Fuel 102 (2012) 545–553

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Effective characterization of petroleum C_{7+} fractions

Egon Eckert [a], Tomáš Vaněk [a,*], Zdeněk Bělohlav [b], Petr Zámostný [b]

[a] Institute of Chemical Technology Prague, Department of Chemical Engineering, Technická 5, 166 28 Prague 6, Czech Republic
[b] Institute of Chemical Technology Prague, Department of Organic Technology, Technická 5, 166 28 Prague 6, Czech Republic

HIGHLIGHTS

- Characterization methods for petroleum fractions by substitute mixtures are studied.
- Establishment and usage of Substitute Mixtures of Real Components (SMRCs) is shown.
- Comparison of SMRC and substitute mixtures of pseudocomponents is provided.
- Examples of separation processes in petroleum refining show the potential of SMRC.
- Example shows that SMRC can be used also in the prediction of pyrolysis yields.

ARTICLE INFO

Article history:
Received 23 August 2011
Received in revised form 1 May 2012
Accepted 2 May 2012
Available online 19 May 2012

Keywords:
Petroleum processing
Characterization of petroleum fractions
C_{7+} fraction
Substitute mixture
Simulation

ABSTRACT

Petroleum fractions are typical complex mixtures. For the simulation of petroleum refining processes they are characterized by substitute mixtures. In this contribution the traditional approach based on pseudocomponents is compared with the newer approach utilizing a Substitute Mixtures of Real Components (SMRCs). The main advantage of SMRC approach is the direct availability of physical property data and the knowledge of the chemical character. The most important task in many applications is to characterize the C_{7+} fraction. It is shown, how it can be characterized by a small number of real components. The examples used for comparison comprise separation processes and also the pyrolysis modeling, where the known chemical character of a SMRC is crucial for feeding an artificial neural network model.

1. Introduction

Petroleum refining industry is obviously the base for many other processes further producing a wide assortment of commodities and products. It is desirable to use modern tools for the modeling of petroleum processing in order to increase the production effectiveness and quality. This is the reason why the employment of recent simulation programs (i.e. Aspen Plus, Aspen HYSYS, PRO II, ChemCAD) increases and the results are utilized in many ways. On the other hand, it is not easy to deal with complex mixtures occurring in this field as crude oil, petroleum fractions and many other mid-products. Their detailed composition is often unknown or partially unknown as the number of present components is extremely high when compared with average mixtures appearing in the rest of chemical industry. Even if we could know the detailed composition of a complex mixture, it would be impossible to import such a large volume of data into simulation programs where a reasonable number of components in a mixture are expected to be at most some tens.

In petroleum processing, there are two main categories of processes where we need to utilize the description or characterization of oil and petroleum fractions. First, the employment of various phase separators, particularly flash units or separation columns, is very frequent [1,2]. The simulation of such processes requires to deal with petroleum fractions treated as complex mixtures and to describe their behavior at the phase equilibrium for various combinations of phases. The main interest is in the description of

Abbreviations: AGO, atmospheric gas oil; ANN, Artificial Neural Network; BIP, Binary Interaction Parameter; EBP, end boiling point temperature of the ASTM D86 distillation curve; IBP, initial boiling point temperature of the ASTM D86 distillation curve; MECM, Molecularly Explicit Characterization Model; MTHS, Molecular-Type Homologous Series; PIONA, paraffins, iso-paraffins, olefins, naphthenes, aromatics; PNA, paraffins, naphthenes, aromatics; PONA, paraffins, olefins, naphthenes, aromatics; SMRCs, Substitute Mixtures of Real Components; TBP, True Boiling Point.

* Corresponding author. Tel.: +420 220 443 106, mobile: +420 604 834 978; fax: +420 220 444 320.
E-mail addresses: Eckert.Egon@centrum.cz (E. Eckert), Tomas.Vanek@vscht.cz (T. Vaněk), Zdenek.Belohlav@vscht.cz (Z. Bělohlav), Petr.Zamostny@vscht.cz (P. Zámostný).

0016-2361/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2012.05.005

Nomenclature

K	number of measured properties or property curves (–)
M	molecular weight (kg kmol^{-1})
p	pressure (Pa)
T	temperature (°C)
x	mole or mass fraction in the liquid phase (–)
y	mole fraction in the vapour/gas phase (–)

Greek symbols

Φ	volume, mole or mass fraction distilled (–)
ρ	standard liquid density at 15.56 °C or liquid density at 20 °C (kg m^{-3})
ζ	symbol for a general property
ω	acentric factor (–)

Subscripts

b	at boiling point
c	critical
i	component index
j	component index
k	index of a property
m	mass

Superscripts

DB	taken from a database of physical properties
exp	experimental value

the vapor–liquid equilibrium but also the vapor–liquid–liquid systems can be encountered in the petroleum processing. The second area of interest is the conversion of petroleum fractions by chemical reactions. Typically, we can mention the pyrolysis or hydrocracking processes. Here, it is crucial to know something about the chemical character of the feedstock.

The most convenient way how to characterize petroleum fractions is based on the usage of substitute mixtures, which enable to decrease the number of considered components dramatically when compared with the original mixture. Otherwise, it would be hardly possible to provide simulation calculations with standard simulation programs. There are other possibilities for the characterization of complex mixtures, i.e. continuous thermodynamics [3] or wavelet models [4], but this will not be discussed here according to their different mathematical background and problems with implementation in standard commercial simulation programs.

The traditional approach to substitute mixtures is based on pseudocomponents (see for example [1,2,5]), i.e. artificial components for which it is necessary to deliver the set of physical properties as a result of empirical estimation methods, often not too reliable as it was proved by Eckert [6]. The impact and importance of a proper choice of the physical property models was also studied in the work of Aladwani and Riazi [7]. Moreover, the pseudocomponent-based substitute mixtures show no chemical character, i.e. no chemical formula or structure of a molecule is defined for a pseudocomponent. A newer approach based on Substitute Mixtures of Real Components (SMRCs) was introduced by Ba et al. [8] and Eckert and Vaněk [9,10]. The substitute mixture is constructed from real components as a result of an algorithm presented further. The main advantage is the direct availability of physical properties from databases and the defined chemical character of the mixture. Certain limitations can be seen in the lack of higher boiling hydrocarbons in majority of databases. Accordingly, heavy petroleum fractions must be usually characterized by substitute mixtures combining real components and pseudocomponents but the chemical character would be partially lost in such cases. Nevertheless, the possibility to use the SMRC approach has been approved on a number of various applications, e.g. the simulation of a crude oil processing [9] and the description of the blending of petroleum fractions [11]. A different type of the application of SMRC is the prediction of pyrolysis products yields [12,13], for which the knowledge of the chemical character is necessary.

We can remark that a slightly modified approach of Eckert and Vaněk [9] has been recently used by Guangying et al. [14] for the simulation of quench systems in the pyrolysis oil processing. Similar method called Molecularly Explicit Characterization Model (MECM) was also published by Albahri [15]. The difference is that a set of representative components to form the substitute mixture is predefined and its composition is optimized in order to match experimental data about the original mixture taking into account a large number of different types of physical and chemical properties. Enhanced version was presented in [16].

The importance and potential utilization of various bulk structural characteristics of a petroleum fraction for kinetic models was recognized by Gomez-Prado et al. [17]. The Molecular-Type Homologous Series (MTHS) approach was originally invented by Peng [18]. Here, the characterization of a petroleum mixture is provided by a MTHS matrix where rows represent the carbon number and columns represent homologous series, i.e. normal or iso-paraffins, olefins, naphthenes, aromatics, etc. Ahmad et al. [19] extended this approach for wider collection of compound types.

This contribution is devoted to the problem how to deal with mixtures containing hydrocarbons with seven or more carbons, which is usually called the C_{7+} fraction. In order to describe such fractions Riazi [1] as well as Whitson and Brulé [2] presented methods and procedures for the definition of substitute mixtures represented by a relatively low number of pseudocomponents. It is shown here how the C_{7+} fraction can be alternatively characterized by the same number of real components with properties defined rigorously by component data retrieved from a suitable database instead of employing empirical estimation methods. Unfortunately, it can happen that some component or some of its properties are not available in the simulation program used later for calculations with the substitute mixture. Then the missing parameters must be also estimated even for real components. The advantage is that we have for this purpose highly reliable basic data from the source database as the input to estimation procedures.

Three examples will be presented here to document the power of the SMRC approach. The first two examples with input data taken from Riazi [1] and Whitson and Brulé [2] comprise the simulation of single- and multistage separation processes for typical mixtures occurring in the petroleum processing industry. The qualitatively different last example shows the usage of the SMRC approach for the characterization of the atmospheric gas oil (AGO) with a small number of real components. Consequently, the substitute mixture served for the prediction of pyrolysis products. In this case, a mixture of pseudocomponents is inapplicable due to the missing chemical character.

2. Methods

2.1. Characterization of complex mixtures

It is very hard, even impossible, to analyze in detail any complex mixture, particularly an oil fraction. However, there are many possibilities to recognize and measure characteristic properties