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Review article

Characterization of crude oils and asphaltenes using the PC-SAFT EoS: A systematic review

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ABSTRACT

In this paper, we present a systematic review of the perturbed-chain statistical associating fluid theory equation of state (PC-SAFT) EoS for thermodynamic modeling with application in asphaltene phase behavior simulation. The SAFT EoS and its modified version known as the PC-SAFT EoS is briefly introduced. Then, uses of the PC-SAFT EoS as a tool for asphaltene phase behavior modeling is highlighted. Crude oil characterization methods and modeling procedures are described with a focus on SARA-based method of modeling. The effects of variations in temperature and pressure on the PC-SAFT asphaltene precipitation models are discussed, as well. An erroneous behavior of PC-SAFT models at low temperatures was noted in the literature for a number of crudes. To address this issue, a summary of approaches developed to deal with such problems is presented. The effect of other modeling aspects on accuracy such as binary interaction parameters, inclusion of association term, and asphaltene polydispersity are discussed. The interaction parameters have a profound effect on modeling of precipitation envelope. Inclusion of association term seems to be especially promising in developing more accurate asphaltene phase behavior models. Modeling asphaltene fraction as polydisperse entities greatly improves the quality of models that aimed at calculation of the amount of precipitated asphaltenes. Finally, a summary of comparative studies between the PC-SAFT and some other thermodynamic models is provided.

1. Introduction

Asphaltenes are commonly defined in terms of their solubility. They do not dissolve in light normal alkanes such as heptane but are soluble in aromatic hydrocarbons such as toluene [1–3]. This fraction is the heaviest parts of crude oil that remain as solid residua during distillation process of crude oil [4]. Asphaltene deposition is a source of flow assurance problems in petroleum reservoirs, production wells, surface facilities, production lines, and transportation facilities [5–12].

Asphaltene precipitation is a prerequisite of consequent deposition on different surfaces and the phenomenon is mainly a function of temperature, pressure, and crude oil composition [2,5,13]. A crude oil phase diagram that accurately depicts the operating conditions at which asphaltenes will start to precipitate is an important tool for early life planning of preventive actions [13]. Experimental investigation of asphaltene fraction behavior is usually conducted at small number of *P-T* points. Thermodynamic models of asphaltene precipitation attempt to obtain accurate match of the model calculations with experimental data and then to give a valid estimation of parameters of interest at a wider selection of pressure, temperature, and composition [2]. One of the main parameters of interest is the asphaltene precipitation onset, which is a point at a phase diagram at which asphaltenes start to split from crude oil. Another parameter of interest that thermodynamic models try to evaluate is the amount of asphaltene fraction that is precipitated from a crude oil at certain *P-T* conditions. Since thermodynamic models perform calculations only at equilibrium conditions, the results of such models are usually further implemented in flow simulators to account for kinetics and dynamics of precipitation. Asphaltene thermodynamic modeling approaches can be roughly divided into two main categories: the colloidal approach and the solubility approach [12–14].

The colloidal approach considers asphaltenes as solids in the crude oil system, which are stabilized by the presence of resins. Leontaritis and Mansoori [15] in their thermodynamic "colloidal" model, considered layers of resins around a solid asphaltene core which act as stabilizers or natural dispersants. Asphaltene precipitation occurs when the volume of resins covering the asphaltene cores is less than a critical threshold necessary for asphaltene fraction stability in solution. Vic-

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torov and Firoozabadi [16] proposed the thermodynamic micellization model that considers asphaltene molecules as micelles with resins residing on the shells. Later, the micellization model was modified by Pan and Firoozabadi [17,18] by modeling precipitation as liquid–liquid equilibrium and assuming the incipient phase to consist only of resins and asphaltenes.

In solubility approach, asphaltenes are considered as particles dissolved in the crude oil and the interactions between them and other crude oil fractions are driven by dispersion forces and not polar interactions [13]. Asphaltenes will start to precipitate when their solubility in the crude oil decreases below the threshold value. The solubility models can be divided into two distinctive categories: solubility theories and the EoS-based approaches [12,13]. The solubility theories consider the bulk phase of the crude oil as one pseudo-component and the system is considered as a binary mixture of crude oil and asphaltenes (i.e., Regular solution theory models [19–26], and Flory-Huggins-Zuo model [27–30]). In contrast, the EoS-based approaches treat the bulk phase as a mixtures of pure and pseudo-components.

The cubic EoSs are widely used in petroleum industry because of their simplicity [13]. This family of EoSs are originated from the van der Waals EoS and require critical temperature (T_c), critical pressure (P_c), and acentric factor (ω) for each component as input parameters [13,31]. The most widely used Cubic EoSs with application to asphaltene modeling are Soave-Redlich-Kwong (SRK) EoS [32,33] and Peng-Robinson (PR) EoS [34]. These two EoSs have demonstrated good results in phase behavior modeling of nonpolar gases. However, it was noted that SRK EoS struggles to accurately model phase behavior of liquid systems that contain components with complex molecular structure, such as asphaltenes or resins [35]. To overcome this shortcoming, Peneloux introduced a correction [36] to the SRK EoS. Both EoSs were implemented for asphaltene precipitation modeling in a number of studies [37–39]. It was noted, however, that the SRK model can sometimes struggle to accurately model systems of complex chemicals such as asphaltenes [13]. Moreover, the obtaining critical properties is problematic for asphaltenes as this fraction disappears before reaching the critical conditions [35]. The cubic-plus-association (CPA) EoS is another type of thermodynamic model that uses cubic EoS (typically SRK EoS) for description of dispersive and repulsive interactions and combines it with association term based on the Wertheim's perturbation theory [40]. In addition to three parameters for the cubic EoSs mentioned above, the CPA requires an additional two parameters to account for association. This type of EoS was successfully implemented for asphaltene phase behavior modeling in several studies [41–47].

The Statistical Associating Fluid Theory (SAFT) is a non-cubic EoS based on the Wertheim's first-order perturbation theory to increase the accuracy of the modeling of the phase equilibria for strongly polar/associating fluids [48–50]. The associative behavior of molecules has a profound effect on phase behavior of mixtures because the associating clusters have different molecular properties as compared to their monomers [49]. These deviations, if unaccounted, can cause profound errors in fluid properties estimation [49]. Several modifications were developed to improve the original SAFT including the Perturbed-Chain SAFT (PC-SAFT) EoS [51]. The PC-SAFT remains the most popular choice among the SAFT-based family of EoSs for modeling the asphaltene precipitation behavior. It has demonstrated excellent abilities throughout two decades of practice. The asphaltene modeling can be conducted with association (WA) or without association (WOA) term. A schematic of modeling approaches is shown in Fig. 1.

The PC-SAFT was first used by Ting et al. [52,53] for asphaltene phase behavior modeling where they described the crude oil characterization procedure based on results of SARA analysis. They also developed several correlations for the PC-SAFT EoS parameter estimation procedure. In their study, the associative interactions of molecules were ignored based on the assumption that asphaltene precipitation is mostly governed by dispersive interactions such as London dispersion forces. This method was later improved by Gonzalez et al. [54–57] and Panuganti et al. [35,58] showed ability of the PC-SAFT asphaltene modeling under various conditions such as gas injection, oil-based mud (OBM) contamination, and polydisperse asphaltene modeling. The PC-SAFT was also used to evaluate reservoir compartmentalization by modeling asphaltene compositional grading and tar mat formation [59]. Punnapala and Vargas [60] presented new correlations for EoS parameter evaluations and modified the procedure by reducing the number of fitting parameters. Tavakkoli et al. [61,62] investigated the effect of asphaltene polydispersity on modeling accuracy and concluded that asphaltene precipitation amount can be more accurately modeled considering asphaltenes as a polydisperse entities. Arya et al. [41] demonstrated that the modeling accuracy can be greatly improved by including the association behavior between the asphaltenes and crude oil components. Several authors conducted modeling by representing the asphaltenes as a solid phase and applying the PC-SAFT for equilibrium calculations of liquid and gas phases [63–65]. The PC-SAFT EoS was used in series of studies for thermodynamic phase behavior calculations as a part of asphaltene deposition simulators [66–71].

In this paper, we provide a comprehensive, systematic, and yet critical review of the current state of research considering asphaltene phase behavior modeling using the PC-SAFT EoS including the most recent developments. First, a short background on SAFT EoS and its modifications is given followed with a description of the existing modeling procedures with a focus on SARA-based models. The effect of temperature–

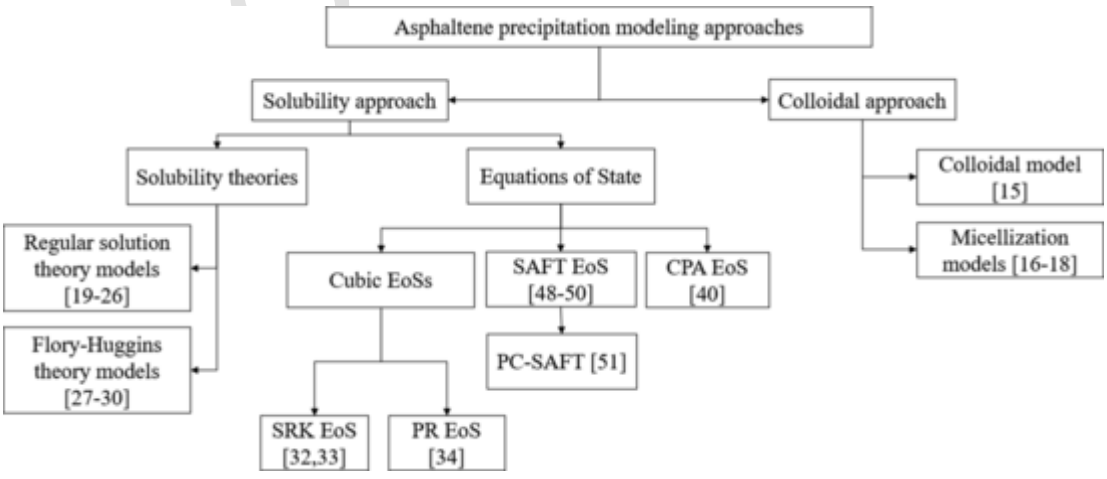

Fig. 1. Generalized schematic of asphaltene precipitation modeling approaches.

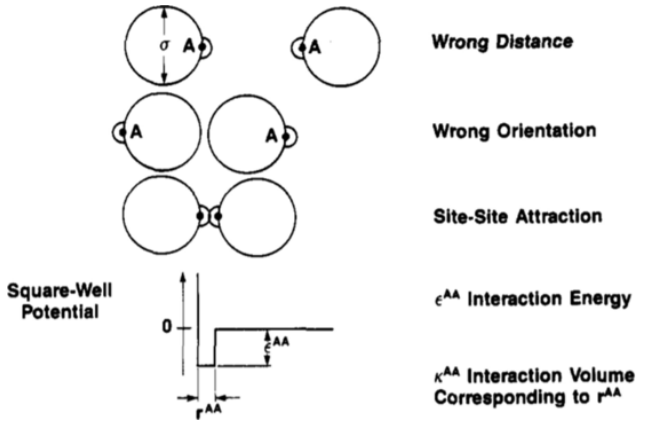

Fig. 2. Square-well potential associative interactions of hard spheres. Reprinted with permission from Chapman et al. [49], Copyright © 1990, American Chemical Society.

pressure changes on accuracy of the PC-SAFT models is discussed, as well. We provide a summary of available methods in the literature that deal with *P-T* related deviations of the PC-SAFT models. Then, we review the effect of compositional changes due to miscible gas injection, oil-based mud contamination, and presence of paraffin wax precipitation problems. We highlight the inclusion of asphaltene polydispersity and association behavior in the PC-SAFT models. Binary interaction parameters and their role in model fitting are also discussed and approaches to generate these parameters are analyzed. We summarize research works that compare the PC-SAFT performance with other EoS in asphaltene phase behavior modeling. To conclude, some recommendations and future perspectives of the PC-SAFT asphaltene phase behavior modeling are provided with some main conclusions.

2. Statistical associating fluid theory (SAFT) EoS

The SAFT EoS is presented in terms of the contribution of different terms to total residual Helmholtz free energy of the system. The residual Helmholtz energy is a characterization of intermolecular forces as the molecules of ideal gases exert no such forces on each other. Alternatively, the EoS can be presented in terms of compressibility factor (Z). SAFT considers a reference fluid consisting of hard-spheres that have only repulsive forces between each other. This reference fluid is assumed to roughly describe the behavior of a fluid of interest; the model is then corrected by perturbations to account for other intermolecular interactions [49]:

$$a^{res} = a^{seg} + a^{chain} + a^{assoc} \tag{1}$$

where a^{res} is the total residual Helmholtz energy per mole of molecules, a^{seg}represents the contribution of the segment formation, $a^{chain}$is for the covalently bonded chain formation, and the term $a^{assoc}$is to account for the associative interactions. The full formulations of SAFT EoS can be found elsewhere [48–50].

Chapman et al. [49] modeled the fluids as a mixture of LJ spheres. This version is sometimes referred to as "SAFT-0" or "original SAFT". A reference fluid is a mixture of hard-spheres for which its contribution to total Helmholtz free energy is given by (a^{hs}), accounting for the repulsive forces. The first perturbation (a^{disp}) adds attractive interactions that exist between the segments. Chapman et al. [49] suggested that the hard-sphere reference contribution to the Helmholtz free energy (a^{hs}) can be expressed by equations of Carnahan et al. [72]. Furthermore, the dispersion term (a^{disp}) for Lennard-Jones spheres can be calculated using correlations from Cotterman et al. [73] for dense fluids. The effect of temperature on segment diameter is accounted by using Barker and Henderson [74] theory and Cotterman et al.[73] formulation (f_{CT}), through the Lennard-Jones potential by introducing temperature-dependent segment diameter ($d(T)$). The other two perturbations to the Helmholtz free energy are aimed to increase the accuracy of model compared to a fluid consisting of only spherical segments. The equations are originally shown for pure components; a mixing rule is required to use them for mixtures. SAFT-0 uses the van der Waals one fluid theory (so-called, one-fluid rule). Most of the modifications follow the same rule, except for the VR-SAFT [75,76].

The perturbation (a^{chain}) accounts for the chain formation from equal size segments. The chain molecules with m number of segments form by the covalent bonding. The chain energy term for mixtures is estimated from hard-sphere radial distribution function $g^{hs}(d)$. The radial distribution function is used in the calculation of both chain and association terms. It is the probability of like (subscript ii – for chain term) or unlike (subscript ij – for association term) segments to be located at a defined distance (d) from each other in a given system [77]. Any assumptions made in the estimation of the probability distribution function have a profound effect on the accuracy of modeling; it is one of the elements of the model that is altered in various formulations of the SAFT EoS [77,78]. The association bonds act at short distances which strongly depend on the number and orientation of the association sites on the associating molecules. The association term (a^{assoc}) represents the contribution to Helmholtz energy from such bonds.

Three SAFT parameters are necessary for each pure component to describe a non-associating fluid, namely: temperature-independent segment diameter (σ), the number of segments per molecule (m), and segment-segment interaction energy ($\in/k_{BT}$).

2.1. Variations of the SAFT EoS

Wertheim's first order perturbation theory that is implemented in SAFT EoS considers energy change due to the bonding of two molecules and does not account for the presence of other molecules [79]. This assumption leads to a series of approximations in SAFT modeling [48,49]: the angle between different bonding sites in one molecule is not considered (i.e., the properties of the fluid will be independent of the angle between sites). Each of bonding sites form bonds independently without interference from other sites on the same molecule. In case one site on a molecule forms a bond with a site on an adjacent molecule, then any other molecules cannot bond to these sites and will be repelled (Fig. 3-a). One site cannot bond to two sites at the same time (Fig. 3-b). Moreover, in this model framework, the formation of double bonds is not possible (Fig. 3-c). A consequence of such limitation is that the model cannot recognize isomers and other configurations of the chain molecules and treat them all the same. Furthermore, no ring-like clusters can be formed. These and other limitations are addressed in numerous modifications of the original SAFT EoS, the most notable ones of which are listed in Table 1.

2.2. pC-SAFT

The PC-SAFT EoS was developed by Gross and Sadowski [51]. Unlike the other modifications, the reference fluid in PC-SAFT is a chain fluid for which the repulsive hard-spheres form covalently bonded chains; dispersion forces are then added at a chain level. Thus, the perturbation applied to account for the attractive interactions is a function of the chain length (m). The EoS is presented as follows [51,100]:

$$a^{res} = a^{hc} + a^{disp} + a^{assoc} \tag{2}$$

$$\frac{a^{hc}}{RT} = \left(\frac{a^{hs}_{o}}{RT}\right)\sum_i X_i m_i + \frac{a^{assoc}}{RT} \tag{3}$$

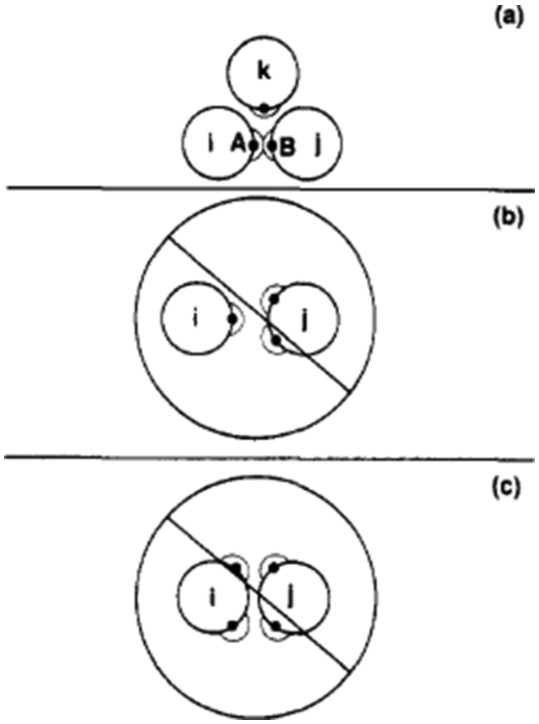

Fig. 3. The SAFT EoS model approximations. Reprinted with permission from Chapman et al. [49]. Copyright © 1990, American Chemical Society.

Table 1
Chronological variations of the SAFT EoS.

Variation	Year	Remarks	Ref.
SAFT	1988	• Sometimes referred to as original SAFT or SAFT-0	[48–50]
CK-SAFT	1991	• Also sometimes referred to as original SAFT. • Dispersion term obtained from Chen and Kreglewski [80]	[81,82]
LJ-SAFT	1992	• Lennard-Jones spheres used as a reference fluid	[83–88]
Simplified SAFT	1995	• Dispersion equation in CK-SAFT is replaced by that from Lee et al. [89] equation.	[90]
BACK-SAFT	1998	• BACK EoS [80] and SAFT EoS are integrated for improved modeling of near-critical regions.	[91]
Soft-SAFT	1997	• The modification based on the work of Johnson et al. [86]. • Repulsive and dispersive interactions are described through Lennard-Jones potential.	[92,93]
VR-SAFT	1997	• Different types of intermolecular potentials (i.e., LJ, Square-Well) are allowed. • The parameter λcan control the shape of these intermolecular forces.	[75,76,94–98
PC-SAFT	2001	• Perturbation added to account for attractive interactions are applied to hard chain molecules. • They correlate to the chain length (m)	[51]
SimplifiedPC-SAFT	2003	• Simplifications applied for T-dependent diameter and hard-sphere terms.	[99]

$$\frac{a^{assoc}}{RT} = \sum_i X_i(1-m_i)\ln g_{ii}\left(d_{ii}\right) \tag{4}$$

$$\left(\frac{a_o^{hs}}{RT}\right) = \frac{1}{\zeta_0}\left[\frac{3\zeta_1\zeta_2}{\left(1-\zeta_3\right)} + \frac{\zeta_2^3}{\zeta_3\left(1-\zeta_3\right)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0\right)\ln\left(1-\zeta_3\right)\right] \tag{5}$$

The temperature-dependent segment diameter (d) is defined through the Square -Well potential model by Chen and Kreglewski [80] as follows:

$$d_{ii} = \sigma_i\left[1 - 0.12\exp\left(-\frac{3\epsilon_{ii}}{k_{BT}T}\right)\right] \tag{6}$$

The dispersion term is expressed through Barker and Henderson's [74] second-order theory for chain molecules. It is extended for mixtures, using the one-fluid rule. PC-SAFT calculates the density of a mixture iteratively by adjusting η until the calculated pressure matches the system pressure. The Newton-Raphson iteration algorithm is used for this purpose [51]. An initial guess is required to initiate the process. Gross and Sadowski [51] suggested to use $\eta = 0.5$for liquids and $\eta = 10^{-10}$ for gases. The calculated density is then used for the calculation of Helmholtz energy terms and fugacity coefficients. The flowchart of PC-SAFT algorithm can be seen in Fig. 4. Thermodynamic algorithms, such as flash calculations, use fugacity coefficients that are calculated by the EoS to perform equilibrium calculations. The fugacity coefficient calculation algorithm and details about the PC-SAFT formulation are available in the paper by Gross and Sadowski [51].

The PC-SAFT EoS was successfully applied for various purposes such as to model phase behavior of pure components, binary and ternary polymer systems [102], and hydrocarbon systems. The limitations of the EoS were noted regarding aqueous systems [78]. Regarding asphaltenes, it was noted [103] that different versions of the SAFT EoS are expected to give comparable results because of the same basic principles. However, the PC-SAFT remains the most applied version to model asphaltene precipitation in the literature due to its presence in thermodynamic software such as Multiflash, VLXE, and PVTSim [78,103].

2.2.1. Simplified PC-SAFT EoS (sPC-SAFT)

Von Solms et al. [99] simplified the original PC-SAFT by introducing two modifications: one to the temperature dependent segment diameter (d) and another one to the hard-sphere term (a^{hs}) to achieve a similar accuracy at a lower computational burden compared to the original PC-SAFT EoS. A significant reduction in the computational time was achieved, with sPC-SAFT, especially for the associating mixtures. The temperature dependent segment diameter (d) is simplified in this model by assuming that all segments in the mixture have the same average diameter [99]. It is also assumed that the reduced density of the mixture calculated with simplified diameter will equal to the actual reduced density of the mixture. These two assumptions applied to sPC-SAFT EoS are expressed in Eqs. (7) and (8).

$$\eta \equiv \zeta_3, \text{where} \eta = \pi d^3/6 \tag{7}$$

$$d = \left(\frac{\sum_i X_i m_i d_i^3}{\sum_i X_i m_i}\right)^{1/3} \tag{8}$$

The usage of a new diameter simplifies the expression for the radial distribution function:

$$g^{hs}(d) = \frac{1-\eta/2}{(1-\eta)^3} \tag{9}$$

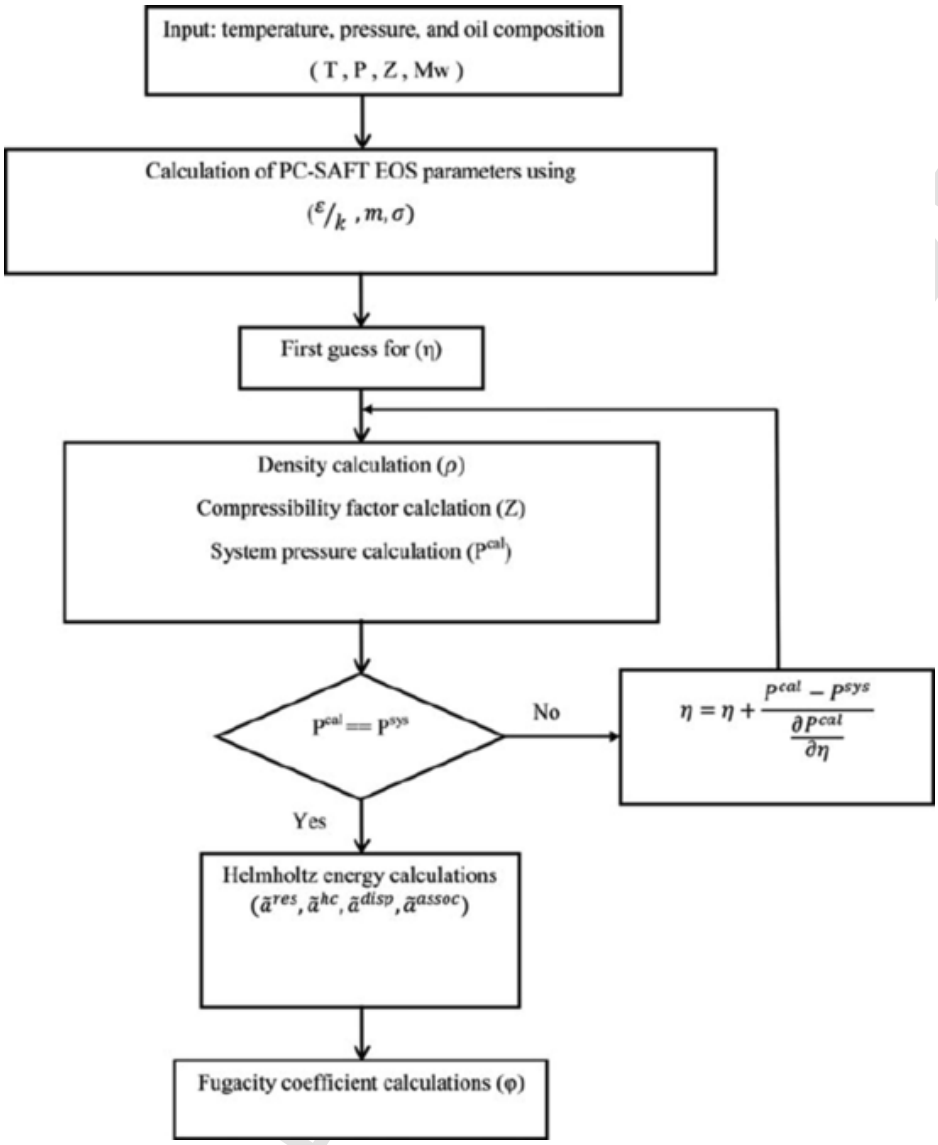

Fig 4. Flowchart of PC-SAFT calculations. Reprinted with permission from Assaf et al. [101], Taylor & Francis Ltd. http://www.tandfonline.com.

The second modification puts the simplified diameter into the expression for the hard-sphere energy term (a^{hs}):

$$\left(\frac{a_o^{hs}}{RT}\right) = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \tag{10}$$

3. Implementation of the PC-SAFT EoS for asphaltene phase behavior modeling

As it was mentioned before, the PC-SAFT EoS is the most widely used variation of the SAFT EoS. It requires three non-associating parameters and two associating parameters in the framework of SAFT EoS. Because a crude oil is a complex mixture, it is computationally expensive to consider all components, individually. Instead, in the thermodynamic modeling, various components with a similar characteristic are lumped into a few pseudo-components. The following sections describes existing crude characterization methods. The list of works that are applying the PC-SAFT in asphaltene phase behavior modeling are presented in Table 2.

The general assumptions for the asphaltene precipitation modeling using PC-SAFT were firstly formulated by Ting [52]:

- The crude oil is a non-associating system (the association term is ignored). Some of researchers later included the association term into the modeling (see section 4.4).
- Asphaltene phase exists in crude in the form of nanoaggregates.
- Asphaltene precipitation is governed by Wan der Waals forces (particularly, London dispersion forces) and the negligible effect of polar interactions.
- Asphaltene precipitation is a thermodynamically reversible process.
- Precipitation is modeled either as liquid–liquid equilibrium (LLE) or vapor–liquid–liquid equilibrium (VLLE), where one of the liquid phases represent the asphaltene rich dense phase. In contrast, there is a group of researchers that have assumed asphaltenes as a solid phase and modeled phase behavior of vapor/liquid phases using PC-SAFT (see section 4.8).

3.1. The SARA-based method

The most widely used method of crude oil characterization for PC-SAFT asphaltene precipitation modeling is the procedure that was first introduced by Ting et al. [52,53] and later modified by various re-

Table 2
The PC-SAFT EoS asphaltene phase behavior modeling works in the literature.

Ref.	PC-SAFT model					Fluid(s)	Remarks
	Objective	Phase equilibrium model	Association term	Polydispersity	Crude oil characterization method		
[53]	Calculations of asphaltene stability boundaries and densities of crude oil	VLLE [1]	WOA [2]	MD [3]	SARA-based method	Model oil (toluene + asph. + C1) and live oil	• Introduction of the SARA-based method
[55]	The study of asphaltene precipitation under gas injection (methane, ethane, N_2, CO_2)	VLLE	WOA	MD	SARA-based method	Model oil (toluene + asph. + C1) [53], and live oil [106]	• Adequacy of modeling under gas injection was demonstrated • C_1 and N_2 are strong asphaltene precipitants
[56]	The study of the effect of OBM contamination and compositional change due to gas addition	VLLE	WOA	MD	SARA-based method	2 deep water reservoir fluids ("A" and "B"), Saudi Arabian crude (fluid "C" [107])	• Oil-based mud contamination showed to a decrease onset and bubble point pressure due to decrease in GOR • Largest in MW asphaltenes will precipitate first
[54]	Investigation of the effect of CO_2 presence on asphaltene precipitation	VLLE	WOA	MD	SARA-based method	Live oil [106], South American STO [108]and model oil [53]	• Modeled CO_2 injection can have a positive or negative effect on asphaltene stability depending on the certain temperature threshold
[109]	Modeling with PC-SAFT, solid model (with SRK EoS), and Flory-Huggins theory	VLLE	WOA	MD	SARA-based method	Iranian crude oil sample	• PC-SAFT showed superior results compared to other models

Ref.	PC-SAFT model					Fluid(s)	Remarks
	Objective	Phase equilibrium model	Association term	Polydispersity	Crude oil characterization method		
[42]	Comparative study between PC-SAFT and CPA EoS	VLLE	WOA	MD	SARA-based method	6 live oils of different origin [106,110,111]	• Temperature dependent deviations from experimental data were demonstrated by PC-SAFT models • CPA gave generally better results than PC-SAFT models
[59]	Isothermal asphaltene compositional grading and tar mat modeling	VLLE	WOA	MD	SARA-based method	Two crude oil samples	• Successful modeling of tar mat formation using PC-SAFT
[35]	The development of improved crude oil characterization methodology. Comparison with the SRK-P EoS	VLLE	WOA	MD	SARA-based method	3 Middle Eastern crudes	• PC-SAFT showed superior results compared to SRK-P EoS
[60]	The improvement of the SARA-based characterization method. Modeling of gas injection	VLLE	WOA	MD	SARA-based method	5 crude samples from Abu Dhabi fields	• New correlations for PC-SAFT parameters. The number of tuning parameters is reduced from 3 to 2

[112]	Modeling of AOPs and precipitation amounts using monophasic oil composition	VLLE	WOA	MD	SARA-based method	3 live oils from literature [106,113,114]
[115]	Modeling with PC-SAFT and SRK-P EoSs	N/A	WOA	MD	Pedersen's method [116]	Recombined Gulf of Mexic (Tahiti) oil

Ref.	PC-SAFT model					Fluid(s)	Remarks
	Objective	Phase equilibrium model	Association term	Polydispersity	Crude oil characterization method		
[62]	Modeling of polydisperse behavior, comparison with monodisperse modeling	VLLE	WOA	PD	SARA-based method	Lagrave oil and Iranian oil [26], 4 heavy oils and bitumens [37] from Canada, Venezuela, Russia and Indonesia	• Sensitivity analysis of aromaticity and MW • 3 asphaltene sub-fractions • Polydisperse modeling showed a more gradual increase in precipitation in comparison with monodisperse modeling
[117]	Polydisperse modeling of heavy oils and bitumens	VLLE	WOA	PD	Zúniga-Hinojosa et al. [117]	7 heavy oils and bitumens from the literature [37]	• Asphaltene fraction was divided into 30 sub-fractions • The gamma distribution function is applied • New correlations for Asphaltene sub-fraction parameters
[118]	Modeling the effect of non-ionic dispersant using Molecular Dynamics simulation and PC-SAFT EoS	VLLE	WA	MD	Sedghi and Goual [118]	1 model oil; 3 live crudes from the literature [60]	• Octylphenol (dispersant) addition to asphaltene-toluene mixture at ambient conditions • Remodeling of three crudes from Punnapala and Vargas [60] at HPHT conditions

[45]	Comparison with CPA EoS, modeling of PVT parameters	VLLE	WOA	MD	SARA-based method	PC-SAFT modeled crude o Panuganti et al.[35]

Ref.	PC-SAFT model					Fluid(s)	Remarks
	Objective	Phase equilibrium model	Association term	Polydispersity	Crude oil characterization method		
[41]	Modeling with the association term and comparison with CPA EoS	VLLE	WA	MD	Arya et al. [41]	5 crudes from the literature [35,106,110,119,120] and 1 model oil	• The inclusion of the association term improved the accuracy of PC-SAFT models • CPA generally gave more accurate results • The PC-SAFT models can be unreliable outside the experimental temperature range
[61]	Polydisperse modeling using the improved methodology	VLLE	WOA	PD	SARA-based method	Middle Eastern light crude	• The "indirect method" of onset detection was used to cope with the limitations of conventional experimental techniques • 3 fitting parameters for asphaltenes • 4 subfractions, the gamma distribution function is applied

Ref.	PC-SAFT model					Fluid(s)	Remarks
	Objective	Phase equilibrium model	Association term	Polydispersity	Crude oil characterization method		
[121]	Modeling of crude oil mixed with aromatic solvents at reservoir conditions	VLLE	WOA	MD	SARA-based method	1 live oil sample	• PC-SAFT and PR EoS (with Peneloux correction) were applied • PC-SAFT demonstrated reasonable calculations of AOPs and the amount of asphaltene precipitated, while the performance of PR-P EoS deteriorated at higher concentrations of aromatic solvents
[101]	Modeling the effect of DBSA dispersant	LLE	WOA	MD	SARA-based method	Iranian dead oil sample	• Average error of the model is 14% • Asphaltene dispersants have a certain critical concentration below which they are not effective. The PC-SAFT has been able to capture this trend

[122]	Comparison between the PC-SAFT and the PR EoSs	VLLE	WOA	MD	SARA-based method	1 Middle Eastern crude [3 1 crude under the lean ga injection.

Ref.	PC-SAFT model					Fluid(s)	Remarks
	Objective	Phase equilibrium model	Association term	Polydispersity	Crude oil characterization method		
[123]	Modeling of precipitation under the gas injection with dynamic reservoir simulation	VLLE	WOA	MD	SARA-based method	2 characterized live oils from the literature [35,54]	• 25–40% improvement of computational speed by the improved root finding algorithm • PC-SAFT is 1.5–2.1 times slower than PR EoS
[124]	Modeling of a polystyrene-asphaltene-toluene mixture	LLE	WOA	MD	AlHammadi and Chapman [124]	Polystyrene-asphaltene-toluene mixture	• The single BIP between asphaltenes and polystyrene was fitted to experimental data • Three SAFT parameters of each component were taken from the literature
[125]	Modeling of asphaltene phase behavior and PVT parameters with one fitting parameter (γ_{Asph})	VLLE	WOA	MD	SARA-based method	8 Abu Dhabi offshore and onshore crude oils	• MW_{Asph} and γ_{A+R} are kept constant
[65]	Modeling with the application of multi solid approach using PC-SAFT and PR EoSs	Solid	WOA	MD + PD	Dehaghani et al. [65]	Two Iranian crudes [126]	• PC-SAFT showed higher accuracy than PR EoS and VR-SAFT EoS models • Polydisperse modeling decreased deviations of models
[127]	The algorithm for generating complete *P-T* and *P-x* diagrams of asphaltenic crude oils	VLLE	WOA	MD	SARA-based method	3 crudes from the literature [35,126,128]	• Complete *P-T* and *P-x* diagrams was constructed using PC-SAFT, CPA and SRK-P EoSs

Ref.	PC-SAFT model					Fluid(s)	Remarks
	Objective	Phase equilibrium model	Association term	Polydispersity	Crude oil characterization method		
[104]	The modification of the SARA-based method to account for the low temperature deviations	VLLE	WOA	MD	SARA-based method	6 crudes from the Middle East and the Gulf of Mexico [104,110]	• The improvement was achieved in the modeling of crudes with atypical low temperature behavior
[43]	Comparative study between the PC-SAFT and CPA EoS.	VLLE	WA	MD	Arya et al. [41]	8 live oils from the literature [44,106,111,114,120,126]	• PC-SAFT models were better than CPA EoS and was stated to be more reliable outside the experimental range
[129]	Modeling of a Brazilian crude using n-C_7 and n-C_6 as precipitating agents	VLLE	WOA	MD	SARA-based method	Brazilian crude oil and a model oil (asph. + toluene)	• Mean relative errors of 3.75% and 10.25% for n-C_6 and n-C_7 cases respectively.
[130]	Asphaltene-wax precipitation modeling using the simplified PC-SAFT EoS	VLLLE [4]	WOA	MD	Xue et al. [130]	2 North Sea blends 3 pipeline dead oils	• BIP correlations for 12 binary n-alkane systems
[131]	The theoretical modification of the dispersion term to account for low temperature deviations	VLLE	WOA	MD	SARA-based method	9 crudes of different origin	• The U-AOP curve is smoothened in comparison with the original PC-SAFT models. The match to the experimental data demonstrated smaller deviations than the original PC-SAFT EoS

Ref.	PC-SAFT model					Fluid(s)	Remarks
	Objective	Phase equilibrium model	Association term	Polydispersity	Crude oil characterization method		
[132]	A modification of PC-SAFT through the linear extrapolation of normalized cohesive energy as a function of temperature along U-AOP line to account for atypical temperature behaviors	VLLE	WOA	MD	SARA-based method The LENCE model	6 crudes from the literature	• It was possible to model both atypical temperature behaviors • At least two U-AOPs are necessary to fit the model • The computational time has been decreased 5 times in comparison with regular PC-SAFT modeling
[133]	Polydisperse modeling using five asphaltene sub-fractions and gamma distribution function	VLLE	WOA	PD	SARA-based method	Deepwater reservoir crude oil sample	• Asphaltenes were represented by four asphaltene and one resin sub-fractions • Monodisperse modeling lead to the overestimation of the amount of asphaltene precipitated
[134]	The development of the new algorithm for VLLE calculations	VLLE	WOA	MD	SARA-based method	6 modeled crudes from the literature	• A four-fold improvement in computing speed has been achieved • Gas injection modeling showed lesser accuracy in comparison with models from the literature

Ref.	PC-SAFT model					Fluid(s)	Remarks
	Objective	Phase equilibrium model	Association term	Polydispersity	Crude oil characterization method		
[64]	Modeling with the application of solid solution approach using PC-SAFT and PR EoSs	Solid	WOA	MD + PD	Dehaghani et al. [65]	Two Iranian crudes [126]	• Solid solution approach improved models in terms of accuracy • This approach requires more tuning parameters than the multi solid approach
[135]	Comparison between PC-SAFT, CPA, modified and original Flory-Huggins models and solid model (with SRK EoS)	VLLE	WA	MD	Arya et al. [41]	12 crudes from the literature	• PC-SAFT showed the least deviation but the highest CPU time for modeling
[136]	The modification of a temperature-dependent density (d) to account for low temperature deviations	VLLE	WOA	MD	SARA-based method	6 crudes of different origin (5 from the literature)	• The substantially lower U-AOP values has been calculated in comparison with the original PC-SAFT EoS

[137]	Modeling of the effect of dead oil reinjection on asphaltene deposition	VLLE	WOA	MD	SARA-based method	3 Middle Eastern crudes [13,60,138] 1 crude from Gulf of Mexi

Ref.	PC-SAFT model					Fluid(s)	Remarks
	Objective	Phase equilibrium model	Association term	Polydispersity	Crude oil characterization method		
[139]	Experimental studies of wax inhibitors. Modeling of AOPs of a crude with different concentrations of paraffin wax and gas injection	VLLE	WOA	PD	SARA-based method	North Sea crude oil	• Increasing wax content had a positive effect on asphaltene stability both in experimental and modeling studies • The relative error in estimating U-AOPs ranged from 1.52% to 5.87%. Error increased with increased wax content
[39]	Modeling of U-AOP with PR EoS using new characterization method. A comparison with PC-SAFT EoS	VLLE	WOA	MD	SARA-based method	6 crudes from the literature 4 new Middle Eastern crudes	• The PR EoS modeling with a new characterization method showed comparable results with PC-SAFT

[140]	Modeling with modified temperature-dependent diameter [136] and the new set of PC-SAFT universal constants [141]	VLLE	WOA	MD	SARA-based method	6 crudes from the literatu

Ref.	PC-SAFT model					Fluid(s)	Remarks
	Objective	Phase equilibrium model	Association term	Polydispersity	Crude oil characterization method		
[105]	Modified algorithm for the estimation of asphaltene PC-SAFT parameters with the Trust-Region based optimization method	VLLE	WOA	MD	SARA-based method	3 crudes from the literature [35,60,106] and one new southwesternIranian crude oil	• A simplified procedure was developed for the estimation of PC-SAFT parameters of asphaltene pseudo-component • Algorithm was validated using three already modeled crudes from the literature

[1] VLLE/Solid– Asphaltene precipitation is modeled as the liquid–liquid (or vapor liquid–liquid below BP and before L-AOP) equilibrium, where one of the liquid phases is the asphaltene-rich dense phase/asphaltenes are represented as solids, and other phases are liquid oil and vapor hydrocarbon gases which are described by an EoS.
[2] WOA/WA – The PC-SAFT model without/with the association term.
[3] MD/PD – Monodisperse/polydisperse modeling (asphaltene fraction represented by one/several pseudo-component(s)).
[4] Liquid phases: Asphaltene-rich and wax-rich phases and bulk crude oil phase

searchers [35,54–57,60–62,104,105]. This method discriminates the stock tank oil (STO) components into four distinct groups including saturates, aromatics, resins, and asphaltenes according to SARA analysis results. The method is referred to as the "SARA-based method" in this text.

The SARA-based method lumps most components of flashed gas and STO into several pseudo-components while treating some of the com-

pounds as pure components. The method then combines these pseudo- and pure components to form a reservoir fluid with a similar GOR value. Then, the values of PC-SAFT parameters are evaluated for all components of the recombined fluid.

Ting et al. [53] and Gonzalez et al. [54–56] characterized flashed gas with C_1, the joint H_2S/CO_2 component, N_2, and with one light alkane pseudo-component for hydrocarbon gas fractions heavier than C_1 (C_{2+}). The concentration of light components has a significant effect on the precipitation behavior of asphaltene from crude oil, because these light components are usually poor solvents for the asphaltene. For this reason, the gas fractions were later recommended treat by representing all impurities such as N_2, CO_2, H_2S, and also by increasing the number of light hydrocarbon pure components (C_1, C_2, C_3) [58]. Only one pseudo-component for hydrocarbon gas fractions heavier than C_3 (C_{4+}) is applied [58].

Saturates are modeled with a single pseudo-component assuming that the entire pseudo-component consists of only *n*-alkanes. Aromatic and resin fractions of SARA analysis are usually combined into one pseudo-component (A + R). However, modeling these fractions separately by using two pseudo-components (resins and aromatics) is also possible [131,136]. Asphaltenes are modeled either by using one pseudo-component (monodisperse modeling) or by several pseudo-components (polydisperse modeling approach) [13].

All above-mentioned pure and pseudo-components are recombined by changing their molar fractions to be consistent with GOR values between flashed gas and STO. As the next step, the PC-SAFT parameters should be estimated for each of the components. As mentioned earlier, the PC-SAFT parameters for the non-associating molecules are the temperature-independent segment diameter (σ), the number of segments per molecule (m), and segment-segment interaction energy (ϵ/k_{BT}) [51]. Parameters can be acquired by applying various correlations, based on the molecular weight of pseudo-components or well-established values (for pure components). Parameters for C_1, C_2, C_3, and impurities such as CO_2 and N_2 are well established and can be found in the original PC-SAFT work reported by Gross and Sadowski (Table 3) [51].

Three PC-SAFT parameters have the following features: 1) the parameters for saturates and aromatics correlate linearly with their molecular weight [51–53]; and 2) parameters of components with aromatic rings and aliphatic chains such as resins and asphaltenes are in the region between parameters of *n*-alkanes and aromatics [52,57]. These two observations led to the development of several correlations that are used in the literature to calculate values of PC-SAFT parameters for non-associating pseudo-components. These correlations, as well as correlations implemented by some other characterization methods, are presented in Table 5 with corresponding references and descriptions. The parameter evaluation procedure for non-associating components and monodisperse asphaltene modeling is as follows [35,52,57,60]:

Pure components – The parameters are obtained from the literature [51].

C_{4+} and Saturates – Both pseudo-components are assumed to consist of only *n*-alkanes. Parameters are calculated using correlations for the saturates.

Table 3
The constant SAFT parameters for pure components [51].

Components	MW (g/mol)	m	σ (Å)	ϵ/k_{BT} (K)
N_2	28.01	1.205	3.313	90.96
CO_2	44.01	2.073	2.785	169.21
C_1	16.04	1	3.704	150.03
C_2	30.07	1.607	3.521	191.42
C_3	44.1	2.002	3.618	208.11

Aromatics + Resins (A + R) – Since this pseudo-component can consist of both aliphatic and aromatic components, parameters are estimated using appropriate correlations from Table 4 by adjusting the aromaticity parameter (γ_{A+R}) in the range from 0 to 1 until a minimal error is reached between the calculated values and the experimental data. The experimental bubble point pressures (BPs) and crude oil densities are the main choices for such tuning. The increase in the aromaticity parameter increases the crude oil density due to the increasing amount of polynuclear aromatic hydrocarbons (PNAs) while it decreases the bubble point value due to the higher volatility of the hydrocarbon gases [59]. The one unknown in this procedure is the aromaticity parameter (γ_{A+R}). During the A + R parameter tuning, asphaltene parameters are set in the range of reported values from the literature. Because the asphaltene concentration is usually low and because the light components control the BP estimations, the asphaltene parameters are expected to have a negligible effect on the BP calculations.

Asphaltenes – Ting et al. [52,53] directly adjusted three SAFT parameters by fitting them to three experimental data points of asphaltene precipitation onsets at constant asphaltene molecular weight of 1700 g/mol. A similar approach was followed by Gonzalez et al. [54–57]. Panuganti et al. [35,58] fitted the parameters to the asphaltene onset pressures (AOPs) for a number of crudes.

Punnapala and Vargas [60] suggested evaluating parameters using correlations as a function of aromaticity parameter (γ_{asph}) and the asphaltene pseudo-component molecular weight (MW_{Asph}). These two parameters must be iteratively changed until the minimal error between the calculated and the experimental AOPs is achieved. Two unknowns require a minimum of two experimental data points for model fitting. The recommended step size for MW_{Asph} and γ_{asph} is 25 g/mol and 0.005, respectively and search should be conducted until the global minimum is found [13]. This method requires changing the molar fraction distribution of the liquid pseudo-components at each step because of the changing MW_{Asph}. The major drawback of this method is time consumptiveness, as the search for a global error minimum can require performing calculations with a very large range of adjustable parameters.

Fouad et al. [125] modeled AOPs and BPs with a constant value of γ_{A+R} and MW_{Asph} for eight Abu Dhabi crudes. The only fitting parameter was γ_{asph}.

Recently, Masoudi et al. [105] suggested using the combination of saturates-benzenes-PNA correlations from Gonzalez [57]. They [105] use two fitting parameters, namely, saturation parameter (α_{Asph}) and aromaticity parameter (γ_{asph}) to tune the model, using Trust-Region based optimization algorithm. They modeled several crudes using the new method and received excellent results in terms of accuracy. Additionally, they [105] provided a detailed description of the characterization method and equilibrium calculation algorithms and a MATLAB code for Trust-Region based method.

3.2. Required input parameters

The list of experimental data that is required for the monodisperse asphaltene precipitation modeling by the SARA-based method as listed by Punnapala and Vargas [60]:

- Compositional analysis of flashed gas and STO for pseudo-component lumping
- Density and average molecular weight of STO for aromaticity tuning and pseudo-component lumping
- Gas-oil ratio (GOR) between STO and flashed gas for recombining flashed gas and liquid crude into reservoir fluid
- The SARA analysis for liquid phase pseudo-component lumping
- Several AOPs and BPs of live oil at different temperatures (and mol% of gas injected, if available) for model tuning and validation

Table 4
Correlations of PC-SAFT parameters for non-associating pseudo-components.

Ref.		Saturates		Aromatics + Resins (A + R)	Asphaltenes	Description
[52]	(11)	$m = 0.0253MW + 0.9263$	(12)	$m = \gamma\,(0.0201MW + 0.7860) + (1-\gamma)(0.0139MW + 1.2988)$	Asphaltene parameter range	Aromaticity parameter defined as follows: $\gamma = 1$ (PNA) $\gamma = 0$ (benzene, bi-phenyl, ter-phenyl) Asphaltene parameters fitted to experimental refractive indices at precipitation onsets. The initial guess is chosen such that parameters are in the region between *n*-alkanes and PNAs parameters correlations and the calculated solubility is in the range reported for asphaltenes (19-24 MPa $^{0.5}$)
	(13)	$m\sigma = 0.1037MW + 2.7985$	(14)	$m\sigma = \gamma\,(0.0782MW + 2.466) + (1-\gamma)(0.0597MW + 4.2015)$	For MW = 1700 g/mol: m− 25-35 σ− 3.389-4.239 ϵ/k_{BT}− 414.77-658.01	
	(15)	$\frac{\epsilon}{k_{BT}} = 32.81\ln(MW) + 80.398$	(16)	$\frac{\epsilon}{k_{BT}} = \gamma\,(40.65\ln(MW) + 112.4) + (1-\gamma)\,(119.41\ln(MW) - 230.21)$	For MW = 4000 g/mol: m− 56-80 σ− 3.902-4.271 ϵ/k_{BT}− 449.55-760.18	
[57]	(17)	$m = 0.0257MW + 0.8444$	(18)	$m = \gamma\,(0.0101MW + 1.7296) + (1-\gamma)(0.0223MW + 0.751)$	Asphaltene parameter range (for MW = 1700 g/mol):	Range of correlations for aromatics and resins was expanded (to include more benzene derivatives as compared to Ting [52] to more accurately calculate parameters for crudes with API gravity lower than 33 Asphaltene parameters fitted as previously
	(19)	$\sigma = 4.047 - \frac{4.8013\ln(MW)}{MW}$	(20)	$\sigma = \gamma\left(4.6169 - \frac{93.98}{MW}\right) + (1-\gamma)(4.1377 - \frac{38.1483}{MW})$		
	(21)	$\ln(\frac{\epsilon}{k_{BT}}) = 5.5769 - \frac{9.523}{MW}$	(22)	$\frac{\epsilon}{k_{BT}} = \gamma\left(508 - \frac{234100}{MW^{1.5}}\right) + (1-\gamma)(0.00436MW + 283.93)$	m− 19-39 σ−4.1-4.5 ϵ/k_{BT}− 296-504	
[60]		Correlations from Gonzalez [57]	(23)	$m = (1-\gamma)\,(0.0257MW + 0.8444) + \gamma(0.0101MW + 1.7296)$		Aromaticity parameter in A+R correlations was redefined as: $\gamma = 1$ (PNA) $\gamma = 0$ (Saturates) Asphaltene parameters are estimated using Eqs. 23-25 by tuning aromaticity (γ) and molecular weight (MW) of asphaltene pseudo-component to experimental onsets
			(24)	$\sigma = (1-\gamma)\left(4.047 - \frac{4.8013\ln(MW)}{MW}\right) + \gamma\left(4.6169 - \frac{93.98}{MW}\right)$		
			(25)	$\frac{\epsilon}{k_{BT}} = \gamma\left(508 - \frac{234100}{MW^{1.5}}\right) + (1-\gamma)\left(\exp\left(5.5769 - \frac{9.523}{MW}\right)\right)$		

Ref.	Saturates and Aromatics + Resins (A + R)		Asphaltenes	Description
[117]	Correlations from Gonzalez [57]	(26)	$m = 0.0257MW + 0.8444$	A+R parameters are estimated using correlations from Gonzalez [57] applying constant value of aromaticity (γ) Asphaltene parameters are estimated using developed correlations Model was fitted to the experimental data by altering BIPs between asphaltenes and *n*-alkanes
		(27)	$\sigma = 0.1097\ln(MW) + 3.3685$	
		(28)	$\frac{\epsilon}{k_{BT}} = 32.81\ln(MW) + 80.398$	
[105]	Correlations from Gonzalez [57]	(29)	$m = (1-\alpha-\gamma)\,(0.0253MW + 0.9263) + \gamma\,(0.0101MW + 1.7296) + \alpha\,(0.0257MW + 0.8444)$	α−Saturation parameter γ− Aromaticity parameter $(1-\alpha-\gamma)$− Benzene derivative The method uses combination of correlations from Gonzalez [57] to iteratively search parameters of asphaltenes in region between parameters of saturates, PNAs and benzene derivatives

	(30)	$\sigma = (1-\alpha-\gamma)\left(4.1377-\frac{38.1483}{\mathrm{MW}}\right) + \gamma\left(4.6169-\frac{93.98}{\mathrm{MW}}\right)+\alpha\left(4.047-\frac{4.8013\ln(\mathrm{MW})}{\mathrm{MW}}\right)$	
	(31)	$\frac{\epsilon}{k_{BT}} = (1-\alpha-\gamma)(0.00436\mathrm{MW}+283.93) + \gamma\left(508-\frac{234100}{\mathrm{MW}^{1.5}}\right)+\alpha\left(\exp\left(5.5769-\frac{9.523}{MW}\right)\right)$	
[116]	(32)	$m_i = C_{7m} + 2.82076 * 10^{-2}\left(\frac{MW_i}{\rho_i}-\frac{C_{7MW}}{C_{7\rho}}\right)$	The method does not use the SARA analysis results and rather divides t SCN fractions and then evaluates parameters of each fraction higher th given correlations for all components Here ϵ, m, ρ and MW subscripts of C_7 stands for two PC-SAFT paramete and MW of the C_7 fraction respectively. The detailed expressions can b [116,142] σ is obtained by fitting to the liquid density of SCN at standard conditi
	(33)	$\frac{\epsilon_i m_i}{k_{BT}} = C_{7\epsilon m} + 7.97066\left(\mathrm{MW}_i * \rho_i^{0.25} - C_{7MW} * C_{7\rho}^{0.25}\right)$	
[143]	(34)	$m = 33.58 + 0.08816\mathrm{MW} - 90.75\mathrm{SG} - 0.07727\mathrm{MW} * \mathrm{SG} + 61.01\mathrm{SG}^2$	Correlations for petroleum fractions as a function of MW and specific g (SG). Original paper [143] used correlations for crude oil PVT paramet Correlations were implemented for SAFT parameter evaluation of satur and resins by Dehaghani et al. [64,65]. Asphaltene parameters were ev correlations from Gonzalez [57]
	(35)	$m\sigma^3 = -75.14 + 2.848\mathrm{MW} + 231.7\mathrm{SG} - 1.288\mathrm{MW} * \mathrm{SG} - 186.9\mathrm{SG}^2$	
	(36)	$\frac{\epsilon m}{k_{BT}} = 3372 + 11.24\mathrm{MW} - 8955\mathrm{SG} - 5.925\mathrm{MW} * \mathrm{SG} + 6136\mathrm{SG}^2$	

Table 5
The set of BIPs for the SARA-based method from Panuganti et al. [35]

	N_2	CO_2	H_2S	C_1	C_2	C_3	C_{4+}	Saturates	A + R	Asphaltenes
N_2	0	0	0.09	0.03	0.04	0.06	0.075	0.14	0.158	0.16
CO_2		0	0.0678	0.05	0.097	0.1	0.12	0.13	0.1	0.1
H_2S			0	0.062	0.058	0.053	0.07	0.09	0.015	0.015
C_1				0	0	0	0.03	0.03	0.029	0.07
C_2					0	0	0.02	0.012	0.025	0.06
C_3						0	0.015	0.01	0.01	0.01
C_{4+}							0	0.005	0.012	0.01
Saturates								0	0.007	−0.004
A + R									0	0
Asphaltenes										0

The main disadvantage of the SARA analysis is the inconsistency in results depending on the method of performing the analysis. Panuganti et al. [58] reported a noticeable difference between the SARA analysis results obtained through thin layer chromatography with flame ionization detection (TLC-FID) and high-pressure liquid chromatography (HPLC) for the same Middle Eastern crude. Also, the results can differ depending on a laboratory that performs the experiments [35]. However, Arya et al. [41] modeled the crude oil (from Panuganti et al. [35]) using three different sets of SARA analysis. It was possible to calculate accurate AOPs for all the used sets with negligible differences. They [41] concluded that the sensitivity of the PC-SAFT model on the SARA analysis is not significant. However, the accuracy of the modeling of the amount of asphaltene precipitated is highly dependent on experimental measurements of the asphaltene concertation.

Compositional analysis of the crude oil and flashed gas is a very important input data; without such data it is impossible to model the asphaltenes phase behavior. The analysis is usually presented using the method proposed by Katz and Firoozabadi [144] or by the later development of this method by Whitson [145] in terms of the single carbon number (SCN). Such analysis [146] commonly groups various components to three categories of 1) pure components 2) SCN fractions that are characterized within certain boiling temperature range and 3) the heavy end fraction that represents all the undefined SCNs with the average boiling point equal and higher than certain SCN. The asphaltenes fall in the third category. Note that there is some level of flexibility in this analysis that contributes to variations in the outcome. For example, for $< C_{10}$ part, Ting et al. [53] considered all nonpolar linear branched and cyclic components to be saturates. All components with one or more aromatic ring were lumped to A + R. The remaining composition is distributed in the C_{10+} part according to the SARA analysis. Asphaltenes are assumed to be present only in the C_{10+} part. Panuganti et al. [35] considered SCN $< C_9$ is a reasonable threshold choice for manual component lumping.

The flashed gas and STO composition are both necessary for an accurate representation of the reservoir fluid. However, for some crudes, only the monophasic oil composition is available at the reservoir condition. In such cases, Tavakkoli et al. [112] suggested to conduct flash calculations (i.e., vapor–liquid phase split) at standard conditions by the PC-SAFT and then to use the resultant flashed gas/STO compositions to perform conventional characterization according to the SARA-based method. The heavy-end fraction (C_{7+}) parameters are suggested to estimate using correlations for A + R by adjusting the aromaticity parameter γ to minimize the error between the calculated and experimental data of GOR and/or C_{7+} fraction density. The schematics of this method can be seen in Fig. 5. Arya et al. [47] suggested that components heavier than C_{6+} can be treated as 100% STO in cases with monophasic composition.

The asphaltene precipitation onset data is very important in tuning the three PC-SAFT parameters of asphaltenes and in generating the asphaltene precipitation envelopes [52,53]. The precipitation onset data are commonly obtained under ambient condition or reservoir (high

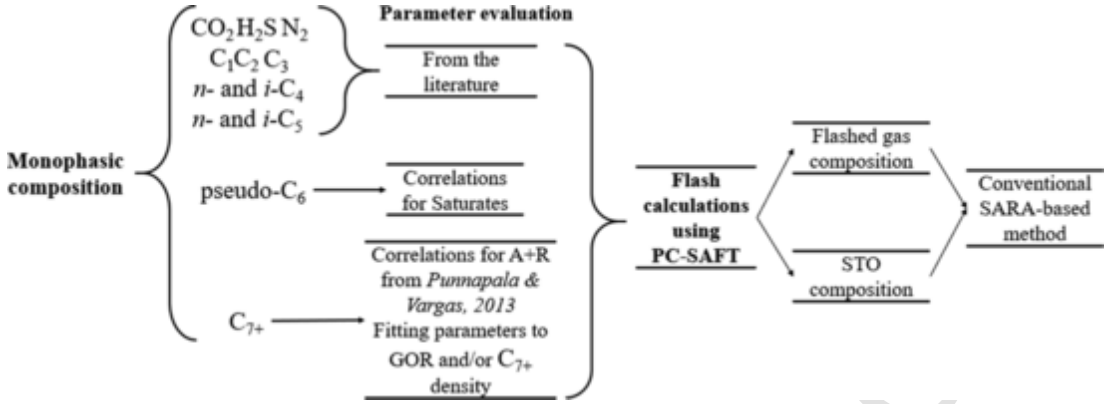

Fig. 5. Schematics of the monophasic composition method by Tavakkoli et al. [112]

pressure and high temperature, or HPHT) conditions. The onset tests at ambient condition experiments are usually conducted by adding asphaltene precipitant (*n*-alkane) while measuring the volume of precipitant required to observe asphaltene precipitation. The HPHT experiments provide more realistic phase behavior for the reservoir fluid; however, they are more expensive and also require live oil samples to simulate the in-situ fluid behavior [147]. Several additional values of upper (U-AOP) and lower AOPs (L-AOP) at different temperatures/compositions are required to validate the model [60]. The common choice for A + R parameter tuning is BPs and crude oil densities [58]. Some authors [52,56,64,129] apply the *n*-alkane dilution onsets for the asphaltene parameter fitting, especially if asphaltenes are considered to be polydisperse [52,53,112].

The U-AOP is the pressure above the BP at which the asphaltene rich phase starts to separate from the crude oil bulk phase which is the onset of asphaltene instability [2]. To cause flow assurance problems, asphaltene aggregates will need to further deposit onto a particular surface which depends on the specific characteristics of the surface and flow hydrodynamics [148]. Precipitation does not always lead to deposition and subsequent asphaltene related problems. However, it is a necessary condition for deposition to happen. The L-AOP, on the contrary, is a pressure below the BP at which the asphaltenes are fully reintegrated into the crude oil [2]. There are several ways to measure onsets at HPHT conditions. Jamaluddin et al. [114], for instance, have conducted measurements of AOPs using four different techniques:

- Gravimetric technique – includes depressurizing a PVT cell by discrete equilibrium steps. Asphaltene fraction will settle at the bottom of the PVT cell due to the gravity effect. The experiment includes taking small samples and measuring the asphaltene content at each step. A drop in the asphaltene concentration in the crude oil samples will indicate an U-AOP [114].
- Filtration technique – Experiments are conducted by depressurizing the crude oil in PVT cell and taking samples though a filter at each step. An increase in the asphaltene content filtered relates to the onset of precipitation. The method, similar to gravimetric, also provides a quantitative measurement of the asphaltene precipitation [114].
- Acoustic Resonance Technique – the technique measures the propagation of sonic waves through crude oil during depressurization. Jamaluddin et al. [114] mention that this technique cannot detect L-AOPs.
- Light Scattering Technique (LST) – The technique measures light transmittance intensity through crude oil to detect the onset of asphaltene precipitation. Depressurization occurs in a visual PVT cell with varying depressurization rates. Jamaluddin et al. [114] used the maximum depressurization rate of 40 psi/min. A sharp decline in the light transmittance relates to the U-AOP state. For dark color crudes, visible light is not feasible; instead, emission at near infrared region (with wavelength 800 to 2200 nm [2]) is required [114].

Among the analytical methods used for the detection of AOP, the LST technique is used the most [149]. The LST method is quick and requires small sample volume [2]. LST (NIR) is usually used in conjunction with High Pressure Microscopy (HPM) to visually identify the formation of the asphaltene aggregates. This combination is the most common commercially applied method for evaluating AOPs [150].

Laboratory measurement techniques used for characterization of petroleum fluids suffer from some limitations. For example, the LST + HPM results are sensitive to depressurizing rate and equilibration time; also, the smallest size of the aggregates that can be detected is limited by the wavelength of the emitted light source [61,103,104,125,151]. These limitations lead to uncertainties in experimental measurements. Dumont et al. [152] demonstrated that experimental AOP measurements using LST(NIR) + HPM on the same crude oil samples from the same depth conducted by different laboratories can differ by about 1000 psi. A rough estimate of the accuracy of recent AOP measurements on three crudes from different origins using LST was ± 250 psi [153]. Moreover, results can vary depending on the chosen laboratory measurement technique [114,149]. As discussed earlier, since the PC-SAFT parameters of asphaltene pseudo-components are fitted to these measurements then, such uncertainties create a challenge in way of evaluation of the actual accuracy of the PC-SAFT EoSs in estimation of asphaltene phase behavior. The A + R parameters are fitted to BP measurements; which, are also suffering from uncertainties. Sisco et al. [13] recommended fitting the A + R parameters with a maximum error of 0.5% for crude oil density and 10% for BPs because of the relative certainty of crude oil density data in comparison with BP measurements.

3.3. Alternative characterization methods

Pedersen et al. [116,142,154] developed a characterization method that was applied to model a number of crude oil PVT parameters and asphaltene precipitation onsets under CO_2 injection. This method gained popularity due to its simplicity [13]. In this method, the heavy-end fractions (i.e., C_{36+}) is divided into SCN fractions up to C_{80} whose carbon numbers are linearly correlated to the logarithm of their molar percentage (mol%). Densities of these fractions are also assumed to correlate linearly with the logarithm of their carbon number, with C_6 density being equal to 0.86 times the density of the C_7 fraction. MWs of these fractions are calculated using the correlation [116]:

$$MW_i = 14CN_i - 4 \tag{37}$$

where CN_i is a carbon number of component *i*. After the SCN split, the

PC-SAFT parameters m and $\in/k_{BT}$ are calculated for each fraction, using correlations (Table 4). The segment diameter σ is determined by matching the liquid density of the carbon number fraction (that was calculated by the linear extrapolation) at standard conditions. After the evaluation, fractions are lumped into several pseudo-components, and their parameters are also combined using mixing rules given by Pedersen et al. [116,142]. This method was applied for the modeling of asphaltene phase behavior by Hustad et al. [115] where the asphaltene fraction was assumed to be in the C_{50+} part and represented by one pseudo-component.

As was mentioned before, the SARA-based method assumes the non-associative behavior for the crude oil system and ignores the association term. Arya et al. [41] developed a modeling procedure with the inclusion of this term. The details of the procedure are described in the corresponding section below.

Xue et al. [130] presented a characterization method for modeling of joint asphaltene-wax precipitation using sPC-SAFT. The characterization is performed by first dividing the C_{7+} into SCN fractions by using Whitson's method [145]. Each SCN is divided into paraffin, naphthene, and aromatic parts by the procedure from Riazi et al. [155] and then the naphthenic and aromatic + resin parts are lumped into Saturates and A + R pseudo-components, respectively. Paraffinic fractions are represented as separate components up to n-C_{36}. Asphaltenes are characterized by a single pseudo-component and the concentration is estimated using SARA analysis. PC-SAFT parameters are estimated using procedure from Liang et al. [146].The adjustable parameters are segment diameters of all model components that are fitted to the specific gravity (SG) of each component. Additionally, the asphaltene segment-segment interaction energy is adjusted to match the experimental onset point. The detailed description of the characterization method can be read in the article by Xue et al [130].

There are several methods of crude oil characterization for performing calculations of crude oil PVT parameters (such as density, compressibility etc.) using PC-SAFT. For example, Saajanlehto and Alopaeus [156] developed a method for characterizing heavy oils for PC-SAFT EoS. The method divides crude into pseudo-components based on their boiling points and Saturate Aromatic Polyaromatic (SAP) distribution. SAP distribution is performed using the developed correlations (see [156]) as a function of boiling temperature of the pseudo-component and the only input data required is the distillation curve of the crude oil. The crude oil is treated as a non-associating system and asphaltenes are represented by one pseudo-component. They estimated three SAFT parameters using correlations from Gonzalez [57] for A + R for both aromatic and polyaromatic pseudo-components with γ equal to 0.1 and 0.6, respectively. Although good results were achieved in calculating the densities and saturation pressures, the method was not tested in the modeling of asphaltene precipitation. There are also other methods available in the literature for calculating the PVT parameters including methods offered by Yan and co-workers [146,157–159], the simplification of the SARA-based method for PVT parameter calculations by Abutaqiya et al. [160], and the method by Rokni et al. [161].

4. Developments in PC-SAFT asphaltene phase behavior modeling

In the following sections, we show the developments in the modeling of asphaltene-crude oil behavior using PC-SAFT and compare to other EoS such as PR, SRK, and CPA. We have modified all results for consistency in unit, and style. Most units in the figures are shown in SI unit. We consistently show the results for the upper asphaltene onset point (U-AOP), lower asphaltene onset point (L-AOP), and the bubble point pressure (BP) curves with black, red and blue colors respectively. The modeling results from literature related to original PC-SAFT are shown with solid line, while modifications to PC-SAFT, or other EoSs are shown with dashed or dotted lines. Also, the experimental data from literature are also shown consistently with black circles (for U-AOP), red squares (for L-AOP), and blue triangles (for the BP).

4.1. The effect of the pressure–temperature change

Temperature and pressure change are one of the main causes of asphaltene related problems both during oil production and laboratory experiments [5,162]. At the starting point of a production system, crude oil is in the reservoir at approximately isothermal conditions. The asphaltene fraction is usually more stable at higher pressures and starts to precipitate at certain pressure above bubble point known as the U-AOP. The amount of the asphaltene rich phase will increase by further decreasing the pressure, and finally it will reach a maximum at the bubble point pressure [2,163].

At the bubble point, the first bubble of gas will liberate from the crude oil. The exsolved gas components such as N_2, CO_2, and light alkanes are considered as poor solvents for asphaltenes. Thus, the stability of asphaltene-crude system increases as these light components are exsolved and the amount of asphaltenes precipitated from crude oil is reduced with decline in pressure [163]. Pressure may eventually reach the L-AOP and asphaltenes will be reintegrated into the solution [2,120].

In general, an increase in temperature will decrease the amount of precipitated asphaltene [5,12]. However experimental results on the effect of temperature are controversial. Burke et al. [164] noted that precipitation amount should decrease at lower temperatures because the solubility of asphaltenes and bulk crude oil phase are very similar. Verdier et al. [108] also has observed that stability of asphaltenes increases with a decrease in temperature. A recent study of asphaltene precipitation kinetics [165] showed that an increase in temperature causes a decrease in the amount of asphaltene precipitation and aggregation; while, simultaneously making the remaining of the crude oil a better solvent for the asphaltene fraction. The U-AOPs seems to decrease with an increase in temperature for most of the crudes studied in the literature. For instance, Boesen et al. [166] analyzed 24 different crudes from the literature and majority of them showed a decrease in U-AOP with an increase in temperature. However, the U-AOPs increased with increase in temperature for some crudes [120]. Boesen et al. [166] suggests that decreasing/increasing trends of the U-AOP can possibly be explained by selected temperature range for the experiments. As shown in Fig. 6, both decreasing and increasing U-AOP curves depend on the temperature range.

The PC-SAFT generally performs well in modeling the asphaltene phase behavior under varying temperatures. However, several authors

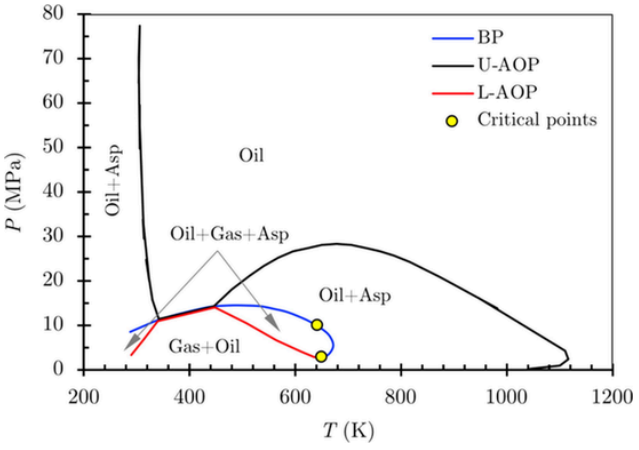

Fig. 6. Complete *P-T* diagram of asphaltene phase behavior generated by the PC-SAFT EoS for light crude oil system. Modified after Agger and Sørensen [127], Copyright © 2018, American Chemical Society.

noted that in some cases, the PC-SAFT model calculations can significantly deviate from experimental U-AOP data at lower temperatures.

As can be seen in Fig. 6, the modeled U-AOP curve tends to have a steep increase in slope at low temperature. This can be consistent with experimental observations in some cases (e.g. [35,60,106]). However, in some cases, experimental values do not follow this trend. Ting [52] noted such erratic behavior in the modeling of asphaltenes/toluene/methane mixtures. A similar problem was mentioned by Arya et al. [41] and Zhang et al. [42] in the modeling of Kuwait crude oil from Kabir and Jamaluddin [110] (Fig. 7) and by Fouad et al. [125] with the two Abu Dhabi crudes. Abutaqiya et al. [132] introduced the terminology minimum upper critical solution temperature (MUCST) as the temperature at which the modeled slope of the U-AOP curve approaches infinity. They also have stated that all SAFT-based models tend to have such a deviation from experimental data at low temperatures [132].

AlHammadi et al. [104] have reported that the experimental onsets that are measured by LST(NIR) and HPM methods generally follow a specific pattern, featuring an abrupt increase in the U-AOP values at low temperatures similar to the modeling trend exhibited by the PC-SAFT. They reported that some crude oils demonstrate atypical behavior with the U-AOP curve increasing linearly with a decrease in temperature, as demonstrated in the case with a crude oil from Kuwait (Fig. 7). The unusual behavior of the model was explained by the nature of experimental procedures that are used for the U-AOP detection. The slow aggregation of asphaltenes at low temperatures combined with lack of sufficient aging time during the experiments are hypothesized to cause the onset of asphaltene precipitation to be detected at lower pressures and the true onset to be bypassed by experiments [104]. Despite of this explanation, the researchers [104] suggested modifications to the SARA-based method that helps match low temperature U-AOP calculations with experimental measurements. Asphaltene parameters are suggested to be estimated by firstly adjusting the asphaltene aromaticity to match the model to the U-AOP at one specific temperature by setting MW_{Asph} to 1700 g/mol. The parameters then further fitted by adjusting the MW_{Asph} to match the U-AOPs at the lowest and the highest temperatures to produce a linear dependency of MW_{Asph} versus T. The proposed method was moderately successful in matching to experimental U- AOPs of a number of crudes with linear U-AOP trends (e.g., Fig. 8). However, as can be seen, in this example, the new characterization technique resulted in an overestimation of high-temperature U-AOP.

Vargas et al. [103] also claim that the NIR + HPM methods may underestimate the true onsets of asphaltene precipitation because of the lack of sensitivity. Tavakkoli et al. [61] reported that a short aging time impedes the system reaching equilibrium conditions. This makes the precipitation process to depend on the system kinetics. Therefore, the amount of precipitated asphaltenes can be affected with the aging time considerably. These authors [61] stated that the parameters obtained from such experimental data should not be used for the tuning of thermodynamic models. Others have also reported lack of measurement sensitivity for NIR and HPM analytical methods where the aggregates smaller from 0.5 μm are not detectible [125,151].

On the other hand, researchers have reported a number of numerical pitfalls for the SAFT-based EoSs in general and for the PC-SAFT in particular [167–172]. For instance, Yelash et al. [171,172] concluded that the PC-SAFT calculates, in addition to the typical gas–liquid phase split, multiple fictional critical points and phase splits for one-component systems of polymers, namely: 1) "liquid–liquid" split at high density and low temperature and 2) "gas–gas" split at low density and high temperature. These erroneous behaviors attributed to inappropriate assumptions in the dispersion term and the fictional "liquid–liquid" split has led to serious discrepancies in calculation of densities of polybutadiene at low temperatures [172]. Later, similar pitfalls have been observed in cases with nearly 60 common pure components, including *n*-alkanes [170]. Privat et al. [170] stated that the PC-SAFT can exhibit about five different volume roots in contrast to the three roots of Cubic EoSs. Such discrepancies are not limited to pure components and might be an issue in parameter estimation for mixtures [168,170]. Polishuk et al. [169] demonstrated that such erroneous behavior of the PC-SAFT can occur at pressure–temperature ranges of interest in the petroleum industry.

Later, Polishuk [173] suggested a new standardized critical point-based approach to numerically evaluate the PC-SAFT parameters. A refitting of the original PC-SAFT universal constants and some changes in the original EoS formulations and mixing rules (see [173]) was suggested. This new approach requires critical pressure, temperature, and triple point liquid density as input data and demonstrated no above-mentioned numerical pitfalls in the modeling of high-pressure densities and sound velocities of non-polar compounds and their mixtures [173]. This approach later demonstrated promising results in modeling of aromatics [174], aqueous solutions [175,176], and various other systems [177–188], although has not been implemented in asphaltene phase behavior modeling yet.

To mitigate some of these numerical issues in asphaltene phase behavior modeling, Cañas-Marín et al. [131] suggested replacing the dispersion term from the second-order perturbation expression of Barker and Henderson [63] with a modified term from Zhang et al. [189–191]. Later, in another work, Cañas-Marín et al. [136] modified the

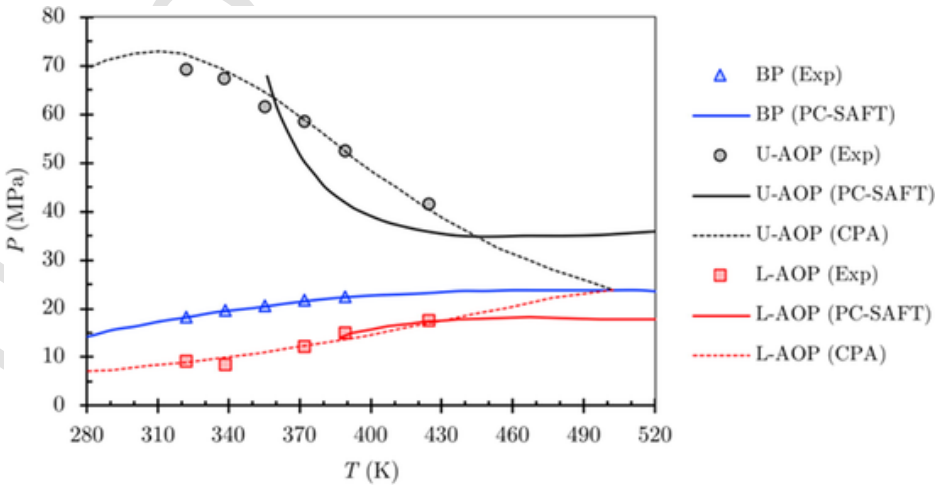

Fig. 7. The linear U-AOP behavior of Kuwaiti crude from Kabir and Jamaluddin [110] and deviations of the PC-SAFT model. Modified after Zhang et al. [42], Copyright © 2012, American Chemical Society.

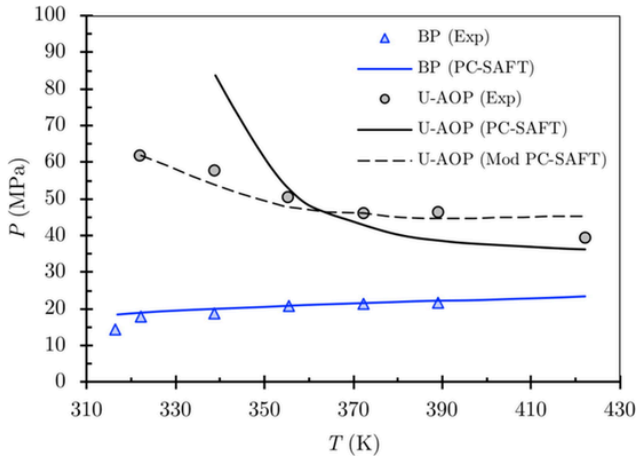

Fig. 8. The modeling of a Kuwaiti crude from Kabir and Jamaluddin [110] using PC-SAFT EoS with regular and modified SARA-based method. Modified from AlHammadi et al. [104], Copyright © 2019, American Chemical Society.

temperature-dependent diameter ($d(T\&\rho)$) to make it a function of both temperature and density. Substantially lower U-AOPs values were calculated at lower temperatures after such modification, compared to the conventional PC-SAFT model. Liang et al. [192] suggested a new set of universal constants for the PC-SAFT to improve the speed of sound calculations in *n*-alkanes. Polishuk et al. [169] concluded that this new set of constants can substantially improve the performance of the SAFT-based EoSs in dealing with the above-mentioned numerical pitfalls. These new constants were later revisited and improved by Liang and Kontogeorgis [141]. Cañas-Marín et al. [140,193] have used the latter set of constants in combination with the modified temperature-dependent diameter ($d(T\&\rho)$). Application of the Liang-Kontogeorgis [141] constants has resulted in lower values of U-AOPs compared with the original set of universal constants by Gross and Sadowski [51]. Overall, the combination of the Liang-Kontogeorgis [141] constants and $d(T\&\rho)$ [136] has found to give the most improved results [140,193].

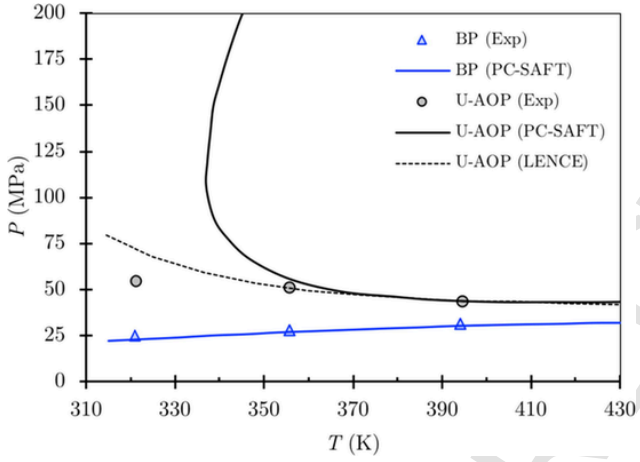

Fig. 9. The modeling of U-AOPs under 30 mol% of CO_2 injection (exp. data from Punnapala and Vargas [60]) with regular PC-SAFT and LENCE. Modified after Abutaqiya et al. [132], Copyright © 2018, with permission from Elsevier.

Abutaqiya et al. [132] followed the approach by Vargas et al. [194] and developed a function that linearly extrapolates the normalized cohesive energy along the U-AOP curve with respect to the temperature (LENCE). The developed LENCE [132] model was tested with several crude oils with atypical temperature behavior (i.e., Fig. 9). The results showed a substantial decrease in the computational time of modeling up to 5 times faster than the regular PC-SAFT modeling.

As mentioned earlier, some crude oils exhibit atypical behavior where the U-AOP values decrease with decreasing temperature. Examples of such crude are the North American (cited by Zhang et al. [42]) and Venezuelan crude oils reported by Gonzalez et al.[120]. The North American crude was modeled by the PC-SAFT [42] and the asphaltene parameter alteration or BIPs adjustments were not able to change the shape of the modeled U-AOP curve and fit the model to the experimental data (Fig. 10). Zhang et al. [42] suggested that the PC-SAFT model match can be improved with the inclusion of the association term. Abutaqiya et al. [132] tested their PC-SAFT LENCE model on Venezuelan crude oil reported by Gonzalez et al. [120] and were able to accurately match the calculated U-AOPs with the reverse temperature U-AOPs, as shown in Fig. 11.

As noted from the mentioned works, the PC-SAFT EoS seems to perform well in pressure ranges of interest in the petroleum industry. However, Abutaqiya et al. [132] have proposed a hypothetical phase boundary for the PC-SAFT models at extremely high pressures called "Hyper Asphaltene Onset Pressure (H-AOP)" curve. Above this hypothetical curve asphaltenes will separate from the crude oil phase (Fig. 12). Abutaqiya et al. state [132] that this kind of phase boundary has not been verified experimentally and may be an artifact of SAFT-family EoSs.

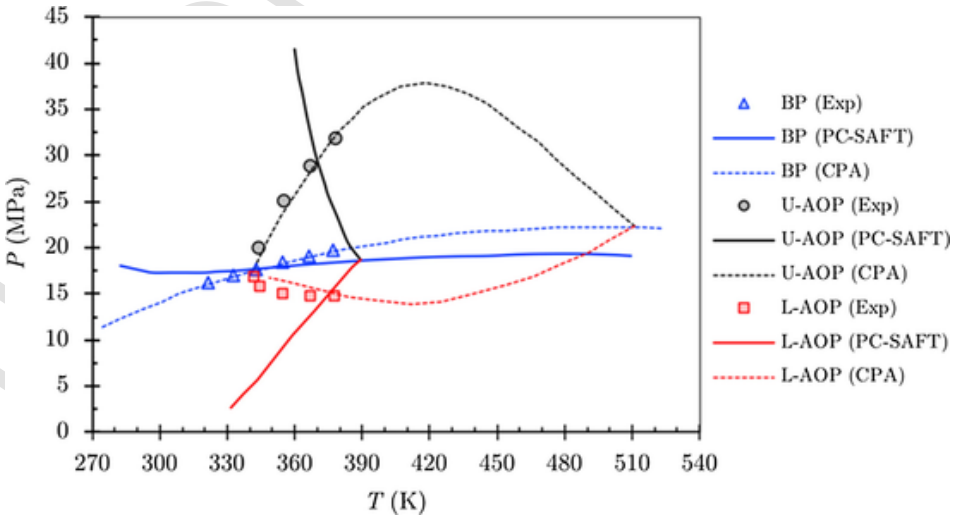

Fig. 10. The reverse temperature behavior of U-AOPs and unsuccessful PC-SAFT modeling results. Modified after Zhang et al. [42], Copyright © 2012, American Chemical Society.

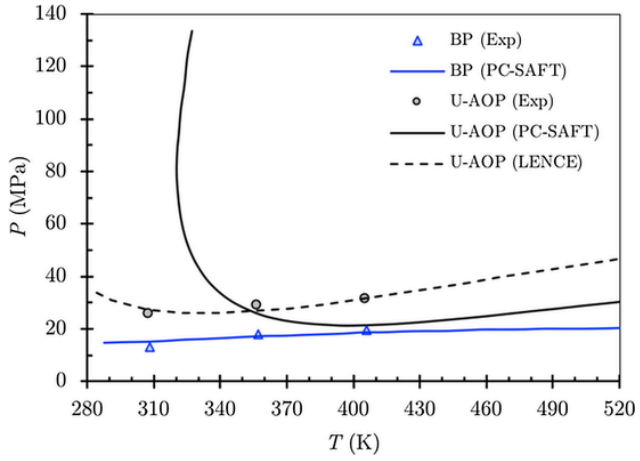

Fig. 11. The reverse temperature behavior of a Venezuelan crude from Gonzalez et al.[120] modeled by the PC-SAFT LENCE model. Modified after Abutaqiya et al. [132], Copyright © 2018, with permission from Elsevier.

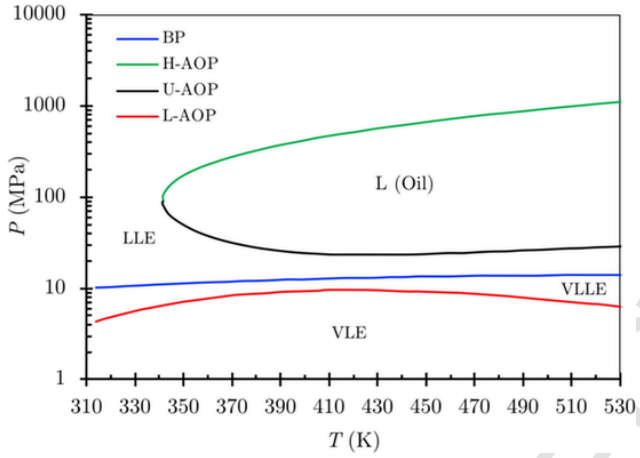

Fig. 12. The H-AOP modeled by PC-SAFT EoS at high pressures. Modified after Abutaqiya et al. [132], Copyright © 2018, with permission from Elsevier.

4.2. The effect of miscible gas injection

Asphaltene related problems are reported when crude oil composition was altered as a consequence of miscible gas injection EOR [7,195]. Since most of the injected gas types (i.e., CO_2 and CH_4) are not good solvents for asphaltene fraction, they can increase the risk of precipitation [9]. Thomas et al. [6] have reported major problems during miscible flooding in Alberta, Canada. The state of the production in some wells required to treat them with solvents every 16 h to keep them producing. Jamaluddin et al. [106] analyzed the asphaltene concentration using NIR analytical method. The tests were conducted on reservoir fluid under the injection of different concentrations of N_2. The U-AOP nearly tripled its value at the maximum (20 mol% of N_2 mixed with crude oil) injected concentration. The negative effect of CO_2 and rich gas injections were also noted during a number of laboratory experiments under both standard and reservoir conditions [113,196,197].

The PC-SAFT models repeatedly showed its ability to accurately calculate the values of experimental U-AOPs under the miscible gas injection for a number of crudes in the literature. The calculation of U-AOP for different amounts of gas injected is often used for model validation purposes. Gonzalez et al. [54,55] modeled the effect of C_1, C_2, N_2, and CO_2 injections and concluded that C_1 and N_2 are the strongest precipitants. CO_2 injection, according to the model, was found to have both positive and negative effects on asphaltene stability depending on a certain temperature threshold. At lower temperatures, CO_2 can stabilize the crude oil and at higher temperatures, it can induce precipitation. This behavior was explained through the change in the solubility parameter. Punnapala and Vargas [60] modeled four different crudes under the injection of rich and lean hydrocarbon gases, as well as their mixtures with N_2, CO_2, and H_2S at different ratios as shown in Fig. 13. PC-SAFT calculations of U-AOPs and BPs were in a good agreement with experimental data in all studied cases. Arya et al. [41] also modeled crude oil systems under the gas injection for a number of crudes from the literature with the inclusion of the associative behavior and have been able to achieve greater accuracy in the modeling of phase in comparison with the WOA modeling. However, sometimes, additional adjustments of a model are required to adequately capture the behavior of a system under the gas injection. Zhang et al. [42] studied the effect of N_2 injection using data from Jamaluddin et al. [106]. The authors concluded that the alteration of N_2 – Asphaltenes BIP was necessary to properly match the model to the experimental U-AOPs at different mol% of N_2 injected.

4.3. Wax-asphaltene precipitation modeling

Experimental evidences suggest that high paraffin content can cause spontaneous flocculation and aggregation of the asphaltenes [198]. Aromatics are good solvents for asphaltenes and are denser than the paraffins (that are considered bad solvents for the asphaltenes). So, in general, the lighter crudes with a higher alkane content are more prone to asphaltene instability than the heavier crudes, with a higher aromatic content [12,199]. Yanes et al. [200] evaluated the effect of long chain paraffins on the asphaltene precipitation. They used three Brazilian crudes for which the asphaltene precipitation was induced by the addition of *n*-heptane. The results showed a decrease in the asphaltene stability (in terms of a decrease of wt% of *n*-C_7 that was necessary to induce precipitation) with an increase in the paraffin content added.

Application of the PC-SAFT for wax precipitation modeling [139,201–203] has been reported in the literature. Meighani et al. [202] used the PC-SAFT EoS for wax precipitation in presence of asphaltenes. In their work, wax and asphaltenes each were represented by a pseudo-component and their three SAFT parameters were fit to the experimental data of onsets. Sensitivity analysis using the Monte Carlo simulation and ANN showed that high asphaltene content positively correlates with the high amount of wax precipitation [202].

Recently, simultaneous wax-asphaltene precipitation was modeled through sPC-SAFT, integrated with UNIQUAC model [130] and using similar assumptions to SARA-based method. These assumptions state non-associating system, thermodynamic reversibility of the precipitation process, and the modeling of precipitation as a phase split between the liquid crude oil phase, and liquid asphaltene rich phase. With the inclusion of wax precipitation, the system is modeled as a four-phase vapor–liquid (crude oil)-liquid (asphaltene rich)-liquid (wax rich) equilibrium. Modeling was performed for two samples of pipeline dead oils and one mix of these oils from Henan Nanyang and three North Sea oil blends. The model was validated by calculating the total (asphaltene + wax) amount of co-precipitation at different temperatures at the atmospheric pressure against experimental data. The mixed oil cloud point was modeled with AARD of 0.17% and the amount of precipitation was modeled with AARD of 34.48% considering all samples (min. error of 12.21% and max. error of 96.16%) [130].

Joonaki et al. [139] used the SARA-based method of characterization to model U-AOPs of a North Sea crude mixed with different concentrations of paraffin, wax, and hydrocarbon gases. Relative error between the experimental and calculated U-AOPs was between 1.52% and 5.87%. The error increased with increase in the wax content in the

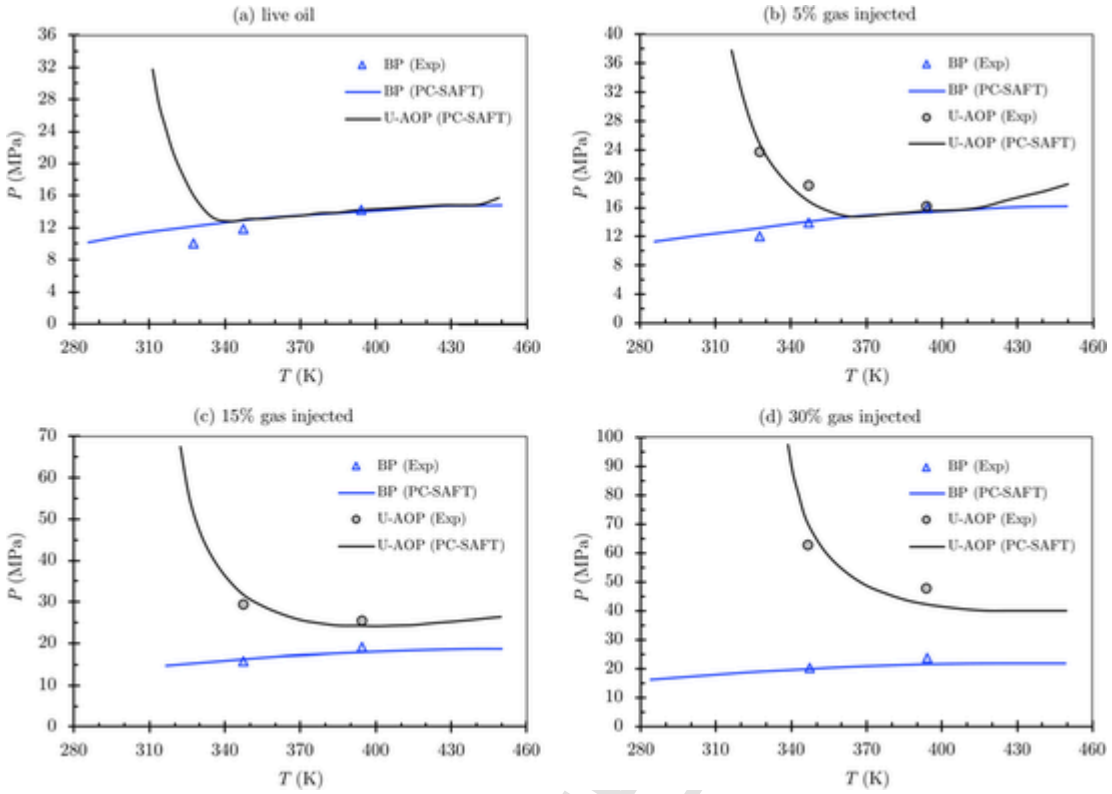

Fig. 13. Modeling of U-AOP and BP curves of light crude oil under the rich hydrocarbon gas injection at different concentrations. Modified after Punnapala and Vargas [60], Copyright © 2013, with permission from Elsevier.

crude oil. It was concluded from both experimental and modeling investigations that higher wax content in crude oil leads to more stable asphaltenes in the solution [139].

Despite the relevance of wax-asphaltene systems in the petroleum industry, the use of PC-SAFT as a tool to study the co-precipitation of asphaltene and wax and the synergic effect of wax on asphaltene precipitation are very limited. Future studies can be focused on this area to show the effect of wax on the asphaltene phase envelope, under reservoir and production conditions.

4.4. The effect of the association term

The model becomes more complex if the association is considered since it increases the number of parameters necessary for each component in the mixture. For associating systems, two additional parameters are required, namely, the association volume ($\kappa^{A_iB_j}$) and association energy ($\epsilon^{A_iB_j}$). Arya et al. [41] performed a PC-SAFT modeling with the association term (PC-SAFT WA) and compared it with the standard non-associating system modeled by the SARA-based method (PC-SAFT WOA). The schematics of methods can be seen in Fig. 14. The essential highlights of the method are as follows [41]:

- The procedure for pure components and C_{4+} is similar to the PC-SAFT WOA.
- Liquid STO is characterized by two pseudo-components: Heavy Component (HC) and Asphaltenes. Associative interactions are between these two pseudo-components. Asphaltene molecules are modeled with 4 associating sites (2 positive and 2 negative). The HC modeled with 1 associating site that can interact with both positive and negative sites of asphaltene molecules.
- Initial estimates of the HC parameters are evaluated using A + R pseudo-component correlations from Punnapala and Vargas [60] with a fixed value of $\gamma_{A+R} = 0.5$. Then, three SAFT parameters are fitted to all available experimental points of BP and STO density.
- Three non-association PC-SAFT parameters of the asphaltenes are fixed. Asphaltene MW is considered to be equal to 750 g/mol.
- Self-association energy (ϵ^{AA}) of the asphaltenes can be a fixed number or can be treated as an adjustable parameter.
- The cross-association energy between HC and asphaltenes (ϵ^{AH}) is fitted to two AOPs at different temperatures.
- The association volume parameters (both cross- and self-association) have a fixed value of 0.05.

One of the main advantages of this method is that the procedure is not a function of asphaltene concentration or MW_{Asph} [41]. Thus, it does not depend on the SARA analysis results, which was sensitive to the analytical method used. It was noted that an increase in the asphaltene concentration increases the value of cross-association energy parameter (ϵ^{AH}) at a fixed value of (ϵ^{AA}) [41].

Arya et al. [41] obtained a match with the experimental onsets in cases with atypical temperature behavior (in both low temperature and reverse temperature cases which were described earlier in this text). The modeling results for the reservoir fluid with a reverse temperature behavior for Lake Maracaibo crude from Venezuela can be seen in Fig. 15. The experimental data are from Gonzalez et al. [120]. Also, the same crude oil from Kuwait [110] that was modeled without association (PC-SAFT WOA) and featured significant deviations (see Fig. 7) was re-modeled with the inclusion of the association parameters which is shown in Fig. 16. An improvement in accuracy was achieved in the modeling of U-AOPs under the miscible gas injection. This WA method with small modifications was later implemented in comparative studies reported by Nascimento et al. [43] and Daryasafar et al. [135] for modeling a number of crude oils from the literature.

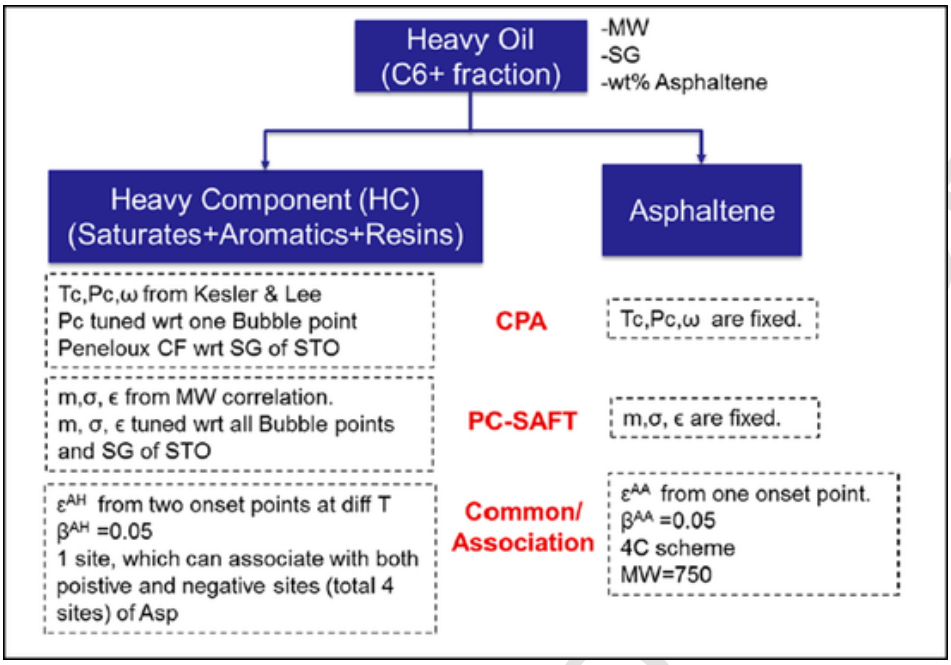

Fig. 14. The PC-SAFT WA and CPA methods. Reprinted with permission from Arya et al. [41], Copyright © 2016, American Chemical Society.

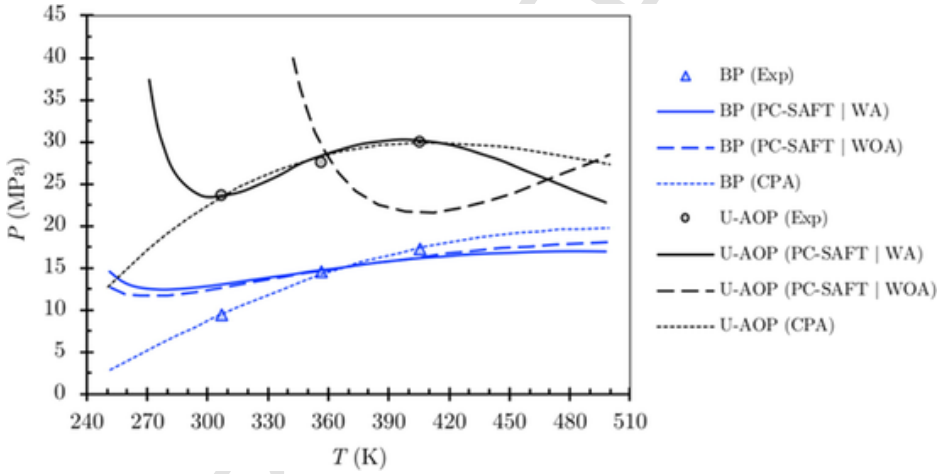

Fig. 15. The reverse temperature U-AOP behavior of Venezuelan crude from Gonzalez et al. [120] and the CPA model/PC-SAFT models with (WA) and without (WOA) the association term. Modified after Arya et al. [41], Copyright © 2016, American Chemical Society.

4.5. The effect of binary interaction parameters (BIPs)

BIPs are temperature independent parameters present in the dispersion term [51]. They are used to improve the modeling accuracy by correcting the calculation of intermolecular interactions between unlike components. There are no established constant values of interaction parameters for the PC-SAFT EoS [199]. BIPs are usually determined by fitting experimental equilibrium data at a corresponding temperature between two pure components [51]. A pseudo-component is represented in the fitting by a specific pure component (within the available components in pseudo-component class) [55]. For example, Gonzalez et al. [55] used VLE for propane and decane to evaluate the BIPs between C_{2+} and saturates pseudo-components respectively. The asphaltenes BIPs in this procedure [55] were set to be equal to those of the aromatics. Then, these asphaltene BIPs were adjusted to achieve the best match with the experimental onset data. Pedersen et al. [199] suggested that the interaction parameters from cubic EoS can be reasonable initial estimates. Gonzalez [57] showed that the asphaltene precipitation onsets are highly sensitive to the values of interaction parameters between asphaltenes and saturates. Change in the BIP between asphaltene and saturates pseudo-components from 0.007 to 0.0024 resulted in a shift in the estimated U-AOP from 105.1 MPa to 68.6 MPa. Tavakkoli et al. [62] also noted a significant effect of the asphaltene-saturates BIP on the onset of precipitation. The difficulties of finding the optimal set of BIPs were also reported by Zhang et al. [42]. Also, in modeling N_2 injection process [42] the adjustment of N_2-asphaltenes BIP was found to control the accuracy of the results. Pedersen et al. [116] also reported high sensitivity of the PC-SAFT model to CO_2 BIPs during CO_2 injection, especially at high gas concentration. Panuganti et al. [35,58] developed a set of BIPs for the SARA-based characterization method that demonstrated a good performance in modeling of a number of crude oils. This set was then successfully used by a number of other researchers [13,60,125]. Furthermore, there are several correlations presented in the literature for some binary systems. For example, Garcia-Sánchez et al. [204] developed a polynomial cor-

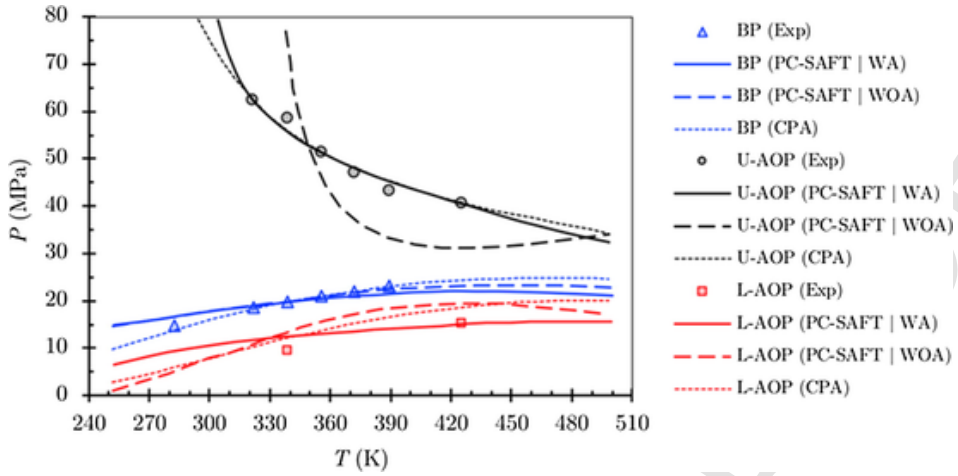

Fig. 16. The linear U-AOP behavior of Kuwait crude from Kabir and Jamaluddin [110] and the CPA model/PC-SAFT models with (WA) and without (WOA) the association term. Modified after Arya et al. [41], Copyright © 2016, American Chemical Society.

relation for N_2-alkane systems as a function of the molecular weight of *n*-alkane. The equation was tested by modeling the *P-x* diagram for the N_2 - *n*-hexadecane system. There are also correlations for methanol-alkane systems [205] and CO_2, methane, and ethane mixtures with high *n*-alkanes [206].

Stavrou et al. [207] proposed a method to estimate the BIPs between pure components based on quantitative structure property relationship model. For each intermolecular interaction type (i.e., dispersive, polar, or association) there are descriptors which are a function of PC-SAFT parameters of the target pair of components. An example of a descriptor for dispersive interactions (D^{LJ}) between components *i* and *j* can be seen in Eq. (38).

$$D^{LJ} = 1 - \left[\frac{\sigma_i^3 \left(\in_i / k_{BT}\right)^2}{\sigma_j^3 \left(\in_j / k_{BT}\right)^2}\right] \tag{38}$$

The resultant BIP is a summation of all descriptors multiplied by the regression coefficients (see [207]). Although a method was successful in modeling phase behavior of pure components in the mixture, but it has not been yet tested for mixtures containing highly heterogeneous pseudo-components such as the asphaltenes.

Abbasi et al. [208] used ANN to estimate the BIPs for PC-SAFT EoS. The algorithm used two sets of input data — either 1) three SAFT parameters or 2) MW, SG, and the normal boiling point for each pair (the best results). The algorithm was tested and demonstrated a good accuracy in calculating the BP and gas composition between several binary mixtures, as well as estimating the BP of a reservoir fluid under nitrogen injection from Jamaluddin et al. [106]. However, the method [208] was not implemented to model asphaltene phase behavior of this fluid.

Abutaqiya et al. [39] applied a modified Chueh and Prausnitz [209] correlation to evaluate the BIPs of pseudo-components in the mixture:

$$k_{ij} = 1 - \left(\frac{2\left(m_i\sigma_i^3\right)^{\frac{1}{6}}\left(m_j\sigma_j^3\right)^{\frac{1}{6}}}{\left(m_i\sigma_i^3\right)^{\frac{1}{3}} + \left(m_j\sigma_j^3\right)^{\frac{1}{3}}}\right)^n \tag{39}$$

where *n* is the constant that should be fitted to experimental data. Abutaqiya et al. [39] used this correlation to evaluate the BIPs between the hydrocarbon pseudo-components (saturates, A + R and C_{4+}) and pure components (C_1, C_2, C_3). The parameter *n* was fitted to experimental data of BPs. BIPs for non-hydrocarbon components were kept constant and taken from Panuganti et al. [35]. Asphaltene BIPs were initially kept constant, and the above correlations were applied only when a good match to the experimental data of U-AOPs was not possible. The above approach was successfully implemented by modeling U-AOPs of ten different crudes [39].

Tavakkoli et al. [61] and Abutaqiya et al. [133], have applied the following linear correlation to estimate BIPs between *n*-alkanes and asphaltene sub-fractions for the polydisperse asphaltene modeling:

$$\begin{aligned} k_{ij} = {} & 8.27 \\ & * 10^{-3} - 2.05 \\ & * 10^{-4} MW_{n-alkane} + 1.23 \\ & * 10^{-5} MW_{asph} \end{aligned} \tag{40}$$

It can be concluded that the BIPs have a profound effect on accurate modeling of asphaltene precipitation envelopes. The fitting of BIPs to experimental equilibrium data for each binary pair in the mixture significantly increases the model complexity and the time consumption of the PC-SAFT EoS modeling. In some cases, experimental equilibrium data for each binary pair may not be available [208]. In such cases, BIPs should be fitted to other available data such as AOPs or treated as constants. While it was shown that in many cases [35,60,125] a set of BIPs from Panuganti et al. [35] can be used and marginally altered when necessary, these cases consider only monodisperse models that are fitted to U-AOPs. Tavakkoli et al. [61], for example, have applied completely different sets for polydisperse models that are fitted to asphaltene precipitation amount data. The development of a reliable and universal method of generating BIPs may greatly increase the simplicity and reliability of the PC-SAFT models.

4.6. Comparison with other EoSs

Panuganti et al. [35] modeled the asphaltene precipitation envelope and bubble point curves for a crude oil from the Middle East with different gas injection scenarios. As can be seen in Fig. 17, the SRK-P EoS failed to accurately model the onsets of asphaltene precipitation at high gas injections. Panuganti et al. [35] argue that SRK EoS fails to accurately model the behavior of mixtures when there is a notable difference between the molecules. In addition, the parameters of cubic EoSs are fitted at the critical point of the mixture where asphaltenes usually are not present due to their decomposition before reaching the critical point [35]. The higher accuracy of the PC-SAFT model compared to VR-SAFT and PR was also verified in several studies, in modeling the phase behavior of the asphaltene systems [64,65]. Another study [121] reported that the accuracy of the PR-EoS decreases sub-

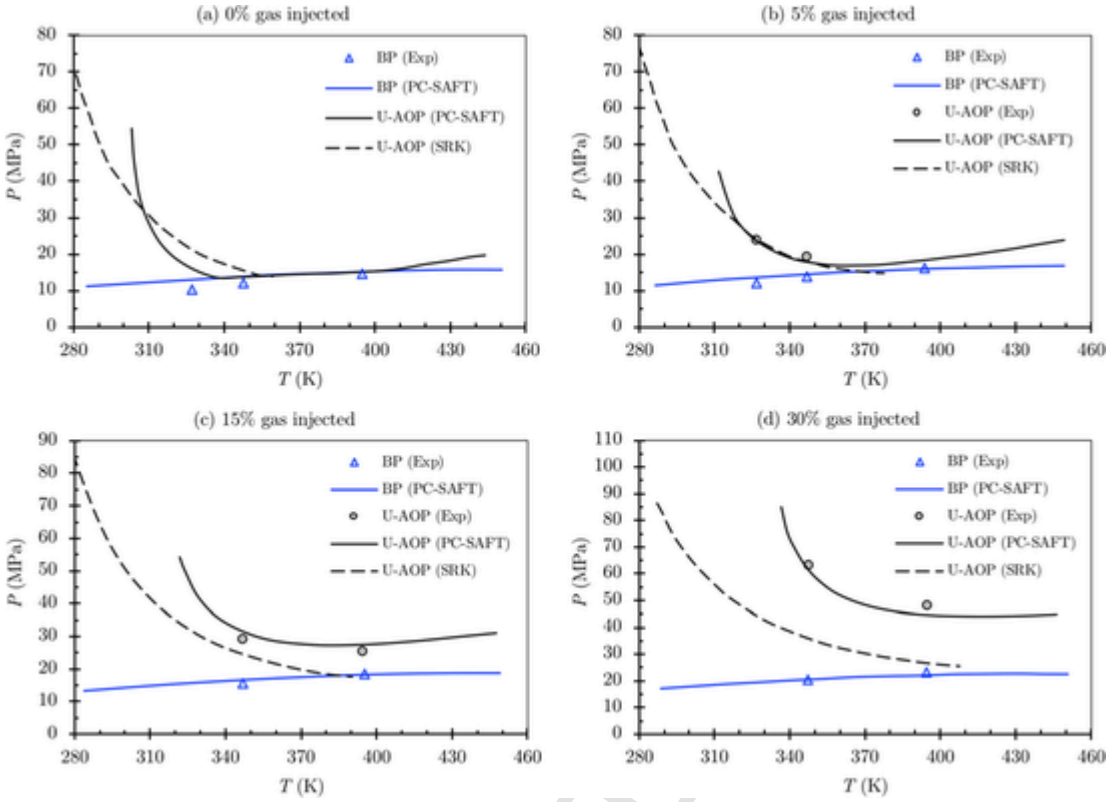

Fig. 17. The comparison between PC-SAFT and SRK-P calculations for light crude oil under different concentrations of rich hydrocarbon gas injected. Modified after Panuganti et al. [35], Copyright © 2011, with permission from Elsevier.

stantially when high concentration aromatic solvent was mixed with asphaltenic reservoir fluid; the PC-SAFT however gave reasonable estimations of system's phase behavior at all concentrations.

Recently, however, the PR EoS has been successfully used [39] to calculate U-AOPs for ten different types of oil using an improved modeling procedure based on SARA analysis. The PR EoS was able to calculate onsets as accurate as the PC-SAFT EoS. In some cases, the PR EoS was more successful, such as in dealing with crudes that demonstrate atypical temperature behavior. This can be seen in the modeling of previously mentioned Venezuelan crude in Fig. 18. Abutaqiya et al. [39] related the poor performance of the cubic EoSs as demonstrated by

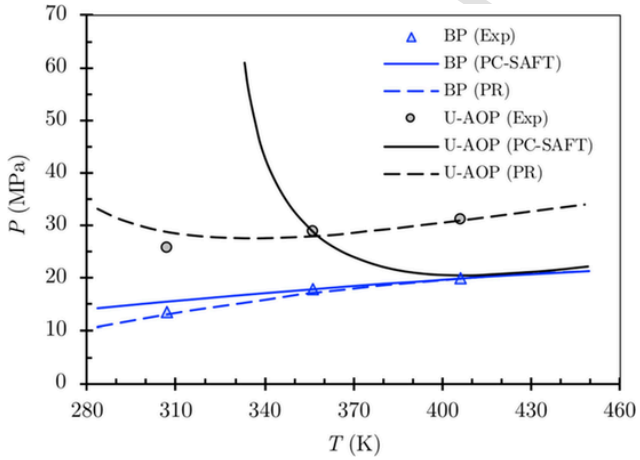

Fig. 18. Modeling of atypical temperature behavior of a Venezuelan crude (from Gonzalez et al. [120]) using PR EoS and PC-SAFT EoS. Modified after Abutaqiya et al. [39], Copyright © 2020, American Chemical Society.

Panuganti et al. [35] to the shortcomings of modeling procedure rather than the cubic EoS itself.

The cubic-plus-association (CPA) [40] EoS has demonstrated a comparable (and, in some cases, even better) results compared to PC-SAFT EoS. Zhang et al. [42] used PC-SAFT WOA and CPA to model asphaltene precipitation from six crudes with asphaltene concentrations ranging from 0.5 to 3.6 wt%. The results indicated that the CPA EoS could be successfully implemented in asphaltene precipitation modeling. Furthermore, in some cases, CPA showed superiority over PC-SAFT in calculating the precipitation amount and phase envelopes (see Fig. 7 and Fig. 10). Also, AlHammadi et al. [45] compared the CPA EoS (with a modeling approach formulated by Zhang et al. [42]) and the PC-SAFT (with adopting modifications from Panuganti et al. [35] for the SARA-based method). The results showed adequate accuracy in modeling the asphaltene phase envelope, with PC-SAFT being closer to the experimental values, demonstrating a greater accuracy in the calculation of GOR. Arya et al. [41] used the newly developed approach for the CPA and the PC-SAFT (WA and WOA) to model asphaltene phase envelopes (see Fig. 15). The CPA model resulted in the lowest deviation from the experimental data both in BP and U-AOP calculations; while, the PC-SAFT WA had a lower deviation in calculating L-AOPs. Nascimento et al. [43] also performed a modeling using a similar method as Arya et al. [41] and concluded that the PC-SAFT is better than CPA (as formulated by Li and Firoozabadi [44] and Nasrabadi et al. [210]) and more reliable outside the experimental range. This claim is based on the fact that the association volume parameter in the PC-SAFT demonstrated a better linear correlation with temperature [43].

In terms of efficiency of computational efforts, the PC-SAFT EoS was found to be slower than four other asphaltene models due to its relative complexity and iterative equilibrium calculations [135]. These four models include 1) the CPA model, 2) SRK EoS (solid model), 3) modified Flory-Huggins model and 4) original Flory-Huggins model [135]

(Fig. 19). It was also shown [123] that the PC-SAFT EoS is about 1.5–2.2 times slower than the PR EoS when performing IMPEC simulations (Fig. 20).

4.7. The effect of asphaltene polydispersity

Asphaltenes are in reality polydisperse. The previously discussed methods treated asphaltenes as monodisperse aggregates for simplicity. It was noted that the model built using the asphaltene monodispersity assumption will model the phase behavior of only the most unstable part of the asphaltene phase; which, should be sufficient if the aim of the modeling is to study the phase boundaries (i.e., AOPs and/or BPs) [13]. However, the amount of asphaltene precipitation is more accurately modeled when the effect of asphaltene polydispersity is included [61].

Ting [52] modeled Lagrave crude oil using four or three pseudo-components for asphaltene sub-fractions based on the type of asphaltene precipitant – n-C_{15+}, n-$C_{7\text{-}15}$, n-$C_{5\text{-}7}$, and n-$C_{3\text{-}5}$ (resins) sub-fractions. The PC-SAFT parameters were then fitted to the experimental n-alkane titration data. A similar method was later implemented in several studies [56,61,62]. Tavakkoli et al. [61] used correlations for A + R pseudo-component by keeping the aromaticity parameter constant for all of the sub-fractions. The gamma function by Yarranton et al. [37,211–213] applied for the description of apparent molecular weight distribution of sub-fractions:

$$f(r) = \frac{1}{M_m \Gamma(\alpha_G)} \left[\frac{\alpha_G}{\left(\bar{r} - 1\right)} \right]^{\alpha_G} \exp\left[\frac{\alpha_G (1 - r)}{\left(\bar{r} - 1\right)} \right] \tag{41}$$

The fitting parameters are MW of each sub-fraction, the aromaticity parameter (γ), and the shape factor of the gamma distribution function (α_G) for all the sub-fractions. The HPHT modeling demonstrated that the calculated U-AOPs were higher than experimental ones detected by means of NIR spectroscopy and HPM. Tavakkoli et al. [61] justify such deviations by the sensitivity limitations and non-sufficient aging time of these experimental procedures. The effect of aging time can be seen in Fig. 21. This method was later modified by Abutaqiya et al. [133], who considered asphaltene fraction consisting of five parts – four asphaltene and one resin pseudo-components. The gamma distribution function was used for all five components.

Zúniga-Hinojosa et al. [117] used the PC-SAFT EoS for the modeling of seven heavy oils and bitumens diluted by n-alkanes. Experimental data is from Sabbagh et al. [37], four crudes from the same source were also modeled by Tavakkoli et al [112]. In contrast with other works, the asphaltene fraction was divided into 30 sub-fractions. Parameters for each of sub-fraction were evaluated using developed correlations [117] as a function of a sub-fraction's MW. Saturates and A + R pseudo-components were evaluated applying correlations from Gonzalez [57] by setting the aromaticity parameter equal to 0.01. In contrast to the SARA-based method, parameters of A + R and asphaltene pseudo-components were not fitted to the experimental data. Instead, the model was fitted by changing BIP between the n-alkanes and asphaltenes to reduce the error between the calculated and the experimental values of the amount of asphaltene precipitated [110].

Polydisperse modeling flattens the asphaltene precipitation curve and makes the process more gradual and the heaviest asphaltene sub-fractions will precipitate first [52,61,62]. Moreover, the inclusion of resins as a sub-fraction of asphaltenes seems to stabilize asphaltenes in terms of a minimal amount of precipitant necessary to induce precipitation even with only dispersion interactions considered [52]. The main disadvantage of such modeling is that experimental data that is used for the model tuning are usually n-alkane dilution onsets obtained at ambient conditions. Therefore, these models may not accurately describe the behavior of fluids under reservoir conditions [13]. Masoudi et al. [105] showed that models that are fitted to the HPHT onsets cannot accurately match the experimental wt% of asphaltene precipitated.

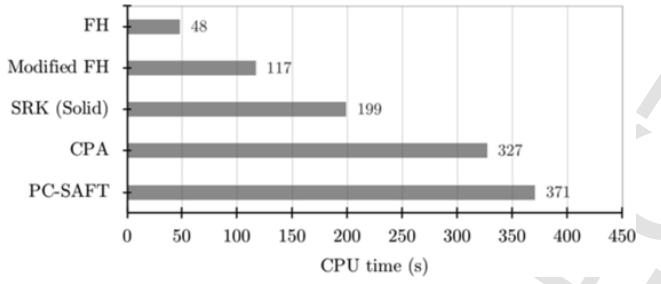

Fig. 19. The CPU time comparison between the PC-SAFT and some other thermodynamic models. Modified after Daryasafar et al. [135], Copyright © 2020, with permission from Elsevier.

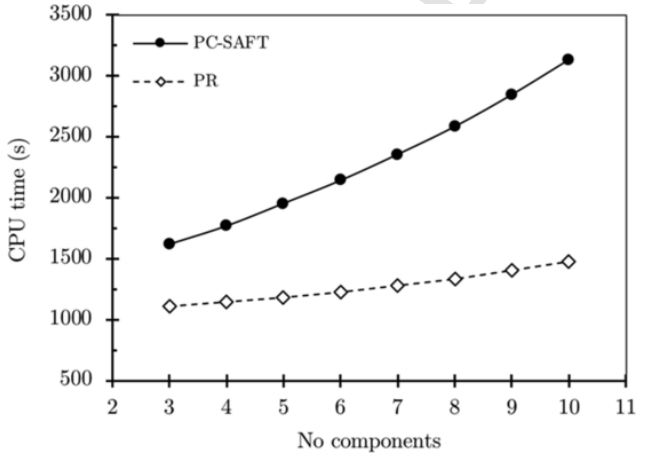

Fig. 20. The CPU time of IMPEC (implicit pressure, explicit concentration) simulations on one pore volume (PV) of gas injection in a two dimensional grid-block reservoir as a function of number of components in the modeled mixture. A comparison between the PC-SAFT and the PR EoSs. Modified after Mohebbinia et al. [123], Copyright © 2017, with permission from Elsevier.

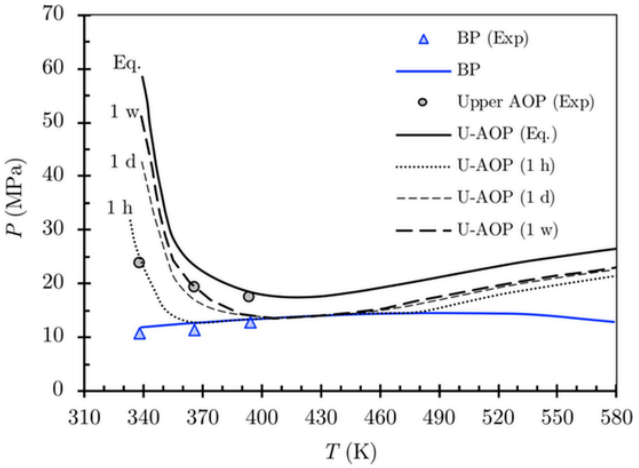

Fig. 21. The PC-SAFT calculations of U-AOPs and BPs with parameters fitted to n-alkane dilution onsets with different aging times (1 hr, 1 day, 1 week and equilibrium conditions) Modified after Tavakkoli et al. [61], Copyright © 2015, with permission from Elsevier.

Khaleel et al. [137,214] concluded that those models that assume asphaltene monodispersity tend to highly overestimate the amount of precipitated asphaltenes. In general, they calculate a slightly lower U-AOP values compared to modeling polydisperse asphaltene media. These observations were also supported by Abutaqiya et al. [133] stating that considering asphaltene monodispersity in the modeling calculates higher amounts of asphaltene precipitated and that the monodisperse asphaltenes require a higher volumes of precipitant to induce instability. It can be concluded that asphaltene polydispersity should be included if the aim is to accurately model the asphaltene precipitation amount. However, models that consider asphaltene monodispersity assumption are sufficient to generate accurate AOP curves [58,60]. Ideally, both the asphaltene precipitation amount data and AOP curves should be used [214].

4.8. Asphaltenes as solid phase

The research works that were mentioned before considered asphaltene precipitation as a phase split between liquid crude oil phase and liquid asphaltene-rich dense phase plus vapor phase, below the bubble point condition. An alternate approach is to represent the precipitated asphaltenes as a solid phase and model the liquid and vapor phase behavior using an EoS. For example, Nghiem et al. [38] used the Peng-Robinson (PR) EoS to model the phase behavior of vapor and liquid phases; they characterized asphaltenes by dividing C_{31+} heavy end-fractions into precipitating (C_{31A+}) and non-precipitating (C_{31B+}) pseudo-components.

The PC-SAFT modeling approaches that consider the precipitated asphaltene as a solid phase were implemented by a number of researchers [63–65]. For example, Dehaghani et al [65] implemented a multi-solid approach that was initially used by Lira-Galeana et al. [215] to model the precipitated paraffin wax as multiple solid phases that are insoluble in other solid phases. They applied this approach for polydisperse asphaltene by considering three pseudo-components, using both PC-SAFT and PR EoSs. Models were applied to two Mexican crudes where a considerable accuracy improvement was achieved in comparison with VR-SAFT models [126]. The asphaltene polydisperse modeling allowed to calculate the onsets and the precipitation amount to have smaller deviations compared to the monodisperse modeling [65]. The crude oil heavy-end characterization procedure was taken from Pedersen et al. [116,142]. Correlations that were developed for saturates, aromatics and resins by Assareh et al. [143] and for asphaltene sub-fractions by Gonzalez [57] were implemented. The PC-SAFT parameters were fitted to the experimental data of U-AOPs, BPs, and *n*-alkane dilution. Recently, models for the same two Mexican crudes were improved by applying the UNIQUAC activity coefficients and using solid-solution approach [64].

4.9. Bitumen phase behavior modeling

Bitumen is classified as a viscous (>10,000 cP in situ) and extremely dense (>1,000 kg/m^3) crude oil that typically regarded as immobile [216]. Asphaltene content generally considered to be high (>10 wt%) [217]. For instance, the most viscous samples from bitumen deposits in Alberta, Canada have asphaltene content ranging from 16 wt% to 25 wt%, as well as a considerable concentration of sulfur [216]. The data of viscosity, density, solvent solubility, and asphaltene precipitation amount of various bitumen/solvent mixtures is crucial in planning of EOR operations for bitumen recovery using various production methods such as solvent-aided recovery, Cyclic Steam Stimulation, and Steam Assisted Gravity Drainage [218]. High asphaltene content of bitumen poses high flow assurance risks for petroleum reservoirs, surface facilities, and transportation pipelines. In addition, depending on solvent type, asphaltenes can influence the solubility of a solvent [219]. CO_2 is less soluble in deasphaltened bitumen than in asphaltene-containing bitumen; while, solubility of C_1 is not significantly affected [219]. Conventional experimental methods of characterization, such as beforementioned SARA analysis or gas chromatography, are not sufficient when it comes to complex mixtures, such as bitumen [220]. Furthermore, asphaltene concentration can affect viscosity of bitumen [219]. Several research works are reported in the literature on modeling bitumen/solvent systems including asphaltene phase behavior using various EoSs. The CPA EoS is successfully applied to evaluate solubility of CO_2 [221] and water [222] in bitumen, asphaltene precipitation modeling in diluted bitumens [223] and phase behavior of bitumen/*n*-alkane systems [224]. Azinfar et al. [218] proposed a generalized EoS modeling method for calculation of properties of bitumen/butane mixtures for design and optimization of solvent-aided recovery processes of bitumen. Bitumen/solvent mixtures were also modeled using PR EoS and SRK EoS [225–227].

The PC-SAFT was also applied for the above-mentioned purposes. Ma et al. [228] proposed a combination of sPC-SAFT and Expanded Fluid Viscosity model [229] to predict viscosities of the Athabasca and the Peace River bitumen with different solvents. The characterization was done by using distillation and molar mass data to divide bitumen into 8 pseudo-components and calculate the mixture density and solvent solubility. Three sPC-SAFT parameters then were fitted to the experimental saturated density data of bitumen with C_1, C_2, and CO_2 and then verified by prediction of undersaturated densities of bitumen with five different liquid solvents. Solubility was then matched with experimental data by fitting BIPs using the developed correlations for *n*-alkane systems [206]. The Expanded Fluid Viscosity model [229] uses density calculated by an EoS (i.e., sPC-SAFT in this case) as an input to calculate the viscosity of the system. Bitumen was characterized by one pseudo-component for the viscosity calculations. The results demonstrate capability of the sPC-SAFT for prediction of density and matching solubility of bitumen systems with AARD between the experimental and calculated values of the respective parameters equaling to 2.3% and 6.6%, respectively [228]. The Expanded Fluid Viscosity model, using densities from sPC-SAFT, calculated viscosities of Athabasca bitumen/C_1 mixture with AARD of up to 55.4%. Ma et al. [228] noted that the results can be further improved (AARD down to 13.5% for the bitumen/C_1 case) by matching the Expanded Fluid Viscosity model parameters to the experimental viscosity data of the modelled systems. The predictive viscosity calculation results for the Peace River were relatively better, with the AARD ranging between 11.9% and 24.9% for different solvents. The Expanded Fluid Viscosity model viscosities for the Peace River bitumen showed greater accuracy compared to viscosities calculated by the Arrhenius and Power Law correlations. Later, this characterization was applied to the model volumetric properties of bitumen/H_2 mixture [230] and multiphase boundaries between bitumen with C_1, C_2, and CO_2 [231].Other examples of PC-SAFT modeling of bitumen/solvent mixtures are reported by Tavakkoli et al. [62] and Zúniga-Hinojosa et al [117]. These studies were concerned with polydisperse modeling of asphaltene precipitation amount and mixture density (see section 4.7).

4.10. The effect of oil-based mud contamination

Oil-based mud is a drilling fluid that is used during drilling operations in clay rich formations that are sensitive to water (such as shale formations). Since such type of drilling fluid consists of hydrocarbons, they are miscible with crude oil. Such mixing is called oil-based mud (OBM) contamination. Laboratory samples can be contaminated with OBM and consequently cause wrong data interpretation [232]. The effect of OBM contamination on two deep water live oils was modeled by Gonzalez et al. [56]. As can be seen in Fig. 22, an increase in OBM contamination decreases the U-AOPs and BPs. In general, OBM is con-

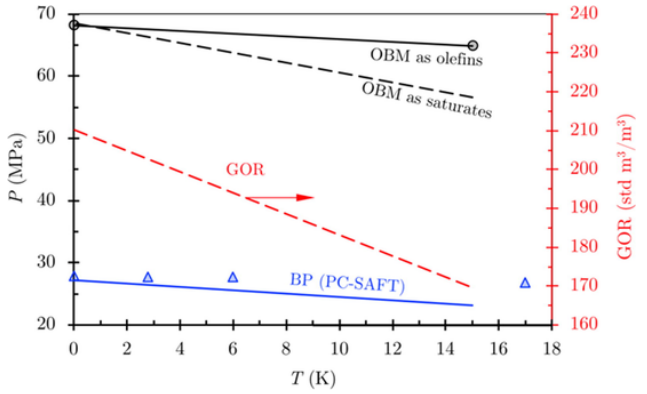

Fig. 22. The OBM contamination effect modeled by PC-SAFT. Modified after Gonzalez et al. [56], Copyright © 2007, American Chemical Society.

sidered as an asphaltene precipitant and addition of such agents should decrease the stability of the system. However, in the case shown in Fig. 22 the increase in the contamination leads to decrease in U-AOPs narrowing the pressure range at which asphaltenes exist as a separate phase. The addition of OBM decreased the concentration of light hydrocarbon components and, consequently, decreased the GOR. Since light hydrocarbons are strong asphaltene precipitants then, the effect of such dilution surpassed the effect of OBM and increased the stability of the system [232]. The U-AOP decrease with an increase in wt% of the contamination was possible to achieve with both options. However, representing the OBM contamination as a part of "Saturates" pseudo-component gave the best match with the experimental data [56].

5. Future perspectives of the PC-SAFT in asphaltene precipitation modeling

In this paper, we showed through an extensive and yet systematic and critical review of the relevant literature that modeling asphaltene phase behavior using the PC-SAFT EoS has seen extensive developments since its first appearance two decades ago. Modifications have been done to improve the existing models in terms of accuracy, reliability, and computational efficiency. Despite this, some areas are still dubious and remain unaddressed which can be further improved through conducting additional research. We highlight some of the areas of future research significance and interest in the text below:

- The temperature dependent deviations from experimental data, both low temperature and reverse behaviors, can be further investigated to generate a general framework for dealing with these problems. Some researchers consider deviations at low temperature as a drawback of the PC-SAFT EoS and have made several attempts to modify the EoS itself or the crude oil characterization procedure. Others relate these problems to the experimental procedures for the AOP determination due to lack of accuracy. Including the association term in models seems to be also a promising method in tackling such temperature-dependent deviations and can be further tested for different types of crudes.
- Several comparative studies have been analyzed. CPA EoS and PR EoS demonstrated that they can give similar (or better) results to the PC-SAFT EoS. Because the basis of CPA and PR is cubic EoS, they have an advantage over the PC-SAFT in terms of computational efforts efficiency. Nevertheless, the performance of these two EoSs varies for different crude oils and applied methods of modeling. A comparative study of optimal methods with a variety of crude types can facilitate the usage of all three models in both the petroleum industry and academia.
- The development of accurate correlations for BIPs for asphaltene-crude oil systems will be a valuable modification to the PC-SAFT modeling procedure. Such improvements have the potential to greatly simplify the modeling process and increase its accuracy, considerably.
- The PC-SAFT is computationally more demanding than other EoS types when modeling asphaltene phase behavior. Although several improvements have been done recently, there is still room for further improvements to its computation efficiency.

6. Closure

The PC-SAFT EoS is a variation of SAFT EoS that considers dispersive forces applied to chains of covalently-bonded hard spheres. Since its appearance two decades ago, it has been extensively applied in many fields of study. In this paper, we provided a systematic and critical review of the relevant high quality literature published on the application of this EoS in asphaltene phase behavior modeling. The following main aspects have been extensively discussed and highlighted:

- Several crude oil characterization methods have been reviewed and described including the SARA-based method that gained the most widespread usage in the literature. Correlations for the evaluation of PC-SAFT modeling parameters have been described.
- Several aspects of performance of the described models are discussed such as the effect of asphaltene polydispersity, pressure–temperature-composition changes, and binary interaction parameters. Recent developments in these directions have been systematically and critically reviewed.
- It was shown in the literature that some crudes have demonstrated an atypical temperature behavior, with U-AOP data points increasing linearly causing low temperature deviations of the PC-SAFT models or, in contrast, decreasing with respect to temperature. Such behaviors cannot be accurately modeled with a regular SARA-based method and original formulation of PC-SAFT and require either inclusion of an association term or a modification in characterization procedure or modification of the EoS itself.
- Accuracy of the PC-SAFT models is shown too dependent on the binary interaction parameter values between the components in a mixture. We reviewed several strategies that deal with this issue. There is still no general and reliable method for generating these parameters for such complex systems as asphaltenic crude oils.
- Polydispersity inclusion in the PC-SAFT model increases the accuracy of calculation of the amount of asphaltene precipitated. Evidences from the literature suggest that monodisperse modeling tends to overestimate the precipitation amount. However, polydispersity does not appreciably affect the estimation of the AOPs for which a monodisperse asphaltene model is satisfactory.
- Comparative studies between the PC-SAFT models and other EoS types were summarized and tabulated. The PC-SAFT is computationally more demanding than other thermodynamic asphaltene models. The CPA EoS seems to demonstrate comparable results with the PC-SAFT. However, the performance of all thermodynamic models highly depends on the problem formulation, modeling approach, and crude oil composition.
- Finally, some recommendations are provided here for future studies. We have noted that there is no general framework for dealing with temperature-dependent deviations of PC-SAFT models. The results from other EoSs seem also to highly vary depending on crude oil type and chosen method of modeling. A comparative study of different methods considering a greater variety of crudes is highly recommended. Development of reliable methods for generating suitable BIPs and improving computational efficiency of the PC-SAFT models are also highlighted as a possible area for further research.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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