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Modelling asphaltene precipitation with solvent injection using cubic-PR solid model

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Cubic equation-of-state solid models are commonly-used to predict asphaltene precipitation behavior. Thermodynamic parameters are needed to model this behavior under different pressures and temperatures, and are usually obtained through fitting the model to multi asphaltene onset experiments. This paper introduces an empirical linear relation (tested on six oil samples) relating Asphaltene Onset Pressure (AOP) with injected solvent amount. In addition, waxes and aromatics correlations are utilized to obtain the thermodynamic parameters within the model. The two modifications decrease the number of tuning parameters of the model, as well as reduce the number of lab measurements needed to apply it. The model is tested on two oil samples, with previously published data, to predict AOPs. Using aromatics correlations provided more rational trends for AOP than waxes correlations. Besides, both correlations create a practical domain inside which the laboratory AOP values lie. The new additions enhance the prediction capabilities of the model in the lack of asphaltene experiments.

KEYWORDS
asphaltene onset pressure; asphaltene precipitation modelling; cubic equation of state; solid model; solvent injection

1. Introduction

Asphaltene(s) precipitation can affect all the components of the production system. A lot of Enhanced Oil Recovery (EOR) projects suffered from the asphaltene precipitation/deposition problem (Kokal and Sayegh 1995). Although adding an EOR solvent (changing the composition) could increase the possibility/amount of asphaltene precipitation; more of the precipitated asphaltene could re-dissolve again into the crude oil, depending on the conditions of pressure and temperature (Abedini et al. 2011). In a similar context, the aggregation of asphaltene particles comes as a middle step between asphaltene precipitation and deposition. The presence of a solvent affects the concentration of asphaltene in the mixture, which controls the mechanisms of the aggregation (Ashoori et al. 2009).

Several screening criteria are available to assess the severity of asphaltene precipitation for a certain crude before going into the experimentation or modeling (Shokrlu, Kharrat, and Ghazanfari 2011). If there is potential of asphaltene precipitation; special PVT experiments are performed to evaluate precipitation amount and conditions. These experiments necessitate specific setup and are, generally, more expensive than traditional PVT experiments (GeoMark 2013).

AOP is the pressure at which asphaltenes precipitation initiates, keeping temperature and composition constant. Figure 1 shows the Asphaltene-Precipitation-Envelope (APE) on a typical phase
AOP laboratory measurements are made at different temperatures, representing points lying on the upper asphaltene envelope. Other experiments seek to measure the amount of precipitate, usually in wt% of live oil, versus (vs.) pressure at constant temperature and composition. Solvent injection experiments are another set of experiments targeting to study the effect of injecting a solvent (e.g. CO₂) on precipitation behavior. This latter set is important to consider for preventing/reducing flow assurance problems during EOR processes.

2. Modelling approaches

The laboratory experimentation phase is usually followed by modeling to predict precipitation behavior at all conditions of production. Different approaches, with a significant number of models in each approach, have been proposed in the literature (K. S. Pedersen and Christensen 2007; Subramanian, Simon, and Sjöblom 2015). The thermodynamic approach is more common in modeling asphaltenes. Thermodynamic equilibrium calculations between all the components and/or pseudo-components of the system are performed to predict the phase behavior of oil at specified conditions. Equations of State (EOSs) models are one of the most common methods for thermodynamic modeling of asphaltenes. Statistical Associating Fluid Theory (SAFT) EOSs (Gonzalez et al. 2005; Panuganti et al. 2012), Cubic Plus Association (CPA) EOSs (Sabbagh et al. 2006; Shirani et al. 2012), and cubic EOSs (Nghiem et al. 1993; Kohse et al. 2000; K. S. Pedersen and Christensen 2007) are all methods belonging to the category of EOS modeling. Non-thermodynamic models exist as well. Rassamdana et al. (Rassamdana et al. 1996) proposed a scaling model to predict the quantity of asphaltene precipitation at different solvents injection and the onset conditions for precipitation. The scaling model was, afterwards, modified and compared with an artificial-intelligence model (Ashoori et al. 2010).

This study comprises the cubic EOS solid model, using Peng-Robinson (PR) EOS, to model onset precipitation conditions of asphaltenes. Researchers have reported different problems concerning this type of models. The problems include (1) less matching outside the tuned experimental range (Abouie, Darabi, and Sepehrnoori 2016); (2) needing more than one set of experiments to obtain parameters within the model (Jafari Behbahani et al. 2011); and (3) inconsistency resulting from manipulation of thermodynamic parameters (Abad 2013). The objectives of this study are to enhance the reliability of cubic-PR solid model of asphaltenes, decrease its dependence on experiments, and improve its predictability (especially with solvent injection).
3. Applied model procedures

3.1. Characterization and tuning

Splitting the reported plus fraction of the sample into Single Carbon Numbers (SCNs), assigning critical properties to the obtained SCNs, and lumping the pseudo-components are done following the methodology mentioned in (Nghiem et al. 1993; Nghiem and Coombe 1997; Tavakkoli et al. 2010).

Binary Interaction Coefficients (BICs) of hydrocarbon-hydrocarbon, excluding asphaltene-hydrocarbon, is given by the following formula (Li, Nghiem, and Siu 1985):

\[
\delta_{ij} = 1 - \left( \frac{2 \frac{\nu_i^c}{\nu_c^i} \frac{\nu_j^c}{\nu_c^j}}{\frac{\nu_i^c}{\nu_c^i} + \frac{\nu_j^c}{\nu_c^j}} \right)^e
\]

where \(e\) and \(\nu_c\) are tuning exponent parameter and critical volume, respectively. Asphaltene-hydrocarbon BICs are considered to have one value for the light components symbolized as \(\delta_{\text{asp}}\), and zero for all the heavy components.

Tuning usually involves precipitate wt% depletion experiments to ensure a consistent shape of precipitate vs. pressure (Kohse et al. 2000; Tavakkoli et al. 2014). In this paper, tuning is performed to match the saturation pressures and AOP experiments, with the target of obtaining an appropriate APE. The tuning parameters are the exponent parameter \(e\), asphaltene-light hydrocarbon BIC \(\delta_{\text{asp}}\), and asphaltene molar volume \(v_{\text{asp}}\). The tuned parameters are then used to predict AOPs at the experimental conditions, and hence checked with the actual measured values.

3.2. Model framework

The solid fugacity is estimated, at any pressure and temperature, from Eq. 2 (L. X. Nghiem et al. 1993; Nghiem and Coombe 1997; Kohse et al. 2000).

\[
\ln(f_s) = \ln(f^*_s) + \frac{v_{\text{asp}}}{R} \left[ \frac{P-P_{\text{atm}}}{T} - \frac{P^s-P_{\text{atm}}}{T^s} \right] - \frac{\Delta H_f}{R} \left[ \ln \left( \frac{T}{T^s} \right) - T \left( \frac{1}{T} - \frac{1}{T^s} \right) \right] - \frac{\Delta C_P}{R} \left[ \ln \left( \frac{T^s}{T} \right) - T^s \left( \frac{1}{T} - \frac{1}{T^s} \right) \right]
\]

Reference conditions are indicated by the superscript “*” (usually taken at one known onset condition). \(v_{\text{asp}}\) is the molar volume of asphaltene at reference conditions, \(R\) is the universal gas constant, and subscript “f” indicates atmospheric-fusion conditions. \(\Delta H_f\) is the enthalpy and \(\Delta C_P\) is the heat capacity difference between liquid and solid. AOP values at different conditions are obtained through Eq. 2. At onset conditions, the fugacity of the solid phase, assumed to contain only precipitated asphaltenes, should equal that of asphaltenes in the liquid phase. This is due to the fact that at onset conditions, the solid phase is just beginning to form. The liquid-phase fugacity is obtained from PR EOS (Peng and Robinson 1976).

3.3. Thermodynamic parameters

In the application of the model, the waxes correlation of fusion temperature (Eq. 3) is the only one that is really used. Enthalpy of fusion \(\Delta H_f\) and heat capacity difference \(\Delta C_P\) are used as matching parameters to adjust the APE using the measured AOPs (Long X. Nghiem et al. 2000; Kohse et al. 2000; Tavakkoli et al. 2014).

\[
T_f = 374.5 + 0.02617 \frac{MW}{MW_s} - \frac{20172}{MW_s}
\]

where \(MW\) is the molecular weight, and the subscript ‘s’ stands for solid (asphaltene).
3.4. Proposed modifications

The first proposed modification is to use several reference conditions (instead of just one) in case of solvent injection. This modification emerged from the fact that Eq. 2 models the change in fugacity with respect to pressure and temperature but not composition. This point was also mentioned in the work of Ebrahimi et al. (2016).

The reference fugacity is usually taken as the liquid fugacity at a known AOP. Therefore, in case of solvent injection experiments, a trend is needed between AOP and amount of injected solvent. This trend is then used to estimate the reference fugacity at any amount of injected solvent (at any composition). Heng et al. (2017) showed that the relationship between AOP and amount of injected solvent is linear. This observation was based on a single sample at three different temperatures. In this work, this relationship is further proved on another six oil samples (with already published laboratory values).

The linearity between AOP and solvent concentration is proven in the “Results” section. This linear relation can be expressed in the form of Eq. 4.

\[ \text{AOP} = A \ n + B \]  

where \( n \) is the mol% of injected solvent. \( A \) and \( B \) are empirical coefficients to be determined from the available solvent experiments. These two parameters depend on the oil, solvent, and fixed temperature; but not on the amount of injected solvent. To obtain the coefficients; a minimum of two AOP experiments, with at least one of them with injected solvent, is needed. After obtaining \( A \) and \( B \); Eq. 4 aids to obtain the reference pressure at any composition before substituting in Eq. 2. The relation is very useful in obtaining AOP at any solvent amount (assuming the linear relationship holds true for the solvent concentration range of interest). However, it cannot be used at more than one temperature.

Another modification is to calculate the thermodynamic parameters (\( T_f \) and \( \Delta H_f \)) using both the waxes correlations reported by Won (1986) and the aromatics correlations developed by Pan, Firoozabadi, and Fotland (1997), along with the \( \Delta C_p \) correlation developed by Pedersen, Skovborg, and Ronningsen (1991). The waxes correlation of enthalpy is listed as:

\[ \Delta H_f = 0.1426 \ \text{MW}_s \ T_f \]  

while the aromatics correlations are given by:

\[ T_f = 333.45 - 419 \ \exp (-0.00855\text{MW}_s) \]  

\[ \Delta H_f = 11.2 \ T_f \]  

and the heat capacity correlation is presented as:

\[ \Delta C_p = 0.3033 \ \text{MW}_s - 0.0004635 \ \text{MW}_s \ T \]  

The heat capacity difference correlation is the same for waxes and aromatics (Schlumberger 2009). The above modification facilitates the model concerning the quick calculation of the thermodynamic parameters for Eq. 2. Instead of fitting \( \Delta H_f \) and \( \Delta C_p \) on multi-AOP points; quick values can be estimated just after characterizing the sample.

4. Samples used in this study

4.1. Samples measured data

For proving the linear trend of AOP vs. injected solvent amount, six oil samples (whose data are listed in Table 1) are used. For the modeling part, the first two of the six samples were used.
Those were the samples with enough data to be utilized in the model. Table 2 shows the properties of the two samples used in the modeling study.

### 4.2. Modelled samples compositions

Since the composition, and hence the characterization, of the samples changes according to the amount of injected solvent; the characterization parameters (e.g. critical pressures, critical temperatures, …) are not constant for the samples. An example of the calculated parameters is given in Table 3 for Sample 2 at 0% solvent.
4.3. Model status of samples

In the utilization of the measured data within the model, the data is divided between tuning and prediction. Table 4 shows the status of the data of each sample whether it is taken into consideration while tuning the model parameters; or used to test the model predictions.

5. Results

5.1. AOP vs. injected solvent

Figure 2 shows the measured AOPs vs. injected solvent % for all six samples. It can be clearly seen from the figure that all samples exhibit linear relationship, taking the form of Eq. 4.

As it can be seen for Samples 1 and 6, the trends are all linear regardless of the temperature. Samples 5 and 6 exhibit an opposite, but still linear, trend. The reason behind this behavior is that the solvents used for both samples are actually asphaltene precipitation inhibitors. Both act to dissolve asphaltene, not to encourage its precipitation.

Based on the model status presented in Table 4, A and B coefficients of the samples are reported on Figure 3. For Sample 1, only the A and B coefficients of the 327.6-K temperature are used. The rest of the temperatures are obtained through running the model.
5.2 Model tuning results

Table 5 shows the tuning results of both saturation pressures and AOPs of the two modeled samples. Sample 1 tuned parameters using waxes correlations were \(e = 1.12\), \(d_{asp} = 0.18\), and \(v_{asp} = 0.986 \text{ m}^3/\text{kg-mole}\), and for aromatics correlations were \(e = 1.24\), \(d_{asp} = 0.27\), and \(v_{asp} = 0.986 \text{ m}^3/\text{kg-mole}\). Tuned bubble point pressures results are in very good agreement with measured values. The tuned results of AOPs using aromatics correlations are, in overall, closer to laboratory-
measured AOPs. In addition, using waxes correlations resulted in inconsistent tuned AOP values, where AOP appears to increase with temperature (at constant composition).

For Sample 2, the tuning results ($e = 1.98$, $\delta_{asp} = 0.29$, and $v_{asp} = 1.023 \text{ m}^3/\text{kg-mole}$) of bubble-point pressures is in an acceptable range with experimental values. Since the tuning procedure in the sample is isothermal; the type of thermodynamic correlations is irrelevant.

### 5.3. Model prediction results

Figure 4 presents the prediction results of Sample 1 at 30 mol% solvent (Left) and Sample 2 (Right). Both samples exhibit good agreement between the model and experimental values regarding the saturation pressures.

For Sample 1, the linear prediction of the 30 mol% solvent AOP at 327.6 K is very close to the measured AOP with an error of around 2.5%. This value is used in the model to predict the rest of values at different temperatures. The predicted AOP of the sample at 30 mol% solvent and $T > 347 \text{ K}$ temperature is unstable when using waxes correlations.

For Sample 2, the aromatics-correlations model shows a more proper upper APE trend than waxes. The modeling of pure oil AOPs includes using the AOP at 422 K as a reference for 0% solvent calculations. Both models (using aromatics correlations and/or waxes correlations) pass through this point. Two points were used in the tuning of the model for this sample. Then, the prediction of five points was performed.

### 6. Discussion

Actual AOP values usually fall between waxes’ and aromatics’ correlations model predictions. The predicted AOP results are sufficiently good when the empirical relation (Eq. 4) is used in modeling. It is best to include all available saturation pressure measurements (often available from the conventional PVT report) in the tuning process.

In solvent injection schemes, the composition changes cover a wide range, and it is difficult to cover the entire expected range with expensive experiments. The conventional approach needs one AOP point for every desired solvent concentration, in addition to two points at two different temperatures (and the same solvent concentration) for fitting the thermodynamic parameters ($\Delta H_f$ and $\Delta C_p$). The application of this modified model is valuable as it uses the minimum amount of data (only two points of AOP measurements, at one temperature, versus two different injected solvent amounts) to generate consistent and reliable results. The linear relationship (Eq. 4) and the thermodynamic correlations replace the needed extra measured points.

### 7. Conclusions
An enhanced PR-cubic solid model has been developed to model AOP. The improvement comes from two additions: (1) the incorporation of a relation to track compositional changes within the model, and (2) the use of both waxes and aromatics correlation in calculating the thermodynamic parameters.

Based on empirical observation, the relation between AOP and injected solvent mole% is linear. This relation can be used to improve the predictability of the current cubic-PR solid model with minimum laboratory experiments.

Using the aromatics correlations enhanced the experimental matching of the two samples tested in this study. The use of waxes correlations only may result in inconsistent trends of AOP.

The use of both aromatics and waxes correlations results in calculated AOPs that often bracket the laboratory measured AOPs.

Pure oil AOPs could be predicted from solvent injection AOPs, leading to valuable savings of additional expenses to perform pure oil AOP experiments.

The proposed modification of cubic-PR solid model can work with only two AOPs, with at least one with solvent injection, in order to model AOP at any composition and/or temperature.

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