Dossier

This paper is a part of the hereunder thematic dossier published in OGST Journal, Vol. 70, No. 6, pp. 909-1132 and available online here

Cet article fait partie du dossier thématique ci-dessous publié dans la revue OGST, Vol. 70, n°6, pp. 909-1132 et téléchargeable ici

Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 70 (2015), No. 6, pp. 909-1132

ENHANCED OIL RECOVERY (EOR)

ASPHALTENES

HYDRATES

Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 70 (2015), No. 6, pp. 1075-1086
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DOI: 10.2516/ogst/2014037

Prediction of the Gas Injection Effect on the Asphaltene Phase Envelope

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Abstract *— Asphaltene instability may occur when pressure, temperature and compositional variations affect the reservoir oil. Permeability reduction, wettability alteration, and plugging of wells and flow lines are the consequences of this phenomenon. Therefore, it is crucial to investigate the asphaltene behavior in different thermodynamic conditions by knowing the Asphaltene Precipitation Envelope (APE) in a preventive way rather than the costly clean-up procedures. The selected reservoir oil has faced a remarkable decline in production due to several years of extraction, and Enhanced Oil Recovery (EOR) has been considered as a solution. Therefore, in this paper, a comprehensive study was carried out to predict the effects of different injected gases on asphaltene onset and to prevent future asphaltene precipitation based on the laboratory data. The Advanced Redlich-Kwong-Soave (RKSA) equation of state was considered to develop APE using Multiflash (*Infochem Co.*). For the selected reservoir oil, with temperature reduction at low temperatures, asphaltene precipitation weakened and made the onset pressure decrease, so this behavior is different from the results obtained in other published reports. On the basis of this model, several sensitivity analyses were performed with different gases (*i.e.*, methane, CO_2, N_2 and associated gases) to compare the risk of each gas for future EOR strategies. APE tend to expand as the amount of injected gases increases, except for CO_2 gas injection, that showed another unconventional behavior for this crude oil. It was observed that for CO_2 gas injection below a certain temperature, asphaltene stability increased, which can be considered as a good inhibitor of asphaltene precipitation.*

Résumé — Prévision de l'effet d'injection de gaz sur l'enveloppe de phase des asphaltènes — L'instabilité des asphaltènes peut se produire lorsque des variations de pression, de température et de composition affectent les réservoirs d'huile conduisant à une réduction de la perméabilité, à l'altération de la mouillabilité et au blocage de l'écoulement dans les puits et les conduites. Par conséquent, il est crucial d'étudier le comportement des asphaltènes pour différentes conditions thermodynamiques en connaissant leur domaine de précipitation (APE, *Asphaltene Precipitation Envelope*) de manière préventive pour limiter les opérations coûteuses de nettoyage. Le réservoir d'huile choisi pour cette étude a subi un déclin remarquable de sa production du fait de plusieurs années d'extraction et la récupération assistée (EOR, *Enhanced Oil Recovery*) a été considérée comme une solution prometteuse. Par conséquent, dans ce document, une étude détaillée basée sur des données de laboratoire est réalisée afin de prévoir les effets d'injection de différents gaz lors du début de la précipitation des asphaltènes et pour empêcher toute précipitation ultérieure. L'équation d'état avancée Redlich-Kwong-Soave (RKSA) a été considérée pour établir l'enveloppe APE en utilisant le logiciel Multiflash (*Infochem Co.*). Pour le réservoir de pétrole sélectionné, une réduction de la température diminua la précipitation d'asphaltènes et fit chuter la pression de départ. Ce comportement diffère des résultats précédemment publiés. De nombreuses analyses de sensibilité ont été réalisées pour différents gaz (méthane, CO_2, N_2 et gaz associé) dans le but de comparer le taux de risque de chaque gaz pour différentes stratégies de récupération EOR. Les enveloppes APE ont tendance à croître lorsque la quantité de gaz injecté augmente, sauf pour de l'injection de CO_2 qui a révélé un comportement non conventionnel avec ce pétrole brut. Il a été constaté qu'avec l'injection de CO_2, en-dessous d'une certaine température, la stabilité des asphaltènes augmentait, ce qui peut être considéré comme un bon système d'inhibition de la précipitation des asphaltènes.

INTRODUCTION

Asphaltene deposition in near-wellbore formations, production tubing and surface facilities can occur upon pressure, temperature and composition variations. The latter may happen when reservoir oil blends with various gases during enhanced oil recovery (CO_2, N_2, dry and enriched gas injection), gas lift and acid stimulation. The effects of different gases on asphaltene stability have previously been studied in various fluids. Experimental investigation of asphaltene aggregation due to N_2 injection showed asphaltene particles tend to precipitate as the amount of injected N_2 increases (Jamaluddin *et al.*, 2002), and other gases such as CO_2, methane and propane could increase the asphaltene instability (Vafaie-Sefti *et al.*, 2003). In addition to the fact that these parameters affect asphaltene stability, they could also change the Asphaltene Precipitation Envelope (APE). Observations showed that as the temperature increases, the onset pressure decreases (Andersen, 1994), whereas it might cause an increase at onset pressure in some cases (Gonzalez *et al.*, 2012). Some authors reported that CO_2 gas injection increases the Asphaltene Onset Pressure (AOP) at any temperature (Novosad and Costain, 1990; Srivastava and Huang, 1997; Takahashi *et al.*, 2003; Vazquez and Mansoori, 2000), while other studies found that at some temperatures asphaltene particles could be more stable (Gonzalez *et al.*, 2007). An oil production system can also experience a significant temperature change from the reservoir to the separator. This effect is even more significant in production of deep-sea reservoirs where seafloor temperatures are about 4°C. The consequences generally include changes in reservoir wettability, formation damage, downhole facility plugging and finally, affect the Enhanced Oil Recovery (EOR) project due to unfavorable economic consequences such as production delays and costly clean-up procedures (Akbarzadeh *et al.*, 2007; Creek, 2005; Escobedo and Mansoori, 1997; Mansoori *et al.*, 2007; Zekri *et al.*, 2007).

The reservoir under study faced asphaltene deposition problems during early production of oil and the problem has become even more severe with further production. The producing interval is in the range of 2 692-2 725 m and the oil is transferred to an operation plant near the well site. After the first appearance of asphaltene deposition in surface facilities, a comprehensive study was performed in the laboratory to evaluate the AOP and contents of Saturates, Aromatics, Resins and Asphaltenes (SARA). In order to maintain the reservoir pressure and also prevent more asphaltene deposition and further problems in the future, it is necessary to investigate different strategies to predict asphaltene precipitation behavior. The amount of gas that can be dissolved in the oil before the asphaltene precipitation is an important parameter to consider in the design of the optimal gas injection scheme. The prediction of the phase behavior of asphaltene is essential in the design of well completion and/or surface facilities.

Although experimental determination of the full set of thermodynamic conditions in which asphaltenes begin to flocculate might be desirable for each specific crude oil, the cost of such a detailed characterization is prohibitive. An alternative is to obtain a minimum amount of laboratory data and incorporate that information into a thermodynamic model to predict the onset pressure over a wide range of conditions. To mimic experimental observations, current thermodynamic models generally require the use of many adjustable parameters, some of which cannot be verified experimentally (Leontaritis and Mansoori, 1987; Nghiem *et al.*, 1993; Pan and Firoozabadi, 1998).

One of the first effective models for asphaltene flocculation was a colloidal model that recognized asphaltene particles in crude oil as a colloid (Hirschberg *et al.*, 1984). They treated the oil phase as a homogeneous liquid and modeled flocculation as a new phase of pure asphaltene. In some models, a solid phase was formed when flocculation occurred (Chung, 1992). Both approaches could result in a model that requires too many adjustable parameters and was very sensitive to small changes in parameter values. This means that the model must be refitted to a large quantity of experimental data for each fluid. Leontaritis and Mansoori (1987) proposed a thermodynamic colloidal model that is able to predict the onset of asphaltene flocculation. According to this model, asphaltene solid particles are stabilized by resin on their surface in a colloidal suspension system, and the state of crude oil and molecular weight of asphaltene can be determined by this model. Single-component solid model is one of the simplest models for asphaltene precipitation that was proposed by Nghiem *et al.* (1993), who used the model along with a flash calculation procedure for vapor/liquid/asphalt systems to predict asphaltene precipitation data under pressure depletion, gas or solvent injection conditions. They discovered that the model could not depict the true behavior of asphaltene precipitation with increasing solvent concentration under gas/solvent injection conditions. The micellization model of asphaltene precipitation is another model and it is assumed that one of the key factors in asphaltene deposition is micelle formation (Victorov and Firoozabadi, 1996). This model has shown good agreement with most experimentally observed results. However, this model could not predict asphaltene behavior under gas titration conditions. Later, another model was proposed to understand asphaltene precipitation with a detailed molecular-thermodynamic framework (Wu *et al.*, 2000). This model considered strong interactions between asphaltene and resin molecules and between asphaltene molecules using the SAFT association theory, where asphaltene precipitation is treated as a liquid-liquid equilibrium with the oil. An effective model that describes solid deposition allows the engineer to carry out a variety of tasks from screening for potential problems through to examination of possible remediation strategies. In this work, the Multiflash commercial software was used for predicting the APE based on the RKSA Equation Of State (EOS). The purpose of this paper is to investigate the AOP for a live oil during pressure reduction, blending with different gases and to demonstrate the future strategies for the selected reservoir.

1 CHARACTERIZATION METHODOLOGY

Asphaltenes may destabilize, and precipitate out of the reservoir fluid when subjected to pressure, temperature or compositional changes. It was used screening criteria to investigate the tendency of asphaltenes particles to precipitate. The crude oil under study was a 20.32 °API fluid with the characteristics shown in Table 1, and the total content of asphaltene was 12.8 wt%.

TABLE 1

Reservoir fluid characterization

Reservoir temperature (°C)	96.1
Reservoir pressure (MPa)	30.82
Bubble point pressure (MPa)	9.87
Gas/oil ratio (m^3/m^3)	56.81
Oil API gravity (deg)	20.32
Molecular weight of residual oil	269
Molecular weight of reservoir oil	169
SARA contents (ASTM D4124-97)	
Saturates (wt%)	24.8
Aromatics (wt%)	45.6
Resins (wt%)	16.8
Asphaltenes (wt%)	12.8

The data required for the screening were PVT properties including the oil density at the bubble point pressure, the reservoir pressure, and the SARA contents of the Stock-Tank Oil (STO). Three plots are used for the screening; namely, the de Boer plot, the Asphaltene-Resin ratio and the ratio of Saturate/Aromatic (S/A) to Asphaltene/Resin (A/R). The preliminary screening was conducted on the selected sample. The de Boer plot was developed based on field observations (de Boer *et al.*, 1995), Figure 1 indicates that the reservoir fluid is in a moderate problem region. Moreover, the Asphaltene-Resin ratio screening method (Jamaluddin *et al.*, 2001), suggests that the asphaltenes are unstable in the given fluid (Fig. 2). The last criterion demonstrated in Figure 3 also shows the reservoir fluid is in unstable zone (Stankiewicz *et al.*, 2002). Thus, the results from the stability screening suggested that there may be potential for asphaltene problems in reservoir conditions. Hence, detailed measurements were conducted to determine the onset of asphaltene destabilization at various temperatures.

The reservoir fluid was flashed from reservoir conditions to ambient conditions to measure the Gas-Oil Ratio (GOR). Thus, it was anticipated that the STO would keep all the solids present in the reservoir fluid.

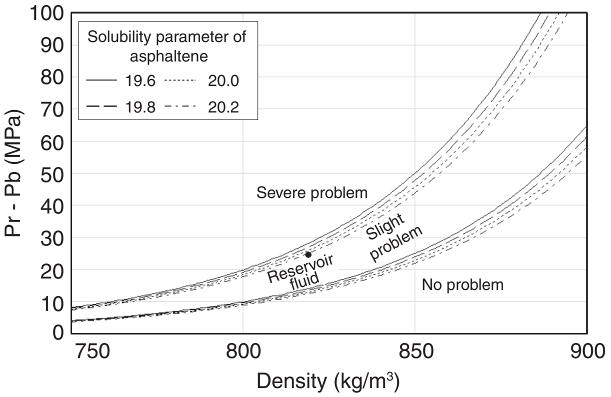

Figure 1

De Boer plot for reservoir sample.

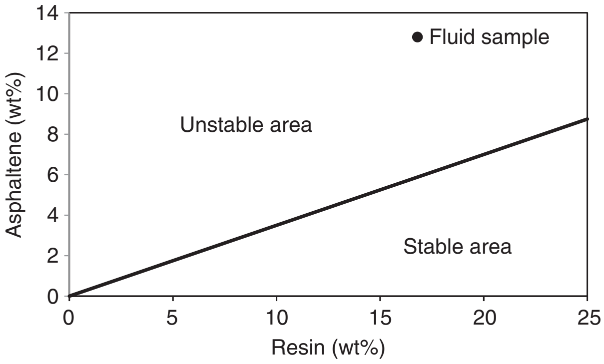

Figure 2

Asphaltene *vs* resin for reservoir sample.

TABLE 2

Reservoir fluid composition

Components	MW (g/mol)	Density (g/cm^3)	STO		Flashed gas		Monophasic fluid	
			(mol%)	(wt%)	(mol%)	(wt%)	(mol%)	(wt%)
N_2	28.04	0.809	0	0	0.91	0.792	0.39	0.065
CO_2	44.01	0.817	0	0	4.10	5.603	1.74	0.458
C1	16.04	0.300	0	0	48.38	24.094	20.55	1.97
C2	30.07	0.356	0	0	17.22	16.078	7.31	1.314
C3	44.1	0.508	0.10	0.016	12.43	17.02	5.34	1.409
i-C4	58.12	0.567	0.13	0.029	2.17	3.917	1.00	0.347
n-C4	58.12	0.586	1.67	0.364	6.34	11.441	3.65	1.269
i-C5	72.15	0.625	3.85	1.041	2.10	4.704	3.10	1.337
n-C5	72.15	0.631	6.44	1.741	2.45	5.489	4.75	2.049
C6	84	0.690	7.73	2.432	2.44	6.364	5.48	2.753
C7	96	0.727	4.82	1.733	1.07	3.189	3.23	1.853
C8	107	0.749	2.03	0.813	0.36	1.197	1.32	0.844
C9	121	0.768	3.93	1.781	0.03	0.112	2.27	1.642
C10	134	0.782	3.80	1.907	0	0	2.19	1.754
C11	147	0.793	3.15	1.734	0	0	1.81	1.59
C12+	370	0.9769	62.35	86.409	0	0	35.87	79.346
Total			100	100	100	100	100	100

Also, the flashed gas and STO were used to measure their molecular composition using gas chromatography and microdistillation, respectively. These compositions were then recombined numerically to obtain the reservoir fluid composition using the measured GOR. In addition, the molecular weight and density of the STO were measured. After measuring the density and the molecular weight of the STO, these properties can be calculated for the plus fraction. The measured and calculated data for modeling purposes are presented in Table 2. It has

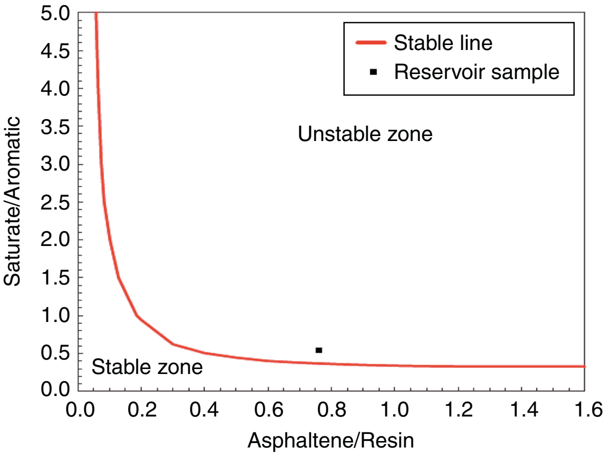

Figure 3

Saturate/Aromatic *vs* Asphaltene/Resin plot for reservoir sample.

been observed that the light components in the oil affect both the bubble pressure and AOP significantly (Gonzalez *et al.*, 2005). Additionally, gas injection typically used for EOR purposes is generally rich in lighter hydrocarbons, and therefore the methodology proposed in the present work will enable good predictions for this type of injection.

2 PRESSURE DEPLETION AND GAS INJECTION EXPERIMENTS

A filtration method was used to measure the asphaltene content in natural depletion and gas injection tests. The reservoir fluid was transferred into the PVT cell to apply the desired pressure and temperature in contact with different ratios of gases. A 0.5-micron metal filter made by the *Swagelok* company was used during the experiments. After the reservoir oil is stabilized in the PVT cell (in the pressure depletion scenario and/or in the gas injection scenario), the fluid passes through the filter during sampling at each stage. All asphaltene particles bigger than 0.5 microns do not pass through the filter, and the asphaltene content of the filtered fluid was determined by the IP-143 method (ASTM D6560-00, 2000). Finally, the differences between the asphaltene content of the original reservoir oil and the filtered samples can determine the amount of deposited asphaltene at each step. The asphaltene that this technique gives is physically extracted from oil, and by using some other techniques such as SARA analysis and molecular weight measurement, it can be further studied. The asphaltene onset points at different temperatures were achieved by extrapolation on asphaltene wt% *versus* the pressure plot by using the Peng-Robinson (PR) EOS (Nghiem *et al.*, 1993; Nghiem and Coombe, 1997), and are summarized in Table 3. Figure 4 is an example of achieving the asphaltene onset pressure at 80°C.

TABLE 3

Upper onset points at different temperatures

Temperature (°C)	96.1	80	60
Upper onset point (MPa)	32.34	34.96	31.36

3 MODELING OF ASPHALTENE PRECIPITATION

In this work, the plus fraction splits into pseudocomponents with different ranges of molecular weight, and single carbon cuts can also be grouped into pseudocomponents (Whitson, 1983). The molecular weight and specific gravity of each component can be obtained by correlation (Riazi and Al-Sahhaf, 1996), and they are adjusted to match the measured values for the whole liquid sample. The mole fraction of each component is obtained by converting the weight fraction using the molecular weight. Then the mole fraction of the monophasic fluid can be calculated. The critical properties and acentric factors of each single carbon cut and pseudocomponents can be predicted by correlations (Kesler and Lee, 1976).

Here, the experimental results are used in the commercial software Multiflash to generate and estimate APE. The models that have been proposed in the past half century have some limitations. Poor prediction of the liquid phase density, lack of asphaltene-asphaltene and asphaltene-resin interactions, and a comprehensive correlation for vapor pressure of polar compounds are some common problems in these models (Edmonds *et al.*, 1999a, 1999b).

The RKSA EOS is able to predict the properties of non-polar molecules in the vapor phase, and it is given by Equation (1) (Soave, 1972):

$$P = \frac{NRT}{V-b} + \frac{a}{V(V+b)} \tag{1}$$

$$a = \sum_{ij} \sqrt{a_i a_j}(1-K_{ij})n_i n_j \tag{2}$$

$$b = \sum_{i} b_i n_i \tag{3}$$

$$a_i = a_{ci}\left(1+\kappa_i\left(1-\sqrt{T/T_{ci}}\right)\right)^2 \tag{4}$$

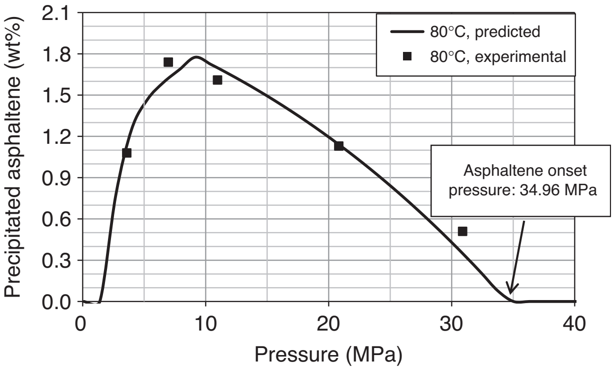

Figure 4

Precipitated asphaltene wt% in natural depletion at 80°C.

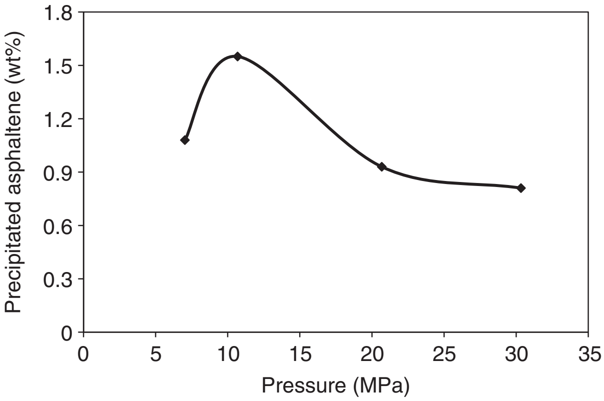

Figure 5

Experimental amount of asphaltene precipitation for reservoir oil at the reservoir temperature during a natural depletion test.

$$a_{ci} = 0.42748\frac{R^2T_{ci}^2}{P_{ci}} \tag{5}$$

$$\kappa_i = c_0 + c_1\omega_i - c_2\omega_i^2 \tag{6}$$

$$b_i = 0.08664\frac{RT_{ci}}{P_{ci}} \tag{7}$$

where $n_{i,j}$ are the molar fractions of components, ω is the acentric factor, P_{ci} and T_{ci} are the critical pressure and temperature, R is the gas constant, and K_{ij} is the binary interaction between components i and j. Equation (6) is a correlation for vapor pressure and c_0, c_1 and c_2 were determined based on vapor pressure data. Poor prediction of vapor pressure correlation at low temperatures, large errors in calculating liquid density and large density deviation at the critical point are some problematic issues in this model.

Pedrosa *et al.* (2013) applied some modifications to the EOS and presented the RKSA EOS to eliminate these issues. For an improved phase behavior prediction, K_{ij} coefficients are fitted to vapor pressure data from the triple point to the critical point for each component. Furthermore, for a better prediction of liquid volume and density, Equation (8) is used (Peneloux *et al.*, 1982).

$$V = V^{\text{RKS}} - \sum c_i n_i \tag{8}$$

where c_i is the temperature-dependent volume shift parameter, and it is fitted to the experimental saturation liquid density. The association and solvation of asphaltene molecules are described by the RKSA cubic EOS. In this model, asphaltene-asphaltene and asphaltene-resin interaction coefficients (K_{AA} and K_{AR}), the temperature-dependent association constants, are used to characterize the interactions between asphaltenes and asphaltene-resin particles (Zhang *et al.*, 2012). This model is a computationally efficient way of considering the complex compounds and it is appropriate for engineering studies.

4 RESULTS AND DISCUSSIONS

4.1 Effect of Pressure and Temperature

The asphaltene phase behavior during a natural depletion test at the reservoir temperature is demonstrated in Figure 5, based on the filtration method (Nakhli *et al.*, 2011). Figure 6 also shows the experimental oil density and calculated solubility parameter at different pressures. In this figure, the solubility is calculated based on the Asphaltene Instability Trend (ASIST) (Wang *et al.*, 2006). As the pressure drops from the reservoir pressure to the bubble point pressure, the density and solubility parameters of the oil will decrease and it makes the asphaltene less stable. Further reduction in pressure below the bubble point pressure causes the solution gas to evolve from the liquid and as a result, the oil becomes richer in heavy-end components. Therefore, the density and solubility parameters of the oil increase and again the oil becomes a better solvent for precipitated asphaltene. The calculated solubility parameter of the oil supports this speculation. The minimum amount of solubility and oil phase density occurs at the bubble

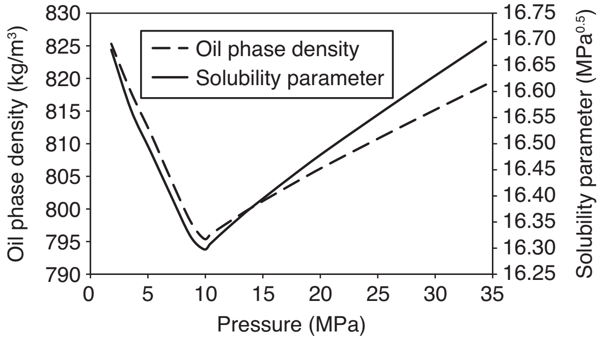

Figure 6

Calculated oil phase density and solubility parameters during a natural depletion test at the reservoir temperature.

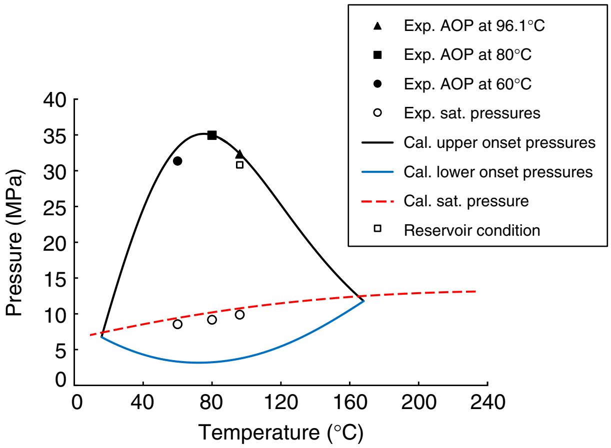

Figure 7

Asphaltene precipitation envelope for reservoir sample.

point pressure where the asphaltene precipitation reaches its maximum.

When the pressure of the reservoir fluid drops at a specified temperature, the asphaltene is in the liquid phase region as the pressure is higher than the upper onset point of precipitation and there is no appearance of asphaltene flocculation. Asphaltene instability occurs when the pressure is between the upper onset and bubble point and between the bubble point and lower onset. The fluid is in oil-asphaltene two-phase and gas-oil-asphaltene three-phase equilibrium respectively. As the reservoir fluid depressurizes below the lower onset point, the asphaltene particles redissolve completely in the liquid phase and the fluid is in the gas-oil two-phase region (Panuganti *et al.*, 2012). Figure 7 presents the APE for the reservoir fluid with the plots of the bubble point and upper and lower onset pressures as a function of temperature and as can be clearly seen, there is good agreement between the calculated and experimental results. The oil is originally unstable, probably due to its initial high content of light components, which has a strong effect on asphaltene stability.

Asphaltenes are polar compounds which are stabilized in crude oil by the presence of resins. When the oil is diluted by light hydrocarbons, the concentration of resins decreases and a point may be reached where the asphaltenes are no longer stabilized. At this point, the asphaltene particles start to grow in size, and finally they flocculate and form a deposit. Since resins, as asphaltene stabilizers, work through the mechanism of polar interactions, their effect becomes weaker as the temperature rises, *i.e.* flocculation will occur as the temperature increases. Also, a decrease in the density of the fluid is another reason for asphaltene precipitation. However, at a specified temperature, the solution entropy increases and the asphaltene melts and redissolves in the oil as the temperature increases. It causes a counterbalancing effect, and make the asphaltene precipitation either stronger or weaker when the temperature increases (Ting, 2003); while in other work, it was proposed that an increase in temperature will redissolve asphaltene particles (Hassanvand *et al.*, 2012; Verdier *et al.*, 2006). When the temperature is below 73.9°C, the density of the oil decreases and causes asphaltene particles to flocculate as the temperature increases, and above this temperature the redissolution phenomenon is stronger. According to Figure 7, the temperature plays a more significant role in the upper onset pressure than lower onset pressure. At higher pressures the fluid non-ideality is stronger than at lower pressures, and non-ideality relates to interaction between molecules. At high pressures, molecules have lower mobility, but an increase in temperature changes the mobility significantly. However, at low pressure the non-ideality is weak and the fluid mobility is higher, therefore temperature plays a less important role. That is why at higher pressures and temperatures the change in the upper onset is greater than in the lower onset.

4.2 Effect of Gas Injection

Based on the model in the natural depletion test, the effect of different light gases was observed on the onset of the asphaltene precipitation. The possibility of asphaltene flocculation increases when light gases are exposed to the oil during miscible gas flooding processes.

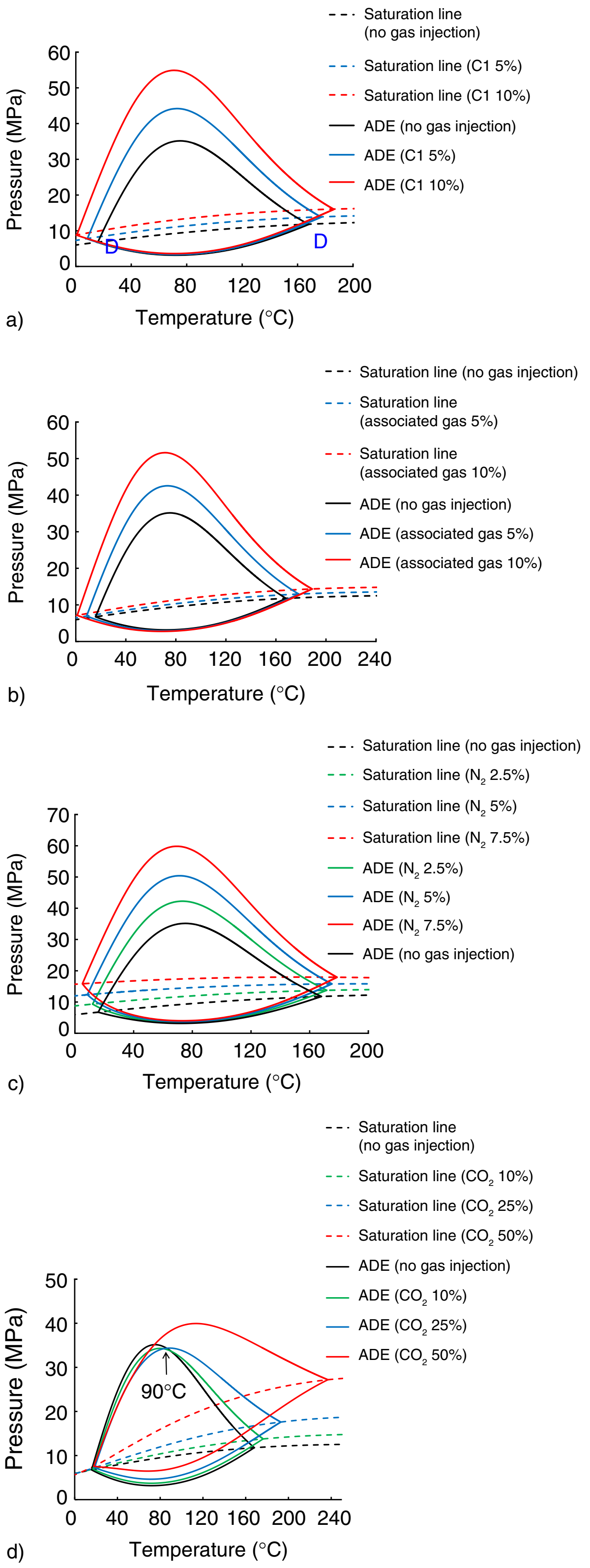

Figure 8

Effect of a) methane, b) associated gas, c) N_2, d) CO_2 on the APE.

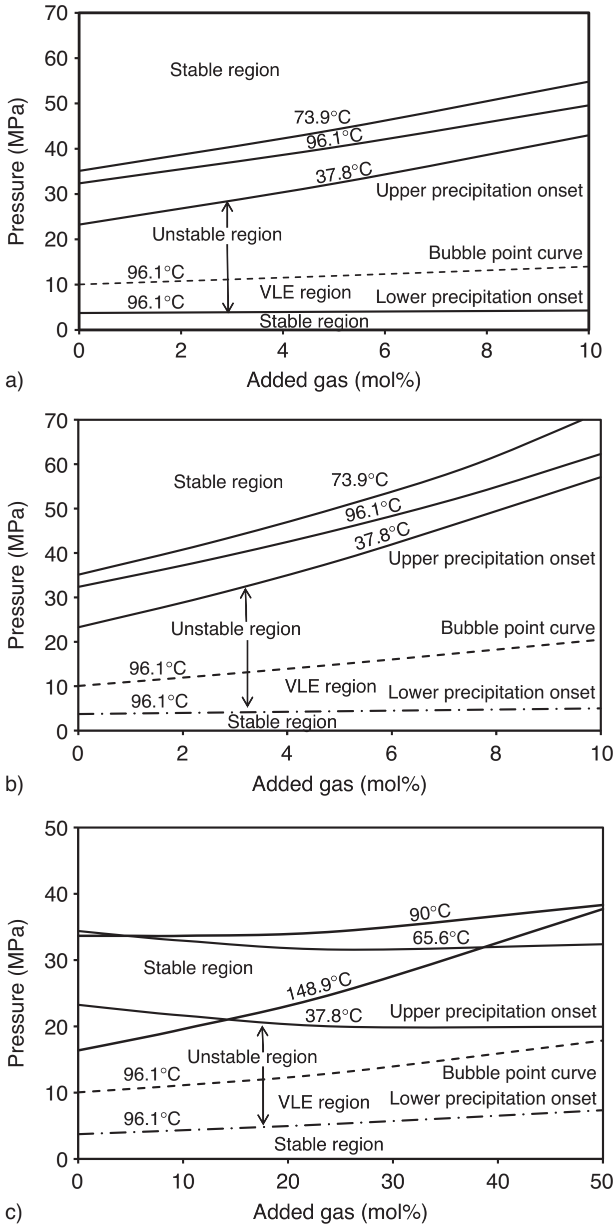

Figure 9

Temperature effect on asphaltene precipitation onset after the addition of a) methane, b) N_2, c) CO_2.

The bubble point curves and the asphaltene stability boundary increase when different compositions of methane, associated gas and N_2 are added to the original fluid, as shown in Figures 8a to 8c. A different behavior is observed upon the addition of CO_2. As shown in Figure 8d, for a known amount of injected CO_2, below a specific crossover temperature, the stability of asphaltene improves (*e.g.*, at 10 mol% of injected gas, the crossover temperature is about 90°C).

TABLE 4

Summary of composition for original fluid and mixtures

	Reservoir fluid	Mixture of reservoir fluid and associated gas			Injected gas
Injected gas added (mol%)	0	10	25	50	100
Component (mol%)					
N_2	0.39	0.442	0.520	0.650	0.91
CO_2	1.74	1.976	2.330	2.920	4.10
C1	20.55	23.333	27.508	34.465	48.38
C2	7.31	8.301	9.787	12.265	17.22
C3	5.34	6.049	7.113	8.885	12.43
i-C4	1.00	1.117	1.292	1.585	2.17
n-C4	3.65	3.919	4.323	4.995	6.34
i-C5	3.10	3.000	2.850	2.600	2.10
n-C5	4.75	4.520	4.175	3.600	2.45
C6	5.48	5.176	4.720	3.960	2.44
C7	3.23	3.014	2.690	2.150	1.07
C8	1.32	1.224	1.080	0.840	0.36
C9	2.27	2.046	1.710	1.150	0.03
C10	2.19	1.971	1.642	1.095	0
C11	1.81	1.629	1.358	0.905	0
C12+	35.87	32.283	26.902	17.935	0
Total	100	100	100	100	100

This behavior can be explained by the solubility parameter of CO_2. At temperatures below the crossover point, the solubility parameter of reservoir oil is lower than the solubility parameter of CO_2, so the probability of asphaltene precipitation in original oil is stronger than the CO_2-induced asphaltene. This phenomenon is in agreement with the one that Gonzalez *et al.* (2007) proved based on the PC-SAFT model. Above the crossover temperature, the asphaltene solubility decreases and the onset pressure increases at higher temperatures. The increase in the amount of gas at different temperatures was also calculated, as shown in Figure 9. The onset pressure of the mixture increases at any temperature when methane, N_2 and associated gases are added, which is why the upper onset curves in Figure 9 always have positive slopes. This behavior is completely different for CO_2. At temperatures below the crossover point, the CO_2 acts as an inhibitor and the upper onset curves have negative or zero slopes, whereas at temperatures above this point, it acts as a strong asphaltene precipitant and therefore the upper onset curves are ascending. The slope variation in the precipitation onset curves above and below the crossover point supports the specific behavior of the CO_2.

This gas can behave as an inhibitor or precursor of asphaltene precipitation, depending upon the temperature of the system for a fixed pressure and live oil composition. This dual effect is not observed with other gases, such as N_2 or methane, which always expand the ADE. Table 4 summarizes the fluid compositions at different mole percentages of associated gas based on the RKSA model.

Figure 10, that was calculated by Verdier in 2006, shows the solubility parameters of N_2, methane and CO_2 *versus* pressure, and among these gases N_2 has the lowest solubility. In a wide range of temperatures, different amounts of N_2 increase the upper onset pressures more than different percentages of methane and CO_2;

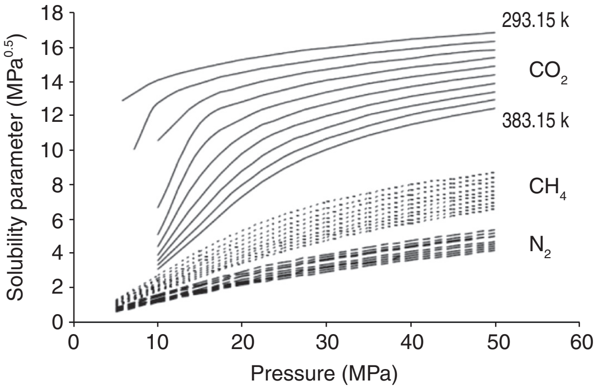

Figure 10

Solubility parameters of N_2, methane and CO_2 calculated every 10 K, starting at 293.15 K for the top curves by Verdier (2006).

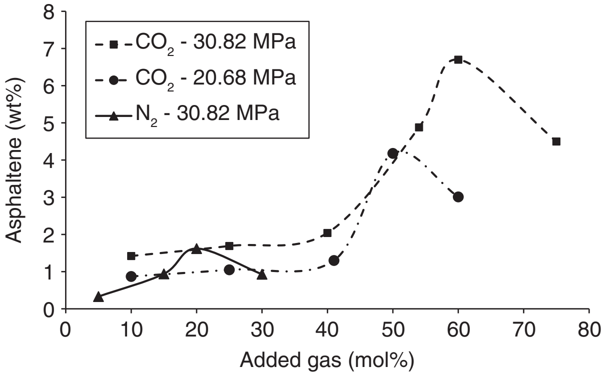

Figure 11

Experimental asphaltene precipitation due to CO_2 and N_2 gas injection at the reservoir temperature.

however, CO_2 is a stronger precipitant agent at a specified temperature and leads to a higher content of asphaltene to precipitate.

Figure 11 proves this behavior of CO_2 and N_2 based on experimental results. CO_2 and N_2 gas injection tests were carried out at different mole percentages. By adding more gas into the system, the saturation pressure of the mixture increases. Therefore, at each pressure point, the asphaltene precipitation will increase, as the saturation pressure is below the test pressure. This means that before the mixture reaches the saturation pressure, all injected gases mix with the oil and the density of the mixture decreases. Based on the solubility theory the asphaltene precipitation increases when density decreases. When the operating pressure is lower than the saturation pressure, the gas does not mix with the fluid, and some light components of the oil can travel to the mixture.

The result of this phenomenon is asphaltene dissolution and an increase in the density of the oil. For a specified amount of gas injection, N_2 increases the saturation pressure more than CO_2, and it reaches its maximum content at lower percentages of injected gas compared with CO_2. It is worth mentioning that if the results obtained here are confirmed by other authors, they need to be verified.

CONCLUSION

The general results are summarized as follows:

1. Depending on a counterbalancing effect of density and solution entropy, the temperature can cause an increase or a decrease in the amount of asphaltene precipitation;
2. Although temperature has a slight effect on the lower onset of asphaltene precipitation and the bubble point, the temperature can lead to a big change in the upper onset of asphaltene precipitation;
3. APE were gradually shifted to the high-pressure side and expanded as C1, N_2 and associated gas content increased. This phenomenon is stronger for N_2;
4. The shape of APE are similar to the original reservoir oil APE;
5. CO_2 injection causes asphaltene precipitation to increase at high temperatures but below a certain crossover, the asphaltene stability increases. Therefore, CO_2 can behave as an inhibitor or precursor of asphaltene precipitation;
6. The APE was gradually expanded to a wide range of pressures and temperatures in a CO_2 injection scenario, while the increase in the onset pressure was more significant in other gas injections;
7. Although at the same mol% of N_2 and CO_2 injection, the APE expands more with N_2 injection; CO_2 is a strong precipitant agent at a specified temperature, which leads to a higher content of asphaltene to precipitate.

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Manuscript submitted in January 2014
Manuscript accepted in August 2014

Cite this article as: P. Bahrami, R. Kharrat, S. Mahdavi and H. Firoozinia (2014). Prediction of the Gas Injection Effect on the Asphaltene Phase Envelope, *Oil Gas Sci. Technol* **70**, 6, 1075-1086.