP curve and phase portraits.

Sulphur contained in petroleum products represents a potential danger for the environment. In simulation calculations, hydrocarbon mixtures with certain compounds containing sulphur, especially thiols, must be handled very carefully according to very low content of sulphur (ppm). There are two possibilities used in simulation programs. In the example below a distinct stream is defined for addition of compounds containing sulphur. Another possibility has been implemented into the Aspen Plus petroleum processing subsystem, namely definition of the sulphur content (mass percent) in each pseudo-component. Nevertheless, the approach to the characterization of complex mixtures using real components provides a uniform treatment of mixtures of all kinds and it is easy to incorporate sulphur-containing compounds. Such compounds can be taken into account when choosing candidate components or simply can be added to the list of components representing the mixture. The difference is that for the second alternative the content of each sulphur-containing component could be known and the algorithm used for the determination of the composition of the substitute mixture should be slightly modified.

RESULTS AND DISCUSSION

Example 1. Blending of Oil Fractions

In order to illustrate the problem, a simulation case described in [9] has been used, but HYSYS 3.2 has been further employed for calculations. Fig. 1 shows the original flowsheet for the first part of the petroleum processing, *i.e.* the pre-flash tower.

The process feed (MIXCRUDE) is a blend of two crude oils: OIL-1 (20 %) and OIL-2 (80 %). A furnace is used to vaporize partially the feed and the pre-flash tower (PREFLASH) removes light gases and some naphtha from the feed while bottoms are used as a feed to crude distillation unit (CDU), which is

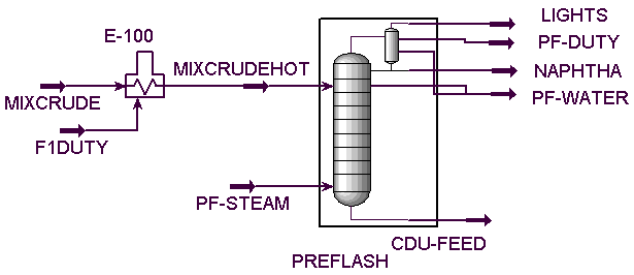

Fig. 1. Flowsheet for Example 1 ("Preflash tower").

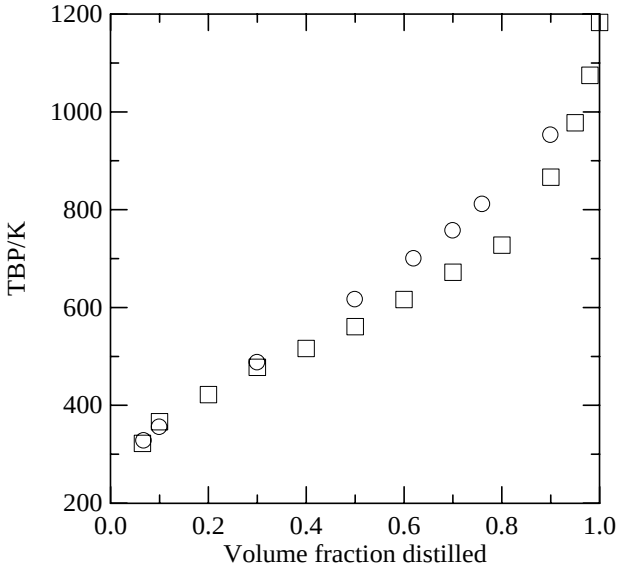

Fig. 2. TBP curves for OIL-1 (○) and OIL-2 (□).

not part of this example. Detailed simulation input data can be found in the original source [9] including the measured characterization data and specification of light end components for both mixtures. Figs. 2 and 3 depict the appropriate characterization curves, from which it can be seen that the approach based on the use of criterion (*9*) can be used. One shall respect the original cutting of the overall temperature range into primary temperature intervals given in Table 1.

Unfortunately, the database of real components used here (taken from HYSYS 2.1) does not cover the entire range. Therefore, a combined approach as in [6] was used, *i.e.* only the first 25 intervals were represented by real components, the rest by pseudo-components. For both crude oils there also predefined light ends are different. The overview of the number of components in substitute mixtures originating from various sources is summarized in Table 2. It should be emphasized that when using the proposed approach to blending, two distinct substitute mixtures (OIL-1 and OIL-2) are considered for partial characterization by real components, but later it is necessary to define only one feed stream in HYSYS.

Therefore, the selected components can be treated

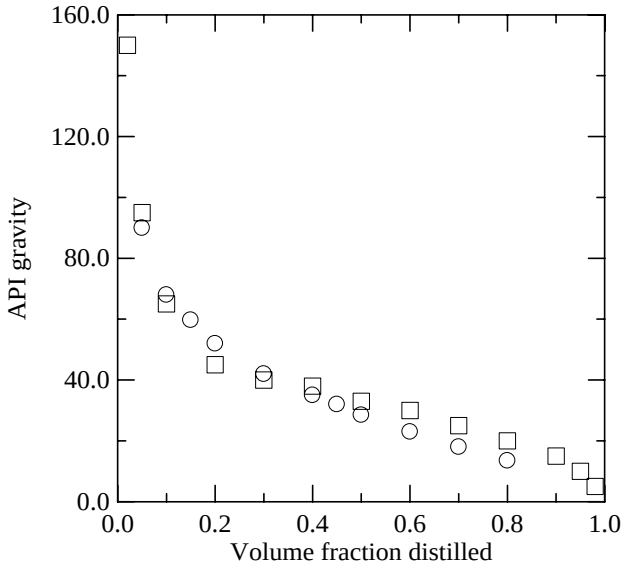

Fig. 3. API gravity curves for OIL-1 (○) and OIL-2 (□).

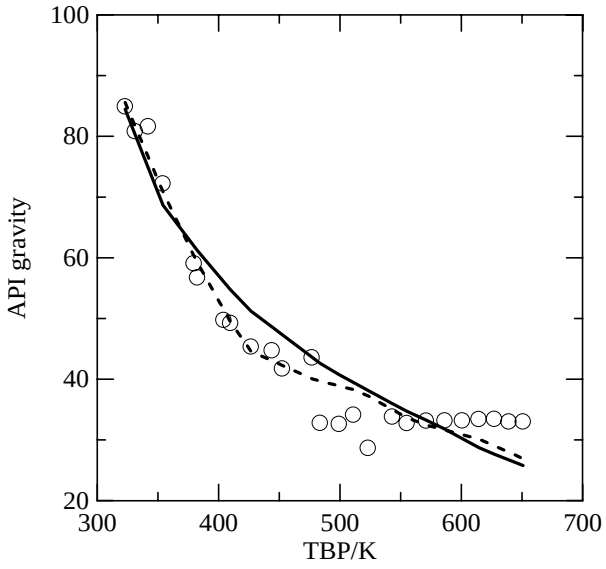

Fig. 4. API gravity phase portraits – database values (○) for selected components and curves for OIL-1 (——) and OIL-2 (– – –) derived from measurements.

Table 1. Primary Temperature Intervals for the Preflash Tower Example

Lower temperature/K	Upper temperature/K	Number of cuts
310.93	699.81	28
699.81	922.04	8
922.04	1033.15	2
1033.15	1166.48	2

as an extension of the original light end. Comparison of the API gravity retrieved from the database for real components selected into the substitute mixture with values expected from the measured API gravity curves is provided in Fig. 4.

The match is better for lower-boiling components but also in the higher boiling region the deviations are acceptable.

The simulation calculations were performed by the HYSYS 3.2 simulation program using HYSYS database to get substitute mixtures of real components. In Fig. 5 the TBP curves of products resulting from the simulation are compared for both approaches.

The match is satisfactory but it could be expected that direct definition of substitute mixture of real components for the characterization curves is obtained, as weighted average would probably give closer match

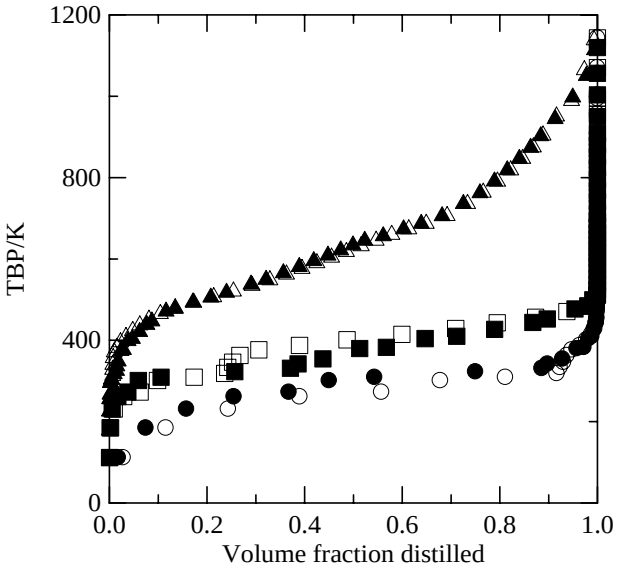

Fig. 5. TBP curves of main products (top to bottom: LIGHTS, NAPHTHA, CDU-FEED) resulting from simulation. Substitute mixture of pseudo-components (△□○), substitute mixture partially defined using real components (▲■●).

Table 2. Number of Components in Substitute Mixtures

Components in streams	OIL-1	OIL-2	MIXCRUDE	MIXCRUDE (original)
Light end	7	8	8	8
Selected real components	25	25	25	–
Pseudo-components	15	15	15	40

Table 3. Mole Fractions of Sulphur-Containing Components in Both Products; PC = Substitute Mixture of Pseudo-Components, RC = Substitute Mixture of Real Components

Component	Light gasoline		Medium gasoline	
	PC	RC	PC	RC
Isopropylsulphane	2.18×10^{-4}	1.78×10^{-4}	1.20×10^{-4}	1.40×10^{-4}
Prop-1-ylsulphane	1.09×10^{-4}	7.44×10^{-5}	1.44×10^{-4}	1.62×10^{-4}
Thiophene	2.33×10^{-5}	8.25×10^{-6}	3.33×10^{-4}	3.45×10^{-4}

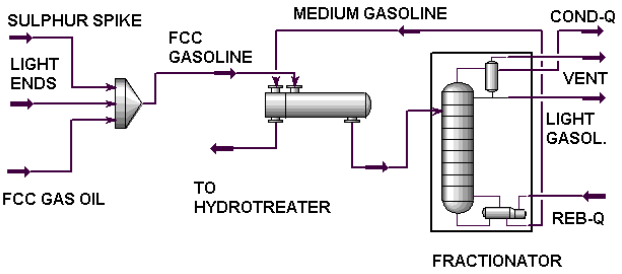

Fig. 6. Flowsheet for Example 2 ("Clean Fuels").

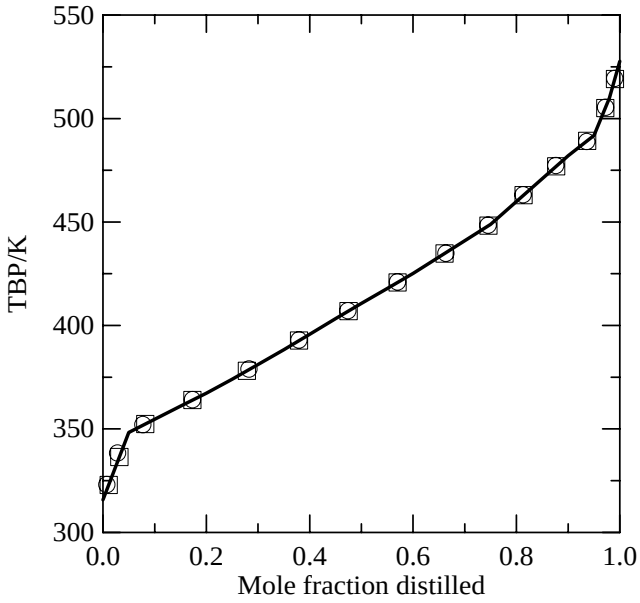

Fig. 7. TBP curves for FCC gas oil stream – experimental (——), substitute mixture of pseudo-components (□), substitute mixture of real components (○).

as implies from our experience. Nevertheless, it is not easy to judge, which curves are closer to reality. This would be possible if measured TBP curves for all products were available.

Example 2. Complex Hydrocarbon Mixtures Containing Sulphur

Again, an example delivered with a simulation program can be used (see HYSYS 3.2 documentation [10], "Clean Fuels" example). In this example,

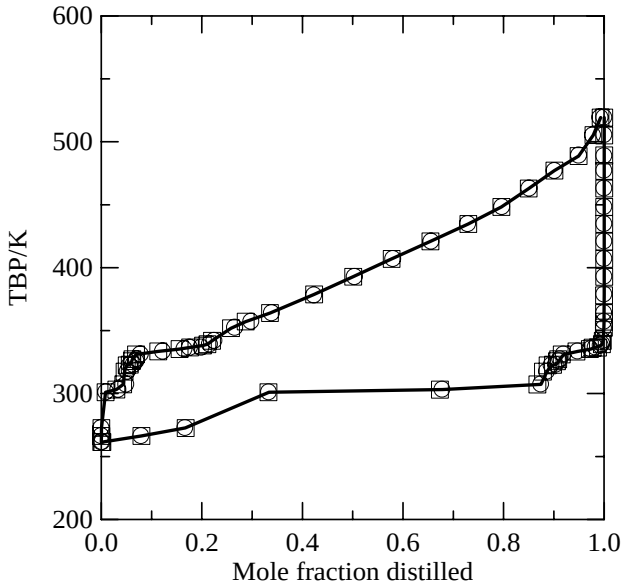

Fig. 8. TBP curves for both products (top to bottom: MEDIUM GASOLINE, LIGHT GASOLINE) – substitute mixture of pseudo-components (□), substitute mixture of real components (○).

a light/medium gasoline is fractionated in a gas plant column. The complete scheme is depicted in Fig. 6.

The amount of sulphur is calculated in the light gasoline and the gasoline endpoint is set to 338.7 K for this design. The case will consist of an FCC gasoline feed stream to the tower and two outlet streams, a light gasoline product stream and an intermediate naphtha which is sent to an upstream hydrotreater for further treating. The design objective is to maximize the yield of light gasoline since hydrotreatment of gasoline results in severe octane loss. For detailed specifications see the original source [10].

Addition of sulphur-containing components is in this example provided by a separate stream as well as the addition of the light end. This illustrates the problem with incorporating real components into an assay, which is usually impossible within simulation programs. With the approach to characterization using real components this is very simple as mentioned above. Nevertheless, in order to compare both approaches all three input streams were preserved. The number of components for both substitute mixtures was set to 15.

The results are summarized in Figs. 7 and 8 using comparison of TBP curves to show the excellent match between both approaches. For the FCC gas oil stream TBP curves of both substitute mixtures are compared also with the measured curve. Another comparison concerns the content of sulphur-containing components in both products (see Table 3). Here the match is not as good according to the absolute value of mole fractions but the trend is preserved.

Acknowledgements. The authors appreciate the support of the fund MSM 6046137306.

SYMBOLS

K	number of measured properties	
L	total number of blended mixtures	
M	molar mass	kg kmol^{-1}
T	temperature	K
TBP	True Boiling Point	K
u	weight of a mixture in criterion (*9*)	
w	weight in criterion (*8*)	
ζ	symbol for property	
η	viscosity	Pa s
ρ	density	kg m^{-3}
Φ	volume or mass fraction distilled	

Subscripts

b	at boiling point
c	index of a candidate component
i, j	index of a component
l	index of a mixture in criterion (*9*)
k	index of a property in criterion (*8*)
m	measured value
r	value calculated or retrieved from the database

REFERENCES

1. Ba, A., Eckert E., and Vaněk, T., *Chem. Pap. 57*, 53 (2003).
2. Eckert, E. and Vaněk, T., in *Proceedings of the 30th International Conference of SSCHE,* Tatranské Matliare (Slovakia), 2003.
3. Eckert, E., *Collect. Czech. Chem. Commun. 64*, 571 (1999).
4. Rätzsch, M. and Kehlen, H., *Fluid Phase Equilib. 14*, 225 (1983).
5. Briesen, H. and Marquardt, W., *Comput. Chem. Eng. 50*, 633 (2004).
6. Eckert, E. and Vaněk, T., in *Proceedings of the 16th International Congress of Chemical and Process Engineering CHISA*, Prague, Czech Republic, 2004.
7. Bělohlav, Z., Zámostný, P., Herink, T., Eckert, E., and Vaněk, T., *Chem. Eng. Technol. 28*, 1166 (2005).
8. Eckert, E. and Vaněk, T., *Comput. Chem. Eng. 30*, 343 (2005).
9. Aspen Technology, Inc., *Aspen Plus 11.1 Documentation*, Cambridge, MA, 2001.
10. Aspen Technology, Inc., *HYSYS Plant 3.2 Documentation*, Cambridge, MA, 2001.