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PREDICTION OF ASPHALTENE ONSET PRESSURES DURING NATURAL GAS AND CARBON DIOXIDE INJECTIONS

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Abstract

Asphaltene precipitation is one of the challenges encountered during the production of heavy crude oils. Precipitation may also be pronounced during gas injection operations performed to improve production of such heavy crudes. Many of the reported models used for predicting Asphaltene Precipitation in order to achieve the best reservoir and production management practices are rather complex for routine applications. This study was designed to develop a simple but accurate model for predicting Asphaltene precipitation onset during gas injection into oil reservoirs. The parameters for the equation were obtained by tuning to experimental PVT data to obtain pressure-temperature phase profiles. Upper Asphaltene Onset Pressures (UAOP) were predicted under carbon dioxide gas injection and natural gas injection. Results were validated using published data, and compared with the Perturbed Chain Statistical Associating Fluid Theory (PCSAFT) Equation of State. The predictions matched experimental data. Generally, UAOP increased with an increasing proportion of injected gases and varied with reservoir fluid and type of injected fluid. This shows that as much as possible, injections of gases into heavy oils reservoirs should be done at the highest possible pressures.

***Keywords**: Asphaltene precipitation; Reservoir fluid modelling; Gas injection operations.*

1. Introduction

Asphaltenes are very complex solid component part petroleum fluids ; they are usually high boiling materials with metals contents and heteroatoms like oxygen and sulphur while Nitrogen exists in various heterocyclic types including pyridine, aniline, quinolin, and pyrrole [1] it also exhibits polymer characteristics being derived from basic hydrocarbon units. Asphaltene precipitation poses challenges in petroleum production and storage systems, reservoir, wellhead, pipelines and process facilities [2-5] and understanding behavior of asphaltene has been a major challenge to the oil industry [6-7]. Numerous studies have been done in areas of asphaltene thermodynamics, structural characteristics, depositional behaviour, mitigation and economics, These studies, however, do not effectively give solutions to the asphaltene problem, [8], observed a rise in the quantity of precipitated asphaltene with temperature increase, although the reverse is the case for asphaltene dispersed in paraffin solutions. Leontaritis [9] suggested the asphaltene precipitation envelope (APE) describe the conditions under which asphaltene precipitation can occur; the asphaltene precipitation envelope shows the region in which precipitation occurs in a temperature-pressure or temperature-composition diagram, the upper asphaltene onset conditions fall within the points on the APE. Studies described asphaltene molecules as undergoing self-association or association with resins, while the resin-to-resin association is not possible, asphaltene-resin association causes asphaltene stability in mixtures. Leontaritis and Mansoori [10] later suggested the steric colloidal model for predicting the onset of flocculation of colloidal asphaltene in oil mixtures based on the phenomenon that

Resin particle are very important in Asphaltene stability and that a streaming potential develops during oil flow, this contains charged colloidal particles which causes the flocculation and precipitation of asphaltene particles.

The thermodynamic behaviour of asphaltene in solution is usually described by the molecular solution theory, which suggests that the stability of asphaltene in oil as a solution and the separation of the oil (solvent) and asphaltene (solid) phase when asphaltene precipitation occurs. This approach has found use in different literature, which includes the Flory-Huggins-(FH) theory, Flory-Huggins-Goldstein theory, Scatchard-Hildebrand equation, Statistical Association Fluid Theory (SAFT) and thermodynamic colloidal Theories. Most models in literature are based on a combination of these theories, for instance, the micellar approach suggests that Asphaltene in aromatic solvents, crudes, and aromatic/alkane mixtures form micelles [11]. This approach suggests that the micelles formed by asphaltene molecules remain stable in crude oil and it can precipitate upon the attainment of a critical concentration when the concentration of asphaltene monomers reaches a critical concentration which causes the solubility of the monomer concentration to be lower than the solubility of the asphaltene micelles, [12]. Studies have shown that asphaltene micelles form when crude oil contains excess hydrocarbon. Priyanto [13], described different stages in asphaltene association, suggesting that at concentrations above CMC asphaltene in solution will self-associate, as concentration further increases the self-associated Asphaltene will form a coacervate, and a continuous increase in concentration will result in the formation of asphaltene aggregates. Asphaltene micelle formation shares structural similarity with surfactant systems [14].

There are other approaches used to study the thermodynamic behaviour of associating fluids these approaches include, the Perturbation theory, Tangent Sphere model, Lattice model, Hole model, Molecular simulation, Scaled Particle theory, and Partition function theory. The Cell and Lattice models provide different adaptations of the compressible lattice model of solid polymers while incorporating compressibility in a different manner. The hole model combines both methods of incorporating compressibility introduced by cell and lattice fluid, it assumes that molecular sized holes exist in a solid state and an increased number of holes will confer fluid like properties to the solids, also during compression vacant holes are replaced by molecules, thereby causing gas to act as a liquid. Perturbation theory is a useful tool in many branches of physics and statistical mechanics of classical fluids. In perturbation theory, the fluid structure is characterised by a set of distribution functions brought about by expanding a fluid about the same properties of its reference fluid. One of the earliest applications of perturbation theory can be seen in the assignment of parameters to VDW EOS in order to account for the two major interacting components namely, the high-density repulsion and the low-density attraction.

Perturbation theory has been widely applied to classical associating fluids in other to understand their thermodynamic behaviours [15]. Wertheim further suggested the Statistical Associated Fluid Theory (SAFT), for describing the thermodynamic behaviour of associating fluids. The basis for the development of the SAFT model was the sequential expansion of the Helmholtz energy about an integral molecular distribution function and the inherent association capability [16]. This resulted in an association between the excess Helmholtz energy of association, the energy formed because of the formation of adjacent molecular chains and a function related to the segment-to-segment interaction.

Where, is the residual energy contribution as a result of the interaction of adjacent segments, refers to contribution due to the formation of adjacent chains, refers to site-site interaction of segments while refers to the association energy contribution.

In recent time, the association theory has been widely used to model asphaltene behaviour, but it is rather complex and used many parameters that are difficult to define. Kontogeorgis and Folas [17] introduced the cubic plus association equation of state, combining the classical equation of state with an association term, in order to describe complex mixtures and hydrocarbon.

The focus of this study will be on the formulation of a simple equation of state to study the asphaltene onset pressure during CO_2 gas injection in oil reservoirs.

2. Methodology

We suggest an expression in the form:

$$P = \frac{RT}{(V-b)} - \frac{a}{v(v+b)} - \frac{c}{(v+b)} \tag{1}$$

The parameter "a" terms represents the attractive term, while parameter "b" is the volume parameter, and "c" the non-physical force term.

The equation can be simplified to the form:

$$P = \frac{RT}{v-b} - \frac{(a+cv)}{v(v+b)} \tag{2}$$

The fugacity coefficient was calculated from the following thermodynamic equation:

$$\varphi_i = \frac{1}{RT}\int_v^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,n,V,n_i} - RT/V\right]dV - ln\,Z \tag{3}$$

where:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} - \frac{c(T)}{V+b} \tag{4}$$

The derivation of the fugacity equation for the equation of state formulation is achieved by incorporating, equation (2) in equation (4) to obtain.

$$ln\,\varphi = (Z-1) - ln\,Z + \frac{1}{RT}\left[-\frac{1}{RT}ln\frac{V}{V-b} + \frac{a}{b}ln(V+b) + c\,ln(V+b)\right]_{\infty}^{V} \tag{5}$$

Simplifying further gives:

$$ln\,\varphi = (Z-1) - ln\,Z - ln(Z-B) + \frac{A}{B}ln\left(1+\frac{B}{Z}\right) + C\,ln(Z+B) \tag{6}$$

The phase liquid-solid phase equilibrium is given in terms of fugacity as

$$\varphi_i^L = \varphi_i^V. \tag{7}$$

where L, S indicate the liquid and solid phases respectively, and i represent the specie.

For a liquid- solid phase formulation at equilibrium, the fugacity of the i^th^ component in the liquid and solid phase can be expressed as.

$$ln\left(\frac{\theta_V}{\theta_L}\right) = Z_V - Z_L - ln\left(\frac{Z_V}{Z_L}\right) - ln\left(\frac{Z_V-B}{Z_L-B}\right) - \frac{A}{B}\left(\frac{Z_V+B}{Z_L+B}\right)\left(\frac{Z_V}{Z_L}\right) - C\,ln\left(\frac{Z_V+B}{Z_L+B}\right) \tag{8}$$

For each n component in a mixture, the equation of state can be expressed in terms of fugacity as:

$$ln\,\varphi = (Z-1)B' - ln\,Z - ln(Z-B) + \frac{A}{B}(A_i' - B_l')ln\left(1+\frac{B}{Z}\right) + C\,ln(Z+B) \tag{9}$$

where,

$$A' = \left(1/2\sum_{i,j=1}^{N}(1-k_{ij})(a_i a_j)^{\frac{1}{2}}\right) \quad (10);\ B' = \frac{b_i}{b};\ C_i' = \frac{c_i}{c} \tag{11}$$

A fitting procedure as suggested by Kontogeorgis and Folas [17] was used to determine the parameters of the equation The parameters were fitted to the vapour pressure and liquid density using the Generalised Reduced Gradient (GRG) non-linear minimization program, the objective function minimized in this study is the root sum of squares errors function defined by the expression:

$$\text{Objective function} = \sqrt{\sum_{j=1}^{k\Sigma}\sum_{j=1}^{m\Sigma}\left(x_{ij}^{exp_{ij}^{est}}\,()^2\right)} \tag{12}$$

where: i=data point number with a group; j=Measured variables for a data point; k=total number of a point in a data group; m=Number of points in a data group; x is the measured or calculated variable.

Reservoir fluid Data from the studies done by Arya et al. [18] and a model oil mixture developed by Marcano *et al.* [19], designated as Fluid-1, and Fluid-2, respectively were investigated. In order to model Asphaltene precipitation in the test petroleum fluid samples, the fluid volume was assumed constant. The Crude oil composition and properties used for the study is shown in Table 2 and Table 3 respectively.

2.1. Determination of molar volume

The molar volume used for the equation was derived from a simple adjustment procedure done in excel software, which can be summarised by the expression:

$$V = V_{fitted} - V_{adjusted} \tag{13}$$

where: V_{fiited} is the volume fitted from experimental data; $V_{adjusted}$ is the adjustment.

Fluid-1 was used by Al-Hammadi et al. [20] (2015) and Arya et al. [18] (2016), the PC SAFT results were obtained by an approach similar to Panuganti [21] (2012), while Fluid-2 has been was used by Jamaluddin et al. [22] (2002), under nitrogen gas injections of 5, 10 and 20wt%.

Table 1. Crude oil compositions gas phase

Component	Fluid 1 (Mol %)	Fluid 2 (Mol %)	Component	Fluid 1 (Mol %)	Fluid 2 (Mol %)
N_2	0.163	0.490	Iso-butane	1.885	0.810
H_2S	1.944	3.220	n-Butane	5.671	3.710
CO_2	0.000	11.370	Iso-pentane	2.993	1.220
Methane	33.600	27.360	n-pentane	2.980	1.980
Ethane	7.673	9.410	C6+	38.236	34.280
Propane	7.282	6.700			

Table 2. Properties of crude oil samples

Properties	Fluid-1	Fluid-1
Saturates (wt. %)	57.4	66.26
Aromatics (wt. %)	30.8	25.29
Resins (wt. %)	10.4	5.25
Asphaltenes (wt. %)	1.40	2.80
MW of C_{6+}	-	208.08
Res. fluid MW (g/mol)	102.04	97.50
STO Density (g/cm^3)	0.906	0.823
GOR (scf/stb)	900	787

3. Results and discussion

Equation (3) represents a 3-parameters equation of state (EOS), it is different from the most commonly used EOS. While parameter "a" is a function of temperature for most equations of state, in this study, parameter "b" is a function of temperature as given in Table 3.

Figures 1-3 show the UAOP and bubble point pressures of Fluid-1 under natural gas injection scenarios of 0, 15, and 30 wt% result of comparison between the PC SAFT model results and this study with respect to experimental model, for the gas injection scenarios showed agreement with experimental data and PC-SAFT data for the bubble point pressures and UAOP at different values of pressure and temperature. The model predicted both the Saturation pressures and Upper Asphaltene onset pressure (UAOP) of the reservoir fluids shown in Tables 2 and 3. The deviations between the PC-SAFT and this study was less pronounced for the saturation pressure especially at a lower temperature, while the deviation for UAOP increased at higher pressures. The result also showed an increase in the gap between the saturation pressure line and the upper Asphaltene onset UAOP as injection increased from 0 to 30wt%. This may be due to an increase in interaction between Asphaltene and STO and increased precipitation as a result of a change in fluid composition during gas injection.

Figures 4-6 show the UAOP and bubble point pressures for Fluid-2 under CO_2 gas injections of 0, 10 and 20wt%. The model prediction shows agreement with the experimental data and

PC SAFT results at 0wt% gas injection, but noticeable deviations were observed at 10 wt% and 20wt% Co2 gas injections, there is also an increase in the difference between UAOP and the saturation pressure with an increase in the amount of injected gas. This agrees with the findings of Gonzalez *et al.* [23]. The "a" and "c" parameters for the model equation were obtained by a parameter fitting procedure while a temperature based correlation was used to obtain the b parameter as shown in Table 3. Generally, the study showed slight deviations in the UAOP as the injected gas increased from 0 wt% to 30 wt% natural gas injection for Fluid-1; 10 and 10 wt% to 20 wt% CO_2 gas Injection for Fluid-2, this shows that changes in the composition of crude oil will affect the asphaltene behavior. These deviations were also proportional to the changes in the values of the liquids volume used in the model equation. The liquid volume also decreased with an increase in the gas injection for Fluid-1, Fluid-2. This may be due to the formation of Asphaltene precipitation in petroleum fluids. Formation of Asphaltene precipitation in the petroleum

Table 3. Fitted parameters used

Fluid	a	b	c
Fluid-1	0.999	$0.0036T^2$-3.760T+1002.9	0.964
Fluid-2	0.998	$0.0128T^2$-9.118T+1588.0	0.918

Table 4. SAFT parameters correlations for saturates (Gross and Sadowski [24])

M	0.0253MW+0.9263
σ	$3.369MW^{0.0271}$
ε/k	$132.11MW^{0.1221}$

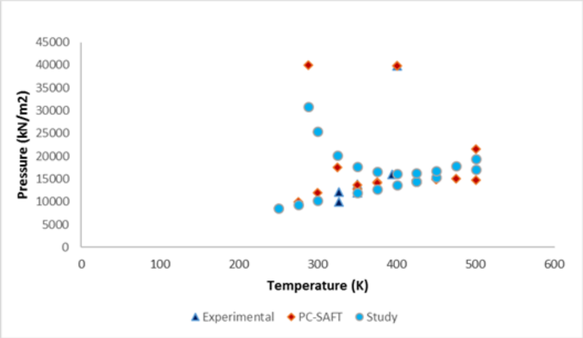

Figure 1. UAOP and Bubble point pressures for Fluid-1 at 0 wt% natural gas injection

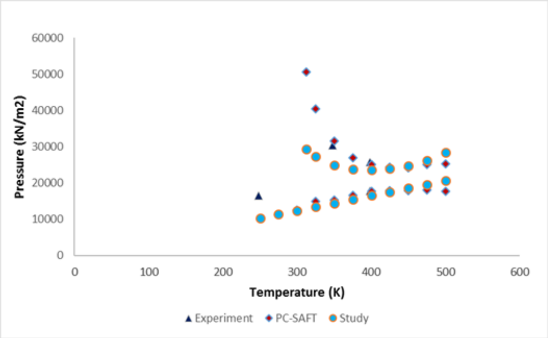

Figure 2. UAOP and Bubble point pressures for Fluid-1 at 15wt. % natural gas injection

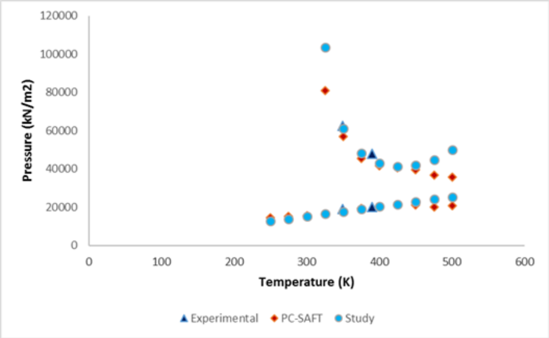

Figure 3. UAOP and Bubble point pressures for Fluid-1 at 30 wt. % natural gas injection

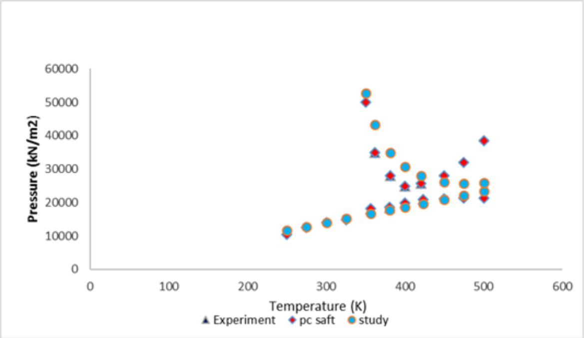

Figure 4. UAOP and Bubble point pressures for Fluid-2 at 0wt. % CO_2 gas injection

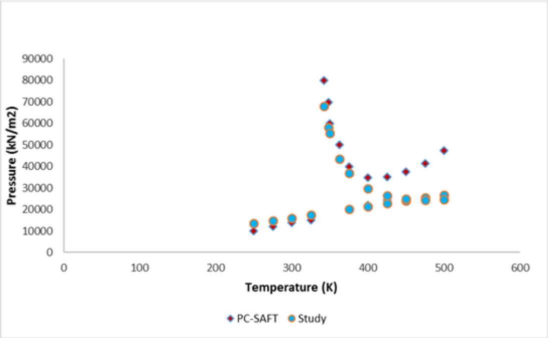

Figure 5. UAOP and Bubble point pressures for Fluid-2 at 10wt. % CO_2 gas injection

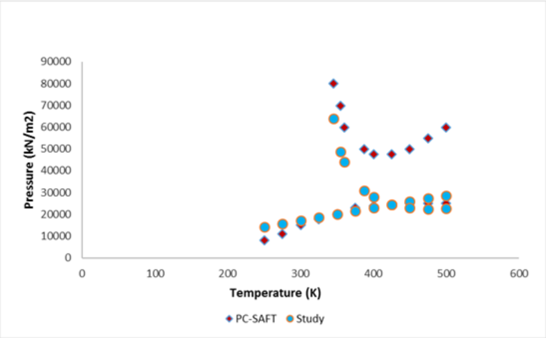

Figure 6. UAOP and Bubble point pressures for Fluid-2 at 20wt. % CO_2 gas injection

4. Conclusion

A simple method was used to predict phase envelopes of heavy crude and determine their upper asphaltene onset pressure. Application to carbon dioxide and Natural gas injection led to the following conclusion:

1. The Upper Asphaltene Onset Pressures UAOP occurred at high pressure and temperature which indicates that asphaltene will form at the reservoir regions rather than at the surface.
2. As gas injections increased, the Upper Asphaltene Onset Pressure increases will little change in temperature.
3. Changes in the composition of crude oil during gas injection will affect the asphaltene behaviour in crude oil.

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