

Precipitated Asphaltene Amount at High-Pressure and High-Temperature Conditions

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ABSTRACT: In the upstream asphaltene flow assurance community, both academics and industries are actively involved to predict the asphaltene deposit profile in wellbores and pipelines. Essential information for such a study is the amount of asphaltenes that can precipitate and, hence, deposit. In this work, the perturbed chain form of the statistical associating fluid theory (PC-SAFT) is applied to predict the asphaltene precipitation onset condition as well as the amount of precipitate under pressure depletion and high-pressure and high-temperature gas injection conditions. Previous PC-SAFT asphaltene studies in crude oil required the compositional data for both flashed gas and flashed liquid. This work shows a PC-SAFT crude oil characterization procedure when only the composition of the monophasic reservoir fluid is available. After the model parameters for asphaltene onset pressure are estimated, the fitted parameters are used to predict the amount of asphaltene precipitation. The modeling results represent a good match for both upper and lower onset pressures. However, the precipitated asphaltene amount shows an overprediction by PC-SAFT with respect to experimental data obtained from different techniques. The study in this paper discusses the accuracy of these experimental techniques at high-pressure and high-temperature conditions. It shows how a small experimental error during the measurement of precipitated asphaltene amount can result in a significant difference between modeled and experimental values. We invite discussion on the possibility of such errors and suggestions of experimental procedures or a new experimental tool for measuring the amount of precipitated asphaltene at high-pressure and high-temperature conditions.

1. INTRODUCTION

Asphaltenes are a major flow assurance problem in the upstream petroleum industry. With deepwater production involving high pressure and high temperature (HPHT), understanding the behavior of asphaltene becomes even more important because of the high cost factors involved with the requirement of precious space on the rig and the ability to pump solvent downhole. For efficient process design, it is important to know when and how much asphaltene precipitation may affect the production of petroleum in all facets of the field development. To predict precipitation, it is useful to develop thermodynamic models for describing the precipitation properties of hydrocarbon-based fluids even at HPHT.

The perturbed chain form of the statistical associating fluid theory (PC-SAFT) is such an equation of state capable of handling HPHT.¹ It is also demonstrated that PC-SAFT can accurately predict the phase behavior of complex mixtures, such as crude oil containing asphaltenes.² Many researchers have shown a remarkable match between experimental data and SAFT modeling results for asphaltene phase behavior, but only a few of them reported the modeling results for the amount of precipitated asphaltenes under HPHT conditions.^{3,4} Moreover, the model predictions of the precipitated asphaltene amount are not compared to the experimental data. Part of the reason is the scarcity of experimental data at HPHT conditions, owing to safety, expense of equipment, and other technical difficulties during setup and measurements.⁵

In this work, the PC-SAFT equation of state is used for characterizing crude oils even when only the composition of

monophasic reservoir fluid is available without the information on flashed gas and flashed liquid. The model after matching the asphaltene phase boundaries is used to predict the amount of precipitated asphaltenes in comparison to the experimental data under pressure depletion and HPHT gas injection conditions. A discussion about the possibility of experimental error during the filtration procedure or gravimetric method, which is used for measuring the amount of precipitated asphaltenes, and its effect on the difference between experimental data and modeled results is initiated.

2. CHARACTERIZATION METHODOLOGY

Before asphaltene phase behavior modeling, each crude oil must be characterized as a number of components or pseudo-components. The characterization procedure is described in detail by Panuganti et al.⁶ The recombined crude oil composition obtained by the previously developed PC-SAFT characterization method for modeling asphaltene phase behavior consists of N₂, CO₂, C₁, and four pseudo-components: heavy gas, saturates, aromatics + resins, and asphaltenes. Both flashed gas and flashed liquid compositions are required to do different steps of this previously developed characterization method to reach final

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Table 1. PC-SAFT Parameter Correlations as Presented by Gonzalez et al.⁹

aromatics + resins pseudo-component (γ is aromaticity)	
saturates pseudo-component	parameter = $(1 - \gamma)(\text{benzene derivatives correlation}) + \gamma(\text{PNA correlation})$
$m = 0.0257M_w + 0.8444$	$m = (1 - \gamma)(0.0223M_w + 0.751) + \gamma(0.0101M_w + 1.7296)$
$\sigma = 4.047 - 4.8013 \ln(M_w)/M_w$	$\sigma = (1 - \gamma)(4.1377 - 38.1483/M_w) + \gamma(4.6169 - 93.98/M_w)$
$\ln(\epsilon/k) = 5.5769 - 9.523/M_w$	$\epsilon/k = (1 - \gamma)(0.00436M_w + 283.93) + \gamma(508 - 234100/(M_w)^{1.5})$

Table 2. PC-SAFT Parameters Correlations for a Cut Fraction, Such as C₇₊ Pseudo-component

C ₇₊ pseudo-component (γ is aromaticity)	
parameter = $(1 - \gamma)(\text{saturates pseudo-component correlation}) + \gamma(\text{PNA correlation})$	
$m = (1 - \gamma)(0.0257M_w + 0.8444) + \gamma(0.0101M_w + 1.7296)$	
$\sigma = (1 - \gamma)(4.047 - 4.8013 \ln(M_w)/M_w) + \gamma(4.6169 - 93.98/M_w)$	
$\epsilon/k = (1 - \gamma)\exp(5.5769 - 9.523/M_w) + \gamma(508 - 234100/(M_w)^{1.5})$	

recombined oil composition. However, for some fluids, only the composition of monophasic reservoir fluid may be available. Some valuable asphaltene experimental data available in the literature could not be modeled using PC-SAFT, because the previous characterization methodology is not applicable for the lack of flashed gas and flashed liquid compositions.

This work presents a PC-SAFT crude oil characterization procedure when only the composition of monophasic reservoir fluid is available. Here, the reservoir fluid is flashed to atmospheric conditions using the PC-SAFT equation of state to calculate both flashed gas and flashed liquid compositions for which SARA analysis is available. The requirement of flashed gas and flashed liquid compositional data for crude oil characterization is eliminated using this approach, while the modeling results are still in reasonable comparison to the experimental data.

To flash a reservoir fluid using PC-SAFT, it is needed to know the SAFT parameters of all components. PC-SAFT parameters for individual components are available in the literature.⁷ For pseudo-components, such as C_{7H₁₆}, the parameter correlations for saturates presented in Table 1 can be used. For a cut fraction, such as C₇₊, the correlations in Table 2 should be used. According to these correlations, a C₇₊ pseudo-component will be linearly weighted by an aromaticity parameter between polynuclear aromatic (PNA) and saturate components. The aromaticity value for C₇₊ is adjusted to meet the gas/oil ratio (GOR) or C₇₊ density.

After flashing the monophasic fluid to atmospheric conditions, the compositions of flashed gas and flashed liquid are available. The flashed liquid is characterized as saturates, aromatics, resins, and asphaltenes based on SARA analysis of a stock tank oil (STO). The flashed gas, saturates, aromatics, resins, and asphaltenes are then recombined as per the monophasic fluid molecular weight to generate reservoir crude oil. During the characterization, asphaltenes can be modeled as polydisperse based on individual asphaltene fraction data. A detailed description on how asphaltenes can be treated as a polydisperse fraction is provided elsewhere.⁸ The PC-SAFT parameter correlations for aromatics + resins pseudo-component presented in Table 1 are also used for calculating the asphaltene PC-SAFT parameters. Here, a constant aromaticity value is assumed for the entire asphaltene distribution. The aromaticity value for asphaltenes and molecular weights of different asphaltene subfractions are fitted to the experimental onset pressure. The aromaticity value is thus typically adjusted between 0 and 1. In this work, on the basis of the available experimental data, both monodisperse and polydisperse asphaltenes are considered.

Asphaltene molecules aggregate even in good solvents, such as toluene. Along with polarizability, polarity of the asphaltenes may also play a role in forming these nanoaggregates. We model these nanoaggregates as dissolved in the oil. However, precipitation of these nanoaggregates is dominated by polarizability.^{10,11} Because of this, the association term in SAFT can be presumed to be negligible in asphaltene modeling work, and the PC-SAFT equation of state requires just three parameters for each non-associating component. These parameters are the temperature-independent diameter of each molecular segment (σ), the number of segments per molecule (m), and the segment–segment dispersion energy (ϵ/k).

3. EXPERIMENTAL DATA

In the literature, very few experimental data are available with information on crude oil composition and both asphaltene onset pressure (AOP) and precipitated asphaltene amount at HPHT. Thus, the following crude oils are chosen because the relevant data are available.

3.1. Oil A. In the experiments performed by Jamaluddin et al., asphaltene precipitation in a crude oil from the Middle East is studied.¹² The fluid and reservoir characteristics are presented in Table 3. The

Table 3. Fluid and Reservoir Properties of Crude Oil A

parameters	oil A
region	Middle East
reservoir temperature (°F)	240
reservoir pressure (MPa) [psia]	62.05 [9000]
bubble point pressure at T _{res} (MPa) [psia]	22.68 [3290]
GOR (m ³ /m ³)	195.90
API gravity (deg)	39
SARA Analysis of STO (% w/w)	
saturates	68.3
aromatics	11.6
resins	18.8
n-C ₅ asphaltenes	1.3

analysis of saturates, aromatics, resins, and asphaltenes of the STO obtained from a direct flashing is also presented in Table 3. In the direct flashing method, the single-phase reservoir fluid is homogenized at the reservoir conditions and rocked for 5 days. Subsequently, a subsample is flashed from the reservoir conditions to the ambient conditions to obtain the STO in a glass vial. This ensures that the STO used for measurements contains all of the solids present in the reservoir fluid. Table 4 presents the composition of oil A.

Jamaluddin et al. used a gravimetric technique in a conventional pressure–volume–temperature (PVT) cell for the measurement of asphaltenes precipitation from oil A.¹² The details of this method have

Table 4. Oil A Composition

components	monophasic fluid composition (mol %)
N ₂	0.48
CO ₂	0.92
H ₂ S	0.00
C ₁	43.43
C ₂	11.02
C ₃	6.55
i-C ₄	0.79
n-C ₄	3.70
i-C ₅	1.28
n-C ₅	2.25
pseudo-C ₆ H ₁₄	2.70
C ₇₊	26.88
total	100
M _w (g/mol)	82.49
C ₇₊ M _w (g/mol)	228.07
C ₇₊ density (g/cm ³)	0.865

been explained by Jamaluddin et al.¹² Oil A gravimetric tests are performed at the reservoir temperature of 116 °C (240 °F). Results of the asphaltene content in oil as a function of the pressure, as both *n*-pentane and *n*-heptane insolubles, are presented in Figure 1. It has not

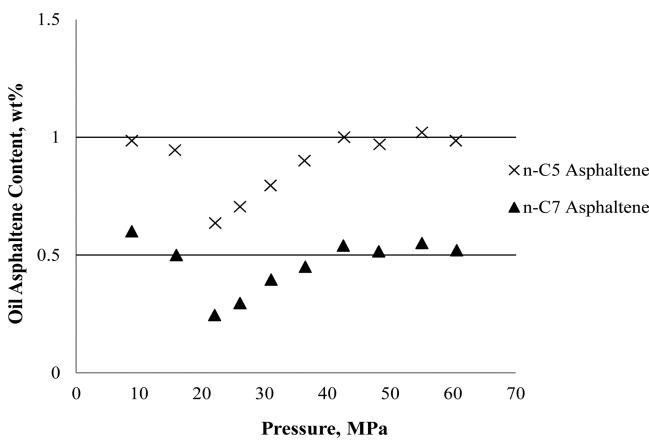


Figure 1. Asphaltene content of oil A at different pressure steps.

been discussed by Jamaluddin et al. whether or not the asphaltene contents determined on the flash oil are corrected for shrinkage of the oil.¹² If *n*-C₅ asphaltene content has been measured by the SARA analysis method without adjusting for shrinkage, the difference between the amount of *n*-C₅ asphaltene in Table 3, which is 1.3 wt %, and the amount of *n*-C₅ asphaltene in oil at HPHT (Figure 1), which is around 1 wt %, could be as a result of measurement uncertainty.

The asphaltene content of supernatant fluid during the gravimetric test starts to decrease at an AOP of 42.75 MPa (6200 psia). The asphaltene content shows a decreasing trend up to a pressure of 22.24 MPa (3235 psia). Subsequently, the asphaltene content increases. This pressure corresponds to the bubble point pressure.

The acoustic resonance technique (ART) is successfully used by different researchers in defining the upper asphaltene precipitation boundary.^{13–15} In the experiments performed by Jamaluddin et al., the asphaltene phase boundary for oil A is measured using ART tests.¹² The results of upper AOP along with the bubble point pressure data are summarized in Table 5.

3.2. Oil B. A summary of the black oil reservoir fluid B properties is provided in Table 6.¹⁶ Jamaluddin et al. investigated the aggravated asphaltene instability because of nitrogen injection, in comparison to the expected benefits of improved oil recovery.¹⁶ Oil B composition is summarized in Table 7.

Table 5. Saturation Pressures along with Upper and Lower AOPs for Oil A at Different Temperatures

temperature (°C)	upper onset pressure (MPa)	bubble point pressure (MPa)	lower onset pressure (MPa)
99	47.26	22.21	
104	45.42	22.64	
110	44.26	22.59	
116	42.92	22.68	13.51

Table 6. Fluid and Reservoir Characteristics for Crude Oil B

parameters	oil B
reservoir temperature (°F)	296
reservoir pressure (psia)	3256
bubble point pressure at 255 °F (psia)	3045
GOR (SCF/STB)	900
API gravity (deg)	32
SARA Analysis of STO (% w/w)	
saturates	57.4
aromatics	30.8
resins	10.4
<i>n</i> -C ₇ asphaltenes	1.4

Table 7. Oil B Composition

component	flashed liquid (mol %)	flashed gas (mol %)	monophasic fluid (mol %)
N ₂	0.00	0.77	0.49
CO ₂	0.00	17.67	11.37
H ₂ S	0.00	5.00	3.22
C ₁	0.00	42.49	27.36
C ₂	0.14	14.54	9.41
C ₃	0.66	10.05	6.70
i-C ₄	0.23	1.13	0.81
n-C ₄	1.48	4.11	3.17
i-C ₅	1.17	1.26	1.22
n-C ₅	2.71	1.57	1.98
pseudo-C ₆ H ₁₄	5.32	0.92	2.49
pseudo-C ₇ H ₁₆	7.38	0.37	2.87
pseudo-C ₈ H ₁₈	8.62	0.10	3.14
pseudo-C ₉ H ₂₀	7.67	0.02	2.74
pseudo-C ₁₀ H ₂₂	6.49	0.01	2.32
pseudo-C ₁₁ H ₂₄	5.31	0.01	1.90
C ₁₂₊	52.82	0.01	18.82
total	100	100	100
M _w (g/mol)	229.21	31.69	102.04
C ₁₂₊ M _w (g/mol)	337.98	167.11	337.94
C ₁₂₊ density (g/cm ³)	0.906		0.906

A HPHT filtration test is conducted by Jamaluddin et al. to quantify the amount of asphaltenes that can precipitate at a specified condition.¹⁶ Details of the experiment are presented in their paper.¹⁶ Table 8 presents the results of filtration tests conducted at 200 psia below the saturation pressure and through a 0.22 μm filter. For dark-colored oils,

Table 8. Filtration Test Result at 200 psi below Saturation Pressure for Oil B

filtration pressure (psia)	percent asphaltenes (%)	
	filtrate	filter paper
2700	93.81	5.15
total	98.96	

such as oil B, a near-infrared (NIR) light scattering is necessary to detect a phase change phenomenon.¹⁷ All of the asphaltene precipitation onset data thus measured are summarized in Table 9, along with respective bubble point pressures.

Table 9. Saturation Pressures and Upper Onset Pressures for Oil B at Different Temperatures

temperature (°F)	upper onset pressure (psia)	bubble point pressure (psia)
190	5400	2500
230	4050	2700
260	3650	2900
300	3800	2060

The saturation pressure and upper onset pressure data for nitrogen-injected reservoir oil B are summarized in Table 10.¹⁶ It can be seen from Table 10 that the asphaltenes are becoming increasingly unstable with an increasing nitrogen concentration. Also from Table 10, the amount of asphaltenes retained by 0.22 μm filter increases with an increasing nitrogen concentration.

3.3. Oil C. Negahban et al. discussed an experimental work associated with the evaluation of asphaltene precipitation from oil C for a United Arab Emirates (UAE) field.¹⁸ A summary of the reservoir fluid properties for oil C is provided in Table 11. The composition of this crude oil and producer gas composition used for gas injection experiments are presented in Tables 12 and 13, respectively.

A HPHT filtration test is conducted by Negahban et al. to quantify the amount of asphaltenes that may form and remain suspended at a given pressure.¹⁸ Table 14 shows the results of filtration experiments at various temperatures as well as different concentrations of injected gas.

Negahban et al. used a fixed wavelength light scattering technique to measure AOP at different conditions.¹⁸ A description of this light scattering technique can be found elsewhere.¹⁹ Table 15 shows both bubble and onset pressures for oil C at various temperatures and concentrations of injected gas. In the data reported by Negahban et al., the light scattering AOP has been found to be too low when compared to filtration results. We have no information about the experimental error bar and the uncertainties in the procedure because they were not been discussed by Negahban et al.

4. RESULTS AND DISCUSSION

4.1. Oil A. **4.1.1. Characterization Results.** For oil A, only the composition of monophasic reservoir fluid is available and, hence, flashed to atmospheric conditions using PC-SAFT equation of state to obtain flashed gas and flashed liquid compositions. For oil A, on the basis of the composition presented in Table 4, PC-SAFT parameters for pseudo-components C_6H_{14} and C_{7+} are needed. For C_6H_{14} pseudo-component, the correlations for saturates from Table 1 are used. For C_{7+} , the correlations in Table 2 are used. The aromaticity value for C_{7+} is adjusted to meet the GOR reported in Table 3. Table 16 compares experimental data and modeling results using 0.12 as the aromaticity value of C_{7+} . Table 17 shows both flashed gas and flashed liquid compositions for the monophasic fluid presented in Table 4.

Table 10. Onset Pressures, Bubble Pressures, and Filtration Test Results for Oil B at Different Concentrations of Injected Nitrogen

injected nitrogen (mol %)	saturation pressure (psia)	upper onset pressure (psia)	asphaltenes on filter (% w/w)	asphaltenes in filtrate (% w/w)	asphaltenes in toluene rinse of cell (% w/w)	total asphaltenes (% w/w)
0	3045	3800	5.15	93.8		99.0
5	4000	5500	21.9	71.3	4.3	97.5
10	4800	7700	27.6	63.4	6.4	97.5
20	7000	11700	30.9	61.8	4.4	97.2

Table 11. Fluid and Reservoir Characteristics for Crude Oil C

parameters	oil C
reservoir temperature (°F)	250
reservoir pressure (psia)	4550
bubble point pressure at T_{res} (psia)	3434
GOR (SCF/STB)	1100
API gravity (deg)	38.4
SARA Analysis of STO (% w/w)	
saturates	61.3
aromatics	31.8
resins	6.4
n-C ₇ asphaltenes	0.49

Table 12. Oil C Composition

components	monophasic fluid C composition (mol %)
N ₂	0.31
CO ₂	3.02
H ₂ S	0.00
C ₁	44.29
C ₂	6.36
C ₃	4.88
i-C ₄	1.40
n-C ₄	3.22
i-C ₅	1.64
n-C ₅	2.07
pseudo-C ₆ H ₁₄	2.89
C ₇₊	29.92
total	100
M_w (g/mol)	84.1
C ₇₊ M_w (g/mol)	213.1

Table 13. Injected Gas Composition

components	injection gas composition (mol %)
N ₂	0.71
CO ₂	4.43
H ₂ S	2.00
C ₁	73.45
C ₂	8.81
C ₃	5.47
i-C ₄	1.20
n-C ₄	2.20
i-C ₅	0.62
n-C ₅	0.60
n-C ₆	0.37
n-C ₇	0.13
n-C ₈	0.01
total	100

Table 18 represents the results of oil A characterization using PC-SAFT characterization methodology. It also reports PC-SAFT parameters of all of the components after characterization. The aromaticity value for the aromatics + resins component is

Table 14. Filtration Test Results for Oil C at Different Temperatures and Concentrations of Injected Gas

injected gas (mol %)	test temperature (°F)	asphaltenes on filter (% w/w)	asphaltenes in filtrate (% w/w)	asphaltenes in the PVT cell (% w/w)	total asphaltenes (% w/w)
0	250	11.6	76.7	6.3	94.6
15% CO ₂	130	13.4	66.4	13.5	93.2
15% CO ₂	250	12.1	70.3	10.4	92.8
15% synthetic gas	130	16.3	62.7	14.6	93.5
15% synthetic gas	250	13.2	68.8	13.1	95.2
45% synthetic gas	130	16.8	61.0	16.2	94.1
45% synthetic gas	250	14.6	66.4	15.6	96.5

Table 15. Saturation Pressures and Upper Onset Pressures for Oil C at Different Temperatures and Concentrations of Injected Gas

injected gas (mol %)	temperature (°F)	bubble pressure (psia)	upper onset pressure (psia)
0	130	2990	
0	250	3434	
15% CO ₂	130	3243	4200
15% CO ₂	250	3700	
15% synthetic gas	130	3627	8087
15% synthetic gas	250	4103	7092
45% synthetic gas	154		14500
45% synthetic gas	250	5193	11889

Table 16. Comparison of Experimental and Modeling Results for Oil A GOR and C₇₊ Density

parameters	experimental value	modeling results
C ₇₊ density (g/cm ³)	0.865	0.847
GOR (m ³ /m ³)	195.90	196.26

Table 17. Flashed Gas and Flashed Liquid Compositions of the Monophasic Crude Oil A

components	flashed gas composition (mol %)	flashed liquid composition (mol %)
N ₂	0.71	0.00
CO ₂	1.31	0.11
C ₁	64.03	0.35
C ₂	15.90	0.70
C ₃	8.99	1.45
i-C ₄	0.99	0.37
n-C ₄	4.25	2.56
i-C ₅	1.11	1.63
n-C ₅	1.65	3.51
pseudo-C ₆ H ₁₄	1.00	6.25
C ₇₊	0.00	83.07

0.03 and is fitted to reproduce both the experimental STO density and bubble point pressure. The experimental STO density, 0.830 g/cm³, and the fitted value, 0.817 g/cm³, show a reasonable match.

To investigate the effect of asphaltene polydispersity, the asphaltene fraction in the characterization process is divided into two subfractions: n-C_{5–7} and n-C₇₊ asphaltenes, on the basis of the experimental amount of n-C₅ and n-C₇ asphaltenes. The aromaticity value for asphaltene as well as molecular weights of different asphaltene subfractions are fitted to the experimental upper onset pressure at different temperatures.

The binary interaction parameters presented by Gonzalez et al. are applied in this work.²⁰ Table 19 shows the binary interaction parameters used for PC-SAFT modeling of oil A. Sensitivity analysis of the binary interaction parameters between asphaltenes and other components show an effect on both the onset and amount of precipitation. Obviously, a component with a higher amount in oil composition will have a larger impact on the asphaltene phase behavior. An increase in the value of a binary interaction parameter between asphaltenes and another component of the oil will result in a wider range of pressures for asphaltene precipitation and also more amounts of precipitated asphaltene.

4.1.2. Modeling Results. With all of the parameters defined, the saturation pressure at different temperatures and both upper and lower onset pressures at various temperatures are calculated using PC-SAFT. A comparison of equation of state and experimental data for the asphaltene phase envelope is shown in Figure 2 for oil A. The equation of state accurately captures the phase behavior.

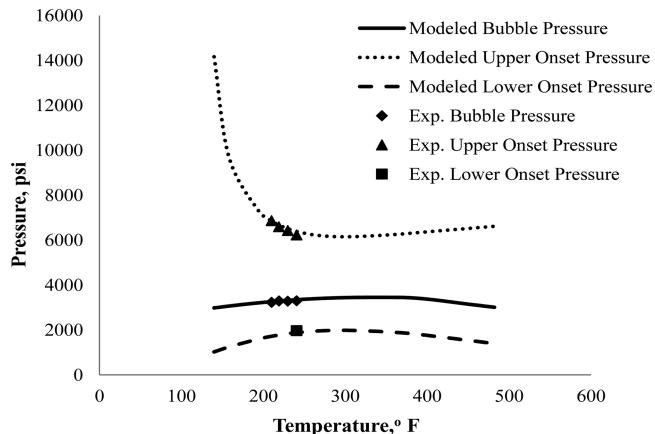
The same set of fitted parameters is used for predicting the amount of asphaltene dissolved in oil during pressure depletion conditions. To calculate the content of both n-pentane- and n-heptane-insoluble asphaltenes for oil A, the gravimetric measurement technique is simulated using PC-SAFT equation of state. First, the monophasic system is depressurized to a predetermined pressure. Because of the relatively higher density, the part of fluid that settles at the bottom of the PVT cell is the asphaltene-rich phase and the fluid sample from the top of the

Table 18. Characterized Crude Oil A as a Combination of Eight Components and Their PC-SAFT Parameters

component	M _w (g/mol)	composition (wt %)	σ (A)	m	ε/k (K)
N ₂	28.01	0.194	3.31	1.205	90.96
CO ₂	44.01	0.562	2.78	2.073	169.21
C ₁	16.04	1.0024	3.70	0.999	150.03
heavy gas	43.13	14.290	3.60	2.017	203.90
saturates	176.43	51.177	3.91	5.378	250.36
aromatics + resins ($\gamma = 0.03$)	277.00	22.779	4.01	6.856	290.30
n-C _{5–7} asphaltenes ($\gamma = 0.29$)	1700.00	0.599	4.24	32.930	353.20
n-C ₇₊ asphaltenes ($\gamma = 0.29$)	2500.00	0.375	4.25	47.940	356.11

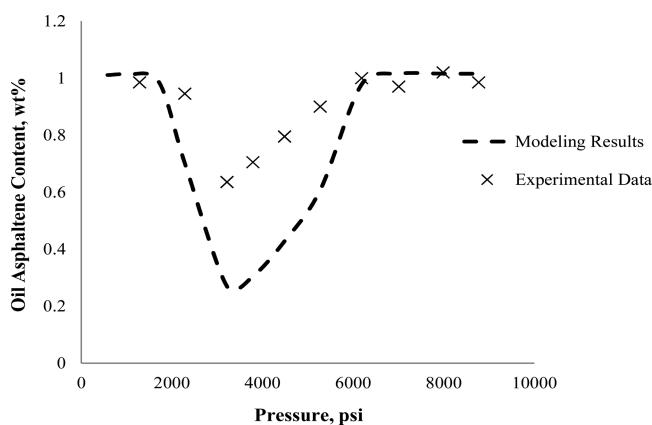
Table 19. Binary Interaction Parameters Used for Modeling of Crude Oil A

component	N ₂	CO ₂	methane	heavy gas	saturates	aromatics + resins	C _{5–7} asphaltenes	C ₇₊ asphaltenes
N ₂	0							
CO ₂	0	0						
methane	0.03	0.05	0					
heavy gas	0.06	0.10	0	0				
saturates	0.12	0.13	0.03	0.01	0			
aromatics + resins	0.11	0.09	0.029	0.01	0.007	0		
C _{5–7} asphaltenes	0.11	0.10	0.029	0.01	0.007	0	0	
C ₇₊ asphaltenes	0.11	0.10	0.029	0.01	0.007	0	0	0

**Figure 2.** Asphaltene phase envelope for crude oil A generated by PC-SAFT.

cell is an asphaltene-lean phase. The asphaltene-lean phase is flashed to atmospheric conditions to obtain a sample stock tank liquid for asphaltene analysis. After that, the stock tank liquid is analyzed for both *n*-pentane- and *n*-heptane-insoluble asphaltenes; aliquots of the flashed stock tank liquid are independently treated with *n*-pentane and *n*-heptane to determine the total asphaltene content of the flashed liquid. Figure 3 and Table 20 compare the PC-SAFT predictions to experimental data for the *n*-pentane asphaltene content of oil A.

It can be seen from Figure 3 that PC-SAFT shows an accurate trend for the precipitated amount but appears to overpredict the precipitated asphaltene amount during pressure depletion conditions. Table 20 reports experimental and modeling results for *n*-C₅ asphaltene content of oil A as well as the corresponding

**Figure 3.** Comparison of experimental and modeling results for the *n*-C₅ asphaltene content of oil A.**Table 20.** Comparison of Experimental and Modeling Results for the *n*-C₅ Asphaltene Content of Oil A

pressure (psi)	experimental <i>n</i> -C ₅ asphaltene content (wt %)	modeled <i>n</i> -C ₅ asphaltene content (wt %)	error (%)
1291.56	0.985	1.014	2.94
2288.84	0.945	0.681	27.85
3220.72	0.635	0.268	57.78
3792.93	0.705	0.305	56.67
4495.93	0.795	0.430	45.89
5280.68	0.900	0.609	32.23
6196.22	1.000	0.980	1.98
7013.66	0.970	1.015	4.73
7994.59	1.020	1.015	0.41
8779.33	0.985	1.015	3.13

error percentage. Here, it is necessary to talk about the PC-SAFT ability to correctly account for the partitioning of the asphaltenes between asphaltene-lean and asphaltene-rich phases. In a recent publication by Tavakkoli et al., asphaltene precipitation onset as well as the precipitated amount were modeled for titration of dead oils with various *n*-alkanes using PC-SAFT equation of state.⁸ They showed a reasonable match between modeling results and experimental data of asphaltene precipitation at ambient conditions. Therefore, one may conclude that the PC-SAFT can model the precipitated amount and correctly account for the partitioning of asphaltenes between asphaltene-lean and asphaltene-rich phases.

4.1.3. Experimental Uncertainties. In oil A, because all predictions for saturation and onset pressures are matched well with the same set of fitted parameters, one might ask about the uncertainties in the experimental measurements for the amount of precipitated asphaltene. It is presumed that experimental methods for measuring saturation and onset pressures involve fewer errors than the techniques for measuring the amount of precipitated asphaltene at HPHT conditions. The uncertainties in experimental data for the precipitated asphaltene amount reported by various experimentalists are a good reason for this belief.^{16,18} A typical uncertainty in the filtration test experimental results is that the sum of the asphaltene amount passed through the filter, the amount retained by the filter paper, and the asphaltene in the PVT cell is not equal to the total asphaltene content of the crude oil sample, and there are some losses in the reported asphaltene amount.^{16,18} Refer to Tables 10 and 14 to see these uncertainties in the experimental precipitated amount. Recently, new experimental procedures and tools, such as an indirect method using NIR spectrometry and an electron paramagnetic resonance sensor, are proposed to investigate asphaltene instability in petroleum fluids with promising results.^{21,22} These new procedures and tools are still under development, and there are no published experimental data on the precipitated amount obtained by these new methods.

Therefore, we did not have a chance to compare the PC-SAFT predictions to the experimental precipitated amount obtained by these methods. We hope to see that these new experimental procedures and tools would close the gap between modeling results and experimental data.

4.1.4. Incorporating Factor W . When the monophasic fluid is depressurized to a predetermined pressure between lower and upper onset pressures, there will be two phases: asphaltene-rich phase and asphaltene-lean phase, or three phases: asphaltene-rich phase, asphaltene-lean phase, and gas phase, depending upon the pressure in which the monophasic fluid is depressurized. In both cases, each phase has a specific portion of the total fluid. If during sampling from the top liquid phase of the PVT cell in the experimental gravimetric technique a very small portion of the asphaltene-rich phase becomes transferred to the asphaltene-lean phase, a small error may happen in experimental results.

To simulate this experimental error during modeling, a small portion of the asphaltene-rich phase (weight fraction factor or W) is added to the asphaltene-lean phase before flashing the sample liquid to atmospheric conditions. Instead of flashing the pure asphaltene-lean phase, the " W " portion of the asphaltene-rich phase plus the " $1 - W$ " portion of the asphaltene-lean phase are flashed to the atmospheric conditions. To match the experimental data for the precipitated asphaltene amount from oil A requires a " W " of only 0.005. Factor " W " is not selected on the basis of the losses in the reported asphaltene amount. The losses show the possibility of error in experimental data. We change the value of " W " to change the modeling results and find the best match between modeling results and experimental data. The final value for " W " is a weight fraction of the asphaltene-rich phase that has been transferred to the asphaltene-lean phase to show the possible small error in experimental data. " W " is small, and it makes sense because a large portion of the asphaltene-rich phase is made of asphaltenes and a small portion of this asphaltene-rich phase has a considerable amount of asphaltenes. To find the amount of asphaltenes transferred from the rich phase to the lean phase, one needs to multiply the factor " W " to the asphaltene weight fraction in the asphaltene-rich phase.

Actually, " W " is not a model fitting parameter but a weight fraction factor that is treated as a matching parameter to show the potential impact of a small error. Figure 4 compares PC-SAFT predictions when factor " W " is 0.005 to experimental results of the asphaltene content, by both *n*-pentane and *n*-heptane insoluble. The measurements are not biased by a constant " W "

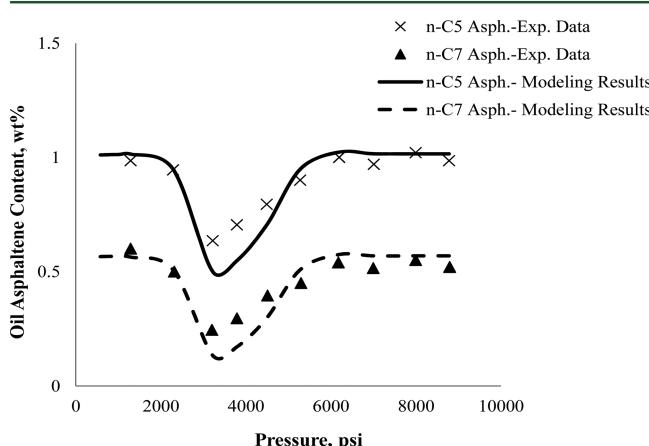


Figure 4. Comparison of PC-SAFT modeling results considering factor " W " and experimental data for the asphaltene content of crude oil A.

factor. There can be different values for factor " W " at different pressure steps, because the gravimetric technique is repeated at those pressure steps. Factor " W " may increase around the bubble point, because the amount of precipitated asphaltenes is at a maximum at the saturation pressure, and factor " W " may decrease around onset pressures. In other words, the probability of experimental error for the amount of precipitation measured around the bubble pressure is more than around the onset pressure. However, here, " W " is treated as a single factor only to show the effect of experimental error on modeling predictions.

Figure 4 shows a good match for the oil asphaltene content during pressure depletion conditions. The value of 0.005 for factor " W " represents a very small error in the experimental procedure. A comparison of Tables 20 and 21 shows the significant decrease in error percentage between experimental data and modeling results when factor " W " is used. It is necessary to mention that, in the current study, no multipliers are applied to the experimental data to match to the model. All of the experimental data presented in this paper are the same as the data presented in the original papers. The " W " factor is used to change the modeling results to simulate the possible experimental error.

It should be mentioned that, after using the same set of parameters, which were fitted to capture asphaltene phase behavior, and finding an unreasonable match between modeling and experimental data on the precipitated amount, we tried to change the fitting parameter values to find a good match. However, all of the parameters that affect the precipitated amount, i.e., asphaltene molecular weight, asphaltene aromaticity, and binary interaction parameters between asphaltenes and other components, also control AOPs. In other words, one can change the fitting parameters to find a better match for the asphaltene amount precipitated, but at the same time, the good match between modeling and experimental results for asphaltene phase behavior is being missed. For instance, decreasing the asphaltene molecular weight will decrease the precipitated amount predicted by PC-SAFT. At the same time, it also decreases the predicted asphaltene upper onset pressure, and therefore, we are missing the previously well-matched asphaltene phase behavior.

4.1.5. Asphaltene Polydispersity. Asphaltenes are a polydisperse class of compounds defined in terms of solubility cut (toluene soluble and *n*-pentane or *n*-heptane insoluble) of this distribution. They are a continuum of aggregates (self-associated asphaltenes) of increasing effective molar mass.²³ Typical molecular weight values using the vapor pressure osmometry technique are in the range of 800–3000 g/mol in good solvents (e.g., toluene and benzene).²⁴ Knowledge on the polydisperse behavior of asphaltenes is important because different fractions precipitate in different amounts under different conditions. In this regard, limited modeling work is available in the literature. In a recent publication by Tavakkoli et al., asphaltenes in real crude oil systems were modeled as polydisperse using PC-SAFT equation of state.⁸ However, their modeling results were limited to titration of dead oils with various *n*-alkanes.

To see the role of each asphaltene subfraction in total asphaltene precipitation at HPHT, plots for the mass distribution of asphaltene subfractions in crude oil A as a function of the pressure are shown in Figures 5 and 6 for *n*-C₅ and *n*-C₇ asphaltenes, respectively. These figures show the contribution of each asphaltene subfraction to the total asphaltene content of oil when pressure decreases from reservoir pressure to atmospheric conditions. As seen in Figure 6, the contribution of C_{5–7} asphaltenes in the *n*-heptane asphaltene content of oil A

Table 21. Comparison of PC-SAFT Modeling Results Considering Factor “W” and Experimental Data for the Asphaltene Content of Crude Oil A

pressure (psi)	experimental $n\text{-C}_5$ asphaltene content (wt %)	modeled $n\text{-C}_5$ asphaltene content (wt %)	error (%)	experimental $n\text{-C}_7$ asphaltene content (wt %)	modeled $n\text{-C}_7$ asphaltene content (wt %)	error (%)
1291.56	0.985	1.014	2.94	0.605	0.564	6.03
2288.84	0.945	0.949	0.43	0.500	0.508	1.68
3220.72	0.635	0.500	21.28	0.245	0.134	45.48
3792.93	0.705	0.548	22.19	0.295	0.171	41.96
4495.93	0.795	0.705	11.25	0.395	0.298	24.57
5280.68	0.900	0.949	5.42	0.450	0.509	13.07
6196.22	1.000	1.023	2.32	0.540	0.575	6.50
7013.66	0.970	1.015	4.73	0.515	0.570	10.51
7994.59	1.020	1.015	0.41	0.550	0.570	3.47
8779.33	0.985	1.015	3.13	0.520	0.570	9.44

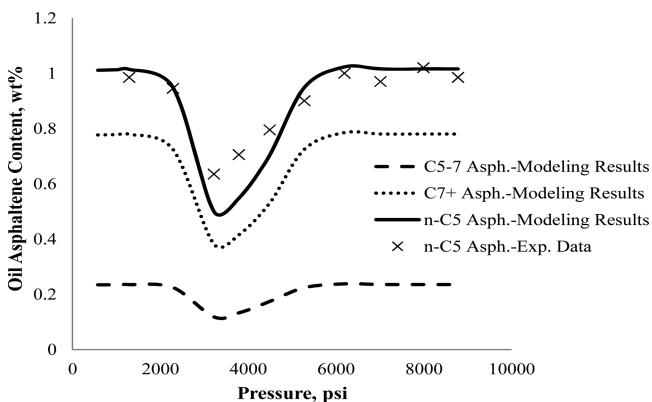


Figure 5. Mass distribution of $n\text{-C}_5$ asphaltene subfractions as a function of the pressure in oil A.

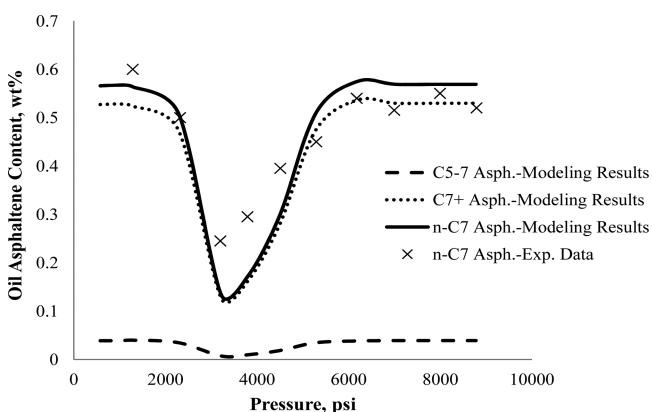


Figure 6. Mass distribution of $n\text{-C}_7$ asphaltene subfractions as a function of the pressure in oil A.

is almost zero when the pressure reaches the bubble point pressure.

C_{5-7} asphaltenes represent the fraction of asphaltenes that is more soluble in $n\text{-C}_7$ (although not completely soluble) than $n\text{-C}_5$. Therefore, $n\text{-C}_7$ asphaltenes contain both C_{5-7} and C_{7+} asphaltene subfractions, and the amount of the C_{5-7} subfraction is very low in total $n\text{-C}_7$ asphaltenes. The maximum asphaltene precipitation happens at the bubble point pressure, and because the amount of the C_{5-7} subfraction is very low in total $n\text{-C}_7$ asphaltenes, C_{5-7} asphaltenes follow the observation in Figure 6.

There is no experimental data on the precipitated amount of each asphaltene subfraction to compare to modeling results obtained by PC-SAFT. Part of the reason can be the difficulties

associated with extracting each asphaltene subfraction from a crude oil. Hence, the results presented here for the role of different asphaltene subfractions are only theoretical predictions.

It is necessary to mention that using asphaltene polydispersity, without considering factor “W”, did not help in successfully predicting the total precipitated amount (see Figure 3). Oil A is a good sample for the case of using two asphaltene fractions. The two fractions are chosen on the basis of the experimental data of the total amount of C_5 and C_7 asphaltenes. To consider more than two asphaltene fractions, we need to tune more parameters: the molecular weight of each asphaltene fraction and its weight fraction in total asphaltenes precipitated. We also implemented the asphaltene polydispersity effect for oil A using more than two fractions (we tried three and four fractions). The already mentioned parameters were first fitted to capture the asphaltene phase behavior. Then, using the same set of parameters, the amount of precipitated asphaltene is predicted. However, the total amount of precipitated asphaltene (C_5 and C_7 asphaltenes) did not show considerable changes in comparison to the case of using two asphaltene fractions. One can try to find a better match for the precipitated amount by changing the values of fitting parameters, but at the same time, as previously mentioned, the good match between modeling and experimental results on asphaltene phase behavior is being missed. Therefore, even in the case of asphaltene polydispersity, one still needs to use the “W” factor to change the modeling results for simulating the possible experimental error.

Therefore, on the basis of the modeling results of oil A, one can say that there is not a single parameter that controls solely the amount of precipitated asphaltenes without having any effect on the AOP. The “W” factor is the only parameter that affects the amount of asphaltenes without affecting the asphaltene phase behavior. From the above discussion, in different ways, we tried to match the experimental precipitated amount, showing that the “W” factor is not due to the particular equation of state characterization treatment in the model. “W” is due to possible experimental error and is small, which shows that a small experimental error may cause a significant difference between modeling results and experimental data.

4.2. Oil B. 4.2.1. Characterization Results. Although oil B has been used by previous researchers for modeling asphaltene phase behavior under nitrogen injection conditions using PC-SAFT equation of state, the amount of precipitated asphaltene under the same conditions has not been modeled by them.^{25,26} For crude oil B, both flashed gas and flashed liquid compositions are available and the PC-SAFT characterization procedure already available in literature can be applied. Table 22 presents the live oil

Table 22. Characterized Crude Oil B as a Combination of Eight Components with Their PC-SAFT Parameters

component	M_w (g/mol)	composition (wt %)	σ (Å)	m	ε/k (K)
H ₂ S	34.08	1.227	3.073	1.651	227.34
N ₂	28.01	0.155	3.313	1.205	90.96
CO ₂	44.01	5.602	2.785	2.073	169.21
C ₁	16.04	4.909	3.704	1.000	150.03
heavy gas	44.56	10.946	3.612	2.053	204.97
saturates	212.89	44.290	3.926	6.315	252.69
aromatics + resins ($\gamma = 0.25$)	248.50	31.790	4.047	5.779	325.82
asphaltenes ($\gamma = 0.292$)	2631.90	1.080	4.257	50.328	357.13

Table 23. Binary Interaction Parameters Used for PC-SAFT Modeling of Crude Oil B

component	H ₂ S	N ₂	CO ₂	methane	heavy gas	saturates	aromatics + resins	asphaltenes
H ₂ S	0							
N ₂	0.09	0						
CO ₂	0.0678	0	0					
methane	0.062	0.03	0.05	0				
heavy gas	0.07	0.075	0.12	0.03	0			
saturates	0.09	0.14	0.13	0.03	0.005	0		
aromatics + resins	0.015	0.158	0.10	0.029	0.012	0.007	0	
asphaltenes	0.103	0.204	0.17	0.035	0.012	0.011	0	0

B along with the PC-SAFT parameters. The aromaticity value of 0.25 for the aromatics + resins component is fitted to reproduce experimental STO density and bubble point pressure at different temperatures. The experimental value for STO density is 0.865 g/cm³, and the fitted value is 0.846 g/cm³, showing a reasonable match.

Here, there is only one asphaltene fraction based on the reported experimental data. The aromaticity value and molecular weight for the asphaltene fraction are fitted to the experimental upper onset pressure upon nitrogen injection. Besides asphaltene aromaticity and molecular weight, the binary interaction parameters between asphaltene and other components are also adjusted to find a good match for the AOPs. The values presented by Panuganti et al. are used as reference values for the binary interaction parameters between different components³ in oil B. Table 23 shows the set of temperature-independent binary interaction parameters used for oil B. The sensitivity analysis of these asphaltene binary interaction parameters is the same as discussed for oil A. Because of nitrogen injection into oil B, the binary interaction parameter between asphaltenes and nitrogen also plays a prominent role.

4.2.2. Modeling Results. With all of the parameters set, Figure 7 is plotted, which shows a good agreement of the PC-SAFT and experimental values for bubble and upper AOPs. Figure 8 drawn on a pressure–composition diagram for various amounts of nitrogen injected, showing a comparison of modeling results and experimental data for the asphaltene phase behavior. The results demonstrate a good match for both bubble and onset pressures at various concentrations of nitrogen. The same set of fitted parameters that is used to predict saturation and precipitation onset pressures is used for predicting the filtrate asphaltene content at different concentrations of injected nitrogen. Figure 9 compares experimental and predicted results, before and after using factor “W”, for the asphaltene content of filtrate at different concentrations of injected nitrogen gas.

From Figure 9 and Table 24, one can see the difference between experimental data and modeling results for the filtrate asphaltene content before using the factor “W”. Actually, PC-SAFT shows the right trend, but similar to the case of oil A, it

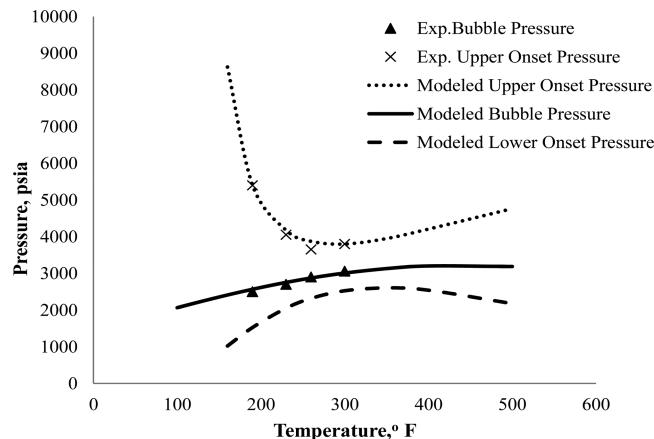


Figure 7. Asphaltene phase envelope for crude oil B generated by PC-SAFT.

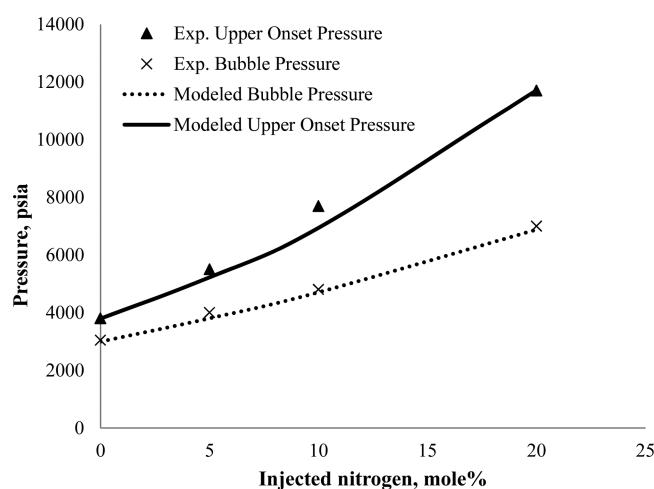


Figure 8. Comparison of PC-SAFT modeling results and experimental data for saturation and AOPs at various concentrations of injected nitrogen into crude oil B.

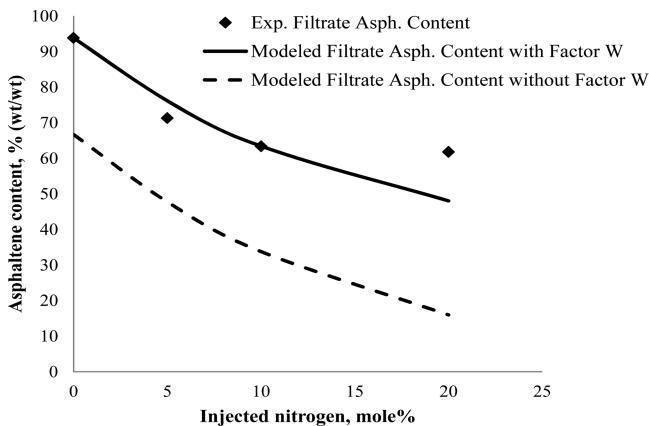


Figure 9. Comparison of PC-SAFT modeling results and experimental data of the filtrate asphaltene content for crude oil B at different concentrations of injected nitrogen. W used is 0.0054.

Table 24. Comparison of PC-SAFT Modeling Results and Experimental Data of Filtrate Asphaltene Content for Crude Oil B at Different Amounts of Injected Nitrogen

injected nitrogen (mol %)	experimental filtrate asphaltene content (% w/w)	modeled filtrate asphaltene content with factor W (% w/w)	modeled filtrate asphaltene content without factor W (% w/w)	error with factor W (%)	error without factor W (%)
0	93.81	93.84	66.67	0.03	28.92
5	71.3	76.19	47.76	6.85	33.01
10	63.4	63.38	33.77	0.03	46.73
20	61.8	48.04	15.98	22.26	74.14

overpredicts the amount of precipitated asphaltene for HPHT gas injection conditions. Similar to crude oil A, a small error in the experiment can explain this difference. During the filtration procedure, even if a very small portion of the asphaltene-rich phase escapes the filter paper and becomes transferred to the asphaltene-lean phase, then the filtrate contains both asphaltene-lean and asphaltene-rich phases instead of only the asphaltene-lean phase.

To simulate this experimental error during modeling, a small portion of the asphaltene-rich phase (weight fraction factor or W) is added to the asphaltene-lean phase before flashing the filtrate to atmospheric conditions for calculating its asphaltene content. Instead of flashing the pure asphaltene-lean phase, the “ W ” portion of the asphaltene-rich phase plus the “ $1 - W$ ” portion of the asphaltene-lean phase are together flashed to atmospheric conditions. For oil B, the value of “ W ” that matches the experimental data for the precipitated asphaltene amount is 0.0054.

Figure 9 and Table 24 compare the PC-SAFT predictions for “ W ” equal to 0.0054 to experimental results of the filtrate asphaltene content. Using a constant value of “ W ” cannot match all of the data points. “ W ” may have different values at various concentrations of injected gas, because more asphaltene precipitation happens when the concentration of injected gas increases (see Table 10). However, here, we treated “ W ” as a single factor only to show the effect of experimental error on modeling predictions. Figure 10 shows the PC-SAFT predicted amount of precipitated asphaltene under pressure depletion conditions at reservoir temperature and different concentrations of injected pure nitrogen gas. It can be seen that the maximum amount of precipitation occurs at the bubble point pressure.

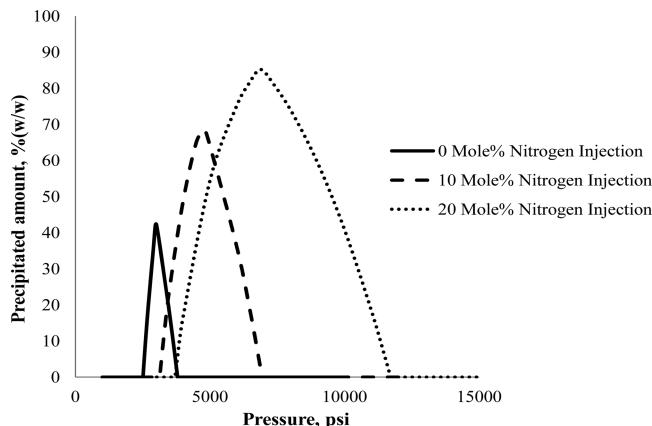


Figure 10. PC-SAFT predictions for the amount of precipitated asphaltene under pressure depletion conditions and various concentrations of nitrogen gas injected into crude oil B.

4.2.3. Binary Interaction Parameter Comparison. By comparing the binary interaction parameters of oil B to oil A, one can understand that the binary interaction parameters of asphaltenes– N_2 , asphaltenes– CO_2 , and asphaltenes– H_2S for oil B differ much from the same binary interaction parameters for oil A. The values for these parameters in oil B are more than the values for oil A. This is because of more amounts of gases N_2 , CO_2 , and H_2S in oil B in comparison to oil A. When the amount of one component is more in oil composition, the binary interaction parameter between that component and asphaltenes has more effect on the asphaltene phase behavior prediction as well as the precipitated amount. Unlike oil B, which has some amount of hydrogen sulfide in its composition, oil A has zero amounts of H_2S . Also, the CO_2 content of oil B is much more than the CO_2 content in oil A. Because oil B has been used for nitrogen injection experiments, the binary interaction parameter between asphaltenes and nitrogen plays an important role for asphaltene phase behavior modeling.

If one sets the values for binary interaction parameters of oil B close to the values of the binary interaction parameters used for oil A, the molecular weight of asphaltenes in oil B needs to be increased from 2631.90 to 2861.30 to find a reasonable match between modeling and experimental results, which does not show a lot of changes in the molecular weight value. If one calculates the error percentage between modeling results and experimental data, it can be found that the error for the asphaltene molecular weight of 2631.90 and the binary interaction parameters presented in Table 23 is less than the error in the case of asphaltene molecular weight equal to 2861.30 and the binary interaction parameters close to the values used for oil A. Although both cases show a reasonable match between modeling and experimental data, the first case has been presented in this study because of a smaller error percentage between model predictions and experimental data. The issue of uniqueness of asphaltene SAFT parameters has been investigated previously by Ting.²⁷ Different values for asphaltene molecular weight and aromaticity result in various asphaltene SAFT parameters. Therefore, it is possible to find reasonable results using different sets of fitting parameters. The phase envelope calculated using these different sets of asphaltene parameters are similar, and therefore, we believe the effects of the non-uniqueness of asphaltene parameters on asphaltene phase behavior in oil will be small. Finally, we choose one set of fitting

Table 25. Effect of Changes in Model Input Parameters on the Predicted Filtrate Asphaltene Content

model parameter	adjusted value based on experimental data	effect of asphaltenes aromaticity	effect of molecular weight	effect of asphaltenes–saturates BIP ^a	effect of the “W” factor
asphaltenes aromaticity	0.292	0.3212	0.292	0.292	0.292
asphaltenes molecular weight	2631.90	2631.90	2895.09	2631.90	2631.90
asphaltenes–saturates BIP ^a	0.011	0.011	0.011	0.0121	0.011
“W” factor	0.0054	0.0054	0.0054	0.0054	0.00489
predicted oil asphaltenes content at 10 mol % injected nitrogen (wt %)	63.38	53.27	49.36	59.75	58.92
decrease in predicted oil asphaltenes content (%)		15.95	22.12	5.73	7.04

^aBinary interaction parameter.

parameters that shows the minimum error percentage between modeling results and experimental data.

From the above two paragraphs, it can be concluded that the difference between the amount of light fractions in oil B and oil A may result in the difference between asphaltene binary interaction parameters for oil B and oil A. Therefore, the difference between asphaltene binary interaction parameters of various crude oils can be justified by the difference in natures of those crude oils as well as the difference in the crude properties, such as composition. Also, the characterization space does not look different depending upon the recovery method, i.e., pressure depletion versus gas injection. Therefore, as an initial estimate, one may use the binary interaction parameters obtained from modeling pressure depletion conditions to predict asphaltene phase behavior under HPHT gas injection conditions. However, for the reservoir under miscible gas injection conditions, the binary interaction parameters between asphaltene and the injected gas are more in comparison to the binary interaction parameters between asphaltene and the same gas when the reservoir is being produced under natural depletion conditions.

When the asphaltene properties of crude oils A and B are compared, one can understand the differences between different asphaltene properties, such as asphaltene aromaticity, asphaltene molecular weight, and asphaltene binary interaction parameters. On the basis of the discussion that we made for asphaltene binary interaction parameters, one can say that the difference between asphaltene properties of various crude oils can be justified by the different natures of those crude oils as well as by the difference between the crude oils properties, such as composition.

4.2.4. Sensitivity Analysis of Model Parameters. A sensitivity analysis is performed here for important model parameters to understand the effect of each parameter on precipitated asphaltene amount. Table 25 shows the effect of 10% change in input parameters on the predicted oil asphaltene content at 10 mol % nitrogen injection. The parameters used in this analysis are asphaltene aromaticity, asphaltene molecular weight, asphaltenes–saturates binary interaction parameter, and “W” factor. Only one asphaltene binary interaction parameter is used because changes in other asphaltene binary interaction parameters show the same trend as the asphaltenes–saturates binary interaction parameter. For asphaltene aromaticity, asphaltene molecular weight, and asphaltenes–saturates binary interaction parameter, the increase of the parameter value will result in more amounts of precipitated asphaltene, which means less amounts of asphaltenes in the filtrate, as shown in Table 25. The decrease in the “W” factor shows the same result as the increase in the other parameters of Table 25, because a decrease of “W” means a decrease in the amount of added asphaltene-rich phase to asphaltene-lean phase, and we will have less amounts of

asphaltenes in the filtrate. It can be found from Table 25 that the model prediction is very sensitive to asphaltene aromaticity and asphaltene molecular weight. Also, one can see that a very small decrease in the “W” factor will result in more than a 7% decrease in the filtrate asphaltene content.

4.3. Oil C. **4.3.1. Characterization Results.** For oil C, only the composition of monophasic reservoir fluid is available. Similar to oil A, the reservoir fluid is flashed to atmospheric conditions using PC-SAFT equation of state to calculate flashed gas and flashed liquid compositions. For oil C, on the basis of the composition presented in Table 12, the PC-SAFT parameters for pseudo-components C₆H₁₄ and C₇₊ are calculated from the correlations for saturates presented in Table 1 and correlations in Table 2, respectively. The aromaticity value for C₇₊ is adjusted to meet the live oil GOR reported in Table 11. The estimated value for GOR, using 0.32 as the aromaticity value of C₇₊, is 193.89 (m³/m³), which shows a reasonable agreement in comparison to the PVT data of 195.9 (m³/m³). Table 26 shows both flashed gas and flashed liquid compositions of monophasic oil C presented in Table 12.

Table 26. PC-SAFT Modeling Results for Flashed Gas and Flashed Liquid Compositions of the Monophasic Crude Oil C

components	flashed gas composition (mol %)	flashed liquid composition (mol %)
N ₂	0.48	0.00
CO ₂	4.47	0.34
C ₁	68.14	0.27
C ₂	9.62	0.34
C ₃	7.04	0.90
i-C ₄	1.87	0.53
n-C ₄	3.94	1.89
i-C ₅	1.57	1.77
n-C ₅	1.67	2.82
pseudo-C ₆ H ₁₄	1.20	6.00
C ₇₊	0.00	85.14

After characterization of crude oil C from the information of flashed gas and flashed liquid, Table 27 shows the components and their parameters. The aromaticity value for aromatics + resins is estimated to reproduce both experimental STO density and bubble point pressure of the original reservoir fluid. As mentioned in section 2, the PC-SAFT parameters for asphaltene are calculated from the correlations for aromatics + resins pseudo-component. The fitting parameters, aromaticity value and molecular weight for the asphaltene fraction, are estimated to the experimental upper onset pressure at 15 mol % of carbon dioxide injection.

Table 27. Characterized Crude Oil C as a Combination of Seven Components and Their PC-SAFT Parameters

component	M_w (g/mol)	composition (wt %)	σ (Å)	m	ε/k (K)
N_2	28.01	0.135	3.31	1.205	90.96
CO_2	44.01	1.983	2.78	2.073	169.21
C_1	16.04	11.022	3.70	0.999	150.03
heavy gas	47.20	12.761	3.63	2.120	206.86
saturates	164.77	45.423	3.89	5.079	249.41
aromatics + resins ($\gamma = 0.1$)	244.00	28.306	4.01	5.992	301.15
asphaltenes ($\gamma = 0.383$)	1700.00	0.370	4.28	31.092	373.04

4.3.2. Carbon Dioxide Injection Modeling Results. Figures 11 and 12 show the PC-SAFT observed asphaltene phase envelope for crude oil C.

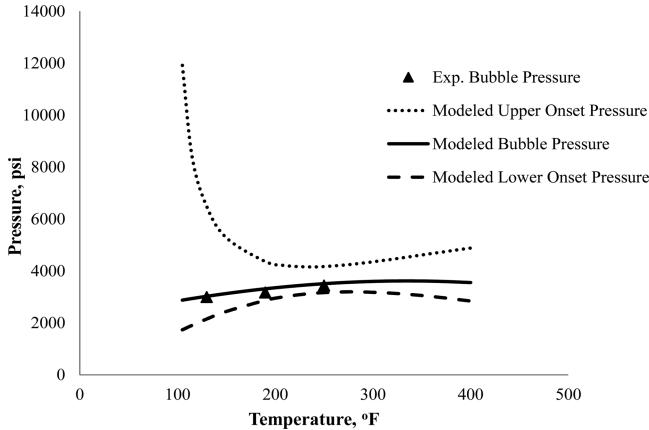


Figure 11. Asphaltene phase envelope for crude oil C generated by PC-SAFT.

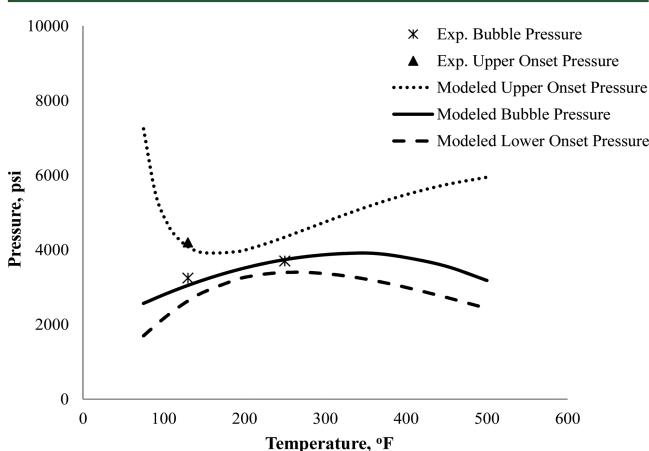


Figure 12. PC-SAFT generated asphaltene phase envelope for crude oil C under 15 mol % of carbon dioxide injection.

behavior for original reservoir fluid and when 15 mol % of pure carbon dioxide is injected into this reservoir fluid. Table 28

Table 28. Comparison of PC-SAFT Predicted Results without Factor “W” and Experimental Data for the Asphaltenes Content of Filtrate at Saturation Pressure in Oil C

injected CO_2 concentration (mol %)	T (°F)	experimental filtrate asphaltenes content (% w/w)	modeled filtrate asphaltenes content (% w/w)	error (%)
0	250	76.7	57.36	25.21
15	130	66.4	51.86	21.89
15	250	70.3	54.23	22.86

compares PC-SAFT model results and experimental data for the asphaltene content of filtrate at saturation pressure, for 0 and 15 mol % of injected carbon dioxide. It can be seen from Table 28 that PC-SAFT overpredicts the amount of precipitated asphaltene for HPHT carbon dioxide injection conditions in comparison to the experiment.

The same discussion as for oils A and B can be introduced for oil C with a factor “W”. For oil C with no external gas injected, “W” is found to be 0.0007, and for the same oil with 15 mol % carbon dioxide injection, “W” is 0.001. Factor “W” is estimated to match the experimental data for the precipitated asphaltene amount. For oil C, two different values for “W” are observed for two different cases. The reason is that “W” may have different values at different concentrations of injected gas as per the amount of asphaltenes precipitated (see Table 14). Table 29

Table 29. Comparison of PC-SAFT Predicted Results Using Factor “W” and Experimental Data for the Asphaltene Content of Filtrate at Saturation Pressure

injected CO_2 concentration (mol %)	T (°F)	experimental filtrate asphaltenes content (% w/w)	modeled filtrate asphaltenes content (% w/w)	error (%)
0	250	76.7	76.02	0.88
15	130	66.4	67.98	2.38
15	250	70.3	67.52	3.95

compares PC-SAFT predictions using factor “W” to experimental results of the filtrate asphaltene content, and it shows a good match when the factor “W” is used. Figure 13 shows the PC-SAFT predicted amount of precipitated asphaltene under pressure depletion conditions at reservoir temperature and different concentrations of carbon dioxide injected into oil C. It

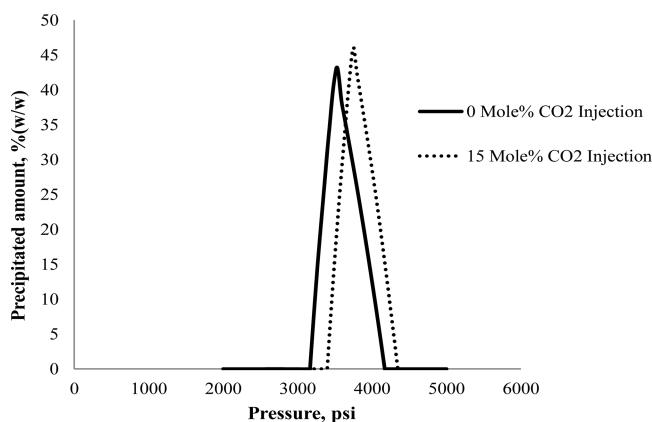


Figure 13. PC-SAFT predictions for the amount of precipitated asphaltene under pressure depletion conditions and at different concentrations of pure CO_2 injected into crude oil C.

can be seen that the maximum amount of precipitation occurs at the bubble point pressure.

4.3.3. Synthetic Gas Characterization Results. The PC-SAFT parameters of oil C, used for modeling of the carbon dioxide injection case, are also used to predict the asphaltene phase behavior under synthetic gas injection conditions. Table 13 shows the composition of producer gas, and the phase behavior results are presented in Table 15. To model this system, first the synthetic gas is characterized for gas injection. The gas contains nitrogen, carbon dioxide, hydrogen sulfide, methane, and one pseudo-component, heavy gas, which contains ethane and heavier hydrocarbons of the gas. The PC-SAFT parameters for this heavy gas pseudo-component, which is mostly composed of alkanes, are obtained from the correlation presented in Table 30. The same correlations are used for heavy gas pseudo-components throughout the paper. Table 31 shows the results of synthetic gas characterization.

Table 30. PC-SAFT Parameter Correlations for *n*-Alkanes⁹

alkane correlations used for heavy gas pseudo-component

$$m = 0.0253M_w + 0.9263$$

$$\sigma = (0.1037M_w + 2.7985)/m$$

$$\varepsilon/k = 32.81 \ln(M_w) + 80.398$$

Table 31. Characterized Synthetic Gas, Used for Gas Injection in Crude Oil C, as a Combination of Five Components and Their PC-SAFT Parameters

component	M_w (g/mol)	composition (wt %)	σ (Å)	m	ε/k (K)
N ₂	28.010	0.865	3.31	1.205	90.96
CO ₂	44.010	8.480	2.78	2.073	169.21
H ₂ S	34.080	2.965	3.07	1.652	227.34
C ₁	16.040	51.250	3.70	0.999	150.03
injected heavy gas	43.163	36.440	3.60	2.018	203.93

The same set of PC-SAFT parameters of oil C used for modeling of the carbon dioxide injection case are also used to predict the asphaltene phase behavior under synthetic gas injection conditions. The binary interaction parameter between asphaltenes and the injected heavy gas pseudo-component is slightly different from the value between asphaltenes and heavy gas to obtain a better match between experimental and modeling results for asphaltene phase behavior. Table 32 shows the binary interaction parameters used for oil C under both CO₂ and producer gas injection conditions. The binary interaction parameters for H₂S are from Panuganti et al., and for the other binary interaction parameters, the values presented by Gonzalez

are applied.^{3,20} To have a good estimate of the saturation pressure, the binary interaction parameters of methane–saturates and methane–aromatics + resins are slightly decreased from their original values. These parameters have a large effect on the saturation pressure, because of the high amount of methane present in the crude oil. For crude oil C and in the case of CO₂ injection, the asphaltenes–CO₂ binary interaction parameter has a large effect on the AOP and precipitated amount. The same result is observed in the case of produced gas injection and for the binary interaction parameters between asphaltenes and synthetic gas components.

4.3.4. Synthetic Gas Injection Modeling Results. A comparison of the equation of state predicted and the experimental data for saturation pressures as well as onset pressures is shown in Figures 14 and 15 for 15 and 45 mol % of

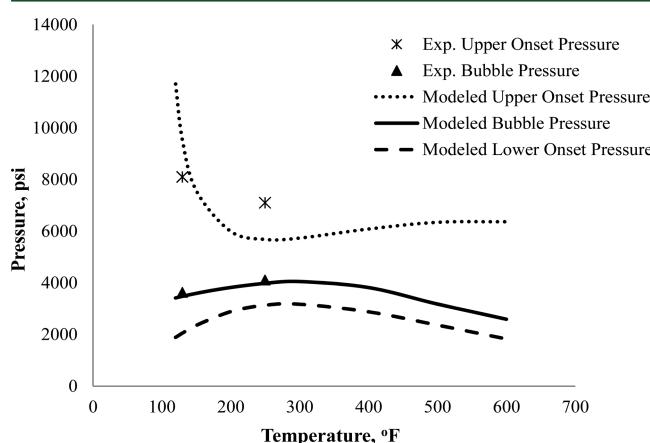


Figure 14. Asphaltene phase envelope for crude oil C with 15 mol % of producer gas injected.

injected synthetic gas, respectively. Figures 14 and 15 demonstrate the influence of injected synthetic gas on asphaltene phase behavior of oil C. Table 33 compares model results and experimental data for the asphaltene content of filtrate at saturation pressure, when 15 and 45 mol % of synthetic gas are injected into the monophasic reservoir fluid C. As observed from Table 33, there is no good match between modeled and experimental results for the filtrate asphaltene content. PC-SAFT constantly overpredicts the amount of precipitated asphaltene for HPHT gas injection conditions, especially for higher amounts of gas injected. When the injected gas amount increases from 15 to 45 mol %, PC-SAFT predictions show an intensive drop in the filtrate asphaltene content, while experimental data show a very small drop.

Table 32. Binary Interaction Parameters Used for PC-SAFT Modeling of Crude Oil C

component	N ₂	CO ₂	H ₂ S	methane	heavy gas	injected heavy gas	saturates	aromatics + resins	asphaltenes
N ₂	0								
CO ₂	0	0							
H ₂ S	0.09	0.0678	0						
methane	0.03	0.05	0.062	0					
heavy gas	0.06	0.10	0.07	0	0				
injected heavy gas	0.06	0.10	0.07	0	0	0			
saturates	0.12	0.13	0.09	0.021	0.01	0.01	0		
aromatics + resins	0.11	0.09	0.015	0.018	0.01	0.01	0.007	0	
asphaltenes	0.11	0.10	0.015	0.029	0.01	0.04	0.007	0	0

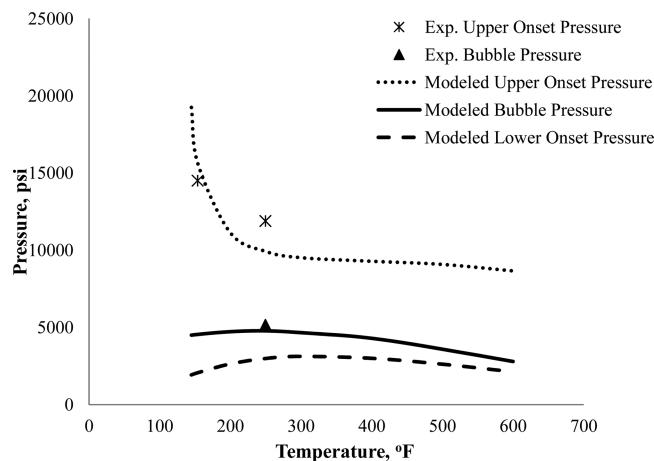


Figure 15. Asphaltene phase envelope for crude oil C with 45 mol % of producer gas injected.

Table 33. Comparison of PC-SAFT Predicted Results without Factor “W” and Experimental Data for the Asphaltene Content of Filtrate at Saturation Pressure

injected synthetic gas concentration (mol %)	T (°F)	experimental filtrate asphaltene content (% w/w)	modeled filtrate asphaltene content (% w/w)	error (%)
15	130	62.7	31.57	49.65
15	250	68.8	44.73	34.98
45	154	61.0	20.90	65.74
45	250	66.4	22.13	66.67

Figures 14 and 15 show that, for upper AOPs, both experimental and modeling results represent a large change when the concentration of injected gas changes from 15 to 45 mol %. It is correspondingly expected to reflect in the precipitated asphaltene amount. However, the experimental data show a very small change, while according to the PC-SAFT predictions, a large portion of the asphaltene content of crude oil C comes out of the oil at saturation pressure and 45 mol % of injected gas. Similar to the discussion for oil C under carbon dioxide injection, a factor “W” is introduced for oil C under synthetic gas injection. In this case “W” is 0.0022 for both 15 and 45 mol % of injected gas. Table 34 compares PC-SAFT

Table 34. Comparison of PC-SAFT Predicted Results Using Factor “W” and Experimental Data for the Filtrate Asphaltene Amount at Saturation Pressure

injected synthetic gas concentration (mol %)	T (°F)	experimental filtrate asphaltene content (% w/w)	modeled filtrate asphaltene content (% w/w)	error (%)
15	130	62.7	61.90	1.27
15	250	68.8	68.20	0.87
45	154	61.0	66.80	9.51
45	250	66.4	60.11	9.47

predictions using factor “W” to experimental results of the filtrate asphaltene content. It shows a good match when factor “W” is used. Figure 16 shows the PC-SAFT predicted amount of precipitated asphaltene under pressure depletion conditions at reservoir temperature and different concentrations of injected synthetic gas. The maximum amount of precipitation occurs at the bubble point pressure.

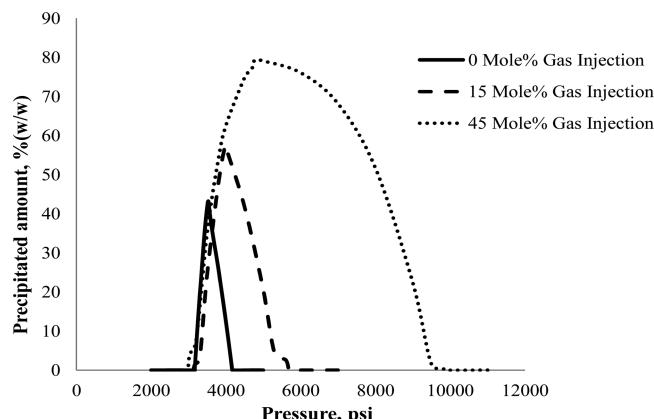


Figure 16. PC-SAFT predictions for the amount of precipitated asphaltene under pressure depletion conditions and at different concentrations of injected producer gas for crude oil C.

4.4. Miscellaneous. For oil A, there is a single point for asphaltene lower onset pressure that is matched well with modeling results (see Figure 2). There are no lower onset experimental data for oils B and C. However, modeling results predict a reasonable trend of asphaltene lower onset curve for oils B and C (see Figures 7 and 11). As per the PC-SAFT model, no asphaltene precipitation is expected at stock tank conditions for all oils A, B, and C.

No error bars are available for all of the experimental data used in this study, for either the precipitated amount or the AOPs. The only error that has been reported is for the amount of precipitated asphaltene, which is that the sum of the asphaltene amount passed through the filter, the amount retained by the filter paper, and the asphaltene in the PVT cell is not equal to the total asphaltene content of the crude oil sample. Refer to Tables 10 and 14 to see these uncertainties in the experimental precipitated amount.

There is no error bar information for the experimental data on the amount of precipitated asphaltene to see if the model prediction is within the reported error bars. However, we guess that the model is within the expected error in the data, because a small experimental error during the measurement of the precipitated asphaltene amount can result in a significant difference between modeled and experimental values. Also, it is very important to say that, in all cases, the difference between data and the model is in the direction that is consistent with the loss of material from the experiments. In other words, the model always overpredicts the amount of precipitated asphaltene for all cases presented in this study.

PC-SAFT modeling results appear to overpredict the amount of precipitated asphaltene at HPHT conditions obtained by the gravimetric technique or filtration method. We hope to see a very small difference between modeled and experimental results in the case of having new experimental data for the precipitated amount obtained from more extensive studies of asphaltene yields at different conditions, including benchtop tests, where the accuracy of the data is usually very good.

5. CONCLUSION

In PC-SAFT characterization of crude oil systems for which the experimental data of flashed gas and flashed liquid compositions are not available, the PC-SAFT equation of state can be used for flashing the monophasic reservoir fluid to atmospheric

conditions for obtaining the required data as per the procedure presented in this paper.

In this work, PC-SAFT equation of state is applied to model the phase stability of asphaltene in crude oils under pressure depletion and HPHT gas injection conditions. PC-SAFT modeling results show a good agreement with respect to experimental data for bubble pressure as well as upper and lower onset pressures of asphaltene precipitation. However, the same set of parameters used for saturation and onset pressure predictions do not show a good match for the amount of precipitated asphaltene. In modeling the precipitated amount, a reasonable prediction can be seen when a weight fraction factor, W , is used. " W " is a very small portion of the asphaltene-rich phase that is added to the asphaltene-lean phase during modeling and shows the possibility of small errors, which may happen in the experimental procedures for measuring the amount of precipitated asphaltene at HPHT conditions.

This study shows that, if a small experimental error happens during the filtration procedure or gravimetric method for measuring the amount of precipitated asphaltene, a significant difference can be seen between modeled and experimental results. We invite discussion on the possibility of such errors and suggestions of experimental procedures or a new experimental tool for measuring the amount of precipitated asphaltene at HPHT conditions.

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Notes

The authors declare no competing financial interest.

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