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Modeling Asphaltene Precipitation in Algerian Oilfields with the CPA EoS

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Abstract

One of the major flow assurance problems afflicting the oil industry is the asphaltene precipitation during the production, transportation and storage of oil. The precipitation of these heavy compounds is responsible for changes in crude oil properties, increases in oil viscosity, and formation of deposits that reduce oil production and disable equipment leading to significant operational costs. In Algeria, the deposition of asphaltene in reservoirs and pipelines is a severe problem. During production the depressurization of reservoir fluid and the variations of thermodynamic conditions create the need to frequently pig the lines and, in some cases, to inject solvents and dispersants to maintain the production. The understanding of the asphaltene behavior and the prediction of its deposition in flow conditions is crucial to implement appropriate strategies for the prevention or remediation, especially in the wellbore region. In this work we used the CPA EoS to describe the asphaltene phase envelope and predict the PT regions of stability for five Algerian live oils. The model provides a very good description of the experimental behavior of live oils without and with gas injection. The sensitivity to SARA analysis data and its effect on the asphaltene phase boundaries were also analyzed.

Keywords: Asphaltene, Cubic Plus Association, equation of state, live oil.

1. Introduction

Asphaltenes are the heaviest constituents of crude oil and are considered a worldwide hazard for the oil industry. The first definition of asphaltene dates from 1837 when JB Boussingault created the term asphaltene to describe the solid, insoluble in alcohol and soluble in dark turpentine, obtained as a distillation residue of bitumen. According to the modern concept, asphaltenes are fractions defined as a solubility class of petroleum which are insoluble in paraffin with low molecular weight (n-heptane, n-pentane) but soluble in aromatic solvents such as toluene and benzene Herzog et al. (1988). Asphaltenes are aromatic-based hydrocarbons of amorphous structure that are present in crude oil in the form of dispersed colloidal particles. The central part of the asphaltene aggregates consists of a high molecular weight component surrounded and peptized by resins and smaller paraffinic hydrocarbons, which present hydrophilic properties when in presence of aromatics and resins Yen and Chilingarian (1994) According to Leontaritis and Mansoori (1987), asphaltenes are polar molecules bearing electrical charges which are involved in the structure of aggregates. Andersen and Speight (1993) also believe that the polarity of asphaltene plays a role in the formation of aggregates presenting a high molecular weight, and playing an important role in self-association and flocculation. Goual and Firouzabadi (2002) measured the polarity of asphaltene and resins for eight petroleum fluids, the dipole moment for resins and asphaltenes was found between (2.4 –3.2 D) and (3.3– 6.9 D) respectively. This high polarity is one of the main causes for the low solubility of asphaltenes in the oil. The molecular weight of these poly-dispersed mixtures of molecules varies depending on the different sources of crude oils and their compositions (Lobato et al., 2007). The asphaltene may also contain small amounts of heteroatoms such as oxygen, vanadium, sulfur and nitrogen (Zhang et al (2012). The metals found in the asphaltene fraction can cause irreversible deactivation of catalysts by depositing on their active sites Butz and Oelert (1995). Although these substances are often present in small quantities they can have a considerable influence on the physico-chemical properties of the crude oil. Their ability to flocculate, adsorb to surfaces and form solid deposits can cause problems during reservoir operation due to the evolution of thermodynamic conditions. Also, the asphaltene deposits can strongly modify the stability of asphaltene and relative permeability of the reservoir. Unstable asphaltenes flocculate, precipitate, and settle on the porous space of the reservoir, eventually leading to the blockage of the crude oil flow from the wells. Asphaltene deposition is not only observed during the operation of heavy oils with a high asphaltene content. These issues can also occur in oils with low asphaltene content (0.1

to 0.5%), as in the case of the Hassi Messaoud field of Algeria, particularly in zone I located in the western part of the field. Several oil wells were closed in this region because of this problem (Haskett and Tartera, 1965; Yonebayashi et al., 2011). Asphaltene precipitation does not only occur during the primary recovery. These problems also occur during the gas injection and the EOR due to the composition change in the fluid (Negahban et al., 2006; Sarma, 2003; Srivastava et al., 1999; Sunil et al., 2003). The risk of asphaltene precipitation due to the addition of light gases or nitrogen to live oils has been studied by many authors (Yonebayashi et al., 2011; Sunil et al., 2003; Negahban et al., 2006; Sarma, 2003; Srivastava et al., 1999).

Over the years, a considerable effort was made to understand the flocculation and precipitation of asphaltenes, and despite the wealth of knowledge on this subject, no general satisfactory explanation has emerged for the asphaltene deposition in oil wells. The main causes have not been fully understood until now, and due to the complex nature of crude oils the evaluation of the factors that affect the stability of this system is very difficult. Many studies were conducted to explain the chemical structure, the effect of the various parameters causing asphaltene flocculation and precipitation, as well as the mechanism causing their instability and precipitation in crude oil. The main factors that have been highlighted as responsible for asphaltene precipitation and flocculation are the composition of the crude oil, the nature of the resins present in the crude oil, the pressure, the temperature and the nature and quantity of the diluents (Goual and Firoozabadi, 2004; Hammami et al., 1998; Carnahan et al., 1999; Speight, 2014). Therefore, studies on the gas effect on asphaltene behavior and the risk of precipitation in flow conditions are important to optimize any gas injection project. Equations of state (EoS) like the Cubic-Plus-Association (CPA) and the Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) have been used by many researchers to model asphaltene precipitation for live oils with or without gas injection, using different approaches. Their applications and limitations to model the phase behavior of asphaltenes have been illustrated in many works (Alhammadi et al., 2015; Gonzalez et al., 2007; Panuganti et al., 2012; Ting et al., 2003; Arya et al., 2016)

Zhang et al. (2012) used both the CPA and PC-SAFT equations of state. In the CPA case, they used an approach where both the asphaltene and the resins are considered as self-associating compounds, while with PC-SAFT they used the modeling approach from Gonzalez et al. (2005), which does not consider association for any of these molecules. The authors concluded that their CPA approach presented better results than those obtained with PC-SAFT. Al Hammadi et al. (2015) also compared this CPA approach and the PC-SAFT

form Panuganti et al. (2012) concluding that the PC-SAFT approach, without considering asphaltene as an associating compound, is more accurate than the CPA approach of Zhang et al. (2012). However, their analysis was only conducted for one type of fluid.

In the work of Arya et al. (2016). Three different modeling approaches were compared based on these equations of state. It was shown that the PC-SAFT without the association term was unable to correlate the phase boundary of asphaltene for some specific cases, in agreement with the results reported by Panuganti et al. (2012). However, the PC-SAFT with the association term was able to correlate the upper onset pressure for all the fluids. The most important observation from their work is the temperature dependency of the model, which may lead to unreliable modeling results outside the experimental temperature range.

Classic cubic equations of state, such as PR and SRK, have been used to correlate the onset precipitation pressures and compared against associating models like CPA and PC-SAFT. Shirani et al. (2012) compare both the PR and SRK EoS as a physical part in addition to an association part as a modeling approach based on the CPA EoS. Based on the data for the live oils studied, they conclude that the SRK EoS is better than the PR. Pederen and Christenen, (2007) also studied live oils with the SRK/PR EoS and concluded that the models can correlate the asphaltene phase boundary after tuning critical pressure and temperature of asphaltene component. However, the effect of gas injection on the asphaltene phase boundary were not studied. Also the work conducted by Jamaluddin et al. (2002) on two live oils concluded that the SRK EoS could correlate asphaltene upper onset pressure boundary by tuning the model parameters. Again, the effect of gas injection on the asphaltene phase boundary was not studied. The PR EoS was used by Sabbagh et al. (2006) to study asphaltene yield from the heavy oil. It was concluded that the PR model was not an universal predictor and it was not better than the previously developed regular solution model.

Thermodynamic models are important tools for the development and optimization of processes. They can be used to characterize and predict the phase equilibria of reservoir fluids, helping in the development of strategies for producing and managing a reservoir. PVT properties are also crucial in reservoir and production computations, namely for material balance calculations, determinations of oil and gas reserves and the amount of gas that can be recovered. Finally, to forecast the deposition tendency of precipitated asphaltene particles and to obtain a profile of deposited asphaltenes using deposition simulators, it is essential to perform a characterization of the live oil in order to obtain an adequate thermodynamic model that describes the phase behavior of asphaltenes in the live oil.

The objective of the present study is to test the accuracy of the CPA EoS to predict the asphaltene phase behavior and PVT properties from Algerian live oils. Five crude oils are here studied with the CPA EoS. The results of the modeling approach using the CPA EoS are compared with the experimental data of the five oil samples that belong to the HMD field and the RAMA field. The effect of gas injection on asphaltene precipitation is also studied.

2. CPA EOS

In the recent years, the CPA equation has been applied to the description of complex systems such as the phase equilibria of mixtures containing water, alcohols, organics solids and hydrocarbons Kontogeorgis and Folas (2010). The CPA EoS combines the conventional Soave-Redlich-Kwong term with the Wertheim association term applied in SAFT Zhang et al. (2012). For the first time, Edmonds et al. (1999) applied the CPA EoS for asphaltene precipitation, from crude oils. The asphaltene model, based on the CPA EoS, integrated in the commercial software Multiflash is a thermodynamic model capable of an efficient description of the association of asphaltene molecules and different fractions of crude oil (“MULTIFLASH, Version 6.1,” 2015). When considering mixtures, the CPA equation of state can be described, in terms of pressure, as presented in equation (1)

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2} \frac{RT}{V_m} \left(1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (1)$$

With

$$a(T) = \sum_i \sum_j x_i x_j a_{ij}(T) \quad (2)$$

$$a_{ij}(T) = \sqrt{a_i(T) a_j(T)} (1 - k_{ij}) \quad (3)$$

Where P , T and $\rho = (1/V_m)$ are the pressure, temperature and the molar density, respectively.

X_{A_i} represents the fraction of sites A on molecule i that do not form bonds with other active sites.

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (4)$$

This value is related to the strength of association ($\Delta^{A_i B_j}$) given by:

$$\Delta^{A_i B_j} = g(\rho) \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (5)$$

In the expression of the association strength ($\Delta^{A_i B_j}$), the parameters $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are referred to as the association energy and the association volume, respectively. These two parameters are only used for associating components. The CPA-EoS requires at least five parameters for each self-associating component.

The radial distribution function is given by:

$$g(\rho) = \frac{1}{1 - 1.9\eta}, \quad \eta = \frac{1}{4} b \rho, \quad b_{ij} = \frac{b_i + b_j}{2} \quad (6)$$

The energy parameter of the cubic term of the EOS is given by

$$a(T) = a_0 (1 + c_1 (1 - \sqrt{T_r}))^2$$

The van der Waals one fluid mixing rules were applied to calculate the parameters for the mixture

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (7)$$

$$b = \sum_i x_i b_i \quad (8)$$

The k_{ij} is the interaction parameter for the energy of the cubic term.

3. Fluid characterization using the CPA model

The crude oil is composed of numerous types of hydrocarbon compounds. According to classic liquid chromatography, they can be subdivided on saturates, aromatics, resins and asphaltenes. Compared to the other crude oil components, the asphaltenes are the heaviest fraction and that with the highest degree of aromaticity. In this work, the modeling approach proposed by Zhang et al. (2012) is applied. The CPA asphaltene model used can handle all the phases, the gas, the liquid and the asphaltene phase. The mechanism behind the asphaltene precipitation considered in the modelling is that asphaltene are monomers supposed to be dissolved in the oil.

The asphaltene phase is modeled as a liquid phase Zhang et al. (2012) and asphaltenes are considered as self-associating compounds. The energy and volume of association for the asphaltene are fixed as $\epsilon^{asp-asp} / R = 3000 \text{ K}$ and $\beta^{asp-asp} = 0.05$ respectively and the two cross associating parameters are optimized from the measured asphaltene onset data, at least at two different temperatures. The properties of asphaltene are based on its solubility parameters ranging from 18.2 to 20.7 Zhang et al. (2012) and the asphaltene critical parameters (P_c , T_c) and the acentric factor [(T_c (K) = 1040, P_c (bar) = 15.44, $\omega = 1.535$] are calculated from the Lee-Kesler correlations Kesler and Lee (1976). The molecular weight and specific gravity are determined from the Whiston table Whitson and Brulé (2000) .

In the present approach, the fluid characterization method most used in the oil industry is used to characterize the oil. The live oils are characterized by considering pure and pseudo-hydrocarbon components (C1, C2, ..., C7, C_{n+}). The heaviest fraction of the crude oil is split into pseudo-components and the number of pseudo-components and the physical properties of these fractions are calculated by the correlations of Lee-Kesler (Kesler, M.G; Lee, 1976) and Riazi (Riazi, M. R.; Al-Sahhaf, 1996) Zhang et al. (2012). Table 1 presents the compositions and properties of the crude oils studied in this work, and Table 2 shows a detailed characterization of Oil1 as an example. Here the pseudo-components start (saturated and aromatics) with C and the resins with R, the asphaltenes are the heaviest fraction followed by the resins considered as the second heaviest fraction.

Table 1

Properties of the five live oils used in this work

| Components | Oil1(wt%) | Oil2(wt%) | Oil3(wt%) | Oil4(wt%) | Oil5(wt%) |
|-------------------------------|-----------|-----------|-----------|-----------|-----------|
| N₂ | 1.77 | 1.61 | 1.76 | 1.62 | 0.90 |
| CO₂ | 1.40 | 2.07 | 2.02 | 1.99 | 0.00 |
| H₂S | 0.00 | 0.00 | 0.00 | 0.00 | 1.99 |
| C1 | 24.01 | 30.59 | 26.06 | 26.20 | 35.04 |
| C2 | 11.51 | 14.05 | 12.56 | 12.50 | 14.70 |
| C3 | 10.40 | 10.48 | 10.66 | 10.44 | 8.85 |
| i-C4 | 1.43 | 1.32 | 1.41 | 1.42 | 1.09 |
| n-C4 | 5.43 | 4.99 | 5.37 | 5.39 | 3.99 |
| i-C5 | 1.50 | 1.43 | 1.50 | 1.52 | 1.17 |
| n-C5 | 2.89 | 2.60 | 2.85 | 2.87 | 2.20 |
| C6 | 3.55 | 3.12 | 3.50 | 3.58 | 2.83 |
| Mcylo-C5 | 0.55 | 0.44 | 0.54 | 0.55 | 0.35 |
| Benzene | 0.71 | 0.68 | 0.34 | 0.34 | 0.43 |
| Cyclo-C6 | 0.52 | 0.45 | 0.40 | 0.40 | 0.39 |
| C7 | 2.93 | 2.32 | 3.14 | 3.13 | 2.38 |
| Mcylo-C6 | 0.96 | 0.80 | 0.81 | 0.81 | 0.69 |
| Toluene | 0.11 | 0.09 | 0.32 | 0.32 | 0.25 |
| C8 | 3.62 | 2.97 | 3.21 | 3.16 | 2.52 |
| C2-Benzene | 0.43 | 0.30 | 0.17 | 0.16 | 0.15 |
| mp-Xylene | 0.64 | 0.60 | 0.37 | 0.36 | 0.36 |
| o-Xylene | 0.15 | 0.13 | 0.18 | 0.18 | 0.12 |
| C9 | 2.55 | 2.04 | 2.68 | 2.67 | 2.08 |
| C10 | 3.31 | 2.62 | 2.97 | 2.95 | 2.57 |
| C11 | 2.54 | 2.00 | 2.31 | 2.30 | 2.00 |
| C12+ | 17.08 | 12.30 | 14.89 | 15.17 | 12.95 |
| MW of C12+ | 265.26 | 260.10 | 267.88 | 265.69 | 259.76 |
| SpG of C12+ | 0.862 | 0.860 | 0.864 | 0.863 | 0.862 |
| Asphalt content (wt %) | 0.11 | 0.05 | 0.5 | 0.4 | 0.5 |

Table 2

Physical Properties of the pure and the pseudo-component of Oil5 used in the CPA model

| Components | MW | SG | T_C (K) | P_C (Bar) | Acentric factor |
|---------------------------|-----------|-----------|-----------------------------|-------------------------------|------------------------|
| Nitrogen | 28.01 | 0.836 | 126.192 | 33.95 | 0.037 |
| CO₂ | 44.00 | 0.146 | 304.128 | 73.77 | 0.223 |
| Methane | 16.04 | 0.366 | 190.564 | 45.99 | 0.010 |
| Ethane | 30.07 | 0.515 | 305.33 | 48.71 | 0.099 |
| Propane | 44.09 | 0.562 | 369.85 | 42.47 | 0.152 |
| Isobutane | 58.12 | 0.583 | 407.85 | 36.40 | 0.184 |
| n-butane | 58.12 | 0.624 | 425.16 | 37.96 | 0.198 |
| Isopentane | 72.14 | 0.630 | 460.45 | 33.77 | 0.227 |
| n-pentane | 72.14 | 0.753 | 469.7 | 33.66 | 0.251 |
| Methylcyclopentane | 84.16 | 0.886 | 532.79 | 37.85 | 0.230 |
| Benzene | 78.11 | 0.782 | 562.16 | 48.98 | 0.208 |
| Cyclohexane | 84.16 | 0.774 | 553.56 | 40.7 | 0.209 |
| Methylcyclohexane | 98.18 | 0.870 | 572.19 | 34.71 | 0.234 |
| Toluene | 92.14 | 0.873 | 591.79 | 41.04 | 0.263 |
| Ethylbenzene | 106.16 | 0.864 | 617.2 | 36.06 | 0.302 |
| p-xylene | 106.16 | 0.867 | 616.2 | 35.11 | 0.318 |
| m-xylene | 106.16 | 0.883 | 617.05 | 35.35 | 0.323 |
| o-xylene | 106.16 | 0.766 | 630.3 | 37.3 | 0.308 |
| C6-13 | 123.00 | 0.76 | 600.09 | 26.19 | 0.423 |
| C14-18 | 220.36 | 0.84 | 733.27 | 17.26 | 0.701 |
| C19-23 | 289.37 | 0.870 | 795.44 | 13.83 | 0.872 |
| C24-26 | 350.41 | 0.89 | 837.93 | 11.76 | 0.999 |
| C27-29 | 390.66 | 0.90 | 861.65 | 10.71 | 1.070 |
| R29-47 | 480.34 | 0.91 | 904.19 | 8.95 | 1.203 |
| R47+ | 672.64 | 0.95 | 972.09 | 6.73 | 1.396 |
| Asphaltene | 672.88 | 1.035 | 1040 | 15.43 | 1.535 |

4. Results and discussion

4.1 Modeling reservoir fluids from literature

In order to evaluate the reliability of the model used in this work, six reservoir fluids from the literature are analyzed. The first reservoir fluids studied are from the work by (Buenrostro-Gonzalez et al. (2004)). The information regarding the composition of the reservoir oils, the amount of asphaltene in STO (stock tank oil), MW and SPG of the heaviest fraction are available in the article. These two fluids (fluid-C1 and fluid-Y3) were previously studied by Li and Firoozabadi (2010) and by Arya et al. (2015), both using the CPA EoS. Li and Firoozabadi (2010) provide a good description of the experimental data for both bubble point

and upper onset pressures. In the work of Arya et al. (2015), the CPA EoS was used to calculate the asphaltene precipitation envelope based on the SARA analysis, but applied a different approach than the one used in this work. As shown in Figure 1, the approach here used, based on the CPA EoS, is able to describe both the phase envelope and the bubble points. For both cases the present method calculates the same shape for the asphaltene envelope. However, in the case of fluid Y-3, a different behavior is obtained by both Arya et al. (2015) and Li and Firoozabadi (2010), where the upper onset pressure seems to be parallel to the saturation line at higher temperatures.

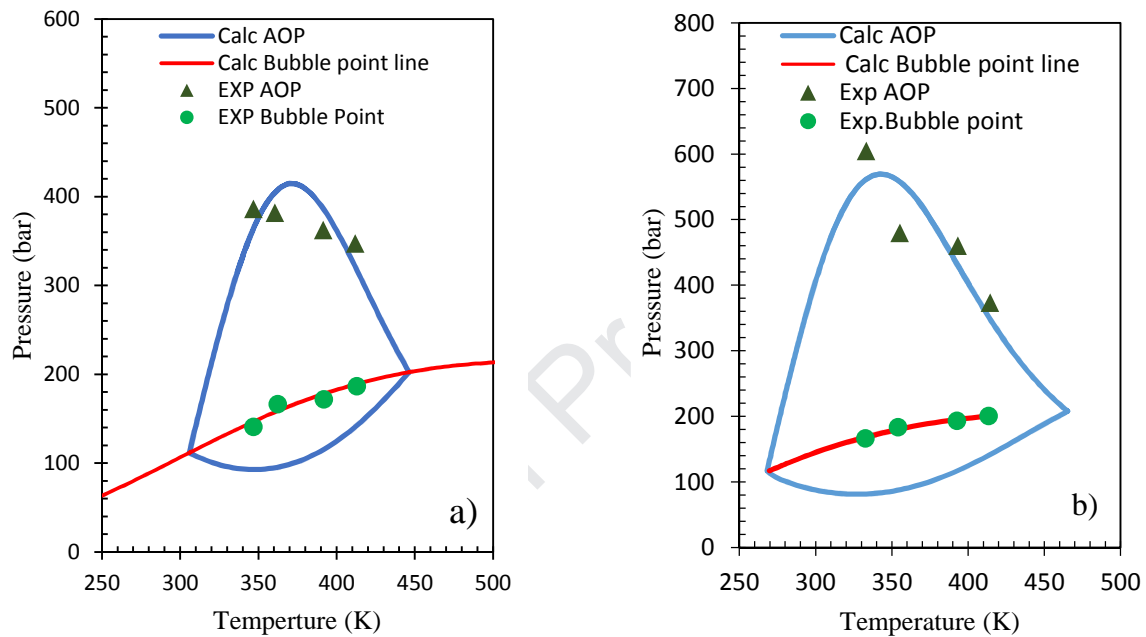


Fig. 1. Upper onset and bubble pressure boundaries for reservoir fluid without gas injection obtained by the Asphaltene CPA model. Plot (a) Fluid C1, Plot (b) Fluid Y3 Experimental data are from (Buenrostro-Gonzalez et al. (2004)). Symbols represent experimental data from Buenrostro-Gonzalez et al. (2004) and lines represent results calculated by the CPA model.

To check if the model is able to calculate the effect of gas injection on asphaltene precipitation, one reservoir fluid from Yonebayashi et al. (2011) was selected, this offshore carbonate field suffers from asphaltene deposition in the tubing of its wells. The experimental saturation points were not provided. The asphaltene onset pressure for the original reservoir fluid and for the cases with gas injection are presented in Figure 2. The composition of the injected gas is shown in Yonebayashi's paper Yonebayashi et al. (2011). As can be seen in Figure 2, the CPA results for the upper onset pressure are in good agreement with the experimental data. The results are similar to those of Zhang et al. (2012). with a maximum in

the upper and a concave shape, whereas those of Arya et al. (2016) do not show any maximum or concavity.

Three fluids from Punnapala and Vargas (2013) with different types and amounts of gas injection were also studied to show the reliability of the model. Model parameters were calculated by correlating experimental data for the case with a 5 mole % of gas injection, being the cases with 10, 15 and 30 mole % of gas injection calculated from these parameters, as it was applied in the approach by Arya et al. (2016). The compositions of the reservoir fluids and of the injected gas were taken from the work of Punnapala and Vargas (2013).

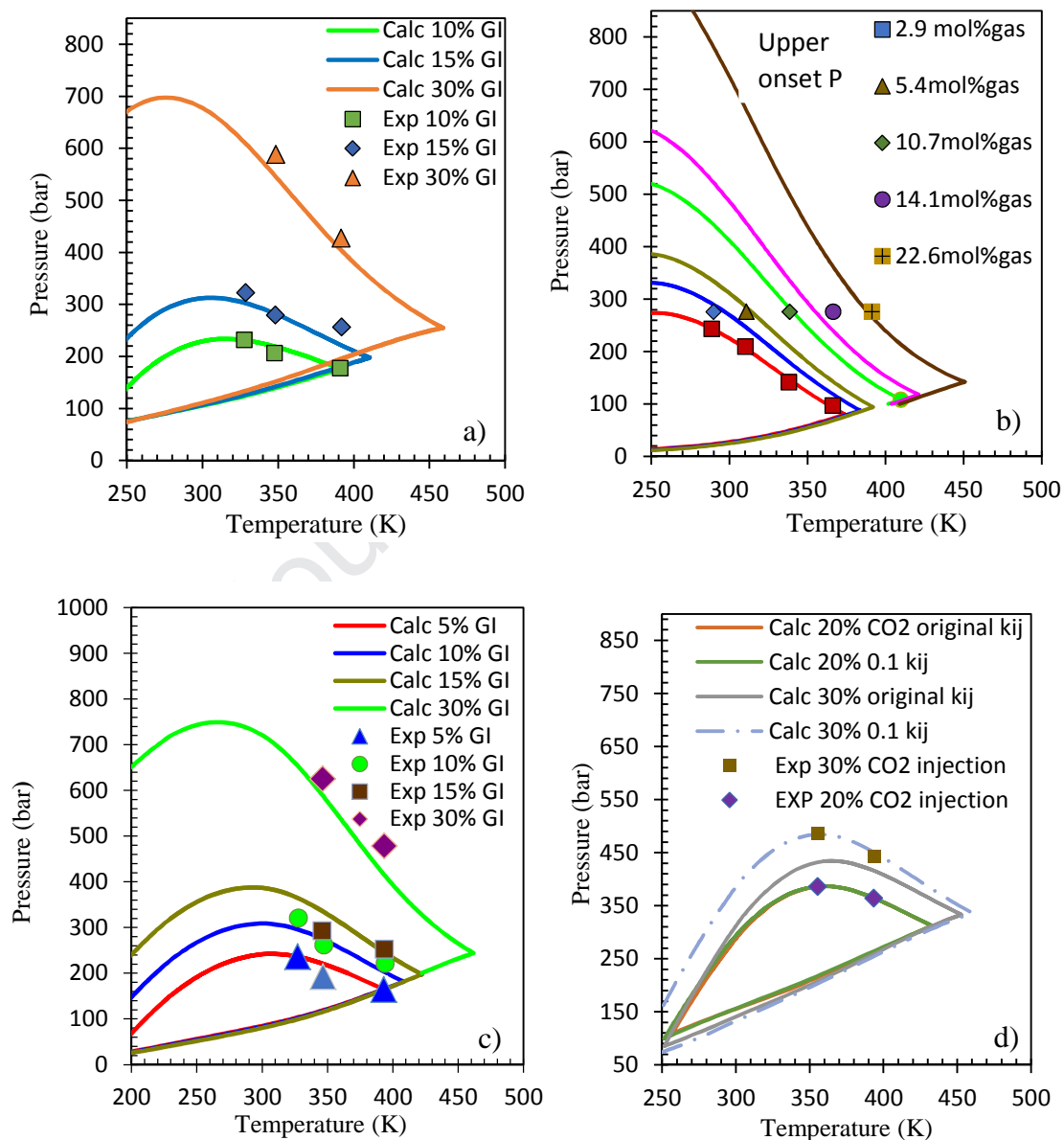


Fig. 2. UOP and bubble points vs temperature for different types of gas injections. Symbols represent experimental data. Plot (a) Lines for upper onset and bubble pressures calculated by the CPA model.

Plot (a) Fluid 1 from Punnapala and Vargas (2013) Plot (b): Experimental Data from Yonebayashi et al. (2011), Plot (c) : Fluid 2 from Punnapala and Vargas (2013), , Plot (d) : Fluid 4 from Punnapala and Vargas (2013).

In Figure 2, a), b), c), the capability of the CPA EoS to calculate the effect of gas injection in reservoir fluids Fluid1 and Fluid2, studied by Punnapala and Vargas (2013) and Arya et al. (2016), is evaluated. It is observed that the proposed approach provides an accurate description of the experimental results for the injections in the experimental temperature range. However, for the case of Fluid4, the model was only able to calculate the effect of 30 % of CO₂ injection after changing the k_{ij} of the Asphaltene-CO₂ pair to 0.1 as indicated in Figure 2d). This change does not affect significantly the results for the other wells, as the amount of CO₂ added is much lower.

The results for these fluids show the ability of the proposed approach to calculate the phase envelope and the asphaltene onset of precipitation for real reservoir fluids.

4.2 Asphaltene Precipitation on the HMD field

The Hassi-Messaoud field, particularly in zone I, exhibits asphaltene deposition problems in the pipelines of certain wells, over an interval of about 400 m, just below the segregated gas zone (gas cap) overlying the oil part. This zone is divided into three parts 1a), 1b) and 1c) and is located at the western periphery of the field, as presented in Figure 3.

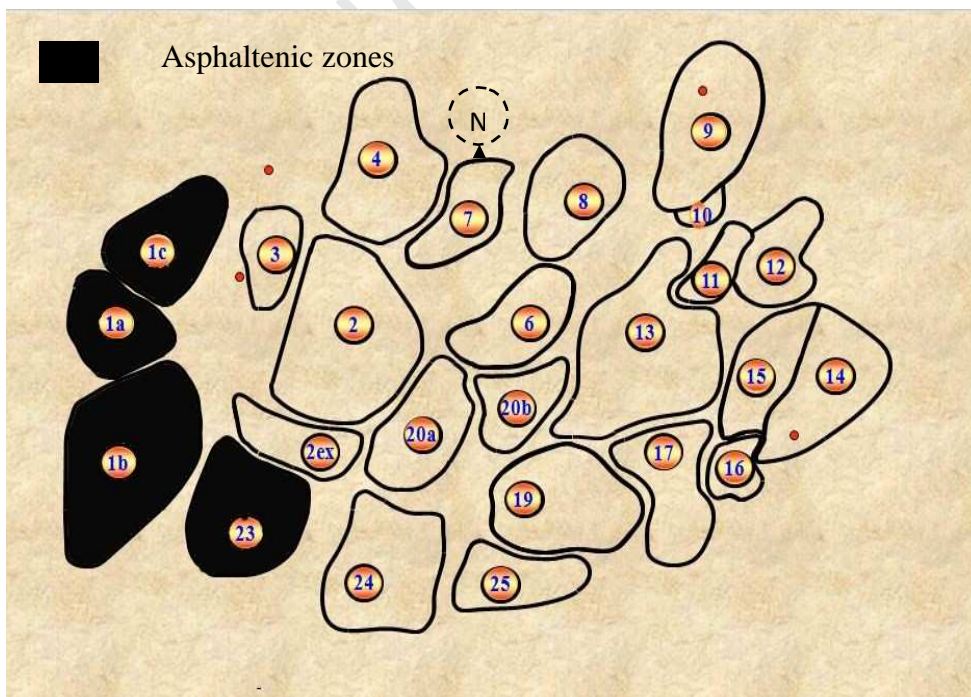


Fig. 3. View of Asphaltenic zones in HMD field

The oil of Hassi Messaoud is produced from the Cambro-Ordovician reservoir. The petrophysical characteristics are weak to mediocre, the producing reservoir is located at an average depth of 3300 m and the reservoir pressure varies between 300 and 400 bar. After several years of production, the reservoir pressure has decreased from about 300 to 160 kg/cm². The temperature is around 119 °C. The crude oil is an intermediate oil with 42.3 degrees API, extremely rich in gasoline. To maintain the layer pressure, most zones are under water and gas injection. The historical analysis of the behavior of the wells of this zone has shown asphaltene deposit problems since the beginning of the production of the field, on the tubing and especially in the upper reservoir. Ten to thirty months after starting in service, many producing wells, stopped production or, in the best case, suffered a significant decrease in their productivity. In addition to the inflow of water and the deposit of salts in some wells, this decrease in productivity index was also attributed to the deposit of an asphaltic substance in zone I between 1500 and 2500 m.

Asphaltene precipitation in Algerian oilfields is a pressure driven process and it is likely to happen around the saturation pressure. In the pipelines, when the pressure falls below the bubble point, the flocculation of asphaltene decreases. Algerian oilfields can be divided into three main categories: Oilfields with severe, mild or no asphaltene deposition problems.

To analyze the asphaltene precipitation risk the de Boer plot Boer et al. (1995) has been used as a preliminary evaluation of the risk induced by asphaltenes. It represents the difference between the reservoir pressure and the bubble pressure as function of the density of the reservoir fluid. The major risk is found for light oils, which is the case of HMD, as shown in Figure 4.

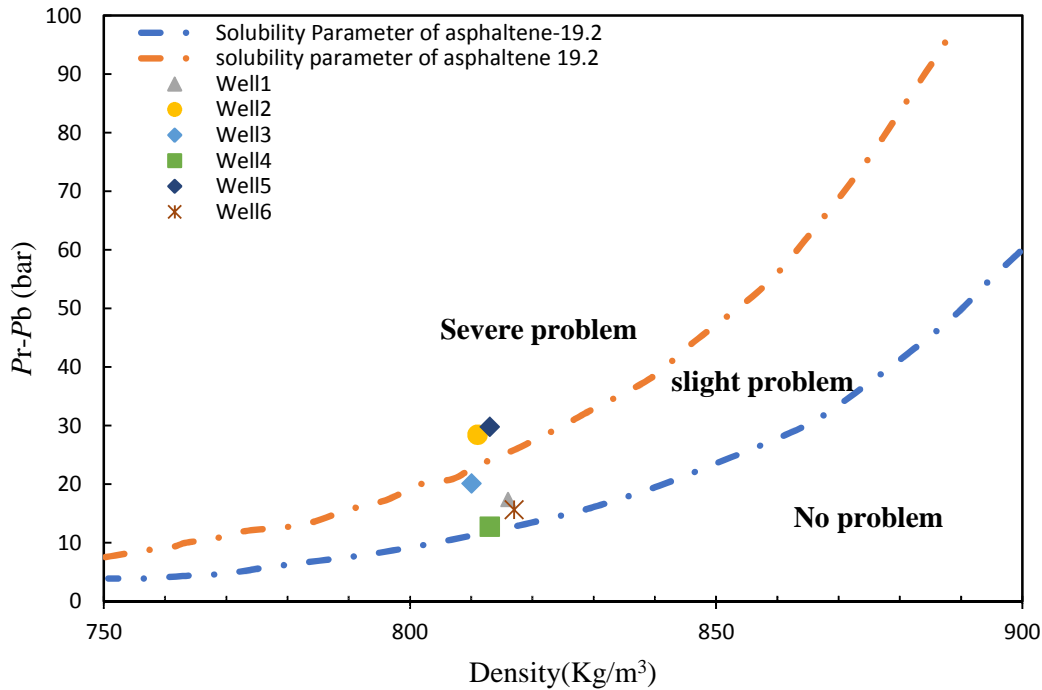


Fig. 4. Asphaltene-precipitation potential risk evaluated by the de Boer plot for the HMD field.

To overcome this issue, many remedial actions have been applied in the field, among these actions, mechanical scraping with the wire-line or performing coiled tubing to wash the well bore with aromatic solvent, and soak it in the formation, were tested. However, the problem was deemed severe, since these practices do not prevent or delay the asphaltene deposition in the affected area. For this reason, more complex studies have been conducted by oil companies for a better understanding of the phenomena of asphaltene precipitation in the field. The fluids from zone I of HMD exhibit asphaltene precipitation. The mechanism of flocculation and precipitation of asphaltenes is very complex and depends on several factors. From a practical point of view, the factors that could influence the deposition of asphaltenes in the HMD field can be cited in the order of greatest influence as: the evolution of thermodynamics conditions; the rate of filtration of the oil in the matrix; the influx of waters; the use of HCl during acidizing job in reservoir; injection of miscible gas and water. During the injection of natural gas or CO₂, the solubility of the oil is modified affecting the solubility of the asphaltene, which may lead to formation damage.

4.2.1 HMD Wells

Oil1 to Oil4 in Table 1 are live oils from the HMD field, zone 1b) with an average asphaltene content which varies from 0.05 to 0.5 wt %. Since the beginning of production life, an anomalous decline in production rate was observed. This decline was attributed to asphaltene

deposition in the near wellbore region and pipelines. Thus, a series of solvent injections operations have been made. To better understand and calculate the precipitation envelope and implement appropriate strategies for preventing asphaltene deposition, five bottom hole samples were analyzed and supplied by the operating company. The samples were scanned by near infrared (NIR). This enabled the detection of the formation of asphaltene during three different isothermal depressurizations tests and with the addition of a portion of gas in the range of operating conditions of interest. This gas is currently being injected back into the reservoir. The composition of the injected gas is shown in Table 3.

The compositions and properties of the five crude oils, such as the MW and specific gravity of the heaviest fractions, are presented in Table 1. The compositional data for the bottom hole sample given by the PVT report was determined by flashing the fluid at ambient conditions. For these wells compositional information for pure components up to C36+ and PVT experiments such as CCE and DLE are available. The measured asphaltene onset precipitation without and with the quantity of the gas added are presented in Table 4.

In all cases studied, the fluid analysis and characterization method applied were the same. The C6+ fraction is divided into 8 pseudo-components. The number of pseudo-components does not significantly affect the description of asphaltene precipitation with the present approach. The properties of the pseudo-components are adjusted to match the saturation points.

The main experimental data used in the present approach are the compositional analysis for the five live oils, the amount of asphaltene content in the stock tank and the experimental bubble point.

To establish an adequate model to assess the asphaltene precipitation conditions and the risk of deposition for the oil from the HMD field at the operating condition during production, the asphaltene phase boundaries were calculated using the asphaltene model from Multiflash. As can be seen from Figure 5 for the five live oils, the asphaltene upper and lower limits were established from the onset precipitation data. The calculated asphaltene phase boundary obtained with the CPA EoS is in a good agreement with the asphaltene onset data and the calculated phase envelope is closed along the bubble point. Moreover, the calculated AOP lines are bell-shaped (Figure 5) with a maximum pressure along the upper AOP line as presented in the work of Zhang (2012). This behavior was also observed for some fluids studied by Arya's using the CPA model Arya et al. (2015). The upper AOP line decreases with temperature after passing through a maximum, as is presented in a dashed line in the phase envelope from the five oils studied, and also observed in Zhang's work Zhang et al.,

(2012), it is probably not a real description of the behavior of asphaltene at lower temperatures, which would require further experimental confirmation of this behavior. To avoid the bell-shaped envelope reported above, we opted for a second approach that is similar to Arya et al. approach. Like in Arya's work, the modeling approach is simple and does not need to split the heaviest fraction into multiples components. Just three pseudo components including the asphaltene fraction are implemented in the characterization method. The asphaltene molecules are self-associating and the universal asphaltene-asphaltene parameters (energy = 3000 and volume $b = 0.05$ in the present work) should be optimized individually for each case in parallel with the cross-associating parameters to match the experimental points. The model will thus not be reduced to the two cross-associating between asphaltene and resin (as in Zhang et al) but will use a set of four associating parameters. This approach will allow the CPA model to give a good description over the entire temperature and pressure range of interest with the upper AOP increasing as the temperature decreases and therefore with no maximum in the upper onset curve as in the results reported above. Even in Arya's work there were maxima in the upper onset curve for some oils which lead to the conclusion that with the associating model (CPA and PC-SAFT), we should be careful about the predicted asphaltene behavior at lower temperatures and more experimental data for onset pressure to live oils are required to validate whether the asphaltene becomes stable or not at low temperature (which is probably not the case).

The Figures 5f) and 5g) below show the asphaltene phase boundaries for two oils (from the five oils studied) as an example using the two different approaches, the red lines represent the upper and lower limit for asphaltene precipitation with the modified approach and the blue lines represent the asphaltene phase boundaries from the Multiflash inbuilt CPA model.

This suggests that with the associating models the user should be aware about this particular behavior and be critical about the results predicted by the model at low temperatures. We can conclude that the CPA is able to correlate experimental data of the onset of precipitation after tuning a set of the associating parameters (self-association and cross-association) but there is still a poor understanding on whether the temperature dependent cross-association could have a physical meaning or not.

Table 3

Composition of the gas injected

| Component | wt% |
|-----------------------|------------|
| N₂ | 3.01 |
| CO₂ | 3.96 |
| H₂S | 0.00 |
| C1 | 52.66 |
| C2 | 24.06 |
| C3 | 9.16 |
| i-C4 | 0.97 |
| n-C4 | 2.85 |
| i-C5 | 0.65 |
| n-C5 | 0.98 |
| C6 | 0.72 |
| Mcyclo-C5 | 0.08 |
| Benzene | 0.06 |
| Cyclo-C6 | 0.05 |
| C7 | 0.35 |
| Mcyclo-C6 | 0.09 |
| Toluene | 0.03 |
| C8 | 0.16 |
| C2-Benzene | 0.01 |
| mp-Xylene | 0.01 |
| o-Xylene | 0.01 |
| C9 | 0.09 |
| C10 | 0.04 |
| C11 | 0.01 |
| C12 | 0.01 |

Table 4

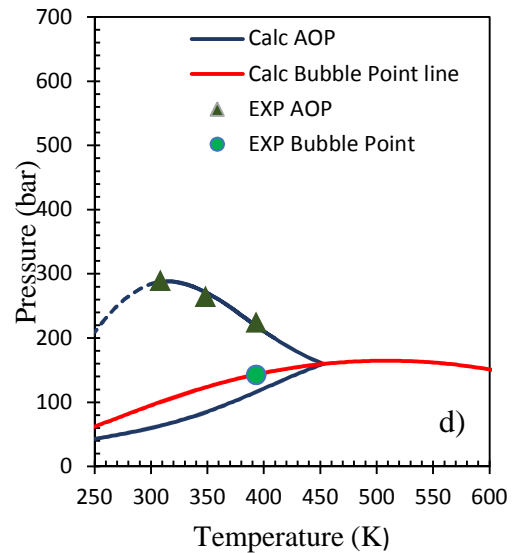
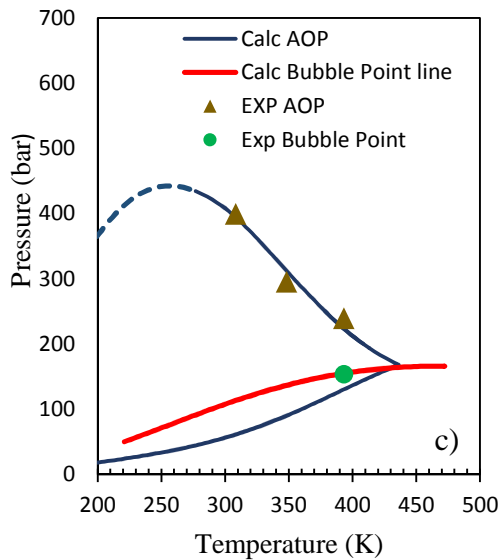
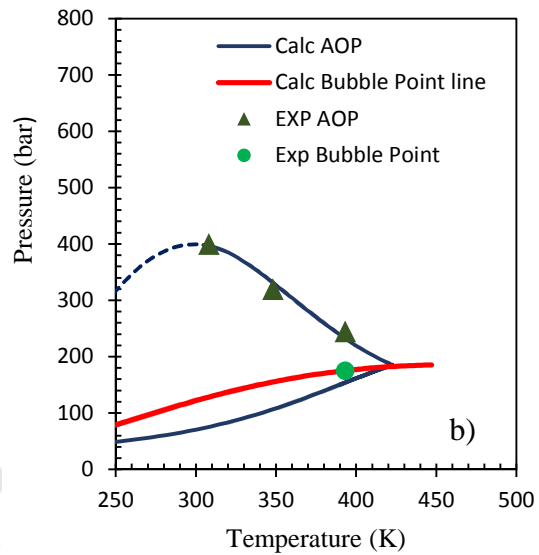
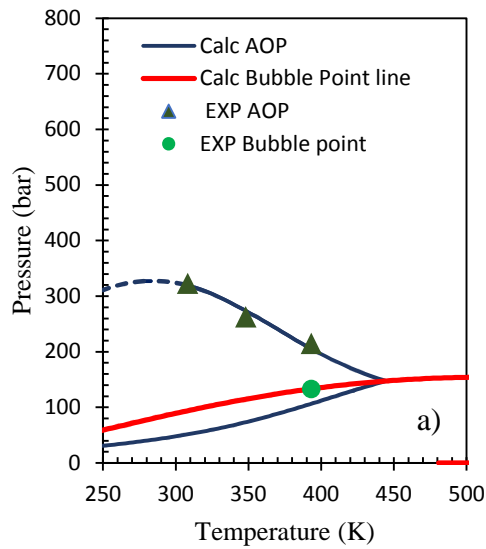
Measured AOP for the five oils without gas injection

| Oils | Oil1 | Oil2 | Oil3 | Oil4 | Oil5 |
|--|-------------|-------------|-------------|-------------|-------------|
| Bubble point at T_{res} | 132.5 | 175.2 | 154.0 | 142.5 | 253.4 |
| P _{AOP} at 120 °C bar | 215.0 | 245.0 | 240.0 | 225.0 | 288.2 |
| P _{AOP} at 75 °C bar | 263.0 | 320.0 | 296.0 | 265.0 | 352.8 |
| P _{AOP} at 35 °C bar | 323.0 | 400.0 | 400.0 | 290.0 | 384.4 |

Table 5

EXP data for AOP after gas injection

| Oils | | Oil1 | Oil2 | Oil3 | Oil4 | Oil5 |
|---------------------|--------|------|------|------|------|------|
| Mole % of Gas added | % mole | 1 | 2.0 | - | - | - |
| P_{AOP} at 120 °C | bar | 235 | 280 | - | - | - |



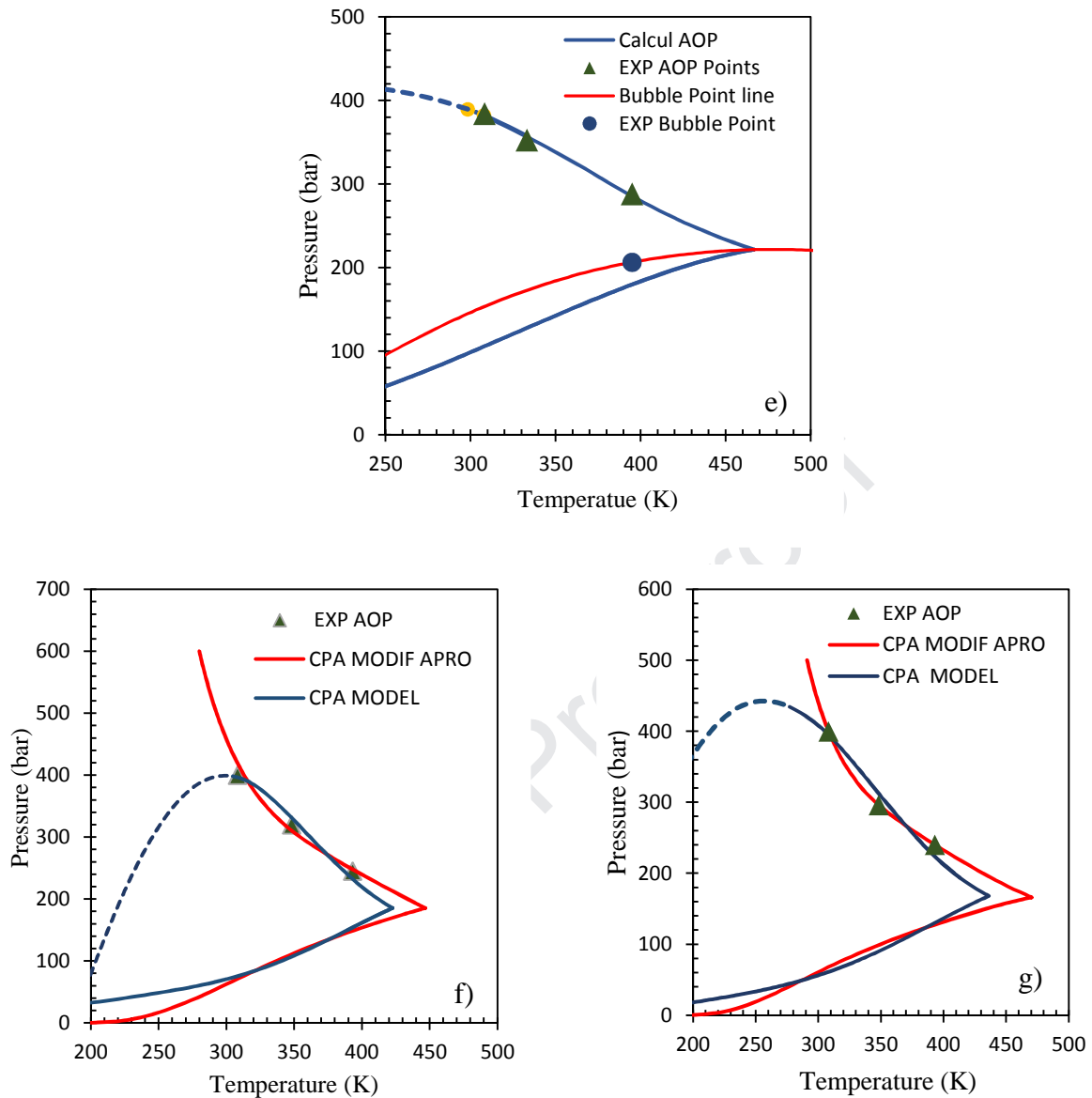


Fig. 5. Asphaltene phase boundaries of the reservoir fluids without gas injection, Plot (a) oil1, Plot (b) Oil2, Plot (c) Oil3, Plot (d) Oil4, Plot (e) Oil5. Solid lines calculated by CPA EoS, dashed line for the calculated bubble point line by the CPA. Symbols represent experimental data. Plot f) Oil2, Plot g) Oil3. Asphaltene phase boundaries using the two different approach.

In order to study the effect of gas on asphaltene, three isothermal depressurization tests (on each sample) to detect the formation of asphaltenes were carried out at the reservoir temperatures of 120°C, 75°C and 35°C. Each portion of sample was filtered prior to analysis and again thereafter. The apparatus was rinsed after each test with toluene. A portion from each well was also examined after approximately 1 or 2 mole % of gas was added. From the

experimental results, all wells indicated precipitation well above the saturation pressure and approaching the reservoir pressure as temperature decreased.

From the cases with gas injection presented in Figure 6, the asphaltene model calculate well the gas effect for Oil1 and Oil2. The 0 mole % injection case was used to calculate model parameters and then the 1 and 2 mole % of injected gas, were calculated using these parameters. As can be seen from Figure 6, a) and b), the model was able to calculate the gas injection effect in agreement with the experimental data.

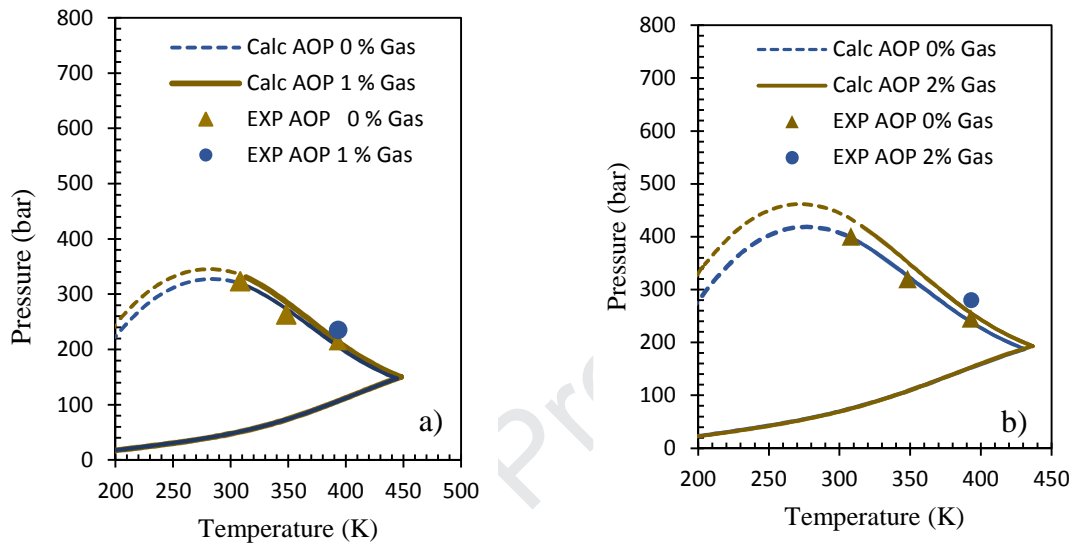


Fig. 6. Asphaltene phase boundaries of the reservoir fluid with gas injection, Plot (a) Oil1, Plot (b) Oil2. Solid lines results calculated the by CPA EoS. Symbols represents experimental data.

4.2.2 Sensitivity of the Asphaltene Phase boundaries to SARA Fractions

The SARA analysis is an indicator of the colloidal stability of asphaltenes in crude. It can vary depending on the analytical method applied. While Panuganti et al. (2012) have shown that the PC-SAFT without association needs an accurate value of SARA analysis, Arya et al. (2016) showed that the PC-SAFT with association and their CPA approach do not depend on the SARA analysis and that diverse sets of SARA values could result in the same phase envelope. In order to check the sensitivity of the approach here proposed on the SARA analysis, seven sets of SARA analysis were selected for Oil2, as shown in Table 7. On Figure 7, it is possible to observe that the CPA Model can calculate the experimental data of asphaltene precipitation without gas injection, the results do not differ much. However, there are concave upward and downward for the phase envelope, as we can see from the sensitivity analyses, the impact of R/A ratio is not significant and different sets of SARA could result in a similar asphaltene boundaries except for SARA5. The effect of asphaltene content could

influence the shape and the concavity of the phase envelope. As can be seen on Table 7, the associating parameters RAEXP (cross associating energy) and RAPREXP (volume of association) vary with the change of SARA fractions. From SARA3 to SARA5, the increase in the saturate with the decrease in R/A ratio increase the volume of association parameter (RAPREXP) from 2.95 to 7.95 and the cross energy associating parameter from 0.84 to 0.93 and in parallel for SARA6 and 7, the decrease in the saturate with R/A equal to SARA3 will increase the cross associating energy (RAEXP) with the same manner (from 0,84 to 0,93). This behavior was also reported by Arya et al. (2015) which attributed that the variation of the cross associating energy are a function of the variation of the SARA fractions and not random fitting values. From our sensitivity study, we can conclude that the approach presented here does not depend upon SARA analysis, only the asphaltene content used from the SARA analysis would affect the modelling results. However, the result in predicting injected gas and particularly at higher concentration could result in inaccurate calculation of the asphaltene phase behavior for different sets of SARA. Therefore, while characterizing a crude oil, care must be taken to fit the equation of state model to accurate data.

Table 7
Sensitivity analysis to different sets of SARA

| | Saturate (wt%) | Aromatic (wt%) | Resin (wt%) | Asphaltene (wt%) | RAPREXP (wt%) | RAEXP (wt%) |
|--------------|---------------------------|---------------------------|------------------------|-----------------------------|--------------------------|------------------------|
| SARA1 | 60 | 30 | 9,95 | 0,05 | 0,54 | 0,92 |
| SARA2 | 65 | 25 | 9,95 | 0,05 | 0,54 | 0,92 |
| SARA3 | 60 | 30 | 9 | 1 | 2,95 | 0,84 |
| SARA4 | 75 | 17 | 7 | 1 | 4,06 | 0,84 |
| SARA5 | 75 | 16 | 6 | 3 | 7,95 | 0,93 |
| SARA6 | 40 | 50 | 9 | 1 | 2,95 | 0,84 |
| SARA7 | 20 | 70 | 9 | 1 | 2,95 | 0,93 |

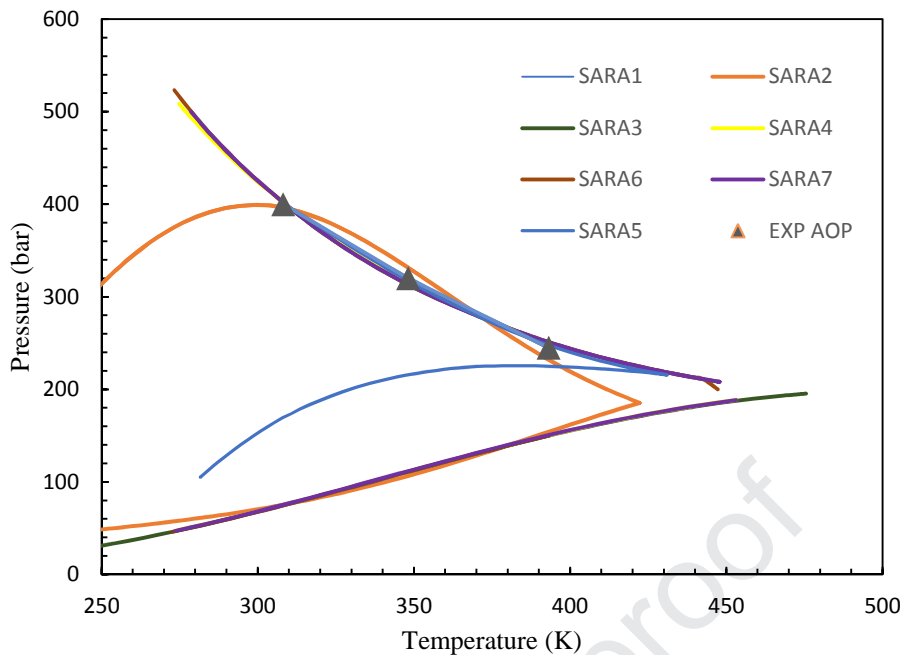


Fig. 7. Sensitivity analysis of Asphaltene phase boundaries based on SARA analysis for the cases without gas injection.

4.2.3 Well 05 (Rama field)

Oil5 from Table 2, is a bottom hole sample which has been taken from another field near HMD, 'RAMA' field. The reservoir studied suffered from asphaltene deposition problems in the earlier stage of the production. The oil is produced from the quartzite formation reservoir with an average reservoir pressure of 360 bars. The detailed analysis and the PVT experiments on the sample are provided in the supporting information, as well as the results obtained using CPA in a predictive manner. After fitting the EOS parameters, the phase behavior is determined, and the same set of parameters are used to predict others PVT properties. The results of the predicted PVT properties are presented in the supporting information.

4.3 Sensitivity Analysis for the Gas effect on the phase envelope

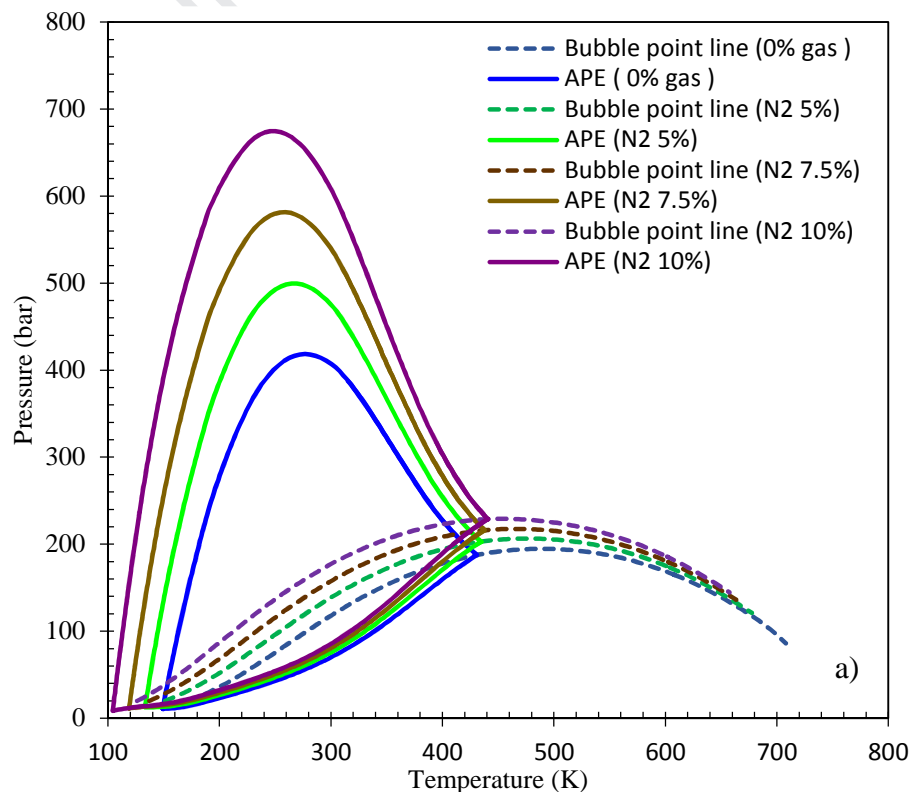
For any EOR project the study of the gas injection in the reservoir to enhance the production and recovery of oil is a challenge. This is due to the risk of asphaltene precipitation and the damage that could be induced by these molecules. Light gases like CO_2 , N_2 and methane can destabilize asphaltene molecules and lead to asphaltene deposition. Therefore, it is essential to

investigate the effect of gas injection on asphaltene precipitation and deposition before implementing any gas injection project.

In this section, the effect of adding N_2 , CO_2 or associated gas on the calculated asphaltene phase boundaries is analyzed for the case of Oil1. As can be observed on Figure 8b), the asphaltene phase envelope becomes larger with the increase in the amount of HC gas. This is attributed to the change of H:C ratio that lead to the reduction of asphaltene solubility in crude oil.

On Figures 8a) and 8c), it can be seen that the non-hydrocarbon gases, such as N_2 and CO_2 , have a larger influence on the asphaltene envelope, introducing a larger increase of the area of the diagram where there's risk of asphaltene precipitation. According to the results from the three figures, the N_2 is the strongest precipitant followed by the associated gas and lastly by CO_2 .

For the non HC gases, CO_2 and N_2 , the calculated results show that N_2 is unfavorable for the asphaltene stability, the increase of N_2 concentration, pushed the upper onset pressure more than CO_2 , even at higher concentrations. As reported by Gonzalez et al. (2008) for CO_2 above the crossover temperature the addition of CO_2 decreases the solubility parameter of the mixture and hence, favors the precipitation of asphaltene.



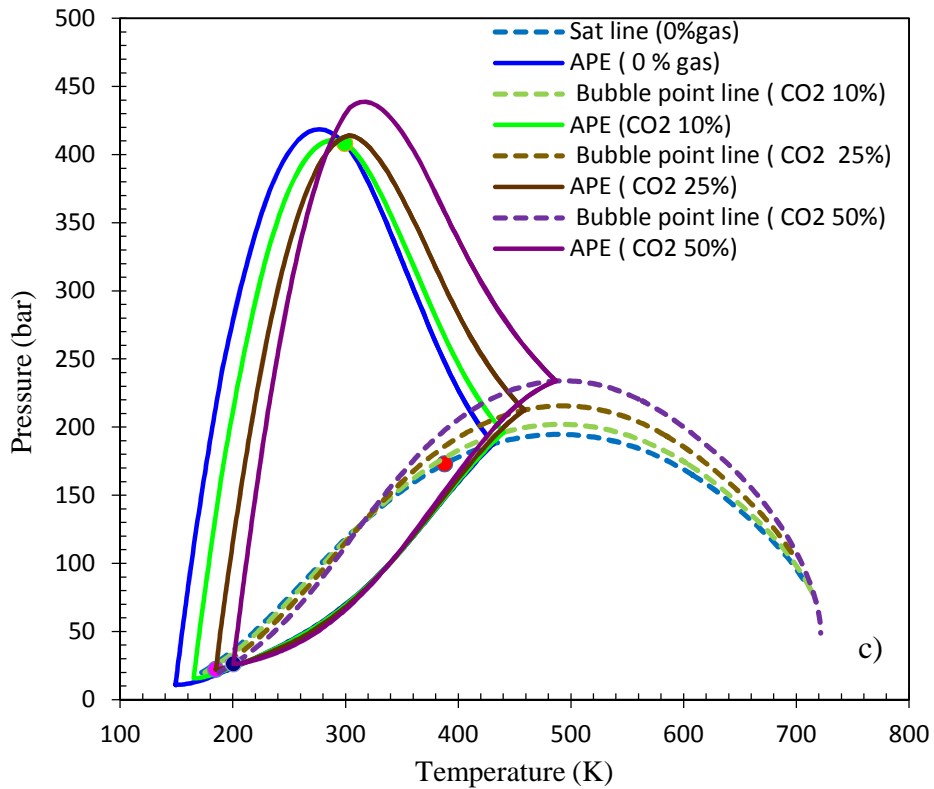
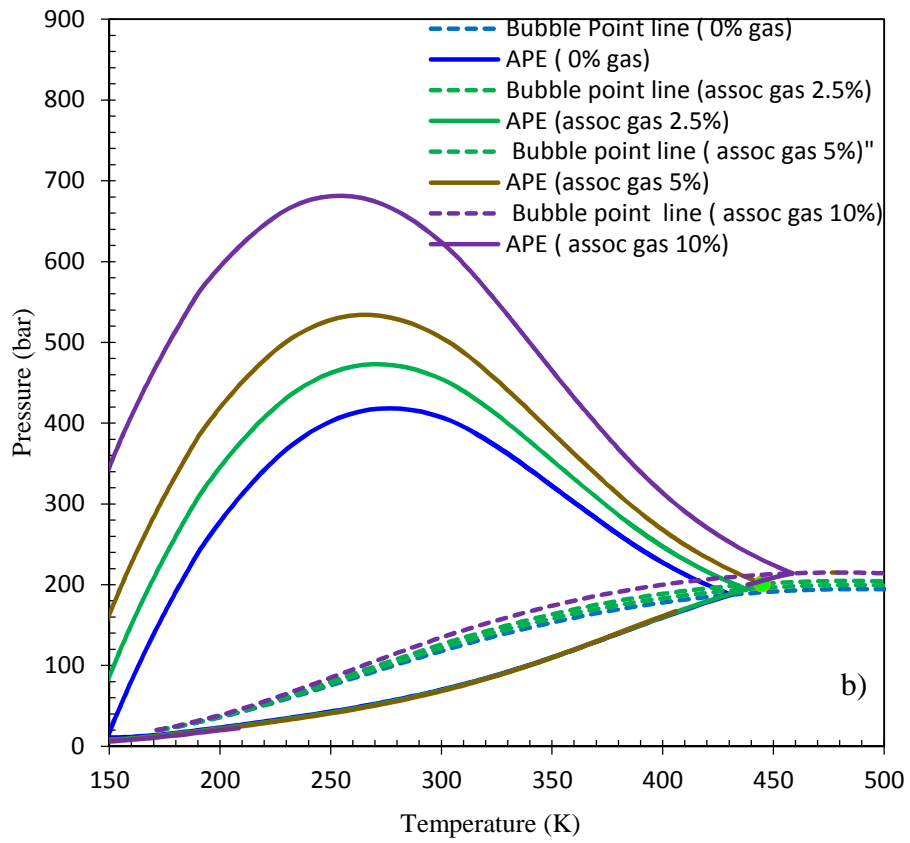


Fig. 8. a), b), c) effect of N₂, associated gas, CO₂ respectively on the asphaltene precipitation envelope (Oil1).

5. Conclusion

In this work, a comprehensive study of the CPA EoS to model asphaltene phase behavior for Algerian crudes is presented. The five oils studied showed the capability of the CPA-EoS based approach for the modeling of asphaltene phase boundary. As was demonstrated in the five cases, the CPA model is able to predict the asphaltene precipitation envelope for both the cases without and with gas injection.

For all the fluids studied, the CPA model accurately correlated the bubble pressure. The model is for the most part fairly insensitive to the SARA analysis and at least two experimental data points for asphaltene precipitation and one bubble point are required for an accurate description of the phase envelope and asphaltene onset of precipitation (AOP).

According to the sensitivity results for gas injection, show N₂ being a very strong precipitating agent. The CO₂ and the associated gas is also shown to increase asphaltene precipitation. However, for these gases the change on the asphaltene envelope is more gradual and is more acceptable in processual terms.

Flow-assurance calculations require more than a thermodynamic model for asphaltene precipitation; they also require a kinetic model to estimate the profile and rate of asphaltene deposition. Developing a physically realistic description of the kinetics of the asphaltene deposition process will be the subject of a future work.

Supporting information

Tables for the PVT experiments (CCE, DL, Viscosity) for Oil5, composition for the five reservoir oils studied and results for the predicted PVT properties using the CPA EoS and relative deviations from other associating based models.

Acknowledgments

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Nomenclature

$A(T)$ = energy parameter of CPA

k_{ij} = binary interaction parameter for the cubic energy term

P = Pressure (bar)

T = Temperature (K)

g = radial distribution function

R = universal gas constant

T_c, P_c = critical temperature, critical pressure

Tr = reduced temperature (T/T_c)

V = molar volume

x = mole fraction

X_i = mole fraction of sites of type i not bonded

Z = compressibility factor

Greek Symbols

β = association volume

Δ_{ij} = association strength between site i and site j

ε = association energy

ρ = molar density

Sub- and Superscripts

bub = value of the property on the bubble

i, j = pure component indices

exp, calc = experimental, calculated

assoc gas = associated gas

Abbreviations

ADE = Asphaltene Deposition envelope

AOP = Asphaltene onset Precipitation

CCE = Constant Composition Experiment

CPA = Cubic Plus Association

DL = Differential liberation

EMV = Electromagnetic Viscometer

EOR = Enhanced Oil recuperation

HMD = Hassi Messaoud

PC-SAFT = Perturbed Chain Statistical Fluid Association Theory

PVT = Pressure, Volume, Temperature

RAPREXP = Resin-Asphaltene pre-exponential

RAEXP = Resin-Asphaltene exponential

SARA = Saturate, Aromatic, Resin, Asphaltene

SRK= Soave-Redlich-Kwong

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Highlights

The CPA-EoS based approach described correctly the asphaltene behavior.

Correct description of phase envelopes and stability regions of Algerian crude oils.

The sensitivity of the model to the SARA analysis is studied.

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Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: