# Integrated Wax-Hydrate Formation in Real Oil Mixtures: What Factors Are Important from Thermodynamic Modelling?

M. Ameri Mahabadian[1], A. Chapoy[1*], R. Burgass[1], B. Tohidi[1]
*[1]Hydrates, Flow Assurance & Phase Equilibria Research Group, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, United kingdom*
[*] Corresponding author: a.chapoy@hw.ac.uk

## Abstract

The presence of unknown fractions in real mixtures, as opposed to synthetic mixtures, necessitates the application of a characterization scheme to provide accurate inputs for the thermodynamic models utilized for modelling wax and hydrate formation. Inappropriate evaluation of these inputs may result in poor predictions, even though accurate thermodynamic models are used to describe phases. On one hand, regardless of the type of the unknown fraction, it is essential for the purpose of wax precipitation modelling, to characterize it to identify the amount and distribution of the wax forming part in the mixture. On the other hand, accuracy of hydrate phase boundary and amount calculation in real oils, is indirectly dependent on characterization of the unknown fraction, meaning that if the fluid phases are described precisely the hydrate dissociation lines can be calculated with acceptable accuracy.

In this work, the modelling of formation of waxes and hydrates in real oils are discussed separately. It will be shown that the main complication for modelling combined wax-hydrate formation in real mixtures is with the wax modelling part and in particular the correct quantification of the distribution of normal paraffins in the unknown fraction. In the wax part, different schemes for characterization of real oils are explained and compared for evaluation of wax precipitation and melting temperatures, highlighting limitations and requirements of different models. It will be explained that amongst all of the existing methods for extending wax precipitation models to real systems, only those which (i) distinguish the wax forming (paraffinic) part from the non-paraffinic part for each unknown fraction and (ii) are capable of identifying the distribution of wax forming fractions in the heavy end, are reliable. Accordingly, the performance of the only two approaches which satisfy these criteria was evaluated. With a comparative approach, it is concluded that the method of Coutinho and Daridon [1] is the best fully-predictive extending scheme which gives the most accurate results with the least experimental information, specifically the distribution of n-alkanes in the mixture.

Our recently proposed UNIQUAC-CPA-vdWP integrated thermodynamic model for wax-hydrate formation [2] with the extension of Coutinho and Daridon method is finally applied for combined solids formation modelling in a real mixture for which experimental WDT data are available. Based on the results obtained it was concluded that hydrate formation could escalate the wax precipitation problem which agrees with the results achieved in our previous study for systems without unknown fractions.

## Introduction

One of the main goals in thermodynamic modelling work for wax, hydrate and combined wax/hydrate forming systems is to validate the developed models by comparison with data for real mixtures. The presence of unknown fractions in real mixtures calls for the application of a characterization scheme to provide the thermodynamic models with accurate inputs. If these inputs are assigned incorrect values, poor predictions might be the outcome of the thermodynamic modelling, regardless of the accuracy of thermodynamic models exploited to describe different phases in equilibria. Examples of such inputs are the critical and physical properties of unknown fractions. The unknown fractions in a mixture can be (i) a plus fraction, which is a single fraction including all the constituents of a mixture with molecular weight/boiling point higher than a specific value, (ii) pseudo/lumped fractions which include the constituents of the mixture with a certain range of molecular weight/boiling point. A Single Carbon Number (SCN) group is defined as a pseudo-component in which all constituents possess the same carbon number. On one hand, regardless of the type of the unknown fraction, it is essential for the purpose of wax precipitation modelling, to

characterise it to identify the amount and distribution of the wax forming part prior to the wax phase boundary and amount calculation. Characterization of heavy end pseudo fraction for estimation of distribution of paraffin wax forming component in the unknown fraction is emphasised, as such data is not usually reported experimentally. On the other hand, the accuracy of hydrate phase boundary and amount calculation in real oils, is indirectly dependent on the unknown fraction characterization, because if the fluid phases are described precisely the hydrate dissociation lines can be calculated with acceptable accuracy. The exactness of the description of the fluids in real systems is, in turn, dependent on the precision of critical/physical properties of the unknown fraction. This is a less important problem as these parameters can be tuned to match experimental saturation data which are usually reported. Additionally, in the absence of such data, there are several correlations to estimate critical and physical properties of unknown fractions with more or less acceptable accuracy.

In this work, first, the modelling of formation of waxes and hydrates in real oils are separately discussed. In the wax part, different schemes for characterization of real oils are explained and compared for evaluation of wax precipitation curve and melting temperature, highlighting limitations and requirements of different models. With a comparative approach, the best fully-predictive scheme, which provides the most accurate results is chosen. Here, the aim is to select a method which requires the least experimental information, specifically when the distribution of n-alkanes in the mixture is not reported. This is due to the high importance of a thermodynamic model to be predictive, making it independent of the system to which it is applied.

The proposed configuration is finally applied for integrated wax-hydrate precipitation modelling of a crude oil, using our recently proposed UNIQUAC-CPA-vdWP (UCV) model [2], which confirms that hydrates can synergistically escalate wax precipitation in real fluids.

## Modelling Wax Precipitation in Real Mixtures

The major calculations in wax precipitation process, from a thermodynamic viewpoint, are (i) wax disappearance (melting) temperature, WDT, at a given pressure and (ii) the amount and composition of waxes formed at a T/P condition inside the wax phase boundary, used to form wax precipitation curve, WPC. As the ultimate goal in any modelling work is to match reliable experimental measurements, the first step is to make sure if the available experimental data are valid or at least fairly accurate representation of the variables under investigation. Therefore, here as a preliminary step, the experimental uncertainties with measuring WDT and WPC are explained. It is then discussed that the evaluations of models by comparing calculation results with the measured WPC data are safe while the same expression is not valid for WDT experimental data. It is assumed here that saturates are the only wax forming part of the mixtures.

## Limitations of Measuring Wax Melting Temperature

It is known that the wax phase boundary of crudes is a strong function of their composition, more specifically the distribution of normal paraffins [3,4] and in particular amounts of the heaviest normal paraffins [4,5], as heavy normal paraffins are the major constituents of petroleum waxes [3,6,7]. Therefore, as long as the distribution of the normal paraffins in the crude is not measured or accurately calculated it is difficult to model the wax precipitation process precisely. Also, the uncertainties with the experimental measurements of WDT and their dependency to the experimental technique utilized undermines measurement accuracy. For example, measurement of WDT using differential scanning calorimetry (DSC) or light transmittance (LT) methods, require sufficient amount of crystallized solid to be present for detecting the phase transition [3]. Due to this experimental limitation, it is a common practice to match WDT modelling results with WDT experimental measurements for real oils assuming that the wax phase boundary is corresponding to a point where a certain percentage of wax has precipitated (see for example [5,8]). Even for the cross-polarized microscopy (CPM) technique, which is believed to be the most conservative method for measuring wax melting point [4], it may be necessary to assume a small finite value for the amount of wax to fit the model with measurements (see for example [9]). However, this percentage varies for different experimental techniques utilized for data points' measurements. This value is believed to be infinitesimal for matching the CPM results, due to its capability to detect wax nucleation by visual observation at the microscopic scale [7]. This is while higher values are required for other techniques such as DSC which requires a higher amount of waxes formed so that it can detect the crystallization onset. The specified percentage may not even be fixed for different mixtures when the same experimental technique is used for WDT measurements, and the same model is used for matching experimental data (see for example [5] for model results matched with laser-based solids detection system (SDS) measurements for two crudes by Hammami and Raines [7]). Overall, the problem of matching WDT is mainly due to the presence of a finite n-paraffin tail at the WDT measured as a result of

experimental techniques incapability in detecting the first wax crystal formed [10]. A complete overview of the limitations of different experimental techniques for determination of the cloud point of waxy mixtures can be found in the work of Coutinho and Daridon [4] where they state that as high as 20 K error in the measurement of WDT is possible due to experimental limitations. Hence, they argue that the cloud point temperature may not be used alone as a single indicator of crudes wax formation conditions and their consequent operational risks. Therefore, here, the aim is not to assess the models for wax phase boundary calculation. Instead, the focus is to check whether the existing schemes can precisely model WPC. This work ends with checking the change in WPC of a real oil mixture due to the presence of hydrates using the UCV model.

## Experimental Uncertainties with WPC Measurements

It is experimentally established that the distribution of n-paraffins in crude oil is of exponential decay type [11–14]. The decay rate of n-paraffin content i.e. (wt% $nC_{n+1}$)/ (wt% $nC_n$) is usually high (lower that 0.9). For such systems, exact identification of the heaviest paraffin in the mixture, in contrast to the wax melting point, would not significantly affect the wax precipitation amount [4]. Therefore, as opposed to WDT data, measured WPC data can be used as a good source to assess the models. Unfortunately, such data are very scarce for mixtures for which the compositional analysis is available. In the current study, the models are mainly assessed with the experimental WPC data of crude oils investigated in the extensive study of Rønningsen et al. [15] and Pedersen et al. [16].

## Description of Existing Methods

There have been several publications on modelling wax precipitation in real mixtures [1,17–21]. Some of the models make no distinction between different classes of hydrocarbons forming waxes and assume that all the constituents of a SCN group or a pseudo component have the same wax forming potential. This assumption is, however, far away from reality as the differences in the structure and morphology of each homologue class of hydrocarbons have a very significant effect on their crystallization behaviour and consequently their wax forming potential. Therefore, the accuracy of results obtained by such approaches are very much dependent on the results of the heavy end characterization method [1] (for example number of pseudo-components and lumping technique) which raises questions about their reliability. Hence, they are not evaluated here. Instead, the focus is on assessment of methods which divide each SCN into different fractions representing PNA ratios in it or at least devise a method for calculating the paraffinic part in each SCN fraction. Amongst these methods, Pan et al. [20] have used exponential decay distribution for estimating the amount of paraffinic portion of each fraction. Assessment of their method is, however, impossible as they have not provided any information about the specification of their estimation method, e.g. the decay rate of the exponential function. Therefore, the only methods left to assess are the methods of Pedersen [18], Ji [21] (which are very similar and are named "Pedersen-Ji" methods and abbreviated as PJ methods hereafter) and the fully predictive method of Coutinho and Daridon [1] (CD method hereafter). Below these methods are described and their pros and cons are discussed. Therefore, the aim here is to (i) evaluate distinct approaches to the problem of wax precipitation modelling in real oil mixtures (ii) discussing each approach's pros and cons and identifying the most robust method between them.

### Pedersen-Ji (PJ) Method
Pedersen [18] suggested that each SCN can be divided into two fractions, i.e. wax-forming and non-wax-forming fraction. Based on perturbation of the density of an SCN group from the density of the n-paraffin with the same carbon number, Pedersen [18] proposed the following formulation for calculation of the normal paraffin (wax forming) fraction in each SCN:

$$x_{P_{SCN,i}} = 1 - \left(A + B \times Mw_{np,i}\right) \times \left(\frac{SG_{SCN,i} - SG_{np,i}}{SG_{np,i}}\right)^{C} \tag{1}$$

Here, $x_{P_{SCN,i}}$ and $SG_{SCN,i}$ are the molar fraction of the paraffinic part and the specific gravity of the $i^{th}$ SCN, and $Mw_{np,i}$ and $SG_{np,i}$ are the molecular weight and specific gravity of the n-paraffin with the same carbon number as that of the $i^{th}$ SCN. Also, A, B and C are positive constants. In the original work of Pedersen [18] the value for the last three parameters are evaluated by matching the experimental wax precipitation data of oils reported by Rønningsen et al. [15] and Pedersen et al. [16]. Later, Pedersen at al. [22] reported different values for these parameters. Expressing that the WDT is a better representative of the true melting point temperature of waxes, Ji [21] re-adjusted the parameters A, B and C to be equal to 0.8133, 5.737×10⁻⁴ and 0.1281, respectively, by matching the WDTs of Rønningsen et al. [15] and Pedersen et al. [16] oils. Furthermore, Ji [21] considered the possibility of a

non-paraffinic fraction to be contributing in solid formation by assigning a 70 K lower fusion temperature to the non-paraffinic fraction of SCN compared to the melting point of the n-alkane with the same carbon number. This high reduction in melting temperature would result in insignificant contribution of non-normal paraffins in the amount of wax precipitated in the temperature range of importance. Therefore, for the assessments made, the assumption that only the paraffinic parts are wax forming part of the fluid, is plausible. To increase the computational efficiency, the non-paraffinic parts can be lumped as a single component. The lumping of non-paraffinic parts has almost no effect on the wax calculations [5]. The critical/physical properties of the lumped component can be evaluated by suitable correlations (here Riazi and Daubert [23] correlations for critical temperature and pressure, and Lee and Kesler [24,25] correlation for the acentric factor) or by matching saturation pressure data if available. The evaluations made here are based on the Ji [21] modification of the Pedersen [18] method. Also, the binary interaction parameter between the non-paraffinic lumped fraction and all the rest of components in the mixture is set to zero in this work.

Estimation of the WPC using the PJ method integrated into UCV model calls for prediction of the amount of heavy SCNs, so that Eq. 1 can be used to evaluate the paraffinic part. Similar to the Pan et al. [20] approach it is here assumed that SCN fractions with molecular weights heavier than about 850 g/gmol are like resins and asphaltenes, not contributing to wax formation. Therefore, the extension of the SCN distribution for fractions lighter than C60 (Mw about 842) is required. However, experimental data for the SCN distribution in a crude oil are scarce and are not commonly reported for fractions heavier than SCN30. Therefore, in PJ method, a splitting scheme is required to extend the distribution to SCN59. Ji [21] applied the Whitson three parameter Gamma distribution function [26] for the extension of the SCNs' distribution. Furthermore, as the application of Eq. 1 requires accurate values of SG for each SCN, Ji [21] proposed a formula to correlate the SG logarithmically to the Mw of an SCN with two unknown parameters to be evaluated using the available information on SCN7 and the dead fluid. According to Ji [21], when the experimental data for calculating unknown parameters are not available, the general correlations of Riazi and Al-Sahhaf [27] can be used:

$$SG_{SCN,i} = 1.07 - \exp(3.56073 - 2.93886 \, M_{w_{SCN,i}}^{0.1}) \qquad (2)$$

Ji [21] argues that the application of Riazi and Al-Sahhaf [27] correlations may result in under/over estimation of specific gravities of SCNs. Due to wider range of application, however, for the purpose of evaluations made in this study, whenever SG of SCNs are not experimentally available, Riazi and Al-Sahhaf [27] correlation is used to evaluate SGs.


## Coutinho and Daridon (CD) Method

By making plausible assumptions that, (i) n-alkanes are the only wax forming components in crudes, and (ii) n-alkanes distribution in a crude obeys the exponential decay behaviour, Coutinho and Daridon [1] proposed that only total wax content and the decay rate are required to define the normal paraffin distribution of a crude. The decay rate, $\alpha_D$, is defined as the ratio of wt% of two consecutive n-alkanes heavier than nC20 in mixture:

$$\alpha_D = \frac{Wt_{nC_{n+1}}}{Wt_{nC_n}} \qquad (3)$$

Coutinho and Daridon [1] suggested that, in absence of experimental data on the normal alkane distribution, a general value of 0.88 can be set for $\alpha_D$, and when the total wax content (in their work for fractions heavier than SCN20) is not available one can use the following formula to estimate it:

$$Wt\%_{(nC_{20}+)} = 0.070 \times Mw - 8.3 \qquad (4)$$

As mentioned by the authors, the above formula provides a good estimation of wax content of paraffinic waxy crudes based on their molecular weight Mw. Coutinho and Daridon [1] have, however, outlined that the application of the general decay rate of 0.88 and Eq. 4 should be done with care. This is indeed important and will be covered later on while discussing the pros and cons of this approach. Contrary to the PJ method, the CD method is fully predictive. Using this method, the predicted WDT and WPC will depend on the paraffin distribution (decay rate), total wax content and the heaviest paraffin in crude, though the dependency of the predicted WPC on the last parameter for normal decay rate of waxy crudes (~0.88) is insignificant [4].

In addition to the evaluation of the two methods described, the applicability of well-known PNA characterization schemes (e.g. Riazi et al. [28,29] and van-Nes and van-Westen [30]) to model the wax precipitation in real oils were assessed. It was observed that uncertainties in the amount of wax forming components using these methods are high. Furthermore, they require experimental information of several properties for each SCN to be available. For example, the method of van-Nes and van-Westen [30] requires the boiling point and specific gravity of the SCNs and Riazi et al. [28,29] method requires information on refractivity index, viscosity gravity or both. Such data are not typically available, and if correlations are used to evaluate them, extra uncertainty is added to calculations. Furthermore, it

was revealed that significant changes in predicted WPC may be observed when a different version of Riazi and co-workers correlations, i.e. Riazi and Roomi [29] formulation are used. Therefore, these methods have limited applicability and are not advised for wax precipitation modelling where accurate estimates of the wax forming components fractions are required as it is hard to evaluate their performance for a broad range of SCNs as outlined by other authors [31]. Below an evaluation of the methods described above, integrated into the UCV model, is presented.

## Methods Evaluation

The assessment of the two approaches for the WPC are made for several crudes, the experimental data of which are taken from the work of Rønningsen et al. [15] and Pedersen et al. [16]. In their work, the authors have provided the WPC data using NMR technique for temperatures as low as −40 ℃. However, as detailed by Coutinho and Daridon [1], the accuracy of their measurements below 0 ℃ is questionable. Therefore, similar to Coutinho and Daridon [1], here, the models are compared with the experimental WPC data for temperatures higher than 273 K.

Figure **1** to Figure **5** provide comparisons of the two methods described combined with UCV model for some of the oils studied by Rønningsen et al. [15] and Pedersen et al. [16]. As can be seen in these figures, the CD method outperforms the PJ method for many of the cases.
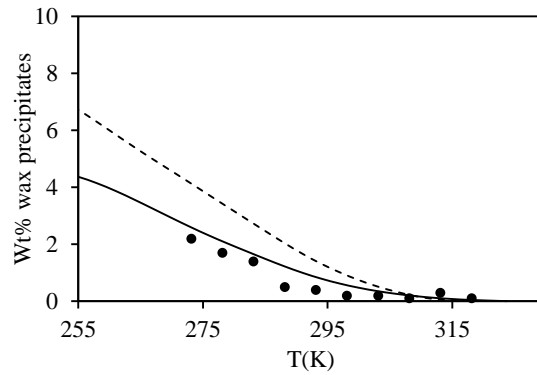


Figure 1: WPC calculated with CD method (solid line) and PJ method (dashed line) for Oil 2 mixture of Pedersen et al. [16]; ●: experimental WPC data
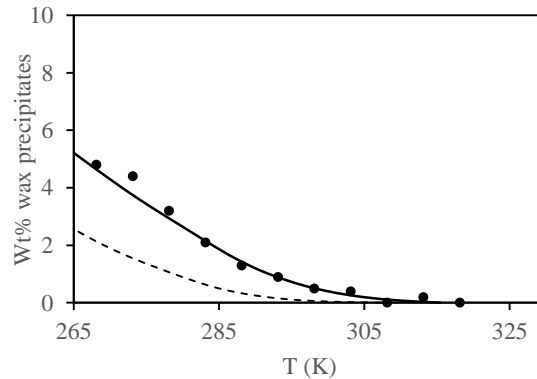


Figure 2: WPC calculated with CD method (solid line) and PJ method (dashed line) for Oil 4 mixture of Pedersen et al. [16]; ●: experimental WPC data.
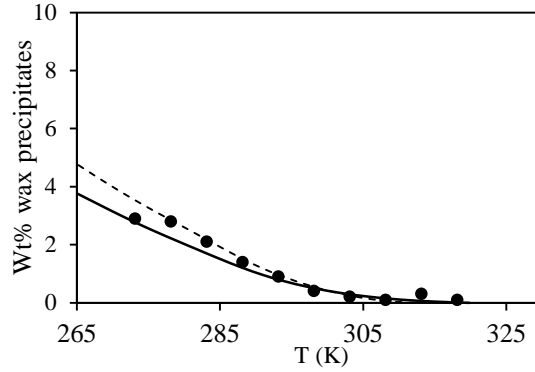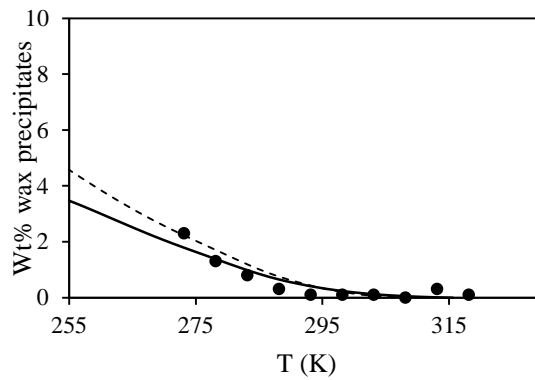
Figure 3: WPC calculated with CD method (solid line) and PJ method (dashed line) for Oil 8 mixture of Pedersen et al. [16]; ●: experimental WPC data



Figure 4: WPC calculated with CD method (solid line) and PJ method (dashed line) for Oil 15 mixture of Pedersen et al. [16]; ●: experimental WPC data
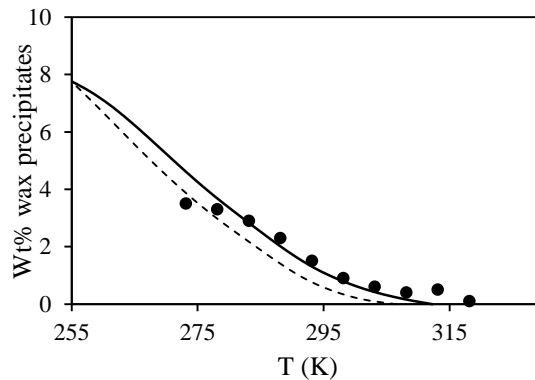


Figure 5: WPC calculated with CD method (solid line) and PJ method (dashed line) for Oil 16 mixture of Pedersen et al. [16]; ●: experimental WPC data

The superiority of the CD method over the PJ method might seem to be at odds with the fact that the same set of experimental data has been used to evaluate three unknown parameters of Eq. 1 of PJ methods. In fact, the results obtained for the same systems in the work of Ji [21] show better agreement with experimental data. It should be noted that the set of correlations used for evaluating the thermophysical properties, the thermodynamic model used for describing the non-ideality of solid and fluid phases in the work of Ji [21] are different from the ones used in the current work. Furthermore, Ji [21] proposed a modified version of UNIQUAC activity coefficient model to describe

solid waxy parts. Therefore, the difference in results of WPC calculation presented here compared to the work of Ji [21], signifies the need to readjust unknown parameters of the PJ methods when changing the correlations used to calculate the thermophysical properties of paraffins and the thermodynamic models for describing solid and fluid phases. This, in turn, again underlines the fact that PJ methods are not predictive, and this severely undermines the robustness of the model. In contrast, due to the sound theoretical basis of the CD method, it is fully predictive, though it has its disadvantages as described later.

Furthermore, as mentioned, when TBP data of heavy fractions are not available the PJ method requires a splitting scheme. The dependency of this method on the splitting scheme utilized is, here, evaluated using the Whitson three-parameter Gamma distribution function [26] and Riazi distribution [32,33] which is a three-parameter modified Weibull distribution function [34]. Both of these three-parameter distribution functions were able to match experimental TBP data and accordingly, the difference of WPC calculated using each of these distributions differ marginally for most of the cases studied here. However, there are some cases for which the difference becomes observable. This is shown for the case of Pedersen et al. [16] Oil 16. As presented in

Figure **6** both distributions can properly match the TBP data. However, their extension to SCNs of very high molecular weight shows a relatively significant difference in mole fractions. A comparison of WPCs obtained using both distributions is presented in

Figure **7**. As shown the WPC obtained by PJ method can be dependent on the distribution function used to match TBP data and split the plus fraction. The impact of changing the distribution function is even greater while calculating WDT as, clearly, the WDT is a strong function of the amount of assumed last normal alkane in the mixture.

Moreover, the accuracy of the PJ method is a function of the specific gravity of SCNs. As mentioned, this issue is discussed in details in the work of Ji [21] in which the author has proposed a new correlation for calculation of the specific gravity of SCNs as a logarithmic function of their molecular weight with two unknown parameters by:

$$SG_{SCN,i} = \frac{a_{SG} \times \ln(Mw_{SCN,i}) + b_{SG}}{1 + (0.0126\,Mw_{SCN,i} - 2.2667) \times 10^{-2}} \tag{5}$$

Here, $a_{SG}$ and $b_{SG}$ are mixture specific constant which are calculated using information on SG and Mw of SCN7 and the dead fluid which might not always be available.
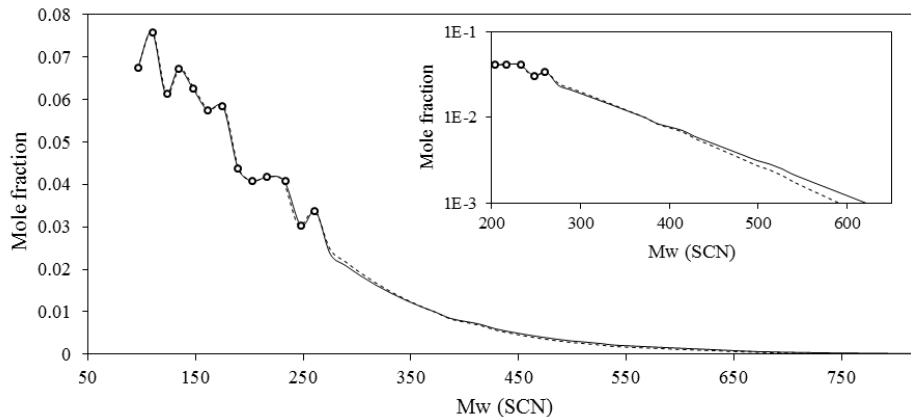


Figure 6: Whitson (solid line) and Riazi (dashed line) distributions used for matching the molecular weight of SCNs and splitting the plus fraction for Pedersen et al. [16] Oil 16; ○: experimental data. The vertical axis of the graph in upper right corner is in logarithmic scale.
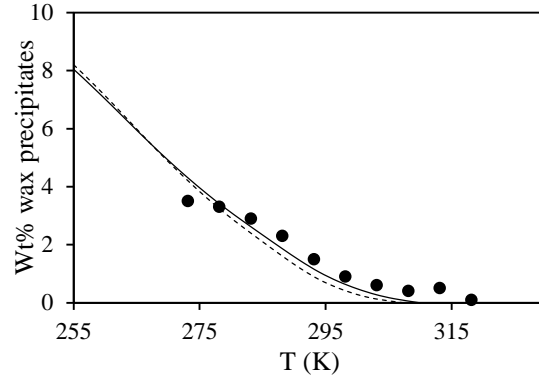
Figure 7: WPC of Pedersen et al. [16] Oil 16 calculated by PJ method with SCNs fractions extended using Whitson (solid line ) and Riazi (dashed line) distributions. ●: experimental WPC.

As opposed to the PJ method, the method of CD is fully predictive and as shown is robust, though the wt% decay rate of 0.88 is questionable in some cases. For example, for the cases of two condensate real mixture studied by Daridon et al. [35] for which the extended distribution of n-alkanes are experimentally available, the molar decay rate of 0.85 is reported which corresponds to the wt% decay rate of 0.9. Generally, the lighter the system is, the higher is the decay rate. The effect of changing the decay rate is shown for the example case of Pedersen et al. [16] Oil 15 in Figure 8. As observed, the higher decay rate would result in higher WDT estimated and larger slopes of WPC at higher temperatures when the nC20+ wax content is kept constant, while the changes on the WPC is marginal. The change in nC20+ wax content can however significantly changes the WPC. In fact, if the total wax content is not experimentally reported and Eq. 4 is used to estimate it for some of the sample cases drastic changes in WPC is observed, as shown for the example case of Pedersen et al. [16] Oil 2 in Figure 9.
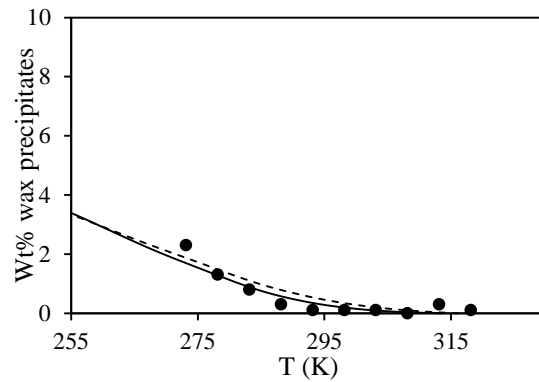


Figure 8: WPC of Pedersen et al. [16] Oil 15 calculated by CD method with n-alkane distribution obtained by wt% decay rates of 0.88 (solid line) and 0.9 (dashed line). ●: experimental WPC.
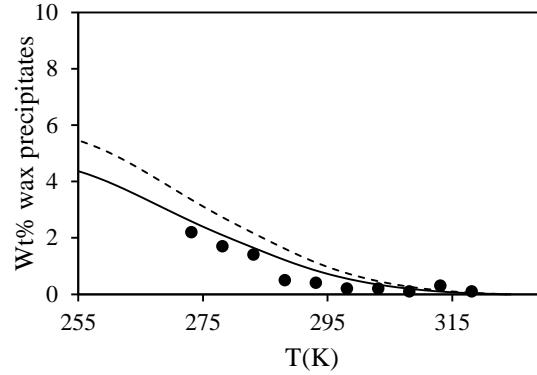
Figure 9: WPC of Pedersen et al. [16] Oil 2 calculated by CD method with nC20+ wax content measured experimentally (solid line) and calculated by Eq. 4 (dashed line). ●: experimental WPC.

Furthermore, Coutinho and Daridon [1] have argued that the distribution of alkanes lighter that n-eicosane may not show an exponential decay behaviour. That is why the total wax content considered in their work (Eq. 4) corresponds to the amount of paraffins heavier than nC20. Therefore, their model is not applicable for wax precipitation in real mixtures with a significant amount of wax forming components lighter than nC20. Nevertheless, the advantage of CD method resides in the fact that both the decay rate and nC20+ wax content can be used as adjustable parameters for matching WPC. Additionally, the fact that the model is fully predictive, along with its acceptable performance and independence from the splitting schemes and requiring lowest amount of experimental data, is convincing enough to choose this approach for calculating n-alkanes (wax forming) components distributions in the crude. Therefore, for the rest of the calculations the CD method is chosen for characterising the paraffin content and distribution in real mixtures.

## Modelling Hydrate Formation in Real Mixtures

The constituents of hydrates are water and light hydrocarbons, therefore, in contrast to wax, the prediction of hydrate phase boundary is not very sensitive to the characterization of the unknown fraction over a moderate pressure range, as long as the saturation pressures are accurately measured. As mentioned earlier, using any of the two PJ and CD schemes presented, similar to the approach applied by Daridon et al. [35] and Coutinho et al. by adjusting the critical properties of the lumped component representing the non-paraffinic parts of SCNs all together, accurate calculation of the hydrate dissociation line can be achieved. Using the CD scheme for characterization, Figure **10** presents the hydrate dissociation for BO1, a black oil system [36] for which experimental hydrate dissociation points, as well as saturation pressure data, are available. The composition and properties of BO1 are provided in
Table **1**.

| Comp. | Mol% | Mw | SG | Comp. | Mol% | Mw | SG | HDPs | |
|-------|------|----|----|-------|------|----|----|------|------|
| Methane | 23.98 | 16 | - | SCN10 | 4.06 | 133 | 0.776 | T(K) | P(MPa) |
| Ethane | 3.98 | 30 | - | SCN11 | 3.31 | 147 | 0.79 | 273.5 | 0.58 |
| Propane | 5.65 | 44 | - | SCN12 | 2.64 | 162 | 0.801 | 278.5 | 1.3 |
| i-Butane | 2 | 58 | - | SCN13 | 2.36 | 173 | 0.815 | 283.5 | 2.79 |
| n-Butane | 4.12 | 58 | - | SCN14 | 2.18 | 188 | 0.831 | 286 | 4.1 |
| i-Pentane | 2.09 | 72 | - | SCN15 | 1.95 | 203 | 0.837 | 287.25 | 4.99 |
| n-Pentane | 2.89 | 72 | - | SCN16 | 1.61 | 220 | 0.844 | 287.33 | 5.06 |
| SCN6 | 4.1 | 85 | 0.666 | SCN17 | 1.28 | 233 | 0.849 | Saturation Points | |
| SCN7 | 6.25 | 94 | 0.714 | SCN18 | 1.27 | 248 | 0.856 | T(K) | P(MPa) |
| SCN8 | 6.55 | 105 | 0.738 | SCN19 | 1.05 | 262 | 0.863 | 373 | 9.4 |
| SCN9 | 5.2 | 119 | 0.761 | C20+ | 11.5 | 483 | 0.947 | - | - |

Table 1: Composition and experimental saturation pressure and HDPs of black oil BO1 [36].
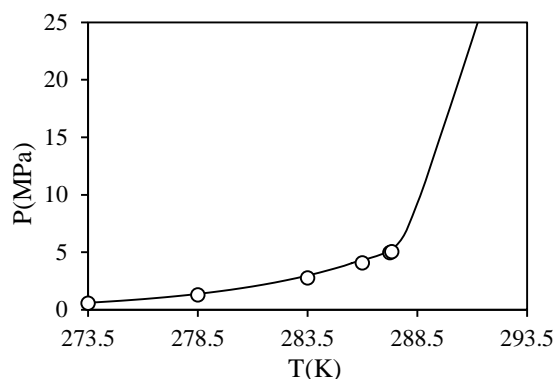
Figure 10: Hydrate dissociation prediction for black oil system BO1; —— Hydrate dissociation line UCV model with the fluid characterised by CD method [1].○: Experimental hydrate dissociation points in the absence of wax [36].

## Integrated Wax-Hydrate Modelling in Real Mixtures

In this section, the UCV model with the extension of the CD method for calculating normal alkanes' distribution is used for evaluation of WPC for a live real mixture LTB98-1. The composition of this system, the properties of its SCNs and its QCM measured WDT data are listed in
Table 2.

| Comp. | Mol% | Mw | SG | Comp. | Mol% | Mw | SG | WDTs | |
|---|---|---|---|---|---|---|---|---|---|
| $CO_2$ | 0.49 | - | - | SCN9 | 7.1 | 116 | 0.778 | T(K) | P(MPa) |
| Nitrogen | 1.16 | - | - | SCN10 | 5.26 | 131 | 0.79 | 311.15 | 0.2 |
| Methane | 31.26 | - | - | SCN11 | 3.9 | 147 | 0.789 | 310.15 | 3.4 |
| Ethane | 2.03 | - | - | SCN12 | 3.05 | 161 | 0.809 | 310.15 | 6.1 |
| Propane | 0.68 | - | - | SCN13 | 2.63 | 173 | 0.822 | 310.15 | 7.9 |
| i-Butane | 0.2 | - | - | SCN14 | 2.63 | 186 | 0.839 | 310.15 | 9.6 |
| n-Butane | 0.68 | - | - | SCN15 | 2.18 | 203 | 0.837 | 311.15 | 13.2 |
| i-Pentane | 0.86 | - | - | SCN16 | 1.73 | 215 | 0.843 | 312.15 | 19.3 |
| n-Pentane | 1.47 | - | - | SCN17 | 1.4 | 229 | 0.841 | 313.15 | 28.8 |
| SCN6 | 3.94 | 89 | 0.678 | SCN18 | 1.35 | 246 | 0.843 | 314.15 | 36.4 |
| SCN7 | 8.55 | 92 | 0.733 | SCN19 | 1.13 | 258 | 0.854 | - | - |
| SCN8 | 10.59 | 103 | 0.757 | C20+ | 5.76 | 384 | 0.88 | - | - |

Table 2: Composition and SCN properties of LTB98-1 live oil

As discussed, tuning of model parameters is inevitable for matching WDT data in real systems. Using the Coutinho and Daridon method [1], the nC20+ wax content, the decay rate and the assumed last alkane present in the mixture, can all be used as an adjustable parameter to match WDT data. For this mixture, assuming the last n-alkane in the mixture is nC59 (as discussed before), the adjusted value of nC20+ wax content to match the experiment WDT data is 1.2 wt%. Also, by changing the last alkane to nC69 and using the same decay rate, but this time with the nC20+ wax content of 0.2, again excellent match with WDT data is achieved. This is shown in
Figure 11. It should be noted that for this mixture Eq. 4 will result in negative nC20+ wax content. To be consistent with the rest of the results, the first set of values for tuned parameters are used to do the rest of the calculations on this system. Using nC20+ wax content of 1.2 and assuming the heaviest alkane is nC59,
Figure 12 shows the phase diagram of the live real mixture LTB98-1.
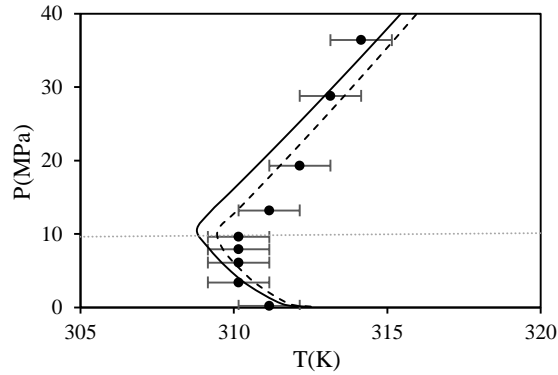
Figure 11: Live real fluid LTB98-1 wax phase boundary calculated using the CD method
integrated to UCV model with the last alkane to be nC59 and nC20+ wt% of 1.2 (solid line) and
nC69 and nC20+ wt% of 0.2 (dashed line). Points: experimental WDT data. The error bars are
corresponding to ±1K for purpose of graphical representation

As shown in
Figure **12**, for this mixture waxes are formed at a higher temperature than hydrates. Therefore the mutual effects of
hydrates and waxes for this mixture are solely presented inside the hydrate phase by comparing the change in WPC
of precipitable alkanes (here alkanes heavier than nonadecane), i.e. WPC of WP, for two pressures, one above and
one below the bubble point in Figure 13. As shown in Figure 13, similar to the observations made in our previous
work for synthetic mixtures [2], (i) hydrates can synergistically increase wax precipitation, and (ii) appearance of sI
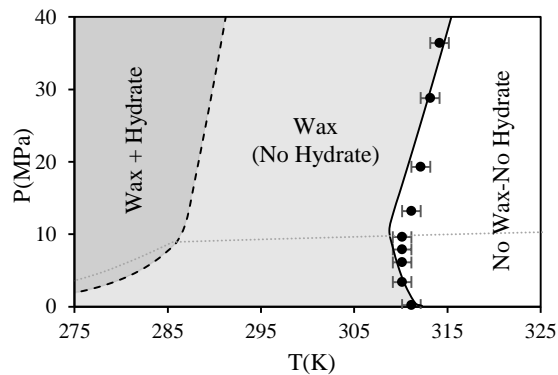hydrate can further increase this effect at lower temperatures.



Figure 12: Live real fluid LTB98-1 wax (solid line) and hydrate (dashed line) phase boundaries as
well as bubble line calculated with UCV model with CD method to extend n-alkane distribution.
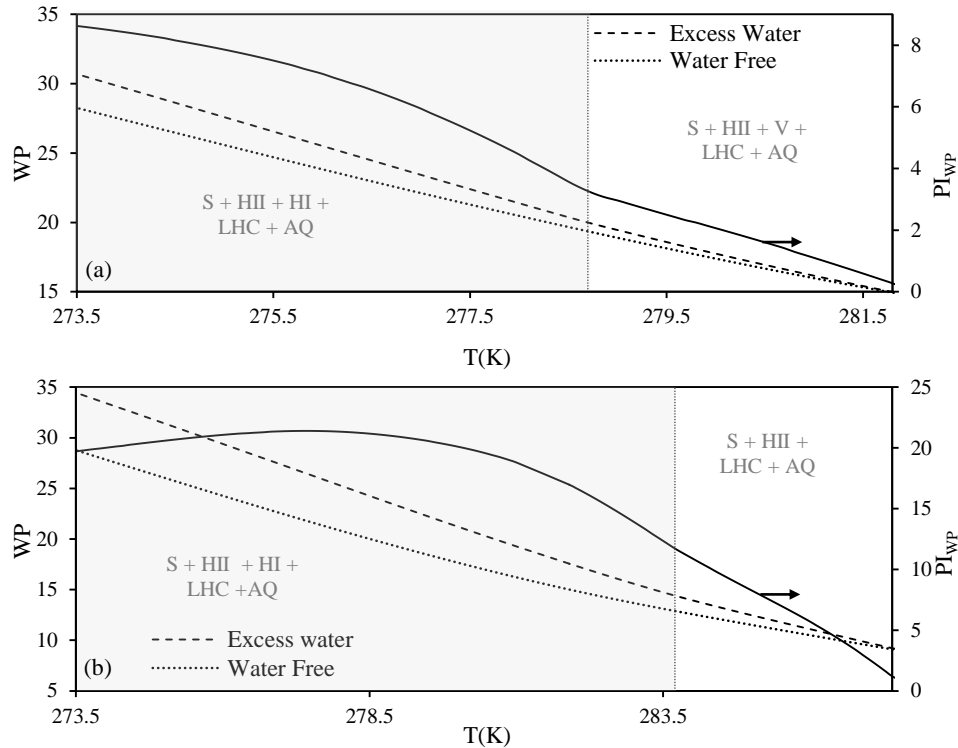Points: experimental WDT.

Figure 13: WPCs for amount of WP shown both in excess water and water free conditions (left axis) and the percentage increase in WP comparing the two conditions (right axis) for LTB98-1 below the hydrate dissociation temperature at (a) 5 MPa (below bubble point) and (b) 15 MPa (above bubble point)

## Conclusions

In this work, the extension of the previously developed integrated thermodynamic model (UCV) for application of solid-fluid equilibria of wax, hydrate and combined wax-hydrate formation in real systems with unknown fractions is explained. The challenges of modelling hydrate and wax formation in real mixtures are described separately.

As discussed, the main complication for modelling combined wax-hydrate formation in real mixtures is with the wax modelling part and in particular the correct quantification of the distribution of normal paraffins in the unknown fraction. In fact, as explained from the existing methods for extending wax precipitation models to real systems, only those which (i) distinguish the wax forming (paraffinic) part from the non-paraffinic part for each unknown fraction and (ii) are capable of identifying the distribution of wax forming fractions in the heavy end, are reliable. Accordingly, the performance of two approaches which satisfy these criteria was evaluated. Based on the evaluations made the method of Coutinho and Daridon [1] was selected for this purpose.

The UCV model with the extension of Coutinho and Daridon [1] method was applied for integrated wax-hydrate modelling in a real mixture for which experimental WDT data are available. Based on the results obtained it is concluded that hydrate formation could escalate the wax precipitation problem which agrees with the results achieved for synthetic systems [2].

## Acknowledgment

## References

[1]     J.A.P. Coutinho, J.L. Daridon, *Low-pressure modeling of wax formation in crude oils*, Energy and Fuels. 15 (2001) 1454–1460.

[2]     M.A. Mahabadian, A. Chapoy, R. Burgass, B. Tohidi, *Mutual effects of paraffin waxes and clathrate*

        *hydrates: A multiphase integrated thermodynamic model and experimental measurements*, Fluid Phase Equilib. 427 (2016) 438–459.

[3]     A. Hammami, J. Ratulowski, J.A.P. Coutinho, *Cloud points: Can we measure or model them?*, Pet. Sci. Technol. 21 (2003) 345–358.

[4]     J.A.P. Coutinho, J.L. Daridon, *The limitations of the cloud point measurement techniques and the influence of the oil composition on its detection*, Pet. Sci. Technol. 23 (2005) 1113–1128.

[5]     J.A.P. Coutinho, B. Edmonds, T. Moorwood, R. Szczepanski, X. Zhang, *Reliable wax predictions for flow assurance*, Energy and Fuels. 20 (2006) 1081–1088.

[6]     M. Sanjay, B. Simanta, S. Kulwant, *Paraffin problems in crude oil production and transportation: a review*, SPE Prod. Facil. 10 (1995) 50–54.

[7]     A. Hammami, M.A. Raines, *Paraffin deposition from crude oils: Comparison of laboratory results with field data*, SPE J. 4 (1999) 9–18.

[8]     J.Y. Zuo, D.D. Zhang, *Wax formation from synthetic oil systems and reservoir fluids*, Energy and Fuels. 22 (2008) 2390–2395.

[9]     B. Edmonds, T. Moorwood, R. Szczepanski, X. Zhang, *Simulating wax deposition in pipelines for flow assurance*, Energy and Fuels. 22 (2008) 729–741.

[10]    J.A.P. Coutinho, M. Gonçalves, M.J. Pratas, M.L.S. Batista, V.F.S. Fernandes, J. Pauly, et al., *Measurement and Modeling of Biodiesel Cold-Flow Properties*, Energy and Fuels. 24 (2010) 2667–2674.

[11]    D.D. Erickson, V.G. Niesen, T.S. Brown, *Thermodynamic measurement and prediction of paraffin precipitation in crude oil*, in: SPE Annu. Tech. Conf. Exhib., Society of Petroleum Engineers, 1993.

[12]    K. Paso, H.S. Fogler, *Influence of n-paraffin composition on the aging of wax-oil gel deposits*, AIChE J. 49 (2003) 3241–3252.

[13]    A.J. Briard, M. Bouroukba, D. Petitjean, N. Hubert, J.C. Moïse, M. Dirand, *Thermodynamic and structural analyses of the solid phases in multi-alkane mixtures similar to petroleum cuts at ambient temperature*, Fuel. 84 (2005) 1066–1073.

[14]    J.A.P. Coutinho, J. Pauly, J.L. Daridon, *Modelling phase equilibria in systems with organic solid solutions*, Comput. Aided Prop. Estim. Process Prod. Des. (2004) 229–249.

[15]    H.P. Rønningsen, B. Bjorndal, A. Baltzer Hansen, W. Batsberg Pedersen, *Wax precipitation from North Sea crude oils: 1. Crystallization and dissolution temperatures, and Newtonian and non-Newtonian flow properties*, Energy and Fuels. 5 (1991) 895–908.

[16]    W.B. Pedersen, A.B. Hansen, E. Larsen, A.B. Nielsen, H.P. Rønningsen, *Wax precipitation from North Sea crude oils. 2. Solid-phase content as function of temperature determined by pulsed NMR*, Energy and Fuels. 5 (1991) 908–913.

[17]    K.S. Pedersen, P. Skovborg, H.P. Rønningsen, *Wax precipitation from North Sea crude oils. 4. Thermodynamic modeling*, Energy and Fuels. 5 (1991) 924–932.

[18]    K.S. Pedersen, *Prediction of Cloud Point Temperatures and Amount of Wax Precipitation*, SPE Prod. Facil. 10 (1995) 46–49.

[19]    C. Lira-Galeana, A. Firoozabadi, J.M. Prausnitz, *Thermodynamics of wax precipitation in petroleum mixtures*, AIChE J. 42 (1996) 239–248.

[20]    H. Pan, A. Firoozabadi, P. Fotland, *Pressure and composition effect on wax precipitation: Experimental data and model results*, SPE Prod. Facil. 12 (1997) 250–258.

[21]    H. Ji, *Thermodynamic modelling of wax and integrated wax-hydrate*, Phd Thesis. Heriot-Watt University, 2004.

[22]    K.S. Pedersen, P.L. Christensen, J.A. Shaikh, *Phase behavior of petroleum reservoir fluids*, CRC Press, 2014.

[23]    M.R. Riazi, T.E. Daubert, *Characterization parameters for petroleum fractions*, Ind. Eng. Chem. Res. 26 (1987) 755–759.

[24]    B.I. Lee, M.G. Kesler, *A generalized thermodynamic correlation based on three-parameter corresponding states*, AIChE J. 21 (1975) 510–527.

[25]    M.G. Kesler, B.I. Lee, *Improve prediction of enthalpy of fractions*, Hydrocarb. Process. 55 (1976) 153–158.

[26]    C.H. Whitson, *Characterizing hydrocarbon plus fractions*, Soc. Pet. Eng. J. 23 (1983) 683–694.

[27]    M.R. Riazi, T.A. Al-Sahhaf, *Physical properties of heavy petroleum fractions and crude oils*, Fluid Phase Equilib. 117 (1996) 217–224.

[28]    M.R. Riazi, T.E. Daubert, *Prediction of molecular-type analysis of petroleum fractions and coal liquids*, Ind. Eng. Chem. Process Des. Dev. 25 (1986) 1009–1015.

[29]    M.R. Riazi, Y.A. Roomi, *Use of the Refractive Index in the Estimation of Thermophysical Properties of*

*Hydrocarbons and Petroleum Mixtures*, Ind. Eng. Chem. Res. 40 (2001) 1975–1984.

[30]  K. Van Nes, H.A. Van Westen, *Aspects of the constitution of mineral oils*, Elsevier Pub. Co., 1951.

[31]  F. Varzandeh, W. Yan, E.H. Stenby, *General approach to characterize reservoir fluids using a large pvt database*, in: SPE Eur. Featur. 78th EAGE Conf. Exhib., Society of Petroleum Engineers, 2016.

[32]  M.R. Riazi, *Distribution model for properties of hydrocarbon-plus fractions*, Ind. Eng. Chem. Res. 28 (1989) 1731–1735.

[33]  M.R. Riazi, *A continuous model for C7+ fraction characterization of petroleum fluids*, Ind. Eng. Chem. Res. 36 (1997) 4299–4307.

[34]  S. Sánchez, J. Ancheyta, W.C. Mccaffrey, S. Sa, J. Ancheyta, W.C. Mccaffrey, et al., *Comparison of probability distribution functions for fitting distillation curves of petroleum*, Energy and Fuels. 21 (2007) 2955–2963.

[35]  J.L. Daridon, J. Pauly, J.A.P. Coutinho, F. Montel, *Solid-liquid-vapor phase boundary of a North Sea waxy crude: Measurement and modeling*, Energy and Fuels. 15 (2001) 730–735.

[36]  A.H. Mohammadi, H. Ji, R.W. Burgass, A. Bashir, B. Tohidi, *Gas hydrates in oil systems*, in: SPE Eur. Annu. Conf. Exhib., Society of Petroleum Engineers, 2006.