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Modeling the characterization of the plus fractions by using continuous distribution function

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ABSTRACT

Heavy oil fluids contain large concentrations of high molecular weight components, hence large content of plus fractions. The hydrocarbon plus fractions that comprise a significant portion of naturally occurring hydrocarbon fluids cause major problems when determining the thermodynamic properties and the volumetric behavior of these fluids by equations of state. These problems arise due to the difficulty of properly characterizing the plus fractions. In order to split the plus fractions into single carbon numbers, generating the mole fraction and the respective molecular weight, a probability model that expresses the mole fraction as a continuous function of the molecular weight has been developed in this work. The developed method is based on the relationship between three parameter gamma distribution, experimental mole fraction, molecular weight and single carbon number data obtained from literature and industrial contracts. In the developed method, the three parameters of gamma distribution are obtained by the statistical regulation of gamma. The characterized mole distribution as a function of single carbon number is generated by integrating the gamma distribution between the limiting molecular weights to fit the characterized and experimental mole fractions. At least two previous carbon numbers and their mole fraction must be known to use the method. The proposed method was validated by using experimental extended fluid composition of different reservoir fluids and was compared to other splitting methods published in the literature. In addition, a worthwhile contribution of this paper is that some of the correlations which have been developed originally to predict the light oil physicochemical properties are tested for oil heavy samples to identify the ranges where they can be applied.

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1. Introduction

Reservoir fluids are composed of a lot of different hydrocarbons and non-hydrocarbons such as CO_2 , N_2 and H_2S . These hydrocarbon components can be classified as follow: (1) Defined components which have well known critical properties and acentric factor. (2) True boiling point (TBP) or single carbon number (SCN) components which have a measured or estimated molecular weight and specific gravity, and those critical properties are difficult to obtain experimentally. (3) Heavy ends (plus fraction) which has a measured mole fraction, molecular weight and specific gravity [1]. A conventional laboratory fluid composition report for reservoir fluids usually comprises the mole fraction or mole percent for non-hydrocarbon and methane through plus fraction, including the molecular weight and specific gravity of the plus fraction [2].

Equations of state (EOS) have been extensively used to generate phase behavior calculations of petroleum fluids. Peng-Robinson equation of state (PR-EOS) was originally developed to predict phase behavior for pure substances with known critical properties [3]. The use of EOS in multi-component mixtures, such as hydrocarbon mixtures, is possible by the application of the mixing rule. This means that critical properties and acentric factor should be known for all components of the mixture. There are several correlations in the literature for calculating critical properties and acentric factor for each SCN. For plus fraction, accurate properties can be calculated by accurate representations of the critical properties and acentric factor. The properties of the plus fraction are very sensitive to the phase behavior [4]. Direct measurement of the critical properties for heavy ends is not practical. So a proper description for the plus fraction is important to effectively predict the phase behavior of the fluid [5].

Characterization of plus fraction usually includes three steps: (1) Split the plus fraction into SCN or distillation cuts with known mole amounts and molecular weights. (2) Estimate the physicochemical properties such as critical pressure, critical temperature,

Abbreviations: TBP, true boiling point; TPG, three parameter gamma distribution; SCN, single carbon number; EOS, equations of state; PR, Peng–Robinson; LMW, limiting molecular weight; ARE, average relative error; AARE, absolute average relative error.

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boiling point, specific gravity and acentric factor of each fraction. (3) Group the generated SCN into pseudo-components and group the properties of the pseudo-components [6].

Proper characterization of the plus fraction has an important effect on phase behavior of the reservoir fluids by using the EOS. It can lead to erroneous prediction and calculation if the plus fraction is used directly as one component in calculations of EOS. Several samples of reservoir oil indicate that the plus C_{10+} contains a molar fraction close to 70% and the fraction C_{80+} is representative with values close to 2% [7]. The importance of characterizing the plus fraction increases when the oil sample has high molecular weight and high density [8].

There are several methods for splitting the plus fraction into SCN groups. The same number of carbon atoms is lumped in SCN with predefined value for properties like: P_C , T_C , T_b , ω and ρ among these methods. Katz [9] proposed the simplest method for splitting the plus fraction. The method used the exponential function which only requires the plus mole fraction of C_{7+} . Pedersen et al. [10] proposed a logarithmic relationship between the mole fraction and the carbon number for SCN. There are two mixture dependent constants determined from the measured weight fraction of the plus fraction.

Ahmed et al. [11] presented a concise method for extending the mole distribution for the heavy fractions of naturally occurring hydrocarbon systems from studying the mole behavior of thirtyfour hydrocarbon systems with a detailed laboratory compositional analyses of the heavy fraction.

Sportisse et al. [12] proposed a fitting based on the characterization of the plus fraction using three continuous distribution functions related to the following families: n-alkanes, n-alkyl benzenes and polyaromatics. The parameters of the distribution are fitted to improve the accuracy of constant composition liquid deposit curve calculation at the reservoir temperature.

Huang and Radosz [13] proposed a characterization procedure for plus fractions. A Gaussian-distribution function was used to split the plus fraction into SCN considering that the no uniform lumping is more efficient. They raised a benchmark to compare efficiency of various lumping approaches which are a continuous thermodynamic model of phase equilibrium.

Among characterization methods, the most general approach is by Whitson [14], who presented a method using the three parameter gamma distribution (TPG) to estimate the mole fraction of SCN. The molecular weights were obtained by the Katz correlation [9] for each SCN.

Each SCN contains hundreds of isomers with the same carbon number. It is not possible to set a unique value of molecular weight, critical properties and acentric factor, because of the uncertain of the isomers presented in each SCN [15]. The object of this study is to find an accurate method for splitting the hydrocarbon plus fraction to a respective numbers of SCN and calculating their mole fraction and molecular weight, and then use the method validating experimental extended fluid compositions of different petroleum fluids. Also, the proposed method will be compared with other methods published in the literature.

Generalized correlations have been developed to predict physicochemical properties originally to work with light oil, such as Kesler–Lee [16], Winn [17], Pederson–Fredenslund [18], Sancet [19], Twu [20], Ahmed [5], and Edmister [21]. Some of these correlations are tested for heavy oil samples to identify the ranges where they can be applied in this work.

2. Theory

2.1. Whitson's method to estimate the mole fraction distribution

Whitson [22] proposed a three parameter gamma (TPG) probability distribution function to describe the relation between mole fraction and molecular weight of SCN components of the C_{7+} fractions. The Gauss–Laguerre quadrature method was used to generate the mole fraction of SCN. This method is widely used recently, especially for heavy oil [23]. The molar fraction for each SCN is calculated by cumulative frequency of occurrence between the limits M_{i-1} and M_i multiplied by the mole fraction of the plus fraction.

$$z_{i} = z_{C_{n+}} \int_{M_{i-1}}^{M_{i}} p(M) dM$$
(1)

where z_i is the mole fraction of each SCN group. $z_{C_{n+}}$ is the mole fraction of the C_{n+} fraction. M_{i-1} and M_i represent the molecular weight of single carbon neighborhood number. *i* is the single carbon number. The probability density function, p(M) is as follow:

$$p(M) = \frac{(M - \gamma)^{\alpha - 1} \exp[-(M - \gamma)/\beta]}{\beta^{\alpha} \Gamma(\alpha)}$$
(2)

where α , β and γ are the characteristic parameters of the gamma distribution. γ is the minimum molecular weight presents in the C_{n+} fraction. α is used to fit the shape of distribution. η is the minimum molecular weight presents in the C_{n+} fraction and Γ is the gamma function. When $\alpha = 1$, the gamma distribution function reduces to a simple exponential distribution form.

$$\gamma = 14n - 6 \tag{3}$$

$$\alpha \cdot \beta = M_{C_{n+}} - \gamma \tag{4}$$

2.2. Physicochemical properties estimation

Each SCN group contains hundreds of isomers with the same number of carbon atom. Due to the uncertainty of the isomers presented in each SCN group, it is not possible to set the unique value of the physicochemical properties such as critical temperature, critical pressure and acentric factor by the experimental and literature database. Several correlations have been developed to estimate the physical properties of petroleum fractions. They are in principal function of the boiling point temperature, the specific gravity and the molecular weight. The correlations are as follows: Kesler–Lee [16], Winn [17], Pederson–Fredenslund [18], Sancet [19], Twu [20], Ahmed [5], Edmister [21], etc.

2.3. Lumping method

By splitting the plus fraction into large number of components with their respective mole fractions and physical properties, an appropriate mole distribution that represents the plus fraction is generated. The use of the components in a reservoir simulation is tedious and time-consuming. So the reduction of the number of components used in equations of state calculations for reservoir fluids is needed, defined as lumping.

Whitson [14] proposed a method for deciding which carbon number fractions to be lumped into the same pseudo-component and the number of multiple carbon numbers groups (MCN). The number of groups (N_g) is defined as:

$$N_{\rm g} = \inf[1 + 3.3 \log(N - n)] \tag{5}$$

where *N* is the number of carbon atoms of the last SCN generated by the characterization process, *n* is the number of carbon atoms of the first SCN within the C_{n+} fraction.

The molecular weights separating each *MCN* group are determined by:

$$M_I = M_{C_{n+}} \left(\frac{M_{N+}}{M_{C_{n+}}}\right)^{I/N_g} \tag{6}$$

where M_{N^+} is the molecular weight of the last SCN, $M_{C_{n^+}}$ is the molecular weight of the first SCN. *I* represents 1, 2, 3, . . . , N_g .

The Hong's mixing rule is used to average T_C , P_C , ω of the individual carbon number fractions to one T_C , P_C , ω to represent the lumped pseudo-components.

The weight fraction average w_i for the mixing parameter in characterizing is defined as:

$$w_i = \frac{z_i M_i}{\sum_{i \in L}^{L} z_i M_i} \tag{7}$$

where *L* is the lumped fraction:

The mixing rule for properties of the MCN is:

$$\Gamma_L = \sum_{i \in L}^{L} w_i \Gamma_i \tag{8}$$

where Γ represents different properties: pseudo critical pressure P_{cL} , pseudo critical temperature T_{cL} , pseudo volume V_{cL} , pseudo acentric factor ω_L and pseudo molecular weight M_L .

3. Methodology

The developed method for splitting the hydrocarbon plus fraction is based on a modification of Whitson's approach [14]. The approach is based on the fact that SCN group with varied contents of paraffine, naphtene and aromatic compounds with the same number of carbon atoms. It is very important to determine the value of parameter α in the gamma distribution method. Whitson [22] used the empirical relation [24] to estimate the value of α . However, it is necessary to have SCN mole fractions and molecular weights accurately measured. It should also constitute a full compositional analysis and such analyses are nearly nonexistent. The method is not available if there is no experimental data of higher carbon. That is, if only the mole fraction of plus fraction is provided, the SCN mole fraction cannot be calculated by this method.

3.1. Determination of α

The modification of Whitson's method [14] includes a simple procedure to determine the value of α and a new definition of the limits used to calculate the frequency of occurrence for each single carbon number.

 α defines the shape of the mole fraction distribution. The mole distribution of normal and heavy oil system is left skewed which means that the value of α is higher than 1 for a characterization with TGB. The exponential distribution characteristic of condensate and light hydrocarbon system means that the value of α is equal to 1, seen from Fig. 1.

If the molecular weight for the maximum mole fraction of experimental data has the same value with the molecular weight of the maximum value of TGB, the best trend fit is found. The value of molecular weight for the maximum mole fraction of the previous carbon, Mw_{max} , can be obtained by the experiment. The derivative with the molecular weight of Eq. (2) is calculated by

$$\frac{dp(M)}{dM} = \frac{(\alpha - 1)(M - \gamma)^{\alpha - 2} \exp[-(M - \gamma)/\beta]}{\beta^{\alpha} \Gamma(\alpha)} - \frac{(M - \gamma)^{\alpha - 1} \exp[-(M - \gamma)/\beta]}{\beta^{\alpha + 1} \Gamma(\alpha)}$$
(9)

If take the molecular weight to Mw_{max} , the value of the Eq. (9) will be 0. So

$$\left. \frac{dp(M)}{dM} \right|_{Mw_{\text{max}}} = 0 \tag{10}$$

The parameters α , β and γ can be determined by combining and solving Eqs. (3), (4) and (10). Once the parameters α , β and η



Fig. 1. The mole fraction characterization of different oil systems.

have been determined, the weight boundaries M_{i-1} and M_i in the integral of Eq. (1) determined by the new limits are different from the Whitson's method [14]. The length between molecular weight boundaries is set to a constant. It may cause a great error because uncertainty of the types and distribution of compounds present in each single carbon number from one sample to another.

3.2. New weight boundaries for cumulative frequency of occurrence of SCN

The new weight boundaries to calculate the cumulative frequency of occurrence are defined by the best fit between TPG and the experimental mole fraction (z_{exp}). Determining the new boundaries is based on the relationship between TPG and the z_{exp} of previous carbon number, such as C_7 through C_{29} , if C_{30+} fraction is characterized. In order to establish the function of limiting molecular weight (*LMW*) versus carbon number of SCN, at least two previous carbon numbers and their mole fraction must be known to use this approach. The relationship between TPG and z_{exp} is found by iteration and described as a function of *LMW* versus carbon number.

The new definition of the limits, *LMW*, is introduced. Eq. (1) is then transformed to:

$$z_{cal}(C_i) = z_{C_{n+}} \int_{LMW_{i-1}}^{LMW_i} p(M) dM$$
(11)

where LMW_{i-1} and LMW_i are the lower and upper limiting molecular weight. The first lower boundary is set by γ (Eq. (3) or by defining molecular weight of the first component). The upper boundary is then varied until the calculated SCN mole, $z_{cal}(C_i)$ is matched with the experimental mole $z_{exp}(C_i)$. The result of upper boundary is then used as the lower boundary for the next SCN. The function of LMW versus SCN from C_7 to C_{n-1} is generated. The use of C_{7+} fraction is arbitrary and any other plus fraction can be used. It is recommended to generate as many values of LMW function of SCN as possible [25].

LMW is calculated by the best fit between $z_{cal}(C_7)$ and $z_{exp}(C_7)$ with the following iterative:

- (a) Get the lower boundary $LMW_6 = \gamma$, $z_{cal}(C_7)$ is obtained by the first estimation of the limiting molecular weight.
- (b) If $|z_{cal}(C_7) z_{exp}(C_7)| > \varepsilon$ then adjust the upper boundary *LMW*₇ for each iteration.
- (c) The process is repeated until $|z_{cal}(C_7) z_{exp}(C_7)| \le \varepsilon$.



Fig. 2. The program frame of the developed method.

(d) The last LMW_7 is regarded as lower boundary in the calculating $z_{cal}(C_8)$.

The process to characterize carbon numbers higher than 7 is similar with the iterative process presented above. The function of *LMW* versus carbon number can be generated for carbon number from 7 to C_{n-1} by the least square fitting. The process is illustrated in Fig. 2.

The approach proposed requires to define the *LMW* that will be used to split the C_{n+} fraction into SCN. The function *LMW* versus SCN generated previously is extrapolated in order to adjust the molecular weight of plus fraction. The simplest function is linear, which demands at least two previous carbon numbers and their respective mole fractions to determine. The calculation precision has a direct relation with the numbers of previous carbon. It requires less experiment data than the Whitson method [14].

The molecular weight for each SCN is given by

$$M_{i} = \gamma + \alpha \beta \frac{P(LMW_{i}, \alpha + 1) - P(LMW_{i-1}, \alpha + 1)}{P(LMW_{i}, \alpha) - P(LMW_{i-1}, \alpha)}$$
(12)

where $P(X, \alpha)$ is the cumulative probability function defined as the integral of $p(x \le X)$ from γ to X:

$$P(x \le X) = \int_{\gamma}^{X} p(x) dx \tag{13}$$

In order to compare the accuracy of proposed methods for splitting the plus fraction into SCN, the first step is to group the experimental extended fluid composition to C_{7+} . The procedure is as follows:

(a) Group the extended experimental composition to a plus fraction of C_{7+} , the mole fraction of C_{7+} is calculated as:

$$z_{C_{7+}} = \sum_{i=7}^{n} z_i \tag{14}$$

(b) The molecular weight and specific gravity of the new plus fraction C₇₊ can be calculated as follows:

$$M_{C_{7+}} = \frac{\sum_{i=7}^{n} z_i M_i}{z_{C_{7+}}}$$
(15)

$$\gamma_{C_{7+}} = \frac{\sum_{i=7}^{N} z_i M_i}{\sum_{i=7}^{N_e} z_i M_i / \gamma_i}$$
(16)

The second step is to split the new plus fraction C_{7+} to original extended experimental plus fraction by using the developed method. Each grouped composition will be extended to C_{n+} in order to observe the values of molecular weight of C_{n+} . The molecular weight of C_{n+} must be greater than the molecular weight of SCN n-1.

The last step is to compare the experimental mole fraction with the calculated, with the average relative error, ARE and the absolute average relative error, AARE:

$$ARE = \frac{\sum_{C_7}^{N} (Z_{icalc} - Z_{iexp}) / Z_{iexp}}{N}$$
(17)

$$AARE = \frac{\sum_{C_7}^{n} |Z_{icalc} - Z_{iexp}| / Z_{iexp}}{N}$$
(18)

where Z_{iexp} and Z_{icalc} are the experimental and calculated mole fractions for component *i*, respectively. *N* is the total number of SCN extended from 7 to the plus fraction.

If hydrocarbon plus fraction C_{7+} is extended to SCN *n*, the mole fraction and molecular weight of the final group are calculated as follows:

$$z_{C_{n+}} = z_{plus} - \sum_{i=7}^{n-1} z_i$$
(19)

$$M_{C_{n+}} = \frac{z_{plus}M_{plus} - \sum_{i=7}^{n-1} z_i M_i}{z_{C_{n+}}}$$
(20)

The developed method has been compared with four different methods that used for splitting the hydrocarbon plus fraction. These methods are as follows: Pedersen method [6], Katz method [9] and Whitson method [14].

4. Results and discussion

The developed method here is a modification of Whitson's approach [14]. The uncertainty association with the molecular weight assigned to carbon number was a motivation to develop this method. In order to validate the developed method, 14 different extended experimental fluid compositions have been used. These fluid compositions have different plus fractions, such as C_{20+} , C_{30+} , C_{35+} , C_{36+} and C_{45+} . The main characterization for these fluids is presented in Table 1. As shown from Table 1, this set of data covers a wide range of C_{7+} mole fraction of 5.45–98.46%, which covers gas condensates, volatile oils, black oil and heavy oils. The range has been selected to check the developed methods whether or not work for all reservoir fluid types used in compositional simulation. Samples 1 through 10 are from Al-Meshari et al. [26], the data for Sample 11 is taken from Rodriguez and Hamouda [27], and Samples 12–14 are from Krejbjerg and Pedersen [28].

 Table 1

 Summary for the fluids used in this study.

Fluid	C_{n^+}	$Z_{C_{n+}}$	$M_{C_{n+}}$	$\gamma_{C_{n+}}$	$Z_{C_{7+}}$	$M_{C_{7+}}$	$\gamma_{C_{7+}}$
Sample 1	C36	0.0003	578	0.93	0.054	158	0.79
Sample 2	C30	0.0031	519.3	0.80	0.061	204	0.82
Sample 3	C20	0.0039	337	0.88	0.065	148	0.79
Sample 4	C20	0.0099	490	0.88	0.10	173	0.80
Sample 5	C20	0.047	478.8	0.92	0.14	255	0.87
Sample 6	C20	0.047	415	0.92	0.15	232	0.86
Sample 7	C30	0.010	588	1.01	0.18	189	0.83
Sample 8	C36	0.015	887	1.01	0.23	261	0.87
Sample 9	C45	0.017	2607.3	1.15	0.28	346.6	0.92
Sample 10	C36	0.040	593	1.01	0.34	245.2	0.87
Sample 11	C35	0.26	1038.1	0.97	0.79	527.9	0.79
Sample 12	C30	0.09	449.1	0.98	0.46	226.3	0.92
Sample 13	C41	0.15	761	1.002	0.98	331.5	0.96
Sample 14	C36	0.25	1038.1	1.11	0.78	539.2	0.94

4.1. Verification of the developed method

The developed method is used to calculate the cumulative frequency of occurrence and the results for each method presented below.

Table 2 shows the average relative errors that were calculated using Eq. (17) for all fluids when the experimental extended composition is grouped to C_{7+} and then extended to the original plus fraction. In the developed method, the first half of experimental extended compositions is used to generate the function *LMW* versus SCN. The rest of the half is used to compare with the mole fraction calculated by Eq. (12) using the extrapolated function *LMW* versus SCN.

As shown in Tables 2–5, the method applied to calculate the cumulative frequency of occurrence of the experimental fluid composition will result a reasonable mole fraction for SCN, which will receive lower average relative error (0.000066, 0.00089) and absolute average relative error (0.00049, 0.0089). The calculation results of the mole fraction are well with those of experiments.

The calculated molecular weight for carbon numbers between C_7 and C_n are generated by using Eq. (12) in the developed method. The molecular weights of C_{n+} calculated using Eq. (20) in this case are all higher than the experiments and reasonable absolute average relative error (0.011, 0.0985), seen in Tables 6–8.

4.2. Comparing the developed method with other methods

The proposed method to split the hydrocarbon plus fraction has been compared with three different methods that were used for splitting the hydrocarbon plus fraction. These methods are as follows: Pedersen method [6], Katz method [9] and Whitson method

Table 2

C	omparison	results	ot	mol	e	trac	tion,	ARE.
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Fluid	Average relative error					
	Method	Pedersen	Katz	Whitson		
Sample 1	0.000066	-0.029	0.38	-0.016		
Sample 2	0.00019	-0.023	0.31	-0.14		
Sample 3	0.00029	-0.011	0.0094	-0.24		
Sample 4	0.00066	-0.0075	0.072	-0.43		
Sample 5	0.00073	-0.0017	-0.14	-2.47		
Sample 6	0.00082	-0.0028	-0.12	-1.06		
Sample 7	0.00049	-0.0097	0.32	-0.11		
Sample 8	0.00051	-0.0041	0.35	-0.089		
Sample 9	0.00056	-0.016	0.44	-0.15		
Sample 10	0.00072	-0.0058	0.41	-0.22		
Sample 11	0.00078	-0.39	-7.43	-2.14		
Sample 12	0.00081	-0.0052	0.21	-0.64		
Sample 13	0.00089	-0.11	-0.065	-0.47		
Sample 14	0.00081	-0.348	-6.78	-1.96		

Table 3
Comparison results of mole fraction, AARE.

Fluid	Absolute average relative error				
	Method	Pedersen	Katz	Whitson	
Sample 1	0.0061	0.16	0.49	0.268	
Sample 2	0.0019	0.17	0.61	0.31	
Sample 3	0.0029	0.11	0.12	0.31	
Sample 4	0.0066	0.098	0.21	0.52	
Sample 5	0.00073	0.052	0.42	2.54	
Sample 6	0.00082	0.069	0.44	1.18	
Sample 7	0.00049	0.11	0.47	0.42	
Sample 8	0.0051	0.071	0.64	0.23	
Sample 9	0.0056	0.13	0.95	0.31	
Sample 10	0.0072	0.091	0.69	0.44	
Sample 11	0.0078	0.81	8.61	2.19	
Sample 12	0.0081	0.076	0.71	0.69	
Sample 13	0.0089	0.33	1.38	2.01	
Sample 14	0.00081	0.72	7.97	0.54	

Table 4

Comparison results summary of mole fraction, ARE.

Method used	z _i Average relative error ((Calc. – Exp.)/Exp.)				
	Maximum	Mean	Minimum		
Method	0.00089	0.00059	0.000066		
Pedersen	-0.0017	-0.068	-0.39		
Katz	0.44	-0.85	-7.43		
Whitson	-0.016	-0.72	-2.47		

Table 5

Comparison results summary of mole fraction, AARE.

Method used	c. – Exp.) /Exp.)		
	Maximum	Mean	Minimum
Method	0.0089	0.0045	0.00049
Pedersen	0.81	0.21	0.052
Katz	8.61	1.69	0.12
Whitson	2.54	0.85	0.23

[14]. Tables 2 and 3 show the comparison results of mole fraction for each carbon number using Eqs. (17) and (20) between the proposed methods and these three methods. Tables 4 and 5 give the summary of the comparison results of average relative error and absolute average relative error respectively. Tables 6–8 show comparison results of molecular weight of C_{n+} .

The proposed method is the most accurate method to split hydrocarbon plus fraction for different reservoir fluids especially those used in compositional simulations compared with the other

Table 6Comparison results of molecular weight of C_{n+}.

Fluid	C_{n+}	$M_{C_{n+}}$				
		Experiment	Method	Pedersen	Katz	Whitson
Sample 1	C ₃₆₊	578	596.03	626.58	654.12	653.83
Sample 2	C_{30^+}	519.3	526.25	569.54	578.28	578.18
Sample 3	C_{20^+}	337	362.2	357.77	378.23	398.21
Sample 4	C_{20^+}	490	504.56	508.21	543.12	542.32
Sample 5	C_{20^+}	478.8	524.52	497.41	644.88	563.23
Sample 6	C_{20^+}	415	455.91	431.57	583.39	478.32
Sample 7	C_{30^+}	588	621.32	652.47	909.55	687.23
Sample 8	C_{36^+}	887	901.45	928.37	1460.91	1123.54
Sample 9	C_{45+}	2607.3	2635.21	2869.91	3433.52	2963.12
Sample 10	C_{36^+}	593	613.88	625.05	756.65	654.32
Sample 11	C_{35+}	1038.1	1068.75	1260.31	1154.24	1130.25
Sample 12	C_{30^+}	449.1	489.21	532.64	569.32	496.32
Sample 13	C_{41+}	761	815.25	986.21	869.52	856.32
Sample 14	$C_{36^{+}}$	1038.1	1098.23	1310.96	1456.31	1125.32

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Table 7						
Comparison	results	of mole	ecular	weight	of	Cn+.

Fluid	C_{n+}	<i>M_{Cn+}</i> Absolute average relative error ((Calc. – Exp.) /Exp.)				
		Experiment	Method	Pedersen	Katz	Whitson
Sample 1	C ₃₆₊	578	0.031	0.084	0.13	0.13
Sample 2	C_{30+}	519.3	0.013	0.097	0.11	0.11
Sample 3	C_{20+}	337	0.075	0.062	0.12	0.18
Sample 4	$C_{20^{+}}$	490	0.030	0.037	0.11	0.10
Sample 5	$C_{20^{+}}$	478.8	0.095	0.039	0.34	0.17
Sample 6	$C_{20^{+}}$	415	0.099	0.040	0.41	0.15
Sample 7	C_{30^+}	588	0.057	0.110	0.54	0.16
Sample 8	C_{36^+}	887	0.016	0.047	0.64	0.26
Sample 9	C_{45+}	2607.3	0.011	0.101	0.31	0.13
Sample 10	C_{36^+}	593	0.035	0.054	0.27	0.10
Sample 11	C_{35+}	1038.1	0.030	0.214	0.11	0.08
Sample 12	C_{30^+}	449.1	0.089	0.186	0.26	0.10
Sample 13	C_{41+}	761	0.071	0.296	0.14	0.12
Sample 14	C_{36^+}	1038.1	0.058	0.263	0.41	0.08

three methods used in this study. The accuracy of this method depends on the previous carbon numbers and their respective mole fraction. The molecular weight of C_{n+} is very well with the experiment and the mole fraction of SCN is also in agreement with the experiment, so calculation on the molecular weight of SCN is accurate using this method. The developed method has a good accuracy for different reservoir fluids. It has more extensively applicable scope than the other three methods.

The Pedersen method [6] is not suitable for multiple samples because each sample has its own coefficients A and B. This method does not honor the properties of plus fraction. This method is more suitable for the gas condensate and volatile oil systems. When this method is used for black oils and heavy oils, the average relative error and absolute average relative error both have higher error.

The Katz method [9] was tested and proposed using gas condensate sample and it does not work for the oil sample. The range of C_{7+} mole % for the samples used to develop the correlation is 1.5–8%. It is the simplest way to use and the least accurate compared with the other methods used in this study. The mean of absolute average relative error is as high as 169.56%.

The Whitson method [14] has a comparable accuracy with the Pedersen method.

4.3. Estimation of critical properties for SCN

The critical physical properties for each SCN are obtained by the correlations that are primary function of boiling temperature, specific gravity, molecular weight and carbon number. These correlations are developed to calculate properties of SCN fraction with low number of carbon atom originally. Prediction of physical properties for oil samples with high carbon number demonstrates the range where different correlations could be used. The physical properties include: critical pressure, critical temperature, boiling temperature, acentric factor and specific gravity.

Table 8

Comparison result summary of molecular weight of C_{n+} .

Method used	M _{Cn+} Absolute average	$M_{C_{n+}}$ Absolute average relative error ((Calc Exp.) /Exp.)				
	Maximum	Mean	Minimum			
Method	0.0985	0.050	0.011			
Pedersen	0.29	0.11	0.037			
Katz	0.64	0.28	0.10			
Whitson	0.26	0.13	0.084			



Fig. 3. Critical pressure calculated with different correlations of SCN.

4.3.1. Critical pressure

Some methods have been studied before. Critical pressure is calculated with eight different correlations. Table 9 shows the properties needed to calculate critical pressure by using the correlations studied. The used correlations for calculating properties are included in Table 9.

The values of critical pressure are presented as a function of carbon number and shown in Fig. 3. As shown, three ranges are identified in Fig. 3 in order to determine the applicable carbon number range.

Region I includes carbon number lower than 20 and shows that all the correlations follow a similar trend, however there are two categories. The Sancet and Twu correlations are in the same category and deviate significantly from the other correlations including the Kesler–Lee, Winn, Pederson–Fredenslund and Ahmed correlations at carbon numbers 7 and 20, respectively.

Region II can be defined as carbon numbers between 20 and 60; in this region, the values calculated by the studied correlations follow a similar trend except for the Ahmed correlation, as shown in Fig. 3. The values predicted by the correlations show significant different, which makes it difficult to identify the accurate critical pressure without experimental verification.

In Region III critical pressures calculated for carbon numbers higher than 60 are approaching asymptotes. None of the six correlations in this region can be identified to be superior to the others. The values predicted by the correlations are very different and the difference between the maximum and minimum is 1.2 MPa at the carbon number 100.

4.3.2. Critical temperature

Table 10 shows the used critical temperature correlations and the used functional variables for each correlation method. Critical temperature is obtained as a function of the carbon number with six correlations, as shown in Fig. 4.

All the correlations applied to calculate critical temperature practically have the similar result for carbon numbers lower than 40, as shown in Fig. 4. Correlations by Pederson–Fredenslund and Ahmed do not seem to be available for carbon higher than 60. Kesler–Lee, Winn and Sancet practically calculate the same values for all the studied carbon number, giving an advantage to the Sancet correlation because it is the just function of molecular weight. Twu correlation has a lower value compared with the three correlations for carbon numbers above 40. Difference in temperature of 100 K is presented between the Winn and Twu correlation at the carbon number 100.

Table 9

Dependency of the correlation for critical pressure.

	Correlation	Functional variable	Origin of the functional variable
	Kesler–Lee	SG and T _b	Logarithmic and Twu correlation
	Winn	SG and T _b	Logarithmic and Twu correlation
Critical management	Pederson–Fredenslund	SG and M	Logarithmic
Critical pressure	Sancet	Μ	Method developed
	Twu	T_b and T_c	Twu correlation
	Ahmed	Cn	

Table 10

Dependency of the correlation for critical temperature.

	Correlation	Functional variable	Origin of the functional variable
	Kesler–Lee	SG and T _b	Logarithmic and Twu correlation
	Win	SG and T_b	Logarithmic and Twu correlation
Critical	Pederson–Fredenslund	SG and M	Logarithmic
temperature	Sancet	Μ	Method developed
	Twu	T_b	Twu correlation
	Ahmed	C_n	

Table 11

Dependency of the correlation for boiling point temperature.

	Correlation	Functional variable	Origin of the functional variable
Boiling point temperature	Sancet Twu Ahmed	M M C _n	Method developed Method developed

Table 12

Dependency of the correlation for acentric factor.

	Correlation	Functional variable	Origin of the functional variable
Acentric factor	Kesler–Lee Pederson–Fredenslund Ahmed Edmister Edmister Edmister Edmister	P_c, T_c and T_b, M and SG SG and M C_n P_c, T_c and T_b P_c, T_c and T_b P_c, T_c and T_b	Kesler-Lee, Twu method developed logarithmic Logarithmic Ahmed Sancet Twu

Table 13

Summary of the application ranges for the different correlations.

Dronoutry	Range of carbon numbers and correlations valid			
rioperty	7-20	7-40	7-60	7-inf
		Kesler-Lee		
		Winn		
	I	Pederson-Fredenslu	und	
Critical Pressure		Sancet		
		Twu		
	Ahmed	l		
		Kesler-Lee		
		Win		
Critical	Pederso	n-Fredenslund		
Temperature		Sancet		
		Twu		
		Ahmed		
		Sancet		
Boiling Point		Twu		
Temperature		Ahmed		
		Ahmed		
Specific Gravity	Logarithmic			
		Kesler-Lee		
	Pederson-Fredenslun	d		
Acentric Factor	Edmister-A	hmed		
	Edmister-Sa	ancet		
		Edmister-Twu		



Fig. 4. Critical temperature calculated with different correlations of SCN.

4.3.3. Boiling point temperature

Boiling point temperature is obtained as a function of carbon number with three correlations. The correlations and the origin of function variables applied to predict the critical temperature are shown in Table 11.

Ahmed, Twu and Sancet correlations are used to predict the boiling point temperature of SCN. Fig. 5 shows the boiling point temperature as a function of carbon number. The three correlations show similar predictions for carbon number lower than 40. Twu and Sancet correlations have a similar trend when the physical property is calculated for carbon number higher than 40. Sancet predict a higher value of physical property if compared with Twu. Values calculated by the Ahmed correlation show that the boiling point temperature for carbon numbers higher than 60 do not follow the same trend as that for the other two correlations.

4.3.4. Specific gravity

The critical properties with Kesler–Lee and Pederson–Fredenslund need specific gravity. The only correlation available for calculating specific gravity as a function of carbon number is Ahmed correlation, as far as we know. The Ahmed has a maximum value of carbon number 70, and at higher carbon number the specific gravity decreases, which does not seem to be logical, so a logarithmic correlation of specific gravity versus carbon number is generated from literature values.

The logarithmic correlation is:

$$SG = 0.1129 \ln(C_n) + 0.5203$$



Fig. 5. Boiling point temperature calculated with different correlations of SCN.



Fig. 6. Specific gravity calculated with different correlations of SCN.



Fig. 7. Acentric factor calculated with different correlations of SCN.

The two correlations used present an almost similar prediction for carbon numbers lower than 70, as shown in Fig. 6. For carbon numbers higher than 70, it is observed that Ahmed correlation shows a decreasing trend but the Logarithmic correlation does not.

4.3.5. Acentric factor

(21)

Acentric factor is obtained as a function of carbon number with four correlations. Correlations for acentric factor depend on some physical properties predicted by some proposed correlations. So the Edmister correlation can combine with the Ahmed, Sancet and Twu correlations. The dependence is shown with the origin of functional variable in Table 12.

All the correlations proposed present almost similar values for carbon numbers lower than 20, as shown in Fig. 7. For carbon numbers between 20 and 40, the Edmister correlation with critical properties obtained by Twu, Kesler–Lee and Ahmed has similar predictions. The values of acentric factor calculated by Kesler–Lee and Edmister–Twu correlation may be correct when carbon numbers are higher than 40.

Table 14
Relationship between number of SCN and number of pseudo-component

Fluid	Number of SCN	Number of pseudo-component
Sample 12	136	8
Sample 13	176	8
Sample 14	297	9

Table 15	
Saturation pressure obtained by developed method and Pedersen method with PR-EOS.	

Fluid	Reservoir temperature (°C)	Experimental saturation pressure (MPa)	aturation pressure (MPa) Calculated saturation pres	
			Method	Pedersen
Sample 12	52	3.64	3.86 (6.04%)	4.08 (12.09%)
Sample 13	63.2	7.61	7.78 (2.23%)	9.06 (19.05%)
Sample 14	66.6	6.01	5.42 (9.8%)	8.02 (33.44%)

4.4. Summary of the used correlation limits to calculate physical properties

The observations identified for each correlation and physical property are used to determine the ranges where the correlations may be used to calculate a specific property, as shown in Table 13.

4.5. Predictions of PVT properties with PR-EOS

A commercial simulator (PVTsim) is used to calculate the saturation pressure of Samples 12–14. The mole fractions of all SCN are calculated by the developed model. Whitson's lumping scheme is used to obtain the number of pseudo-components. The applied physical-chemical properties are: critical pressure and critical pressure generated by Sancet correlation, and the acentric factor obtained by Kesler–Lee correlation. The mole fraction of each pseudo-component is calculated by adding the mole fraction of all SCN within the pseudo-components carbon number. The critical property of each MCN is obtained by the Hong's mixing rule.

Table 14 shows the number of pseudo-components and single carbon numbers for the studied fluid.

In order to study the effect of the characterized plus fraction on saturation pressure, the fraction of each SCN is calculated by the developed method and Pedersen method, respectively, because the Pedersen method [6] is more accurate than the Katz method [9] and Whitson method [14], seen from Table 5 in this study. The other parts, such as the critical properties, the lumping scheme and the mixing rule, are all the same.

Table 15 compares experimental and predicted values of saturation pressure by the developed method and Pedersen method with PR-EOS at reservoir temperature. The error in the prediction of saturation pressure is different for each fluid, from 2.23% for sample 13 until 9.8% for sample 14 by using values of the developed method. For all the three fluids, the saturation pressure using developed method has higher accuracy than the Pedersen method.

5. Conclusions

The developed method for characterizing plus fraction is not only limited to heptanes-plus (C_{7+}). In order to establish the function of limiting molecular weight to SCN, at least two previous carbon numbers and their mole fractions must be known to use this approach. The parameters of gamma probability function are obtained by the frequency of occurrence for the previous carbon fraction. Linear extrapolation of the limiting molecular weight as a function of carbon number is used to extend the characterization to the missing data of higher carbon number. So the accuracy of computation is affected by the distribution features of previous carbon.

Classical cubic equations of state are applicable to simulate the phase behavior of heavy reservoir oil mixtures. In this work, a method is proposed to characterize plus fraction (C_{7+}) of crude oil by using literature database. Due to the exponential increase of components number with the increasing carbon number, the molecular weight did not uniquely relate to the carbon number, and based on which the developed method. In the method, the TPG distribution from Whitson's method [14] is used to characterize plus

fraction. The α , β , η parameters of TPG distribution are obtained based on the statistical property of TPG in the method. It is applied to find the best trend to fit to the experimental data and obtain the limiting molecular weight. The extrapolating of the limiting molecular weight as a function of carbon number is used to extend the characterization to the missing data of higher carbon number. It is necessary that at least two previous carbon numbers and their respective mole fractions must be known.

The developed method was applied to 14 different oil samples that cover gas condensates, volatile oils, black oil and heavy oils. Different methods have been used to compare with it. The predicted mole fraction is shown to be the most close to experimental data associated with carbon number using the method. The method is appropriate for every reservoir fluid type. The molecular weight is different from one sample to another, which perhaps reflects the difference in the molecular weight for each single carbon number.

Different correlations have been used to determine the critical properties, which may be summarized as follows:

The calculated critical pressure as a function of carbon number can be divided into three regions: the first region, from 7 to 20, shows that all the correlations follow a similar trend. In the second region from carbon number 20 to 60, the values calculated by the studied correlations follow a similar trend except for the Ahmed correlation. In the third region for carbon number higher than 60, none of the six correlations can be identified to be superior to the others. The Sancet and Kesler–Lee correlations have similar values of critical pressure, while the Winn and Pederson–Fredenslund overestimate it the Twu underestimate it, and the value obtained by Ahmed correlation largely deviates from the Sancet and Kesler–Lee's.

The predicted critical temperature as a function of carbon number shows that the correlations by Kesler–Lee, Win, Pederson–Fredenslund, Sancet, Twu and Ahmed result in a good agreement for carbon number less than 40 However, the correlation follow a same trend except Pederson–Fredenslund and Ahmed correlations for carbon number higher than 40. The other four correlations have the similar values.

The calculated boiling point temperatures by Sancet, Twu and Ahmed correlations are merely same for carbon number less than 60. Ahmed method does not follow the same trend as the Sancet and Twu's for carbon number higher than 60.

The specific gravity is needed for Kesler–Lee and Pederson–Fredenslund correlations to calculate critical properties. The Ahmed correlation that calculates the specific gravity as a function of carbon number is the only correlation in literature to our knowledge. It is available only to carbon number 70. In this work, a logarithmic curve is similar with Ahmed correlation on specific gravity for carbon number lower than 70, and it is available for the carbon number higher than 70.

Acentric factor is calculated by different correlations. Abbreviations used are Edmister using critical properties from Sancet (E–S), Edmister using critical properties from Twu (E–T), Edmister using critical properties from Ahmed (E–A). Calculated acentric factor are similar to all correlations for carbon number below 20 except the Pederson–Fredenslund correlation. For carbon number between 20 and 40, Kesler–Lee and E–T have similar predictions, and E–A and Ahmed show similar predictions, while Pederson–Fredenslund and E–T correlations show a large deviation. It is shown that the values calculated by all correlations are significant different which makes it difficult to identify the accurate acentric factor without experimental verification except the E–T and Kesler–Lee's. They all have different values for carbon number higher than 40. The E–A deviates and tends to minus infinite around carbon number 60. The Kesler–Lee correlation and E–T correlation are valid for carbon number than 40, to our knowledge.

The saturation pressure generated by the developed method for calculating the fraction of each SCN with Peng–Robinson equation of state shows a difference compared with experimental data. The error is from 2.23% to 9.8% and it finally reaches a satisfactory agreement between the predicted and experimental data.

List of symbols

- *P*_C critical pressure (Pa)
- *T*_C critical temperature (K)
- *T_b* boiling point temperature (K)
- ρ density (kg/m³)
- z_i the mole fraction of the carbon number
- $z_{C_{n+}}$ the mole fraction of the C_{n+} fraction
- p(M) the probability density function
- *C_i* the value of carbon number
- M_i molecular weight (g/mol)
- α , β , γ the parameter of the gamma distribution
- *N* the number of carbon atoms of the last SCN
- *n* the number of carbon atoms of the first SCN within the C_{n+} fraction

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