



Thermodynamic modeling of asphaltene phase behavior using PC-SAFT EoS with two different methods for asphaltene characterization

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Abstract

Asphaltene precipitation and deposition have always been a major issue in the oil industry. In this research, asphaltene precipitation in a live oil has been modeled using PC-SAFT EoS. Two different methods for characterization of asphaltene are employed and compared. The first method of characterization has been applied for modeling of the oil in previous researches. According to this method, aromaticity of aromatics + resins, aromaticity of asphaltene, as well as molecular weight of asphaltene should be tuned. But in the second method, molecular weight of asphaltene is considered fixed, and the number of adjustable parameters is reduced to two. Asphaltene onset pressure is predicted using both methods. The results obtained from the first method show better agreement to the experimental data, and its AAD is 12% to 40% less than method #2.

Keywords: Asphaltene precipitation, PC-SAFT EoS, Thermodynamic modeling, Characterization, Asphaltene onset pressure, Aromaticity, Asphaltene molecular weight, phase behavior

Introduction

Asphaltenes are a polydisperse mixture of the heaviest and the most polar fraction of crude oil [1]. The studies of asphaltene first started in the 1930s. They are defined based on their solubility that are completely miscible in aromatic solvents, such as benzene, toluene, and xylenes, but insoluble in light paraffinic solvents, such as, n-pentane and n-heptane [2]. Due to their tendency to precipitate and deposit, which decrease oil production efficiency, asphaltenes are known as “cholesterol of petroleum” [3].

One of the most challenging issues in the oil industry is to achieve a flow assurance program which ensures continuous and economic production of oil and gas. Modeling of asphaltene precipitation and deposition could reduce the inessential costs due to equipment installation and injection of asphaltene precipitation inhibitors [2].

Despite popularity and simplicity of usage of cubic equations of state (CEoS), these EoS did not have an accurate prediction in the case of asphaltene precipitation. Panuganti et al. [4] showed that the main defect of CEoS is their poor description of phase behavior of mixtures containing components with vastly different molecular sizes and inaccurate prediction of precipitated phase density.



Arya et al. (2015) [5], used CPA EoS to model asphaltene onset pressure and amount of precipitated asphaltene for eight live oils during N₂, CO₂ and CH₄ injection.

The perturbed chain form of the statistical associating fluid theory (PC-SAFT) is demonstrated that is capable to predict phase behavior of complex mixtures such asphaltene at high-pressure high-temperature conditions.

Punnapala and Vargas (2013) [6] presented a new characterization method for PC-SAFT EoS based on Gas Chromatography (GC) compositional analysis of dead oil. Asphaltene molecular weight, aromaticity of aromatics + resin and aromaticity of asphaltene pseudo components were three adjustable parameters of this model. Their model showed good agreement with respect to experimental asphaltene onset pressure and bubble pressure.

AlHammadi and AlBlooshi (2019) [7] compared two characterization method in predicting asphaltene precipitation using PC-SAFT EoS. They first modeled asphaltene onset pressure by standard characterization method and then considered asphaltene molecular weight as a function of temperature. Both methods showed good agreement with experimental data and the second one presented better match with respect to experimental data especially at low temperatures.

In order to reduce computation time, it has always been desirable to reduce the number of adjustable parameters. But sometimes reducing the number of adjustable parameters, increases the error significantly. In this research, asphaltene phase behavior of crude oil U8, which was modeled by Vargas and Tavakkoli [2] in previous researches, is remodeled by considering a fixed molecular weight for asphaltene and the results are compared to the Vargas and Tavakkoli work.

Thermodynamic model

Chapman et al. [8-10] presented SAFT EoS by applying Wertheim's perturbation theory and extending it to mixtures. Gross and Sadowski (2001) [11] applied perturbation theory for chain molecules and did some modification on SAFT EoS and introduced PC-SAFT EoS. In this EoS, compressibility factor is calculated by the following equation:

$$Z = 1 + Z^{hc} + Z^{disp} \quad (1)$$

In equation (1), Z^{hc} and Z^{disp} are the residual hard-chain contribution and the dispersion contribution to the compressibility factor, respectively. Detailed description of the EoS is available in Gross and Sadowski paper [11].

Oil characterization

Before modeling asphaltene phase behavior, the crude oil should be characterized as a number of pure or pseudo components. To do this, the flash gas is divided into seven components, including N₂, CO₂, H₂S, methane, ethane, propane, and heavy gas. Heavy gas includes all C₄₊ fractions, and its molecular weight is the molar average of molecular weight of gases heavier than propane. Also, stock tank oil (STO) is characterized by dividing it into three pseudo components, including saturates, aromatics + resin (A+R), and asphaltene. For this oil, the plus fraction is defined as C₁₀₊. The components which are reported in compositional analysis of STO are distributed according to their chemical structure into saturates, A+R, and asphaltene. Also, the plus fraction is divided into these three pseudo components such that the reported SARA analysis is satisfied. Molecular weights of saturates and A+R pseudo components are set such that overall molar mass of plus fraction is equal to the reported value. In this research, for characterization of asphaltene fraction, two methods are used, and the results are compared together. Method #1 is the procedure which Vargas and Tavakkoli [2]



have used. They have tuned the asphaltene molecular weight as an adjustable parameter. In method #2 a fixed molecular weight (1700 [12]) is considered for asphaltene.

Parameters of PC-SAFT EoS for pure components are reported in literature [11]. PC-SAFT parameters for pseudo components are obtained by the correlations [6], which are presented in table (1). In these correlations, M is molecular weight, and γ is aromaticity. Aromaticity determines the tendency of a pseudo-component to behave as a polynuclear aromatic (PNA) ($\gamma = 1$) or as a benzene derivative component ($\gamma = 0$) [13]. According to these correlations, if asphaltene molecular weight is considered as a tuning parameter, the model has three adjustable parameters, including aromaticity of aromatics + resins, aromaticity of asphaltene, and molecular weight of asphaltene. But if a fixed molecular weight is considered for asphaltene, the model only has two adjustable parameters. To tune these parameters, initially, PC-SAFT parameters for asphaltene are set as: $m = 33$, $\sigma = 4.3$ and $\varepsilon/k = 400$ [13], then aromaticity of aromatics + resins is adjusted to match experimental bubble pressure and density. In the next step, depending on the characterization method, aromaticity of asphaltene and molecular weight of asphaltene is tuned to match the given asphaltene onset pressure (AOP).

Table 1. Correlations for PC-SAFT parameters of heavy gas, saturates, aromatics + resins, and asphaltene [2]

Parameter	Heavy gas and Saturates	Aromatics + Resin, and Asphaltene
m	$0.0257M_i + 0.8444$	$(1-\gamma_i)(0.0257M_i + 0.8444) + \gamma_i(0.0101M_i + 1.7296)$
σ (Å)	$4.047 - \frac{4.8013lm(M_i)}{M_i}$	$(1-\gamma_i)\left(4.047 - \frac{4.8013lm(M_i)}{M_i}\right) + \gamma_i\left(4.6169 - \frac{93.98}{M_i}\right)$
ε/k (K)	$\exp\left(5.5769 - \frac{9.523}{M_i}\right)$	$(1-\gamma_i)\exp\left(5.5769 - \frac{9.523}{M_i}\right) + \gamma_i\left(508 - \frac{234100}{M_i^{1.5}}\right)$

In the experiments performed by Vargas and Tavakkoli [2], asphaltene onset pressures of crude oil U8 were measured for live oil and live oil + gas injection at different gas percentages. The properties of the reservoir oil and dead oil are shown in table (2).

As mentioned before, Vargas and Tavakkoli [2] adjusted asphaltene molecular weight. The final set of simulation parameters which are used by them are presented in table (3). Aromaticity of asphaltene is tuned to minimize the objective function which is presented in equation (2) by considering fixed molecular weight for asphaltene. In this equation, $P_{Onset}^{Exp.}$ and P_{Onset}^{Model} are experimental asphaltene onset pressure and predicted onset pressure by the model, respectively. The result of optimization is presented in table (4).

$$OF = \left(\left| \frac{P_{Onset}^{Exp.} - P_{Onset}^{Model}}{P_{Onset}^{Exp.}} \right| \right) \times 100\% \quad (2)$$

After obtaining the optimal values for the model's parameters, the oil characterization is complete.

The binary interaction parameters implemented for PC-SAFT modeling of the used live oil are reported in literature [2].



Table 2. Properties of crude oil U8 [2]

Reservoir fluid	
Reservoir temperature (K)	400
Bubble pressure at T ^{res} (MPa)	7.61
GOR (Sm ³ /m ³)	68.1
Molecular weight	130.4
Stock tank oil	
Saturates (wt %)	80.64
Aromatics (wt %)	17.44
Resins (wt %)	1.47
Asphaltene (wt %)	0.45
Molecular weight	195.5
Density (kg/m ³)	823.9

Table 3. Final set of simulation parameters for crude oil U8 in method #1 presented by Vargas and Tavakkoli [2]

Component	Molecular weight	Composition (mol %)	m	σ	ϵ/k	γ
N ₂	28.01	0.40	1.205	3.313	90.96	-
CO ₂	44.01	1.09	2.073	2.785	169.21	-
H ₂ S	34.08	0.69	1.652	3.074	227.34	-
Methane	16.04	19.06	1.000	3.704	150.03	-
Ethane	30.07	4.29	1.607	3.521	191.42	-
Propane	44.10	4.74	2.002	3.618	208.11	-
Heavy gas	71.78	10.32	2.689	3.761	231.42	0.000
Saturates	188.41	49.72	5.686	3.914	251.23	0.000
Aromatics + Resins	227.10	9.67	5.356	4.067	346.10	0.498
Asphaltene	6300	0.008298	125.74	4.254	356.45	0.380

Table 4. Simulation parameters for asphaltene in method #2

Component	Molecular weight	m	σ	ϵ/k	γ
Asphaltene	1700	26.544	4.4015	432.336	0.7010

Results and discussion

After obtaining the adjustable parameters of the model and characterizing the crude oil, the model must be validated. Vargas and Tavakkoli [2] reported asphaltene onset pressures at various temperatures as well as different concentrations of injected gas. Table (5) shows the injected gas composition. Asphaltene onset pressure is modeled by both characterization methods, and the results are presented in Figure (1). The absolute average deviations (AAD) between experimental and predicted data for both models are reported in table (6). According to the results, both methods could predict trends of experimental data, but method #1 has much more accuracy for the prediction of experimental data.

Table 5. The injected gas composition [2]

Component	Composition (mol %)
N ₂	0.83
CO ₂	4.96
H ₂ S	0.49
Methane	73.54
Ethane	11.34
Propane	5.19
Heavy gas	3.65



Table 6. The calculated AAD in asphaltene onset pressure using method #1 and method #2 for asphaltene characterization

Method	Live oil	Live oil + 10% gas injection	Live oil + 20% gas injection	Live oil + 30% gas injection
Method #1	0.57 %	8.18 %	4.18 %	0.52 %
Method #2	12.31 %	48.75 %	30.45 %	28.51 %

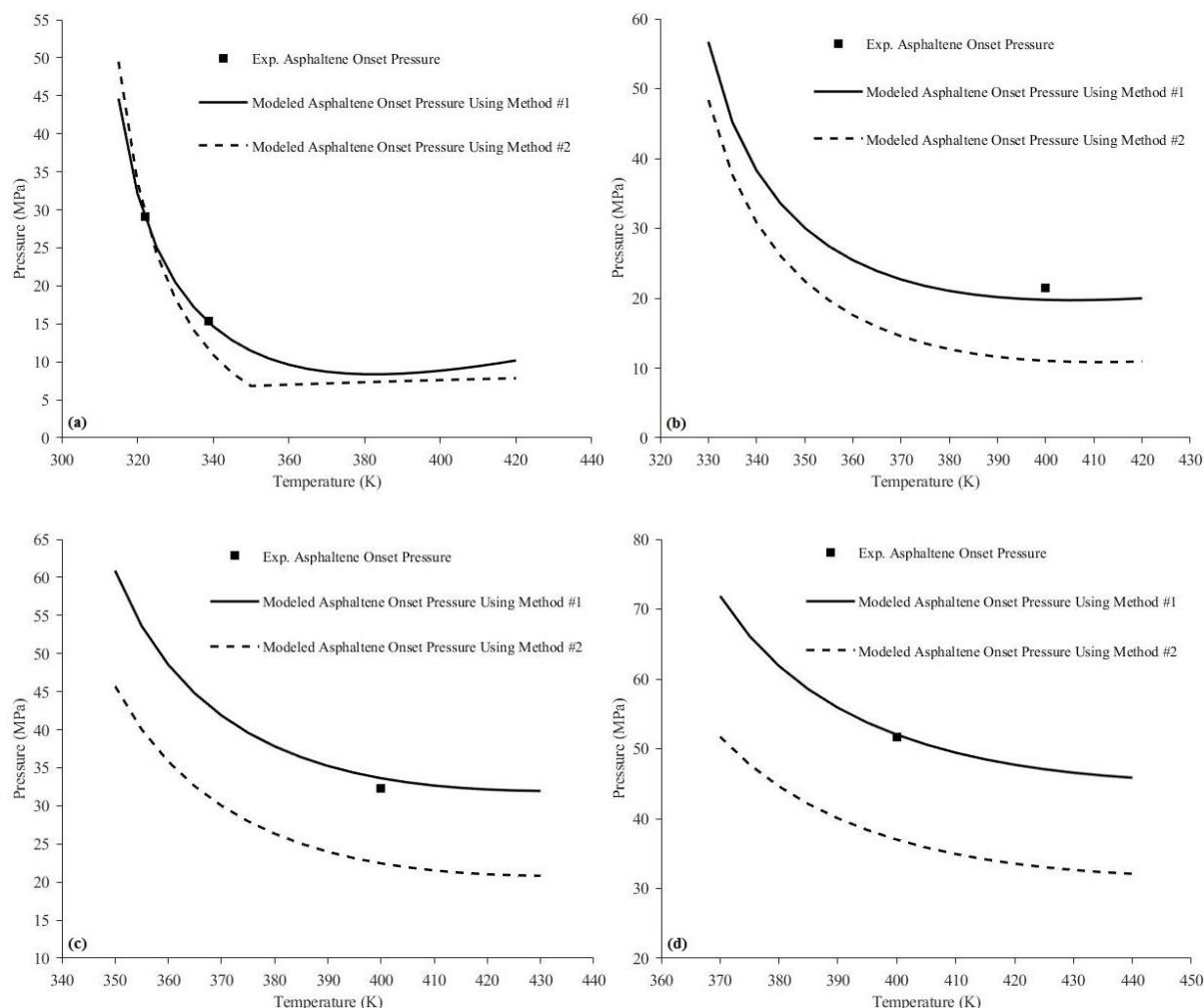


Figure 1. Comparing the predicted asphaltene onset pressure using Method #1 and Method #2 for asphaltene characterization for crude oil U8 (a) live oil, (b) Live oil + 10% gas injection, (c) Live oil + 20% gas injection, (d) Live oil + 30% gas injection with experimental data [2]

Conclusions

In this work, asphaltene phase behavior in a live oil was modeled using PC-SAFT EoS. In characterization of the oil, two different methods were compared. Method #1 was presented by Vargas and Tavakkoli [2]. In their implemented method three adjustable parameters including aromaticity of aromatics + resins, aromaticity of asphaltene and molecular weight of asphaltene were tuned. Since increasing the number of adjustable parameters increases the required time for tuning, the authors examined another method with less adjustable parameters. In method #2, the molecular weight of asphaltene was considered to be equal to 1700 constant and the two other parameters were adjusted. Asphaltene onset pressures for live oil and gas injection at 10%, 20% and 30% were computed using both models. Although



method #1 needed more computational time but its prediction results showed better agreement with respect to experimental data in comparison to method #2.

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