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Thermodynamic Characterization of Undefined Petroleum Fractions of Gas Condensate using Group Contribution

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Abstract — *A methodology proposed in a previous paper [Carreón-Calderón et al. (2012) Ind. Eng. Chem. Res. **51**, 14188-14198] for thermodynamic characterization of undefined petroleum fractions was applied to gas-condensate fluids. Using this methodology, input parameters of cubic equations of state and their mixing rules, critical properties and chemical pseudostructures are determined for undefined fractions by minimizing their Gibbs free energy. The results show the feasibility of applying this approach to gas-condensate fluids without making use of either cubic equations of state or mixing rules with specific adjusted parameters for petroleum fluids. Besides, it is shown that the phase equilibrium envelopes of gas-condensate fluids are highly dependent on the critical properties assigned to the undefined petroleum fractions of such fluid fractions and less dependent on the equation used for modeling gas-condensate fluids as a whole. The Absolute Average Error (AAE) considering the best arrangement is 1.79% in predicting the dew point.*

Résumé — **Caractérisation thermodynamique des fractions indéfinies d'un condensat de gaz à l'aide de la méthode de contribution de groupes** — Une méthodologie proposée dans un article précédent [Carreón-Calderón *et al.* (2012) *Ind. Eng. Chem. Res.* **51**, 14188-14198] pour la caractérisation thermodynamique des fractions de pétrole non définies a été appliquée à des gaz à condensats. En utilisant cette méthodologie, les paramètres d'entrée de l'équation d'état cubique et leurs règles de mélange, propriétés critiques et pseudo-structures chimiques, sont déterminés pour les fractions non définies en minimisant l'énergie libre de Gibbs. Les résultats montrent que l'application de cette approche est appropriée aux fluides provenant des condensats de gaz sans utiliser, pour l'équation d'état cubique ou les règles de mélange, de paramètres caractéristiques ajustés pour les fluides pétroliers. En plus, il est montré que les courbes d'équilibre de phases des fluides de condensat de gaz sont fortement dépendantes des propriétés critiques associées aux fractions de pétrole non définies et moins dépendantes de l'ensemble des équations modélisant les fluides de condensat de gaz. Pour la prédiction du point de rosée, l'erreur moyenne absolue est 1,79 % pour le meilleur arrangement.

NOTATION

<i>AAD</i>	Absolute Average Deviation
<i>FG</i>	Number of functional group types
<i>JR</i>	The Joback-Reid method
<i>MW</i>	Molecular weight
<i>MHV1</i>	Modified Huron-Vidal mixing rule of one parameter
<i>P</i>	Pressure (MPa)
<i>P_C</i>	Critical pressure (MPa)
<i>p_c</i>	Contribution to <i>P_C</i> by functional groups
<i>PSRK</i>	Predictive Soave-Redlich-Kwong mixing rule
<i>PR</i>	Peng-Robinson equation of state
<i>R</i>	Gas constant, 8.31441 J/mol.K
<i>SRK</i>	Soave-Redlich-Kwong equation of state
<i>T</i>	Temperature (K)
<i>T_b</i>	Boiling temperature at 0.101325 MPa (K)
<i>T_c</i>	Critical temperature (K)
<i>t_c</i>	Contribution to <i>T_c</i> by functional groups
<i>V</i>	Volume (m ³ /mole)
<i>V_c</i>	Critical volume (m ³ /mol)
<i>VDW</i>	van der Waals mixing rule
<i>v_c</i>	Contributions to <i>V_c</i> by functional groups
<i>x</i>	Mole fraction
<i>Z_c</i>	Critical compressibility factor

GREEK LETTERS

α	Coefficient in Equation (14)
β	Coefficient in Equation (14)
χ	Coefficient in Equation (14)
Δv	Group volume increment, Equation (13)
ϕ	Fugacity coefficient
γ	Activity coefficient
ρ	Mass density (kg/m ³)
ν	Number of functional groups
ω	Acentric factor

SUPERSCRIPTS

<i>EOS</i>	Equation Of State
<i>EXP</i>	Experimental value

SUBSCRIPTS

<i>c</i>	Critical property
<i>i</i>	Functional group <i>i</i> or pure component <i>i</i>
<i>k</i>	Undefined petroleum fraction <i>k</i> or pure component <i>k</i>

INTRODUCTION

Gas-condensate fluids from reservoirs are composed of hydrocarbon compounds from C₁ to C₆ and at least one undefined fraction, containing unidentified compounds ranging from C₇ to heavier hydrocarbon compounds. Similar to other petroleum fluids, gas-condensate fluids are very complex to model, not only because of the presence of unidentified compounds but also because of the presence of non-hydrocarbon compounds such as hydrogen sulfide, carbon dioxide and nitrogen.

In the same way as heavier petroleum fluids, the characterization of undefined fractions has a great effect on phase equilibrium simulations of gas-condensate fluids. Several methods have been proposed for characterizing undefined fractions, where experimental information in the form of molar distributions, the mole fraction against the Carbon Number (CN), is taken as starting point. For instance, it has been observed that a single straight-line relationship exists between the logarithm of the mole fraction and the molecular weight of the CN (Ahmed, 1989; Hosein and McCain, 2007). On the other hand, Whitson (1983, 1984) used a gamma distribution to establish the molar distribution. Soreide (1989) modified Whitson's method using a *K* factor in order to generate the distribution of specific gravities. When an experimental molar distribution of undefined fractions is absent, the methods commonly employed in the oil industry are those given by Whitson *et al.* (1990) and Pedersen *et al.* (1992).

Once the molar distribution has been defined, the characterization procedure requires the estimation of the critical properties for each CN or a mixture of them. Such mixtures are better known as pseudocomponents. The estimation of critical properties is usually performed using empirical correlations. Some examples of such correlations are those obtained by Kesler and Lee (1976) and Pedersen *et al.* (1980) among others. Sinayuc and Gumrah (2004) established that different sets of correlations provide very dissimilar results. These differences may be explained by the fact that the empirical correlations are obtained from specific experimental data banks of pure compounds; hence, they cannot be used in a general way irrespective of the type of petroleum fraction under study. On the other hand, attempts have been made to obtain a more generalized methodology. For instance, Sinayuc and Gumrah (2004) proposed an optimization method that consists of finding the global minimum of Gibbs energy using critical properties obtained from correlations as independent variables and a genetic algorithm as an optimization tool.

Recently, Carreón-Calderón *et al.* (2012) proposed a methodology, the so-called CURR (Carreón-Urbe-Ramírez-Ramírez's) approach, to estimate the critical properties of undefined petroleum fractions using an approach based on group contribution methods. Using classical thermodynamics, a molecular pseudostructure and critical properties are assigned to a given undefined petroleum fraction by minimizing its corresponding free energy. The CURR approach was applied to light petroleum fluids, where an experimental molar distribution was available. The results obtained appeared to be acceptable, irrespective of both the equation of state and the mixing rule used. Hence, the aim of this work is to test the functionality of the CURR approach under more difficult situations; for example, when an experimental molar distribution is not provided and therefore it has to be estimated, which is usually the case of gas-condensate fluids.

1 METHODOLOGY

The CURR approach was described in detail in a previous work (Carreón-Calderón *et al.*, 2012). In that methodology, one molecular pseudostructure, a set of non-integer functional groups, is simultaneously determined for a given petroleum fraction of unknown composition. Such properties allow undefined petroleum fractions to be treated as hypothetical pure components. This means that any method developed for handling components with known molecular structure can now be applied to petroleum mixtures containing undefined petroleum fractions. Thus, petroleum fluids, which are mixtures formed of unidentified compounds mostly, turn into mixtures formed of identified and pseudocompounds.

It should be noted that this procedure has been evaluated for the characterization of undefined fractions of light petroleum, where their corresponding experimental molar distributions were available. Hence, in this work, an additional step to estimate this distribution is included because experimental molar distributions are not provided for the condensate-gas fluids under study. As will be seen in what follows, this estimation consists of splitting the heavy undefined petroleum fraction, the C_{7+} fraction, into carbon numbers by assuming a probability distribution. In Figure 1, starting with such an estimation, the stages of the CURR method described in the following sections are summarized.

1.1 Molar Distribution of the Heavy Fraction (C_{7+})

Pedersen *et al.* (1992) proposed that, for naturally-occurring hydrocarbon mixtures, an exponential

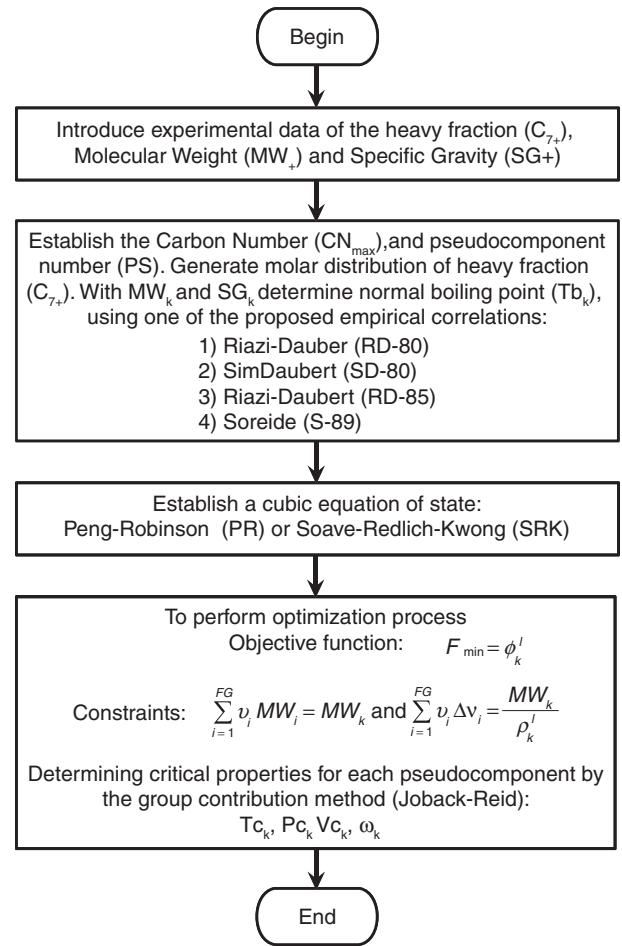


Figure 1

Flow diagram of the CURR method.

relation exists between the mole fraction of a component and the corresponding CN. They expressed this relationship using the following expressions:

$$\ln x_k = A + B(CN)_k \quad (1)$$

$$\rho_k = C + D \ln(CN)_k \quad (2)$$

$$MW_k = 14(CN)_k - 4 \quad (3)$$

where x_k symbolizes the mole fraction, ρ_k the density, MW_k the molecular weight and $(CN)_k$ the k -th carbon number. The heaviest carbon number is usually considered to be CN_{80} . The constants A , B , C and D are determined from experimental values of the mole fraction, molecular weight and density of the heavy petroleum fraction C_{7+} together with mass balances as follows:

$$x_+ = \sum_{k=+}^{CN_{max}} x_k \quad (4)$$

$$MW_+ = \frac{\sum_{k=+}^{CN_{\max}} x_k MW_k}{x_+} \quad (5)$$

$$\rho_+ = \frac{x_+ MW_+}{\sum_{k=+}^{CN_{\max}} \frac{x_k MW_k}{\rho_k}} \quad (6)$$

The subscript + indicates properties of the C₇₊ fraction to be split up. These expressions allow calculating the mole fraction, the molecular weight and the liquid density for each carbon number (Pedersen and Christensen, 2007). In order to solve the system of equations, it is considered that Equation (1) can be equally written in terms of the molecular weight instead of the carbon number, that is:

$$\ln x_k = A + B MW_k \quad (1a)$$

If this equation is inserted into Equations (4) and (5), and Equation (3) is used to determine the molecular weight for each carbon number k (MW_k), then we have a system of two equations with two unknowns (A and B). This system can be solved by any numerical method, such as Newton-Raphson. A similar procedure is performed for determining the liquid density for each carbon number k from the liquid density of the C₇₊ fraction through Equation (2) and Equation (6), but in this case, the previously determined molar distribution, MW_k against x_k , is used together with the density of the last carbon number fraction before the C₇₊ fraction, that is, the n -hexane liquid density. Once the molar distribution has been determined, the characterized petroleum fluid is formed by 80 carbon numbers and defined compounds. Hence, it is advisable to lump carbon numbers into pseudocomponents to reduce the total number of components, and consequently to make the phase equilibrium calculations easier. In Pedersen's methodology, a weight-based grouping is recommended, where each group (pseudocomponent) contains approximately the same weight amount. However, unlike Pedersen's methodology, where critical properties are found as weight mean averages, in this work, they are found from the density, molecular weight and boiling temperature of each pseudocomponent directly by the minimization procedure described below.

1.2 Determination of the Molecular Pseudostructure

In this step, one hypothetical structure, set, is non-integer functional groups are assigned to each pseudocomponent. This molecular pseudostructure may not

correspond to the actual structure obtained from experimental data, but it is expected that it allows properties entering into cubic equations of state to be estimated correctly.

Critical Properties and Liquid Density Group Contribution

Estimating critical properties and the acentric factor from known chemical structure is the greatest advantage of group contribution methods. There have been various proposals for their application to characterize petroleum; for example, Ruzicka *et al.* (1983) and Auaullee *et al.* (1997a-c, 2001). In the latter works, one molecular pseudostructure is assigned to the C₂₀₊ fraction by solving systems of equations developed for a fixed set of non-integer functional groups, whereas, starting with the knowledge of paraffinic-naphthenic-aromatic analysis, two or three key compounds are used to represent undefined fractions from C₆ to C₁₉. For every undefined fraction, either one pseudostructure or key compounds are found by matching the experimental molecular weight and molar volume to calculations. Although the PR equation of state is also employed with C₆ to C₁₉ fractions for such a purpose, it is worth pointing out that, unlike the current treatment, in those studies any minimization procedure subject to constraints was not suggested in order to obtain optimized functional groups in accordance with the thermodynamic laws. This issue allows, in principle, any group contribution method to be used in the current characterization procedure, as will be shown in future work.

Group contribution methods applied to a wider variety of chemical species have been developed to estimate the properties of a pure compound; for example, those proposed by Jöback and Reid (1987) (JR), and by Marrero and Gani (2001). In the current work, the former is suggested to be employed for estimating critical properties (T_c , P_c and V_c) of pseudocomponents; the respective expressions are:

$$T_c = \frac{T_b}{0.584 + 0.965 \sum_{i=1}^{FG} v_i t_{ci} - \left(\sum_{i=1}^{FG} v_i t_{ci} \right)^2} \quad (7)$$

$$P_c = \frac{0.1}{\left(0.113 + 0.0032 n_A - \sum_{i=1}^{FG} v_i p_{ci} \right)^2} \quad (8)$$

$$V_c = \frac{17.5 + \sum_{i=1}^{FG} v_i v_{ci}}{10^6} \quad (9)$$

TABLE 1
Correlations for estimating normal boiling point

	Normal boiling point	Source
RD80	$T_b = \frac{5}{9} \left[\left(\frac{MW \times SG^{1.0164}}{4.5673 \times 10^{-5}} \right)^{\frac{1}{2.1962}} \right]$	Riazi and Daubert (1980)
SD80	$T_b = \frac{5}{9} \left[\left(\frac{MW \times SG^{0.9371}}{1.4350476 \times 10^{-5}} \right)^{\frac{1}{2.3776}} \right]$	Sim and Daubert (1980)
RD87	$T_b = \frac{5}{9} [6.77857 \times MW^{0.401673} SG^{-1.58262} EXP(3.7741 \times 10^{-3} MW + 2.984036 SG - 4.25288 \times 10^{-3} SG)]$	Riazi and Daubert (1987)
S89	$T_b = \frac{5}{9} (1928.3 - 1.695 \times 10^5 MW^{-0.03522} SG^{3.266} e^{-4.922 \times 10^{-3} MW - 4.7685 SG + 3.462 \times 10^{-3} MW \times SG})$	Soreide (1989)

where T_c , P_c and V_c are the critical temperature, pressure and volume, respectively. Similarly, t_{ci} , p_{ci} and v_{ci} represent the corresponding contributions to T_c , P_c and V_c by the i -th functional group, being v_i the number of the functional groups of type i . In the above equations, n_A is the number of atoms in the molecule, T_b is the normal boiling point, and FG is the total number of types of functional groups. The units for temperature, pressure and volume are K, MPa and m^3/mol , respectively. As observed from Equation (7), the normal boiling point is required for the critical temperature to be calculated. Generally, the experimental value of such a boiling point is not available; consequently, the use of some empirical correlations found in the literature is recommended, which are displayed in Table 1.

Another property required to calculate phase equilibrium calculations is the acentric factor. Unfortunately, in the JR method there is not any expression suggested; hence, in this work, we consider the following expression to estimate the acentric factor (Poling *et al.*, 2001):

$$\omega = - \frac{\ln(P_c/1.01325) + f_0(T_{br})}{f_1(T_{br})} \quad (10)$$

$$\begin{aligned} & f_0(T_{br}) \\ &= \frac{-5.97616\tau + 1.29874\tau^{1.5} - 0.60394\tau^{2.5} - 1.06841\tau^5}{T_{br}} \end{aligned} \quad (11)$$

$$\begin{aligned} & f_1(T_{br}) \\ &= \frac{-5.03365\tau + 1.11505\tau^{1.5} - 5.41217\tau^{2.5} - 7.46628\tau^5}{T_{br}} \end{aligned} \quad (12)$$

$T_{br} = T_b/T_c$ is the reduced normal boiling point and $\tau = 1 - T_{br}$.

According to Equation (2), liquid density is part of the exponential molar distribution, which implies that a methodology based on functional groups is also required to estimate liquid densities. In the CURR approach, the liquid density of a given pseudocomponent is estimated by the group contribution method GCVOL (Group Contribution method for predicting Saturated Liquid Density) (Elbro *et al.*, 1991; Ihmels and Gmehling, 2003), where the liquid density ρ is calculated from:

$$\rho = \frac{MW}{V} = \frac{MW}{\sum_{i=1}^{FG} v_i \Delta v_i} \quad (13)$$

Here, MW is the molecular weight and Δv_i is the group volume increment expressed as a function of temperature as follows:

$$\Delta v_i = \alpha_i + \beta_i T + \chi_i T^2 \quad (14)$$

where α_i , β_i , and χ_i are specific parameters of a given functional group.

Calculation of Functional Group Number

In order to estimate the number of functional groups for an undefined petroleum fraction, either the carbon number or the pseudocomponent, each fraction is considered as an independent system at a fixed pressure and temperature. It is well known that the equilibrium of the Gibbs free energy has a minimum value at a fixed value of pressure and temperature. From the PVT experiments carried out in the petroleum industry, the temperature and pressure measurements established for this purpose are 288.7 K (60°F) and 0.1013 MPa (1 atm). Thus, starting with the residual Gibbs energy, it was shown in the CURR approach that the above assumptions lead to

minimizing the liquid fugacity coefficient of the respective undefined petroleum fraction (pseudocomponent), which is treated as a hypothetical pure compound. In other words, the objective function to be minimized becomes:

$$\phi_k^l(T_{ck}(v_1, v_2, \dots, v_{FG}), P_{ck}(v_1, v_2, \dots, v_{FG}), \omega_k(v_1, v_2, \dots, v_{FG})) \quad (15)$$

Taking as constraints: the pseudocomponent volume expressed in Equation (13) and the corresponding molecular weight, expressed in turn by the following expression:

$$\sum_{i=1}^{FG} v_i MW_i = MW_k \quad (16)$$

Using a cubic equation of state and the fundamental expression of fugacity coefficients, Equation (15) can be rewritten as:

$$\phi_j = -\ln(Z - B) + Z - 1 + \frac{A}{B(\gamma + \beta)} \ln \left(\frac{Z + B\gamma}{Z - B\gamma} \right) \quad (17)$$

$$\beta = \frac{\sqrt{u^2 - 4w} - u}{2} \quad (18)$$

$$\gamma = \frac{\sqrt{u^2 - 4w} + u}{2} \quad (19)$$

$$A = \frac{Pa}{(RT)^2} \quad (20)$$

$$B = \frac{Pb}{RT} \quad (21)$$

$$Z = \frac{PV}{RT} \quad (22)$$

where R is the gas constant. In the expressions above, u and w are parameters that depend on the equation of state, as shown in Table 2. On the other hand, a and b depend on the critical properties, as will be shown in the following section.

1.3 PVT Property Calculation

The cubic equations of state were chosen here because they are relatively simple mathematical models relating the pressure-volume-temperature behavior for fluid

TABLE 2
Equation of state parameters

Parameter	PR	SRK
u	2	1
w	-1	0
Ω_a	0.45724 ^a	0.42747 ^b
Ω_b	0.07780 ^a	0.08664 ^b
r_1	0.37464 ^a	0.480 ^b
r_2	1.54226 ^a	1.574 ^b
r_3	-0.26992 ^a	-0.176 ^b

^a Peng and Robinson (1976).

^b Soave (1972).

phases, along with the fact that these equations have been used successfully in the oil industry. The Peng-Robinson (PR) (Peng and Robinson, 1976) and Soave-Redlich-Kwong (SRK) (Soave, 1972) equations of state were used in this work. The corresponding generalized expression is shown below:

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + ubV - wb^2} \quad (23)$$

The parameters u and w define the cubic equation of state; v is the molar volume, while a and b are specific to a given component or, in the context of the current work, a given pseudocomponent through its critical properties, in accordance with the following expressions:

$$a = \frac{\Omega_a (RT_c)^2 f}{P_c} \quad (24)$$

$$f = \left[1 + (r_1 + r_2\omega + r_3\omega^2) \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (25)$$

$$b = \frac{\Omega_b RT_c}{P_c} \quad (26)$$

where Ω_a , Ω_b and r_i are specific parameters for each equation of state, as can be seen in Table 2. It is important to emphasize that Equations (7) and (8) along with Equations (24) to (26) connect functional groups of pseudocomponents with the fugacity coefficient for a pure compound given by either Equation (15) or Equation (17).

TABLE 3
UNIFAC functional groups

Chemical formula	Main group	Sub-group
CH ₃	1	1
CH ₂	1	2
CH	1	3
C	1	4
ACH	3	9
AC	3	10
CO ₂	56	117
CH ₄	57	118
N ₂	60	115
H ₂ S	61	114

Once one molecular structure and the critical properties are simultaneously determined for an undefined petroleum fraction (pseudocomponent) from the procedure described previously, the undefined petroleum fraction becomes a hypothetical pure component from the calculation standpoint. Thus, the whole mixture of hydrocarbons can be treated as a mixture of known components. This means that any approach developed for handling chemical structures can be applied to petroleum fluids regardless of the lack of experimental information about compounds forming undefined fractions and their chemical structures. To verify this assertion in the case of gas-condensate fluids, the Modified Huron-Vidal mixing rule of one parameter – MHV1 – (Horstmann *et al.*, 2005) using the group contribution method UNIFAC (Universal Functional group Activity Coefficients) as an activity coefficient model was used for PVT calculations. The set of UNIFAC functional groups used in the MHV1 mixing rule is shown in Table 3. In the same context, another mixing rule was used, the so-called Predictive Soave-Redlich-Kwong, PSRK (Horstmann *et al.*, 2005). There are other mixing rules such as MHV2 (Dahl and Michelsen 1990), Wong-Sandler (Wong and Sandler, 1992) a PPR78 (Jaubert and Mutelet, 2004; Jaubert *et al.*, 2010), that have been proved to work adequately in predicting the equilibrium of hydrocarbon mixtures, but the aim of this study is to evaluate the CURR method's performance and not mixing rules in general. In other words, we intend to characterize undefined petroleum fractions of gas-condensate fluids so that models requiring chemical structures, the UNIFAC approach inserted into mixing rules in this case, can be employed with such fluids; something that

is not routinely seen in phase equilibrium calculations involving petroleum because of the unknown numbers v_i . Otherwise, the so-called classical mixing rule or the Van Der Waals mixing rule (VDW) (Peng and Robinson, 1976; Soave, 1972), or its variations (Jaubert *et al.*, 2010), is the only available mixing rule for performing such calculations. The reader is referred to the original paper (Carreón-Calderón *et al.*, 2012) for additional information about the use of these mixing rules in the context of the CURR approach.

Although in the original CURR approach, correction in the molar volume was introduced by applying the concept of the volume translation (Peneloux *et al.*, 1982) and GCVOL approach (Eq. 13), the concept of volume translation was not introduced here because the only calculations performed were the phase equilibrium ones. However, it is important to make a distinction between the liquid density of the pseudocomponent and the liquid density of the petroleum fluid as a whole. The former is required for determining the chemical pseudostructure of the corresponding pseudocomponent through the optimization problem given by Equation (15), whereas the latter is not required for phase equilibrium calculations.

2 APPLICATIONS

The methodology described previously was used first of all to characterize thermodynamically the undefined petroleum fraction of five gas-condensate fluids found in the literature. Then, inserting the calculated chemical pseudostructures and associated critical properties into the cubic equations of state and mixing rules described above, the phase equilibrium calculations were performed. The experimental data employed in this work are shown in Table 4.

As mentioned before, first, it is necessary to determine the exponential molar distribution from the only undefined petroleum fraction provided, the C₇₊ fraction in this case (Tab. 4), using the split method proposed by Pedersen. Thus, carbon numbers together with their corresponding molecular weight, specific gravity and molar fraction were obtained. These carbon numbers were then lumped together into pseudocomponents (PS) of approximately the same weight fraction.

As the next step, the critical properties were estimated for every pseudocomponent from the previous step through the minimization process of Gibbs energy given by Equation (15) and related expressions. As observed in Table 4, the boiling temperatures are not available, which, according to Equation (7), are required to estimate critical temperatures; consequently, empirical

TABLE 4
Gas condensate composition, (Elsharkawy, 2002). Composition of the mole fraction. Density of the C₇₊ fraction is in g/cm³

Name	GC1	GC2	GC3	GC4	GC5
Mole fraction					
H ₂ S	0.0000	0.0000	0.0000	0.0001	0.0000
CO ₂	0.0000	0.0010	0.0095	0.0045	0.0098
N ₂	0.0000	0.0000	0.0077	0.0047	0.0066
C ₁	0.8238	0.9522	0.5980	0.6073	0.6810
C ₂	0.0428	0.0168	0.1415	0.1383	0.0700
C ₃	0.0351	0.0091	0.0689	0.0633	0.0505
<i>i</i> -C ₄	0.0161	0.0026	0.0140	0.0130	0.0179
<i>n</i> -C ₄	0.0303	0.0033	0.0252	0.0238	0.0198
<i>i</i> -C ₅	0.0060	0.0016	0.0102	0.0100	0.0162
<i>n</i> -C ₅	0.0068	0.0011	0.0119	0.0109	0.0108
C ₆	0.0099	0.0025	0.0175	0.0165	0.0177
C ₇₊	0.0292	0.0098	0.0956	0.1076	0.0997
MW _{C7+}	125	122.6	163	162	162
Density _{C7+}	0.74	0.723	0.791	0.789	0.807
Reservoir temperature (K)	278	378	416	416	398
DPP (MPa)	21.345	23.069	28.986	28.779	35.993

correlations were employed in accordance with Table 1. For illustrative purposes, the results obtained for the Gas Condensate 1 (GC1) are shown below, which correspond to the lowest Average Absolute Deviation (AAD) obtained for the Dew Point Pressure (DPP).

The molar distribution shown in Table 5 was carried out using 40 CN which were then lumped into 12 pseudocomponents. The boiling temperature correlation employed was S89 (*Tab. 1*), and the equation of state used for the minimization procedure was PR, giving rise to the critical properties also shown in Table 5. Similarly, the numbers of functional groups obtained for GC1 with CN = 40, PS = 12, Tb = S89 and EOS = PR are shown in Table 6.

As shown in Table 6, the proposed methodology allows the values of the number of functional groups to be non-integer numbers, unlike what is considered in traditional methods of group contribution. It should be noted that these values are hypothetical; that is, they do not correspond to those obtained from experimental analysis; they represent the amount of energy and mass needed from such groups, so that the free energy is minimum. Ultimately, the aim of this work is to find

structures that allow bulk properties to be estimated properly for phase equilibrium purposes.

Similarly to the results obtained by Carreón-Calderón *et al.* (2012), the numbers of functional groups shown in Table 6 are not distributed randomly; the same trends can be observed. For example, although incorporated simultaneously in calculations, some functional groups vanish for some pseudocomponents. It can be seen that the lightest pseudocomponents are characterized only by paraffinic functional groups, while cyclic and aromatic functional groups are incorporated into the molecular pseudostructure for the heavier pseudocomponents. In order to accomplish a sensitivity analysis of the different variables involved in the implementation of the CURR method, different tests for the five condensed gases under study were performed. To illustrate this, the results obtained for the condensate gas GC1 are shown in Table 7, where it can be seen that for different equations of state, mixing rules and numbers of pseudocomponents, the highest average absolute deviation is 3.75 for dew point pressure.

The results are similar to those obtained previously applying the CURR approach to light petroleum fluids,

TABLE 5
Molar distribution and critical properties calculated in this work for GC1

	Molar distribution			Critical properties calculated			
	Mole fraction	MW	SG	T_c (K)	P_c (MPa)	V_c (m ³ /mol)	ω
PS94	0.00908	94.0	0.6985	540.40	2.9563	4.0161E-04	0.3451
PS108	0.00626	108.0	0.7209	564.77	2.6760	4.5725E-04	0.3941
PS122	0.00431	122.0	0.7375	588.40	2.4317	5.1300E-04	0.4422
PS136	0.00297	136.0	0.7508	610.86	2.2209	5.6806E-04	0.4859
PS150	0.00205	150.0	0.7619	642.37	2.1217	6.0459E-04	0.4534
PS164	0.00141	164.0	0.7716	674.71	2.0619	6.3919E-04	0.4119
PS178	0.00097	178.0	0.7801	694.20	1.9187	6.8979E-04	0.4371
PS192	0.00067	192.0	0.7877	712.23	1.7901	7.4035E-04	0.4617
PS206	0.00046	206.0	0.7946	728.96	1.6737	7.9055E-04	0.4856
PS225	0.00054	225.7	0.8034	750.60	1.5277	8.6077E-04	0.5175
PS258	0.00033	258.6	0.8162	782.72	1.3242	9.7779E-04	0.5652
PS320	0.00016	321.0	0.8359	843.99	1.1560	1.1697E-03	0.6104

TABLE 6
Number of functional groups calculated for GC1, with 12 pseudocomponents

	Number of functional groups v								
	-CH ₃	-CH ₂	>CH-	>C<	-CH ₂ - (cyclic)	>CH- (cyclic)	>C< (cyclic)	ACH	AC-C
PS94	1.7752	4.7986	0	0	0	0	0	0	0
PS108	1.7236	5.8520	0	0	0	0	0	0	0
PS122	1.6962	6.8795	0	0	0	0	0	0	0
PS136	1.7966	7.6572	0.1215	0	0	0	0	0	0
PS150	3.1988	4.5371	1.6479	0	1.1983	0	0	0	0
PS164	3.7952	2.6892	1.5863	0.3940	2.7951	0	0	0.3554	0
PS178	4.0409	2.8788	1.7202	0.4690	2.9883	0	0	0.5315	0
PS192	4.2856	3.0683	1.8546	0.5453	3.1812	0	0	0.7073	0
PS206	4.5218	3.2470	1.9758	0.6060	3.3636	0.0707	0	0.8732	0
PS225	4.8435	3.4854	2.1312	0.6736	3.6076	0.2541	0	1.0945	0
PS258	5.3759	3.8823	2.3928	0.7924	4.0134	0.5612	0	1.4629	0
PS320	6.8420	3.9583	1.0824	0	4.2046	2.3387	3.2558	1.5336	0

TABLE 7
Percent Absolute Average Deviation (AAD) of Dew Point Pressure (DPP), for gas condensate GC1

Equation of state	Mixing rule	Tb correlation	Pseudocomponent			
			1	6	12	18
			% AAD			
PR	VDW	S89	3.08	0.21	0.52	0.33
	MHV1		2.87	0.16	0.10	0.18
	PSRK		3.75	1.38	1.51	1.59
RKS	VDW		3.35	3.56	3.47	3.30
	MHV1		2.68	2.83	2.73	2.62
	PSRK		1.52	1.25	1.43	1.12

where any combination of cubic equations of state and mixing rules provided similar results provided that the properties of undefined petroleum fractions came from the minimization problem given by Equation (15) and related expressions. The possible explanation is that the CURR approach provides optimized properties, satisfying the fundamental thermodynamic relationships and the mass balance for every undefined petroleum fraction under study. Thus, the pressure-volume-temperature behavior predicted by any fluid model should improve by using such optimized properties.

The boiling point correlation used to determine the critical temperature has a higher impact on the phase envelope than both the cubic equation of state and the mixing rule, as shown in Figure 2. These results confirm that the pseudocomponent properties to be used in fluid models have a higher impact on the phase equilibrium prediction than the fluid model itself, at least in the case of cubic equations of state and their respective mixing rules. The Absolute Average Deviation (AAD) for Dew Point Pressure (DPP) for every case is shown in Table 8.

It should be noted that the results obtained with an exponential distribution employing 12 pseudocomponents had lower AAD than those obtained employing less pseudocomponents, which agrees with the results obtained by Elsharkawy (2002), who established that splitting up the plus fraction into 10 to 12 pseudocomponents leads to minimum absolute average relative deviation. Another interesting result from Table 8 is that, in contrast to Pedersen's suggestion, the best carbon number is not 80; the influence of the carbon number on phase envelope was undetectable for practical purposes. Finally, it can also be observed that the best results are

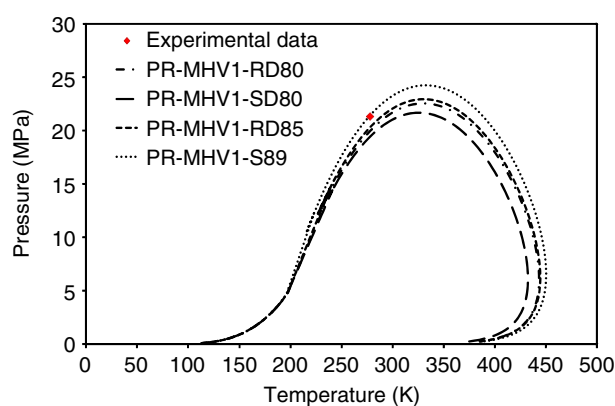


Figure 2

Phase envelope of CG1 using different correlations to estimate normal boiling temperature.

not always obtained using the same correlation for estimating boiling temperature, which shows again that properties to be used in cubic equations of state have a higher impact on the phase envelopes than the equations themselves.

Another aspect highlighted in the methodology shown in this work is that it is not necessary to adjust the parameters belonging to equations of state or their mixing rules in order to obtain a suitable estimation of the experimental data, as has been suggested elsewhere (Coats and Smart, 1986; Slot-Petersen, 1989; Merrill and Newley, 1993; Merrill *et al.*, 1994). Besides, the information needed to characterize the undefined heavy fraction is small: the molecular weight and specific

TABLE 8
Absolute Average Deviation (AAD) of equilibrium estimation of five gas condensates

Fluid	Mole fraction CH ₄	Mole fraction C ₇₊	CH ₄ /C ₇₊	Number of pseudocomponents	CN	Tb correlation	AAD (%)
GC1	0.8238	0.0292	28.21	12	40	S89	0.10
GC2	0.9522	0.0098	97.16	12	40	S89	1.65
GC3	0.598	0.0956	6.26	12	80	SD80	2.18
GC4	0.6073	0.1076	5.64	12	80	SD80	4.79
GC5	0.681	0.0997	6.83	12	80	SD80	0.24

gravity of just one undefined petroleum fraction: the C₇₊ fraction.

CONCLUSIONS

The results showed that the gas-condensate phase envelopes depend more on the properties assigned to the undefined heavy fraction than on the pressure-volume-temperature equations modeling such fluids. The procedure applied here provides optimized values of the critical properties and chemical pseudostructures. Thus, the choice of cubic equations of state or mixing rules with adjusted parameters is of little consequence to predict phase behavior properly.

It is also concluded that the CURR method of characterizing thermodynamically undefined heavy petroleum fractions of crude oil is also applicable for thermodynamic characterization of corresponding heavy fractions belonging to gas-condensate fluids, where experimental molar distribution is not provided. The experimental data required is minimal: the fluid global composition, and the molecular weight, specific gravity and the normal boiling point of the corresponding undefined heavy fraction.

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