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THERMODYNAMIC MODELING OF ASPHALTENE PRECIPITATION AND COMPARISON OF THE EOS, SCALING, SOLUBILITY AND PC-SAFT MODELS

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Abstract

Asphaltene modeling is a complex multifaceted problem. This complexity is associated with the reservoir oil; which is a multi-component multi-structure and potentially multi-phase substance. Different authors have proposed different models to predict the thermodynamic behavior of asphalttene in the reservoir oil mixture. These models study asphaltene solid phase transition with different perspectives toward asphaltene. In the solubility model asphaltene is considered a soluble polymer in the liquid oil media. In the scaling model, dimensionless numbers are used to characterize asphaltene behavior. The equation of state (EOS) model considers asphaltene as an independent constituent of oil.

In this study, the thermodynamic behaviors of two live (heavy and light) oil samples are determined via extensive laboratory experiments. Then the performance of each asphaltene precipitation model is analyzed and compared. Finally, few modifications are proposed for improving these models.

Keywords: Asphaltene; Solid- Liquid- Gas Equilibrium; Flory- Huggins solubility model; Thermodynamic; Equation of State model.

1. Introduction

Asphaltenes are the heaviest fraction of crude oil that precipitate as solid particles upon the addition of paraffins such as normal heptane and normal pentane [1-3]. They are the most polar constituents of crude oil. Asphaltenes transform from a liquid to a solid phase due to changes in pressure, temperature and/or composition [2,4]. Some researchers consider asphaltene to be partly soluble (to a degree depending on their polarity and size) and partly in a colloidal suspension in the crude oil [5-7].

Asphaltene deposition during oil production is one of the most challenging topics in petroleum production. Asphaltenes can deposit at various locations such as the reservoir, well bore, well column, production pipelines and storage tanks. Deposition of asphaltene restricts production (by plugging flow conduits), damages equipment and requires expensive treatment. Transformation of asphaltene into suspended solid particles increases crude oil viscosity and imposes an extra pressure drop during fluid flow [8-10].

During production, asphaltenic crude oil undergoes various solid-liquid, solid-liquid-gas, and liquid-gas equilibrium conditions. Problems associated with asphaltene occur when asphaltene particles precipitate but remain suspended in the flowing fluid. This reversible phenomenon lowers fluidity of the crude oil. Figure 1 shows potential crude oil conditions at various stages of production for a typical well column.

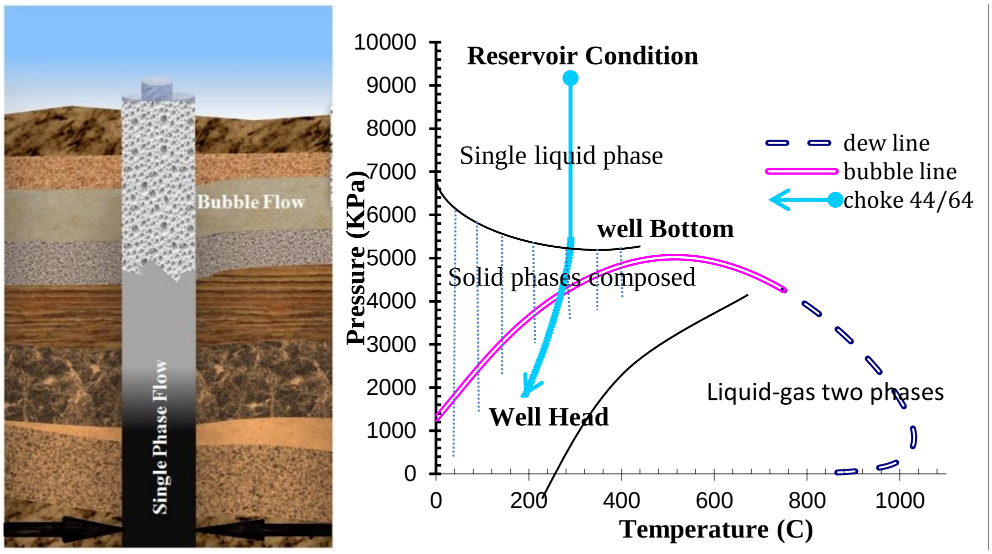

Figure1. Thermodynamic path of petroleum in the production line and related solid-liquid-vapor phase diagram

As shown in Figure 1, oils a single phase homogeneous mixture at reservoir conditions. During production, the temperature and pressure of the reservoir fluid changes (usually decreases). As pressure decreases, the thermodynamic conditions become more stable for phase transition of asphaltene from liquid to solid. The lowest pressure where asphaltene precipitates out of solution is known as the upper onset pressure (UPO). Below the UPO and up to the bubble point pressure (P_b), the reservoir fluid is at two-phase solid-liquid equilibrium of asphaltene precipitates and reservoir oil. As the fluid enters the well column, pressure and temperature of reservoir fluid further decreases. When the pressure reaches P_b, gas bubbles begin to evolve and thus a third phase forms. This point is the beginning of the three phase solid-liquid-gas region. In this region, solid asphaltene nuclei and gas bubbles are transported in a liquid oil medium. Experiment has shown that maximum asphaltene precipitation occurs at P_b. At pressures below P_b, asphaltene precipitation is a reversible process (i.e. solid asphaltene particles redissolve in the oil medium). Therefore the amount of solid asphaltene particles start to decrease as pressure is lowered below P_b until all asphaltene precipitates have redissolved in the liquid phase. This pressure is called the lower onset pressure (LOP) of asphaltene precipitation. At pressures below LOP, the oil mixture is at a two phase, liquid-gas equilibrium.

To predict the amount and location of asphaltene deposition in the well column it is important to model the thermodynamic behavior of the asphaltenic oil. The thermodynamic modeling of asphaltenic oil is quite complex because the studied system is a multi-phase multi-component multi-structured system.

An oil system consists of four categories of compounds: inorganic non-polar components (e.g. N_2), inorganic polar components (e.g. H_2S and CO_2), organic non-polar components (e.g. paraffins and aromatics) and organic polar components (e.g. resins and asphaltenes). Asphaltene thermodynamic modeling is challenging because modeling an oil system requires understanding such a multi-phase, multi-component, multi-chemical structured system.

There are two main approaches in asphaltene thermodynamic modeling. In the first approach, asphaltenes and resins are considered to have molecular entities in the crude oil solution. In the second approach, they are suspended aggregates in the crude oil medium. There are four different models based on the first approach:

1. Burke and Kashou [11], Kawanaka and Mansoori [12], Mannistu and Masliyah [13] and Mousavi *et al.* [5,14] proposed the molecular solubility approach. In this approach, asphaltene is considered a real liquid solute in a crude oil solvent. The Flory-Huggins polymer solution theory is used in this approach for asphaltene modeling.

2. Nghiem *et al.* [59] and Aggrawal *et al.* [17] used EOS models which treats asphaltene as an independent oil component. They used fugacity equality as the governing equation and the molar volume and binary interaction coefficients of asphaltene as regression parameters in defining equilibrium conditions in their model.
3. Ting *et al.* [19] and Tavakoli *et al.* [20] used Perturbed Chain version of the Statistical Association Fluid Theory (PC-SAFT) which models asphaltene thermodynamic behavior based on molecular forces and molecular size.
4. In the last model, asphaltene precipitation is modeled using scaling models based on the corresponding state principle (Scaling model) [21-24].

In this study, four models (the solubility, Peng-Robinson EOS, PC-SAFT EOS, and scaling model) are used for thermodynamic modeling of asphaltene precipitation. The Miller-modified Flory Huggins model is used in the solubility model, the Gibbs free energy minimization concept along with the Peng-Robinson (PR) EOS as the first and the PC-SAFT EOS as the second EOS models are employed, and the Corresponding State Principle is used in the scaling model. The results of these different approaches are evaluated for the studied oil systems and modifications are suggested for improving models.

2. Thermodynamic modeling

Thermodynamic modeling is the characterization of effective thermodynamic properties of a system at equilibrium conditions. The most important thermodynamic properties of a system are its energy, temperature, pressure, volume and composition. In the oil production process, the thermodynamic systems a multi-component multi-phase system. This system is initially a homogeneous single-phase liquid at reservoir temperature and pressure. During oil production, solid asphaltene precipitates come out of solution and form a two-phase solid-liquid system. After the pressure reaches P_b, lighter oil components (C_1 to C_4, CO_2, and N_2) vaporize and form the third phase of the system. A three phase solid-liquid-gas system is presserved until all the precipitated asphaltene redissolves back into oil. After the complete redissolution of asphaltene back into oil, a two phase system forms. The system remains two phase until atmospheric pressure at which all of the gas leaves oil.

In this study asphaltene phase behavior is studied via three models: the EOS, solution and scaling models.

2.1. Equation of State Model

An equation of state (EOS) is a relationship that represents the state of the system. Available Equations of state are only applicable to the gas and liquid phase and other relationships need to be introduced in the equations to account for a potential solid phase [25].

The most stable state in a multi-phase system is defined as the state at which the Gibbs free energy is minimized. The Gibbs free energy can be calculated using the flow chart demonstrated in Figure 2.

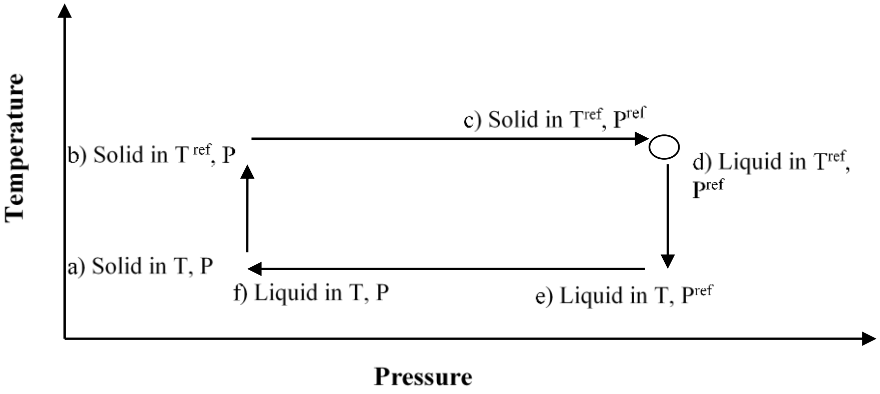

Figure 2. Proposed thermodynamic path for calculating Gibbs free energy for asphaltene precipitation modeling.

The change in the Gibbs free energy (Δg) for substance which changes phase from a liquid to a solid can be calculated usng Equation 1 [6].

$$\Delta g_{a\to f} = \left(\frac{\Delta \mu}{RT}\right)_{a\to f} = \left(\frac{\Delta h}{RT}\right)_{a\to f} + \left(\frac{\Delta s}{R}\right)_{a\to f} \tag{1}$$

In this equation μ , h , s , T and R are the partial molar Gibbs free energy(chemical potential), enthalpy, entropy, temperature and universal gas constant, respectively. The subscripts *a* and *f* represent the liquid and solid phases, respectively.

By re-arranging Equation 1, introducing the defining equation for enthalpy and entropy, Equation 1 can be written in terms of the fugacity coefficient. The change in the solid molar volume (v_i) with pressure is also assumed negligible in the studied pressure range. With these assumptions, Equation 1 simplifies to Equation 2 which shows the relationship for the fugacity of component *i*in the solid phase (f_i^S)

$$f_i^S(P,T) = f_i^{ref}(P,T)\exp\left[\frac{v_i(P-P_i^{ref})}{RT}\right] \tag{2}$$

In Equation 2, f_i^{ref} is the fugacity of component *i* in the solid phase at the asphaltene onset pressure (P^{ref}_i).

At equilibrium, the fugacity of each component should be equal in all phases. Equation 3 represents this equality.

$$f_i^S = f_i^L = f_i^G \tag{3}$$

The subscripts S, L and G represent the solid, liquid and gas phase, respectively. Based on Equation 3, f_i^{ref}can be set equal to the fugacity of component *i* in the liquid phase at the onset pressure in equilibrium.

Furthermore, the fugacity of component *i* in the liquid and gas phases can be calculated using the PR EOS. The relationship between pressure, temperature and system volume is defined with Equation 4 in the PR EOS [25].

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

In Equation 4, v is the system molar volume b and a are constants which have physical theoretical meanings related to the molecular volume and intermolecular forces, respectively. For a multi-component system the mixing rules for calculating b and a are as shown by Equations 5 to 7.

$$b = \sum_{i=1}^{m} x_i b_i \tag{5}$$

$$a(T) = \sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j a_{ij}(T) \tag{6}$$

$$a_{ij}(T) = \left[a_{ii}(T)a_{jj}(T)\right]^{1/2}(1-l_{ij}) \tag{7}$$

In Equation 7, l_{ij} is the interaction parameter between components *i* and *j*.

Based on the PR EOS, the fugacity of component *I* in a multi-component system in the liquid or gas phase can be calculated using Equation 8 [26].

$$f_i = x_i P \times \exp\left(\frac{b_i}{b}\left(\frac{Pv}{RT}-1\right) - \ln\frac{P(v-b)}{RT} - \frac{a}{2\sqrt{2}bRT}\left[\frac{2\sum_j x_j a_{ij}}{a} - \frac{b_i}{b}\right]\ln\frac{v+\left(1+\sqrt{2}\right)b}{v+\left(1-\sqrt{2}\right)b}\right) \tag{8}$$

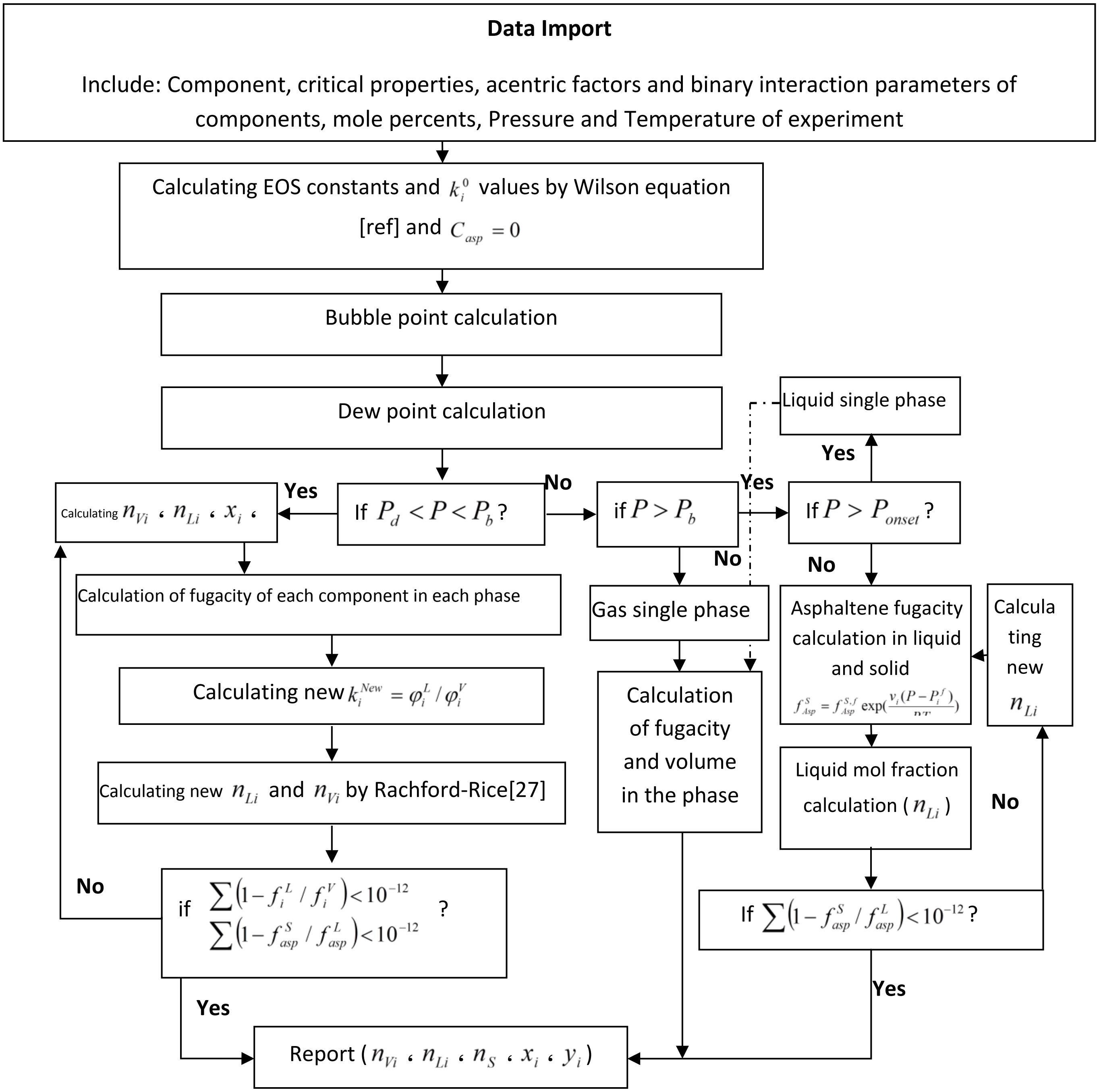

Figure 3. Algorithm for three phase (solid-liquid-vapor) equilibrium calculation

The PR EOS is a cubic equation relative to the system volume. This equation can also be written in terms of the gas/liquid compressibility factor. Furthermore, like any cubic equation, Equation 16 has three roots. These roots may consist of three real roots or two real and an imaginary root. The Gibbs free energy minimization concept is used to determine the root that represents the most stable state of the studied system. The minimum Gibbs free energy can be calculated based on the largest (Z_h) and smallest (Z_l) real roots obtained after solving the PR EOS for the compressibility factor (Equation 9).

$$\frac{(G_h - G_l)}{RT} = (Z_h - Z_l) + \ln\left(\frac{Z_l - B}{Z_h - B}\right) + \frac{A}{B(2\sqrt{2})}\ln\left[\left(\frac{Z_l + (1+\sqrt{2})B}{Z_l + (1-\sqrt{2})B}\right)\left(\frac{Z_h + (1-\sqrt{2})B}{Z_h + (1+\sqrt{2})B}\right)\right] \quad (9)$$

If the left hand side of Equation 9is positive, the Gibbs free energy for Z_l is lower than that for the other root and Z_l is selected as the right root (and vice versa).

A MATLAB code is written based on the aforementioned equations for modeling the asphaltenic oil system. Figure 3 shows various stages of this algorithm.

In this algorithm, a modified version of the Rachford-Rice equation is used for calculating the mole percent of components in all phases [27]. The solid mole percent (n^s) was introduced in the Rachfor-Rice equation for taking the solid phase into account (Equation 10 to 13).

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} \quad (10)$$

$$x_i = \frac{z_i}{1 - n^S + (K_i - 1)n^V}, \quad (11)$$

$$y_i = \frac{z_i K_i}{1 - n^S + (K_i - 1)n^V}, \quad (12)$$

$$x_{asp} = \frac{x_{asp}}{puresolid = 1} = \frac{\phi_{asp}^S}{\phi_{asp}^L} = \frac{f^S}{P\phi_{asp}^L} \quad (13)$$

In these equations K_i is the K-value of component *i*, x_i and y_i are mole fractions of component *i* in the liquid and gas phases and ϕ_i^L and ϕ_i^V are the fugacity coefficients of component *i* in the liquid and vapor phases, respectively.In this equation ϕ_{asp}^S is the fugacity coefficient of asphaltene component and f^S is the fugacity of solid phase.

2.2. Solution Theory Model

In the solution theory model asphaltene is treated as a polymeric molecule in a crude oil solution. Thus Equation 1 can be written for the polymeric asphaltene molecule in the solution theory model.

The change in enthalpy and entropy of asphaltene can be calculated according to the Miller-modified Flory-Hugging model (Equations 14 and 15) [28-29].

$$\Delta\bar{h}_a = v_a(\phi_L)^2\left[(\delta_a - \delta_L)^2 + 2l_{aL}\delta_a\delta_L\right] \quad (14)$$

$$\Delta\bar{s}_a = -R\left[\ln\phi_a - \frac{z}{2}\ln\left[1 - \frac{2}{z}\left(1 - \frac{v_a}{v_L}\right)\phi_L\right]\right] \quad (15)$$

In these equations the change in enthalpy ($\Delta\bar{h}_a$) and entropy ($\Delta\bar{s}_a$) of asphaltene are written in terms of partial properties (denoted with a line above the property). The symbols v, δ and ϕ are the molar volume, solubility parameter and volumetric fraction, respectively. The subscripts *a* and*L* represent asphaltene (the polymer) and the asphaltene free oil (solvent), respectively. In this modified version of the Flory-Huggins equation, an interaction parameter between asphaltene and oil (l_{aL}) is introduced in the equation for enthalpy change [4]. Furthermore, a coordination number (z) is introduced in the equation for entropy change. This parameter represents the number of neighboring molecules surrounding the asphaltene molecule and has a typical value between 3 and 4[14].

Finally, combining Equation 1, 14 and 15 gives Equation 16 for asphaltene chemical potential in the solution theory model.

$$\frac{\Delta\mu_a^L}{RT} = \frac{v_a(1-\phi_a)^2}{RT}\left[(\delta_a-\delta_L)^2 + 2l_{aL}\delta_a\delta_L\right] + \ln\phi_a^L - \frac{z}{2}\ln\left[1-\frac{2}{z}\left(1-\frac{v_a}{v_L}\right)(1-\phi_a^L)\right] = 0 \quad (16)$$

2.3 Scaling Model

The scaling model, similar to the Pie-Backingham model of fluid dynamics, is based on the extraction of dimensionless numbers from effective thermodynamic parameters[30]. This model is regularly used for modeling the temperature profile and compositional changes in gas transportation pipelines [31].

The scaling model consists of the following stages:

1. Identification of effective thermodynamic properties of the studied system.
2. Extraction of dimensionless numbers based on the identified parameters.
3. Finding a relationship between the dimensionless numbers.

The proposed relationship between the dimensionless parameters should be applicable to other systems which have similar effective thermodynamic parameters.

The scaling method was first used for asphaltene precipitation modeling by Rassamdana *et al* [21]. They used the scaling model to predict the amount of asphaltene precipitation as a result of adding paraffins to crude oil. They proposed that asphaltene precipitation is a function of precipitant molecular weight, dilution ratio and the original asphaltene weight percent. Equation 17 and 18 shows their suggested dimensionless numbers.

$$X = D_r/(M_s)^z \quad (17)$$

$$Y = W_r/(D_r)^{z'} \quad (18)$$

In Equation 17 and 18, D_r, W_r and M_s are the dilution ratio, precipitated asphaltene weight percent and the precipitant molecular weight, respectively. The symbols Z and Z' are fitting parameters.

Hu and *et al.* [22] examined the typical ranges of these fitting parameters ($0.1 \le Z \le 0.5$ and $Z' = -2$) and proposed an improved equation for measuring precipitated asphaltene weight percent. They included the effect of temperature as well as the dilution ratio, asphaltene weight percent and the precipitant molecular weight (Equation 19) [32].

$$Y = 2.909 - 50.51X + 82.88X^2 - 4.15X^3, Z = 0.1, Z' = -2 \quad (19)$$

Where X and Y are defined as:

$$X = D_r/(M_s{}^Z T^c) \quad (20)$$

$$Y = W_r/(M_s D_r)^{z'} \quad (21)$$

Moradi *et al.* [24] modeled asphaltene precipitation in a gas injection process. They further improved the weight percent prediction equation by accounting for the effect of pressure (P) besides other parameters (Equation 22 to 24).

$$X = D_r'/(M_s{}^Z T^c) \quad (22)$$

$$Y = W_r/(D_r')^{z'} \quad (23)$$

$$D_r' = D_r \times e^{-h\left(\frac{P_b}{P}-1\right)^2} \quad (24)$$

In equations 22 to 24, h is the fitting parameter and P_b represents the bubble point pressure. Moradi *et al.* [24] proposed values of 7, 0.11 and -2 for h, Z and Z', respectively.

The majority of efforts on asphaltene modeling using scaling model have been focused on dilution processes. This study investigates asphaltene precipitation during naturally pressure depletion. In a hydrocarbon reservoir, the only changing parameter is the reservoir pressure which reduces as production proceeds (the reservoir temperature remains constant).

2.4 PC-SAFT EOS

SAFT EOS [18] is classified as a molecular EOS based on statistical mechanics. It is an extension of the first-order perturbation theory proposed by Wertheim [33-34].In this theory the Helmholtz free energy is expanded around the free energy of a reference fluid. Therefore, The Helmholtz free energy of the system in SAFT EOS is described as a sum of two contributions: (i) an unperturbed system (i.e. referred to as a reference fluid) where the only interaction between molecules is repulsive forces and (ii) a perturbation because of attractive forces such as dispersion and association interactions.

Gross and Sadowski [35] developed PC-SAFT EOS by applying the perturbation theory of Barker and Henderson [36] to the SAFT EOS. They used hard-chain fluid as the reference instead of spherical segments, which seems to be more realistic for molecules like asphaltene.

Ting et al. [37] introduced a new model based on PC-SAFT EOS that considers asphaltenes as mono-dispersed nano-aggregates. This model assumes that precipitation is mainly governed by van-der-Waals dispersion forces. However, due to lack of knowledge about the nano-aggregates size, experimental data is used to fit the PC-SAFT parameters for asphaltene. This EOS recently is used a lot in academic and industrial application for modeling the phase equilibrium of systems containing heavy molecules such as asphaltene [38-45].

The main assumptions and implications made in this modeling approach are [46]:

- Asphaltenes are dissolved in the crude oil like other species. So PC-SAFT EOS follows the solubility theory.
- Reversibility of Asphaltene precipitation is thermodynamically possible and precipitation is modeled as liquid–liquid equilibria (LLE).
- Pre-aggregates (also known as nano-aggregates) are formed via Asphaltenes association even in good solvents like Toluene; further aggregation is possible due to van der Waals interactions. The effect of polar interactions or Hydrogen bonding is reported to be insignificant by different researchers [37,47-48].
- Liquid phase that is rich in Asphaltenes contains some amounts of other non-asphaltenic materials.

For each non-associating component three parameters are required in PC-SAFT EOS, namely: the number of segments per molecule (i.e., chain length) (m), temperature-independent diameter of each molecular segment (σ) and the segment–segment interaction energy (ε/k). Interested readers can follow up the background theory of PC-SAFT EOS and required equations in references [35,38,49].

The characterization scheme developed by Panuganti *et al.* [48] is followed in this work. Compositions, SARA analysis, and gas-oil-ratio (GOR) data are employed to characterize the flashed gas and stock tank oil (STO) and then recombining them according to GOR to simulate the live oil. The gas phase is represented by seven components: N_2, CO_2, H_2S, C_1, C_2, C_3, and heavy gas pseudo-component (lumped C4+ components). The liquid phase is characterized to consist three pseudo-components: saturates, aromatics + resins (A + R), and Asphaltenes. This is done based on the STO composition and SARA analysis. The "saturates" pseudo-component represents normal, branched, and cyclic alkanes which is the nonpolar and soluble fraction of STO in n-heptane at room temperature. Aromatics and resins are lumped into a single pseudo component named A+R. Aromaticity parameter, γ, is used as the weighting factor to characterize A+R Pseudo component by linearly weighting the parameters of ploy-nuclear-aromatics (PNA) and benzene derivatives components with.

3. Procedure

Extensive laboratory tests have been performed on two live heavy and light oil samples to determine their thermodynamic behavior during pressure depletion. These experiments include:

1. Crude oil compositional characterization
2. Pressure-volume-temperature tests
3. Asphaltene studies.

3.1. Crude oil compositional characterization

The composition and fractions of crude oil and associated gas is determined by fractional distillation and gas chromatography. Each component present in the sample is identified with a molecular weight and mole percent. Furthermore, the weight percent of the four main fractions of crude oil (i.e. saturates, aromatics, resins and asphaltenes (SARA)) are also determined. These fractions are different in polarity and aromaticity. The SARA measured fractions are important for analyzing stability of the asphaltene fraction in oil. Different methods are common to measure the SARA fractions of oil and the applied method is based on the concept introduced by Vasquez and Mansoori [50-52].

In this analysis, 20 cm^3 of crude oil is weighed and put under the laboratory hood at 200 mm Hg pressure to evaporate light fractions of oil. After 24 hours, the sample is reweighed and de-asphaltenated by the standard IP-143 process (ASTM D-3279). The de-aspaltenated crude oil (a.k.a. maltene) is fractionated by the SARA column [50-52]

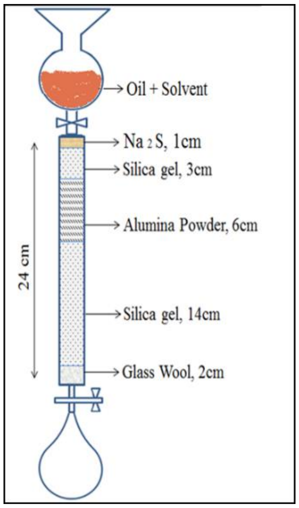

Figure 4. SARA chromatography column

The SARA column is a glassy degreed pipette filled by glass wool. The column is initially wetted by normal hexane, and later filled by silica gel up to a height of 14 cm. Then, 6 cm height of alumina is added to the column followed subsequently by 3 cm height of silica gel. Finally, 1 cm height sodium sulfate is added to the column to absorb any present water. This adds up to a 24 cm height column which can be used as a chromatography apparatus for separating different fractions of maltene. Figure 4 shows the SARA column. In this process, the non-polar solvent (normal hexane), semi polar solvent (50% benzene + 50% normal hexane) and polar solvent (ethanol) are used as the mobile phase of the chromatograph to separate saturates, aromatics and resins, in the mentioned order. After separation, the solvents of each fraction are evaporated under the laboratory hood and the resulting undiluted fraction is weighed.

In the first experiment, 60 cm^3 of the oil samples were flashed from reservoir conditions to atmospheric conditions. The composition of the dead oil and flashed gas were analyzed using micro-distillation equipment and a gas chromatograph (GC). The GC measures the composition of non-hydrocarbon gas components (such as H_2S, N_2 and CO_2) and light hydrocarbons (up to C_9). The micro-distillation tool measures the composition of C_2 to C_{12+} in the liquid phase.

3.2. Pressure-volume-temperature tests

Generally, two common tests are performed for measuring the volumetric behavior of an oil sample and other essential properties such as bubble point pressure, density, formation volume factor, gas oil ratio and viscosity.

In the first test, the oil samples are expanded in a visual PVT cell from reservoir pressure to atmospheric pressure at a constant temperature (reservoir temperature). The change of volume with respect to pressure is recorded and used to determine the bubble point pressure. Volume changes linearly with pressure from reservoir pressure down to bubble point pressure, but it changes exponentially at pressures lower than bubble point pressure [27-28]. Then, the sample is re-pressurized and subsequently re-combined by a magnetic mixer. The cell pressure is lowered stepwise. In each step, the produced gas is discharged from the cell and the volume of the produced gas and the remaining oil is measured. In each pressure step, the density, formation volume factor and gas oil ratio is calculated. In this study, reservoir pressure and temperature of heavy and light oil samples were 65.8 kPa and 408.3K and 34.6 kPa and 368.4K, respectively.

3.3. Asphaltene studies

There are different methods for measuring the content of heavy organic precipitations. The onset of asphaltene precipitation can be detected by solid detector system (SDS) and high pressure microscopy (HPM), the weight percent of asphaltene can be measured by high pressure – high temperature filtration and WAT can be determined by the cross polar microscope (CPM).

As mentioned previously, the main reason for asphaltene precipitation and wax crystallization is changes in pressure and temperature. Consequently, in the asphaltene studies, tests are performed at a constant (reservoir) temperature during a pressure depletion process and, in the wax studies, tests are performed at constant (atmospheric) pressure and depleting temperatures.

Figure 5 shows the solid detection system (SDS). In this apparatus, 60 cm^3 of the live oil sample is charged into a visual PVT cell. The sample is pressurized and heated to reservoir pressure and temperature and is then allowed to rest at reservoir conditions for 24 hours. A near infra-red (NIR) beam (with 800 to 2200 nm wave-length) is sent though the PVT cell and the homogenous mono-phase oil media. The power of transmitted light is measured in a receiver behind the cell. After one hour, when the quantity of power loss becomes stable, the pressure of PVT cell is reduced with a speed of 70 kPa/min. Pressure depletion decreases the density of oil and, as a result, the transmissibility of oil media increases. The change in the lost light power is recorded as a function of pressure. At the onset of precipitation, because of formation of solid particles, some light beams refract and the power of transmitted light decreases drastically. The point at which the power of light changes drastically is the onset of asphaltene precipitation. The performance of SDS depends on solid particle size. A disadvantage of SDS is that in heavier oils (API degree lower than 24), the oil becomes opaque and light beam cannot pass through oil medium [5].

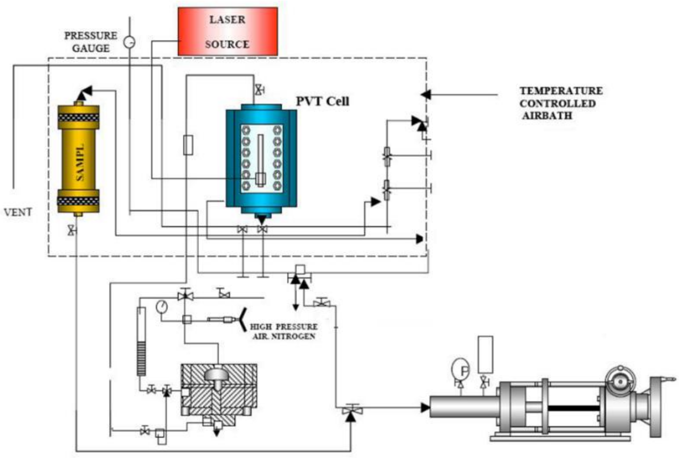

Figure 5. Solid detector system set up

Another method which is used to measure asphaltene weight percent or wax content at high pressure – high temperature condition is filtration. In this study, ash-less paper filter of Watman number 42 was used in a steal cover to filtrate particles greater than o.22 μm. In this method the asphaltene content of oil is measured by the standard IP-143 method before and after filtration. The difference of asphaltene contents is equal to weight percent of precipitated asphaltene. Unlike the SDS method, the filtration method is not limited to oil heaviness and the asphaltene content is measurable at every pressure and temperature. A picture of Watman filters before and after filtration and related steal cover is presented in Figure 6.

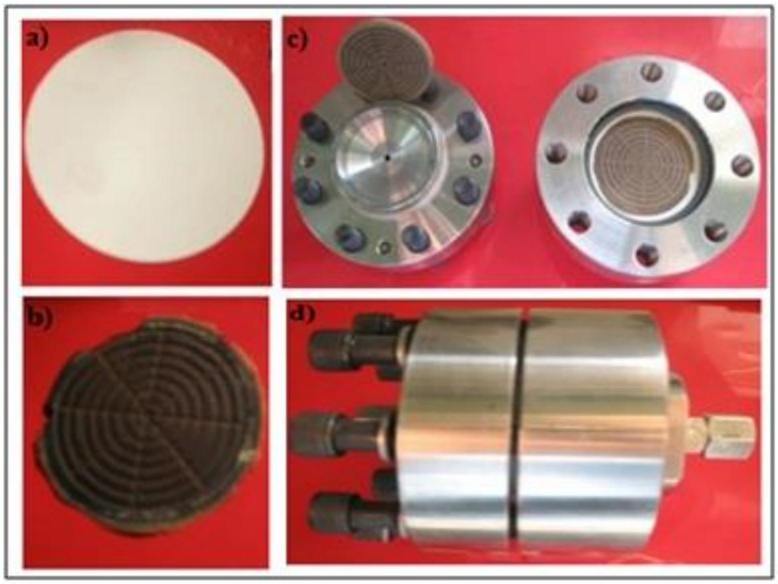

Figure 6.Watman paper filter a) before filtration, b) after filtration, c) oil distributer and d) stainless steel cover of filtration test

The rolling ball viscometer consists of a stainless steel sphere (0.635 cm diameter) which is dropped on top of the viscometer's column which is filled with live oil. The time required for the sphere to reach the bottom of the viscometer is a function of gravitational force on the sphere and the viscosity of the fluid. The relationship which relates this time to fluid viscosity is given by Eq. 25:

$$v = a \times t \times (\rho_b - \rho_o) - b \tag{25}$$

where v , t , ρ_b and ρ_o are fluid viscosity, falling time, ball density and oil density, respectively. a and b are constants. To reduce measurement errors, time measurements are performed with the column set at three different inclinations (70, 45 and 230).

Viscosity measurements can be used in a method known as viscosimetry to determined asphaltene onset of precipitation and precipitated volume percent. Krieger formula is used to convert viscosity data to asphaltene precipitated volume percent [53].

Another set of experiments are performed on the oil samples to determine a range for the asphaltene precipitate molecular weight and weight percent in oil. For this reason, the IP-143 procedure is repeated two more times but with nC_5 and nC_6 instead of nC_7. The molecular weight of crude oil and SARA fractions are measured using the OSMOMAT010 device. This device measures the change in freezing point when a hydrocarbon is added to Benzene (forming a Benzene-hydrocarbon solution). Freezing point of the solution changes in accordance with the properties of the added hydrocarbon because it's a colligative property [54]. The density of liquid phases (i.e. dead oil and C_{12+}) are measured using a digital electro-magnetic density meter, SVM^{TM}3001 [55].

4. Results and discussion

According to the compositional analyses obtained form the micro-distillation and GC tests, the amount of polar inorganic components (such as CO_2 and H_2S) in both the heavy and light oil samples is low. Furthermore, the mole percent of lighter hydrocarbons (C_1 to C_4) is about two times greater in the lighter oil sample. Oil and gas compositions are presented in Table 1.

Table 1. Micro-distillation and GC results: compositional analysis of reservoir oil samples.

Components	Light Oil			Heavy oil		
	Flashed Oil	Associated Gas	Reservoir Oil	Flashed Oil	Associated Gas	Reservoir Oil
H_2S	0.00	0.58	0.42	0.00	0.08	0.04
N_2	0.00	0.11	0.08	0.00	0.77	0.34
CO_2	0.00	2.81	2.02	0.00	7.28	3.27
C_1	0.00	68.15	48.91	0.00	60.33	27.12
C_2	0.15	12.67	9.14	0.11	16.68	7.56
C_3	1.40	8.08	6.19	0.73	9.03	4.46
iC_4	0.57	1.48	1.22	0.39	1.05	0.69
nC_4	1.90	3.75	3.22	1.27	2.61	1.87
iC_5	1.16	0.97	1.02	2.40	0.59	1.59
nC_5	1.53	0.86	1.05	2.98	0.60	1.91
C_6	10.81	0.25	3.23	15.55	0.48	8.78
C_7	9.59	0.18	2.83	8.56	0.31	4.85
C_8	9.62	0.11	2.79	6.67	0.14	3.74
C_9	10.79	0.02	3.06	6.71	0.05	3.72
C_{10}	7.68	0.00	2.17	5.43	0.00	2.99
C_{11}	5.61	0.00	1.58	6.03	0.00	3.32
C_{12+}	39.19	0.00	11.06	43.17	0.00	23.76

The SARA test results show that asphaltene content of the heavy oil is about ten times greater than the light oil (Table 2). But higher asphaltene content doesn't necessarily entail higher instability. The instability of asphaltene to form a solid phase upon pressure reduction is predicted using the colloidal instability index (CII) [56]. According to the CII of the oil samples, while the weight percent of resins and asphaltenes is higher in the heavy oil, the lighter oil is predicted to be more unstable.

Table 2. SARA test results: weight percent of Saturates, Aromatics, Resins and Asphaltenes in the oils.

Oil Type	Saturates (Wt%)	Aromatics (Wt%)	Resins (Wt%)	Asphaltenes (Wt%)	Colloidal Instability Index
Light	64.9	29.1	5.1	0.9	1.92
Heavy	44.7	31.9	12.2	11.2	1.26

Table 3 demonstrates essential thermodynamic fluid properties as determined by the CCE, DL and viscosimetry tests.

Table 3- General thermodynamic data of light and heavy oils.

Property	Unit	Light oil	Heavy oil
Reservoir Temperature	K	408.4	368.4
Reservoir Pressure	MPa	65.90	34.72
Bubble Pressure	MPa	25.66	11.39
Gas Oil Ratio	m^3/m^3	255.92	68.69
Oil Formation Volume Factor	Rm^3/Sm^3	1.9539	1.2781
Dead Oil API	°API	33.79	20.42
Thermal Expansion Factor	$(K)^{-1}$	2.23×10-4	2.41×10-4
Compressibility Factor	$(KPa)^{-1}$	2.01×10-6	1.02×10-6
Oil Viscosity in Bubble Pressure	mPa.s	0.2409	3.0276
Oil Viscosity in Reservoir Pressure	mPa.s	0.3545	4.0843

The point of change in the light power trend versus pressure (which is marked as the asphaltene onset pressure) begins at 42.32 MPa for the light oil sample in the SDS test. The opaqueness of the heavier oil sample prevented any light detection.

The onset pressure of solid precipitation for the heavy oil and weight percent of precipitated solid were measured using a high pressure-high temperature filtration system and a viscometer. Solid precipitation versus pressure is shown in Table 4 and Figure 7.

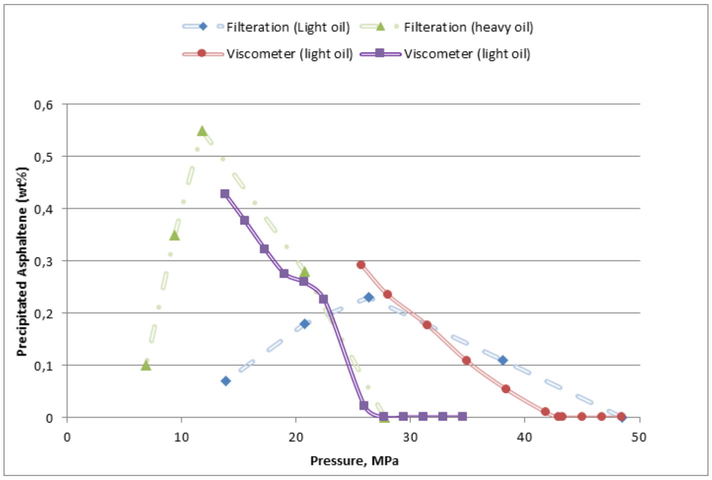

Figure 7. Asphaltene precipitated weight percent change versus pressure in the light and heavy oil samples.

According to Figure 5, the filtration and viscosimetry data have good analogy with the results. They coincidently indicate an increase in the precipitation of solid asphaltene particles with decreasing pressure, above bubble point pressure. The number of measurements of asphaltene weight percent and onset pressure made using the viscosimetry method is higher compared to the filtration method. Therefore changes are more precisely captured using the viscosimetry method.

According to Table 4, asphaltene precipitation occurs at a higher pressure in the lighter oil. As previously noted, this is understandable due to the higher CII of the lighter oil. Furthermore, the maximum weight percent of solid precipitation takes place at the bubble point pressure for both fluids but it is higher for the heavier oil.

Table 4. Asphaltene weight percent variation in light and heavy oil samples at different pressures at reservoir temperature

Filtration method				Viscometer method			
Pressure, MPa	Precipitated Asphaltene in heavy oil (wt%)	Pressure, MPa	Precipitated Asphaltene in light oil (wt%)	Pressure, MPa	Precipitated Asphaltene in heavy oil (wt%)	Pressure, MPa	Precipitated Asphaltene in light oil (wt%)
27.58	0.00	48.26	0.00	27.71	0.00	42.95	0.00
20.68	0.28	37.92	0.11	25.98	0.02	41.88	0.01
11.72	0.55	26.20	0.23	20.78	0.26	34.99	0.11
9.31	0.35	20.68	0.18	19.05	0.27	31.53	0.18
6.89	0.10	13.79	0.07	17.32	0.32	28.06	0.23
				15.59	0.38	25.79	0.29
				13.86	0.43		

Asphaltene molecular weight (MW_a) is measured using an osmometer (OSOMETER 010) after precipitating it with three different precipitants. The measured light oil MW_a is 978, 1627 and 2050 gr/mole and the heavy oil MW_a is 1313, 1970 and 2495 gr/mole when using nC_5, nC_6 and nC_7as precipitants, respectively. The standard method for determining MW_a is based on the use of nC_7. Therefore MW_a is selected as 2050 and 2495 gr/mole for the light and heavy oils.

Modeling asphaltene precipitation using equations of state requires determination of solid-liquid-gas equilibrium properties of the system. A MATLAB code is written based on the algorithm in Figure 3 to model the three phase behavior of the system. CMG's Winprop software data library is used for fluid component properties. Other required properties necessary for for the PR EOS are shown in Table 5. Lee-Kesler correlations were used for determination of critical temperature, pressure, volume and compressibility and acentri factor of the plus fraction (C_{12+}) [57].

Table 5. Equation constants for various components of the PR EOS

Components	Mol. Weight	Pc (MPa)	Tc (K)	Omega A	Omega B	Acentric Factor
N_2	28	3.394	126.4	0.45724	0.077796	0.040
H_2S	34.1	8.936	373.8	0.45724	0.077796	0.100
CO_2	44	7.384	304.9	0.45724	0.077796	0.225
C_1	16	4.604	190.8	0.45724	0.077796	0.013
C_2	30.1	4.884	305.6	0.45724	0.077796	0.098
C_3	44.1	4.246	370.0	0.45724	0.077796	0.152
iC_4	58.1	3.648	408.3	0.45724	0.077796	0.184
nC_4	58.1	3.797	425.4	0.45724	0.077796	0.201
iC_5	72.2	3.389	460.6	0.45724	0.077796	0.227
nC_5	72.2	3.370	469.8	0.45724	0.077796	0.251
C_6	84	3.010	507.7	0.5341	0.067084	0.299
C_7	96	1.920	579.2	0.61428	0.049933	0.658
C_8	107	1.882	607.8	0.58672	0.054978	0.684
C_9	121	1.719	637.4	0.55608	0.059073	0.763
C_{10}	134	1.581	661.7	0.51985	0.065119	0.844
C_{11}	147	1.457	684.9	0.49429	0.069534	0.919
C_{12+}	398	0.521	949.3	0.31495	0.068226	1.776

The following procedure is applied for the modeling:

1. Defining asphaltene as an independent oil and correcting plus fraction properties.
2. Liquid – gas equilibrium modeling by correction of properties of heavy components (C_{10}, C_{11}, C_{12+} and asphaltene).
3. Calculating asphaltene properties (e.g. fugacity and molar volume) at the onset pressure
4. Regression of molar volume, asphaltene binary interaction parameters.

In this modeling, asphaltene is treated as an independent component. We considered the Asphaltene in an ideal solution in the C_{12+}. Separating asphaltene from the plus fraction as an independent component changes the plus fraction mole percent, molecular weight and specific gravity (Table 6).

Table 6. Composition, molecular weight and specific gravity correction of the plus fraction after defining asphaltene as an independent component.

	C_{12+} Mole%	Asp Mole%	MwC12+ (gr/Mole)	MwAsp (gr/Mole)	SG C12+ gr/cc
Light oil	11.06	0.00	398	-	0.8955
Corrected Light Oil	11.01	0.05	390.6	2051	0.8860
Heavy oil	23.76	-	607.0	-	0.9731
Corrected Heavy Oil	23.53	0.24	588.1	2495	0.9533

A model was generated based on the above procedure. This model was used to reproduce the results of laboratory experiments. CCE test results show that oil volume trend versus pressure changes at a temperature of 408.4 and 368.4 K for the light and heavy oil samples, respectively. Figure 6 shows the fractional oil volume (oil volume relative to that at P_b) at various pressures as measured during the CCE test. Figure 8 shows experimental results alongside modeled predictions using the PR EOS.

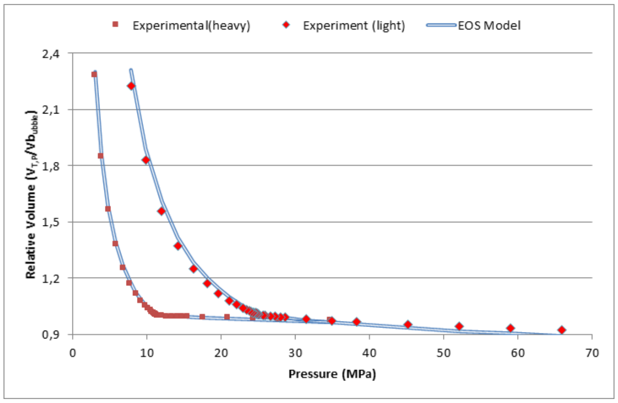

Figure 8. System volume change at equilibrium conditions during pressure reduction at reservoir temperature (408.4K for the light and 368.4 K for the heavy oil sample), experimental data and PR EOS model

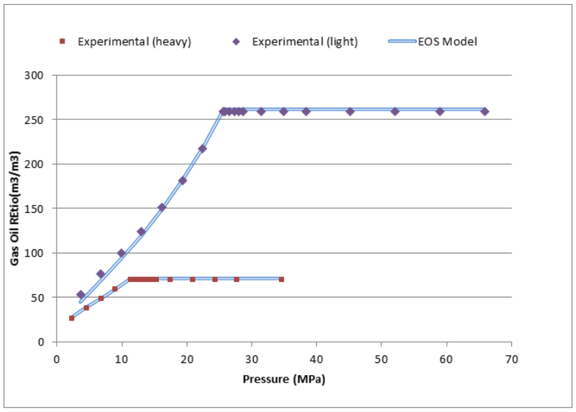

Figure 9. DL experimental data and model prediction for the ratio of soluble gas in the oil at equilibrium conditions at reservoir temperature (408.4K for the light and 368.4K for the heavy oil sample), experimental data and PR EOS model

The output of the model shows that it has predicted the thermodynamic behavior of the oil mixture appropriately.

In the DL test, in which oil is flashed iso-thermally in a step-wise manner, the pressure is reduced about 5 MPa at a time. After this pressure reduction, the cell is given time to reach equilibrium. After equilibrium conditions are achieved in the test cell, the liberated gas is exited from the cell and analyzed. The solution gas oil ratio is then back calculated. Figure 9 shows the test results and PR EOS model prediction for the gas oil ratio.

The solid-liquid-gas equilibrium is modeled as an isothermal process based on the algorithm of Figure 3 using the PR EOS for the liquid and gas fugacity and Equation 12 for the solid fugacity. The Gibbs free energy minimization concept (Equation 23) is used for the PR equation root selection.

The modeling results show that solid asphaltene weight percent changes as a function of asphaltene molar volume and binary interaction parameters. Increasing the binary interaction parameters decreases the precipitated asphaltene weight percent at pressures below P_b. Another corrective parameter in the model is the asphaltene molar volume. The solid phase weight percent decreases with molar volume reduction. After some trial and error calculations, the optimum values for various properties required for the solid-liquid-gas equilibrium modeling is found (Table 7). Figure 10 shows the modeling result for both oil samples.

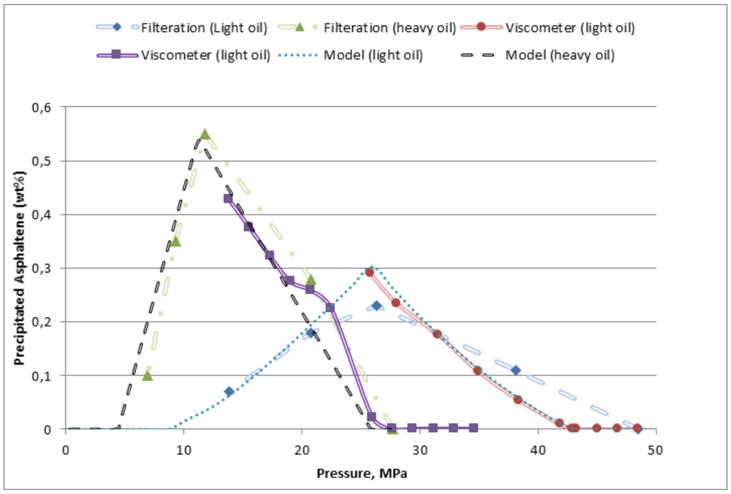

Figure 10. Model output and experimental data of precipitated Asphaltene weight percent versus pressure in an isothermal process at reservoir temperature

Table 7. Regressed parameters for modeling the solid-liquid-gas equilibrium of the light and heavy oil samples

	Asp Mole%	Molar Volume ($10^{-3}m^3$/Mol)	BIP C1-Asp	BIP C2-Asp	BIP C3-Asp	BIP C4-Asp
Light oil	0.05	0.605	0.095	0.0795	0	0.0
Heavy oil	0.24	1.2	0.25	0.2295	0.2295	0.0617

As seen in Figure 10, the model best predicts asphaltene weight percent as found in the viscosimetry test. Asphaltene weight percent can also be measured indirectly in the filtration test. In the filtration test, the oil mixture is filtered and the asphaltene content of the filtrated oil is measured. Then the test is repeated for the filtrated oil. Due to the repetitive nature of the filtration test, the accuracy of the final result diminishes. But volume percent of solid is calculated using Kriger equation from viscosity versus pressure data in the viscosimetry method [53]. Therefore the calculated value for onset pressure of asphaltene precipitation is more accurately calculated in the viscosimetry test.

To model the natural depletion process of asphaltene precipitation using the scaling model, the Moradi *et al.* [24] scaling modeling approach was applied (Equations 22 to 24). In the Moradi model, a parameter is defined to account for gas injection (D_r). In natural depletion, there is no gas injection. But at pressures below P_b, lighter oil components vaporize. The vaporized gas consists mainly of C_1. Therefore, natural depletion can be assumed a methane extraction process. In this process, the pressure, temperature and C_1mole percent most affect asphaltene precipitation. The Moradi *et al.* [24] scaling model parameters for asphaltene precipitation process during natural depletion are developed as shown by Equations 25 to 27.

$$D_r' = D_r \times e^{-h\left(\frac{P_b}{P}-1\right)^2} \tag{25}$$

$$X = D_r'/(D_r^{Z} T^{c}) \tag{26}$$

$$Y = W_r/(D_r')^{z'} \tag{27}$$

In above equations, D_r is methane mole percent in the liquid phase. The unit of temperature in Equation 26 is Fahrenheit. Equation constants are given in Table 8.

Table 8. Regressed constants of the CSP model

Parameter	Z	Z'	h	c
Quantity	0.78	-2	7	0.04

After tuning equation constant, the scaling equation becomes as shown by Equation 28. The variation of X versus Y is shown in Figure 11.

$$Y = 54.86X^3 + 76.08X^2 - 43.21X + 3.56 \tag{28}$$

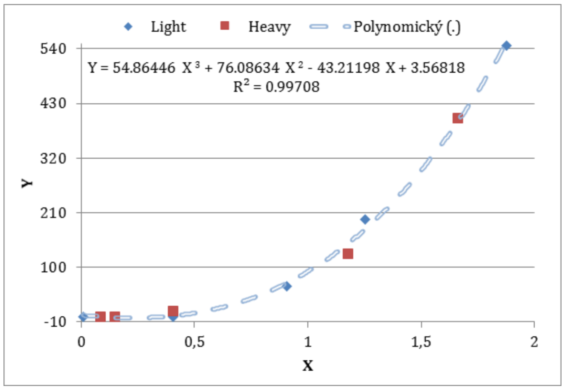

Figure 11. Variation of X and Y in the scaling model for the light and heavy oil samples

Asphaltene weight percent versus pressure was calculated by the back calculation of Equation 28. The final results of the scaling model and experimental data are presented in Table 9 and Figure 12.

Table 9. Back calculated data of the CSP model for asphaltene precipitation in natural depletion and experimental data of the light and heavy oil samples.

			Light Oil		
P (MPa)	S'	X	Y	Asphaltene wt% (CSP)	Asphaltene wt% (Experiment)
48.26	10.54186	0.139046	1.840779	0.016564	0
37.92	23.54251	0.310523	67.76927	0.122272	0.110238
26.20	48.76761	0.643238	551.8842	0.232052	0.22981
20.68	32.59129	0.429875	177.7241	0.167318	0.184343
13.79	0.27201	0.003588	3.439542	46.48696	0.0693

			Heavy Oil		
P (MPa)	S'	X	Y	Asphaltene wt% (CSP)	Asphaltene wt% (Experiment)
27.58	2.429969	0.051255	-1.11425	-0.1887	0.00
20.68	6.596568	0.139141	1.853415	0.042593	0.28
11.72	26.96834	0.568841	392.0786	0.539094	0.55
9.31	19.11506	0.403192	147.7287	0.404309	0.35
6.89	1.386083	0.029237	0.531309	0.276547	0.10

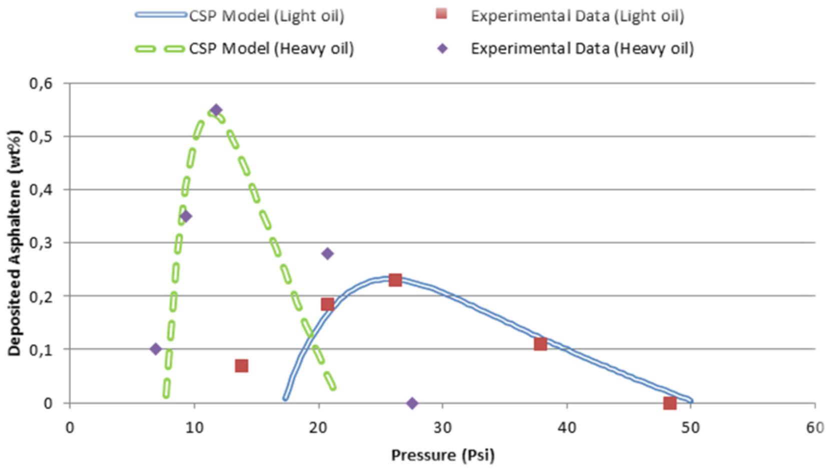

Figure 12. Scaling model output and experimental data of asphaltene precipitation in the light and heavy oils

Figure 12 shows that the scaling model can predict the asphaltene precipitation in a specific pressure region. For the light oil the results of the scaling is accurate at pressures higher than P_b and for the heavy oil, at pressures lower than P_b.

To model asphaltene precipitation in a natural depletion process using the solubility model, the modified Miller-Flory-Huggins [14] method was applied. After programming and modeling the system, optimum values for model constants were found by trial and error (Table 10).

Table 10. Optimum Asphaltene properties for asphaltene modeling using the modified Miller-Flory-Huggins model in the light oil.

Variable	Asphaltene molecular weight, gr/mol	Solubility parameter $Pa^{0.5}$	Binary interaction	Coordinate number
Value	500	17090.8	0.08369	1

Equation 26 was then used to calculate the weight percent of solid asphaltene. The variation of precipitated asphaltene weight percent versus pressure is presented in Figure13 for the light oil sample.

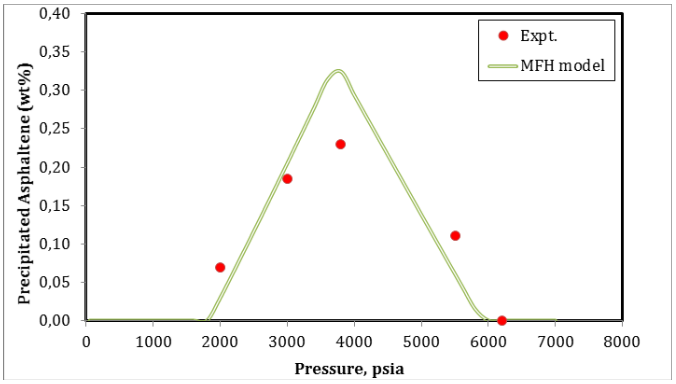

Figure 13. The Miller- Flory- Huggins model results and experimental data (filtration method) for asphaltene precipitation in the light oil

The results of Miller-Flory-Huggins (MFH) model are as accurate as the EOS model. But the number of regressed parameters of this model is greater. Furthermore, the MFH model underestimates MW_a. The reported values for MW_ain literature is in a range of 1200 to 4000 gr/mole [58]. In our study, MW_a in the light and heavy oil samples were measured 2050 and 2495 gr/mole, respectively. But the MFH model regression value of MW_a is about 650 gr/mole, which is much lower than what is expected in reality.

PC-SAFT parameters (m, σ and ε/k) for the pure species are from Gross and Sadowski [40]. These parameters for heavy gas/saturates, aromatics + resins are also well established through the work of Ting and Gonzalez [42,44]. The correlations of these parameters are shown in Table 11.

Table 11. Correlations of PC-SAFT parameters for saturates and aromatics + resins pseudo components

Saturates	Aromatics + resins
$m = (0.0257 \times MW) + 0.8444$	$m = (1-\gamma)(0.0223 \times MW + 0.751) + \gamma(0.0101 \times MW + 1.7296)$
$\sigma = 4.047 - \frac{4.8013 \times \ln(MW)}{MW}, A$	$\sigma = (1-\gamma)\left(4.1377 - \frac{38.1483}{MW}\right) + \gamma\left(4.6169 - \frac{93.98}{MW}\right), A$
$\ln\left(\frac{\varepsilon}{k}\right) = 5.5769 - \frac{9.523}{MW}, K$	$\frac{\varepsilon}{k} = (1-\gamma)(0.00436 \times MW + 283.93) + \gamma\left(508 - \frac{234100}{MW^{1.5}}\right), K$

The aromaticity parameter, γ, which is used in these correlations, is adjusted to match the given density and bubble pressure simultaneously. After setting γ, PC-SAFT parameters of asphaltene are fitted to match the experimentally observed onset pressures. Table 12 and 13 includes compositions, molecular weights, and PC-SAFT parameters of components for characterized Light and heavy oils respectively.

Table 12. PC-SAFT characterization of light oil sample.

Component	Composition (mol%)	MW (g/mol)	m	σ (A)	ε/k (K)
H_2S	0.450	34.10	1.65	3.07	227.34
N_2	0.085	28.00	1.21	3.31	90.96
CO_2	2.179	44.00	2.07	2.78	169.21
C_1	52.845	16.00	1.00	3.70	150.03
C_2	9.818	30.10	1.61	3.52	191.42
C_3	6.266	44.10	2.00	3.62	208.11

Component	Composition (mol%)	MW (g/mol)	m	σ (A)	ε/k (K)
Heavy gas	5.910	64.10	2.49	3.74	227.77
Saturates	15.646	205.04	5.97	3.93	224.05
Resins+Aromatics	6.261	270.00	10.00	4.10	280.52
Asphaltene	0.022	2051.00	17.00	4.68	370.20

Table 13. PC-SAFT characterization of heavy oil sample.

Component	Composition (mol%)	MW (g/mol)	m	σ (A)	ε/k (K)
H_2S	0.045	34.1	1.65	3.07	227.34
N_2	0.433	28	1.21	3.31	90.96
CO_2	4.096	44	2.07	2.78	169.21
C_1	33.944	16	1	3.7	150.03
C_2	9.385	30.1	1.61	3.52	191.42
C_3	5.081	44.1	2	3.62	208.11
Heavy gas	3.280	66.8	2.56	3.74	229.16
Saturates	24.743	249.4	7.25	3.94	254.35
Resins+Aromatics	18.366	336	8.58	4.26	285.39
Asphaltene	0.628	2495	20	4.3	330.04

The temperature independent binary interaction coefficients (K_{ij}) for all components except those of asphaltene are set as reported in references 42, 48 and 52. To predict experimental results of precipitated asphaltene at reservoir temperature for light and heavy oils the Asphaltene Binary interaction coefficient are set as shown in table 14 and 15 respectively.

Table 14. PC-SAFT binary interaction parameters used in the model for light oil

	H_2S	N_2	CO_2	C_1	C_2	C_3	Heavy gas	Saturates	R+A	Asphaltene
Asphaltene	0.160	0.100	0.015	0.125	0.100	0.070	0.068	0.052	0.050	0

Table 15. PC-SAFT binary interaction parameters used in the model for heavy oil

	H_2S	N_2	CO_2	C_1	C_2	C_3	Heavy gas	Saturates	R+A	Asphaltene
Asphaltene	0.160	0.100	0.015	0.060	0.055	0.045	0.035	0.030	0.007	0

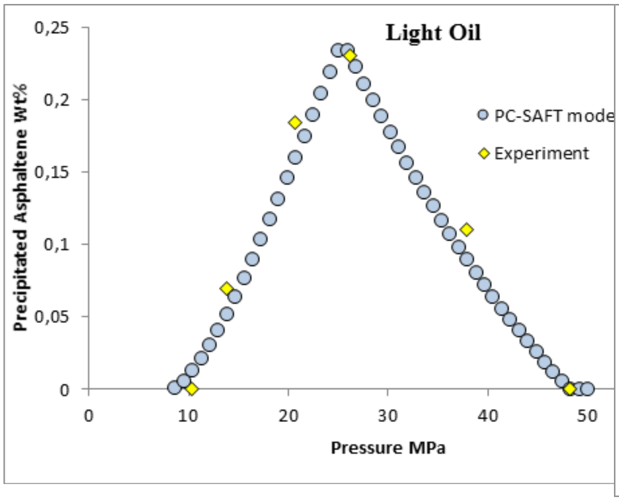

Figure 14. Comparison of PC-SAFT prediction and experimental data (filtration method) of

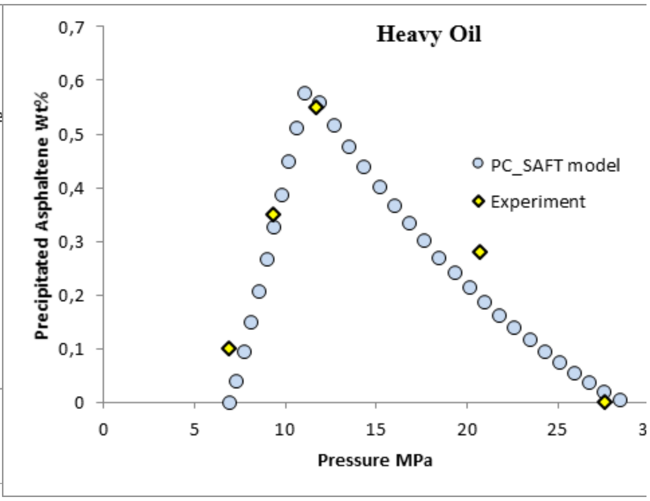

Figure 15. Comparison of PC_SAFT prediction and experimental data of Asphaltene precipitated

Asphaltene precipitated weight percent change versus pressure in the light oil at 275^{0}F

weight percent change versus pressure in the heavy oil at 203^{0}F

The results of PC-SAFT modeling of weight percent of asphaltene precipitation versus pressure in an isothermal process were depicted in figures 14 and 15. The temperature of process is reservoir temperature (275 ^{0}F in light oil sample and 203 ^{0}F for heavy oil sample). In figure 16 effect of temperature on asphaltene precipitation for light oil sample was predicted by PC-SAFT model. In this model the precipitation of asphaltene increases as temperature decreases.

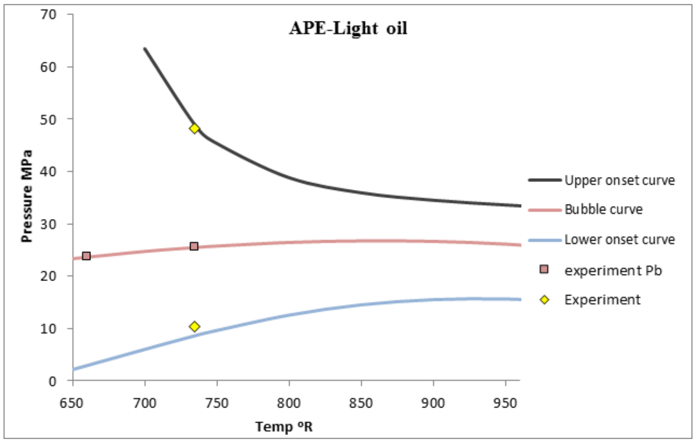

Figure 16. APE plot and bubble curve of light oil: Comparison of PC_SAFT prediction and experimental data

5. Conclusion

One of the drawbacks of the asphaltene precipitation models is the inaccurate characterization of the solid phase. It was proposed that treating asphaltene as an independent component improves the prediction of the thermodynamic behavior of reservoir oil.

For this purpose, three different models were applied for asphaltene precipitation modeling. The PREOS was used for determination of equilibrium conditions of two multi-component multi-phase live reservoir oils. Fugacity equality was considered as the equilibrium condition. The fugacity of liquid and gas components and asphaltene fugacity at the onset pressure are calculated using the PR EOS. Equilibrium was predicted in trial and error loops based on the proposed algorithm. The roots of the PR EOS were selected based on the Gibbs free minimization concept.

In the proposed algorithm, which considered asphaltene an independent component, the asphaltene weight percent, onset of precipitation, solution gas oil ratio and the volume and bubble point pressure of the system were calculated.

In the scaling model, pressure, temperature, asphaltene weight percent, methane mole percent and the bubble point pressure were considered parameters that affect precipitation behavior. Modeling results show that the scaling model was regionally accurate. It is recommended to add extra effective parameters (such as resin, aromatic and saturation concentration) for increasing the accuracy of the model predictions.

The MFH model was generated based on the solution theory. The results of the MFH model are as accurate as the EOS model. But the MFH model suffers from two drawbacks. First, the high number of regression parameters (such as the molecular weight, coordinate number and binary interaction parameters) increases the computational requirements. Second, predicted values for asphaltene molecular weight are far from ranges determined experimentally.

PC-SAFT is a superior model for predicting asphaltene behavior in both light and heavy oils. The number of regressed parameters and input data of the PC-SAFT model are fewer compared to the MFH model. Overall, PC-SAFT and solid models have better accuracy and are simpler to implement for modeling the thermodynamic behavior of asphaltene.

The solid asphaltene weight percent can be measured more accurately in the viscosimetry method, compared to the filtration test. This is because asphaltene weight percent is measured indirectly in the filtration method. The viscosimetry method also allows for the calculation of asphaltene onset pressure; however it cannot measure the quantity of precipitated asphaltene at pressured below P_b. At pressured lower than P_b, the filtration method can be used.

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