

Research note

Effect of Hydrocarbon Fluid Characterization on Wax Precipitation Modeling

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Abstract

The hydrocarbon plus fractions that comprise a significant portion of naturally occurring hydrocarbon fluids create 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 (heavy ends). Proper characterization of the heavier components is important when cubic equations of state and/or solid formation thermodynamic models are used to describe complex phase behavior of reservoir fluids. The effect of heavy fractions characterization on thermodynamic modeling of wax precipitation has been investigated using different models including Won, Pan and Proposed Models. In order to characterize the plus fraction (heavier part) as a series of pseudocomponents, a probability model that expresses the mole fraction as a continuous function of the molecular weight has been used. The study has been conducted using several mixtures. Two different SCNs (Single Carbon Number), C_{7+} and C_{10+} , were chosen. The chosen SCNs were distributed to multicomponents of five, six, and/or ten using continuous method. The results showed that the fractioning is required to be able to predict wax precipitation. Distribution of C_{10+} using a proper distribution function has shown improvement in predictions of WAT and the amount of wax deposited in comparison with the characterization of C_{7+} using semi-continuous approach. In predicting WAT and the amount of wax build up the developed model showed superiority over the others.

Keywords: Plus Fraction,, Characterization, Modeling, Wax Precipitation, Pseudocomponent, Semi-continuous

1. Introduction

The majority of crude oil and gas condensate fluids contain a certain proportion of heavy hydrocarbon compounds, some of which may precipitate as a waxy solid phase if the fluid is cooled below a certain temperature. Waxes are essentially mixtures of long-chain paraffins with carbon lengths ranging from C_{15} to C_{75+} . They are mainly formed from

normal paraffins but isoparaffins and naphthenes are also present. Some waxes also have an appreciable aromatic content [1-2].

Problems caused by wax precipitation, such as decreased production rates, increased power requirements, and failure of facilities are a major concern in the production and transportation of heavy hydrocarbon fluids.

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Wax deposition usually leads to increased viscosity, increased pipeline roughness, and reduction in the effective cross sectional area of the pipelines which all result in increased pressure drop. In extreme cases it may lead to plugging of the pipe. When designing pipelines and separation plants it is, therefore, of importance to be able to determine the conditions under which wax precipitation takes place, and the amount of wax likely to form.

Techniques such as thermal treating of pipelines, addition of chemical inhibitors, and/or pigging are commonly used to prevent wax accumulation. The costs associated with such measures could be reduced significantly if accurate means to predict the wax precipitation region were available. Therefore, it is crucial to develop reliable experimental techniques and/or predictive tools for determining wax equilibria [1-7]. One approach to cope with the deposits which may form in reservoirs, pipelines and production facilities is to predict their occurrence through mathematical (thermodynamical) models to design proper systems preventing their formation as well as dissolving them if already formed.

Proper characterization of the heavy end (heavier) hydrocarbons has an important effect on thermodynamic modeling of wax precipitation. This is due to its important role in predicting the phase behavior of hydrocarbon fluids different methods of characterization and their effects on the prediction of the conditions under which wax precipitation has been investigated using different thermodynamic models including the proposed model [8-12] and the models developed by Won and Pan. The proposed model uses regular solution theory to describe solid phase (wax) non-ideality, while the liquid and gas phases are described by an equation of state [8-12]. Different mixtures covering a wide range of reservoir fluids have been used to investigate the effect of characterization on the aforementioned thermodynamic models.

2. Fluid characterization

Petroleum reservoir fluids are complex mixtures composed of light compounds including N_2 , CO_2 , H_2S , C_1 , and C_2 , intermediate hydrocarbons C_3 to C_6 , and heavier components with varying contents of paraffinic, naphthenic, and aromatic compounds. Proper characterization of the heavier or "heptanes-plus" (C_{7+}) components is important when cubic equations of state (EOS's) and/or solid formation thermodynamic methods are used to describe the complex phase behavior of reservoir fluids. The basis for most characterization methods is true boiling point (TBP) data that includes mass, mole, and volume fractions of distillation cuts with measured molecular weight, specific gravity, and boiling point. Each distillation cut may be considered as a pseudocomponent with a critical pressure, critical temperature, and acentric factor. If the distillation cuts are collected within the range of neighbouring normal alkane boiling points, they are referred to as single carbon number (SCN) groups. Correlations for estimating pseudocomponent critical properties are usually based on specific gravity and boiling point.

An alternative method to characterising the heptanes-plus (heavier part) fraction as a series of pseudocomponents is to use a probability model that expresses the mole fraction as a continuous function of the molecular weight. There are several advantages to using the continuous approach. First, the residue or the heaviest (C_{7+} or higher) cut can be readily divided into discrete fractions by extending the distribution to molecular weights greater than that which can be measured directly [13]. Another advantage is the definition of C_{7+} heavier into a series of pseudocomponents based on statistical reasoning and the model parameters used to describe molar distribution [14]. A continuous description can also be used directly in EOS [15-19].

To indicate the difference between a discrete mixture and a continuous mixture, Fig.1-a

shows how the composition in a discrete mixture is being represented by using mole fractions as composition variables. In this case, the mixture has been identified by 10 components; the mole fraction x_i for component i is given by a bar and the summation of all x_i is shown in Fig.1-b. For a continuous mixture, Fig.1-c, there are no discrete identified components, but instead the mixture has been characterized using a single distribution variable I , such that the fraction of molecules (in the mixture) within the range I and $I + \Delta I$, is given by $\int_I^{I+\Delta I} F_p(I)d(I)$. The normalization is done by

integrating over the whole range (Fig.1-d). To characterize the single carbon number (SCN) groups or pseudocomponents, the properties (physical and critical) of the heavy fractions are estimated depending on the availability of the data. If molecular weights and specific gravities are available, then the Riazi's [20] correlation has been used. If only molecular weight is available, then Whitson [13] general correlation has been used. In the following sections, a brief discussion on implementation of the continuous approach and its application into the EOS will be presented.

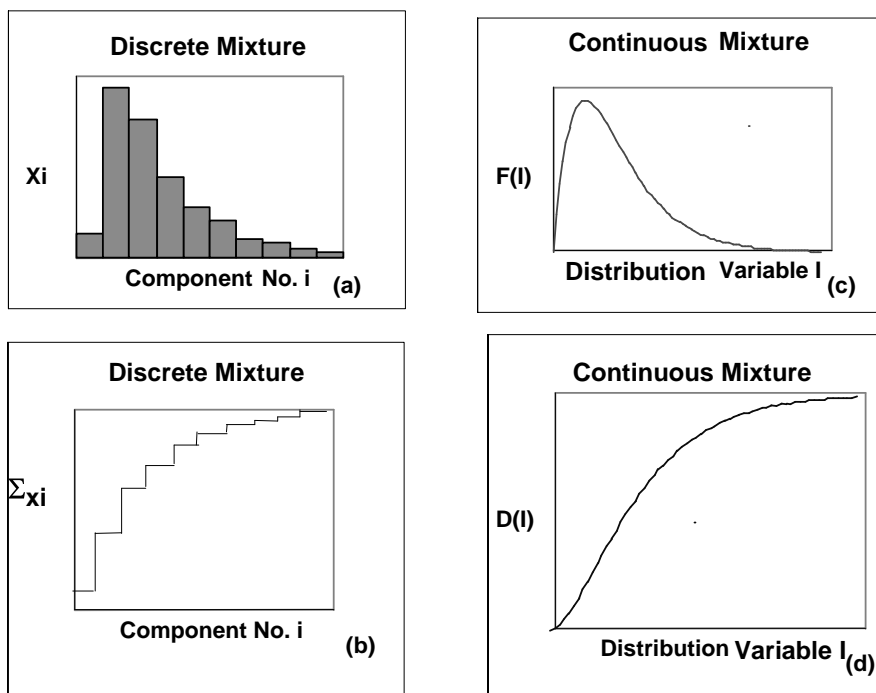


Figure 1. Discrete and continuous description for a multicomponent mixtures.

3. Distribution function

To describe the composition of a continuous mixture, not only the appropriate distributed variables $I, J \dots$ but also some function F_P must be chosen to indicate how these variables are distributed. In general, a function $F_P(I, J \dots)$ is required, however, in this study we have considered only the simplest case where one distribution variable seems to be sufficient.

In statistics, the function F_P is referred to as a probability density function and the integral of F_P is a cumulative density function. To avoid interpretation of the term “density function” to mass, F_P has been referred to as a probability distribution function, or simply, a distribution function, and the integral of F_P as a cumulative distribution function.

The choice of F_P is determined primarily by its ability to represent reality to a sufficient degree of approximation. However, another consideration in the choice of F_P is mathematical convenience; hence, to solve $\mu^\alpha(I)=\mu^\beta(I)$ analytically, some functions of F_P are more suitable than others. For our purpose, we sought mathematical simplicity. A useful distribution function for that purpose is the gamma distribution, the one suggested by Cotterman [16-18].

$$F_P(I) = \frac{(I - \gamma)^{\alpha-1}}{\beta^\alpha \Gamma(\alpha)} e^{-\frac{(I-\gamma)}{\beta}} \quad (1)$$

Where Γ is the gamma function (Johnson and Kotz) [21]. Parameter γ fixes the origin, whereas α and β are the distribution parameters (also called adjustable parameters). The mean θ and the variance σ^2 are given by

$$\theta = \alpha\beta + \gamma \quad (2)$$

$$\sigma^2 = \alpha\beta^2 \quad (3)$$

$$\beta = (\theta - \gamma) / \alpha \quad (4)$$

where θ is the average, say, molecular weight of the continuous part, comprised with molecular weights beginning from γ to infinity. The normalization condition is given by;

$$\int_{\gamma}^{\infty} F_P(I) d(I) = 1 \quad (5)$$

Fig. 2 represents examples of the Γ density distribution for the specific chosen cases. As can be seen, when $\alpha = 1$ Eq.1 (the gamma distribution function) reduces to simple exponential distribution form.

Many fluid mixtures, which are in part continuous, may also contain appreciable amounts of components, which are more conveniently described as discrete components (i.e. light hydrocarbons in a gas condensate system, volatile oil, etc.). Therefore, to obtain a realistic representation of the mixture composition, one can describe a mixture containing both discrete and continuous components as a semi-continuous mixture. The distribution function is generally selected such that the value of Eq.5 becomes equal to 1. Hence, in the semi-continuous approach, the continuous fraction is weighted with its mole fraction, n , and each discrete component, by its concentration, x_i . For k discrete components, followed by continuous ones for $k+$, the normalisation is

$$\sum_i^k x_i + n \int_I F_P(I) d(I) = 1 \quad (6)$$

This can further be extended to allow for multiple continuous fractions, each weighted by an overall mole fraction, n_m , and each described by a distribution function, $F_{P,m}(I)$. Hence, the normalisation equation for systems of k discrete component and l continuous fractions by analogy to the Eq.5,

$$\sum_i^K x_i + \sum_m^l n_m \int_I F_{P,m}(I) d(I) = 1 \quad (7)$$

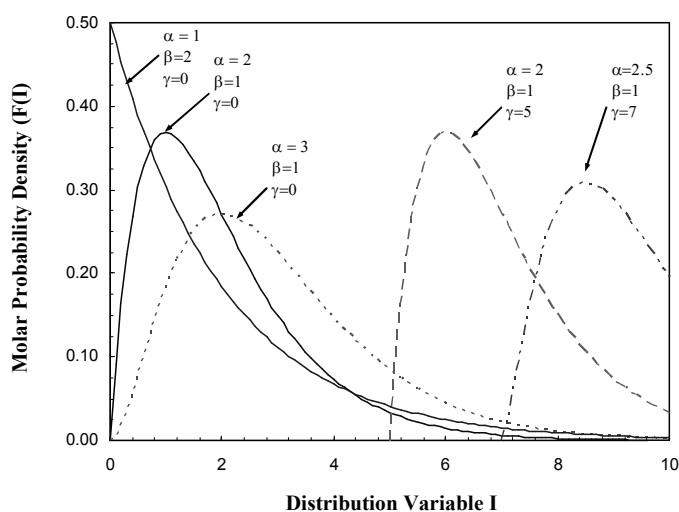


Figure 2. Gamma density function for continuous or semi-continuous distributions.

Where Eq.1 applies to each of the continuous fractions, i.e. the integral of the $F_P(I)d(I)$ for each of the continuous fractions becomes equal to 1.

4. Application of the continuous distribution function in EOS

The continuous distribution function can be used in the calculations of phase behaviour. The two parameters (a and b) van der Waals type equation of state, for a system with k discrete components and l continuous fractions are calculated as,

$$b = \sum_i^k x_i b(i) + \sum_m^l n_m \int_I F_{P,m}(I) b(I) d(I) \quad (8)$$

$$a = \sum_i^k \sum_j^k x_i x_j \left(a_i a_j \right)^{0.5} + 2 \sum_i^k \sum_m^l x_i a_i^{0.5} n_m \int_I F_{P,m}(I) (a(I))^{0.5} d(I) + \sum_m^l \sum_n^l n_m n_n \int_I \int_J F_{P,m}(I) F_{P,n}(J) (a(I) a(J))^{0.5} dI dJ \quad (9)$$

where x_i and n_n are mole fractions for discrete and continuous fractions. A proof on the

equations (8) and (9) is given in Appendix B. If a third or a fourth parameters EOS is used then the above equation should be extended to calculate the parameter(s) as well. For example, for the Valderrama-Pate-Teja (VPT) EOS [22], which has introduced a third parameter, c , and has been used in this study, the parameter c has been evaluated as,

$$c = \sum_i^k x_i c(i) + \sum_m^l n_m \int_I F_{P,m}(I) c(I) d(I) \quad (10)$$

The terms $a(I)$, $b(I)$ and $c(I)$ are some continuous functions of I with values equal to parameters a , b and c , respectively, for compounds described by the continuous description. In this study the parameters $a(I)$ and $b(I)$ were taken from Cotterman for the Peng-Robinson (PR) [23] and Soave-Redlich-Kwong (SRK) [24] EOS and for the VPT EOS, we have developed the following forms using the molecular weight as the variable I .

$$b(I) = b_0 + b_1 I \quad (11)$$

A similar equation with a different coefficient was developed for $c(I)$ continuous parameter.

$$c(I) = c_0 + c_1 I \quad (12)$$

$$\sqrt{a(I, I)} = a_0(T) + a_1(T)I \quad (13)$$

where I is molecular weight. The temperature dependence of $a_0(T)$ and $a_1(T)$ is given by

$$a_0(T) = a_0^{(0)} + a_0^{(1)}T + a_0^{(2)}T^2 \quad (14)$$

$$a_1(T) = a_1^{(0)} + a_1^{(1)}T + a_1^{(2)}T^2 \quad (15)$$

where T is in Kelvin. Table 1 gives the constant for the above equations.

At equilibrium, the equality of fugacity of each component in liquid and vapour phases for the discrete and the continuous parts are expressed as:

$$f_i^L = f_i^V \quad (16)$$

$$f^L(I) = f^V(I) \quad (17)$$

The material balance equation required for the phase behaviour of the discrete is defined by,

$$z_i = (1 - V)x_i + Vy_i \quad (18)$$

where V is the vapour mole fraction. The modified Eq.(18) for the continuous fraction becomes,

$$\eta^F F_P^F(I) = (1 - V)\eta^L F_P^L(I) + V\eta^V F_P^V(I) \quad (19)$$

where $F_P^F(I)$, $F_P^L(I)$, and $F_P^V(I)$ are the distribution functions for the continuous fractions of feed, liquid and vapour respectively. The expression to determine the fugacity coefficients, when using the distribution function, would lead to a complex equation, which can only be solved numerically. Amongst the numerical methods applied successfully (Cotterman et al), the method of Gaussian quadrature has proved to be reliable and practical.

Gaussian quadrature provides an efficient method of integrating a function by summing a finite number of weighted functions evaluated at specified values of the integration variable called quadrature points [25]. For s quadrature points,

$$\int_I f_p(I) dI = \sum_{p=1}^s w(I_p) f_p(I_p) \quad (20)$$

where $w(I_p)$ is the weighting factor and $f_p(I_p)$ is the function value at the quadrature point, I_p . Details of describing quadrature integration can be found in texts on numerical methods [26-27]. A complete description of the quadrature method is explained in Appendix A. This approach has been implemented in this study to the liquid-solid (L-S) phase equilibria calculation, using molecular weight as the variable I.

Table 1. Constants for EOS parameters (equations 11,12,14 and 15).

Parameters	a0,bar-cm6/mol2	a1,bar-cm6/mol2	b, cm3/mole	c, cm3/mole
0*	411.474	89.374	-0.343	- 380.74
1*	-52.178	-7.62	1.286	4.7818
2*	1.574	0.276	-	-

* **0,1** and **2** represents subscript regarding **b** and **c** and superscript for **a₀** and **a₁**.

The numerical evaluation of the integral in Eq. (20) is accomplished by the summation of the products of the values of the function $f_p(I_p)$ at the quadrature point I_p multiplied by the corresponding weights $w(I_p)$. Thus the use of discrete pseudocomponents chosen at the quadrature points with mole fractions determined by the weighting of the quadrature point is exactly analogous to the Gaussian quadrature of the gamma distribution of continuous species. This means that semicontinuous thermodynamics may be used in existing discrete component equation of state programs by simply choosing the pseudocomponents to be at the correct quadrature points.

5. Fractioning analysis

Using the aforementioned method of semi-continuous functions to describe the heavy fractions of petroleum mixtures would require a proper strategy of distributing the heavy fraction. In other words, how many quadrature points are necessary to provide an adequate result.

In order to assess a suitable method to describe the heavy part of the mixture, an analysis was performed on several mixtures, using single carbon number (SCN), five or six and/or ten quadrature points. Most of the experimentally tested data are of the dead oils and only a few of others (i.e. black oil, volatile oil and gas condensate) have been reported. In this study five mixtures with different characteristics were chosen and the following approaches in distributing the heavies were taken to predict the WAT and the amount of wax precipitated;

- Single C_{7+}
- C_{7+} was distributed to six and ten quadrature points using semi-continuous method.
- Single C_{10+}
- C_{10+} was distributed to five quadrature points in one mixture, six quadrature points in all other mixture and ten quadrature points using semi-continuous method.

These mixtures include; three dead oils reported by Hansen et al [28], one volatile oil reported by Pan and Firoozabadi [29] and one gas condensate reported by Won [30]. The reason that three experimental data from Hansen et al [28] were chosen was that their characteristics were reported to be different from one another. They have been reported to be aromatic, paraffinic and waxy oil respectively. Pan and Firoozabadi's data [29] is a volatile oil with the reported wax appearance temperature (WAT) at three different pressures.

Using different fractioning (i.e. semi-continuous and single plus fraction) methods, the WAT was predicted. The amount of wax precipitated was predicted for four of the mixtures, using the aforementioned procedures. In order to analyse the fractioning methods further, besides the developed model, two other models were also tested. In the following sections the results and the discussion of the results for each of the mixtures used in this study are being presented. The adjusted values of the parameters of Gamma distribution function used to calculate wax appearance temperature of different mixtures are given in Appendix C.

6. Results and discussion

Mixture # 1

Mixture #1 was reported to be a biodegraded, aromatic oil [28]. Using the given data, first the C_{7+} fraction was used as a single component and then C_{7+} was described with a gamma distribution function using six or ten quadrature points. Next, the C_{10+} was used as a single component and the same as C_{7+} , a gamma distribution function was used to recapitulate the C_{10+} to five and then ten quadrature points.

Tables 2 and 3 present the predicted wax appearance temperature (WAT) using the aforementioned criterion. The results indicate that all three models have under predicted the WAT when either single C_{7+} or single C_{10+}

was used to describe the heavy part of the mixture. When the continuous function was used to present the distribution of the heavy's, the Won model over predicted the WAT in all cases. Using the Pan's correlation, WAT was under predicted in all cases, while the developed model was able to predict the WAT for this mixture with a good accuracy. Even though the WAT was slightly over predicted when C_{10+} was presented with ten quadrature points, the over prediction was about 4 K.

Regarding the prediction of the amount of wax, using the above fractioned scheme, the following tests were conducted:

- Comparing the amount of wax precipitated using single C_{7+} or C_{10+} for the heavy, by testing all three models.
- Comparing the amount of wax precipitated by different models using six and ten quadrature points to define C_{7+} for the heavy and using five and ten quadrature points to describe the C_{10+} fraction.

Figures 3 to 5 show the prediction of the

amount of wax precipitated using different models and different fractions for this mixture. Figs. 3-5 represent the comparison of the results obtained by using the C_{7+} as single component and as six and ten quadrature points. As can clearly be seen from these figures, by using a single C_{7+} , the prediction of the amount of wax, especially when the temperature was lowered, were very poor using any of the three models. While using the continuous distribution, i.e. defining the C_{7+} as a continuous fraction, the prediction was very much improved. Figure 4 represents a comparison of the results using the C_{10+} as a single component and as five and ten quadrature points, and again, describing the C_{10+} as several quadrature points, shows superiority to the use of single C_{10+} . Overall, as expected, fractioning has improved the prediction of both WAT and the amount of the precipitation of the wax. Also, as these figures indicate, distribution of C_{10+} seems to give a better prediction of the amount of wax precipitated than the C_{7+} distributions. Moreover, it appears that the 10 points distribution does not improve the results considerably.

Table 2. Comparison of the predicted WAT by different methods using different fractioning of C_{7+} (Measured WAT = 308 K).

Model/ WAT(K)	single C_{7+}	6-quadrature points	10-quadrature points
Won	286	321	318
Pan	288	304	300
Proposed Model	293	312	309

Table 3. Comparison of the predicted WAT by different methods using different fractioning of C_{10+} (Measured WAT = 308 K).

Model/ WAT(K)	single C_{10+}	5-quadrature points	10-quadrature points
Won	299	321	323
Pan	294	302	304
Proposed Model	301	311	312

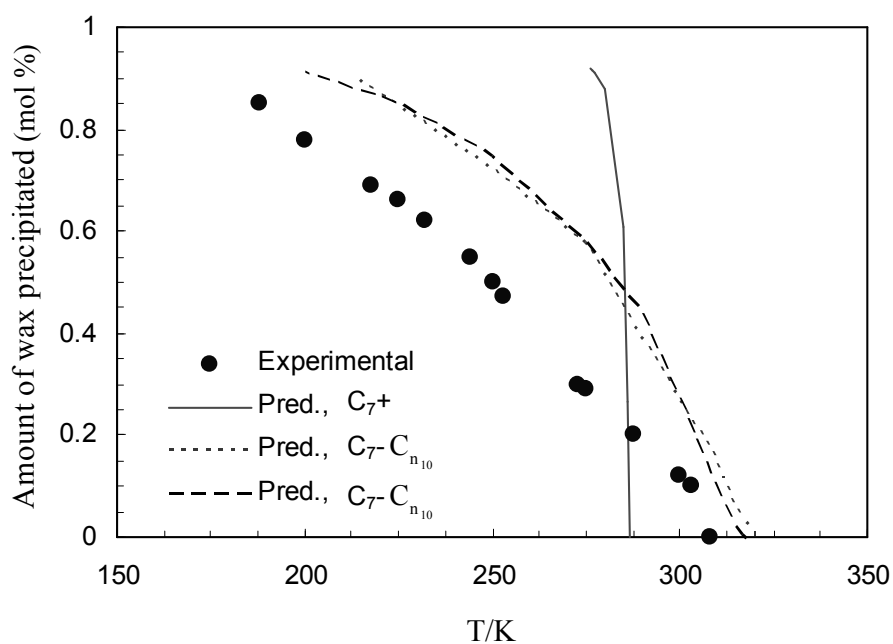


Figure 3. Comparison of the amount of wax precipitated between measured and predicted using the Won model and different fractioning for Mix # 1.

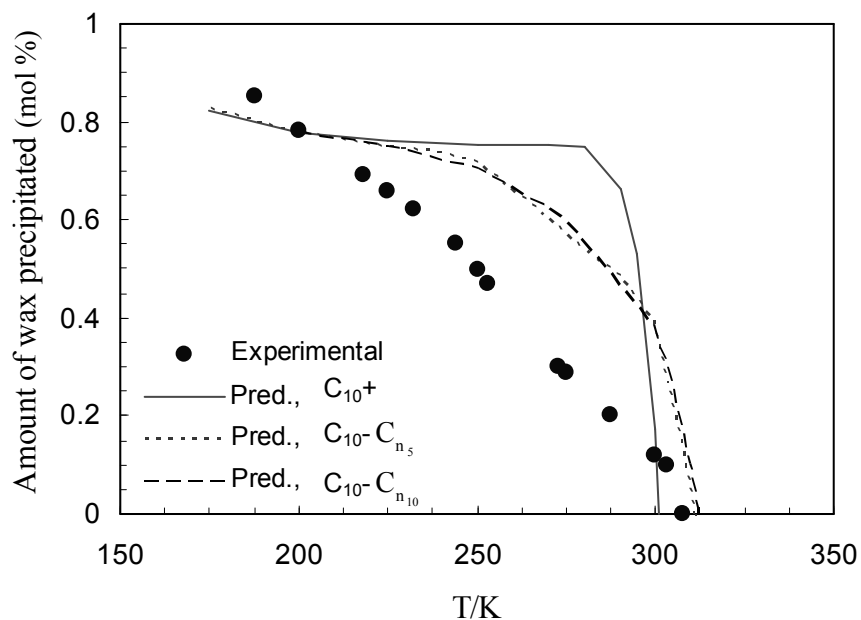


Figure 4. Comparison of the amount of wax precipitated between measured and predicted using the proposed model and different fractioning for Mix # 1.

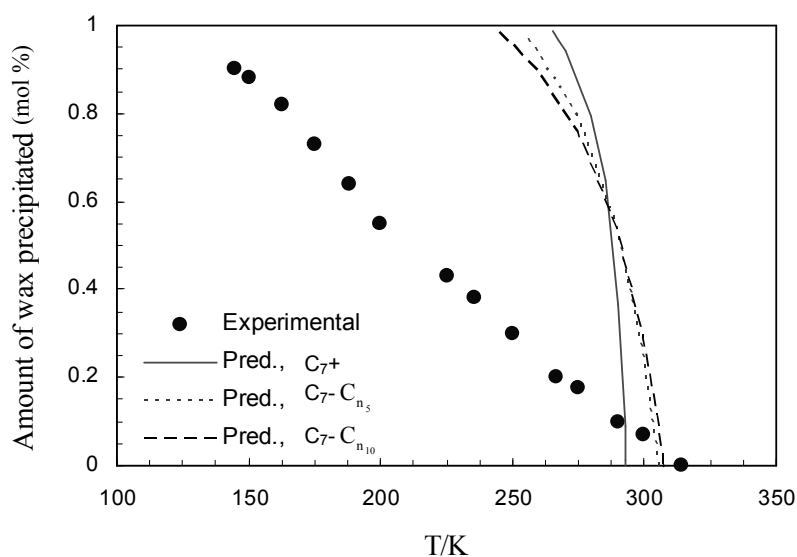


Figure 5. Comparison of the amount of wax precipitated between measured and predicted using the Pan model and different fractioning for Mix # 2.

Mixture # 2

This mixture was reported to be a paraffinic oil with a reported WAT of 314.15 K [28]. Using the given data as it was performed for the mixture-1, the analysis was completed for single C_{7+} and C_{10+} . Using gamma distribution function, six and ten quadrature

points were established for C_{7+} and C_{10+} . WAT and the amount of wax were predicted using different models and different fractions. The results of the comparison of the WAT are presented in Tables 4 and 5.

Table 4. Comparison of the predicted WAT by different methods using different fractioning of C_{7+} (Measured WAT = 314 K).

Model/ WAT(K)	single C_{7+}	6-quadrature points	10-quadrature points
Won	297	317	343
Pan	293	306	308
This work	296	313	315

Table 5. Comparison of the predicted WAT by different methods using different fractioning of C_{10+} (Measured WAT = 314 K).

Model/ WAT(K)	single C_{10+}	6-quadrature points	10-quadrature points
Won	311	325	329
Pan	301	304	307
This work	309	314	314

Again, the same as in mixture-1, and as can be seen from Tables 4 and 5, all three models have under predicted the WAT when either single C_{7+} or C_{10+} was used. These under predictions are much more when C_{7+} was used as a single component, however, when C_{10+} was used, the prediction was much better. When the C_{7+} was used as continuous function, the Won model predicted the WAT fairly well, while only six quadrature points were used. However, when ten quadrature points were used the Won model over predicted the WAT by almost 30 K. On the other hand, when C_{10+} was distributed to six and ten quadrature points, the Won model over predicted the WAT by about 10 and 15 K, respectively. Even after the fractioning, the Pan's model has under predicted the WAT in both cases. The developed model has been able to predict the WAT with a very good accuracy, especially when C_{10+} fractions (six or ten) were used. On the contrary, when continuous distribution was used the prediction was improved considerably. Prediction of the amount of wax seems to be better by using C_{10+} distributions than using C_{7+} distributions. Over all, fractioning has improved the prediction of the WAT and to

some extent the amount of the precipitation of the wax, even though they generally over predicted the wax build up. Similar to the mixture # 1, the ten point distributions did not improve the results considerably for this mixture.

Mixture # 3

This mixture has been reported to be a volatile oil. The WAT were reported at three different pressures [29]. Based on the experience achieved through the previous mixtures, C_{10+} was chosen to be used as a single component and also distributed as six quadrature points. When C_{10+} was used as a single C_{10+} , all three models have predicted the WAT at all pressures below the reported values. The developed model and the Pan model both predicted the WAT better than the Won's model, as shown in Table 6. When C_{10+} was distributed to six quadrature points, the developed model and the Pan model provided better overall predictions of the WAT, while the Won model has over predicted the WAT at all three pressure points by 20 to 30 K. As indicated previously, in order to achieve better results, characterization of the heavy fraction is necessary.

Table 6. Comparison of the predicted WAT(in K) using C_{10+} and 6-quadrature point distributions (Mix # 3, volatile oil)

P/Bar	Exp.	Won		Pan		Proposed Model	
		C_{10+}	C_{10}^*	C_{10+}	C_{10}^*	C_{10+}	C_{10}^*
1	313	305	333	297	306	304	311
50	309	300	332	282	306	298	309
120	301	297	332	272	299	295	307

C_{10}^* is the C_{10+} distributed to six-quadrature points.

Mixture # 4

This mixture was reported to be a gas condensate (GC). Similar to the previous mixture, based on the achieved experience, only C_{10+} and its six quadrature point distribution was considered. Table 7 presents the WAT prediction using different models. As can be seen, Won has over predicted the WAT especially when six quadrature points were used. Pan's model under predicted the WAT, while the developed model has slightly over predicted the WAT. The noticeable points are; the fractioning is required to be able to present the amount of wax precipitation properly. Pan's model has been able to predict the amount of wax better than the previous mixtures. Even though the developed model has over predicted the amount of wax precipitated, when the distribution function was used, the overall prediction of the wax build up shows very good improvements. All models tend to have better results for the wax build up as the temperature was reduced.

7. Conclusions

A study was conducted on the characterisation of the heavy part of several mixtures. The mixtures were chosen such that they would cover most types of reservoir fluids. Two different SCN, C_{7+} and C_{10+} , fractions were chosen. The chosen SCN were distributed to multi-components of five, six and/or ten using the continuous method. Based on the study conducted, using the aforementioned technique, the following conclusions were achieved:

Single C_{7+} provide poor predictions of both WAT and the amount of wax precipitated. The fractions of C_{7+} would provide a better prediction of WAT, but would still give a relatively poor prediction of the amount of wax. Hence, C_{7+} is not recommended to be used in predicting the WAT and the amount of wax precipitate.

Single C_{10+} would also result in poor predictions of WAT and wax build up in most cases. But in contrast, using fractions of

C_{10+} , has shown improvement in predictions of WAT and the amount of wax deposited. It has been proven that by using ten quadrature points over six, the results would not substantially improve, hence the six quadrature points seem to be sufficient for the prediction of the WAT and wax build up. In predicting WAT and the amount of wax build up, the developed model showed superiority over the others. It has to be noted that the Pan model normally under predicted the WAT, while the Won model has over predicted the WAT and the amount of wax precipitated.

Table 7. Comparison of the predicted WAT by different methods using different fractioning of C_{10+} (Measured WAT = 309 K).

Model/ WAT(K)	single C_{10+}	6-quadrature points
Won	315	326
Pan	300	304
Proposed Model	311	314

List of symbols

- a Parameter of the Van der Waals EOS
- a_0 Constant used in Eq. (13)
- a_1 Constant used in Eq. (13)
- $a_0^{(0)}$ Constant used in Eq. (14)
- $a_0^{(1)}$ Constant used in Eq. (14)
- $a_0^{(2)}$ Constant used in Eq. (14)
- $a_1^{(0)}$ Constant used in Eq. (15)
- $a_1^{(1)}$ Constant used in Eq. (15)
- $a_1^{(2)}$ Constant used in Eq. (15)
- b Parameter of the Van der Waals EOS
- b_0 Constant used in Eq. (11)
- b_1 Constant used in Eq. (11)
- c The parameter used in Valderama-Patel -Teja EOS
- c_0 Constant used in Eq. (12)

c_1	Constant used in Eq. (12)
f_i^L	fugacity of component i in liquid phase
f_i^V	fugacity of component i in vapor phase
f_p	function value at the quadrature point, I_p
F_p	distribution function for continuous fraction
F_p^F	distribution function for continuous fraction of feed
F_p^L	distribution function for continuous fraction of liquid
F_p^V	distribution function for continuous fraction of vapor
I	distributed variable e.g. molecular weight
I_p	quadrature point
k	number of discrete components
l	number of continuous fractions
n	mole fraction of the continuous fraction
T	temperature
V	vapor phase mole fraction
w	weighting factor
x_i	mole fraction of each discrete component
z_i	overall composition of component i
α	The parameter used in gamma distribution function (Eq. 1)
β	The parameter used in gamma distribution function (Eq. 1)
γ	The parameter used in gamma distribution function (Eq. 1)
θ	average, say, molecular weight of the continuous part

Subscripts & superscripts

F	feed
i	discrete component i
j	discrete component j
L	liquid phase
m	continuous fraction m
n	continuous fraction n
V	vapor phase

Appendix A

Gaussian quadrature formulas

There is a large family of numerical integration formulas that conform to the following pattern :

$$\int_a^b f(x) dx = A_1 f(x_1) + A_2 f(x_2) + \dots + A_n f(x_n) \quad (\text{A-1})$$

In using such a formula, it is only necessary to know the “nodes” x_1, x_2, \dots, x_n and the “weights” A_1, A_2, \dots, A_n . There exist tables in which the numerical values of the nodes and weights are listed. One major source of the formula (A.1) is in the theory of polynomial interpolation. If the nodes have been fixed, then there is a corresponding Lagrange interpolation formula

$$p(x) = \sum_{i=1}^n f(x_i) l_i(x) \text{ where } l_i(x) = \prod_{\substack{j=1 \\ j \neq i}}^n \left(\frac{x - x_j}{x_i - x_j} \right) \quad (\text{A-2})$$

This formula provides a polynomial p of degree $\leq n-1$ that interpolates f at the nodes; that is, $p(x_i) = f(x_i)$ for $1 \leq i \leq n$. If the circumstances are favorable, p will be a good approximation to f , and $\int_a^b p(x) dx$ will be a good approximation to $\int_a^b f(x) dx$. Therefore,

$$\int_a^b f(x) dx = \int_a^b p(x) dx = \sum_{i=1}^n f(x_i) \int_a^b l_i(x) dx = \sum_{i=1}^n A_i f(x_i) \quad (\text{A-3})$$

where we have put $A = \int_a^b l_i(x) dx$. From the way in which formula (A.3) has been derived, we know that it will give correct values for the integral of every polynomial of degree $\leq n-1$.

Appendix B

Proof on the equations (8) & (9)

Given a random variable and a function $g(x)$, we form the random variable $y = g(x)$. The mean of this random variable is given by

$$E(y) = \int_{-\infty}^{\infty} y f_y(y) dy \tag{B-1}$$

It appears, therefore, that to determine the mean of y , we must find its density $f_y(y)$.

This, however is not necessary. $E(y)$ can be expressed directly in terms of the function $g(x)$ and the density $f_x(x)$ of x [31].

$$E\{g(x)\} = \int_{-\infty}^{\infty} g(x) f_x(x) dx \tag{B-2}$$

According to the above theorem, the mean value of parameter $b(I)$ which is a function of I with distribution function $F_{p,m}(I)$, is calculated using the following equation:

$$b_m = \int_I b(I) F_{p,m}(I) dI \tag{B-3}$$

For a system consisting of k discrete components and l continuous fractions, parameter b is calculated as follows:

$$b = \sum_i^k x_i b(i) + \sum_m^l n_m b_m \tag{B-4}$$

$$= \sum_i^k x_i b(i) + \sum_m^l n_m \int_I b(I) F_{p,m}(I) dI$$

The average value of parameter $[a(I)]^{0.5}$ which is a function of I with a distribution function of $F_{p,m}(I)$ is calculated using the following equation :

$$(a_m)^{0.5} = \int_I [a(I)]^{0.5} F_{p,m}(I) dI \tag{B-5}$$

For a system composed of k discrete and l continuous fraction, the following relations can be obtained for parameter a :

$$a = \sum_i^k \sum_j^k x_i x_j (a_i a_j)^{0.5} + 2 \sum_i^k \sum_m^l x_i a_i^{0.5} n_m (a_m)^{0.5} + \sum_m^l \sum_n^l n_n n_m (a_m)^{0.5} (a_n)^{0.5} = \sum_i^k \sum_j^k x_i x_j (a_i a_j)^{0.5} \tag{B-6}$$

$$+ 2 \sum_i^k \sum_m^l x_i a_i^{0.5} n_m \int_I F_{p,m}(I) (a(I))^{0.5} d(I) + \sum_m^l \sum_n^l n_n n_m \int_I \int_J F_{p,m}(I) F_{p,n}(J) (a(I) a(J))^{0.5} dI dJ$$

Appendix C

The adjusted values of the parameters of Gamma function

Table C1. The adjusted values of the parameters of Gamma distribution function used to calculate wax appearance temperature of different mixtures.

Mix No.	Mw _{C7+}	Mw _{C10+}	γ	α
1	165.125		98.0787	1.92
1		308.340	142.7726	2.40
2	208.075		99.3809	2.40
2		319.378	141.7134	2.60
3 at 1 bar		289	140.740	1.86
3 at 50 bar		289	140.880	1.95
3 at 120 bar		289	141.508	2.20
4		180	98.2041	1.40

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