

On the Development of an Asphaltene Deposition Simulator[†]

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Received August 30, 2009. Revised Manuscript Received January 15, 2010

The potential problem of asphaltene deposition during oil production has motivated the development of several experimental techniques and theoretical models to understand and predict asphaltene behavior. Although important progress has been made in this area, prediction of the rate of asphaltene deposition remains an unsolved problem. We have previously reported the successful application of the perturbed chain version of the statistical associating fluid theory equation of state (PC-SAFT EOS) in modeling asphaltene phase behavior under both ambient and reservoir conditions. In this work, we present the development of a simulation tool that simultaneously accounts for asphaltene precipitation, aggregation, and deposition. The thermodynamic modeling using the PC-SAFT EOS is coupled with kinetic models and transport equations. The mechanism for asphaltene precipitation and deposition, proposed in this work, has been found to be consistent with various experiments and field observations. Furthermore, it also provides an explanation to some paradoxes, such as why some asphaltene precipitation inhibitors worsen asphaltene deposition or why strong asphaltene precipitants, such as propane, produce less amount of deposit. The creation of this asphaltene deposition simulator is a significant advance for understanding and predicting asphaltene precipitation and deposition under reservoir conditions.

Introduction

Asphaltenes are a polydisperse distribution of the heaviest and most polarizable fraction of the crude oil. They represent a potential flow assurance problem because of their tendency to precipitate and deposit because of changes in pressure, temperature, and composition. Such deposition can in extreme cases plug a wellbore completely, resulting in large costs associated with remediation and loss of production. In some cases, the risk of plugging a well has led companies to spend a significant amount of money in chemicals that could prevent asphaltene deposition. Sometimes chemicals might not even be necessary, and some other chemicals might worsen the problem. Despite the work devoted to understanding asphaltene molecular structure and the mechanisms of asphaltene precipitation and deposition, asphaltene deposition still represents a challenging unresolved operational problem. A better understanding of the mechanisms by which asphaltenes precipitate and deposit is needed to improve the prediction and avoid associated production and processing problems.

The objective of this paper is to provide a macroscopic modeling approach for understanding how asphaltenes are transported in a wellbore, including different phenomena, such as precipitation, advection, aggregation, and deposition. The creation of a computer program based on this modeling approach is also described. It is also intended to provide an explanation to some paradoxes, such as why some asphaltene precipitation inhibitors worsen asphaltene deposition or why

strong asphaltene precipitants, such as propane, produce less amount of deposit. Preliminary results obtained with this new simulation tool have been qualitatively validated with experimental work and field observations.

One of the most important components of the proposed mechanism is the precipitation term. Asphaltene stability in crude oil and the mechanisms of its precipitation have been the subject of continuous investigation over many years.^{1–5} Two theories have been proposed to explain such phenomena. The first one is based on colloidal models, whereas in the second one, solubility models are used. The idea of asphaltene colloidal particles stabilized by resins was first introduced by Nellensteyn.⁶ This concept was then refined by Pfeiffer and Saal.⁴ In the solubility theory (or molecular solution approach), asphaltenes are assumed to be part of a solution (oil).⁷ Asphaltene precipitation can be treated as liquid–liquid or solid–liquid equilibria. Resins and aromatics solubilize asphaltenes, whereas saturates destabilize them. Examples of models based on the solubility approach are the Hirschberg model⁸ and the work of de Boer,⁹ Redelius,⁵ Park and

[†] Presented at the 10th International Conference on Petroleum Phase Behavior and Fouling.

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Mansoori,³ Wiehe,^{10–13} and Buckley and Wang,^{14–18} among others. Recent results suggest that the solubility model is more appropriate to study the stability of asphaltenes in crude oils.¹ Using impedance analysis, Goual¹⁹ has demonstrated that resins are unlikely to coat asphaltene nanoaggregates, and therefore, resins are not able to provide the steric stabilizing layer that the colloidal model proposes. Czarnecki²⁰ has determined that the hydrophilic–lipophilic balance (HLB), which provides an approximate measurement of polarity of surfactants, is negative for asphaltenes. Czarnecki²⁰ concludes that asphaltenes are not polar, do not aggregate to form micelles, are not similar to surfactants, and do not stabilize water/oil emulsions. Hirasaki and Buckley¹⁴ have reported that, for asphaltenes in crude oil systems, it is polarizability (and not polar interactions) that determines the asphaltene phase behavior. Recent results obtained by both experimental²⁰ and molecular²¹ simulation schemes have validated this hypothesis. Thus, the solubility model is currently the most accepted theory for modeling asphaltene phase behavior. Among the solubility models, the thermodynamic modeling using the statistical associating fluid theory (SAFT)^{22–24} based equation of state has demonstrated excellent performance and predictive capabilities applied to a wide range of mixtures, including petroleum systems containing asphaltenes.

We have previously reported the successful application of the perturbed chain version of the statistical associating fluid theory equation of state²⁵ (PC-SAFT EOS) in modeling asphaltene phase behavior under both ambient and reservoir conditions.^{26,27} The analysis of the effects of pressure, temperature, composition, and asphaltene polydispersity has been presented. Applications to different field cases, such as CO₂ injection in miscible flooding,²⁸ oil-based mud contamination during drilling and sampling,²⁹ and commingling of oils³⁰ have also been reported.

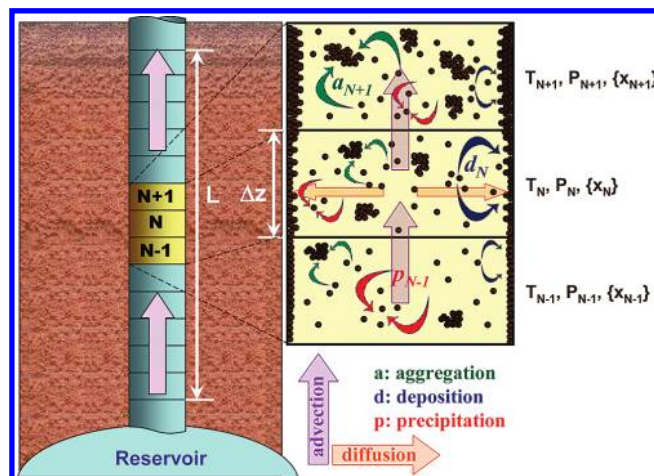


Figure 1. Proposed mechanism for asphaltene transport in the wellbore.

Proposed Mechanism

Transport of asphaltenes in the wellbore may follow a multi-step process, including precipitation, aggregation, advection, and deposition. The mechanism is summarized in Figure 1. At reservoir conditions, asphaltenes are soluble in oil. However, during pressure depletion, the oil expands, reducing the oil solubility parameter, and becomes a poor solvent for asphaltene. At low enough pressures, the asphaltene precipitation onset is reached and asphaltenes begin to precipitate at a certain rate. According to the mechanism, asphaltene precipitation leads to the appearance of the first particles, represented in Figure 1 as dark circles. These particles, which we will call micro-aggregates, can stick to one another undergoing an aggregation process, forming bigger particles, or can follow a diffusion mechanism to the surface of the tubing, where they stick and build up a deposit. Additionally, both small and big particles are transported upward by the moving fluid, in a process known as advection.

The rate of asphaltene precipitation is assumed to be proportional to the supersaturation degree of asphaltenes, which is defined as the difference between the actual concentration of asphaltenes dissolved in the oil and the concentration of asphaltene at equilibrium, according to eq 1

$$\frac{dF_A^*}{dV} = r_P = -k_P(C_A^* - C_A^{eq}) \quad (1)$$

where F_A^* is the rate at which dissolved asphaltenes precipitate forming micro-aggregates in units of mass per unit time, V is the system volume, r_P is the precipitation rate in units of mass per unit time and unit volume, k_P is the specific precipitation rate constant, C_A^* is the actual concentration of asphaltenes in the oil, and C_A^{eq} is the concentration of asphaltenes in the oil at equilibrium, at the given operating conditions.

In other words, the precipitation rate is determined by the degree of supersaturation; i.e., the greater the supersaturation degree of asphaltenes in the crude oil, the quicker the precipitation rate. When the supersaturation degree is zero, the system is right at the onset of asphaltene precipitation. According to the model, a negative supersaturation implies that the system is undersaturated and redissolution of micro-aggregates is possible. Reversibility of precipitated asphaltene has been a subject of extensive discussion. However, it seems a reasonable assumption that the small particles can be redissolved more rapidly than big particles. In fact, it has been experimentally demonstrated³¹ that insoluble asphaltene particles can be readily dissolved under the effect of ultrasonic waves, which break the big aggregates down into small particles. Thus, redissolution of micro-aggregates is

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likely to occur, whereas redissolution of big particles could be neglected, at least in the time frame of interest. A condition where redissolution of micro-aggregates can occur is when the system pressure falls below the bubble point pressure, where the light components, which are asphaltene precipitants, come out from the liquid phase. As this happens, the solubility parameter of the oil increases until the oil becomes a better asphaltene solvent. All of the remaining micro-aggregates are readily redissolved. Big aggregates remain, because they are redissolved much more slowly. In our model, the big aggregates are assumed to be insoluble.

Note that eq 1 can be solved to find the concentration of dissolved asphaltenes, C_A^* , at any position given that

$$\frac{dF_A^*}{dV} = \frac{\langle v_z \rangle dC_A^*}{dz} = -k_P(C_A^* - C_A^{eq})$$

$$C_A^* - C_A^{eq} = (C_0^* - C_A^{eq}) \exp\left(-\frac{k_P}{\langle v_z \rangle} z\right) \quad (2)$$

where C_0^* is the concentration of dissolved asphaltenes at inlet conditions, $z = 0$.

Letting τ be the space time, i.e., $\tau = z/\langle v_z \rangle$

$$r_P = k_P(C_0^* - C_A^{eq}) \exp(-k_P \tau) \quad (3)$$

where r_P is the precipitation rate, k_P is the precipitation rate constant, C_0^* is the concentration of asphaltenes in solution at inlet conditions, and C_A^{eq} is the concentration of dissolved asphaltenes at equilibrium.

r_P in eq 3 represents the rate at which asphaltenes come out of solution, which is assumed to be equal to the rate of formation of micro-aggregates.

The micro-aggregates formed from precipitation can continue the aggregation process, diffuse in both axial and radial directions, deposit at the surface of the pipe, or travel along with the fluid. In our model, axial diffusion is neglected, because the transport in that direction is assumed to be dominated by the advection term.

Diffusion and advection are modeled using the traditional equations of mass transport. The aggregation and deposition steps are modeled using a pseudo-first order reaction, according to eqs 4 and 5

$$-r_A = k_A C_A^{m_A} \quad (4)$$

$$-r_D = k_D C_A^{m_D} \quad (5)$$

where r_A and r_D are the rates of asphaltene aggregation and deposition, respectively, and k_A and k_D are the corresponding rate constants.

All of these phenomena can be incorporated into a mathematical model that tracks the transport of micro-aggregates. The material balance in the transient state for these particles is represented by eq 6

$$\underbrace{\frac{\partial C_A}{\partial t}}_{\text{Accumulation}} = \underbrace{-v_z \frac{\partial C_A}{\partial z}}_{\text{Advection}} + \underbrace{\frac{1}{r} \frac{\partial}{\partial r} \left(D \cdot r \cdot \frac{\partial C_A}{\partial r} \right)}_{\text{Diffusion}} - \underbrace{\left(\underbrace{k_A C_A^{m_A}}_{\text{Aggregation}} + \underbrace{k_P (C_0^* - C_A^{eq}) \exp\left(-k_P \frac{z}{\langle v_z \rangle}\right)}_{\text{Precipitation}} \right)}_{\text{Precipitation}} \quad (6)$$

subject to the following boundary and initial conditions:

$$\text{BC}_1 : \frac{\partial C_A}{\partial r} = 0 \quad \text{at } r = 0, \text{ for all } z$$

$$\text{BC}_2 : C_A = C_0 \quad \text{at } z = 0, \text{ for all } r$$

$$\text{BC}_3 : D \frac{\partial C_A}{\partial r} = -k_D C_A^{m_D} \quad \text{at } r = R, \text{ for all } z$$

$$\text{IC} : C_A = C_0 \quad \text{at } t = 0, \text{ for all } r, z$$

where C_A is the concentration of micro-aggregates, t is the time, v_z is the velocity of the fluid, z is the axial distance, r is the radial distance, R is the radius, D is the diffusion coefficient, C_0 is the concentration of micro-aggregates at inlet conditions, C_A^{eq} is the concentration of dissolved asphaltenes at equilibrium, and k_A and k_P are the aggregation and precipitation rate constants, respectively. m_A and m_D represent the reaction orders for aggregation and deposition, respectively. Because no information was available to determine reaction orders m_A and m_D , they were assumed to be equal to 1 for simplicity. As more information becomes available, reaction orders m_A and m_D can be adjusted accordingly.

Boundary condition 3, BC_3 , represents the deposition of asphaltenes.

The velocity of the fluid, v_z , is a function of the radius for laminar flow. For flow in a circular pipe

$$v_z = v_z(r) = 2\langle v_z \rangle \left(1 - \left(\frac{r}{R}\right)^2\right) \quad (7)$$

Velocity can be assumed constant and equal to the average velocity, $\langle v_z \rangle$, in a turbulent regime (except at $r = R$, where $v_z = 0$).

Equation 6 can be expressed in dimensionless form, letting $\psi = C_A/C_0^*$, $\theta = t\langle v_z \rangle/L$, $\zeta = z/L$, and $\eta = r/R$, to obtain eq 8

$$\frac{\partial \psi}{\partial \theta} = -2(1 - \eta^2) \frac{\partial \psi}{\partial \zeta} + \left(\frac{L}{R}\right) \frac{1}{Pe} \frac{1}{\eta} \frac{\partial}{\partial \eta} \left(\eta \frac{\partial \psi}{\partial \eta} \right) - Da_A \psi$$

$$+ Da_P (1 - \psi^{eq}) \exp(-Da_P \zeta) \quad (8)$$

subject to the boundary conditions in the corresponding dimensionless form

$$\text{BC}_1 : \frac{\partial \psi}{\partial \eta} = 0 \quad \text{at } \eta = 0, \text{ for all } \zeta$$

$$\text{BC}_2 : \psi = \psi_0 \quad \text{at } \zeta = 0, \text{ for all } \eta$$

$$\text{BC}_3 : \frac{\partial \psi}{\partial \eta} = -Da_D \psi \quad \text{at } \eta = 1, \text{ for all } \zeta$$

$$\text{IC} : \psi = \psi_0 \quad \text{at } \theta = 0, \text{ for all } \eta, \zeta$$

Transformation of the partial differential equation into a dimensionless form yields the definition of dimensionless variables: Pe , the Péclet number, and Da_A , Da_P , and Da_D , the Damköhler numbers of aggregation, precipitation, and deposition, respectively

$$\text{where } Pe = \frac{\langle v_z \rangle R}{D}, \quad Da_P = \frac{k_P L}{\langle v_z \rangle}, \quad Da_A = \frac{k_A L}{\langle v_z \rangle}, \quad Da_D = \frac{k_D R}{D}$$

If m_A and m_D were different than 1

$$Da_A = \frac{k_A (C_0^*)^{m_A - 1} L}{\langle v_z \rangle}, \quad Da_D = \frac{k_D (C_0^*)^{m_D - 1} R}{D}$$

The Péclet number physically represents the ratio

$$Pe = \frac{\text{rate of transport by advection}}{\text{rate of transport by diffusion}}$$

Damköhler numbers represent the ratios

$$Da_P = \frac{\text{rate of production of micro-aggregates by precipitation}}{\text{rate of transport of micro-aggregates by advection}}$$

$$Da_A = \frac{\text{rate of consumption of micro-aggregates by aggregation}}{\text{rate of transport of micro-aggregates by advection}}$$

$$Da_D = \frac{\text{rate of consumption of micro-aggregates by deposition}}{\text{rate of transport of micro-aggregates by diffusion}}$$

After solving eq 8, the dimensionless deposition flux, j_A , can be calculated according to eq 9

$$j_A = \frac{RJ_A}{DC_0^*} = \left(\frac{\partial \psi}{\partial \eta} \right) \bigg|_{\eta=1} = Da_D(\psi) \big|_{\eta=1} \quad (9)$$

where j_A is the dimensionless deposition flux, R is the tube radius, J_A is the deposition flux in units of mass per unit time and per unit area, D is the diffusion coefficient, C_0^* is the concentration of dissolved asphaltenes at inlet conditions (used to normalize all of the concentrations in the model), ψ is the normalized concentration of micro-aggregates ($= C_A/C_0^*$), η is the normalized radius ($= r/R$), and Da_D is the Damköhler number of deposition.

The current stage of the deposition model considers an isothermal system with simple micro-aggregate units, which are assumed to be the entities that could stick to the surface and form a deposit, neglecting bigger aggregates. It has been shown, both experimentally³² and by molecular simulations,³³ that the bigger the aggregates, the less suitable they are for deposition. The extension of the current mechanism to include aggregates of bigger size is possible and may be pursued in the future.

A distinction between precipitation and aggregation is also important in the proposed model. Although at first the mechanism of both phenomena could be assumed identical, it has been shown experimentally that this might not be the case. Kraiwattanawong et al.³⁴ have reported that none of the asphaltene chemical inhibitors that they tested in their study prevented the phase separation of asphaltenes but some of them did slow or stop flocculation and growth. The assumption of two distinct steps of phase separation and particle growth seems reasonable.

Model Implementation and Simulator Structure

The proposed model has been implemented in both transient and steady-state forms. The systems studied are at two different scales: wellbore and capillary. The objective of simulating asphaltene deposition in a capillary system is to obtain a better understanding of the variables affecting the process. New experiments can be proposed on the basis of this new knowledge. A conventional numerical technique of finite differences has been used for solving the partial differential equation in dimensionless form with the corresponding boundary conditions. A parametric study has been conducted, where the effect of the different parameters of the model are tested. Furthermore, the effect of the temperature on asphaltene precipitation/aggregation/deposition has also been analyzed. For this purpose, typical Arrhenius functional forms for the temperature dependence of reaction rates and viscosity and the Wilke and Chang³⁵ model for the diffusion

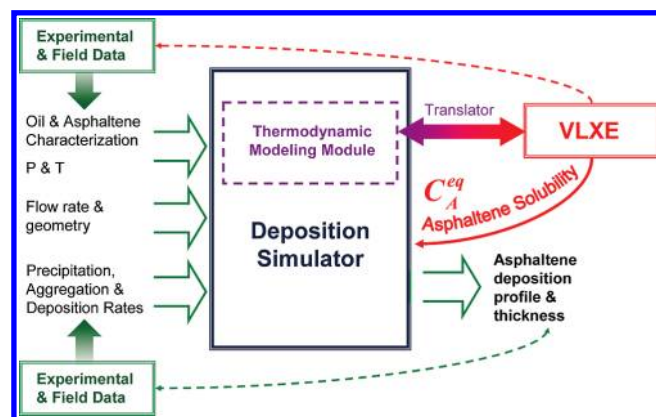


Figure 2. Simulator structure including input parameters and the interface for thermodynamic modeling.

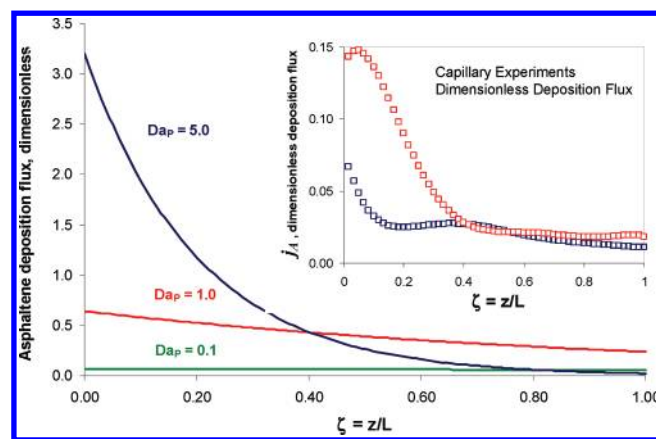


Figure 3. Sensitivity analysis of the Damköhler number of precipitation: Effect on asphaltene deposition flux. $R = 0.01$ in, $L = 106$ ft, $Da_A = 1.2$, $Da_D = 67$, $Pe = 3758$, $\psi_A^{eq} = 0.359$. Qualitative comparison with experimental data from Wang and Buckley³² is presented.

coefficient have been assumed. The diffusion coefficient of 0.35×10^{-5} cm²/s reported by Andrews et al.³⁶ for asphaltenes in toluene is assumed as a rough approximation. Activation energies have typical values according to the literature³⁷ of 20–150 kJ/mol. A value of 85 kJ/mol is assumed as a first approximation. Simulation results are then compared to experimental and field observations to see the qualitative behavior.

The simulator structure is represented by Figure 2. Input variables are shown on the left-hand side. Operation variables, such as pressure, temperature, flow rate, and system geometry, are needed, as well as the characterization of oil and asphaltenes. The method for obtaining the PC-SAFT parameters for oil fractions and asphaltenes has been previously described by Gonzalez et al.^{29,38} Additionally, the rates of precipitation, aggregation, and deposition are needed to define the corresponding dimensionless numbers of the model. Alternatively, deposition profiles can be matched by tuning the values of unknown variables. The thermodynamic modeling using the PC-SAFT EOS for estimating the asphaltene stability is performed in the commercial software VLXE. Because the native language of VLXE, is different than the

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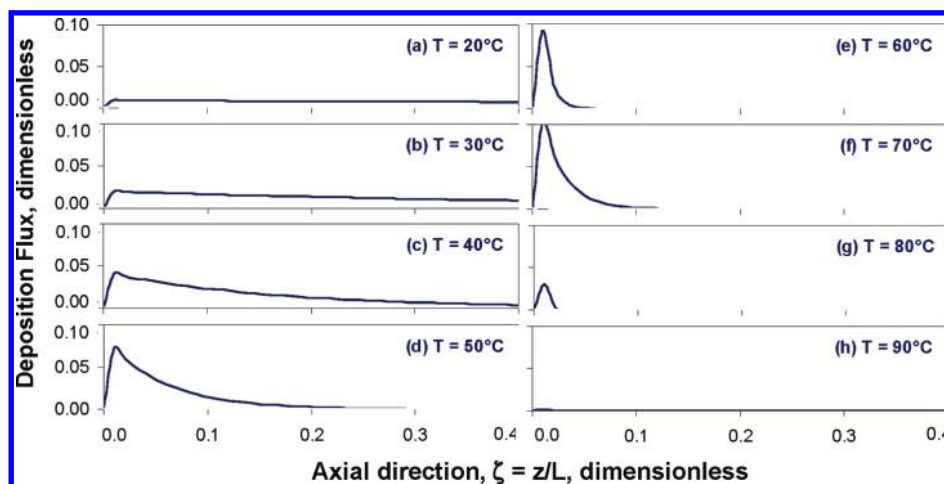


Figure 4. Simulation results of the temperature effect on deposition, in a capillary system. $\zeta = 0$ represents the capillary inlet.

deposition simulator, written in Fortran, a translating interface had to be coded. This interface allows for the operation of both simulators in their native languages and live interaction, as well as the flexibility of future individual upgrades without affecting the performance of the assembled simulation tool. VLXE is used to calculate the concentration of asphaltenes at equilibrium (asphaltene solubility), which, along with the actual concentration of asphaltenes in the oil, determines the supersaturation degree and, consequently, the precipitation rate, according to eq 3.

However, the thermodynamic calculations performed in VLXE and controlled by the translating interface are reported in the form of a look-up table, which is then the input file to the deposition simulator. Therefore, the deposition simulator is not restricted to be operated in connection with VLXE. Other commercial simulators can be used to generate the look-up table containing the information of asphaltene solubility at different operation conditions. The deposition simulator then reads the information necessary as the calculations are executed. The look-up table approach is used instead of a fully compositional simulator to reduce the computational time necessary to perform the calculations.

Preliminary Results

Simulations have been performed, and a mechanism that explains the competition between asphaltene aggregation and deposition has been identified. This competition follows directly from the mechanism of formation and consumption of micro-aggregates described in the previous section. If conditions are favorable for enhancing aggregation, the amount of available micro-aggregates decreases rapidly, diminishing the deposition rate, and vice versa. Most of the asphaltene precipitation inhibitors act as asphaltene dispersants, decreasing the population of big aggregates and, thus, enhancing the permanence of micro-aggregates. Consequently, asphaltene deposition could be promoted. Therefore, this competing phenomenon explains why some asphaltene dispersants actually worsen the deposition problem.³⁹

Another interesting experimental observation has been reported while conducting capillary tests. When oil with

pre-existing asphaltene aggregates is pumped through the capillary tube, no deposition is seen.⁴⁰ To observe deposition, the oil has to be mixed with an asphaltene precipitant and fed to the capillary immediately.⁴⁰ The explanation of this experimental observation can also be drawn from the proposed mechanism. In the former case, aggregation of asphaltene micro-aggregates was undertaken, depleting the population of the simplest and smallest particles and, thus, preventing deposition. In the latter case, both aggregation and deposition can take place, because of the existence of micro-aggregates along the capillary tube.

Additionally, the unexpected poor deposition produced by strong asphaltene precipitants, such as propane, can also be explained in terms of the given mechanism. The addition of a strong asphaltene precipitant rapidly increases the supersaturation degree, and consequently, the precipitation occurs quickly. As the concentration of micro-aggregates in the bulk of the fluid rapidly increases, the aggregation process that can take place at any point of the system is favored over deposition that can occur only at the boundary layer.

The temperature effect has also been studied. The preliminary results show that in a capillary, as temperature increases, the asphaltene deposition flux increases toward the capillary inlet and rapidly decreases toward the outlet. This behavior is in good agreement with experimental data obtained from capillary experiments.³² The comparison is shown in Figure 3. Furthermore, it has been obtained that, at lower temperatures, the amount deposited not only decreases but is also more uniform. It was found that there is a temperature at which asphaltene deposition is at its maximum, according to Figure 4. Beyond that temperature, asphaltene deposition flux decreases and finally stops. This is an expected behavior, as we can anticipate from a typical asphaltenic crude oil phase diagram shown in Figure 5, where data from Jamaluddin et al.⁴¹ for asphaltene precipitation are compared to simulation results,^{27,28} using the PC-SAFT EOS. Asphaltene precipitation and, consequentially, deposition stop because, at temperatures above the upper critical end point (UCEP) boundary, asphaltenes become stable in crude oil. However, the model also predicts that, at very high temperatures above

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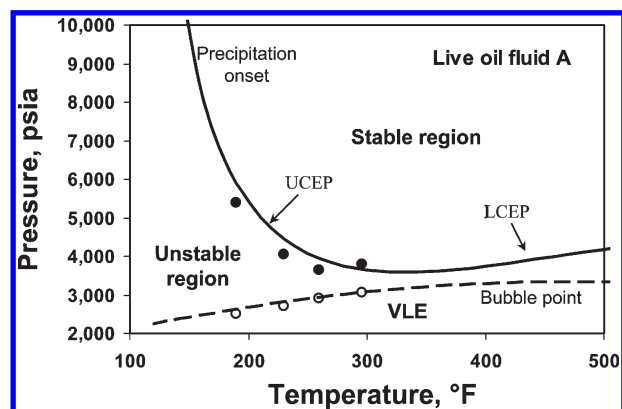


Figure 5. Onset of asphaltene precipitation and bubble points for reservoir fluid A. UCEP- and LCEP-type behaviors are shown. Data are from Jamaluddin et al.⁴¹ Curves correspond to simulations using the PC-SAFT EOS.

the lower critical end point (LCEP) boundary, asphaltenes become unstable again and may deposit. This is more likely to happen inside heat exchangers, at a later stage of the refining process, and not in the wellbore.

Wellbore simulations were also performed, where the objective was to study the flexibility of the model to match the reported measurements of the Hassi-Messaoud field.⁴²

There are two ways of obtaining the appropriate parameter values: one is by matching one by one the different terms of the model (precipitation, aggregation, and deposition rates) against the corresponding experimental data. Because this information is not available most of the time, the alternative is to tune the parameter values simultaneously to match a deposition profile and the data that might be available.

Current Stage and Future Work

A pseudo-transient simulator is under development. The idea is that, by sequentially solving multiple steady-state simulations, updating the deposit thickness, it could be possible to estimate the evolution of the operation variables on time. However, it is expected that the computational time will be reduced considerably with respect to a full transient simulator. Momentum and heat-transfer equations are also being incorporated to include the flow field effects and temperature

change. Additionally, it is also intended to incorporate the effect of bigger aggregates on asphaltene deposition.

Conclusion

A macroscopic approach for providing insight into the mechanism of transport of asphaltenes in the wellbore has been presented. A complex multi-step process that includes precipitation, aggregation, advection, and deposition of asphaltenes has been coded in a simulation tool, and the results obtained have been validated with experimental data and field observations.

A competing phenomenon between aggregation and deposition has been identified. This competition is useful in providing an explanation to interesting observations including the adverse effect of some asphaltene precipitation inhibitors on asphaltene deposition and the poor deposition obtained when strong asphaltene precipitants are used, among others.

Simulations of capillary systems have also been performed. The effect of the temperature on the deposition rate in isothermal capillary systems has been studied, and the first results in this area have been obtained. Asphaltene deposition may or may not be uniform along the capillary depending upon the temperature, keeping all of the other variables constant. As the temperature increases, the amount deposited toward the capillary inlet increases but reduces elsewhere. After reaching a maximum at a certain temperature, deposition decreases as the temperature increases, because we approach the UCEP boundary, above which asphaltene is stable in the oil.

The simulation results obtained in a wellbore system, while performing a sensitivity analysis of the model parameters, are comparable to those reported from the Hassi-Messaoud field.

Although fine-tuning of the different parameters of the model is still necessary, the ideas behind the development of this asphaltene deposition simulator should contribute significantly to understanding and predicting asphaltene precipitation and deposition under reservoir conditions.

Acknowledgment. The authors acknowledge DeepStar for financial support and thank Doris L. Gonzalez (Schlumberger), George J. Hirasaki (Rice University), Jianxin Wang and Hariprasad Janakiram Subramani (Chevron Energy Technology Company), Jill Buckley (New Mexico Institute of Mining and Technology), and Torben Laursen (VLXE) for fruitful discussions. F.M.V. acknowledges support from Tecnológico de Monterrey, through the Research Chair in Solar Energy and Thermal-Fluid Sciences (Grant CAT-125).

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