Development of a Predictive Molecular Model for Abu Dhabi Crude Oils Phase Behavior

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Summary

A new approach based on the statistical associating fluid theory (SAFT) is presented here to model eight light crudes, with the SARA analysis as the only input for the model. Within the characterization procedure of Punnapala and Vargas (2013), the aromaticity parameter and the asphaltene molecular weight were fixed to all crude oil samples, while the asphaltene aromaticity is the only fitted parameter of the model. A correlation for this parameter with the flashed gas molecular weight allows full predictions of the phase behavior without the need of any asphaltene onset data. The predictive molecular model was used to study asphaltene instability as a function of injected CO_2 and natural gas concentration. The model can also accurately reproduce routine PVT experiments such as constant composition expansion, differential vaporization and multi-stage separation tests performed on the crude oils, thereby providing a unified framework for phase behavior studies.

Introduction

Asphaltenes are defined as fossil fuel derived constituents that are insoluble at ambient conditions in large excess of light hydrocarbons such as n-pentane and n-heptane and soluble in toluene. Their exact chemical structure vary from one crude oil to another, but in general, they are known to be the heaviest and the most polar fraction of crude oil consisting of polyaromatic molecules surrounded by aliphatic and heteroatomic chains.

Asphaltene deposition can occur during different stages of production and processing due to changes in pressure, temperature and composition. Oilfield reports indicate that asphaltene deposition in a well can lead to complete cease of fluid flow and production. Moreover, the cost of a typical asphaltene remediation job can get as high as $500,000 onshore or $3,000,000 offshore. Downstream wise, asphaltene deposition can cause fouling in rotating equipment and plug tubing and flow lines.

In this work, we report new asphaltene precipitation onset conditions and PVT properties for eight Abu Dhabi crude oils that were subjected to gas injection in lab. In addition, a predictive PC-SAFT model based on the characterization procedure of Punnapala and Vargas (2013) is developed here and used to predict the crude oils pressure-volume-temperature (PVT) properties and asphaltene phase behavior. Following Punnapala and Vargas (2013), no association forces are considered in this work, the implications of this assumption on the performance of the model will be seen when checking its predictive capabilities.

Molecular Theory

The SAFT equation of state models molecules as chains of spherical segments with long range dispersion interactions among them. An advantage of the model is that the contributions to the free energy are derived from statistical mechanics-based theory and validated versus molecular simulation results of the same underlying model. In addition, the structure of the molecules is built into the equation from its inception. Thus, the equation of state requires a minimal number of physical parameters that can be fit to pure fluid properties such as vapor pressure and saturated liquid density.

Similar to a cubic equation of state, the model requires only three pure-component parameters for the case of a non-associating fluid. Furthermore, these parameters have physical meaning and correlate well with molecular weight for a given homologous series. The complete equation of state in PC-SAFT, in terms of the reduced Helmholtz free energy, is given as the sum of an ideal gas contribution (a^{id}), a hard-sphere contribution (a^{hs}), a chain formation contribution (a^{hs}) and a dispersion contribution (a^{disp}). Additional terms are added in the case of polar compounds.

Following the latest characterization method proposed by Punnapala and Vargas (2013), hydrogen sulfide (H_2S), carbon dioxide (CO_2), nitrogen (N_2), methane (CH_4), ethane (C_2H_6) and propane (C_3H_8) are explicitly modeled within the SAFT framework. These components make up

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the flashed gas phase in addition to a pseudo-component named "heavy gas" to represent C_{4+} fractions found in the compositional analysis. The stock tank oil is composed of three pseudo-components namely: “saturates”, “aromatics + resins (A+R)” and “asphaltenes (Asphalt)” to represent different molecular structures found in the liquid phase. The SARA analysis is used to determine the composition of each of the pseudo-components. The molecular model requires three fitting parameters namely: the A+R aromaticity parameter (γ_{A+R}), the asphaltene aromaticity parameter ($\gamma_{Asphalt}$) and the asphaltene molecular weight ($MW_{Asphalt}$). These parameters were fitted to BP and AOP data in previous SAFT modeling works.

In this work, and seeking to develop a predictive molecular model for Abu Dhabi region crude oils, γ_{A+R} and $MW_{Asphalt}$ were fixed to 0.7 and 3000 g mol^{-1} respectively. The molecular weight of C_{11+} saturates was fixed to a value of 290 g mol^{-1} in this work and the corresponding molecular weight of C_{11+} A+R was then calculated based on the STO molecular weight. The one remaining asphaltene aromaticity parameter ($\gamma_{Asphalt}$) was fitted to AOP data at bottom hole temperature of 250/260ºF. However, it was found that the fitted $\gamma_{Asphalt}$ correlates well with the flashed gas molecular weight as shown in Fig. 1. The latter procedure not just reduces the number of fitting parameters to zero, but also allows the pure prediction of the behavior of crude oils with no experimental data.

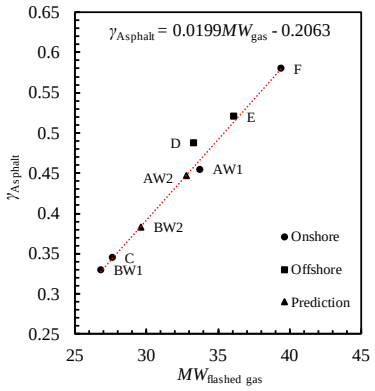

Fig. 1 Correlation of the asphaltene aromaticity parameter with the flashed gas molecular weight.

Results and Discussion

Asphaltene instability measurements were done for six crude oil samples at different flooding conditions and experimental data were used to fit the PC-SAFT model parameter ($\gamma_{Asphalt}$). Fig. 2 depicts asphaltene phase behavior at constant temperature for crude AW1 as a function of injected CO_2 concentration. Asphaltene instability occurs in the region found between the bubble (dashed) and the onset (solid) curves. It can be seen that increasing the amount of CO_2 injected widens the area in which asphaltene instability is expected to occur. Similar good agreement with experimental data was also achieved with the same γ_{A+R} and $MW_{Asphalt}$ values for other crude oils and are omitted here for the sake of brevity.

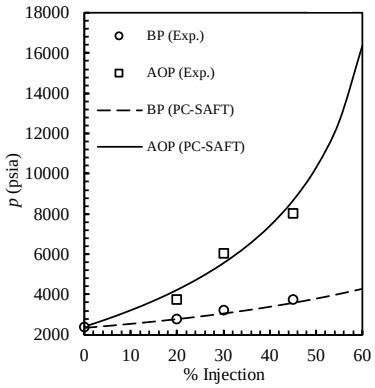

Fig. 2 Asphaltene instability as a function of injected CO_2 mass concentration for crude AW1 at 250ºF.

As shown in Fig. 1, the fitted $\gamma_{Asphalt}$ follow a linear correlation with the flashed gas molecular weight. It is worth noting that Fig. 1 represents data obtained from six different Abu Dhabi oil fields. Assuming that the correlation holds for other crude oil samples, $\gamma_{Asphalt}$ can now be estimated for cases where AOP data does not exist. Fig. 3 demonstrates results obtained for crude AW2 at 260ºF using this fully predictive approach. The latter approach can be applied to other Abu Dhabi oil fields, hence reducing the required experimental efforts and their expenses.

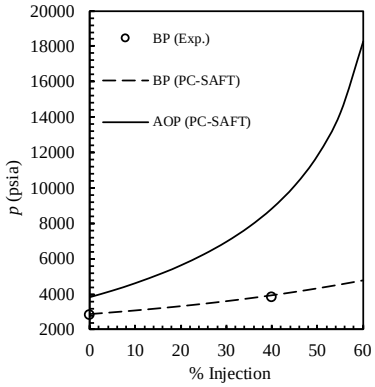

Fig. 3 PC-SAFT predictions of the asphaltene instability in crude AW2 as a function of injected CO_2 mass concentration at 260ºF.

Fig. 4 exhibits oil densities obtained from the constant composition expansion test performed on crude BW1 at 250ºF. It can be seen that decreasing the pressure from 8000 psia down to the bubble point leads to a decrease in the oil density. Below the bubble point, light hydrocarbon gases are released which, in return, leads to an increase in oil density. It is worth noting that PC-SAFT results shown here are pure predictions of PVT properties with no fitting included.

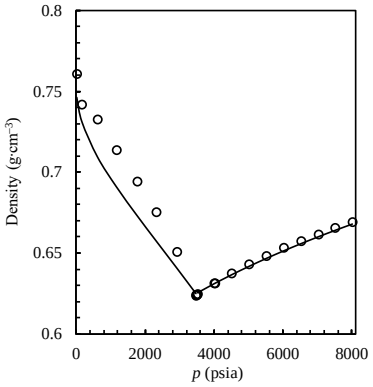

Fig. 4 Oil density from the constant composition expansion test performed for Crude BW1 at 250ºF.

Finally, Fig. 5 shows the CO_2 composition of the differentially liberated gas as a function of pressure. It can be seen that the model was able to predict the maximum in composition found at low pressures for carbon dioxide. Similar accuracy in simulating differential vaporization was observed for other crude oils examined in this work.

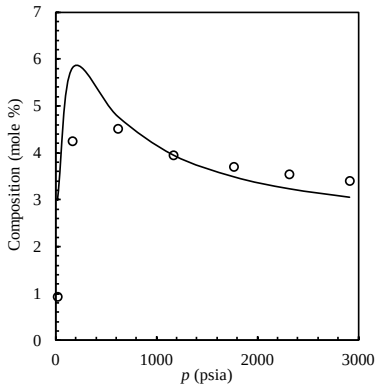

Fig. 5 Carbon dioxide composition in differentially liberated gas from Crude BW1 at 250ºF. Symbols: (o) experiment; (□) PC-SAFT predictions.

Conclusions

Bubble and asphaltene onset pressures as a function of temperature and concentration of injected gas are provided in this work for eight Abu Dhabi crude oils. Together with the SARA analysis, these experimental data were used to characterize the crude oils with PC-SAFT, searching for a predictive model. The proposed SAFT model requires only one fitting parameter which is the asphaltene aromaticity ($\gamma_{Asphalt}$). A simple correlation for this fitting parameter was developed which allows for the pure prediction of the phase behavior without the need of any asphaltene onset data. Results show that decreasing the temperature or increasing the amount of injected gas leads to increasing the asphaltene instability. The model was then used to predict PVT properties and compositional analyses measured from constant composition expansion, differential vaporization and multi-stage separation tests, without performing any fitting. In general, good agreement with experimental data was observed throughout the work exhibiting the model applicability as a predictive tool for the phase behavior of Abu Dhabi region crude oils. Future work includes to assess the applicability of the model to other crude oils, in an attempt to develop a fully predictive model not just for asphaltenes instability but also for routine PVT experiments. By increasing the number of SARA analysis studies or removing the model dependence on them, we believe that the model may eventually become an integral part of the fluid characterization workflow for UAE reservoirs.

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