Iraqi Journal of Oil & Gas Research

Journal homepage: https://ijogr.uotechnology.edu.iq/

A Critical Review of Challenges in Thermodynamic Modeling of Asphaltene Precipitation: Insights from Experimental Complexity and Diverse Approaches

*[1]Seyed Abdollah Shojaei**

[1]Chemical engineering, Department of Applied Chemistry, Faculty of Science, Malayer University, Malayer, Iran

Article information

Article history:
Received: January, 23, 2025
Revised: April, 11, 2025
Accepted: September, 06, 2005
Available online: October, 04, 2025

Keywords:
Thermodynamic,
Asphaltene Precipitation,
Polymer solution

Corresponding Author:
Seyed Abdollah Shojaei
Abdollahshoja@malayeru.ac.ir

Abstract

The reliable prediction of asphaltene precipitation is critical for mitigating operational challenges in oil production, yet existing thermodynamic models face persistent limitations due to the complex composition and self-association behavior of asphaltenes. This study evaluates two dominant modeling frameworks: solubility-based approaches, which treat asphaltenes as dissolved macromolecules, and colloidal stability-based models, which conceptualize asphaltenes as suspended particles stabilized by resin interactions. Solubility models, including Flory-Huggins's theory and cubic equations of state, correlate precipitation with solubility parameters and Gibbs free energy changes, but are constrained by assumptions of molecular homogeneity and reliance on ill-defined critical properties. Colloidal models, such as micellization theory, link precipitation to resin depletion and micelle destabilization.

Statistical Associating Fluid Theory (SAFT) models, particularly the Perturbed-Chain (PC-SAFT) variant, bridge two modeling approaches by incorporating molecular-specific parameters—such as segment size, interaction energy, and chain length—to describe complex behaviors like molecular size variations and clustering in fluids. While SAFT models offer strong predictive accuracy, their reliance on carefully calibrated inputs and computational complexity highlights a trade-off between scientific rigor and practical application. Experimental studies demonstrate that no single model reliably predicts asphaltene precipitation across all crude oil types, underscoring the need for hybrid methods.

This article critically reviews model-based predictions in the context of asphaltene behavior, addressing their necessity, strengths, and limitations. It investigates the most widely adopted models in both academic literature and industrial software, analyzing the underlying reasons for their prevalence. Furthermore, the study explores the similarities and differences among existing models and their classification criteria.

DOI: http://doi.org/10.55699/ijogr.2025.0502.1083 , College of Oil and Gas Engineering, University of Technology-Iraq

1. Introduction

Asphaltenes, the heaviest and most polar components of crude oil, have a multi-aromatic core structure connected to the alkane chains [1]. Asphaltene precipitation and deposition pose significant challenges for oil producers, affecting reservoir formation, production wells, and refining equipment. Therefore, oil experts have conducted numerous theoretical and experimental studies to predict the time, manner, and amount of asphaltene deposition. A comprehensive solution for predicting asphaltene precipitation remains elusive. This limitation arises from the heterogeneity of the asphaltene composition and the complexity of their self-association behavior. Asphaltene, a complex compound with over 100,000 molecular types [2], varies significantly among different oil sources. This variation has led to the proposal of various thermodynamic models for predicting the asphaltene precipitation. Accurate predictive models should be aligned as closely as possible with experimental asphaltene precipitation data. Studies on asphaltene characteristics have revealed that it is a polar compound containing polyaromatic hydrocarbons with functional groups of oxygen, nitrogen, sulfur, and heavy metals, such as nickel and vanadium [3].

Asphaltene aggregation and precipitation are governed by their intrinsic molecular complexity, structural diversity, and environmental interactions. These macromolecules, characterized by polar functional groups and polyaromatic cores [1], exhibit pronounced heterogeneity across size, shape, and polarity [2]. Aggregation progresses hierarchically from nanometric clusters to micron-sized aggregates [4, 5], following non-uniform kinetics where monomers associate at variable rates [6]. Deposits often include non-asphaltene components (e.g., resins, waxes) [7], lack defined phase-transition properties [8], and manifest as semi-solid sludge in pipelines [9]. Fractal theory aptly describes their aggregation patterns [10-12], while their stability in oil hinges on resin content [15, 16] and molecular architecture. The various macromolecules in asphaltene differ in terms of stability in oil, molecular weight, and molar volume [13] and their aggregation is non-uniform and effectively operates under multiple conditions, meaning that some particles aggregate in pairs, others in triplets, etc. [14]. Structurally, asphaltenes adopt two configurations: the island motif (single aromatic core with aliphatic branches) and the archipelago motif (linked aromatic nuclei) [17-21], with the former dominating deposition models due to its alignment with steric and π-π interaction dynamics [18].

Divergences between heavy and light oil asphaltenes further complicate modeling. Heavy oil derivatives exhibit higher H/C ratios, reduced aromaticity, elongated alkyl chains, and broader molecular weight distributions [22], favoring solubility through steric stabilization. Conversely, light oil asphaltenes resemble low-solubility subfractions, with heteroatom-rich structures and stronger π-π interactions that exacerbate deposition [22]. These distinctions necessitate context-specific modeling frameworks. Current approaches bifurcate into two paradigms: (1) solubility-based models, treating asphaltenes as dissolved macromolecules governed by phase equilibria [23], and (2) colloidal models, conceptualizing them as resin-stabilized suspended particles [24].

This article seeks to address critical gaps in asphaltene precipitation modeling by systematically evaluating the theoretical foundations, practical applications, and limitations of existing thermodynamic frameworks. It aims to elucidate why model-based prediction is indispensable for mitigating operational risks in oil production, critically assess the strengths and weaknesses of solubility-based and colloidal stability-based approaches, and identify the most prevalent models in academic literature and industrial software. By establishing a comparative framework that highlights differences and similarities between models—classified by their treatment of asphaltene state (dissolved vs. colloidal).

2. Models Based on Asphaltene Solubility in Oil

One of the oldest modeling approaches uses lattice and regular solution theories to determine the change in the Gibbs free energy associated with polymer formation from monomers. This Gibbs energy change was derived using the Flory-Huggins equation [25, 26]:

$$\Delta G_M = RT\left[n_{Sol.}\, ln\, \phi_{Sol.} + n_{Asph.}\, ln\, \Phi_{Asph.} + n_{Sol.}\Phi_{Asph.}\frac{v_{Asph.}(\delta_{Sol.} - \delta_{Asph.})^2}{RT}\right] \quad (1)$$

Where, $n_{Sol.}$ and n_{Asph}, represent the mole number of solvent and asphaltene, respectively, $v_{Asph.}$ is the molar volume of the asphaltene phase, $\delta_{Sol.}$ is the solvent solubility parameter, and $\delta_{Ply.}$ is the asphaltene solubility parameter. $\phi_{Sol.}$ and $\Phi_{Asph.}$ represent the volume fractions of solvent and asphaltene, respectively, and ΔG_M represents the change in the Gibbs free energy of mixing. The temperature T is measured in Kelvin, and R is the universal gas constant. In polymer thermodynamic models, asphaltene precipitation occurs in two distinct stages. Initially, the phase separation between gas and liquid was evaluated using cubic equations of state. Subsequently, asphaltene precipitation from the liquid phase was assessed. In the simplest model, the initial phase separation uses the SRK (Soave-Redlich-Kwong) equation, assuming that asphaltenes behave like polymers [23]. In other words, the dissolved asphaltene monomers in the oil phase connect to form a polymer chain. Precipitation began when the chain reached a sufficient size. Under this assumption, the chemical potential change for asphaltene precipitation formation is defined as follows [27]:

$$\Delta\mu_{Asph} = \Phi_{PM}^2 v_{Asph}\left(\delta_{PM} - \delta_{Asph})^2 + RT\left[ln\,\Phi_{Asph} + \left(1 - \frac{v_{Asph}}{v_{PM}^{Modefied}}\right)\Phi_{PM}\right)\right] \quad (2)$$

Where, v_{Asph} , $v_{PM}^{Modefied}$, δ_{Asph}, δ_{PM} , Φ_{PM} and Φ_{Asph} are the molar volumes of asphaltene, the molar volume of the petroleum mixture in the liquid phase after correction with the volume shift, the asphaltene solubility parameter, the oil mixture solubility parameter, volume fraction of liquid petroleum mixture and volume fraction of asphaltene in the liquid phase, respectively. Equating the chemical potentials determined the maximum soluble asphaltene fraction. Comparing the maximum soluble fraction to tank deposits estimates the asphaltene phase formation under the given conditions. According to this theory, the quantity and precipitation conditions are highly sensitive to the solubility parameter and molar volumes of asphaltene and the solvent. Adjustments in calculating the solubility parameter of the oil solvent enhance the model predictions [28, 29]. Even when assuming that the volume fractions of asphaltene and solvent are unknown, significant improvements in the model accuracy can be achieved [30]. The experimental determination of these parameters is impractical; therefore, they are often estimated thermodynamically, compromising the model reliability. Further research indicates that pure asphaltene deposits are rarely observed, and usually include asphaltene, resin, and wax. In this study required concentrations, molar volumes, solubility parameters, asphaltene-asphaltene aggregation constant, and resin-asphaltene cohesion constant to describe the system and perform equilibrium calculations. This model shows a slight improvement over the simplest model but remains inaccurate under high-temperature and high-pressure conditions [31].

Although qualitatively insightful, this model's quantitative accuracy is limited by assumptions about asphaltene phase purity, regular solution theory, and vapor-liquid equilibrium. The changes in the molecular weight of asphaltene and the adhesion of resin and asphaltene molecules during deposition cause regression data to be problematic. This problem can be solved using suitable regression [32]. To develop this model, it is assumed that asphaltene is not homogeneous and is a multiple polymer. In this model, Scott and Magat multiple polymer development was used. Therefore, the changes in the Gibbs energy at a given temperature and pressure are as follows [33]:

$$\begin{aligned}\Delta\mu_i^{Asph} = {} & \Phi_{PM}^2 v_i^{Apha}[(\delta_{PM} - \delta_{Asph})^2 + 2\Gamma\delta_{PM}\delta_{Asph}] \\ & + RT\left[ln\,\Phi_i^{Aspha} + \frac{v_i^{Apha}\Phi_{PM}^2}{v_{PM}^{Modefied}Zcor} + 1 - \frac{v_i^{Apha}}{\sum x_i^{Apha}v_i^{Apha}}\right. \\ & \left. + \left(\frac{v_i^{Apha}}{\sum x_i^{Apha}v_i^{Apha}} - \frac{v_i^{Apha}}{v_{PM}^{Modefied}}\right)\Phi_{PM}\right]\end{aligned} \quad (3)$$

In this equation, the coordination number is between two consecutive parts of the asphaltene molecule. This number is typically between three and four. This is an adjustable binary-interaction coefficient. This model has better predictability at higher pressures and temperatures. In addition, this model shows that asphaltene with a higher molecular weight precipitated earlier than asphaltene with a lower molecular weight. Adjustable weight distribution functions render this model computationally complex and less generalizable.

Applying the polymer solution theory with Miller's and Flory-Huggins corrections yields the Gibbs energy change for asphaltene phase formation as follows [33]:

$$\begin{aligned} \Delta G_{Asph} = \Delta\mu_{Asph} &= \Delta H - T\Delta S \\ &= \Phi_{PM}^2 v_{Asph}\left[(\delta_{PM} - \delta_{Asph})^2 + 2\Gamma\delta_{PM}\delta_{Asph}\right] \\ &+ RT\left[ln\,\Phi_{Asph} - \frac{Zcor}{2}ln\left(1 - \frac{2}{Zcor}\left(1 - \frac{v_{Asph}}{v_{PM}^{Modefied}}\right)\Phi_{PM}\right)\right] \end{aligned} \quad (4)$$

This model neglects the multiplicity of asphaltene species, providing slightly improved predictions compared with earlier models. However, its applicability to diverse oil types remains untested, which limits its generalizability.

Various polymer thermodynamic models have been employed to simulate asphaltene deposition, demonstrating a greater sensitivity to changes in oil composition than to pressure and temperature. Figure 1 shows flowchart of polymerization thermodynamic model [23]. Software packages, such as PVTsim and PVTsim Plus, utilize both simple and multiple polymer models for asphaltene deposition modeling. In addition, the Iranian software Pars asphaltene deposition simulator employs a modified Flory-Huggins and Miller model.

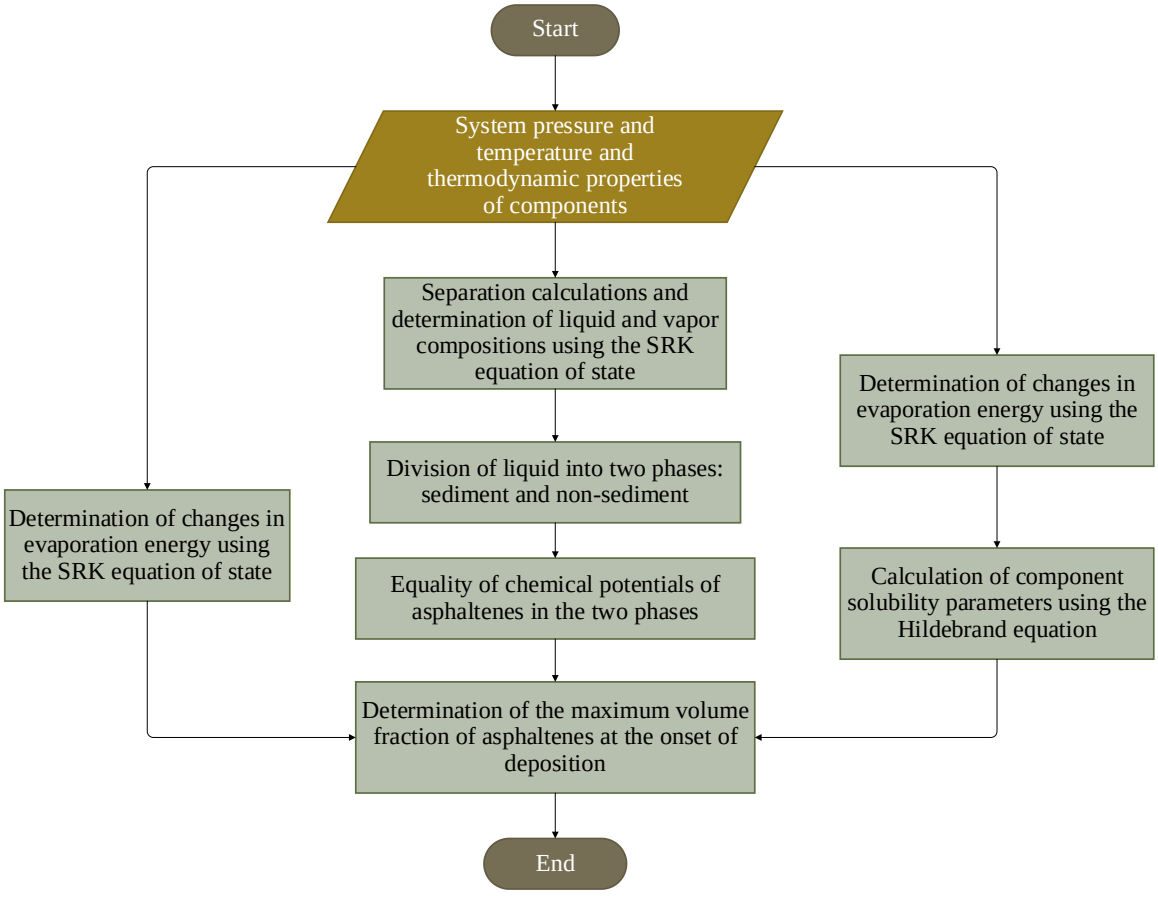

Figure 1: Flowchart of the polymerization thermodynamic model calculations [23].

Another common assumption in asphaltene deposition modeling is that asphaltene macromolecules are soluble in oil and can form a solid phase under specific temperature and pressure conditions. This model relies on the calculation of the fugacity of the pure solid asphaltene phase in equilibrium with the oil solution. As illustrated in Figure 2, the initial step involves calculating the Gibbs energy change associated with the transition from the liquid phase to the solid phase at a given temperature and pressure.

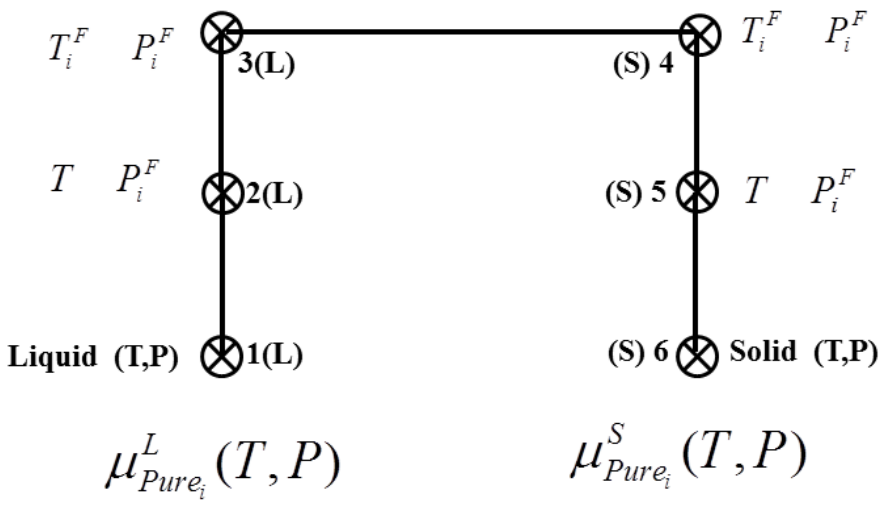

Figure 1: Change of chemical potential of pure component from liquid phase to solid phase

This state change is in the form of chemical potential, enthalpy, and entropy changes. By putting together, the changes of each stage until reaching the solid phase, a relation for the fugacity of the precipitated phase is obtained as follows:

$$f^S_{Pure_i}(T,P) = f^L_{Pure_i}(T,P) \times exp[\frac{\Delta h_i{}^F}{RT_i^F}(1-\frac{T_i^F}{T}) - \frac{\Delta c_{P_i}}{R}(1-\frac{T_i^F}{T}) - \frac{\Delta c_{P_i}}{R}[ln(\frac{T}{T_i^F}) - \frac{1}{RT}\int_{P_i^F}^{P}\Delta v_i dP] \quad (5)$$

Where, Δv_i the difference between the molar volume of pure component i in the solid state and in the liquid state, Δc_{P_i} is the specific heat difference of the pure component i at constant pressure, $\Delta \square_i{}^F$ the latent heat of fusion of the pure component i, T is the temperature and P is also the pressure.

After performing liquid-vapor equilibrium calculations, assuming the deposited asphaltene to be a pure phase, the heaviest petroleum components are divided into two groups: precipitating and non-precipitating. These groups share the same eccentricity coefficients and critical properties but differ in their interaction coefficients with light components. Figure 3 presents the flowchart calculations of solid model [34]. This model is widely adopted in commercial software like WinProp, PVTi, and PVTsim. While it effectively predicts sedimentation conditions qualitatively, its quantitative accuracy is limited. One major drawback is the assignment of critical properties to the precipitating asphaltene component, which compromises the model's reliability.

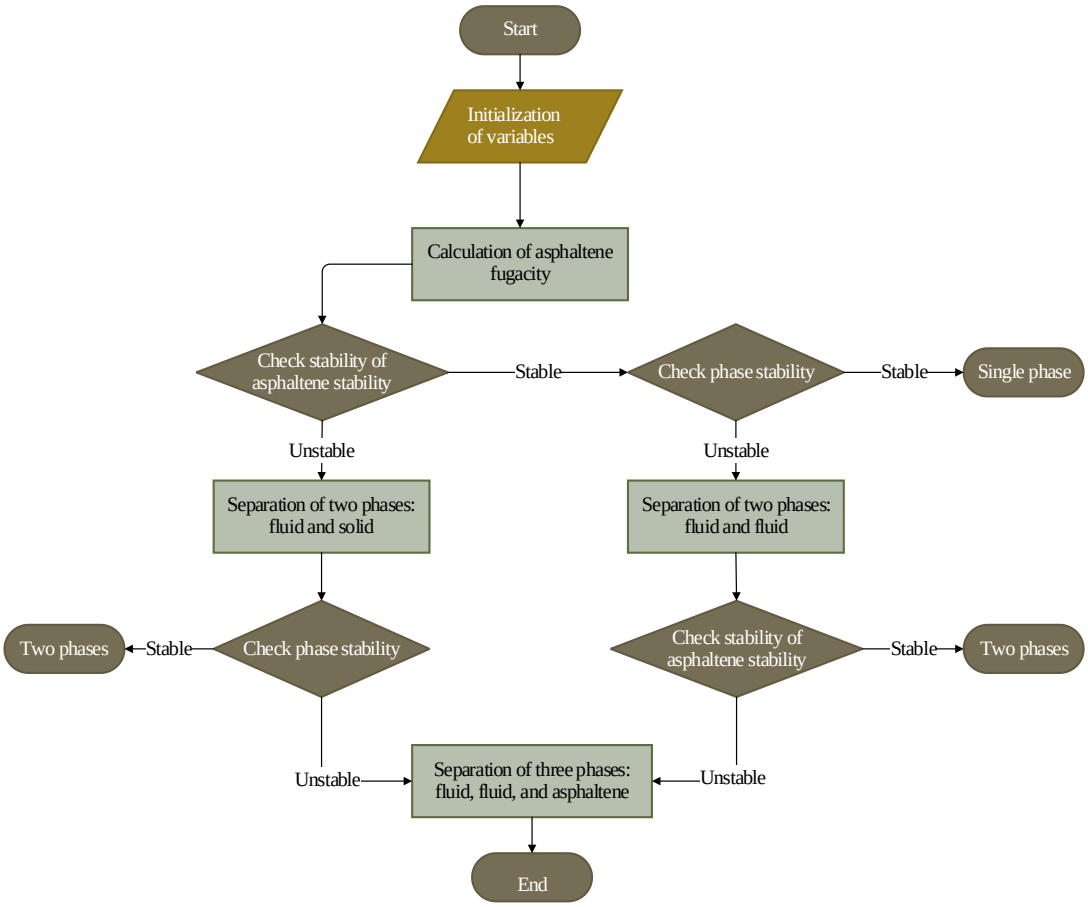

Figure 3:Flowchart of three-phase separation calculations in the solid phase model [34].

Statistical Associating Fluid Theory (SAFT) models, which are based on the aggregation of polar asphaltene macromolecules dissolved in oil, circumvent the need for asphaltene critical parameters. Fugacity coefficients are determined from the residual Helmholtz free energy [35].

$$ln\, f_i = A^{res} + (\frac{\partial A^{res}}{\partial x_i})_{T,v,x_{j\neq i}} - \sum_{k=1}^{N}\left[x_k(\frac{\partial A^{res}}{\partial x_k})_{T,v,x_{j\neq k}}\right] + z - 1 - ln\, z \quad (6)$$

Where, A^{res} and z are the residual Helmholtz free energy and the compressibility coefficient, respectively. The compressibility coefficient is also related to the remaining Helmholtz free energy, using the following equation:

$$z = 1 + \rho_r(\frac{\partial A^{res}}{\partial \rho_r})_{T,x_i} \quad (7)$$

According to the above equations, if the value of A^{res} is obtained, then the other parameters can be obtained. Many developments have been made to determine the value of the Helmholtz residual free energy. For association fluids, the excess free energy consists of the following:

A) Contribution of the intramolecular repulsive and attractive forces $A^{Fundamental}$. Choosing the type of attraction and repulsion between basic particles (square well, Leonard Jones, and hard sphere) will change the relations of this part.

b) The contribution of the interconnection of molecules $A^{C\square ain}$ and the formation of double, triple and higher

chains

c) The share of interconnection of chains formed in the form of branches or rings $A^{Association}$

By collecting the contributions of the Helmholtz free energy and using statistical thermodynamics, it is possible to calculate the contribution of each of the remaining Helmholtz free energy contributions and then obtain the Fuga coefficient for different compounds:

$$A^{res} = A^{Fundamental} + A^{C\square ain} + A^{Association} \quad (8)$$

Various statistical associating fluid theory (SAFT) models, including basic SAFT [29, 36], PC-SAFT [37-50] and Cubic Plus Association (CAP) [43, 51-58] have been applied to asphaltene deposition modeling. Among these models based on the statistical associating fluid theory (SAFT), the PC-SAFT model has been used more than other models for modeling asphaltene deposition. The PC-SAFT equation of state considers three parameters for each non-associated component. These parameters are: the temperature-independent diameter of each molecular segment (θ), the number of segments per molecule (m), and the segment-segment interaction energy (ε/k). All three of these parameters are related to the molecular weight and aromaticity of aromatic compounds [37, 38]. Figure 4 shows three chain molecules model that are used in SAFT model.

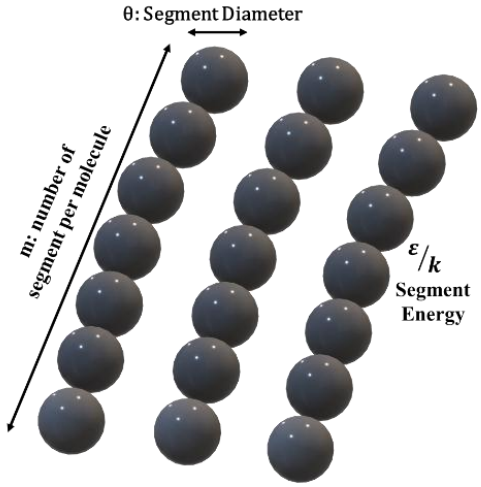

Figure 4: A chain molecule composed of several hard spheres used in SAFT models.

These models, grounded in sound physical principles, offer promising quantitative and qualitative results. However, due to the complex nature of asphaltene as a group of compounds, obtaining accurate molecular parameters for SAFT modeling remains challenging. Model calibration and parameter adjustment are often necessary to achieve satisfactory results, which can limit the general applicability of these models. Figure 5 presents flowchart of calculation steps in PC-SAFT model.

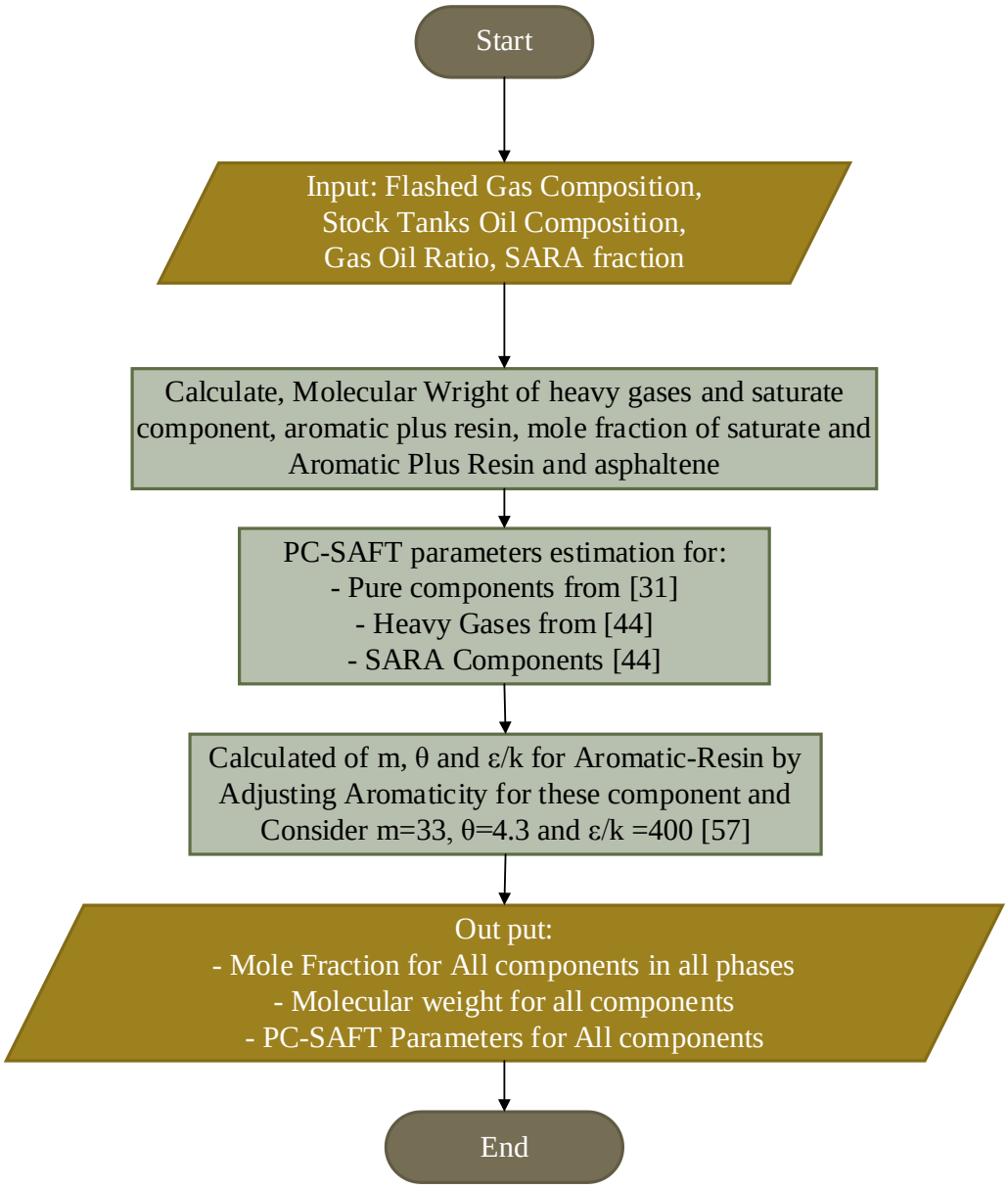

Figure 5: Flowchart of Asphaltene precipitation in PC-SAFT model [50].

Given the relatively recent application of SAFT to asphaltene modeling, most studies focus on using SAFT to analyze and evaluate asphaltene macromolecule aggregation and deposition conditions. The PC-SAFT model has been integrated into PVTsim software for predicting petroleum fluid phase separation. A summary of the comparison between the models presented, considering the presence of dissolved asphaltene macromolecules within the oil medium, is provided in table 1.

Table 1: Comparative analysis of thermodynamic models based on asphaltene solubility in oil

Model	Key Parameters	Strengths	Limitations	References
Flory-Huggins Model	Mole numbers of solvent and asphaltene, volume fractions, solubility parameters, molar volumes	Foundational framework for solubility-based models; calculates Gibbs energy of mixing.	Homogeneous assumptions; limited accuracy under high-pressure/high-temperature (HP/HT) conditions.	[22], [24–29]
SRK Equation (Phase Separation)	Volume fractions, solubility parameters, modified molar volumes	Predicts phase separation using cubic EoS; widely used in industrial software.	Requires empirical adjustments; neglects polydispersity and resin interactions.	[22], [24–29]
Scott-Magat Model (Multiple Polymers)	Coordination number, interaction coefficient, molecular weight distribution	Improved predictability at HP/HT; accounts for molecular weight effects.	Computationally complex; calibration-dependent.	[29]
Miller & Flory-Huggins Corrected Model	Enthalpy, entropy, solubility parameters	Includes enthalpy-entropy trade-offs; better predictions than early models.	Untested for diverse oil types; ignores asphaltene multiplicity.	[29]
Solid Phase Fugacity Model	Molar volume differences, specific heat differences, latent heat of fusion	Predicts solid-liquid equilibrium; used in commercial software (WinProp, PVTsim).	Assigns critical properties to asphaltenes, reducing reliability.	[30]
SAFT/PC-SAFT Models	Segment diameter, chain length, interaction energy	Captures polydispersity and association; aligns with experimental data.	Requires calibration; complex parameterization limits generalizability.	[25], [31–46], [46]

3. Models Based on Colloidal Stability of Asphaltene Particles in Oil

The This category of models is based on the assumption that asphaltene macromolecules remain suspended in oil rather than dissolving, regardless of temperature or pressure. However, this assumption is not accurate under dilute asphaltene concentrations in toluene.

While the colloidal nature of asphaltenes in oil has been recognized since the 1930s, Leontaritis and Mansoori were the first to develop a thermodynamic model based on this concept [59]. Their model is particularly relevant when asphaltene precipitation occurs under conditions where resin-asphaltene micelles are present. Initially, vapor-liquid equilibrium calculations are performed using an equation of state to characterize the liquid phase. Resins play a critical role in stabilizing asphaltene molecules within this liquid phase. Repulsive interactions between resins prevent asphaltene aggregation, maintaining their suspension in the oil. Thus, the stability of asphaltenes is strongly influenced by the presence of resins. The addition of alkanes to dead oil can lead to resin detachment from asphaltenes, making the asphaltene surfaces more active and promoting aggregation. The maximum resin concentration that stabilizes asphaltenes in dead oil can be used as a criterion for predicting asphaltene precipitation onset. Based on experimental data, a critical chemical potential for resins can be estimated using Flory-Huggin's theory to predict precipitation under different conditions.

Another approach views crude oil as a stable colloidal medium, a three-phase micellar system. Crude oil is a complex mixture of paraffinic, naphthenic, and aromatic hydrocarbons, along with polar polyaromatic compounds. While asphaltenes can dissolve in aromatic solutions, the low concentration of aromatic hydrocarbons in crude oil makes it more akin to a three-component system: an organic solvent, a surfactant (resin), and a polar compound (asphaltene).

Figure 6 depicts the various species present in crude oil according to the micellar model. Resin molecules, asphaltene monomers, and micelles are dissolved in the continuous phase (β), representing the crude oil fluid. The micelles consist of an asphaltene core surrounded by a resin shell. Some asphaltenes may also exist in a separate precipitated phase (δ).

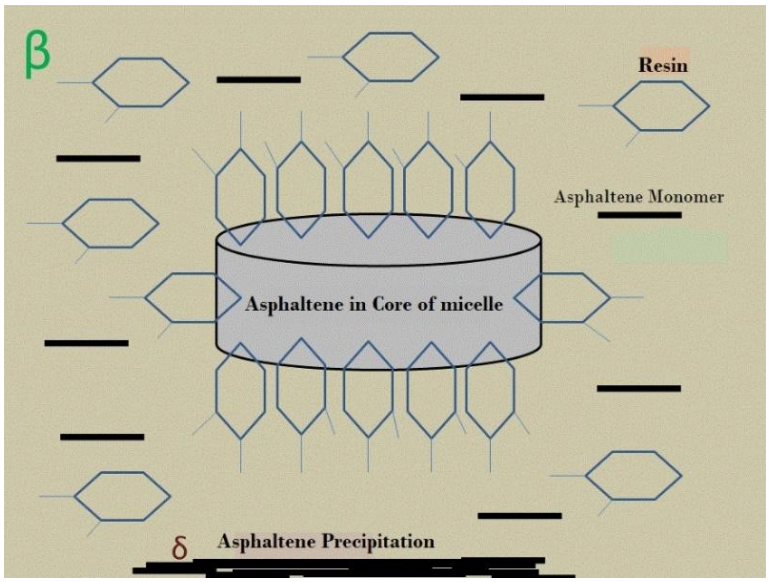

Figure 6: A view of the species presents in the crude oil based on the micellization model

In contrast to colloidal models, where resin concentration is used as the basis for phase change and precipitation, in this model, the concentration of asphaltene in the solvent triggers phase change and precipitation:

$$x_{Mic.}^{\beta} = x_{Asph}^{\beta\ N_{Asph}^{\beta}} x_{Resin}^{\beta\ N_{Resin}^{\beta}} exp[\Delta G_M/RT] \quad (9)$$

Where, N_{Resin}^{β} represents the number of resin molecules attached to the core and forming the micelle shell and N_{Asph}^{β} is the number of asphaltene molecule in core of micelle. x_{Asph}^{β} , x_{Resin}^{β} , and $x_{Mic.}^{\beta}$ represent the mole fractions of asphaltene, resin, and micelle, respectively. As micelles are formed, some asphaltene molecules remain, leading to precipitation and instability. The minimum concentration of asphaltene x_{Asph}^{ons} needed to initiate precipitation serves as an equilibrium criterion.

x_{Asph}^{ons} is the concentration of asphaltene monomers in equilibrium with the micelles, and the precipitate represents the maximum amount of asphaltene that the solvent can dissolve in. An increase in the asphaltene monomer concentration beyond this threshold resulted in asphaltene precipitation. This concentration can be considered the critical micelle concentration in a three-component system. In fact, x_{Asph}^{ons} is the main parameter in the thermodynamic model of micelle formation.

In a three-species system like crude oil, the change in Gibbs free energy for micellization encompasses several components:

1. **Hydrophobic Gibbs Energy:** This term accounts for the energy changes associated with micelle formation from asphaltene monomers, resin, and precipitated asphaltene monomers. It also includes the energy changes due to resin molecules moving from the solvent to the micelle, involving the breaking of resin-solvent bonds and the formation of resin-asphaltene and resin-resin bonds.

2. **Interfacial Gibbs Energy:** This term considers the interfacial energy changes between the resin-micelle surface and the solvent, as well as the micelle core surface not covered by resin.

3. **Electrostatic Gibbs Energy:** Given that oil typically behaves as a dielectric medium, the influence of electrostatic forces on micelle formation is considered negligible. Therefore, the electrostatic term is omitted from this thermodynamic model of micelle formation.

$$\Delta G_M = -N_{Asph}^{\beta} kT\, ln\, X_{ASph}^{ons} + N_{Resin}^{\beta}(\Delta U_R + Tk\, ln(1-\Theta)) - \frac{\sigma_0 a N_{Resin}^{\beta}(1-\Theta)}{\Theta}) \quad (10)$$

In this equation, $\Theta = Ar_{Resin}(N_{Resin}^{\beta})/Ar_{\Sigma}$ where $Ar_R(N_{Resin}^{\beta})$ and Ar_{Σ} denote the sizes and geometry of asphaltene and resin molecules, respectively. σ_0 represents the interfacial tension of the micelle with the solvent without any resin on the micelle core surface. ΔU_R is the change in energy due to interactions between the resin head group with asphaltene in the micelle core and the solvent [60].

This equation captures the change in Gibbs energy for resin-asphaltene micelle formation, with hydrophobic interactions driving resin attraction and shell formation around the asphaltene core ($N_{Resin}^{\beta}\Delta U_R$). The hydrophobic term, represented by $N_{Asph}^{\beta} kT\, ln\, X_{Asph}^{ons}$, and the interfacial tension term, $\frac{\sigma_0 a N_{Resin}^{\beta}(1-\Theta)}{\Theta}$), and $N_{Resin}^{\beta} Tk\, ln(1-\Theta)$ constrain resin adsorption onto the micelle core. By substituting equation (10) into equation (9), taking the logarithm, and differentiating with respect to Θ to zero, the optimal concentration for asphaltene is obtained. Figure 7 shows calculation steps of micellization thermodynamic model for asphaltene precipitation.

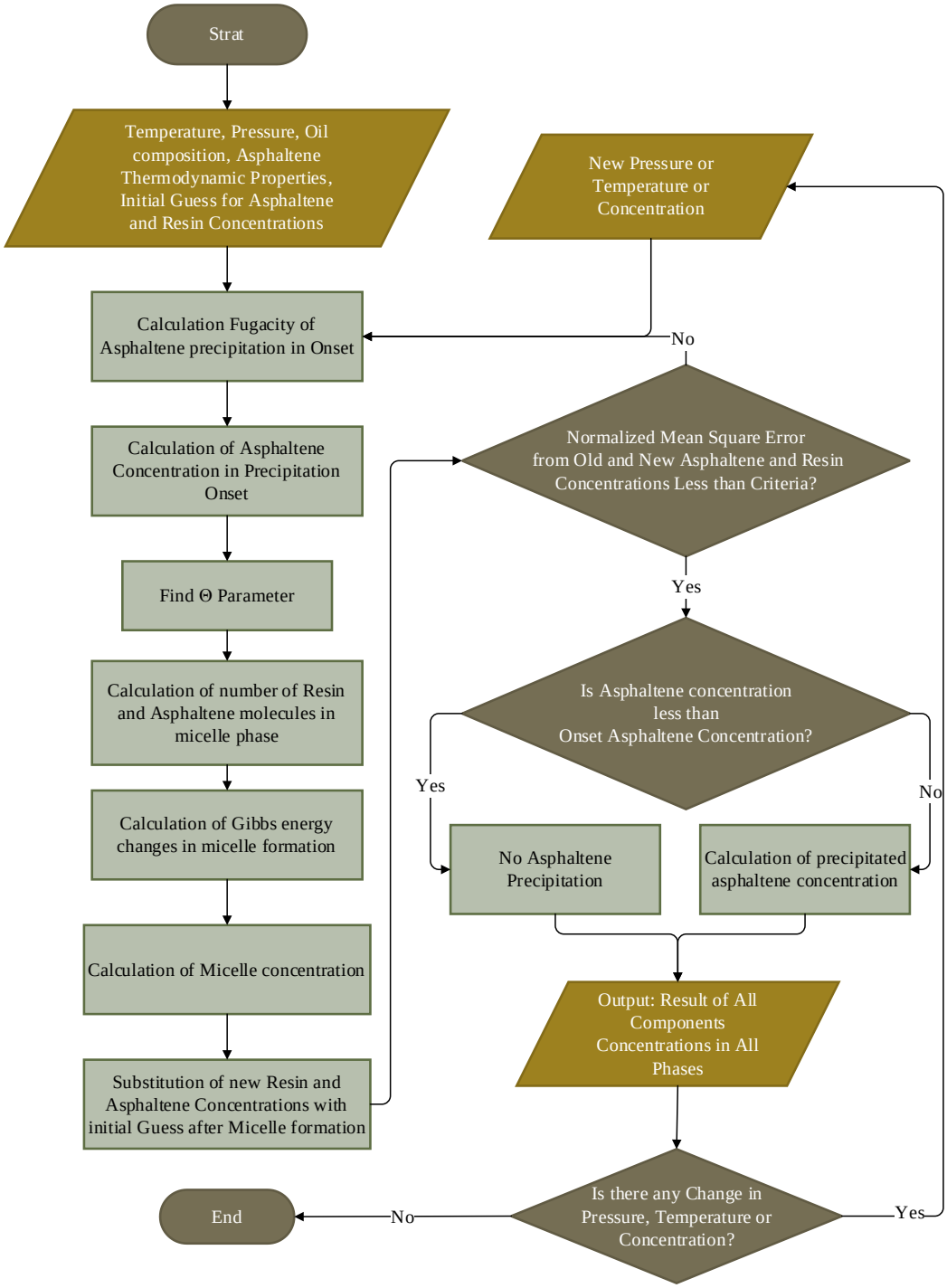

Figure 7: Flowchart of micellization thermodynamic model for asphaltene precipitation [61].

Experimental investigations by [62] explored the onset of asphaltene precipitation under various conditions, employing different precipitants (n-pentane, n-hexane, n-decane, n-dodecane, and gas mixtures) and pressures. A comparison of experimental results with the micellization thermodynamic model reveals that, while the model qualitatively captures experimental trends, it falls short in terms of quantitative prediction.

Subsequent refinements to the thermodynamic model have incorporated modifications to the geometry and deformation of the resin coating surrounding the asphaltene micelle core [63]. These refinements have demonstrated the significant impact of the geometric factor of the resin shell on the modeling results.

Further research has explored the concept of multiple micelle formation, conducting calculations for an oil sample exposed to different alkane precipitants (n-pentane, n-heptane, n-decane, and n-dodecane) [64] . Additionally, the inclusion of resin in the sediment, along with the fractionation of asphaltene into three components and the consideration of micelle core and shell deformation energy, has led to improved model predictions. This model accurately predicts the increase in micelle size with increasing precipitant ratio, aligning well with experimental observations[65].

The incorporation of asphaltene distribution multiplicity has brought the model closer to experimental findings on asphaltene distribution in crude oil. By comparing singular and multiple asphaltene distribution calculations with experimental data, [66] demonstrated that the multiplicity assumption significantly enhances the quantitative accuracy of the thermodynamic model.

The development of micelle-based thermodynamic models for asphaltene deposition has been driven by considerations of interaction coefficients between heavy and light oil components. Initial modeling results have shown quantitative improvements, and the impact of varying these interaction coefficients on model predictions has been investigated [61].

Despite advancements, colloidal-based models still face challenges due to limitations in accurately determining molecular parameters and their relevance to real-world asphaltene deposition scenarios. Further research is necessary to address these limitations and enhance the predictive capabilities of these models. Table 2 provides a comparative analysis of models developed considering the colloidal state of asphaltenes in oil.

Table 2: Comparative Analysis of Colloidal Stability-Based Models for Asphaltene Precipitation

Model	Key Parameters	Strengths	Limitations	References
Leontaritis-Mansoori Colloidal Model	Resin chemical potential, micelle stability criteria, resin-asphaltene interaction coefficients	Pioneering framework for resin-stabilized micelles; predicts precipitation onset via resin depletion.	Assumes constant resin concentration; limited to dead oil systems.	[55], [56]
Micellization Thermodynamic Model	Mole fractions of asphaltene/resin/micelles, Gibbs energy components (hydrophobic, interfacial), micelle size/geometry	Captures micelle formation dynamics; explains resin shell stabilization.	Qualitative alignment with experiments; lacks quantitative precision.	[56], [57]
Geometric Refinement Model	Resin shell geometry, micelle core deformation energy, interfacial tension adjustments	Improves micelle size predictions; aligns with experimental precipitant ratios.	Computationally intensive; requires empirical geometric factors.	[58], [60]
Multiple Micelle Formation Model	Alkane precipitant ratios, asphaltene distribution multiplicity, core-shell deformation energy	Accounts for polydispersity; predicts micelle growth with precipitant addition.	Limited validation for mixed precipitants (e.g., gas + alkane).	[59], [60]
Multi-Component Interaction Model	Heavy-light oil interaction coefficients, resin-asphaltene cohesion constants	Enhances quantitative accuracy for real-world deposition scenarios.	Relies on poorly defined molecular parameters (e.g., resin-asphaltene cohesion).	[56], [61]

4. Conclusion

Thermodynamic modeling of asphaltene precipitation remains a pivotal challenge for the petroleum industry, requiring a balance between theoretical rigor and operational practicality. This study rigorously evaluates two foundational frameworks:

- Solubility-based models (e.g., Flory-Huggins theory, cubic EoS):
  - Strengths: Excel in predicting phase separation in dissolution-dominated systems.
  - Limitations: Oversimplify polydispersity, rely on ill-defined critical properties, and falter under high-pressure/high-temperature conditions.
- Colloidal models (e.g., micellization theory):
  - Strengths: Capture resin-asphaltene micelle dynamics, particularly in heavy oils.
  - Limitations: Struggle to reconcile assumptions with asphaltene solubility in aromatic solvents.

The perturbed-chain statistical associating fluid theory (PC-SAFT) emerges as a promising intermediary, leveraging molecular-specific parameters (segment diameter, interaction energy) to model polydispersity and aggregation. However, its dependency on calibrated inputs highlights a persistent trade-off between physical fidelity and practical applicability.

Critical Gaps and Hybrid Solutions:

Existing models fail to universally predict asphaltene behavior due to inherent heterogeneity (molecular weight, aromaticity) and experimental inconsistencies. Hybrid approaches—such as embedding resin-asphaltene interaction coefficients into PC-SAFT or integrating solubility parameters into colloidal frameworks—could bridge molecular-scale dynamics with macro-scale phase behavior. Key challenges include:

- Standardizing protocols for parameterizing asphaltene-resin interactions.
- Reconciling deterministic models with asphaltene's aggregation kinetics.

Future Directions:

1. Experimental Innovations:
   - Advanced spectroscopy/nanoimaging to resolve aggregation mechanisms under reservoir conditions.
2. Computational Advances:
   - Machine learning for parameter optimization.
   - Multi-scale simulations linking quantum mechanics to continuum thermodynamics.
3. Industry Collaboration:
   - Aligning models with operational needs (e.g., aging wells, unconventional reservoirs).

Ultimate Goal:

Unified frameworks harmonizing molecular insights, colloidal dynamics, and data-driven analytics are essential to refine predictions, mitigate operational risks (e.g., pipeline clogging), and optimize hydrocarbon recovery. As a summary Figure 8 shows categories of various thermodynamic models for prediction of asphaltene precipitation.

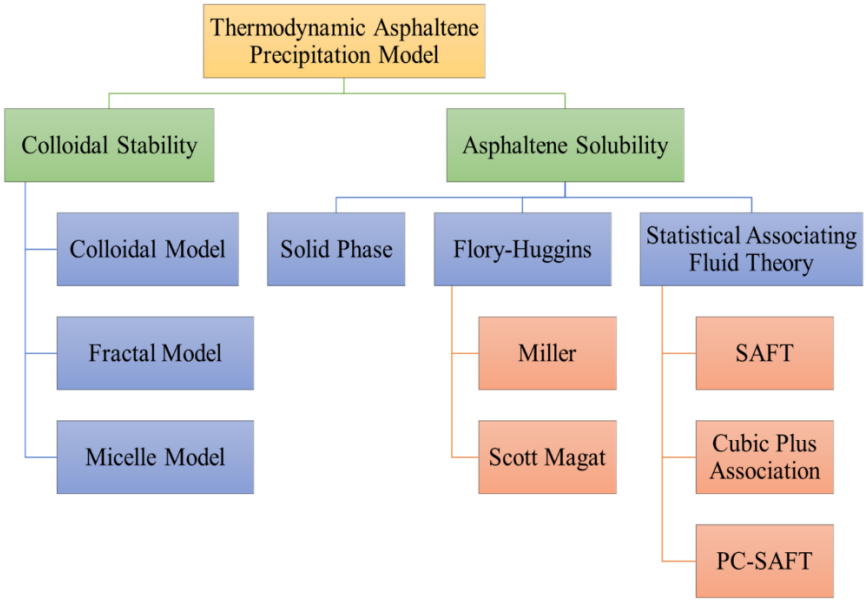

Figure 8: Categories of different thermodynamic model.

List of Symbols and Acronyms

n	Number of Mole	μ	Chemical Potential
δ	Solubility Parameter	x	Mole Fraction
R	Universal Gas Constant	$Zcor$	Coordinate Number
T	Temperature	Γ	Interaction Coefficient
ϕ	Volume Fraction	S	Entropy
G	Gibbs Free Energy	H	Enthalpy
v	Molar Volume	f	Fugacity
P	Pressure	A	Helmholtz Free energy
z	Compressibility Factor	ρ	Density
N	Number of molecules	σ	Interfacial Tension
k	Boltzmann Constant	Ar	Area
ε	Segment Energy	θ	Segment Diameter
m	Number of segments	Θ	Parameter from the sizes and geometry of asphaltene and resin molecules

Subscripts and Superscripts

$Sol.$	Solvent	S	Solid Phase
$Asph.$	Asphaltene	L	Liquid Phase
M	Mixture, Micelle	F	Fusion
PM	Petroleum Mixture	res	Residual
i, j, k	Component	$Mic.$	Micelle
β	Micelle Phase	ons	Onset

References

[1] H. Groenzin and O. C. Mullins, "Molecular Size and Structure of Asphaltenes from Various Sources," *Energy and Fuels,* vol. 14, pp. 677-684, 2000.

[2] A. Wiehe and K. S. Liang, "Asphaltene, Resins, and Other Petroleum Macromolecules," *Fluid Phase Equilibria,* vol. 117, pp. 201-210, 1996.

[3] T. Fergoug and Y. Bouhadda, "Detemination of Hassi Messaoud Asphaltene Aromatic Structure from H and C NMR Analysis," *Fuel,* vol. 115, pp. 521-526, 2014.

[4] A. H. Nikoo, M. Ghaedi, and M. R. Malayeri, "Impact of various aggregation kinetics on thermophoretic velocity of asphaltene deposition," *Scientific Reports,* vol. 14, no. 1, p. 18430, 2024/08/08 2024, doi: 10.1038/s41598-024-69503-3.

[5] S. A. Mousavi-Dehghani, M. R. Riazi, M. Vafaei-Sefti, and G. A. Mansoori, "An Analysis of Methods for Detemination of Onsets oof Asphaltene Phase Separations," *Journal of Petroleum Science and Engineering,* vol. 42, pp. 145-156, 2004.

[6] M. H. Rada, M. Tavakolian, I. Najafi, M. H. Ghazanfari, V. Taghikhani, and M. Amani, "Modeling the kinetics of asphaltene flocculation in toluene–pentane systems for the case of sonicated crude oils," *Scientia Iranica C,* vol. 20, no. 3, pp. 611-616, 2013.

[7] E. Chouparova *et al.*, "Characterization of Petroleum Deposits Formed in a Producing Well by Synchrotron Radiation-Based Microanalyses," *Energy and Fuels,* vol. 18, pp. 1199-1212, 2004.

[8] S. R. Panuganti, "Asphaltene Bahavoir in Crude Oil System," Doctor of Philosophy, Chemical and Boimolecular Engineering, Rice University, Houston, Texas, USA, 2013.

[9] E. W. MOORE, W. C, CROWE, and R. A, HENDRICKSON, "Formation, Effect and Prevention of Asphaltene Sludges During Stimulation Treatments," *Journal of Petroleum Technology,* pp. 1023-1028, 1956.

[10] Y. C. Liu, E. Y. Sheu, S. H. Chent, and D. A. Storm, "Fractal Structure of Asphaltenes in Toluene," *Fuel,* vol. 74, no. 9, pp. 1352-1356, 1995.

[11] N. H. G. Rahmani, T. Dabros, and J. H. Masliyah, "Fractal Structure of Aspahtlene Aggregation," *Journal of Colloid and Interface Science,* vol. 285, pp. 599-608, 2005.

[12] J. S. Amin, S. Ayatollahi, and A. Alamdari, "Fractal characteristics of an asphaltene deposited heterogeneous surface," *Applied Surface Science,* vol. 256, pp. 67-75, 2009.

[13] G. A. Mansoori, D. Vazquez, and M. Shariaty-Niassar, "Polydispersity of heavy organics in crude oils and their role in oil well fouling," *Journal of Petroleum Science and Engineering,* vol. 58, pp. 375-390, 2007.

[14] M.Tavakkoli, S. R. Panguganti, V.Taghikhani, M. R. Pishvaie, and W. G. Chapman, "Understanding the polydisperse behavior of asphaltenes during precipitation," *Fuel,* vol. 117, p. 12, 2014.

[15] S. Acevedo and C. Zuloaga, "Aggrigation-Dissociation Studies of Asphaltene Solutios in Resins Performed Using the Combined Freeze Fracture-Transmission Electron Microscopy Technique," *Energy and Fuels,* 2008.

[16] J. I. S. Aguiar and C. R. E. Mansur, "Study of the interaction between asphaltenes and resins by microcalorimetry and ultraviolet–visible spectroscopy," *Fuel,* vol. 140, pp. 462-469, 2015.

[17] O. C. Mullins, "Review of the Molecular Structure and Aggregation of Asphaltenes and Petroleomics," *SPE Journal,* vol. 13, no. 01, pp. 48-57, 2008, doi: 10.2118/95801-pa.

[18] B. Schuler *et al.*, "Overview of Asphaltene Nanostructures and Thermodynamic Applications," *Energy & Fuels,* vol. 34, no. 12, pp. 15082-15105, 2020/12/17 2020, doi: 10.1021/acs.energyfuels.0c00874.

[19] M. Hassanzadeh and M. Abdouss, "Molecular Structure: The First and Most Significant Factor in the Precipitation of Asphaltenes," *SPE Journal,* vol. 28, no. 02, pp. 894-907, 2023, doi: 10.2118/212311-PA.

[20] M. Morimoto, "Historical changes in the molecular model of asphaltene," *TANSO,* vol. 2023, no. 303, pp. 22-30, 2023, doi: 10.7209/tanso.2023.22.

[21] A. K. Sharma *et al.*, "Machine learning to identify structural motifs in asphaltenes," *Results in Chemistry,* 2024.

[22] M. Salehzadeh, M. M. Husein, C. Ghotbi, B. Dabir, and V. Taghikhani, "In-depth characterization of light, medium and heavy oil asphaltenes as well as asphaltenes subfractions," *Fuel,* vol. 324, p. 124525, 2022/09/15/ 2022, doi: https://doi.org/10.1016/j.fuel.2022.124525.

[23] A. Hirschberg, L. N. J. deJong, B. A. Schipper, and J. G. Meijer, "Infuence of Temperature and Pressure on Aspaltene Flocculation," *Society of pertoleum Engineering Journal*, p. 11, 1984.
[24] K. L. Leontaritis and G. A. Mansoori, "Asphaltene Flocculation During Oil Production and Processing: A Thermodynamic Colloidal Model," presented at the The SPE International Symposium on Oilfield Chemistry San Antonio, Texas, 1987.
[25] L. Vicente, C. Soto, H. Pacheco-Sánchez, J. Hernández-Trujillo, and J. M. Martinez-Magadán, "Application of molecular simulation to calculate miscibility of a model asphaltene molecule," *Fluid Phase Equilibria*, vol. 239, no. 1, pp. 100-106, 2006/01/05/ 2006, doi: https://doi.org/10.1016/j.fluid.2005.11.001.
[26] A. H. Mohammadi and D. Richon, "A monodisperse thermodynamic model for estimating asphaltene precipitation," (in en), *AIChE Journal*, vol. 53, no. 11, pp. 2940-2947, 2007/11// 2007, doi: 10.1002/aic.11304.
[27] S. A. Mousavi-Dehghani, B. Mirzayi, and M. Vafaie-Sefti, "Polymer solution and lattice theory applications for modeling of asphaltene precipitation in petroleum mixtures," *Braz. J. Chem. Eng.*, vol. 25, no. 3, pp. 523-534, 2008/09// 2008, doi: 10.1590/S0104-66322008000300010.
[28] S. L. Kokal, J. Najman, S. Sayegh, and A. E. George, "Measurment and Correlation of Asphaltene Precipitation from Heavy Oils by Gas Injection," *The Juornal of Canadian Pertoleum Technolgy*, vol. 31, no. 4, pp. 24-30, 1992.
[29] K. AKBARZADEH, S. AYATOLLAHI, M. MOSHFEGHIAN, H. ALBOUDWAREJ, and H. W. YARRANTON, "Estimation of SARA Fraction Properties With the SRK EOS," *Journal of Canadian Petroleum Technology*, vol. 43, no. 9, pp. 1-9, 2004.
[30] A. M. Mofidi and M. Edalat, "A Simplified Thermodynamic Modeling Procedure for Predicting Asphaltene Precipitation," *fuel*, vol. 85, pp. 2616-2621, 2006.
[31] Z. Novosad and T. G. Costain, "Experimental and Modeling Studeis of Asphaltene Equilibria for a Reservoir under CO2 Injection," presented at the Annual Technical Conference and Exhibition of SPE, New Orleans, Louisian, 1990.
[32] N. E. Burke, R. E. Hobbs, and S. F. Kashou, "Measurement and Modeling of Asphaltene Precipitation " *Journal of Petroleum Technology*, pp. 1440-1446, 1990.
[33] s. A. Mousavi-Dehghani, B. Mirzayi, and M. Vafaie-Sefti, "Polymer Solution and attice Theory Applications for Modeling of Asphaltene Precipitation in Petroleum Mixtures," *Brazilian Journal of Chemical Engineering* vol. 25, no. 03, pp. 523-534, 2008.
[34] L. X. Nghiem, M. S. Hassam, R. Nutakka, and A. E. D. George, "Efficient Modelling of Asphaltene Precipitation," in *The 68th Annual Technical Conference and Exhibition of the SPE*, Houston, Texax, 1993, vol. 26642: SPE.
[35] J. Gross and G. Sadowski, "Perturbed-Chain SAFT: An Equation of State Based on a Pertubation Theory for Chain Molecules," *Industerial & Engineering Chemistry Research*, vol. 40, pp. 1244-1260, 2001.
[36] P. D. Ting, G. J. Hirasaki, and W. G. Chapman, "Modeling of Asphaltene Phase Behavior with the SAFT Equation of State," *Petroleum Science and Technology*, vol. 21, no. 3, pp. 647-661, 2003.
[37] D. L. Gonzalez, P. D. Ting, G. J. Hirasaki, and W. G. Chapman, "Prediction of Asphaltene Instability Gas Injection with the PC-SAFT Equation of State," *Energy and Fuels*, vol. 19, pp. 1230-1234, 2005.
[38] D. L. Gonzalez, G. J. Hirasaki, J. Creek, and W. G. Chapman, "Modeling of Asphaltene Precipitation Due to changes in Composition Using the Pertubed Chain Statistical Associating Fluid Theory PC-SAFT Equation of State," *Energy and Fuels*, vol. 21, pp. 1231-1242, 2007.
[39] D. L. G. Rodriguez, "Modeling of Asphaltene Precipitation and Deposition Tendency using the PC-SAFT Equation of State," Doctor of Philosophy, Chemical and Biomolecular Engineering, Rice University, HOUSTON, TEXAS, USA, 3309879, 2008.
[40] F. M. V. Arreola, D. L. Gonzalez, G. J. Hirasaki, and W. G. Chapman, "Modeling Asphaltene Phase Behavior in Crude Oil Systems Using the Pertubed Chain Form of the Statistical Associating Fluid Theory (PC-SAFT) Equation of State," *Energy and Fuels*, vol. 23, pp. 1140-1146, 2009.
[41] T. j. Behbahani, C. Ghotbi, V. Taghikhani, and A. Shahrabadi, "Experimental Investigation and Thermodynamic Modeling of Asphaltene Precipitation PC-SAFT," *Scientia Iranica*, vol. 18, no. 6, pp. 1384-1390, 2011.

[42] S. R. Panuganti, F. M. Vargas, D. L. Gonzalez, A. S. Kurup, and W. G. Chapman, "PC-SAFT Characterization of Crude Oils and Modeling of Asphaltene Phase Behavior," *Fuel*, vol. 93, pp. 658-669, 2012.

[43] X. Zhang, N. Pedrosa, and T. Moorwood, "Modeling Asphaltene Phase Behavior: Comparison of Methods for fow Assurance Studies PC-SAFT and CPA," *Energy and Fuels*, vol. 26, pp. 2611-2620, 2012.

[44] S. Punnapala and F. M. Vargas, "Revising thr PC-SAFT Characterization Procedure for an Improved Asphaltene Precipitation Prediction," *Fuel*, vol. 108, pp. 417-429, 2013.

[45] O. S. Hustad, N. Jia, K. S. Pedersen, A. Memon, and S. Leekumjorn, "High-Pressure Data and Modeling Results for Phase Behavoir and Asphaltene Onsets of Gulf Mexico Oil Mixed With Nitrogen PC-SAFT," *SPE Reservoir Evaluation and Engineering*, pp. 1-12, 2014.

[46] M. Sedghi and L. Goual, "PC-SAFT modeling of asphaltene phase behavior in the presence ofnonionic dispersant," *Fluid Phase Equilibria* vol. 369 pp. 86–94, 2014.

[47] M. A. Zú˜niga-Hinojosaa, D. N. Justo-Garcíab, M. A. Aquino-Olivosc, L. A. Román-Ramírezd, and F. García-Sáncheza, "Modeling of asphaltene precipitation from n-alkane diluted heavy oilsand bitumens using the PC-SAFT equation of state," *fluid phase equilibria*, vol. 376, pp. 210-224, 2014.

[48] M. Tavakkoli, A. Chen, and F. M. Vargas, "Rethinking the modeling approach for asphaltene precipitation using the PC-SAFT Equation of State," *Fluid Phase Equilibria*, pp. 1-10, 2015.

[49] S. Mohebbinia, K. Sepehrnoori, R. T. Johns, A. Kazemi, and N. Korrani, "Simulation of asphaltene precipitation during gas injection using PC-SAFT EOS," *Journal of Petroleum Science and Engineering*, vol. 10.1016/j.petrol.2017.09.008, 2017.

[50] M. Masoudi, R. Miri, H. Hellevang, and S. Kord, "Modified PC-SAFT characterization technique for modeling asphaltenic crude oil phase behavior," *Fluid Phase Equilibria*, vol. 513, p. 112545, 2020/06/01/ 2020, doi: https://doi.org/10.1016/j.fluid.2020.112545.

[51] Z. Li and A. Firoozabadi, "Cubic-Plus-Association CPA Equation of State for Asphaltene Precipitation in Live Oils," *Energy and Fuels*, vol. 24, pp. 2956-2963, 2010.

[52] Z. Li and A. Firoozabadi, "Modeling Asphaltene Precipitation by n-Alkanes from Heavy Oils and Bitumens Using Cubic-Plus-Association Euation of State CPA," *Energy and Fuels*, vol. 24, pp. 1106-1113, 2010.

[53] B. Shirani, M. Nikazar, and S. A. Mousavi-Dehghani, "Prediction of Aspahltene Phase Behavoir in ive Oil with CPA Equation of State," *fuel*, vol. 97, no. 89-96, 2012.

[54] H. Nasrabadi, J. Moortgat, and A. Firoozabadi, "A New Three-Phase Multicomponent Compositional Modeling for Asphaltene Precipitation Using CPA-EOS," presented at the The SPE Resevoir Simulation Symposium The Woodlands, Texas, USA, 2013.

[55] M. Sattari, J. Abedi, M. Zirrahi, and A. K. Mehrotra, " Modeling the Onset of Asphaltene Precipitaion in Solvent-Diluted Bitumens Using CPA EoS," presented at the The SPE Canada Heavy Oil Technical Conference Calgary, Alberta, Canada, 2016.

[56] L. Dehdari and M. J. Amani, "Prediction of water solubility in ill-defined hydrocarbons at high temperatures: Modeling with the CPA-EoS," *Fluid Phase Equilibria*, vol. 10.1016/j.fluid.2017.09.009, 2017.

[57] Z. Taherian, M. V. Sefti, M. M. S. , M. Z. Talavaki, A. Afsharpour, and S. Veisi, "Determination of asphaltene precipitation using a new CPA-based equation of state," *Petroleum Science and Technology*, vol. 35, no. 4, pp. 377-384, 2017.

[58] M. Z. Talavaki, A. Afsharpour, and Z. Taherian, "Determination of asphaltene precipitation using a CPA equation of state," *Petroleum Science and Technology*, vol. 35, no. 9, pp. 839-844, 2017.

[59] K. J. Leontaritis, J. O. Amaefule, and R. E. Charles, "A Systematic Approach for the prevention and Treatment of Formation Damage Caused by Asphaltene Deposition," *Old Production and Facilities*, vol. 9, no. 3, pp. 157-164, 1994.

[60] M. Tavakkoli, M. Masihi, M. H. Ghazanfari, and R. Kharrat, "An improvement of thermodynamic micellization model for prediction of asphaltene precipitation during gas injection in heavy crude," *Fluid Phase Equilibria*, vol. 308, no. 1, pp. 153-163, 2011/09/25/ 2011, doi: https://doi.org/10.1016/j.fluid.2011.06.025.

[61] M. Tavakkoli, M. Masihi, M. Ghazanfari, and R. Kharrat, "An Improvement of Thermodynamic Micellization Model for Prediction of Asphaltene Precipitation During Gas Injection in Heavy Crud," *fluid phase equilibria,* vol. 308, pp. 153-163, 2011.

[62] A. I. Victorov and A. Firoozabadi, "Thermodunamics Micellization Model of Asphaltene Precipitation from Petroleum Fluids," *American Institute Chemical Engineering Journal,* vol. 42, no. 6, pp. 1753-1764, 1996.

[63] A. I. Victorov and N. Smirnova, "Thermodynamic Model of Petroleum Fluids Containing Polydisperse Asphaltene Aggregates," *Industerial & Engineering Chemistry Research,* vol. 37, pp. 3242-3251, 1998.

[64] A. I. Victorov and N. A. Smirnova, "Description of Asphaltene ploydispersity and Precipitation by Meas of Thermodynamic Model of Self-Assembly," *fluid phase equilibria,* vol. 158, no. 160, pp. 471-480, 1999.

[65] H. Pan and A. Firoozabadi, "Thermidynamic Micellization Model for Asphaltene Aggregation and Precipitation in Petroleum Fluids," *SPE Production & Facilities,* vol. 36741, pp. 118-127, 1998.

[66] N. A. Smirnova, A. Victorov, and G. Kuranov, "New Applications of Equations of State in Molecular Models of Complex Fluid Mixtures," *fluid phase equilibria,* vol. 150, no. 151, pp. 161-171, 1998.