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New approach to the characterisation of petroleum mixtures used in the modelling of separation processes

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Abstract

Characterisation of complex mixtures is a common tool especially in oil processing industry. Characterisation procedures result in experimentally gained characterisation curves, but for the simulation of industrial processes the definition of a substitute mixture is required. Traditionally, a system of pseudocomponents is derived from the True Boiling Point (TBP) characterisation curve, but there are a number of disadvantages, e.g. the physical properties of pseudocomponents must be estimated by unreliable empirical methods. The new approach to the characterisation of complex mixtures is based on representing the original mixture by a system of real components. Such substitute mixture is fully defined, it has a chemical character, and physical properties can be simply retrieved from databases. Utilisation of a substitute mixture of real components in the simulation of crude oil processing proved that the new approach could replace the traditional one in normal boiling temperature ranges where real components are available. Both approaches could be also easily combined.

Keywords: Refinery processes; Oil processing; Characterisation procedures; Complex mixtures; Pseudocomponents

1. Introduction

Mixtures containing an extremely large number of various components can be often encountered in industrial chemical technologies, particularly in oil processing and refining. Briesen and Marquardt (2003, 2004a, 2004b) analysed thoroughly the past, present and future trends in this branch of industry and pointed out the need to increase the accuracy in the modelling of oil refining processes. There are direct economical and environmental consequences of any progress in this point and improved treatment of complex mixtures is probably the most promising direction. In order to deal with such mixtures in modelling and simulation calculations, it is necessary to simplify the problem by utilising a substitute mixture possessing reasonably lower number of components or to use an alternative representation of the mixture. For this purpose, the continuous thermodynamics can be employed (see, e.g. Rätzsch & Kehlen, 1983), or, more recently, the wavelet-Galerkin discretisation has been proposed (Briesen & Marquardt, 2003, 2004a, 2004b). While continuous thermodynamics has received only a little attention in industrial practice, the adaptation of wavelet-Galerkin discretisation method for the modelling of unit operations, where complex mixtures are processed, is intensively being studied. Its main advantage is the possibility to tune the representation of the mixture by means of adaptive control of the problem discretisation. On the other hand, this approach uses a non-trivial mathematical background and also the standard models of unit operations must be reformulated in order to incorporate the continuous representations (distributions) of some model variables, e.g. of the vector of composition (Briesen & Marquardt, 2003, 2004a, 2004b). Moreover, physical properties dependent on the composition (e.g. *K*-values) must be also converted to distribution-based functions. Such methods can be employed only for physical processes as distillation or absorption, but not for processes with chemical reactions. Since the last decade of 20th century, methods for the “reconstruction” of the chemical composition have been developed presuming that some other information was available beside the usual distillation curve. It might be data from elemental analysis, gas chromatography, mass spectrometry, ^{1}H and ^{13}C NMR analyses, etc. (e.g. Whitson & Brulé, 2000).

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Nomenclature

C	number of candidate components in the primary temperature interval
F	objective function
I	total number of real components
K	number of measured properties
K_W	Watson factor
M	molecular weight
S	standard specific gravity
T	temperature
x	volume or mass fraction
w	weight in criterion (11)

Greek letters

Φ	volume or mass fraction distilled
η	viscosity
ρ	density
ζ	symbol for property

Superscripts

L	left edge of an interval
R	right edge of an interval
–	mean value

Subscripts

b	at boiling point
c	index of a candidate component
HE	index of the first heavy-end component
i	index of a component or temperature interval
j	index of a component
k	index of a property in criterion (11)
LE	index of the last light-end component
m	measured value
r	value calculated or retrieved from the database

When using substitute mixtures in steady state or dynamic simulation, the classical unit operation models can be employed. In fact, in simulation programs the solution engine deals equally with real components as well as with pseudocomponents if properly defined during the data input phase. The number of components used for the substitute mixture is usually up to 10^2, which is considerably lower than for original complex mixtures, i.e. 10^4–10^7 or more in case of crude oils. It might be felt that in the age of powerful computing machinery the number of components in chemical engineering calculations could be practically unlimited. Nevertheless, there are at least two good reasons why to keep lower number of components. First, the dimension of unit operation models is dependent on the number of components involved and especially equation-oriented simulators could still run into troubles according to memory requirements and internal limits. Second, it is very hard to analyse the results of simulation run when the number of components is high, e.g. thousands or more, and no new information could be obtained. Probably, there would be subsets of components behaving almost equally, the content of each being on the ppm level. It could be noticed that also for well-defined mixtures in practical calculations it is often desired to decrease the number of components or even pseudocomponents. The method called lumping is based on representing groups of components with close boiling points and/or some other properties by a selected single member component inheriting in the mixture the "weight" of the entire group (Riazi, 2005). Montel and Gouel (1984) suggested to optimise the lumping scheme for the substitution of a group of known components in order to preserve the PVT behaviour.

The approach based on pseudocomponents had been developed quite a long time ago (Edmister, 1955; Katz & Brown, 1933) and first was used for flash calculations on an early computer (Hariu & Sage, 1969). As the main advantage it was appreciated that the characterisation procedure was non-iterative. It is still widely accepted as a convenient method in the simulation of separation equipment, but a number of problems arise. Above all:

- The chemical character of components forming the mixture could also play a role in chemical reactions occurring in the studied processes. For pseudocomponents, we cannot define any chemical character.
- A pseudocomponent is primarily defined only by its (pseudo) boiling point and by some additional parameters, mostly by specific gravity, molecular weight or viscosity. All other physical properties, e.g. needed for simulation calculations, must be estimated. Unfortunately, the reliability of common estimation methods (listed, for example, by Whitson & Brulé, 2000) for critical properties, the acentric factor, etc. is rather low according to the results of testing published, for example, by Lindqvist, Markkanen, and Happonen (1994), Riazi (2005) and Twu (1984).
- For pseudocomponents, we cannot use group contribution methods (e.g. UNIFAC) requiring information about the molecular structure of compounds in order to estimate some parameters (e.g. binary interaction parameters for vapour–liquid equilibrium).
- The information about the type of the mixture, e.g. if paraffinic or aromatic compounds are prevailing, or about the type of some of its important components (e.g. polar compounds) could not be easily utilised.
- Arbitrary combinations of pseudocomponents and compounds identified in the original mixture are not supported in commercial simulation programs. That is, it is not possible to place a real component into the middle of the temperature range used for the definition of pseudocomponents without knowing its content.

When modelling distillation and absorption processes for complex hydrocarbon mixtures within simulation programs, the original mixture is traditionally substituted by a mixture comprising two different groups of components. For the light-end, real components usually up to C_5 are employed if they are present and if their content can be determined. For the remaining part, a system of pseudocomponents is derived from certain global characterisations of the mixture based on its distillation behaviour. This approach is implemented in recent major