



# Modeling asphaltene precipitation in a compositional reservoir simulator using three-phase equilibrium



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## ABSTRACT

Predicting asphaltene precipitation and its deposition in the porous media is key in understanding costly productivity impairment caused by formation damage. This work presents the development and application of a compositional reservoir simulator including the effects of asphaltene precipitation on production. Precipitation from the liquid mixture occurs as its solubility is reduced either by changes in pressure (natural depletion), or by composition (mixing with another fluid, such as in gas injection). Our approach represents asphaltene as the dense liquid phase computed from a three-phase flash (vapor/liquid/liquid equilibrium VLLE) using the Peng Robinson equation of state.

The multi-phase and multi-component reservoir simulator developed in this study uses a volume-based formulation, with pressures calculated implicitly and compositions explicitly (IMPESC approach). A cubic equation of state solves a three-phase flash to determine the number of phases co-existing in equilibrium. As asphaltene precipitates and deposits in the rock, the model dynamically calculates new porosities and permeabilities to represent the reduced pore space and effective flow path. We validated our model by matching experimental asphaltene precipitation data while predicting the expected phase behavior envelope and response to key thermodynamic variables (i.e. fluid composition, asphaltene molecular weight and its characterization in terms of pseudo critical properties).

Previous modeling techniques were computationally inefficient, exhibit thermodynamic inconsistencies, and/or required special laboratory experiments to characterize the fluid. Our three-phase VLLE flash algorithm coupled with the reservoir model provides superior thermodynamic predictions compared to existing commercial techniques. This model offers the robustness and speed of a flash calculation while maintaining thermodynamic consistency, enabling efficient optimization of reservoir development strategies to mitigate the detrimental effects of asphaltene precipitation on productivity.

## 1. Introduction

Asphaltene is a highly viscous hydrocarbon constituent that contains large and highly concentrated molecules, mainly hydrogen and carbon with some heteroatoms and metals. It can precipitate from the oil during the production process triggered by changes in pressure (depletion by production), temperature (heat transfer along the production path), or oil composition (gas injection or diffusion in strongly compositional reservoirs). Once precipitated, asphaltene can deposit along the reservoir and production system plugging pore throats, wellbore, flowlines, or surface facilities, thus causing serious production impairment (Leontaritis and Ali Mansoori, 1988). Understanding and modeling the conditions at which asphaltene precipitates is key for properly designing and optimizing development

programs for reservoirs with high concentration of asphaltene. Reservoir simulation is an important tool for predicting performance of asphaltenic reservoirs.

To understand the mechanistic behavior of asphaltene, Leontaritis (1996) proposed the deposition envelope displayed in Fig. 1. It represents the relationship between pressure and temperature, where two curves defined the region exhibiting asphaltene precipitation: upper boundary, above which asphaltene does not precipitate, and lower boundary, below which asphaltene does not precipitate.

The complexity of asphaltene molecules has resulted in multiple theories and models explaining the precipitation process within a reservoir. Li and Firoozabadi (2010a, 2010b) classified the theoretical approaches into two main categories depending on the mechanisms of precipitation and stabilization: lyophobic and lyophilic. Lyophobic

Abbreviations: ADE, Asphaltene depositional envelop; AOP, Asphaltene offset pressure; EOS, Equation of state; IMPESC, Implicit-pressure, explicit-saturations and explicit-compositions; VLE, Vapor/liquid equilibrium; VLLE, Vapor/liquid/liquid equilibrium

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**Nomenclature**

$A$	Area perpendicular to flow direction
$\hat{f}_i^l$	Fugacity of component $i$ in the mixture of phase $l=v$ (vapor), $l$ (liquid)
$f_i^{dl}$	Fugacity of pure component $i$ in dense-liquid phase
$f_i$	Mole fraction of phase $l=v$ (vapor), $l$ (liquid), $dl$ (dense-liquid)
$k$	Permeability
$k_r$	Relative permeability
$K_i$	Equilibrium ratio of component $i$
$M_W$	Molecular weight of component $i$
$N_c$	Number of components
$N_l$	Number of phases
$n$	Time level
$n_x$	Number of blocks in $x$ -direction
$n_y$	Number of blocks in $y$ -direction
$n_z$	Number of blocks in $z$ -direction
$p$	Pressure
$p_c$	Critical pressure

$q_i$	Net molar rate of component $i$ from sources and sinks
$S_i$	Volume fraction of phase $l=v$ (vapor), $l$ (liquid), $dl$ (dense-liquid)
$t$	Time
$T_c$	Critical temperature
$V$	Volume (Pore $-p$ or Bulk $-b$ )
$\bar{V}_i$	Partial molar volume of component $i$
$V_m$	Molar volume
$w_i\%$	Weight fraction
$x_i$	Mole fraction of component $i$ in the liquid phase
$y_i$	Mole fraction of component $i$ in the vapor phase
$z_i$	Overall mole fraction of component $i$
$\alpha$	User-defined reduction parameter
$\phi$	Porosity
$\iota$	Phase
$\rho$	Density
$\rho_m$	Molar density
$\Phi$	Potential
$\mu_i$	Viscosity of phase $\iota$
$\omega_i$	Acentric factor of component $i$ .

models assume that asphaltene is insoluble in the oil mixture, but their surface adsorbs resins that stabilize the asphaltene molecule. Asphaltene precipitation occurs as a result of resin desorption from the asphaltene surface. The resins help asphaltene to disperse in oil as a suspension by means of hydrogen-bonding and irreversible acid/base reactions of asphaltene and resin molecules. This theory includes the colloidal model proposed by [Leontaritis and Mansoori \(1987\)](#) and the micellization model proposed by [Pan and Firoozabadi \(2000\)](#).

The lyophilic theory assumes that asphaltene precipitates when the hydrocarbon fluid reduces its solvent power. This theory has had a greater acceptance in the industry for reservoir simulation. The simplest model is a look-up table describing the concentration of asphaltene precipitated with respect to another variable, usually pressure or mole fraction of a specific component ([Schlumberger 2012a](#); [Yi et al., 2009](#)). In this approach, calculation of asphaltene precipitation is independent from the phase behavior of the mixture, which performs only conventional two-phase vapor/liquid equilibrium. The main advantage of this technique is its rapid implementation and fast calculations; however, it does not incorporate a physical model for asphaltene phase behavior and neglect its effect on system equilibrium potentially leading to serious material balance violations.

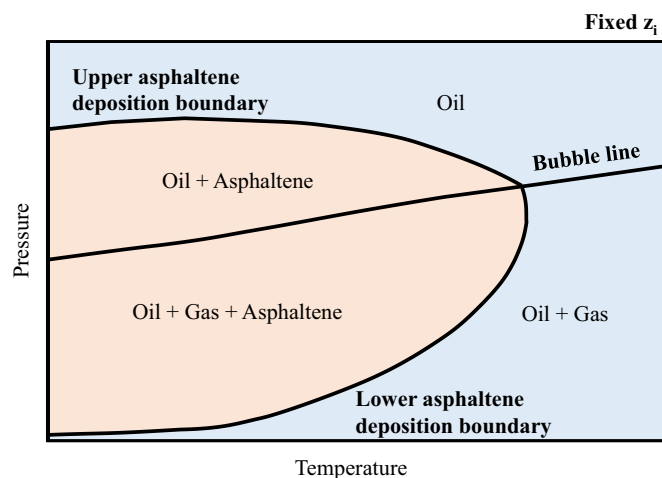
[Wang and Civan \(2005a\)](#) incorporated an asphaltene precipitation

model into a compositional reservoir simulator by combining the polymer solution theory with the Hildebrand solubility concept ([Hirschberg et al., 1984](#)). The model considers two equilibria types: vapor/oil (conventional 2-phase equilibrium) and oil/oil using the solubility theory. The asphaltene solubility in the oil/oil equilibrium uses solubility parameters where crude oil acts as the solvent phase and precipitated asphaltene as the solute phase. Although this approach predicts the solvent/solute interaction, asphaltene description has no direct relationship with the equation of state (EOS) parameters or general equilibrium conditions. It assumes that the second and first equilibrium are independent.

The perturbed chain form of the statistical associating fluid theory (PC-SAFT) assumes that molecular size and nonpolar van der Waals interactions dominate asphaltene phase behavior ([Gonzalez et al., 2007](#); [Vargas et al., 2009](#)). This model describes the molecules as a chain of bonded spherical segments, using the number of segments and the van der Waals attraction forces between segments to model the fluid behavior. This theory predicts the effect of association between molecules of different sizes and provides accurate densities of well-defined components ( $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ , etc.) commonly used in downstream analyses. However, its mathematical complexity significantly increases CPU consumption particularly in multi-phase flow, and it requires additional laboratory experiments to characterize the plus fraction ([Yan et al., 2011](#)).

[Li and Firoozabadi \(2010a, 2010b\)](#) proposed a more rigorous approach for modeling asphaltene precipitation using the cubic plus association equation of state, a model originally proposed by [Kontogeorgis et al. \(1996\)](#). The modified EOS combines a conventional cubic equation with the association term derived from statistical associating fluid theory. The model has two contributing parts: 1) physical, modeled with a cubic EOS, representing the interaction of short-range repulsion and attractions forces of non-association molecules; and 2) association, derived from the perturbation theory, describing the polar/polar interaction of self-association and cross-association. The equation is capable to predict the effect of association between molecules of different sizes and polarities, including the asphaltene/resin interaction. However, it requires additional laboratory experiments to characterize the fluid and its mathematical complexity may significantly increase the computational requirements for reservoir simulation.

[Nghiem et al. \(1998\)](#) developed a model for predicting precipitation based entirely on a cubic EOS. Using a three-phase equilibrium, the model accounts for the thermodynamic balance between vapor, liquid,



**Fig. 1.** Typical  $p$ - $T$  asphaltene precipitation envelope as proposed by [Leontaritis \(1996\)](#) where precipitation occurs only within the region defined between the ADE upper boundary and the ADE lower boundary [adapted from [Leontaritis \(1996\)](#)].

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