THERMODYNAMIC MODELING OF WAX PRECIPITATION IN CRUDE OIL BASED ON PC-SAFT MODEL

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Abstract

Wax precipitation may occur in production or transportation of crude oil form field which is a serious problem in petroleum industry. Flow assurance issues concerning wax precipitation make it necessary to develop a precise thermodynamic model to predict the wax appearance temperature and amount of precipitation at different conditions. In this work a new procedure has been proposed to characterize crude oil based on the SARA test considering the wax and asphaltene as single pseudo components. Two scenarios have been chosen for the survey of the crude oil characterization, with and without asphaltene pseudo component. Also, in this work, the Perturbed Chain form of the Statistical Associating Fluid Theory, PC-SAFT, has been developed to evaluate its ability for modeling of wax precipitation prediction. It is demonstrated that the developed PC-SAFT model can correlate the wax precipitation amount better than basic models (multiple solid and solid solution) typically used in the industry. The results obtained with the proposed model show a remarkable matching with the experimental data for wax precipitation values. The obtained results are very promising in providing better approach to model wax precipitation.

Key words: Flow assurance, Wax precipitation, characterization, PC-SAFT model**.**

Nomenclature

A	[J]	Helmholtz free energy
AD		Average deviation
D	[g/cm^3]	Density
K	[J/K]	Boltzmann constant
MW	[g/gmol]	Molecular weight
N		Avogadro's number
Ns		Number of solid phases
P	[Pa]	Pressure
R	[Jmol^{-1}K^{-1}]	Gas universal constant
T	[K]	Temperature
V	[m^3]	Volume
Z		Compressibility factor
a		Peng Robinson equation parameter
b		Peng Robinson equation parameter
d	[Å]	Temperature dependent segment diameter
f	[Pa]	Fugacity
g_{ii}		Redial distribution function
k_{ij}		Binary interaction coefficient
m		Number of segments
n		Total number of components
t		Target variable
x		Mole fraction
z		Feed mole fraction
Δh	[J/mol]	Enthalpy change
ΔC_p	[Jmol^{-1}K^{-1}]	Heat capacity change
γ		Activity coefficient
δ		Solubility parameter
φ		Volume fraction
σ_{ii}	[Å]	Segment diameter
ρ	[1/Å^3]	Total number density of molecules
ε	[J]	Depth of pair potential
η		Packing fraction
ω		Acentric factor
θ		Physical property

Superscripts

L	Liquid
V	Vapor
S	Solid
f	Fusion
Res	Residual
hc	Hard chain
hs	Hard sphere
$disp$	Dispersion

Subscripts

cal	Calculated value
exp	Experimental value
p	Parrafin
n	Naphtene
a	Aromatic
c	Critical property

Introduction

Crude oil is a complex mixture of hydrocarbon groups consisting of saturates asphaltenes, resins, and aromatics. The change of temperature, pressure and oil composition may cause the precipitation of some hydrocarbons such as heavy paraffins or wax [1]. The wax precipitation may result in many problems such as decreasing the efficiency of transportation processes especially in subsea facilities. Prediction of the temperature at which the first crystals of wax are formed, known as wax appearance temperature or WAT, and the amount of wax precipitation is crucial in the design of oil production and transportation processes. Therefore, describing the solid-liquid equilibrium of hydrocarbons by development of a thermodynamic model is necessary to deal with all the processes involving wax crystallization. Several thermodynamic models were proposed for wax precipitation investigation but their predictions are not in good agreement with experimental data and usually overestimate the wax precipitation.

A literature review indicates that models of wax precipitation can be classified into two different categories. The first

category is based on the assumption that all the hydrocarbon components in precipitated solid phase are miscible and form a solid solution (SS). In this approach a cubic equation of state is used for vapor–liquid equilibrium and an activity coefficient model for solid–liquid equilibrium. Won [2-3] proposed regular solution models for wax precipitation. In Won's model, the SRK equation of state was employed to describe the vapor and liquid phases equilibrium. A modified regular solution theory was used to describe the liquid phase along the liquid–solid coexistence curve. Hansen et al. [4] used Flory's theory [5-6] of multi-component polymer solutions for activity coefficient of liquid phase to propose a modified regular solution. The model proposed by Hansen et al. exhibits limitations of Won's model. Pedersen et al. [7] developed the Won [2] modified model for WAT calculations. The model was validated using the experimental WAT data for the North Sea oils. Coutinho and Stenby [8] applied Wilson's model to describe orthorhombic solid phases. Later, Coutinho [9] modified UNIQUAC model to accurately describe orthorhombic solid phase behavior. Zuo et al. [1] developed the solid solution model to predict wax in crude oils and gas condensates. Their model considers the Poynting correction in the solid fugacity calculation and predicts wax appearance temperatures over a wide range of pressures and wax contents. Bhat and Mehrotra [10] measured and predicted wax–solvent mixtures phase behavior using the Flory free-volume model for liquid phase and the predictive UNIQUAC model for the solid phase. Ji et al. [11] succeeded to achieve wax disappearance temperature for binary and multi-systems by applying the UNIQUAC thermodynamic model. Firstly they estimated thermodynamic properties of the normal paraffins to calculate terms on fugacity coefficient equation and then then a new approach for describing wax solids, based on the UNIQUAC equation, was described. Esmaeilzadeh et al. [12] investigated various activity coefficient models and showed that predictive Wilson model is appropriated to explain the ideal behavior of the solid phase (prediction of wax precipitate in the atmospheric pressure). They used binary, ternary, quaternary and multi-component systems as experimental data to validate the model. Coutinho and Ruffier Me´ray [13] studied wax deposition using experimental and thermodynamics methods. They used the predictive UNIQUAC model for modeling the wax formation in hydrocarbon liquids. Nasrifar and Fani Kheshty [14] used the UNIQUAC model with a pressure dependence term resulting from the Clapeyron equation to predict the wax disappearance temperature of pure, binary and multicomponent paraffin mixtures for wide ranges of temperature, pressure and composition.

The second category of thermodynamic models is based on multiple solid (MS) phase model which considers each precipitated component as a separate solid phase which is not miscible with others. Lira-Galeana et al. [15] presented a wax thermodynamic model in which a multi pure-solid approach was used for description of wax solids. The Peng Robinson equation was used for calculating fugacity in the liquid and vapor phases. Vafaie Sefti et al. [16] applied multiple solid phase model to predict the equilibrium phase in oil mixtures. Liquid and gas phases were described using Peng Robinson equation. Dalirsefat and Feyzi [17] used the modified multiple solid phase thermodynamic model for predicting WAT and wax

precipitate amount. They have utilized Modified Peng Robinson (MPR) equation for calculating the fugacity of liquid and gas phases.

Statistical Associating Fluid Theory SAFT equation of state was developed by Chapman, et al. [18] based on extensions and simplifications of Wertheim's theory [19] for associating fluids. SAFT determines the free energy of a fluid as the sum of the free energy for a collection of spherical segments plus the change in free energy on bonding these spherical segments in a prescribed manner to form the molecules of interest. This change in free energy can be calculated from Wertheim's theory. Numerous forms of the SAFT equation of state have been proposed. These forms differ only in the segment term used to account for the van der Waals attraction between molecules; all use the same chain and association terms as introduced in the original SAFT papers by Chapman, et al. Gross and Sadowski [20] developed the perturbed chain modification (PC-SAFT) to SAFT, by extending the perturbation theory of Barker and Henderson [21] to a hard-chain reference. PC-SAFT employs a hard sphere reference fluid, described by the Mansoori et al. [22] equation of state. This version of SAFT properly predicts the phase behavior of high molecular weight fluids.

The different inconsistencies or overestimations resulted in from solid solution and multiple solid approaches make it necessary to look for a more precise model. In this work, a new characterization of oil based on the SARA test results was used to consider wax as a pseudo component in low asphaltene content crude oils. Asphaltene also was considered as a single pseudo component for highly asphaltenic crude oils to minimize the model deviation from experiments. The wax precipitation data in Iranian crude oil under different temperature at atmospheric pressure were used to develop a model using the perturbed chain form of the statistical associating fluid theory, PC-SAFT.

Theory
Thermodynamic models

Multiple solid model considers each solid phase as a pure component which does not mix with other solid phases. Therefore, the criterion of vapor, liquid and solid equilibria is equality of the fugacities for every component i, as the following equations:

$$f_i^L = f_i^V = f_{pure,i}^S \quad i = n - Ns + 1, \dots, n \qquad (1)$$

$$f_i^L = f_i^V \qquad i = 1,2, \dots, n - Ns \qquad (2)$$

where f is the fugacity, n is the total number of components, and Ns is the number of solid phases determined by Michelsen's stability analysis [23]. Fugacities of liquid and vapor phases are calculated directly from the equations of state but the solid phase fugacity must be calculated from the below expression.

$$ln\left(\frac{f^S}{f^L}\right)_{Pure,i} = \frac{\Delta h_i^f}{RT}\left(\frac{T}{T_i^f} - 1\right) - \frac{\Delta C_{pi}}{R}\left[1 - \frac{T}{T_i^f} + ln\left(\frac{T_i^f}{T}\right)\right] \quad (3)$$

where T_i^f is the fusion temperature, $\Delta C_{pi} = C_{pi}^L - C_{pi}^S$, where C_{pi}^L and C_{pi}^S are the heat capacity of pure component i at constant pressure corresponding to liquid and solid phases, respectively. In the above Eq. Δh_i^f is the fusion enthalpy.

Using above equations and an equation of state, fugacities are calculated. Among the equations of state, Peng Robinson equation of state is used:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)}$$ (4)

where a and b parameters are described by critical properties.

In solid solution model, the fugacities in the solid and liquid phases are expressed by:

$$f_i^S(p,T,x_i^S) = x_i^S \gamma_i^S f_{Pure,i}^S$$ (5)
$$f_i^L(p,T,x_i^L) = x_i^L \gamma_i^L f_{Pure,i}^L$$ (6)
$$f_i^L(p,T,x_i^L) = f_i^S(p,T,x_i^S)$$ (7)

By combining Eqs.(5), (6) and (7) the criterion of equal fugacities can be expressed as:

$$\frac{x_i^S}{x_i^L} = \frac{\gamma_i^L f_{Pure,i}^L}{\gamma_i^S f_{Pure,i}^S}$$ (8)

In order to determine the activity coefficients, Won [2] has used regular solution theory which means that the activity coefficients are dependent to solubility parameters δ_i for each component as the following equations.

$$\ln \gamma_i^L = \frac{V_i^L (\bar{\delta}^L - \delta_i^L)^2}{RT}$$ (9)

$$\ln \gamma_i^S = \frac{V_i^S (\bar{\delta}^S - \delta_i^S)^2}{RT}$$ (10)

$$\bar{\delta}^L = \sum_i \varphi_i^L \delta_i^L$$ (11)
$$\bar{\delta}^S = \sum_i \varphi_i^S \delta_i^S$$ (12)
$$\varphi_i^L = \frac{x_i^L V_i^L}{\sum_i x_i^L V_i^L}$$ (13)
$$\varphi_i^S = \frac{x_i^S V_i^S}{\sum_i x_i^S V_i^S}$$ (14)

where δ_i^L and δ_i^S are the solubility parameters of component i in the liquid and solid phase, respectively. The terms φ_i^L and φ_i^S represent the volume fraction of component i in the liquid and solid phases. The solubility parameters in liquid state can be calculated from a correlation proposed by Riazi and Al-Sahhaf [24] for paraffins in crude oil:

$$\delta_i^L = 8.6 - \exp(2.219195 - 0.54907 MW_i^{0.3})$$ (15)

The solubility parameters of other components are estimated by the correlations proposed by Leelavanichkul et al. [25] as follows. For naphthenic components:

$$\delta_i^L = 8.7 - \exp(2.219195 - 0.54907 MW_i^{0.3})$$ (16)

For aromatic components:

$$\delta_i^L = 8.8 - \exp(2.219195 - 0.54907 MW_i^{0.3})$$ (17)

The solubility of component i in the solid phase can be calculated as:

$$\delta_i^S = \left(\frac{\Delta h_i^f}{V_i} + \delta_i^{L^2}\right)^{0.5}$$ (18)

Won used the following expression for the liquid and solid molar volumes:

$$V_i = V_i^L = V_i^S = \frac{MW_i}{D_{i,25}^L}$$ (19)

where $D_{i,25}^L$ is the liquid phase density of component i at 25 ºC for which can be calculated as follow:

$$D_{i,25}^L = 0.8155 + 0.6272 \times 10^{-4} MW_i - \frac{13.06}{MW_i}$$ (20)

The PC-SAFT model for non-associating fluids in terms of the residual Helmholtz free energy is expressed as [20]:

$$\tilde{a}^{res} = \frac{A^{res}}{NKT} = \tilde{a}^{hc} + \tilde{a}^{disp}$$ (21)

Hard chain reference contribution is as follow:

$$\tilde{a}^{hc} = \bar{m}\tilde{a}^{hs} - \sum_i x_i(m_i - 1)\ln g_{ii}^{hs}(\sigma_{ii})$$ (22)

where $\bar{m}$ is the mean segment number in the mixture.

$$\bar{m} = \sum_i x_i m_i$$ (23)

The Helmholtz free energy of the hard sphere fluid is given by:

$$\tilde{a}^{hs} = \frac{1}{\zeta_0}\left[\frac{3\zeta_1\zeta_2}{(1-\zeta_3)} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0\right)\ln(1-\zeta_3)\right]$$ (24)

and the radial distribution function of the hard sphere fluid is:

$$g_{ii}^{hs} = \frac{1}{(1-\zeta_3)} + \left(\frac{d_i d_j}{d_i+d_j}\right)\frac{3\zeta_2}{(1-\zeta_3)^2} + \left(\frac{d_i d_j}{d_i+d_j}\right)^2 \frac{2\zeta_2^2}{(1-\zeta_3)^3}$$ (25)

where ζ_n is defined as:

$$\zeta_n = \frac{\pi}{6}\rho \sum_i x_i m_i d_i^n \qquad n \in \{0,1,2,3\}$$ (26)

The temperature dependent segment diameter d_i of is given by:

$$d_i = \sigma_i\left[1 - 0.12 \exp\left(-3\frac{\varepsilon_i}{KT}\right)\right]$$ (27)

The dispersion contribution to the Helmholtz free energy is given by:

$$\tilde{a}^{disp} = \tilde{a}_1 + \tilde{a}_2 = -2\pi\rho I_1 \overline{(m^2 \varepsilon \sigma^3)} - \pi\rho\bar{m}C_1 I_2 \overline{(m^2 \varepsilon^2 \sigma^3)}$$ (28)

where C_I is defined in terms of compressibility expression as:

$$C_1 = \left(1 + Z^{hc} + \rho\frac{\partial Z^{hc}}{\partial\rho}\right)^{-1} = \left(1 + \bar{m}\frac{8\eta - 2\eta^2}{(1-\eta)^4} + (1 - \bar{m})\frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^2}\right)^{-1}$$ (29)

Lorentz Bertholet combining rule is employed for a pair of unlike segments as:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$$ (30)
$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j(1 - k_{ij})}$$ (31)

I_1 and I_2 are dependent to the system packing fraction and average segment number and are substituted by simple power series in density [20]. In this model, there are 3 parameters for each component (in non-associating fluids) which must be determined. Some correlations have been proposed by various researchers to determine mentioned parameters in terms of

molecular weight. In this way, average molecular weight can be used for pseudo components of crude oil.

Fusion properties

As mentioned in previous sections, the fugacity ratio of each solid component depends on fusion properties, i.e. the melting point temperature, enthalpy of fusion, and heat capacity change. Various types of components existing in the crude oil such as saturates, aromatics and etc. causes different proposed correlations for determining the aforementioned properties. The fusion temperature of normal alkanes can be calculated using the proposed correlation by Won [2]:

$$T_i^f = 374.5 + 0.02617MW_i - \frac{20172}{MW_i} \qquad (32)$$

Pan and Firoozabadi [26] also proposed a correlation to estimate the fusion temperature of naphtenes and aromatics.

$$T_i^f = 333.46 - 419.01\exp(-0.008546MW_i) \qquad (33)$$

Chen et al. [27] described the fusion temperature of waxy phase as follow:

$$T_i^f = 411.4 - \frac{32326}{MW_i} \qquad (34)$$

Enthalpy of fusion for paraffinic components can be calculated using developed correlation by Won [2]:

$$\Delta h_i^f = 0.1426MW_iT_i^f \qquad (35)$$

Feyzi and Dalirsefat [17] optimized the above correlation to consider the effect naphthenes and aromatics on the enthalpy of fusion.

$$\Delta h_i^f = 0.06599MW_iT_i^f \qquad (36)$$

The correlation proposed by Pedersen et al. [7] is used to calculate heat capacity change.

$$\Delta C_{pi} = 0.3033MW_i - 4.635 \times 10^{-4}MW_iT \qquad (37)$$

Materials

Table 1 and 2 represent the SARA test results and carbon number distribution four Iranian crude oils. WAT and wax precipitation percentage of these crude oils at several temperatures and atmospheric pressure are also available.

Table 1: SARA test results reported for crude oils

	Oil #1 (wt %)	Oil #2 (wt %)	Oil #3 (wt %)	Oil #4 (wt %)
Saturate	35.8	41.6	39.4	42.3
Aromatic	48.5	39.1	42.1	39.5
Asphaltene	2.5	1.4	0.3	0.5
Resin	13.2	17.9	18.2	17.7

Table 2: Compositional analysis of crude oils

Component	Oil #1 Mole %	Oil #2 Mole %	Oil #3 Mole %	Oil #4 Mole %
C1	0.01	0.0	0.01	0.01
C2	0.13	0.13	0.18	0.8
C3	2.12	1.98	2.52	2.41
C4	1.0	1.0	1.0	0.85
C5	3.01	3.01	2.96	2.95
C6	3.26	3.26	3.47	3.12
C7	2.96	2.96	2.96	3.59
C8	8.24	8.24	7.16	7.54
C9	13.25	13.25	13.25	11.32
C10	10.21	10.21	10.21	8.59
C11	8.22	8.21	8.22	8.56
C12	6.26	6.26	6.26	6.58
C13	4.88	4.88	4.56	4.18
C14	3.15	3.15	3.15	3.65
C15	3.49	3.49	3.49	2.32
C16	2.96	2.96	2.96	2.69
C17	2.15	3.2	2.1	3.58
C18	2.14	2.14	2.23	4.78
C19	3.5	2.1	4.1	6.36
C20+	19.09	19.58	19.63	16.12
C20+ MW	395	412	362	343

In this work, PC-SAFT and multiple solid models describe the crude oil as a four pseudo components mixture for low asphaltenic crude oils. These sub-fractions are Light hydrocarbons (up to C_6), Saturates (distributed from C_7 to C_{19+}), Aromatics+Resines (distributed from C_7 to C_{19}) and wax pseudo component (in C_{19+} cut). The relative amount of each pseudo component can be calculated based on compositional data and SARA test results. Despite of the SARA test which considers Asphaltene as a sub-fraction, low concentration of Asphaltene make it acceptable to consider the Asphaltene precipitate within the wax precipitation. To calculate the wax pseudo component mole percent and average molecular weight, the correlation by Pedersen et al. [28] has been used. Pedersen suggest that there is a probability for each component to precipitate as wax. In other word, each component may precipitate depending on its molecular weight, structure and density.

$$Z_i^s = Z_i\left[1 - (A + BMW_i)\cdot\left(\frac{\rho_i - \rho_i^p}{\rho_i^p}\right)^C\right] \qquad (38)$$

where ρ_i and ρ_i^p represent the density of component i and the density of its equi-molecular weight normal paraffin respectively. Using this correlation, the Wax sub-fraction properties (mole percentage and molecular weight) can be estimated. The characterization of sample crude oils has been represented in the table 3.

Table 3: Characterization of crude oils

Component	Oil #1		Oil #2		Oil #3		Oil #4	
	Mole %	MW	Mole %	MW	Mole %	MW	Mole %	MW
Light Hydro-carbons	10.0	68.54	9.0	68.91	9.0	68.92	10.0	65.20
Aromatics+ Resines	58.26	161.94	58.27	164.81	59.72	157.79	55.23	170.06
Saturates	30.55	210.22	31.68	214.39	29.66	205.18	33.64	204.21
Wax	1.19	398.25	1.047	426.01	1.62	324.52	1.13	363.11

In PC-SAFT model, three parameters for each pseudo component are required. Gross and Sadowski [20] identified the three pure component parameters required for non-associating molecules of n-alkanes (up to C_{20}) by correlating their vapor pressures and liquid volumes. The average molecular weight of the light pseudo component is used to estimate the corresponding PC-SAFT parameters as follow:

$$m = 0.0263MW + 0.8161 \tag{39}$$
$$m\sigma = 0.1071MW + 2.4498 \tag{40}$$
$$\left(\frac{\varepsilon}{k}\right) = 40.802\ln(MW) + 54.209 \tag{41}$$

The PC-SAFT parameters for saturates and aromatics+resins pseudo components are also calculated from their average molecular weight. Saturates sub-fraction is treated as n-alkanes; therefore, PC-SAFT parameters are calculated using Eqs. (42)–(44).

$$m = 0.0253MW + 0.9263 \tag{42}$$
$$m\sigma = 0.1037MW + 2.7985 \tag{43}$$
$$\left(\frac{\varepsilon}{k}\right) = 32.8\ln(MW) + 80.398 \tag{44}$$

The proposed correlation by Gonzalez et al. [29] estimates the PC-SAFT parameters for aromatics+resines pseudo component.

$$m = 0.0139MW + 1.2988 \tag{45}$$
$$m\sigma = 0.0597MW + 4.2015 \tag{46}$$
$$\left(\frac{\varepsilon}{k}\right) = 119.4\ln(MW) - 230.21 \tag{47}$$

Wax pseudo component parameters are determined as adjustable parameters by modeling the wax precipitation. In other words, the PC-SAFT parameters for wax have been tuned to match the experimental data for wax precipitation amount. Table 4 shows the values of adjusted parameters for the PC-SAFT model based on the properties of crude oils.

Table 4: PC-SAFT parameters for non-associating crude oils

Component	Oil #1			Oil #2		
	m	σ $(\dot{A})$	ε/k (K)	m	σ $(\dot{A})$	ε/k (K)
Light Hydrocarbons	2.6187	3.736	226.7	2.629	3.739	226.9
Aromatics +Resines	3.5498	3.907	377.2	3.589	3.911	379.3
Saturates	6.2451	3.939	255.8	6.351	3.942	278.9
Wax	10.771	3.973	257.8	10.05	3.968	257.3
Component	**Oil #3**			**Oil #4**		
	m	σ $(\dot{A})$	ε/k (K)	m	σ $(\dot{A})$	ε/k (K)
Light Hydrocarbons	2.629	3.739	226.9	2.531	3.727	224.7
Aromatics +Resines	3.478	3.899	373.3	3.663	3.919	383.1
Saturates	6.117	3.936	255.0	6.093	3.935	254.9
Wax	10.98	3.974	257.9	10.72	3.973	257.8

Use of cubic equation of state in multiple solid thermodynamic model requires critical properties for each sub-fraction to determine the model constants. As suggested by Riazi and Al-Sahhaf [24], properties of petroleum fractions such as a SCN group may be estimated using the pure hydrocarbon properties with PNA composition in the following form:

$$\theta = x_p\theta_p + x_n\theta_n + x_a\theta_a \tag{48}$$

where x_p, x_n, and x_a are the fraction of paraffins, naphthenes and aromatic content of the mixture. θ is physical property of the mixture to be estimated and θ_p, θ_n and θ_a are the same property for pure hydrocarbons from paraffin, naphthene and aromatic groups having the same molecular weight as the mixture. These properties can be estimated from molecular weight by:

$$\theta = \theta_\infty - exp(a - bMW^c) \tag{49}$$

where θ is a property such as T_b and θ_∞ is the limiting value for that property as M tends to ∞. Therefore, required critical properties as well as acentric factor may be calculated by corresponding constants reported by Riazi and Al-Sahhaf [24] for each pseudo component. Wax pseudo component parameters are adjusted using the experimental data. Table 5 shows the values of the adjusted parameters for the multiple solid model based on the properties of crude oils.

Table 5: Multiple solid model properties

Component	Oil #1			Oil #2		
	T_c (K)	P_c (bar)	ω	T_c (K)	P_c (bar)	ω
Light Hydrocarbons	458.99	34.68	0.236	460.1	34.58	0.238
Aromatics +Resines	695.36	24.12	0.485	700.2	23.70	0.495
Saturates	704.59	15.05	0.691	708.8	14.76	0.703
Wax	884.94	10.99	0.419	1158.0	14.05	0.167
Component	Oil #3			Oil #4		
	T_c (K)	P_c (bar)	ω	T_c (K)	P_c (bar)	ω
Light Hydrocarbons	460.1	34.58	0.238	448.7	35.65	0.223
Aromatics +Resines	691.9	24.74	0.471	706.0	22.97	0.513
Saturates	699.3	15.41	0.677	698.3	15.48	0.674
Wax	1108.0	6.474	0.939	772.7	10.49	0.239

The proposed procedure which considers 4 pseudo components to characterize the crude oil may have some inconsistencies in the case of asphaltenic crude oil. This may happen for the cases which have several problems due to asphaltene deposition although they have low asphaltene content. So, a second scenario has been considered which divides the crude oil to 5 pseudo component and asphaltene in the fifth one. This characterization scenario has been applied for two sample and the results are shown in table 6. Asphaltene molecular weight and mole fraction has been adjusted to match the SARA test and plus fraction molecular weight of crude oil. In this case, the values of PC-SAFT parameters have been adjusted for asphaltene and the parameters of wax have been calculated by the correlations proposed for saturates.

Table 6: Characterization of crude oils and adjusted asphaltene parameters

	Oil #2		Oil #5	
Asphaltene content (wt%)	1.4		12	
Component	Mole %	MW	Mole %	MW
Light Hydrocarbons	9.0	68.91	12.0	60.800
Aromatics+Resines	60.4	164.81	48.46	155.389
Saturates	29.5	214.39	37.2	190.670
Wax	0.57	396.01	1.1	348.97
Asphaltene	0.12	2000	1.24	1800
PC-SAFT parameters	M	σ (Å)	ϵ/k (K)	m	σ (Å)	ϵ/k (K)
Asphaltene	33.81	4.66	667.64	8.06	3.13	550.12

Results and discussion

In this work, thermodynamic models of the wax precipitation in four Iranian crude oils under different temperature and atmospheric pressure is developed and compared for their benefits. According to experimental data, taken from the Research Institute of Petroleum Industry (RIPI) labs, the wax precipitation results of the studied crude oils are given in Table 7. The algorithm of wax precipitation calculations (for PC-SAFT and multiple solid models) for the first characterization

scenario has been shown in Fig. 1. The mass fraction of precipitated wax form feed is calculated from the following equation.

$$Wax\ weight\ \% = \frac{Total\ precipitated\ mass}{Mass\ of\ feed\ oil} \times 100 = \frac{n^{wax}MW^{wax}}{\sum_{i=1}^{n} z_i MW_i} \times 100 \qquad (50)$$

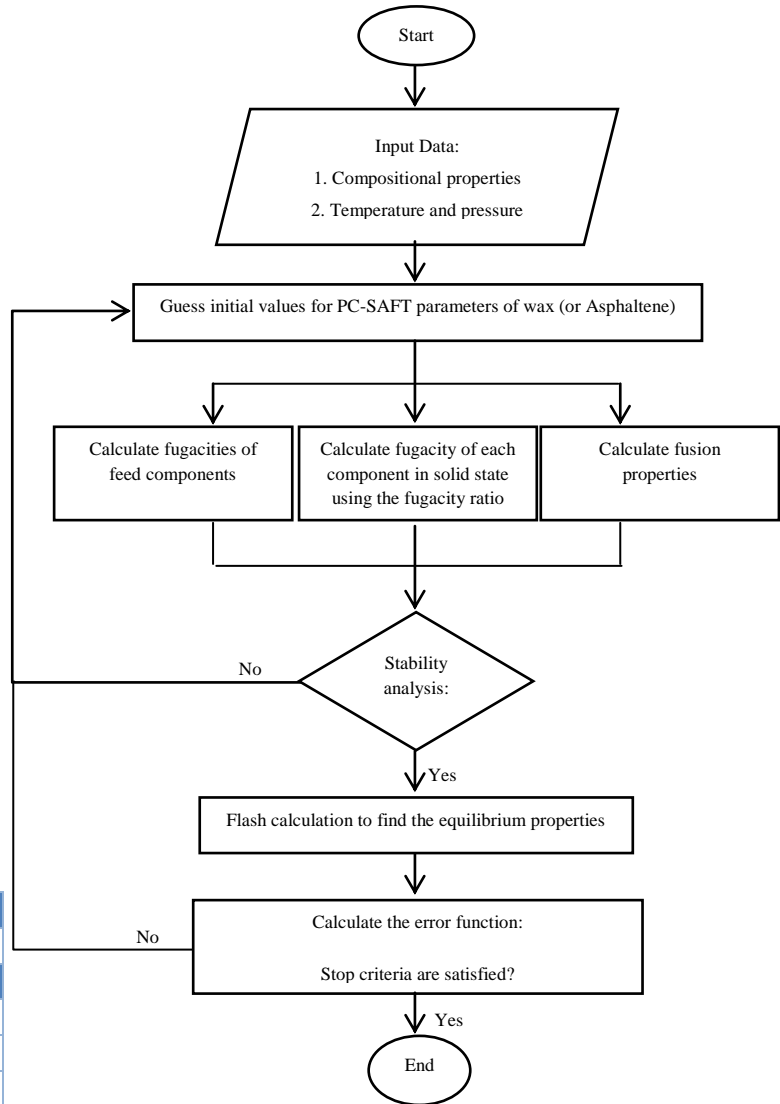Figure 1: Calculation algorithm of the first characterization scenario

Table 7: Weight percent of precipitated Wax at different temperatures

Temperature (K)	Oil #1	Oil #2	Oil #3	Oil #4
273	0.64	0.85	2.02	2.47
285	0.58	0.72	1.85	2.16
290	0.52	0.63	1.12	1.85
295	0.32	0.35	0.98	1.26
300	0.18	0.28	0.74	0.98

Scenario 1: Characterization of crude oil without asphaltene pseudo component

Figs. 2-5 compare the quality of the predicted results of wax precipitation weight percent in crude oil from the experimental data. As shown in these figures, PC-SAFT model performance in prediction of experimental data is acceptable especially in higher temperatures and near the wax appearance temperature. In Figs. 2-5, the predictions of PC-SAFT model by correlated parameters for wax pseudo component are also represented. In other words, the values of PC-SAFT parameters (m, σ and ε/k) for wax sub-fraction has been calculated by the correlations used for saturates. In this way, three other parameters including wax pseudo component molecular weight, wax-light hydrocarbons interaction coefficient and wax-aromatics+resines interaction coefficient has been adjusted to match the experimental data. As it is clear in the figure, the second method of model tuning has more accurate prediction of wax precipitation.
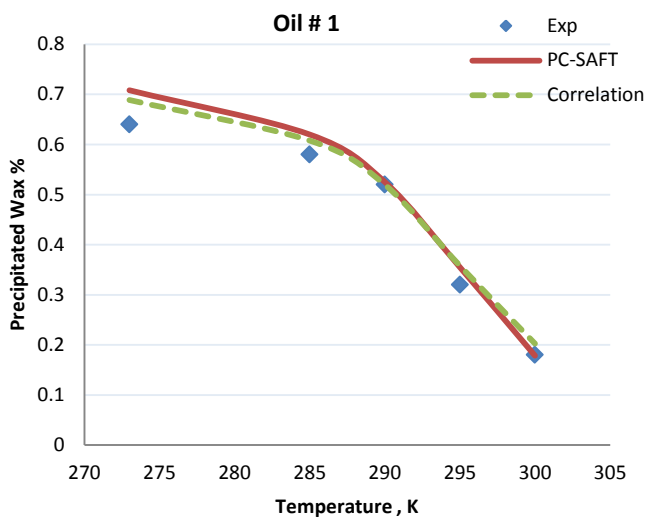

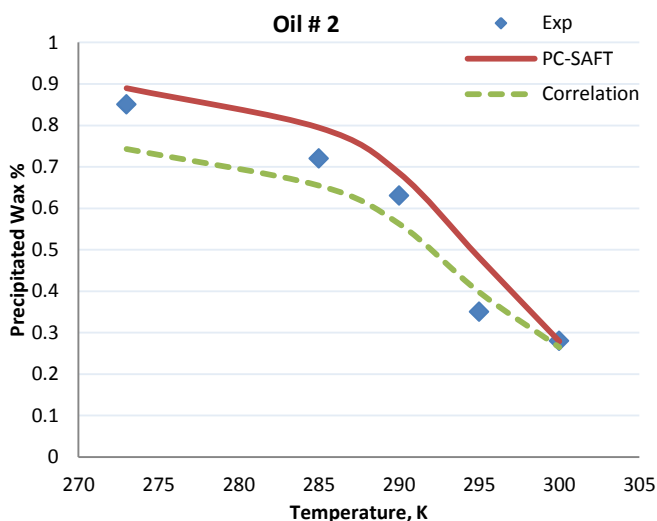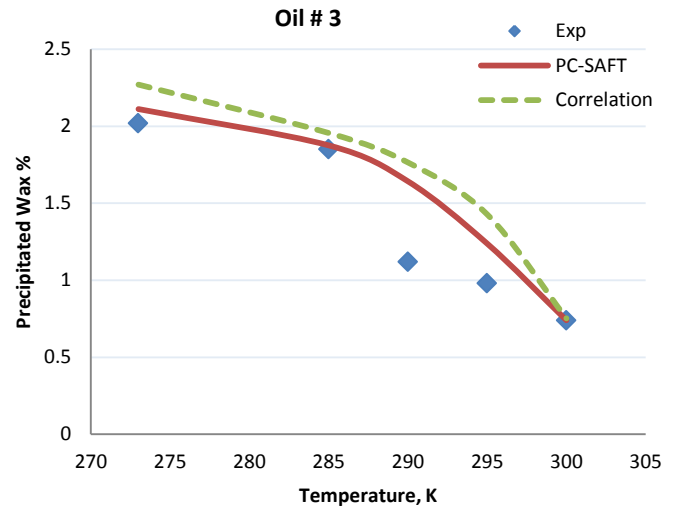Figure 4: Predicted and experimental wax precipitation results for oil 3 at 1 bar

Figure 2: Predicted and experimental wax precipitation results for oil 1 at 1 bar
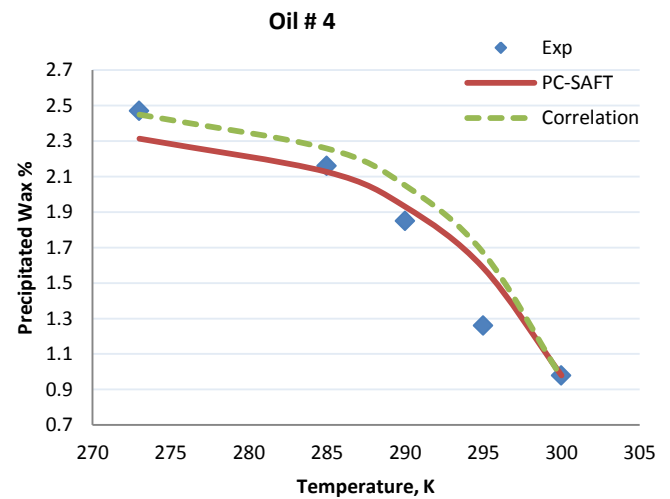
Figure 5: Predicted and experimental wax precipitation results for oil 4 at 1 bar

Figs. 6-9 compare the quality of the correlated results of wax precipitation weight percent in crude oil from the experimental data for the studied models. As shown in these figures, multiple solid model generally overestimate the wax weight fraction but has the same trend as the PC-SAFT model. Solid solution model has higher deviation from experimental data and PC-SAFT model has better correlation through the data points. In Table 8 the prediction of PC-SAFT model is compared with the corresponding values obtained from the multiple solid and solid solution models. In this table the average deviation (AD) is defined as below:

$$AD \% = \sum_{i=1}^{n} \frac{|t_{cal} - t_{exp}|}{t_{cal}} \tag{51}$$

Figure 3: Predicted and experimental wax precipitation results for oil 2 at 1 bar

Table 8: Average deviation of three developed model

	AD %			
	Oil # 1	Oil # 2	Oil # 3	Oil # 4
PC-SAFT model	0.304079	0.616382	0.78932	0.38124
Multiple solid model	0.686717	1.19769	1.011303	0.455587
Solid solution model	1.097626	1.082606	0.884007	0.69292

As it can be observed in Table 8, results obtained with PC-SAFT model proposed in this work, show less deviation from experimental data than results of other basic models. Deviation values for crude oils 2 and 3 show better performances of solid solution model but multiple solid model has better agreement to experimental data for crude oils 1 and 4.
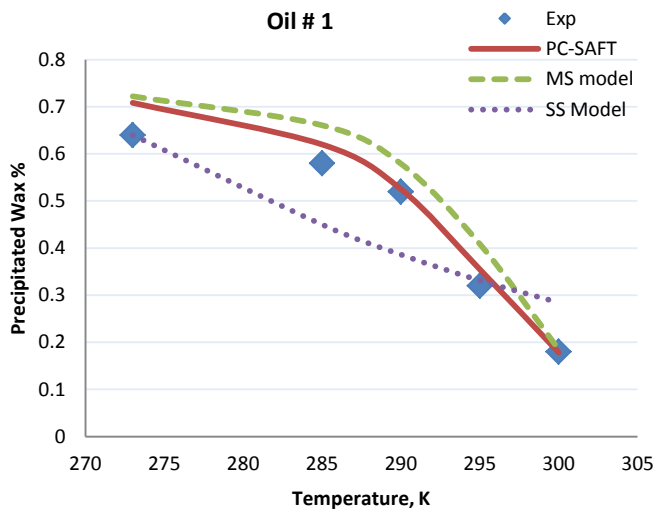

Figure 6: Wax precipitation prediction of PC-SAFT, multiple solid and solid solution models for oil 1
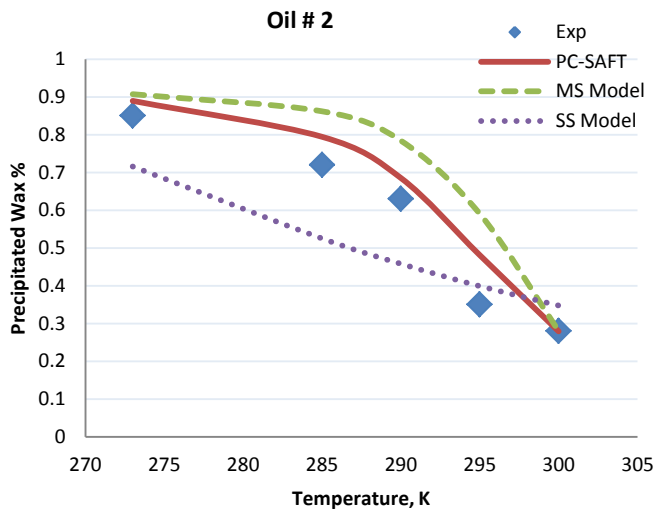

Figure 7: Wax precipitation prediction of PC-SAFT, multiple solid and solid solution models for oil 2
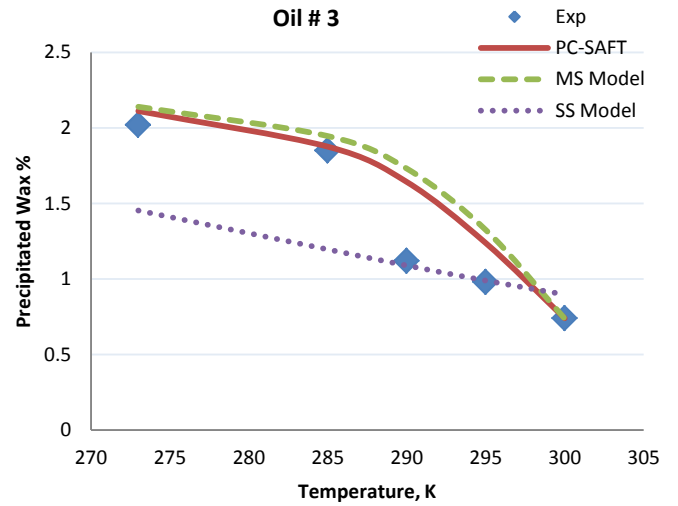

Figure 8: Wax precipitation prediction of PC-SAFT, multiple solid and solid solution models for oil 3
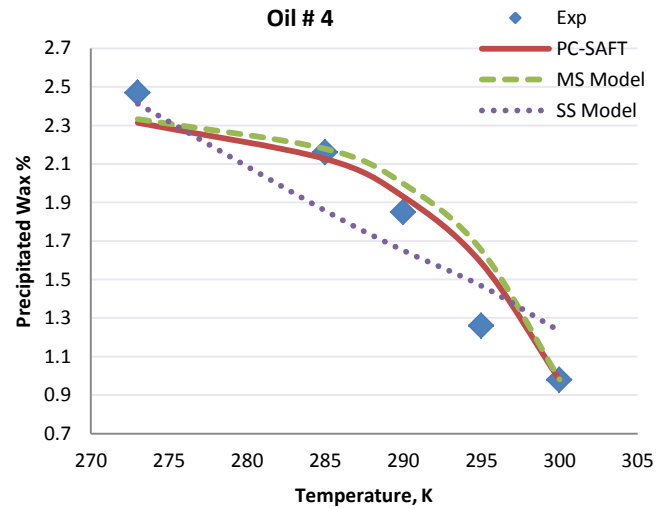
Figure 9: Wax precipitation prediction of PC-SAFT, multiple solid and solid solution models for oil 4

Scenario 2: Characterization of crude oil with asphaltene pseudo component
In the case of high asphaltenic crude oils, the assumption of 4 pseudo components characterization may not be reasonable. In Figs 10 and 11, the results of PC-SAFT calculations have been shown comparing to experimental data points. Therefore characterization of crude oil with asphaltene pseudo component (5 pseudo components characterization) has been proposed for high asphaltenic crude oils as Scenario 2.
The values of AD for proposed characterization with asphaltene pseudo component have been calculated for oils 2 and 5 in Table 9. The remarkable decrease in AD values of high asphaltene content oil (oil 5) is obvious in this table. As clear the deviation of model may be negligible for low asphaltenic sample (oil 2) but it is necessary to consider asphaltene as a pseudo component in characterization of high asphaltenic crude oils.

Table 9: Absolute deviation of model for two characterization approaches

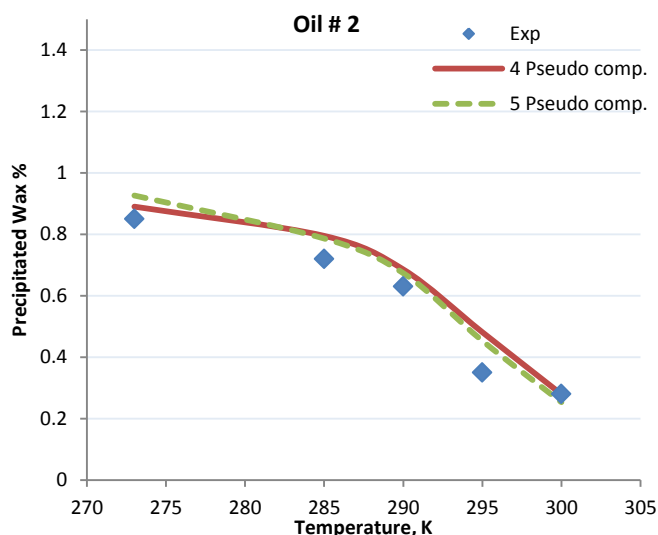| AD %		
	Oil # 2	Oil # 5
4 pseudo components characterization	0.616382	1.563997
5 pseudo components characterization (asphaltene added)	0.639789	0.409708

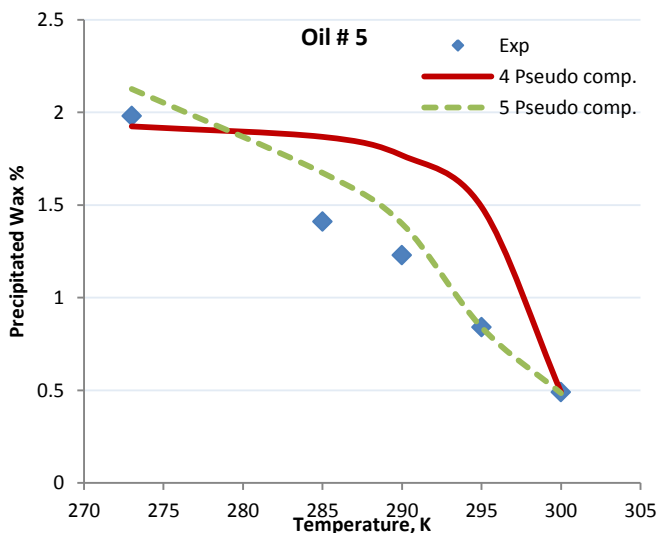Figure 10: Wax precipitation prediction of PC-SAFT for oil 2

Figure 31: Wax precipitation prediction of PC-SAFT for oil 5

Conclusion

In this work, PC-SAFT model which is a statistical thermodynamic method was developed to evaluate the wax precipitation in crude oils below the wax appearance temperature. In this way, this model was tuned by three parameters related to Wax pseudo component to match the experimental data. The obtained results in wax precipitation

prediction were in quite agreement with experimental data. To compare the mentioned model with basic thermodynamic models proposed in wax precipitation researches, a multiple solid model (based on Lira-Galeana model) and a solid solution model (based on Pedersen model) were developed. In order to have better evaluation on the performance of mentioned models, the average deviation of predicted values of model were calculated and PC-SAFT model had more accurate results according to experimental data. In this work the effect of asphaltene was denied for low asphaltene crude oils. In the case of higher asphaltenic crudes it was shown that it is necessary to consider the asphaltene in characterization of oil. The PC-SAFT model has higher level of proficiency than classic models in case of high asphaltene concentration oil. The simultaneous effect of wax and asphaltene precipitation on each other will be investigated using the PC-SAFT model in the future paper.

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