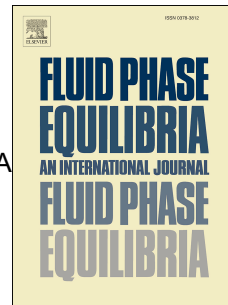


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CRedit authorship contribution statement

Amin Daryasafar: Conceptualization, Methodology, Software, Investigation, Validation, Formal analysis, Writing-Review & Editing. **Mohammad Masoudi:** Conceptualization, Methodology, Software, Validation, Formal analysis, Writing-Review & Editing. **Shahin Kord:** Conceptualization, Methodology, Formal analysis, Supervision, Writing-Review & Editing. **Mohammad Madani:** Conceptualization, Validation, Formal analysis, Writing-Review & Editing

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Evaluation of Different Thermodynamic Models in Predicting Asphaltene Precipitation: A Comparative Study

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Abstract

One of the major issues in the oil industry is asphaltene precipitation. Modeling asphaltene precipitation is still considered as a complex problem due to various characteristics of different heavy components existing in the crude oil. Thermodynamic models have been found as accurate models for studying asphaltene precipitation in the past few years and a great deal of effort has been devoted to model this process by using different empirical models and equations of state. In this study, the obtained results of asphaltene precipitation from different models based on perturbed-chain statistical associating fluid theory (PC-SAFT), cubic-plus-association (CPA), solid model, Flory-Huggins (FH), and the modified Flory-Huggins (MFH) are compared and their accuracy and reliability are analyzed in detail. For this purpose, twelve crude oil types with different characteristics and asphaltene precipitation behavior are used. Additionally, the performance of the introduced models in predicting asphaltene precipitation during gas injection into the studied oil is investigated. Results demonstrated that PC-SAFT and CPA models have the highest accuracy for both precipitation estimation and behavior trend prediction. Afterward, sensitivity analysis is performed by using Monte-Carlo algorithm for better understanding of the

effect of different adjusting parameters, which were used during the tuning process, on each model outputs. Results indicated that cross-association energy between asphaltene and heavy component (HC), self-association energy of asphaltene, and binary interaction coefficient between asphaltene and CO₂ are the most sensitive tuning variables for PC-SAFT, CPA, and solid models, respectively. Finally, the CPU times of various models for simulating this process were compared. This comparison showed that the PC-SAFT model has more computational time due to the involved iterative processes for phase equilibrium calculations.

Keywords: Asphaltene Precipitation; Equation of State; PC-SAFT; CPA; Solid Model; Flory-Huggins; Modeling

1. Introduction

Formation damage which basically refers to permeability impairment in reservoir formations, could be triggered by undesired operational issues, and ultimately decline well production functionality and production rate. Precipitation and further deposition of solid materials such as organic and inorganic scales including asphaltene in surface facilities, wellbore, and porous media are the main causes of formation damage [1].

Crude oil contains four disparate structural constituents of resins, saturates, asphaltenes, and aromatics. Asphaltene fraction of the oil which is inherently heavy is insoluble in light normal alkanes while soluble in aromatic solvents such as benzene. Spectroscopic techniques have implied the poly-nuclear aromatic structure of asphaltene molecules with heteroatoms such as sulfur, oxygen, and nitrogen, and alkyl chains [2]. Any change in a number of parameters including pressure, temperature, and oil composition can result in the phenomenon of asphaltene precipitation, and further drives acute issues such as absolute and relative permeability reduction, rise of pressure drop, and undesirable wettability alteration [3-6]. In addition, gas-based

enhanced oil recovery approaches such as nitrogen or carbon dioxide flooding may lead to precipitation of asphaltene [7]. Hence, it is essential to predict asphaltene precipitation onset reliably.

Modeling asphaltene precipitation is literally difficult since there is still not well-versed knowledge in the nature of asphaltene molecules, and how they interact with other oil constituents. Thus, several modeling methods have been developed to help better understand asphaltene behavior, and further their effective mechanisms that are involved in the process of precipitation. These methods fall into two principal categories, namely colloidal and solubility models [8]. In the colloidal model, asphaltene acts like aggregates dispersed in the bulk oil, and resin structures having more propensity to the oil, stabilize the asphaltene. This model implies that the main reason of asphaltene precipitation is a decline in the stabilizing strength of resin portion, and further assumes that asphaltene precipitation is an irreversible process. The published research works of [9-11] are all of this modeling type. In the solubility model, a true homogenous solution exists owing to solubilization of asphaltene portion in the bulk oil taking into account interactions of asphaltene portions with other oil components. Solubility parameter is applied to explicate the behavior of asphaltene solubility as the most prevailing thermodynamic technique. As the solubility parameter of asphaltene and solvent becomes more differentiated, the more likely asphaltene precipitation takes place. In this technique, the asphaltene precipitation is presumed reversible, and can generally be predicted either via liquid-liquid or solid-liquid equilibrium. Flory-Huggins model, Scott-Magat and regular solution theories all belong to solubility modeling technique; the difference between such methods is the heterogeneity assumption of asphaltene structure [7, 8, 12-16].

Arya et al. [17] determined asphaltene precipitation onset for a variety of reservoir fluid samples by applying CPA (cubic-plus-association) equation of state differently than previous modeling techniques. In their methodology, they made use of a simple oil characterization method in line with SARA analysis to categorize oil plus fraction into two subsections of asphaltene and heavy component, and took the account of asphaltene self-association, and asphaltene-heavy components cross-association terms. Zhang et al. [18] provided a comparison between the capability of CPA and PC-SAFT (perturbed-chain statistical associating fluid theory) equation of states in accurately predicting asphaltene precipitation in live oils on different sets of experimental data. Panuganti et al. [19] presented an in-depth methodology to model asphaltene phase behavior with the aid of PC-SAFT equation of state in disparate sets of temperature and pressure datasets with better accuracy than typical cubic equation of states generally utilized in the oil industry even when composition data as far as C+9 fraction is available. Tavakkoli et al. [20] focused on predicting the precipitation of polydisperse asphaltene via PC-SAFT over a wide range of density data belonging to crude oil, and further provided a description of observed behavior according to Flory-Huggins theory. Kord and Ayatollahi [21] introduced a novel scaling equation for the purpose of predicting live oil based asphaltene precipitation, and then compared its efficiency with widely thermodynamic models of single component and modified Flory-Huggins techniques. The proposed scaling equation was then extended by Kord et al. to be applicable for estimating asphaltene precipitation due to water and gas injection, and also pressure variation [22]. Hemmati-Sarapardeh et al. [6] applied two intelligent techniques including radial basis function, and multilayer perceptron neural network optimized with several algorithms such as genetic algorithm, differential evolution, ant colony optimization, gravitational search algorithm, particle swarm optimization, imperialist competitive algorithm,

scaled conjugate gradient, resilient back propagation, Levenberg-Marquardt, and Bayesian regularization to predict asphaltene precipitation as a function of crude oil characteristics such as temperature, pressure, API gravity, bubble point pressure, and SARA (saturate, aromatics, resin, asphaltene) fractions as the input parameters. The obtained results were compared with those based on Flory-Huggins thermodynamic model. Arya et al. [23] examined the effect of gas injection on the behavior of asphaltene precipitation using SRK (Soave-Redlich-Kwong), Soave-Redlich-Kwong-Plus-Huron-Vidal mixing rule and cubic-plus-association (CPA) equations of states. They performed their study using six different fluid samples during hydrocarbon gas, nitrogen, and carbon dioxide injection schemes.

In this study, the performance of various thermodynamic models in accurate prediction of asphaltene precipitation is investigated from a comparative perspective. Twelve crude oil samples from the literature are evaluated and the obtained results of PC-SAFT, CPA, solid model, Flory-Huggins, and the modified Flory-Huggins are compared. The fluids studied in this research are suitable for checking the proficiency of the models in modeling asphaltene precipitation due to depressurization, addition of n-alkanes, and gas injection. Association terms, physical parameters of the lumped pseudo-component, and a few number of binary interaction coefficients were used as tuning variables for the models. For better understanding of the effect of these adjusted parameters on the results of each model, a sensitivity analysis is performed by using Monte-Carlo algorithm, and the most sensitive parameters are determined.

2. Theoretical background

2.1 Flory-Huggins (FH) model

Flory-Huggins theory signifies that asphaltenes act as large polymer molecules, and can be represented by a pseudo-component with averaged properties. In this technique, vapor-liquid

equilibrium (VLE) is implemented to obtain the liquid characteristics first. Oil-rich part of the oil, and asphaltenes represent the solvent and polymer solute in the liquid-liquid equilibrium (LLE), respectively [24, 25]. In Flory-Huggins theory, which was initially put forward by Hirschberg et al., the mixture Gibbs energy may be derived by [6, 26]:

$$\frac{\Delta G}{RT} = \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi_{FH} \phi_1 \phi_2 \quad (1)$$

In which r and T signify relative molar volume, and temperature respectively. Subscripts 1, and 2 denote fractions of components 1, and 2 correspondingly. r_1 is assumed 1. χ_{FH} indicates the Flory-Huggins interaction parameter. r_2 is obtained based on the following expression:

$$r_2 = \frac{v_2 MW_2}{v_1 MW_1} \quad (2)$$

Where v_1 and v_2 are correspondingly the specific solvent, and polymer volumes, and MW_1 and MW_2 are the solvent and polymer (asphaltene) molecular weights.

2.2 Modified Flory–Huggins (MFH) model

The initial form of Flory–Huggins model was implemented in myriad works, and modified later by many researchers [27-30]. Mohammadi and Richon [31] divided oil and precipitated phases into asphaltene and non-asphaltene portions. They implied that one can assess the amount of asphaltene fraction in equilibrium with other petroleum mixtures via the solution of the below two equations derived by combination of asphaltene-maltene activity coefficients as well as LLE relationship based on polymer theory of Flory-Huggins:

$$\ln \left(\frac{\phi_m^{oil}}{\phi_m^{Asph}} \right) + \left(1 - \frac{v_m}{v_a} \right) \left(\phi_a^{oil} - \phi_a^{Asph} \right) + \chi \left(\left(\phi_a^{oil} \right)^2 - \left(\phi_a^{Asph} \right)^2 \right) = 0 \quad (3)$$

$$\ln \left(\frac{\phi_a^{oil}}{\phi_a^{Asph}} \right) + \left(1 - \frac{v_a}{v_m} \right) \left(\phi_m^{oil} - \phi_m^{Asph} \right) + \chi \left(\left(\phi_m^{oil} \right)^2 - \left(\phi_m^{Asph} \right)^2 \right) = 0 \quad (4)$$

In the above equations, v_a , and v_m are molar volume of asphaltene and maltene respectively. Φ_a , ϕ_m denote volume fraction of asphaltene and maltene respectively. χ which is independent of concentration, is asphaltene-maltene interaction parameter, defined by:

$$\chi = \frac{v_m \left[(\delta_m - \delta_a)^2 + 2l_{am} \delta_a \delta_m \right]}{RT} \quad (5)$$

Wherein solubility parameter is defined by parameter δ and subscripts a, and m indicate asphaltene and maltene, respectively. l_{am} denotes the binary interaction parameter. It is worth noting that a value of 0.01 has usually been incorporated for the binary interaction coefficients in FH-based methods [26]. Solubility parameter and molar volume of the asphaltene components are vital in the performance of this modeling approach. This modeling form is considered the most typical formulation of FH theory [15, 21].

2.3 PC-SAFT EOS

PC-SAFT equation of state is formulated with the definition of reduced Helmholtz free energy as [32]:

$$\tilde{a}^{res} = \tilde{a}^{hc} + \tilde{a}^{disp} + \tilde{a}^{assoc} \quad (6)$$

Where \tilde{a} is the reduced Helmholtz free energy. Superscripts hc, disp, and assoc stand for hard chain, dispersion, and association, respectively. Eq. (6) is used for associating fluids. Hard chain contribution of reduced Helmholtz free energy (\tilde{a}^{hc}) is defined by:

$$\tilde{a}^{hc} = \bar{m} \tilde{a}^{hs} - \sum_i x_i (m_i - 1) \ln g_{ii}^{hs}(\sigma_{ii}) \quad (7)$$

Where x , m , g_{ii} , and σ_{ii} represent mole fraction, number of segments, radial distribution function, and segment diameter, respectively. Mean segment number (\bar{m}) is calculated as:

$$\bar{m} = \sum_i x_i m_i \quad (8)$$

The hard sphere term of Helmholtz free energy (\tilde{a}^{hs}) is given by:

$$\tilde{a}^{hs} = \frac{1}{\zeta_0} \left[\frac{3\zeta_1\zeta_2}{(1-\zeta_3)} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1-\zeta_3) \right] \quad (9)$$

The radial basis function of the hard sphere fluid (g_{ii}^{hs}) used in Eq. (7) may be calculated via the below equation:

$$g_{ii}^{hs} = \frac{1}{(1-\zeta_3)} + \left(\frac{3\zeta_2}{(1-\zeta_3)^2} \right) \left(\frac{d_i d_j}{d_i + d_j} \right) + \left(\frac{2\zeta_2^2}{(1-\zeta_3)^3} \right) \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \quad (10)$$

In Eq. (10), temperature-dependent segment diameter of component i (d_i) and ζ is defined by the following equations, respectively:

$$\zeta_n = \frac{\pi}{6} \rho \sum_i x_i m_i d_i^n \quad n \in \{0, 1, 2, 3\} \quad (11)$$

$$d_i = \sigma_i \left[1 - 0.12 \exp \left(-3 \frac{\varepsilon_i}{KT} \right) \right] \quad (12)$$

Wherein ε is the depth of pair potential, K is the Boltzmann constant, T is the temperature and ρ is the total number density of molecules.

The dispersion term of Helmholtz free energy (\tilde{a}^{disp}) is defined by:

$$\tilde{a}^{disp} = -2\pi\rho I_1 \left(\overline{m^2 \varepsilon \sigma^3} \right) - \pi\rho\bar{m} C_1 I_2 \left(\overline{m^2 \varepsilon^2 \sigma^3} \right) \quad (13)$$

C_1 is the compressibility term defined as:

$$C_1 = \left(1 + m \frac{-8\eta - 2\eta^2}{(1-\eta)^4} + (1-m) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^2} \right)^{-1} \quad (14)$$

In which η is the packing fraction.

Pairs of unlike segments are defined via Lorentz Bertholet combining rule as:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (15)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j (1 - k_{ij})} \quad (16)$$

In Eq. (13), I_1 and I_2 both depends on average segment number and system packing fraction, and are calculated by simple density power series [4, 7].

The association term of Helmholtz free energy (\tilde{a}^{disp}) is given by:

$$\tilde{a}^{assoc} = \sum_i x_i \left[\sum_{A_i} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{M_i}{2} \right] \quad (17)$$

In which, M_i is the molar mass of component i , and X^{A_i} is given by:

$$X^{A_i} = \left[1 + \sum_j \sum_{B_j} \rho_j X^{B_j} \Delta^{A_i B_j} \right]^{-1} \quad (18)$$

In which, $\Delta^{A_i B_j}$ signifies association strength between sites A and B on two disparate molecules, and is given by:

$$\Delta^{A_i B_j} = d_{ij}^3 g_{ij}^{hs} \beta^{A_i B_j} \left[e^{\frac{\varepsilon^{A_i B_j}}{kT}} - 1 \right] \quad (19)$$

Two additional parameters of the association term in the PC-SAFT equation of state, association energy, $\varepsilon^{A_i B_j}$, and volume, $\beta^{A_i B_j}$, are usually adjusted via the available experimental data.

2.4 CPA EOS

The CPA model utilizes a cubic equation of state, and an association term in Wertheim theory the same as SAFT model [33]. In fact, two major contributions co-exist: 1- physical part, which describes the non-associating molecular interactions such as attractive and repulsive forces, and 2- association part, which explicates the associative impacts such as hydrogen bonding. The overall CPA equation in terms of compressibility factor, Z , is defined by [34-36]:

$$Z = Z^{ph} + Z^{assoc} = Z^{ph} - \frac{1}{2} \left(1 + \frac{1}{\nu} \frac{\partial \ln g}{\partial \left(\frac{1}{\nu} \right)} \right) \sum_i x_i \sum_{A_i} (1 - X^{A_i}) \quad (20)$$

Where, X^{A_i} is given by Eq. (18). For CPA, the association strength can be found using the following equation through association energy, ε^{AiBi} , and interaction volume, β^{AiBi} :

$$\Delta^{A_i B_j} = g(\nu) \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{\kappa T}\right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (21)$$

The mixing rules used for cross-association energy, cross-association volume, and cross-association strength are as follows:

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2} \quad (22)$$

$$\beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}} \quad (23)$$

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}} \quad (24)$$

In addition, a simple relation for $g(\nu)$ is used which was introduced by Kontogeorgis et al. (1999) [35], defined by:

$$g(\nu) = \frac{1}{1 - 1.9 \left(\frac{b}{4\nu} \right)} \quad (25)$$

In this study, SRK is made use of to calculate physical part. The corresponding equations in this regard are [37, 38]:

$$Z^{ph} = \frac{v}{v-b} - \frac{a(T)}{RT(v+b)} \quad (26)$$

$$a(T) = 0.42747 \times \alpha \frac{(RT_c)^2}{P_c} \quad (27)$$

$$\alpha = \left[1 + (0.48 + 1.574 \times \omega - 0.176 \times \omega^2) (1 - \sqrt{T_r}) \right]^2 \quad (28)$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (29)$$

In the above equations, v is the molar volume, R is the gas universal constant, T_r is the reduced temperature, T_c and P_c are the critical temperature and pressure respectively, and ω is the acentric factor. For mixtures, a and b in Eq. (26) are defined as:

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij}), \quad b = \sum_i x_i b_i \quad (30)$$

In which k_{ij} , and x_i denote i - j components binary interaction coefficient, and i component mole fraction.

2.5 Solid Model (Monodisperse Asphaltene Modeling) and EOS

In this part, monodisperse asphaltene modeling together with SRK equation of state for the fugacity calculations is described to predict asphaltene precipitation from crude oil. In this approach, for component i to be able to exist as a solid phase, the following inequality must hold [5]:

$$f_i(T, P, z_i) - f_i^s(T, P) \geq 0 \quad i = 1, 2, \dots, N \quad (31)$$

Any component fulfilling Eq. (31) can precipitate, and other components prevail in the form of liquid and vapor phases. In addition, all components that are precipitated must honor the below equation [5]:

$$f_i^l(T, P, x_i^l) = f_i^s(T, P) \quad i = (N - N_s + 1), \dots, N \quad (32)$$

In the above equations, f_i , f_i^s and f_i^l represent the i 'th component fluid mixture fugacity, pure solid phase fugacity, and pure liquid fugacity, respectively. N and N_s are the number of components, and solid layers, respectively.

The material balance equations belonging to non-precipitating, and precipitating components are as follows, respectively [39]:

$$z_i - x_i^l \left[1 - \sum_{j=(N-N_s+1)}^N \frac{n_j^s}{F} - \frac{V}{F} \right] - K_i^{vl} x_i^l \frac{V}{F} = 0 \quad i = 1, \dots, (N - N_s) \quad (33)$$

$$z_i - x_i^l \left[1 - \sum_{j=(N-N_s+1)}^N \frac{n_j^s}{F} - \frac{V}{F} \right] - \frac{n_j^s}{F} - K_i^{vl} x_i^l \frac{V}{F} = 0 \quad i = [(N - N_s + 1), \dots, N - 1], \quad N_s > 1 \quad (34)$$

Where V , F , and n_j^s denote mole number of vapor phase, mole number of initial fluid mixture (feed), and moles of solid phase, respectively.

The vapor-liquid equilibrium (VLE) which should be satisfied by all components, is given as:

$$f_i^v(T, P, x_i^v) = f_i^l(T, P, x_i^l) \quad i = 1, 2, \dots, N \quad (35)$$

The following two constraint equations must be satisfied in the liquid and vapor phases:

$$\sum_{i=1}^N x_i^l = 1 \quad (36)$$

$$\sum_{i=1}^N x_i^v = 1 \quad (37)$$

Total number of equations are $2N+N_s+1$ as we have the following number of equations: N_s in Eq. (32), $(N-N_s)$ in Eq. (33), (N_s-1) in Eq. (34), N in Eq. (35), and two in Eqs. (36) and (37). In addition, total number of unknowns are $2N+N_s+1$ as: V/F (one unknown), n_j^s (N_s unknowns), x_i^l (N unknowns), and x_i^v (N unknowns). If one single pure solid phase is assumed (that is, $N_s=1$ and $x_N^s=1$), Eq. (34) is simplified to the following equation for the solid component [39]:

$$z_i - x_i^l \left[1 - \frac{S}{F} - \frac{V}{F} \right] - \frac{S}{F} - K_i^{vl} x_i^l \frac{V}{F} = 0 \quad (38)$$

Where, S signifies the total moles number of solid phase. Assuming one single pure solid component, the number of unknowns and equations reduces to $2N+2$.

In this study, the method of Nghiem [40] is used for multiphase flash calculations, and liquid/vapor phase fugacity of the available components are estimated with the aid of SRK equation of state. However, for calculating the solid phase fugacity of a pure component ($f_{pure,i}^s$), the following typical equation is used to compute solid-to-liquid fugacity of pure component i [41]:

$$\ln \left(\frac{f_{pure,i}^s}{f_{pure,i}^l} \right) = \frac{\Delta H_{f,i}}{RT} \left(1 - \frac{T}{T_{f,i}} \right) + \frac{1}{R} \int_T^{T_{f,i}} \frac{\Delta C_{p,i}}{T} dT - \frac{1}{RT} \int_T^{T_{f,i}} \Delta C_{p,i} dT + \frac{1}{RT} \int_{P_f}^P (v_i^s - v_i^l) dP + \frac{\lambda}{RT} \quad (39)$$

In which λ , ΔH_f , ΔC_p , P_f , T_f , v^s and v^l represent change in molar Gibbs free energy owing to solid-solid phase transition, melting point enthalpy of fusion, heat capacity of fusion, melting pressure and temperature, and solid and liquid molar volume, respectively. For solid-liquid equilibria, there is an equilibrium factor which can be shown as:

$$K_i^{sl} = \frac{\gamma_i^l}{\gamma_i^s} \left(\frac{f^l}{f^s} \right)_{pure,i} \quad (40)$$

Where, γ is the activity coefficient. At any pressure and temperature, the ratio $(f^l/f^s)_{\text{pure},i}$ can be determined using Eq. (39).

Using SRK equation of state, the fugacity of pure liquid phase and liquid molar volume are calculated. Moreover, melting point temperature is assessed via the following correlation [42]:

$$T_{f,i} = 374.5 + 0.02617MW_i^s - \frac{2017}{MW_i^s} \quad (41)$$

In which MW represents molecular weight.

The following term is used to estimate the enthalpy of fusion, ΔH_f [43]:

$$\Delta H_{f,i} = 0.22089MW_i^s T_{f,i} \quad (42)$$

For the heat capacity of fusion, ΔC_p , the following correlation is used [44]:

$$\Delta C_{p,i} = 1.2698MW_i^s - 1.9406 \times 10^{-3} MW_i^s T \quad (43)$$

In this paper, solid molar volume is selected in such a way to be close to liquid molar volume. In addition, λ in Eq. (39) is assumed adjustable and regressed via experimental data. It is worth noting that the correlations expressed in Eqs. (41) to (43) were proposed for waxy components, for the first time. However, Hosseinzadeh Dehaghani et al. [39] showed the applicability of these correlations for modeling phase equilibria of asphaltene component.

3. Modeling

3.1 Fluids Characterization

Reservoir oil samples from different sources found in literature were utilized in this study. Details of each oil compositions and properties can be found in their sources [1, 6, 21, 45, 46]. Fluid characterization proposed by Arya et al. [7] was used in this study for reduction of the number of components. Therefore, oil samples (oil 1 to oil 12) were divided into CO₂, H₂S, N₂,

C1, C2, C3, iC4, nC4, iC5, nC5, C6, heavy component (HC) and asphaltene. The pseudo-component, HC, includes normal paraffin, iso-paraffin, cycloalkanes, poly-nuclear-aromatic, and all resins. Asphaltene pseudo-component mole fractions in various oils are found based on the results of SARA analysis performed by different researchers [1, 6, 21, 45, 46]. It must be noticed that HC participates in cross-associating with asphaltene. Splitting and grouping of the components heavier than C6 into HC and asphaltene pseudo-components are based on the molar mass of different components as well as asphaltene. In reality, fraction of asphaltene is poly-dispersed in heavy component medium. In this study, molar mass of asphaltene is considered to be a fixed value of 750 g/mol and asphaltene molecules are present as monomers. Different oil samples with their compositions as well as HC molar mass are illustrated in Table 1.

Table 1 Composition and characteristics for the characterized oil samples

Component	Oil 1 Mole%	Oil 2 Mole%	Oil 3 Mole%	Oil 4 Mole%	Oil 5 Mole%	Oil 6 Mole%	Oil 7 Mole%	Oil 8 Mole%	Oil 9 Mole%	Oil 10 Mole%	Oil 11 Mole%	Oil 12 Mole%
CO ₂	1.57	1.59	2.45	1.28	6.98	3.68	4.36	1.33	1.01	1.21	2.46	1.42
H ₂ S	5.39	1.44	0.59	0	3.1	1.72	2.04	-	-	-	-	-
N ₂	0.91	0.47	0.06	0	0.15	0.19	0.22	-	-	-	0.57	0.51
C1	24.02	32.22	38.65	0	19.21	24.27	22.21	0	0.01	0	36.37	6.04
C2	10.09	12.42	6.66	0	5.59	7.42	6.84	0.09	0.12	0.09	3.47	7
C3	9.58	10.29	5.33	1.44	6.79	5.39	5.11	1.12	0.52	1.12	4.05	6.86
iC4	1.83	2.03	1.01	0.84	1.19	0.93	0.84	-	-	-	0.59	0.83
nC4	4.83	4.87	2.92	3.37	3.74	2.71	2.48	1.36	0.95	1.35	1.34	3.35
iC5	2.27	2.22	1.24	1.49	1.55	0.9	0.81	-	-	-	0.74	0.7
nC5	2.74	2.71	1.51	1.53	1.52	1.04	0.95	2.59	2.56	2.23	0.83	3.46
C6	4.77	4.12	4.67	9.39	5.44	3.21	0.92	3.21	3.48	3.26	1.62	3.16
HC	31.86	25.54	33.35	77.80	42.96	46.34	51.48	88.44	89.63	88.68	45.72	64.65
Asphaltene	0.14	0.08	1.56	2.86	1.78	2.2	1.74	1.86	1.72	2.06	2.24	2.02
HC Molar Mass (g/mol)	333.23	282.01	310.43	268.59	274.52	271.84	225.24	230.78	209.08	220.15	308.03	265.98
Oil Molar Mass (g/mol)	132.58	98.62	135.16	247.85	152.86	159.10	143.98	227.13	208.63	219.34	171.34	202.39
Temperature (K)	393.15	406.82	356.48	352.04	393.15	397.04	394.26	298.15	298.15	298.15	373.15	376.48

3.2 Modeling Using PC-SAFT and CPA EOSs

The pure component parameters of the PC-SAFT EOS (σ , ϵ/K , and m) and the physical parameters of CPA EOS (T_c , P_c , and ω) for the well-defined components (CO_2 , H_2S , N_2 , C1, C2, C3, iC4, nC4, iC5, nC5, and C6) were found in literature [19]. Parameters of asphaltene for PC-SAFT and CPA are different. According to Arya et al. [7], these parameters are fixed for asphaltene with molar mass of 750 g/mol based on the assumption that the solubility parameter of asphaltene changes between 19 to 23 $\text{MPa}^{1/2}$ at ambient pressure and temperature [26]. Details of the values of the well-defined components as well as asphaltene are indicated in Table 2 and Table 3 for PC-SAFT and CPA EOSs, respectively.

Table 2 PC-SAFT parameters for the well-defined components

Component	σ (\AA)	ϵ/K (K)	m
CO₂	2.7852	169.21	2.0729
H₂S	3.0737	227.34	1.6517
N₂	3.313	90.96	1.2053
C1	3.7039	150.03	1
C2	3.5206	191.42	1.6069
C3	3.6184	208.11	2.002
iC4	3.7574	216.53	2.2616
nC4	3.7086	222.88	2.3316
iC5	3.8296	230.75	2.562
nC5	3.7729	231.2	2.6896
C6	3.7983	236.77	3.0576
Asphaltene	4.2200	367	15.25

Table 3 CPA parameters for the well-defined components

Component	T_c (K)	P_c (KPa)	ω
CO₂	126.21	3390	28
H₂S	304.14	7375	44
N₂	373.2	8940	34.1
C1	190.56	4599	16
C2	305.32	4872	30.1
C3	369.83	4248	44.1
iC4	407.8	3604	58.1
nC4	425.12	3796	58.1
iC5	460.4	3380	72.2
nC5	469.7	3370	72.2
C6	507.4	3012	86.2
Asphaltene	1040	1544	1.535

Initial values of PC-SAFT parameters for the pseudo-component HC were found using Punnapala and Vargas equations [47] assuming 0.5 as the value of aromaticity (γ). Since the molar mass of HC is different for different oil samples, each oil has specific values of PC-SAFT parameters for HC. In this study, the PC-SAFT parameters for HC were considered as the adjusting parameters for each oil type based on the amount of asphaltene precipitated. In addition, the initial values of CPA variables for HC were calculated using correlations found in literature. The procedure of estimating the initial values of CPA parameters can be found in Nascimento et al. [48]. Again, the values of T_c , P_c , and ω of HC were used as the tuning parameters of CPA EOS for matching the model results with experimental values of asphaltene precipitation amount.

3.3 Modeling Using Solid Model and EOS

In this work, in order to use SRK EOS in a solid framework for accurate modeling of asphaltene precipitation, asphaltene is assumed to be monodisperse with constant molar mass that could be precipitated as a pure solid phase. Initial values of EOS parameters for well-defined components and asphaltene and HC pseudo-components were found using the procedure discussed in the previous section. Again, the physical parameters of HC were used as the adjusted variables in this model. The optimization process is performed by using an optimization algorithm and the model with the minimum objective function is introduced as the best model. The following objective function was used for all the models presented in this study.

$$\text{Objective Function} = \frac{1}{N} \sum_{i=1}^N |Y_i^{\text{Calc}} - Y_i^{\text{Exp}}| \quad (44)$$

In the above relation, N is the total number of data points, Y_i^{Calc} and Y_i^{Exp} are the calculated output and experimental output, respectively.

3.4 Modeling Using FH and MFH

In this study, Flory-Huggins (FH) and the modified Flory-Huggins (MFH) models were also used for modeling asphaltene precipitation behavior in various oils with different compositions. The objective of using these models is to show their ability in asphaltene precipitation estimation with the latest solubility models such as PC-SAFT and CPA models. For estimating asphaltene precipitation by using this model, solubility parameters of maltene and asphaltene, and molar volumes of maltene and asphaltene are required. Asphaltene and maltene solubility parameters can be calculated by using Hirschberg et al. relations [26]. Additionally, SRK-EOS was used for estimation of maltene molar volume. Physical properties of petroleum fractions and binary interaction coefficients were used as same as the ones used in CPA EOS. The adjustable parameters in this model were considered to be the molecular weight of asphaltene (polymer), binary interaction parameter (l), and asphaltene molar volume. In this study, these parameters were tuned by using experimental datasets considering SRK equation of state for gas/liquid equilibria.

4. Results and Discussion

In this study, various thermodynamic models, including PC-SAFT, CPA, solid model, FH, and MFH, are used for simulating asphaltene precipitation behavior of 12 oil samples at different conditions. For each model, with knowing the main characteristics of each oil sample, i.e. pressure, temperature, and composition, the bubble point pressure is determined. If the system pressure is higher than the bubble pressure, calculation for liquid-liquid equilibria (LLE) is performed and the amount of asphaltene precipitated is estimated. Otherwise, first of all, a two-phase gas/liquid flash is done, and then LLE calculation is performed. It is worth noting that

before LLE calculations, an asphaltene stability analysis or phase stability analysis using Gibbs free energy minimization is required to check if $P_{oil} < P_{onset}$ or $P_{oil} > P_{onset}$. It is assumed that asphaltene pseudo-component is negligible in gas phase and hence, it is not considered in gas/liquid flash calculation. Therefore, the association term of the models is neglected in vapor-liquid flash calculation. For each model, different sets of parameters were considered as tuning variables. These parameters were found by minimizing the objective function (Eq. (44)) for the experimental values and the model results.

As mentioned in previous sections, for PC-SAFT and CPA models, the models' parameters for HC were used as tuning variables. The adjusted parameters are indicated in Table 4.

Table 4 Adjusted model parameters of PC-SAFT and CPA for HC pseudo-component

Oil	PC-SAFT Variables			CPA Variables		
	σ ($^{\circ}\text{A}$)	ϵ/K (K)	m	T_c (K)	P_c (KPa)	ω
1	4.17	362.14	7.34	829.01	1178	0.89
2	4.14	356.04	6.41	773.48	1074	0.94
3	4.16	361.21	6.61	847.79	1557	0.73
4	4.15	356.18	6.19	820.09	1743	0.68
5	4.13	354.47	6.35	824.24	1656	0.68
6	4.14	355.98	6.03	830.17	1775	0.66
7	4.15	347.65	5.74	800.67	2201	0.59
8	4.12	347.99	5.99	797.39	2009	0.62
9	4.09	340.25	4.09	778.96	2162	0.59
10	4.11	346.15	5.36	788.47	2051	0.61
11	4.18	362.74	6.94	847.55	1584	0.72
12	4.12	355.89	6.15	802.49	1564	0.74

Binary interaction coefficients (k_{ij}) for these two models were set to zero, except the binary interaction parameters between asphaltene- CO_2 , asphaltene- N_2 , asphaltene- H_2S , asphaltene-C1, and asphaltene-HC. Only asphaltene-HC interaction coefficient was used as an adjusting variable for both PC-SAFT and CPA models. The k_{ij} values between asphaltene and CO_2 , N_2 , H_2S , and C1 were originally proposed by Arya et al. [7] and were used in this work. The used values for

binary interaction coefficients as well as the adjusted one for oil 1 to oil 12 are illustrated in Table 5.

Table 5 Binary interaction coefficients used in PC-SAFT and CPA models

Oil	Component				
	Asphaltene	CO ₂	H ₂ S	N ₂	C1
		0.16	0.015	0.175	0.04
		HC_PC-SAFT		HC_CPA	
1		0.41		0.48	
2		0.68		0.29	
3		0.27		0.34	
4		0.19		0.57	
5	Asphaltene	0.61		0.22	
6		0.72		0.12	
7		0.68		0.66	
8		0.96		0.99	
9		0.91		0.87	
10		0.32		0.75	
11		0.33		0.25	
12		0.93		0.99	

After setting the binary interaction coefficients and pure-component parameters of the pseudo-component HC, self-association energy of asphaltene (ϵ^{AA}/κ), cross-association energy between asphaltene and HC (ϵ^{AH}/κ), self-association volume (β^{AA}) and the cross-association volume (β^{AH}) for both PC-SAFT and CPA models should be determined. Fraction of asphaltene is poly-dispersed, in reality. Each asphaltene sub-fraction may have various ϵ^{AA} and since the HC pseudo-component is a lumped component, the sub-fraction of asphaltene may exhibit different ϵ^{AH} due to various local composition. In this study, it is assumed that sub-fraction of asphaltene have the highest value of ϵ^{AA} , which firstly precipitates and is responsible for precipitation onset. This assumption is true because the only concern is the onset conditions and the approach could be simplified through this assumption [7]. It must be noticed that a 4C scheme was considered for asphaltene association in both PC-SAFT and CPA models. According to Prausnitz and Firoozabadi, ϵ^{AA}/κ has a default value of 3000K [49]; however, this parameter can be used as an adjustable parameter. For both PC-SAFT and CPA models, this variable was used as a tuning

parameter in this work. For determining $\varepsilon^{\text{AH}}/\kappa$, it is assumed that there is a certain value of $\varepsilon^{\text{AH}}/\kappa$ for the entire medium of heavy component. This parameter is considered to be temperature dependent in literature [7]. In this study, since simulation of asphaltene precipitation behavior for each oil is performed at a certain temperature, this parameter is reported as a constant value, not as a function of temperature. The parameter $\varepsilon^{\text{AH}}/\kappa$ is another tuning variable for matching with experimental data. These adjusted parameters are shown in Table 6 for each oil sample. Self-association and cross-association volume parameters, β^{AA} and β^{AH} , for using in PC-SAFT and CPA EOSs were considered to be 0.05.

Table 6 Self-association energy of asphaltene ($\varepsilon^{\text{AA}}/\kappa$) and cross-association energy between asphaltene and HC ($\varepsilon^{\text{AH}}/\kappa$) for both PC-SAFT and CPA EOSs

Oil	PC-SAFT Variables		CPA Variables	
	$\varepsilon^{\text{AA}}/\kappa$ (K)	$\varepsilon^{\text{AH}}/\kappa$ (K)	$\varepsilon^{\text{AA}}/\kappa$ (K)	$\varepsilon^{\text{AH}}/\kappa$ (K)
1	3300	4562.40	3000	4435.93
2	3500	3704.14	4000	3722.83
3	3000	4038.32	4000	4061.45
4	6500	4219.07	4000	4263.47
5	7000	1680.10	6000	1661.54
6	3000	1776.78	3500	1780.57
7	4000	1885.26	2500	1884.79
8	3000	2348.35	3000	2487.14
9	2500	3684.25	4000	3348.97
10	3500	2947.64	3000	3001.28
11	4500	4012.35	4000	3943.18
12	3500	3846.24	3000	3999.49

According to Table 6, each oil has a specific value for the association terms. This is due to the variation in the characteristics of each fraction from oil to oil, and because of this, obtaining an average value for these terms, especially for $\varepsilon^{\text{AH}}/\kappa$, is not possible. By comparing Tables 1 and 6, it can be seen that there is not a general trend between the association parameters and oil or HC molar masses. It must be included that during tuning process, for PC-SAFT and CPA models, the models' parameters were found using bubble pressure experimental data, and the other adjusted

variables, including cross-association energy, self-association energy, and the BIC between asphaltene and HC, were calculated using experimental asphaltene upper onset pressure (UOP).

Bubble point pressure values and UOP of the oil samples can be found in their sources.

Solid model together with SRK EOS was also used for asphaltene precipitation modeling. As discussed before, the physical parameters of HC (T_c , P_c , and ω) were used as adjustable parameters. In addition to these variables, the transition energy (λ), asphaltene-HC, and asphaltene-CO₂ binary interaction coefficients were also used as tuning variables. Values for the other binary interaction parameters were used as the same as the ones used in other models, which are illustrated in previous section. It is worth noting that for this part, $k_{\text{asphaltene-CO}_2}$ was used in addition to $k_{\text{asphaltene-HC}}$ and this is due to this fact that for better comparison between the performance of this model and the performance of PC-SAFT and CPA models, the number of tuning parameters is better to be the same. In addition, the binary interaction coefficient of asphaltene-CO₂ was shown to be effective for matching the model results in Shirani et al. [5]. Table 7 shows the regressed results for the model parameters for different oil samples. For this model, during tuning process, the model's parameters (T_c , P_c , and ω) were adjusted using bubble point pressure data and the transition energy (λ) as well as asphaltene-HC and asphaltene-CO₂ BICs were found using asphaltene UOP values.

Table 7 Adjusted parameters for solid model together with SRK EOS

Oil	SRK Variables for HC				Binary Interaction Coefficients	
	T_c (K)	P_c (KPa)	ω	λ (J/mol)	Asph-HC	Asph-CO ₂
1	911.24	1203	0.88	2160	0.52	0.89
2	794.54	1075	0.95	2330	0.83	0.16
3	832.14	1542	0.70	2180	0.28	0.92
4	801.68	1802	0.68	2220	0.55	0.10
5	809.23	1694	0.68	2210	0.36	0.21
6	854.17	1762	0.67	2100	0.94	0.19
7	811.19	2285	0.54	2300	0.65	0.25
8	799.84	2008	0.60	2230	0.80	0.98

9	781.49	2200	0.59	2290	0.91	0.14
10	783.75	2052	0.62	2290	0.59	0.29
11	887.63	1506	0.71	1990	0.97	0.34
12	836.29	1560	0.73	2010	0.30	0.93

As discussed, for these three models, PC-SAFT, CPA, and solid model, binary interaction coefficients between asphaltene and HC pseudo-component and also CO₂ were used as tuning parameters. BIC shows the strength of interaction between molecules. Generally, these coefficients should be less than one. However, according to Tables 5 and 7, for some oil samples, the k-value between asphaltene and HC or asphaltene and CO₂ is nearly close to one. This may be due to the high polarity and complexity of components (asphaltene, and resin in HC) in some oil samples, which make the interaction between these components more significant and hence, results in increasing the k-values. These high values can also be seen in Shirani et al. [5, 50]. They used CPA and association equation of state (AEOS) for modeling asphaltene precipitation at different conditions and found high BIC values between asphaltene and CO₂, N₂, and H₂S for the studied oil samples.

For better comparison and showing the capability of the previously described models in asphaltene precipitation estimation, the FH and MFH models were also utilized for simulating the asphaltene precipitation behavior of the twelve oil samples. Asphaltene molecular weight, asphaltene molar volume, and binary interaction parameter (l) were found to be an average of 785g/mol, 0.72m³/kgmol, and 0.01 for the oil samples.

Results obtained by the five models are compared with each other and with experimental data for different oil samples. Figures 1 to 10 illustrate the performance of various models in predicting asphaltene precipitation at different environmental conditions of pressure, temperature, solvent type, and solvent ratio. Experimental datasets used in this study can be found in Appendix A.

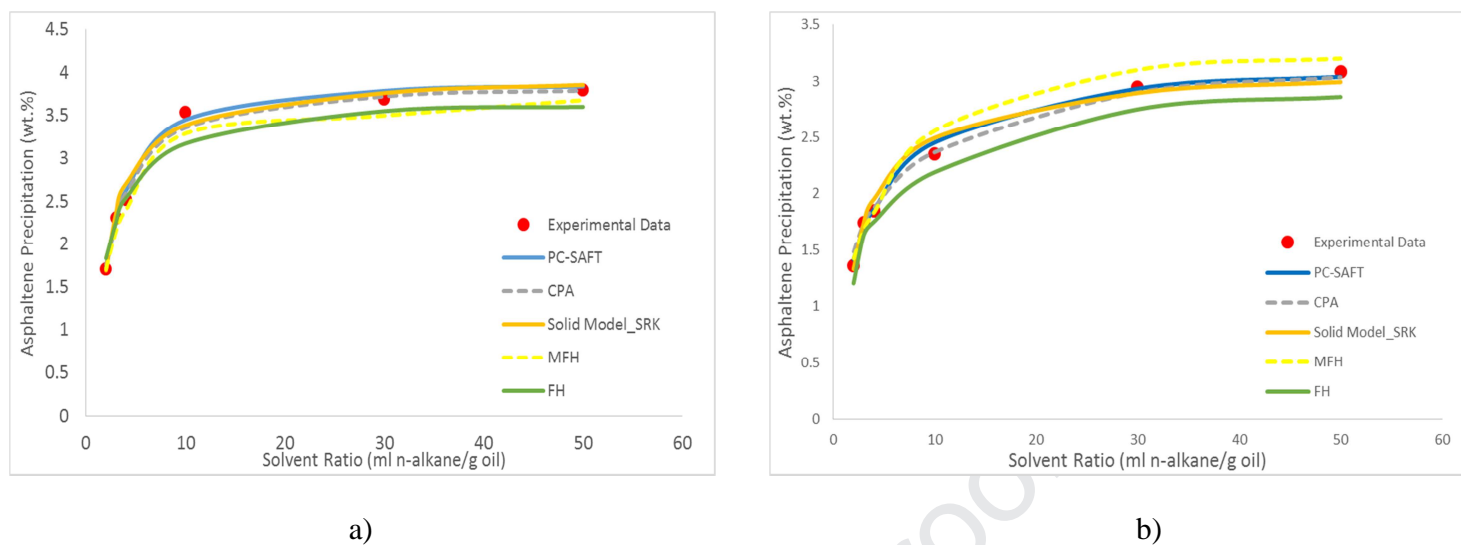


Figure 1 Comparison between different models in predicting asphaltene precipitation for oil sample 1: a) nC5 as solvent, b) nC7 as solvent

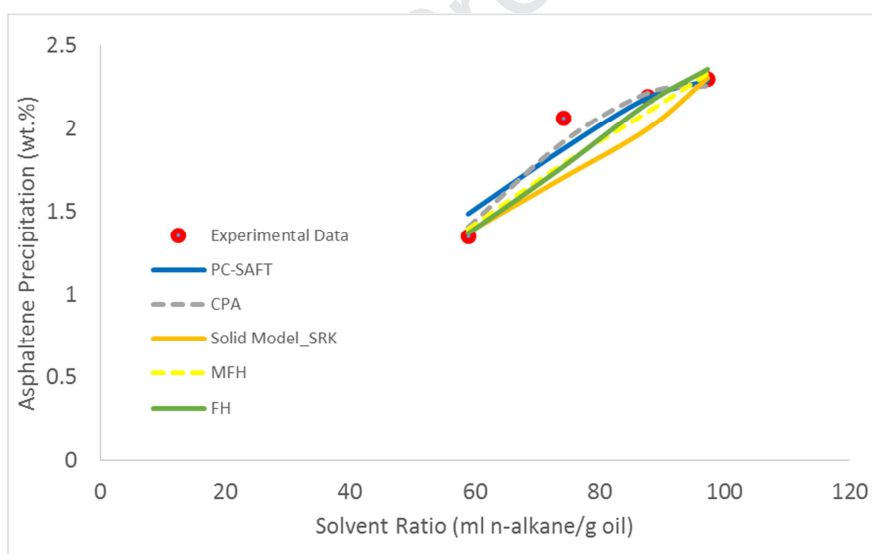


Figure 2 Comparison between different models in predicting asphaltene precipitation for oil sample 2. nC9 is used as solvent

For oil samples 1, it can be seen from Figure 1 that PC-SAFT, CPA, and solid models can accurately predict asphaltene precipitation with solvent ratio, for both nC5 and nC7, while FH and MFH models under-estimate or over-estimate the actual values. However, the general trend

of precipitation behavior for this oil sample is detected clearly by all the models. As shown in Figure 2, for oil sample 2, only PC-SAFT and CPA models are able to accurately simulate asphaltene precipitation behavior with increasing nC9. Hosseinzadeh Dehaghani et al. [39] used these oil samples for comparing the performance of PC-SAFT and Peng-Robinson (PR) EOS in asphaltene precipitation calculation in a multi-solid framework. However, a different characterization was performed for the oils. Both monodisperse and polydisperse asphaltene modeling were utilized in their work. They used volume shift for PR EOS, and the physical parameters of PC-SAFT and PR, and transition energy for asphaltene and (saturates+aromatics) pseudo-components were considered to be the adjustable variables for the models. Due to the sharp changes in the mixtures composition, binary interaction parameters were not included in their model. Results of their study showed that monodisperse modeling in solid model cannot predict the asphaltene precipitation accurately, and polydisperse modeling is needed. By comparing the modeling results of this study and the work done by Hosseinzadeh Dehaghani et al. [39], one can conclude that with a proper oil characterization and tuning parameters selection, single solid phase (monodisperse) modeling could be accurate enough in some cases; the results for oil sample 1 confirm this fact. In addition, using other models such as PC-SAFT and CPA, without usage in multi-solid framework, can be highly efficient, as the results for oil samples 1 and 2 indicate this fact.

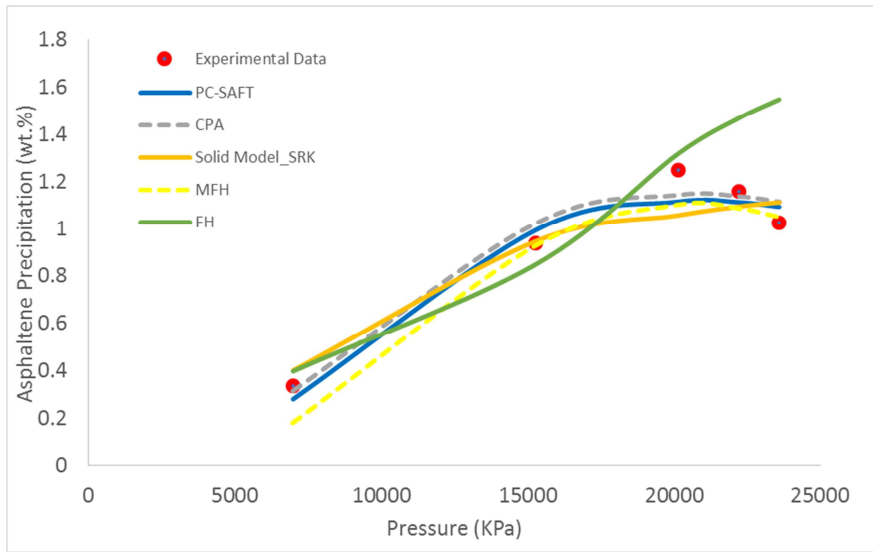


Figure 3 Comparison between different models in predicting asphaltene precipitation versus pressure for oil sample 3

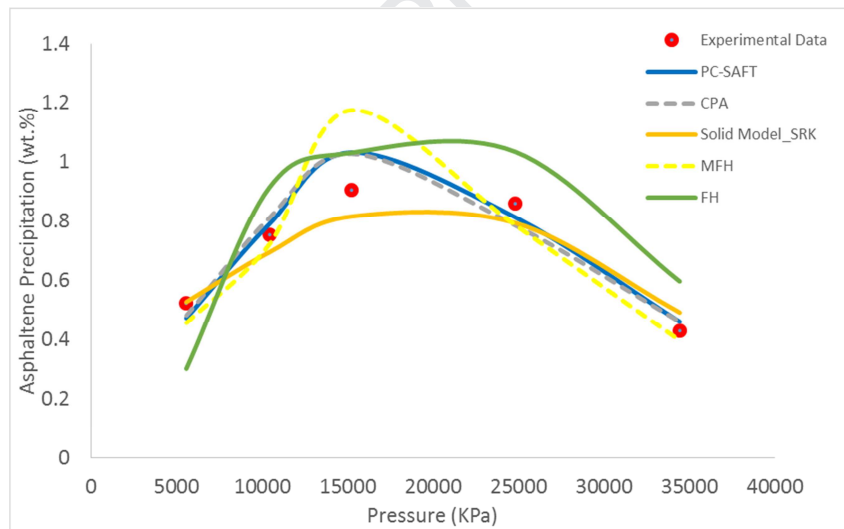


Figure 4 Comparison between different models in predicting asphaltene precipitation versus pressure for oil sample 4

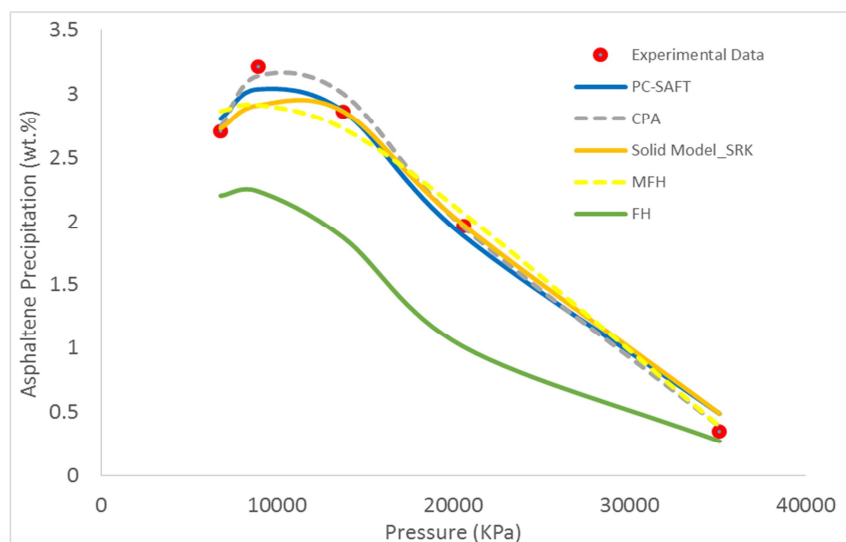


Figure 5 Comparison between different models in predicting asphaltene precipitation versus pressure for oil sample 5

Based on the results shown in Figure 3-5, PC-SAFT and CPA models exhibit higher accuracy compared to other models. Solid model seems to provide acceptable results; however, for oil sample 4, it is not as accurate as PC-SAFT and CPA. This is also true for the results obtained by MFH model. Among different models, only FH fails to predict the behavior trend of asphaltene precipitation in these oil samples. These oil samples were studied by Hemmati-Sarapardeh et al. [6]. They used intelligent tools and also FH model for estimating asphaltene precipitation. Artificial intelligent tools could accurately predict the amount of asphaltene precipitation at different conditions; however, since these tools act as black boxes and are highly dependent on the dataset that is utilized during their training process, they are not suggested for studying the mechanisms involved in processes such as asphaltene precipitation or deposition.

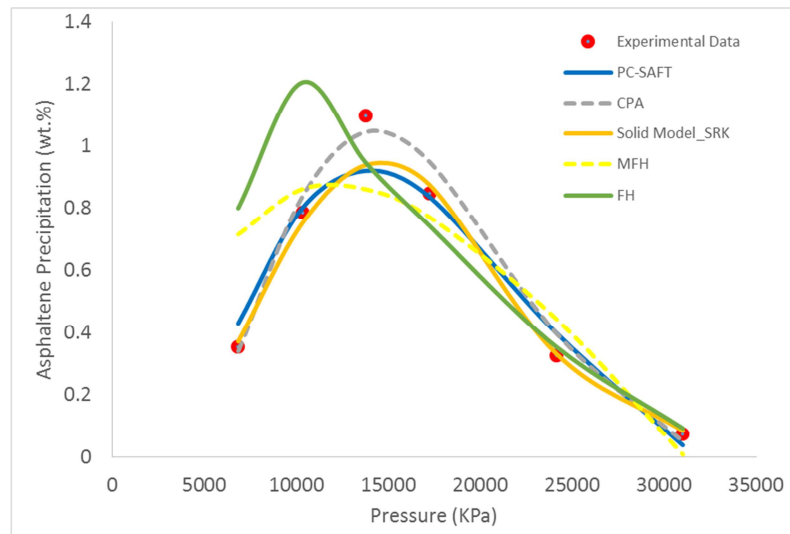


Figure 6 Comparison between different models in predicting asphaltene precipitation versus pressure for oil sample 6

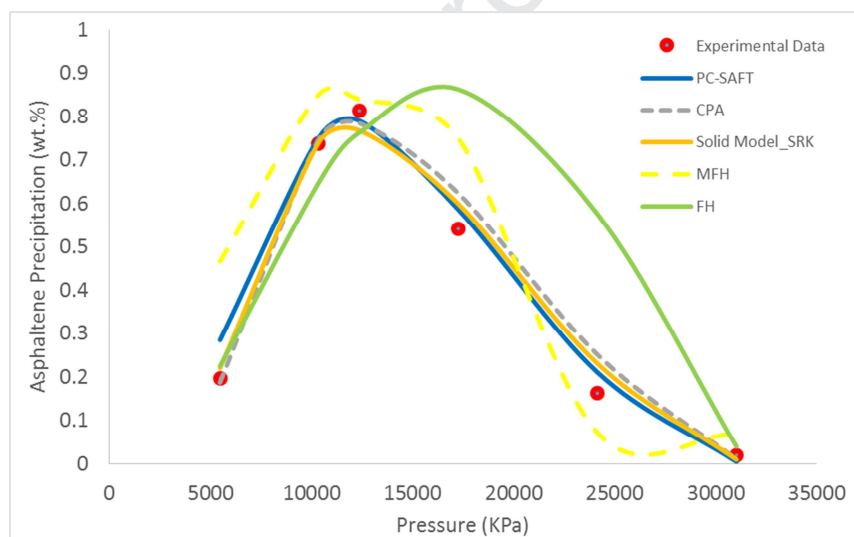


Figure 7 Comparison between different models in predicting asphaltene precipitation versus pressure for oil sample 7

Figures 6 and 7 show that for both the trend prediction and precipitation estimation, PC-SAFT, CPA, and solid model obtain acceptable results. For oil sample 6, CPA EOS exhibits higher accuracy than the other models, and for oil sample 7, solid model and PC-SAFT have the best performance. From Figure 7, it seems that MFH and FH models fail to predict the behavior

trend. Kord and Ayatollahi [21] used different models of FH, MFH, and solid models for studying asphaltene precipitation in these oil samples. The solid model methodology used in their study is different with the one used in this work. Results of their study demonstrated that solid model yields more accurate amounts for asphaltene precipitation than those of the other models. This is also confirmed in the results illustrated in Figures 6 and 7. Asphaltene precipitation has a linear behavior with pressure from upper onset pressure to bubble point and from bubble point to the lower onset pressure. This behavior was confirmed by the most accurate thermodynamic models, i.e. PC-SAFT and CPA, and also the solid model. As shown in figures 3 to 7, the results of these models are nearly on a linear line before and after the deflection point (bubble point pressure). The other models (FH and MFH) fail to predict this trend for some cases.

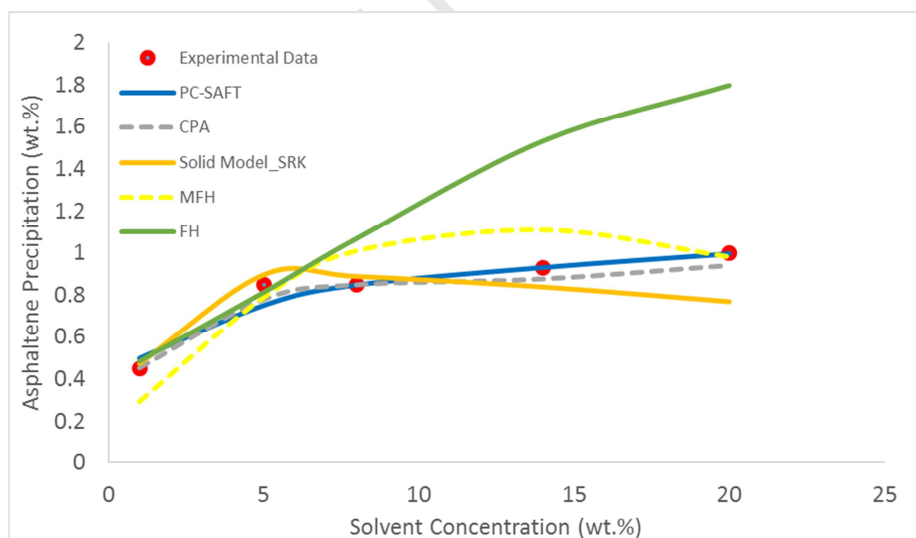


Figure 8 Comparison between different models in predicting asphaltene precipitation for oil sample 8. nC7 is used as solvent

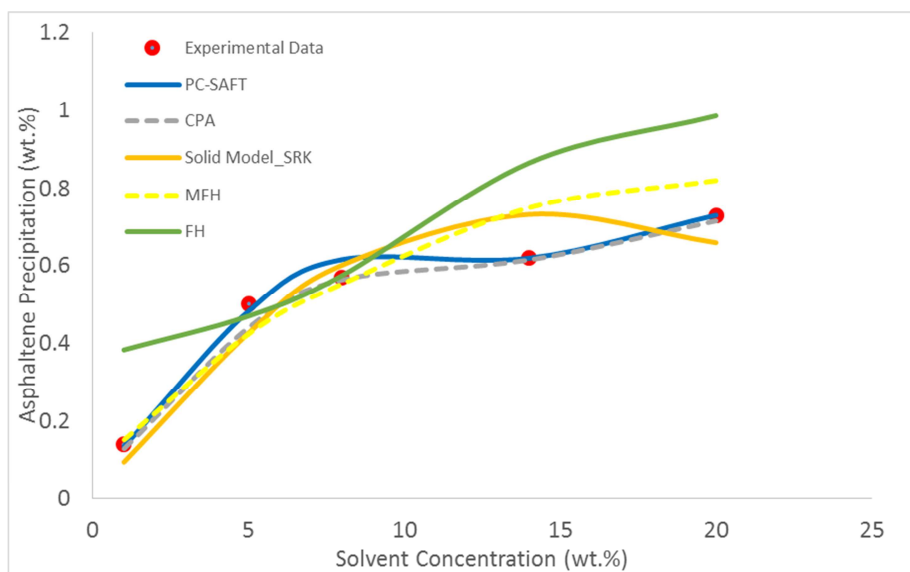


Figure 9 Comparison between different models in predicting asphaltene precipitation for oil sample 9. nC7 is used as solvent

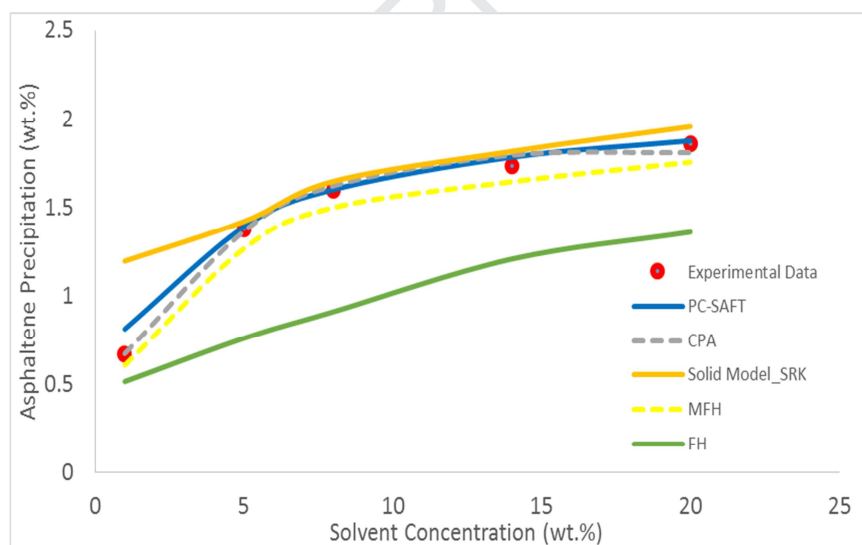


Figure 10 Comparison between different models in predicting asphaltene precipitation for oil sample 10. nC7 is used as solvent

Figures 8-10 indicate that PC-SAFT and CPA models are the most accurate models for estimating asphaltene precipitation versus nC7 concentration, for oil samples 8 to 10. For oils 8 and 9, only PC-SAFT and CPA could predict the trend of precipitation behavior and the other

models fail to predict the same behavior. However, for oil 10, nearly all the models could accurately find the trend of asphaltene precipitation in a titration process with nC7 as solvent. Mashhadi Meighani et al. [1] used PC-SAFT for modeling asphaltene precipitation behavior in these oil samples. They used a different characterization for oils and considered a higher value (1500g/mol) for asphaltene molar mass. Additionally, physical parameters of PC-SAFT and self-association energy and volume of asphaltene were considered to be the tuning parameters. They found lower values for ε^{AA}/κ and higher values for β (for each oil sample) compared to the values obtained in this study.

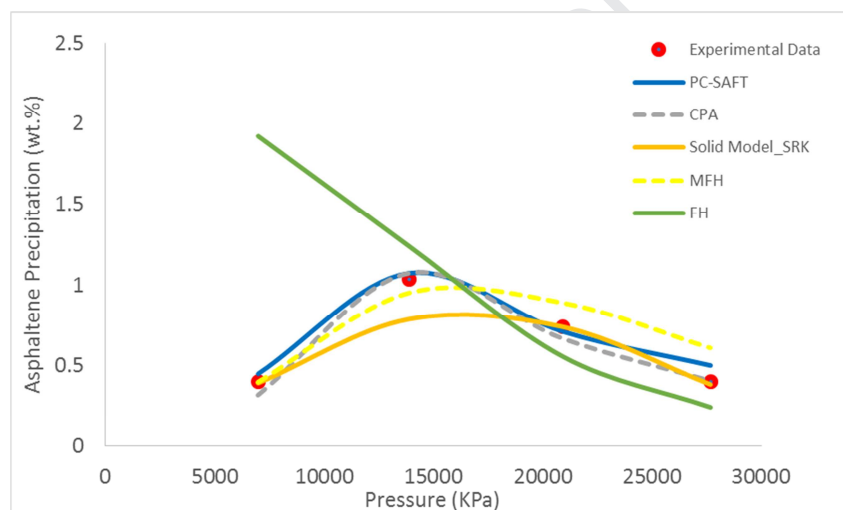


Figure 11 Comparison between different models in predicting asphaltene precipitation versus pressure for oil sample 11

As illustrated in Figure 11, CPA and PC-SAFT can estimate the amount of asphaltene precipitation accurately, and only FH model fails to demonstrate the behavior trend of asphaltene precipitation in oil sample 11. Shirani et al. [5] used CPA equation of state for predicting the amount of asphaltene prediction in this oil sample. A different oil characterization was used for this sample. Association energy, association volume, and binary interaction coefficients between asphaltene and light components, including CO₂, N₂, C1, and H₂S, and also resin were selected

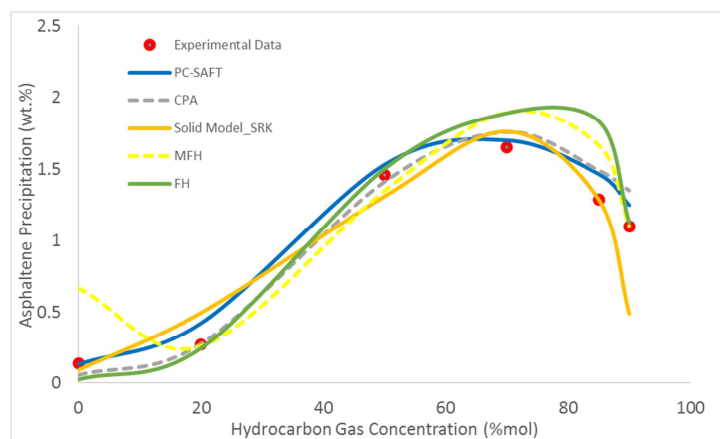
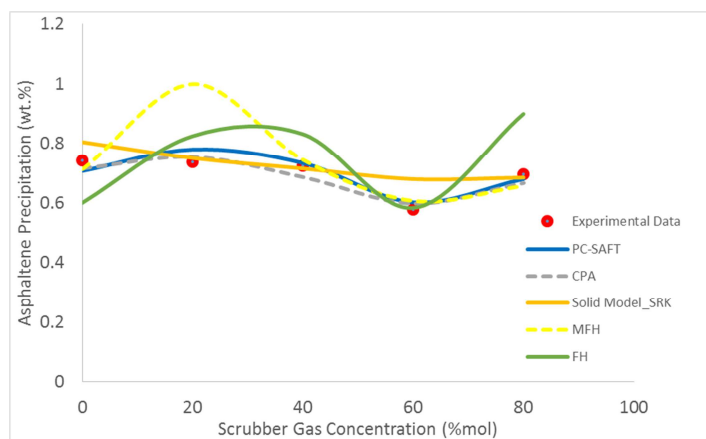
as tuning parameters. Two EOSs including SRK and PR were used for the physical part of CPA. Their results showed that using SRK for the physical part of CPA obtains higher accuracy. Comparing the adjusted variables in their study with the ones in this work, they found lower values for cross association energy and volume, but high values for BIC between asphaltene and light components, even more than one.

For oil samples 11 and 12, the effect of gas injection on the behavior of asphaltene precipitation was investigated and the performance of various models in predicting this behavior was demonstrated. For this purpose, two gases (scrubber gas and hydrocarbon gas) were used as solvents. Compositions of these two gases are shown in Table 8.

Table 8 Compositions of the used gases for asphaltene precipitation in oil samples 11 and 12

Component	H ₂ S	N ₂	CO ₂	C1	C2	C3	iC4	nC4	iC5	nC5	C6
Scrubber Gas, Mole%	0.15	0	0.85	0	0	0	0	0	0	0	0
Hydrocarbon Gas, Mole%	0	0.0317	0.1776	0.3033	0.2692	0.1309	0.0126	0.0466	0.0077	0.00126	0.0078

The effect of increasing gas content on the amount of precipitated asphaltene was studied by using the tuning parameters, which were discussed before for these two oil samples and for each model. The results of various models are indicated in Figure 12.



a)

b)

Figure 12 Modeling the effect of injecting scrubber and hydrocarbon gases on asphaltene precipitation; a) Oil sample 11, b) Oil sample 12

According to Figure 12, PC-SAFT and CPA models are accurate enough for predicting the effect of injecting scrubber and hydrocarbon gases into oil samples 11 and 12. Despite the differences between various models, PC-SAFT, CPA, and solid models respond to increasing gases concentration almost similar for both oils. Also, for oil 12, all models exhibit a similar trend for asphaltene precipitation due to gas injection.

Statistical analysis was performed for comparing the performance of different thermodynamic models in predicting asphaltene precipitation for different oil samples studied in this work. Coefficient of determination (R^2), mean square error (MSE), and average absolute relative error (AARE) are the commonly used statistical variables that are utilized for showing the models robustness. These parameters are calculated using:

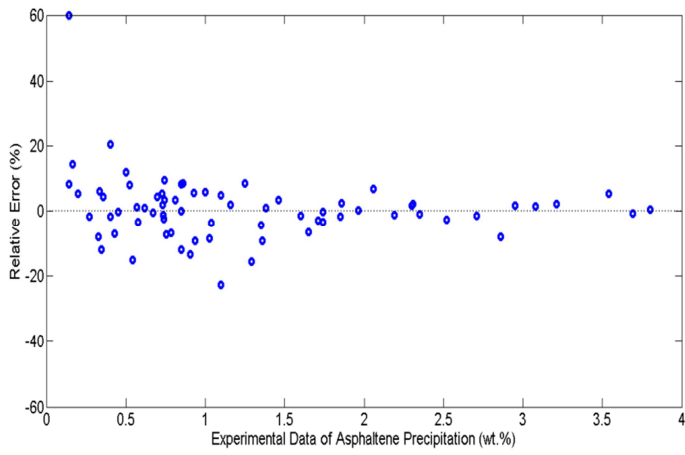
$$R^2 = 1 - \frac{\sum_{i=1}^N (X_{i,\text{exp}} - X_{i,\text{est}})}{\sum_{i=1}^N (X_{i,\text{exp}} - X_{\text{ave,exp}})} \quad (45)$$

$$MSE = \frac{1}{N} \sum_{i=1}^N (X_{i,\text{exp}} - X_{i,\text{est}})^2 \quad (46)$$

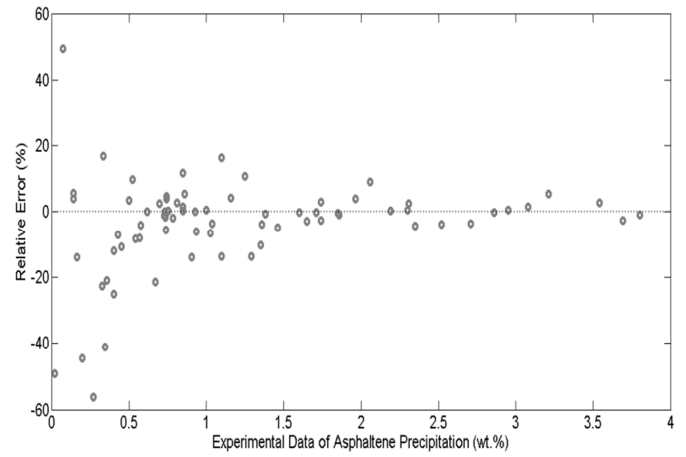
$$AARE (\%) = \frac{100}{N} \sum_{i=1}^N \left| \frac{X_{i,\text{exp}} - X_{i,\text{est}}}{X_{i,\text{exp}}} \right| \quad (47)$$

In the above equations, $X_{i,\text{exp}}$ and $X_{i,\text{est}}$ are experimental and estimated asphaltene precipitation amount, respectively, $X_{\text{ave,exp}}$ is the mean value of experimental values, and N is total data number.

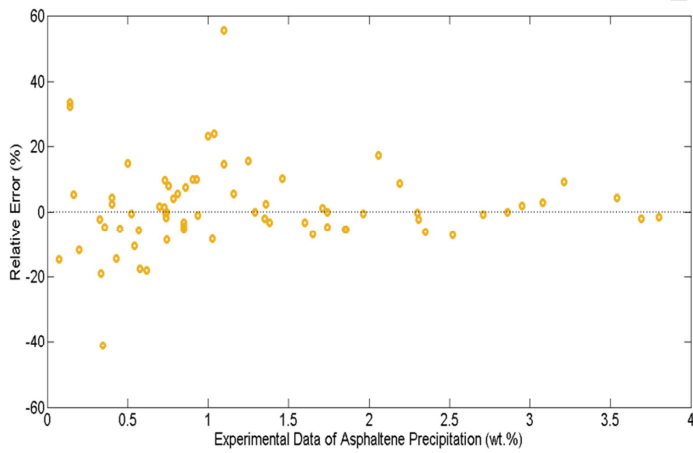
The relative error of the model estimations versus experimental values is shown in Figure 13, and statistical parameters values for the models are illustrated in Table 9.



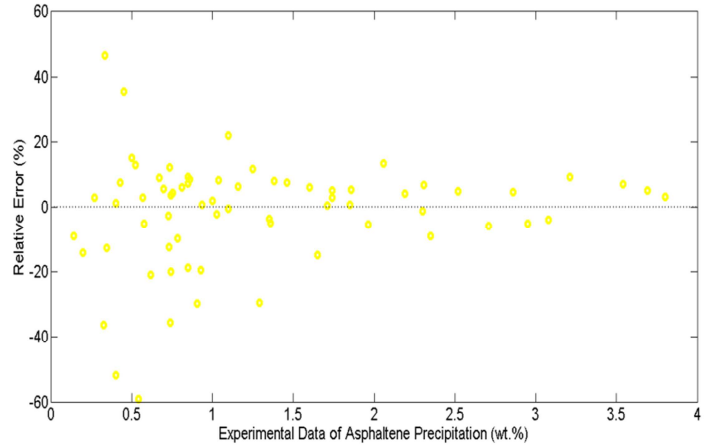
a)



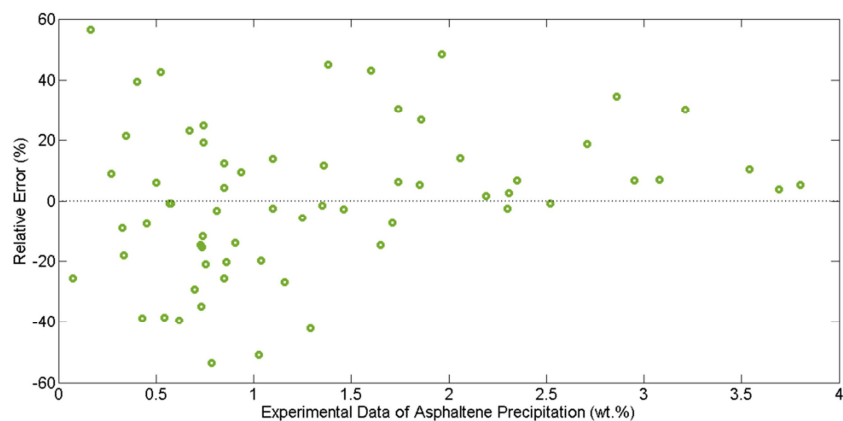
b)



c)



d)



e)

Figure 13 Relative error distribution for various models in estimating asphaltene precipitation; a)

PC-SAFT, b) CPA, c) Solid model_SRK, d) MFH, e) FH

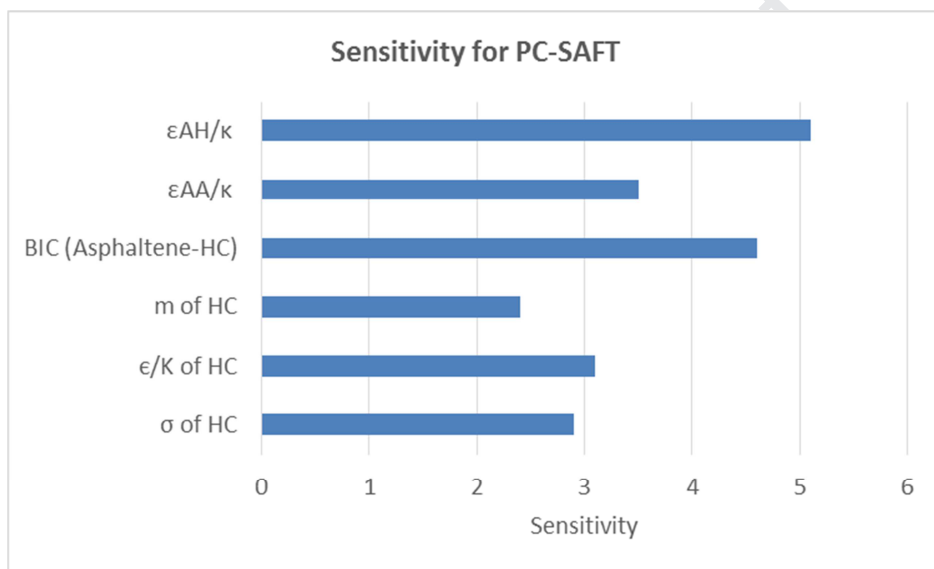
Table 9 Statistical parameters for different models

Parameter	PC-SAFT	CPA	Solid Model_SRK	MFH	FH
R^2	0.9957	0.9835	0.9756	0.9693	0.9372
AARE (%)	7.1367	10.5994	14.2921	17.2886	27.1942
MSE	0.0068	0.0076	0.0098	0.0202	0.0829

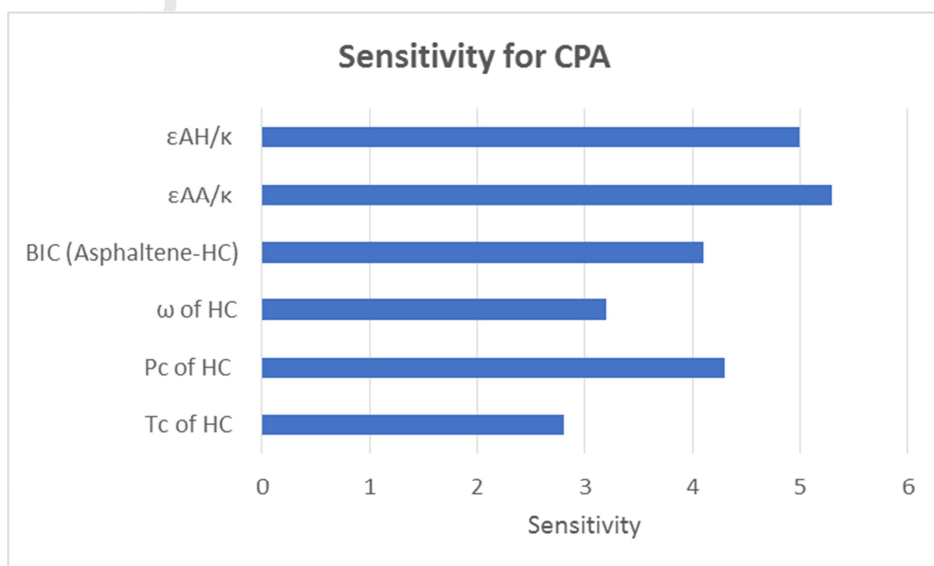
As shown in Figure 13, relative errors of PC-SAFT model outcomes are more compacted around the line of error=0; therefore, this model is more reliable compared to other models. Table 9 confirms this fact that PC-SAFT model provides more accurate results with R^2 , AARE, and MSE of 0.9957, 7.1367%, and 0.0068, respectively for the total data. According to Figure 13 and Table 9, PC-SAFT and CPA models are accurate for predicting asphaltene precipitation; however, similar to other models, experimental data points are needed for fitting the model results and adjusting parameters. This problem is major for most of thermodynamic models. These models cannot accurately predict asphaltene precipitation behavior, if enough experimental data points are not available. One way for solving this issue is to develop models, which can relate oil parameters to its characteristics. Based on this, unknown parameters can be

estimated for each oil sample and hence, predicting the amount of asphaltene precipitated can be performed without requiring experimental values for tuning process.

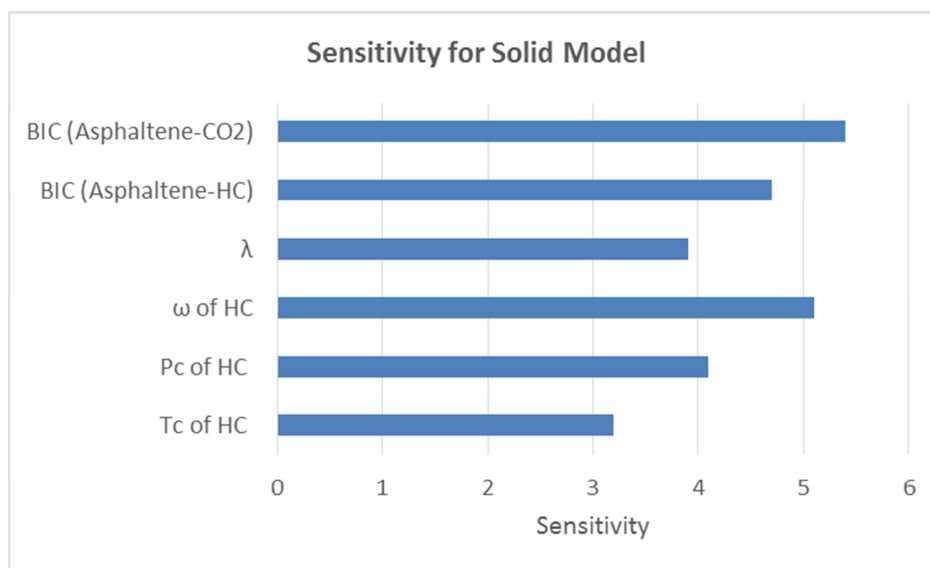
Moreover, for better understanding of the effect of the selected tuning parameters on the models outcomes, a sensitivity analysis was performed on the most accurate models, PC-SAFT, CPA, and solid model. Monte-Carlo algorithm was used for this analysis. Details of this procedure can be found in literature [51, 52]. Results of sensitivity analysis are shown in Figure 14.



a)



b)



c)

Figure 14 Sensitivity analysis on thermodynamic models for simulating asphaltene precipitation behavior; a) PC-SAFT, b) CPA, c) Solid model_SRK

As shown in Figure 14, for PC-SAFT model, cross-association energy between asphaltene and HC, BIC between asphaltene and HC, and self-association energy of asphaltene have the highest impact on the model results and should be considered during the tuning process. For CPA model, self-association energy of asphaltene, cross-association energy between asphaltene and HC, and P_c of HC pseudo-component are the most sensitive factors. In addition, for solid model, binary interaction coefficient between asphaltene and CO₂, and acentric factor of HC have the highest effect on the model outcomes. The importance of the parameters with high sensitivity on the models outputs was confirmed previously by other authors [7]. Additionally, the importance of BIC between asphaltene and CO₂ is related to the increase in asphaltene instability and

precipitation rate due to increase in carbon dioxide concentration. This fact was also confirmed in previous researches [53, 54].

Furthermore, Figure 15 compares the CPU time of various models including PC-SAFT, CPA, solid model, MFH, and FH. As illustrated in this figure, FH and MFH models are much faster and less computationally expensive compared to other models such as PC-SAFT and CPA. However, FH and MFH models are less accurate than others. Higher CPU time of models such as PC-SAFT and CPA is due to the iterative processes involved in these models for phase equilibrium calculations.

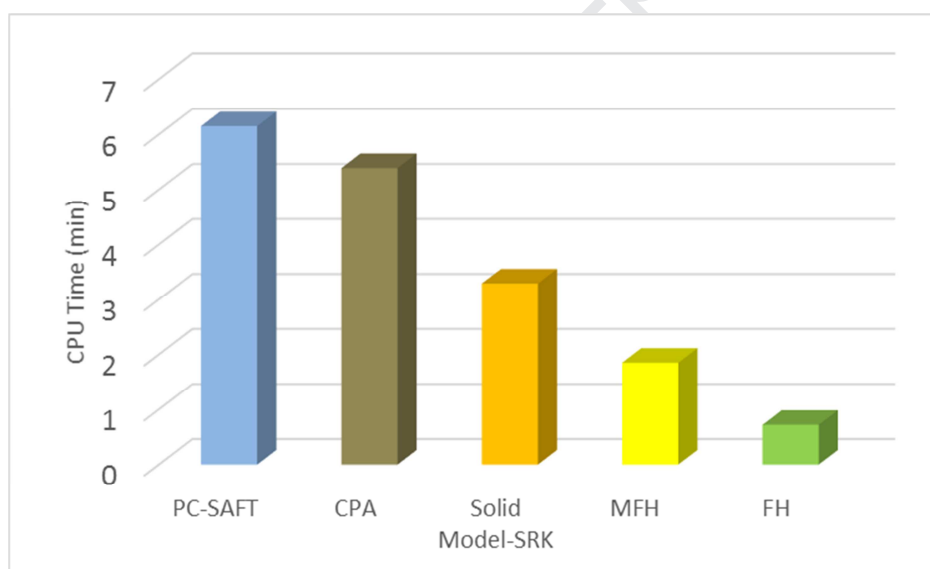


Figure 15 Comparison between the CPU times of different models

5. Summary and Conclusions

In this study, performance of different models in predicting asphaltene precipitation in twelve crude oils was compared in order to shed some lights on appropriate selection of a model for accurate simulation of asphaltene precipitation behavior at different environmental conditions.

For this purpose, PC-SAFT, CPA, solid model together with SRK, MFH, and FH models were used. The following conclusions can be drawn from this work:

- Results of different models demonstrated that PC-SAFT and CPA models are the most accurate models for predicting asphaltene precipitation. This is also confirmed through statistical and graphical analyses.
- Only CPA and PC-SAFT EOSs could accurately predict the behavior trend of asphaltene precipitation for different cases. The other models fail in some cases.
- The models were used for estimation of asphaltene precipitation during scrubber and hydrocarbon gases injection into the studied oil samples. The obtained results indicated high efficiency and accuracy of the developed PC-SAFT and CPA models.
- Physical parameters of the lumped pseudo-component, association terms, and binary interaction parameters were used as tuning variables of the models. Sensitivity analysis was performed on these parameters using Monte-Carlo algorithm. Results showed that cross-association energy between asphaltene and HC for PC-SAFT, self-association energy of asphaltene for CPA, and BIC between asphaltene and CO₂ for solid model have the highest effect on each model outputs; therefore, they should be considered during the tuning process.
- Results of the adjusted binary interaction coefficients showed that for some cases, the values of BICs between the components are close to one. Due to high polarity and complexity of some components such as resin and asphaltene in that systems, the interaction between those components becomes significant and hence, the value of BIC increases.

- Comparison between the simulation times of various models indicated that PC-SAFT is slower than the others and hence, is computationally more expensive.

Appendix A

Experimental datasets used in this work for modeling asphaltene precipitation can be found in "Data.xlsx" in supplementary material.

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Declaration of Interest Statement:

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