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Evaluation of different methodologies to determine the n-paraffin distribution of petroleum fractions

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HIGHLIGHTS

- ▶ Paraffin distribution curves for petroleum mixtures can be obtained by HTGC, SDA and DSC techniques.
- ▶ Results obtained by different techniques are in good agreement.
- ▶ Average boiling temperatures and WAT can be related with pure n-paraffin values.

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ABSTRACT

Petroleum fractions are complex mixtures composed of a large number of components, which makes impossible to obtain their detailed composition and difficult to apply conventional thermodynamic equations to carry out phase equilibrium calculations. Consequently, alternative approaches as the pseudo-component or the continuous thermodynamic methods are used to describe the composition of petroleum mixtures, required as input information for the thermodynamic models.

The purpose of this work is to evaluate the capabilities of different experimental techniques to calculate the n-paraffin distribution of petroleum mixtures. A number of petroleum cuts of a paraffinic crude oil were selected and analyzed by High Temperature Gas Chromatography (HTGC), obtaining their n-paraffin distribution by direct integration of the chromatograms. In addition, the n-paraffin distribution was determined from the simulated distillation curves (SDA). Each distillation curve was fitted to a continuous model to obtain the distribution of boiling temperature for each mixture and thereafter, the boiling temperature distribution was converted into composition. Finally, both the n-paraffin distribution and the average molecular weight of the mixture were obtained. Differential Scanning Calorimetry (DSC) was also used in this work to obtain the wax appearance temperature (WAT) and the n-paraffin distribution. The comparison of the n-paraffin distributions obtained by the different techniques shows a reasonable agreement, despite their different approaches.

1. Introduction

To optimize the design and operation of the processes in which petroleum mixtures are involved, a good knowledge of the process is necessary. However, experimental determination is time and money consuming and therefore, the modeling is a good tool to simulate changes in the operation conditions or feed quality [1–3]. The key of a simulation model is to properly describe the phase equilibrium involved, and consequently a consistent thermodynamic model based on accurate experimental information is crucial.

Petroleum fractions are complex mixtures composed of a huge number of components. It makes impossible to apply conventional thermodynamic equations to phase equilibrium calculations since a complete chemical analysis should be required. Although this analysis was available, the inclusion of all components would lead to massive calculations. Therefore, petroleum mixtures must be described by using approaches requiring as less experimental information as possible. In this sense, the pseudo-component [4–8] and continuous thermodynamics methodologies [9–12] have been the most common approaches for equilibrium calculations involving these mixtures.

The pseudo-component approach has been widely used to describe the composition of petroleum mixtures by a reduced number of key components based on the distillation curve, usually True Boiling Point (TBP) distillation curve [6].

The core idea of the continuous thermodynamic method is the use of a continuous distribution function of a measurable variable (temperature, molecular weight or carbon number) to describe the

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composition of these mixtures. This approach is suitable for phase equilibrium calculations of complex mixtures containing many similar components as in the case of petroleum fractions [13].

Very often, the knowledge of the composition of petroleum mixtures, expressed in terms of n-paraffin, is crucial since it is required as input information for the thermodynamic models [14]. As reported in the literature, the n-paraffin distribution of petroleum mixtures has been traditionally obtained by means of High Temperature Gas Chromatography (HTGC) [15–18]. However, some problems remain unsolved in obtaining the n-paraffin distribution by HTGC, as the uncertainty in the determination of the baseline to integrate the chromatogram because of the low signal/noise ratios and the interference created by other components of different natures.

DSC analysis is a fast technique widely used in the calculation of cold properties as the wax appearance temperature and the wax precipitation curve of petroleum mixtures. Nevertheless, it presents some limitations related to the baseline determination, the integration process to transform heat flow into the corresponding mass, and to identify separated components. Recently, a new method has been developed to overcome such limitations and to determine the n-paraffin distribution. Such procedure was applied to petroleum mixtures obtaining promising results [15,19,20].

The aim of this work is to determine the n-paraffin distribution for a number of crude oil cuts from a paraffinic crude oil by using different experimental techniques. HTGC was used to determine the n-paraffin distribution by direct integration of the chromatograms and to obtain the ASTM D2887 distillation curve (simulated distillation curves or SDA) [21]. Each distillation curve was fitted to a continuous model proposed by Riazi [22] in order to obtain a distribution function of boiling temperature for each mixture. Thereafter, the boiling temperature distribution was converted into composition, and finally both the n-paraffin distribution and the average molecular weight of the mixture were obtained following a previously developed methodology [23]. The crude oil cuts were also analyzed by DSC to obtain the wax appearance temperature (WAT) and the n-paraffin distribution using a calculation method reported elsewhere [19]. The comparison of the n-paraffin distribution experimentally obtained by HTGC, SDA and DSC analyses shows values in reasonable agreement and it can be concluded that both techniques yield consistent and similar results, despite their different approaches.

2. Experimental

2.1. Materials

Petroleum fractions (covering the boiling temperature range 105–535 °C) of a paraffinic crude oil were used in this work. The main features of the crude oil used are summarized in Table 1. All the samples were supplied by Repsol.

Table 1
Characteristics of the crude oil used in this work.

Crude oil	
Origin	North Sea
Density (° API)	35.92
API Classification	Light
Density 15 °C (g/cm^3)	0.8448
Pour point (°C)	−15
Viscosity 20 °C (cSt)	8.49

2.2. High Temperature Gas Chromatography (HTGC)

The samples were analyzed in a chromatograph 3900 Varian GC with an automatic injector, a cryogenic system, a flame ionization detector (FID) and an on-column injection system. Column was a 10 m length × 0.53 mm internal diameter with a 0.17 mm width silicone stationary phase. The studied mixtures were dissolved in CS_2 (5 wt.%), and analyzed. A mixture of n-alkanes (C_5–C_{80}) was used as calibration. The distillation curve of each sample was obtained by using specific software (STARSD™) provided by Varian.

The analyses of the samples were performed in different conditions regarding their nature (light or heavy) as follows:

- Light samples ($T_b \leqslant 335$ °C):
  - Injector: 40–400 °C (10 °C/min). Hold time at maximum temperature: 10.5 min.
  - Column Oven: 35–400 °C (10 °C/min). Hold time at maximum temperature: 10.5 min.
  - Detector: 420 °C
- Heavy samples ($T_b \geqslant 335$ °C):
  - Injector: 40–425 °C (10 °C/min). Hold time at maximum temperature: 10.5 min.
  - Column Oven: 35–425 °C (10 °C/min). Hold time at maximum temperature: 10.5 min.
  - Detector: 450 °C.

The simulated distillation curves (SDA curves) were obtained by HTGC analysis according to ASTM D-2887 method [21] and they were used to obtain the n-paraffin distribution, following a methodology reported elsewhere [23].

The SDA curves were fitted to a two-parameter distribution model developed by Riazi and given by the following equation [22]:

$$P^* = \left[\frac{A}{B}\ln\left(\frac{1}{x^*}\right)\right]^{\frac{1}{B}} \quad P^* = \frac{T_b - P_0}{P_0}, \quad x^* = 1 - x_w \tag{1}$$

where x_w is the cumulative mass fraction and T_b is the absolute boiling temperature. P_0, A, and B are specific parameters for each sample. Values for these parameters were obtained by fitting SDA data for each sample by minimizing the objective function:

$$\delta\ (\%) = 100\frac{1}{n}\sum\frac{|T_{bi} - T_{bi,calc}|}{T_{bi}} \tag{2}$$

which represents the percent average relative deviation, where T_{bi} is the SDA absolute boiling temperature for a given $x_{w,i}$, $T_{bi,calc}$ is the corresponding absolute boiling temperature calculated by Eq. (1), and n is the number of experimental points of the SDA curve.

From Eq. (1) an analytical expression can be directly obtained for the distribution function as published elsewhere [23]:

$$F(P^*) = \frac{B^2}{A}\cdot P^{*B-1}\cdot \exp\left(-\frac{B}{A}\cdot P^{*B}\right) \tag{3}$$

In order to convert the continuous distribution function in concentration of individual compound the following equation was used:

$$x_i = \frac{(T_{bi+1} - T_{bi})\cdot F_i}{\sum_j (T_{bj+1} - T_{bj})\cdot F_j} \tag{4}$$

where T_{bi} is the boiling temperature, x_i the mass fraction and F_i is the distribution function of i component obtained from Eq. (3) at T_{bi}. T_{bi} was calculated by using the equation proposed by Marano et al. [24] for n-alkanes:

$$T_{bi} = T_{b\infty} - (T_{b\infty} - T_{b0})\cdot \exp(-\beta\cdot(n - n_0)^{\gamma}) \tag{5}$$

where n is the carbon atom number for the different n-paraffins. The values of the rest of parameters were taken from Marano et al. [24]: $n_0 = -1.487453$; $T_{b0} = -164.93$; $T_{b\infty} = 1091.11$; $\beta = 0.153505$; $\gamma = 0.602490$.