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INVESTIGATION OF ASPHALTENE PRECIPITATION IN MISCIBLE GAS INJECTION PROCESSES: EXPERIMENTAL STUDY AND MODELING

S. Moradi^{1*}, M. Dabiri², B. Dabir³, D. Rashtchian⁴ and M. A. Emadi⁵

 ¹Petroleum University of Technology, Iran.
 *E-mail: moradi.s@put.ac.ir
 ²National Iranian South Oil Company, Iran. E-mail: mehdidabiri@yahoo.com
 ³Amirkabir University of Technology, Iran. E-mail: drbdabir@aut.ac.ir
 ⁴Sharif University of Technology, Iran. E-mail: rashtchian@sharif.ir
 ⁵National Iranian Oil Company, Iran. E-mail: ema2di@yahoo.com

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Abstract - Asphaltene precipitation during natural depletion and miscible gas injection is a common problem in oilfields throughout the world. In this work, static precipitation tests are conducted to investigate the effects of pressure, temperature and gas type and concentration on asphaltene instability. Three different oil samples have been studied under reservoir conditions with/without nitrogen and methane injection. Besides applying common thermodynamic models, a new scaling equation is presented to predict asphaltene precipitation under HPHT gas injection. Extensive published data from the literature are also used in model development. The scaling approach is attractive because it is simple and complex asphaltene properties are not involved in the calculations. Moreover, the proposed model provides universal parameters for different fluid samples over a wide range of pressure and temperature that makes it novel for evaluation of future gas injection projects when simple PVT data are available.

Keywords: Nitrogen injection; Asphaltene precipitation; Pure solid modeling; Scaling equation.

INTRODUCTION

Miscible/partially miscible gas injection is a promising enhanced oil recovery technique for many reservoirs (Huang *et al.*, 1993). It is well known that the injection of CO₂, N₂ and hydrocarbon gases changes the solubility of heavy components in the reservoir oil and causes asphaltene instability (Yang *et al.*, 1999; Srivastava *et al.*, 1999; Jamaluddin *et al.*, 2002; Takahashi *et al.*, 2003; Hu *et al.*, 2004; Negahban *et al.*, 2005; Verdier, 2006; Dehghani *et al.*, 2008).

Hirschberg *et al.* (1988) applied polymer solution theory to develop a solubility model for asphaltene precipitation. In this approach, asphaltene was treated as a heavy liquid and phase behavior calculations were performed for gas-oil and oilasphaltene systems. The model was later modified to account for asphaltene polydispersity (Monteagudo *et al.*, 2001). Yang *et al.* (1999) proposed a modified Hirschberg model and defined the asphaltene solubility parameter as a function of specific gravity, molecular weight and boiling point. Vafaie-Sefti

^{*}To whom correspondence should be addressed

et al. (2006) and Mousavi-Dehghani et al. (2008) incorporated association terms in the Peng-Robinson equation of state. Simple association factors were obtained from the molecular weight distribution (fractional molecular weight) and average asphaltene molecular weight. However, this model includes more uncertain matching parameters compared to previous attempts. Pazuki et al. (2006) defined an interaction parameter between polymer and solvent and correlated it to the molecular weights of the solution and asphaltene. Later, they applied perturbation theory and proposed a new equation of state to study phase behavior of crude oil and asphaltene (2007). In more recent efforts, Gonzalez et al. (2005, 2008) also applied a thermodynamic liquid-liquid phase approach with the perturbed chain-statistical associating fluid theory (PC-SAFT) equation of state. This thermodynamic model was verified with experimental data for methane, ethane, and N₂ with quite good results. Vargas et al. (2009, 2010) further improved this model to make it applicable to more working criteria with better predictions.

Leontaritis and Mansoori (1987) presented a colloidal model by applying statistical thermodynamics. They defined a critical resin concentration (CRC) to estimate the critical chemical potential of resins. According to this approach, asphaltene precipitation will occur if the chemical potential of resins in the mixture is less than the critical value. Escobedo and Mansoori (1994) concluded that this model is accurate for determination of the onset of asphaltene precipitation but does not quantify the precipitates. Later, Wang *et al.* (2001) mentioned some experimental evidences against this model.

Pan and Firoozabadi (1998, 2000) proposed a thermodynamic micellization model that describes asphaltene precipitation by minimizing the total free Gibbs energy of the system (including asphaltene monomers and micelles). Although their model considers the colloidal nature of oil, it must be optimized to include the effect of resins and precipitants successfully.

Nghiem *et al.* (1997) developed a pure solid model based on their previous work on three-phase equilibrium calculations of gas, liquid and solid under isothermal conditions (Nghiem and Li, 1984). The effects of pressure and temperature on asphaltene precipitation were later introduced in the model by Kohse *et al.* (2000).

The solubility, colloidal and micellization models are based on activity coefficients, whereas the solid model is based on fugacities. In the activity coefficient approach, a two-phase oil-gas flash calculation is first performed to split the mixture into oil and gas phases. The oil phase is then divided into different sets of components for modeling asphaltene precipitation. This approach ignores the effects of asphaltene precipitation on the oil and gas phase equilibrium and may introduce errors in the phase behavior calculations since heavy components such as asphaltene have an important effect on the saturation pressures.

Almost all of the models mentioned involve asphaltene properties (e.g., density, molecular weight) in their calculations. Accurate determination of asphaltene mean molecular weight and the molecular weight distribution of aggregates is difficult because of association of asphaltene particles and their polydisperse nature in molecular size and polarity (Speight et al., 1985; Andersen et al., 1999). To overcome this difficulty, common thermodynamic models consider asphaltene as a heavy pseudo-component and tune its properties to match experimental data. This is accurate only under static test conditions (i.e., a specified pressure range, temperature and injected gas concentration); under reservoir conditions, where different grid blocks can have different gas saturations and temperatures, the results of such a model could be misleading.

Rassamdana *et al.* (1996) presented a scaling equation based on aggregation/gellation phenomena to predict the results of asphaltene precipitation experiments under standard conditions.

In this report, the following objectives are considered.

An experimental study of asphaltene instability due to gas injection is described; the experiments include the effects of gas type (methane and nitrogen), gas concentration, pressure and temperature and the pure solid approach is employed to model the experimental data.

Extensive data collection from the literature is used in the development of a new scaling model for the prediction of asphaltene precipitation due to gas injection; sensitivity analysis is performed on the model parameters and its predictive capability investigated for different gas injection processes.

EXPERIMENTAL

Sample Characterization

Three single-phase bottom-hole samples were taken from representative wells of southwest Iranian oil reservoirs. Reservoir fluid compositions and other basic properties (API, molecular weight and solution GOR) were determined by means of the GC-MS (Gas-Chromatography Mass-Spectroscopy) technique and differential liberation tests. The samples were also characterized for weight percents of saturates (S), aromatics (A), resins (R) and asphaltenes (A) using the SARA method as described in the Institute of Petroleum handbook (IP, 1985). The results are presented in Tables 1-3.

Table 1: Properties of crude oil samples

Sample		Α	В	С
Reservoir Temperature	°F	250	185	255
Saturation Pressure	psia	3950	2747	1722
Solution GOR	SCF/STB	1523	598	450
API Gravity of Residual Oil	°API	31	24	20

Table 2: SARA analysis

Sample		Α	В	С
Saturated	Wt%	52.49	65.46	30.10
Aromatic	Wt%	41.04	19.44	42.10
Resin	Wt%	5.48	6.4	13.36
Asphaltene	Wt%	0.99	8.7	13.75

Table 3: Composition of oil samples

Commonant	Mole Percent			
Component	Α	В	С	
H ₂ S	1.87	0.59	2.70	
N_2	0.31	0.06	0.21	
CO ₂	3.37	2.45	5.14	
C ₁	43.59	38.65	22.00	
C_2	8.58	6.66	7.10	
C ₃	6.27	5.33	5.34	
i-C ₄	1.64	1.01	0.99	
n-C ₄	4.89	2.92	2.78	
i-C ₅	2.20	1.24	1.12	
n-C ₅	2.49	1.51	1.41	
C ₆	1.91	4.67	5.55	
C_7	0.89	4.56	3.84	
C ₈	3.01	3.75	4.02	
C9	2.05	2.24	2.85	
C ₁₀	1.84	2.55	2.83	
C ₁₁	1.39	2.26	2.58	
C_{12}^{+}	13.71	19.56	29.54	
MW of C ₁₂ ⁺ Fraction	300	492	418	
MW of Reservoir oil	75	111	149	
SG. of C ₁₂ ⁺ Fraction @ 60/60 °F	0.9025	0.9569	0.9760	

Asphaltene Precipitation Experiments without Gas Injection

In these sets of experiments, a conventional pressure depletion process was performed at the reservoir temperature in order to examine whether asphaltene precipitation occurred in the absence of gas injection or not. The schematic diagram of the experiments apparatus is shown in Figure 1. The main part of the system is a mercury-free, visual JEFRI equilibrium cell which operates in the temperature range of 30-200 °C with a maximum operating pressure of 10000 psi.

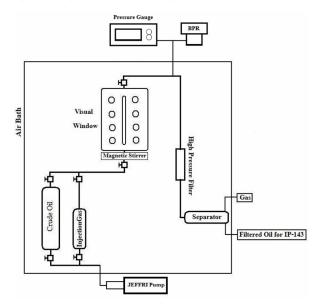


Figure 1: Schematic of the HPHT experimental setup

The experimental procedure in this step is described as follows.

The equilibrium cell is cleaned and maintained at reservoir temperature. The feed oil is first filtered through an appropriate filter paper to remove any possible solid particles present in the oil and then charged into the cell under single-phase conditions at reservoir pressure. A magnetic stirrer is used to agitate the sample overnight and accelerate the equilibrium process. The cell pressure is lowered in subsequent predefined steps; at each point, a high pressure filtration process is performed with a 0.2 µm filter paper. To do this, a limited volume of sample (about 10 cc for each pressure step) is allowed to flow into the filter manifold at constant pressure and temperature. In order to avoid alteration of the asphaltene solubility, only a small pressure drop must occur across the filter. Therefore, high pressure helium is used to maintain a back-pressure on the downstream of the filter so that the fluid sample can flow gradually through the filter with only a small pressure drop.

Filtered oil is then flashed in a separator and the asphaltene content of the residual oil is measured using the standard IP procedure; thus, the difference between the asphaltene content of the original sample and the filtered oil at each pressure determines the weight percent of precipitated asphaltene. The weight of precipitated asphaltene is then divided by the weight of the oil sample that is used in the IP procedure to give the weight percent of precipitated asphaltene. Since the experimental procedure is designed to characterize the asphaltene content of the filtered fluid, the asphaltene deposition problems in the equilibrium cell and the connection flowlines do not affect the accuracy of the experiments and reliable data could be gathered. The results in Table 4 show that noticeable precipitation occurs for samples B and C under reservoir conditions.

Asphaltene Precipitation Due to Gas Injection

In this step, a series of experiments was performed to study the effect of different factors on the asphaltene precipitation behavior of oil samples through the gasinjection process. In these experiments, methane and nitrogen gases were used for injection in miscible conditions as described below.

In the first step, a swelling test is performed to determine the alteration of the bubble point pressure for the mixtures of oil samples and injected gas. The results are presented in Figure 2.

A known volume of fresh oil is fed into the equilibrium cell at the desired temperature while the cell pressure is maintained above the mixture saturation pressure to avoid phase separation during fluid transfer and recombination of oil and gas samples. A preset amount of gas (nitrogen or methane) is introduced into the cell under isothermal conditions. The mixture is allowed to equilibrate and settle down overnight to ensure full asphaltene precipitation. A high pressure filtration is performed to quantify asphaltene precipitation vs. pressure. The sampling, filtration and evaluation processes are similar to natural depletion experiments. To examine the effect of nitrogen injection on asphaltene instability, 10 mole percent of nitrogen was recombined with sample A at a reservoir temperature of 250 °F. Although gas injection showed negative effects on asphaltene precipitation, it was not clearly detected because the asphaltene content of this sample is very low (less than 1 wt %). Nitrogen injection was repeated for sample B with 10 and 20 mole percent of nitrogen at a reservoir temperature of 185 °F (Table 4).

In another effort, in order to investigate the effect of gas type on asphaltene precipitation, methane injection was carried out; Sample C was recombined with methane in GOR of 600 SCF/STB (43.3 mole percent) at a reservoir temperature of 255 °F and asphaltene precipitation was determined at different pressure levels, as shown in Table 4.

The test was repeated at 180 °F to investigate the effect of temperature on asphaltene instability. The results showed that the effect of temperature was different above and below the bubble point pressure. Above P_b , asphaltenes become more unstable as the temperature increases; it can be expected that the energy required to promote the aggregation and precipitation of asphaltene clusters decreases with increasing temperature, i.e., the solubility parameter of the oil decreases with increasing temperature. The asphaltene re-dissolution rate below P_b is controlled by the amount of liberated gas rather than the temperature.

Sample B (T=185 °F)			
	Pressure	Precipitated Asphaltene	
	(psi)	(wt%)	
Natural	3418	1.03	
Depletion	3218	1.16	
Depiction	2918	1.25	
	2216	0.94	
	1015	0.34	
	7054	1.14	
Nitrogen	6043	1.46	
Injection 10	4933	1.93	
Mole %	4033	1.25	
	3028	0.65	
	8561	2.26	
Nitrogon	8058	2.36	
Nitrogen Injection 20 Mole %	7554	2.44	
	6043	2.25	
	4033	1.67	
	2022	1.1	

Table 4: Asphaltene precipitation vs. pressure for nitrogen and methane injection

	Sample C			
	Pressure	Precipitated Asphaltene		
	(psi)	(wt%)		
	5021	1.07		
Natural	3516	1.99		
Depletion	2016	2.54		
-	1315	1.86		
	1015	1.38		
	715	0.93		
	6543	8.49		
Methane	6043	8.95		
Injection	5537	9.04		
255 °F	4537	6.93		
	3531	4.88		
	6543	8.36		
Methane	5743	8.85		
Injection	4937	9.05		
180 °F	4036	7.1		
	3028	4.44		

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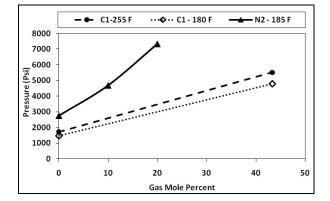


Figure 2: Results of swelling tests

MODELING

Pure Solid Model

In this approach, the heaviest pseudo-component is split into a non-precipitating and a precipitating component. These components have the same critical properties and acentric factors, but different interaction parameters with the light components. The equations for thermodynamic equilibrium between oil, gas and s1 (solid phase in equilibrium with hydrocarbon fluid) are:

$$\ln f_{io} = \ln f_{ig} , \quad i = 1,...,n_c$$

$$\ln f_{n_c o} = \ln f_{S1}$$
(1)

The general solubility equation that relates the solid fugacity to the liquid fugacity of a pure component is (Firoozabadi, 1999):

$$\ln f_{S}(P,T) = \ln f_{1}(P,T) - \frac{\Delta H_{tp}}{R} \left[\frac{1}{T} - \frac{1}{T_{tp}} \right]$$
$$- \frac{\Delta C_{p}}{R} \left[\ln \left(\frac{T_{tp}}{T} \right) + \left(1 - \frac{T_{tp}}{T} \right) \right]$$
$$+ \frac{1}{RT} \int_{P_{tp}}^{P} (v_{s} - v_{1}) dp$$
(2)

This equation can be used to derive an expression relating the fugacity of the solid at any pressure and temperature to the solid fugacity at a reference condition (Kohse *et al.*, 2000):

$$\ln f_{\rm S} = \ln f_{\rm S}^* + \frac{\mathbf{v}_{\rm s}}{R} \left[\frac{\mathbf{P} - \mathbf{P}_{\rm tp}}{T} - \frac{\mathbf{P}^* - \mathbf{P}_{\rm tp}}{T^*} \right]$$
$$- \frac{\Delta H_{\rm tp}}{R} \left[\frac{1}{T} - \frac{1}{T^*} \right]$$
$$- \frac{\Delta C_{\rm p}}{R} \left[\ln \left(\frac{T^*}{T} \right) - T_{\rm tp} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right]$$
(3)

This is the form of the asphaltene fugacity equation used for predicting the effect of pressure and temperature on asphaltene precipitation and can be simplified for isothermal conditions to give:

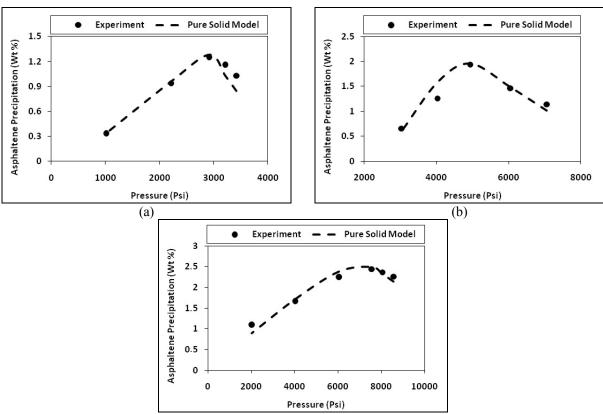
$$\ln f_{S1} = \ln f_{S1}^{*} + \frac{v_{S1} \left(P - P^{*} \right)}{RT}$$
(4)

In this model, the regression parameters are asphaltene molar volume and binary interaction parameters of the asphaltene fraction with the light components (i.e. N₂, CO₂, and C₁). The most accurate regression results, which were achieved with optimum matching parameters, are listed in Table 5. Figures 3 and 4 compare the experimental data with predictions of the pure solid model. It is observed that this model successfully predicts the experimental data at low gas concentrations (natural depletion and 10 and 20 mole percent of nitrogen injection). However, the results for high gas concentration (43.3 mole % methane injection) are not promising above the bubble point pressure.

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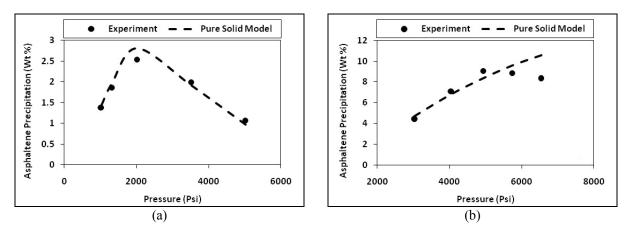
	Asphaltene Molar Volume	K _{ij} (C ₃₁₊ - N ₂)	K _{ij} (C ₃₁₊ - CO ₂)	K _{ij} (C ₃₁₊ - C ₁)
Sample B – Natural Depletion	1.05	0.2	0.2	0.2
Sample B – 10% N ₂	1.02	0.27	0.27	0.27
Sample B – 20% N ₂	1.068	0.25	0.25	0.25
Sample C – Natural Depletion	0.84	0.22	0.22	0.22
Sample C – 43.3% C ₁ – 180 °F	0.7	0.15	0.05	0
Sample C – 43.3% C ₁ – 255 °F	0.6	0	0	0

Table 5: Optimum matching parameters of the pure solid model



(c)

Figure 3: Comparison of experimental data for Sample B with predictions of the pure solid model: (a) Natural depletion; (b) Recombined with 10 mole percent of nitrogen; (c) Recombined with 20 mole percent of nitrogen



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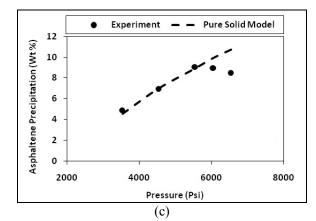


Figure 4: Comparison of experimental data for Sample C with predictions of the pure solid model: (a) Natural depletion; (b) Recombined with 43.3 mole percent of methane ($T = 180 \text{ }^{\circ}\text{F}$); (c) Recombined with 43.3 mole percent of methane ($T = 255 \text{ }^{\circ}\text{F}$)

Conventional Scaling Equation

Rassamdana *et al.* (1996) conducted asphaltene precipitation experiments with different normal alkanes. Since the Flory-Huggins model was not able to predict the experimental results accurately, a scaling equation was developed based on the aggregation/gelation phenomenon:

$$X = \frac{S}{M^{Z}} \qquad Y = \frac{W}{S^{Z'}} \tag{5}$$

where S is the ratio of the volume of injected solvent to the weight of the crude oil, M is the molecular weight of the solvent and W is the weight percent of precipitated asphaltene. For Z' = -2 and Z = 0.25, all data points collapsed onto a single third-order polynomial curve of the general form:

$$Y = a_0 + a_1 X + a_2 X^2 + a_3 X^3 \qquad (X \ge X_C)$$
(6)

Hu *et al.* (2000) checked the predictive capability of the scaling equation and universality of the exponents Z and Z'. They concluded that Z' = -2was a universal constant regardless of the oil composition and the optimum value of Z varied between 0.1 and 0.5.

Ashoori *et al.* (2003) performed asphaltene precipitation experiments for Iranian dead oil samples at different temperatures and introduced the effect of temperature in the original scaling equation:

$$X = \frac{S}{T^{n}M^{Z}} \qquad Y = \frac{W}{S^{Z'}}$$
(7)

The temperature exponent, n, was defined in the range of 0.1 to 0.25 whereas the other constants (Z, Z') were unchanged.

Bagheri *et al.* (2009) proposed the following scaling equation to model their experimental work:

$$X = \frac{S \times C_t \times GOR}{X_{C31+} \times R_t} \qquad Y = \frac{W \times S \times R_t}{C_t}$$
(8)

where S is the solvent to oil dilution ratio (cm^3/g) , GOR is the gas oil ratio (SCF/STB), R_t and C_t are resin and asphaltene contents (wt %), W is the amount of precipitated asphaltene (wt %) and XC₃₁₊ is the mole fraction of the C₃₁₊ fraction in the oil sample. Model results were compared with original scaling predictions; experimental asphaltene precipitation data (at ambient pressure and temperature) were predicted better by the new model.

New Scaling Equation for High Pressure Gas Injection

The conventional scaling equation was developed for standard conditions. Compared to standard conditions, more effective parameters have to be accounted for in HPHT gas injection. Reservoir pressure and temperature, bubble point pressure of the sample, mole percent of precipitant (injected gas) and gas molecular weight were considered in the new model.

Different configurations of the effective parameters were examined considering their physical effect on precipitation. The most simple and accurate X and Y definitions were found to be:

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$$X = \frac{S'}{M^Z T^n} \qquad Y = \frac{W}{S'^{Z'}}$$
(9)

where

$$\mathbf{S}' = \mathbf{S} \, \mathbf{e}^{-\mathbf{h} \left(\frac{\mathbf{P}\mathbf{b}}{\mathbf{P}} - 1\right)^2} \tag{10}$$

M is the molecular weight of injected gas, W is the weight percent of precipitated asphaltene, P is pressure, P_b is the bubble point pressure of the mixture, T is temperature in °F and S is the ratio of the volume of injected gas to the weight of crude oil. The exponential function was applied to model the effects of both increasing and decreasing pressure on asphaltene precipitation above and below the bubble point pressure.

Different sets of gas injection data were collected from the literature to determine the optimized model exponents. Integrated data were mostly for CO₂ injection and data for other gases were sparse. Novosad et al. (1990) evaluated the stability of asphaltene under CO₂ injection. Srivastava et al. (1999) presented the results of dynamic and static precipitation tests for the Weyburn reservoir at reservoir pressure for three oil samples. Takahashi et al. (2003) investigated the effect of CO_2 concentration on asphaltene precipitation at the reservoir temperature for a range of pressures. Other investigations with vague experimental details or incomplete data were excluded from the modeling. Jamaluddin et al. (2002) investigated the effect of nitrogen injection on asphaltene instability due to isothermal depressurization at reservoir temperature. Hu et al. (2004) studied the effects of operating pressure, injected CO₂ concentration, and multiplecontact on the onset and amount of asphaltene precipitation. Negahban et al. (2005) discussed experimental work associated with the evaluation of asphaltene precipitation due to the injection of a synthetic gas for a field in the UAE. Idem et al. (2002) used a molar CO₂ programmed titration technique to evaluate the kinetics of CO₂-induced asphaltene precipitation from three Saskatchewan crude oils under isothermal and isobaric reservoir conditions and formulated a kinetic model for the data.

Using defined X and Y parameters, it was observed that the plot of Y vs. X collapses all literature data onto the following third-order polynomial function (Figure 5):

$$Y = 3.3877 X^{3} + 0.4831 X^{2} - 0.0099 X + 8 \times 10^{-6} (11)$$

The exponents, Z, Z', n and h were carefully determined for best fit of the literature experimental data. Afterwards, the coefficients of the 3^{rd} order polynomial (a_i) could be extended to other samples.

Our experimental data were used to evaluate the new model. Although the general equation was developed for literature CO_2 data, Figure 5 shows that data for methane injection also collapse onto the general curve.

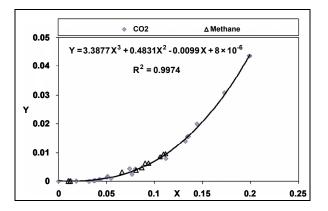


Figure 5: Collapse of literature CO_2 data onto a 3^{rd} order polynomial and overlap of our methane injection data with the curve

Swelling test results confirmed that the effect of nitrogen on fluid phase behavior is different from that of methane (and carbon dioxide) since it increases mixture saturation pressure more compared to other gases, mainly because of its unique critical properties (very low critical temperature of nitrogen compared to methane and carbon dioxide). As a result, a distinct 3rd order polynomial is defined for nitrogen injection data (Figure 6):

$$Y = 34.112 X^{3} - 2.4023 X^{2} + 0.0688 X - 6 \times 10^{-4} (12)$$

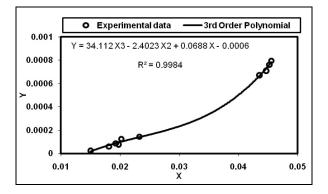


Figure 6: Collapse of Nitrogen injection data onto a 3rd order polynomial

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DISCUSSION

One of main advantages of the new scaling equation is the prediction of asphaltene instability under gas injection without involving asphaltene properties. When simple PVT data, including the molecular weights of the oil and injected gas sample, the mixture bubble point pressure and the asphaltene content of the oil sample are available, the scaling equation should be applicable.

As mentioned before, in thermodynamic–based models asphaltene is considered to be a pseudocomponent and its properties are tuned to match the experimental data. However, this is valid only for static test conditions and the resultant model does not accommodate any changes in thermodynamic conditions (e.g., gas concentration and temperature). Under reservoir conditions, the injected gas concentration is different from point to point and applying the original model to different grid blocks would be misleading. The scaling equation is more reliable because, in this approach, a unique X can be estimated for each grid block depending on its

properties; afterwards, the corresponding asphaltene precipitation would be calculated from the 3rd order polynomial that has been tuned to precipitation data. The working procedure for estimation of asphaltene precipitation by applying the scaling equation can be summarized as follows.

Preliminary characterization of the oil and gas samples (i.e., measurement of oil and injected gas molecular weight and mixture bubble point pressure).

Determination of the asphaltene content by SARA analysis.

Calculation of the X parameter from Equation (9) for the desired pressure, temperature and gas concentration.

Evaluation of the Y parameter from the corresponding 3^{rd} order polynomial (Equation (11) or (12)).

Determination of the precipitated asphaltene weight percent from the Y definition (Equation (9)).

Comparison of experimental data with the new model predictions in Figures 7 and 8 shows that this approach successfully described asphaltene precipitation behavior due to gas injection.

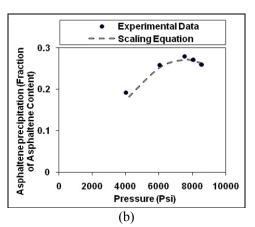


Figure 7: Scaling model prediction vs. experimental data for sample B: (a) 10 Mole % of N₂, (b) 20 Mole % of N₂.

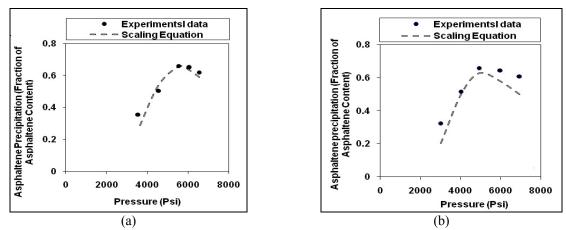


Figure 8: Scaling model prediction vs. experimental data for sample C: (a) T= 255 °F, (b) T= 180 °F.

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Sensitivity analysis was performed to investigate the universality of the model parameters. Z' = -2was found to be universal in agreement with the original scaling equation. Different Z' values resulted in dispersion of the XY plot.

Rassamdana *et al.* (1996) and Hu *et al.* (2000) suggested a range of 0.1 to 0.5 for the Z exponent. The optimum Z value was found to be Z = 0.11 in this work.

Since h is related to the pressure function with important impact on precipitation, it should be tuned more accurately. The best value for h is suggested to be 7 for CO_2 and methane and 1 for nitrogen injection data. Different values for h disperse the data points from the general curve.

Different values between -0.05 and 0.05 were examined for the temperature exponent. The best fit was obtained for n = -0.04, although excluding the temperature term (n = 0) did not produce a large regression error. This is in agreement with literature observations that the effect of temperature is negligible compared to the other parameters and is different above and below the bubble point pressure (Verdier, 2006).

CONCLUSIONS

Experimental results show that the asphaltene redissolution rate below the bubble point pressure decreases at high gas concentrations. This is due to formation of complex clusters when more precipitated particles are present in the mixture.

Comparison of gas injection results shows that the effect of nitrogen on asphaltene precipitation is more severe compared to methane.

The effect of temperature is much less than those of pressure and injected gas concentration and is different in the upper and lower bubble point pressure regions.

Although the pure solid model successfully predicts asphaltene precipitation for the natural depletion process and low gas injection, its results are not promising at high gas concentrations.

A new scaling equation is presented to predict asphaltene precipitation behavior without including complex properties of the asphaltene. Universal parameters of this model make it novel for evaluation of future gas injection projects when simple PVT data are available.

Collapse of the data is often possible by defining dimensionless parameters. Although X and Y are not dimensionless, excellent collapse of the data from different oil and gas samples was achieved for various temperatures and pressures. The scaling model is more reliable for dynamic reservoir conditions since its parameters can be redefined if any change in thermodynamic conditions occurs.

NOMENCLATURE

Ct	Asphaltene content	wt %
\mathbf{f}_{l}	Liquid fugacity	
${{{{\mathbf{f}}_{{\mathrm{s}}}}}\atop{{{\mathbf{f}}_{{\mathrm{s}}}}^{*}}}$	Solid fugacity	
f_s^*	Reference solid fugacity	
h	Pressure exponent	
GOR	Gas oil ratio	SCF/STB
K _{ij}	Binary interaction parameter	
M	Molecular weight	g/mol
n	Temperature exponent	_
Р	Pressure	psi
P _b	Mixture bubble point	psi
	pressure	-
S	Solvent to oil dilution ratio	cm ³ /g
R _t	Resin contents	wt %,
Т	Temperature	Κ
T^*	Reference temperature	Κ
T _{tp}	Triple-point temperature	Κ
Vı	Liquid molar volume	cm ³ /mol
Vs	Solid molar volume	cm ³ /mol
W	Precipitated asphaltene	wt%
X _{C31+}	Mole fraction of C_{31+}	
	fraction	
ΔC_p	Heat capacity difference	cal/mol K
ΔH_{tp}	Enthalpy of fusion at the triple-point	cal/mol

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REFERENCES

- Andersen, S. I. and Pedersen, C., Thermodynamics of asphaltene stability by flocculation titration. AICHE National Spring Meeting, March 14-18 (1999).
- Andersen, S. I. and Speight, J. O., Thermodynamic models for asphaltene solubility and precipitation. Journal of Petroleum Science and Engineering, 22, 53-66 (1999).

- Ashoori, S., Jamialahmadi, M., Muller-Steinhagen, H. and Ahmadi K., A new scaling equation for modeling of asphaltene precipitation. Paper SPE 85673 presented at the SPE International Technical Conference and Exhibition, Nigeria, August 4-6 (2003).
- Bagheri, M. B., Mirzabozorg, A., Kharrat, R., Dastkhan, Z. and Ghotbi, C., Developing a new scaling equation for modelling of asphaltene precipitation. Canadian International Petroleum Conference (CIPC), Calgary, Alberta, Canada, June 16-18 (2009).
- Dehghani, A. K., Gholami, V., Moghadasi, J. and Abdi, R., Formation damage through asphaltene precipitation resulting from CO₂ Gas injection Iranian carbonate reservoir. SPE Production & Operations, May 210-214 (2008).
- Escobedo, J. and Mansoori, G. A., Theory of viscosity as a criterion for detection of onset of asphaltene flocculation. Paper SPE 28729 presented at the SPE International Conference and Exhibition of Mexico Field, Veracruz, October 10-13 (1994).
- Firoozabadi, A., Thermodynamics of Hydrocarbon Reservoirs. McGraw-Hill, New York, 298-299 (1999).
- Gonzalez, D. L., Ting, P. D., Hirasaki, G. J. and Chapman, W. G., Prediction of asphaltene instability under gas injection with the PC-SAFT equation of state. Energy Fuels, 19, 1230-1234 (2005).
- Gonzalez, D. L., Vargas, F. M., Hirasaki, G. J. and Chapman W. G., Modeling study of CO₂-induced asphaltene precipitation. Energy Fuels, 22, 757-762 (2008).
- Hirschberg, A., De Jong, L. N. J., Schipper, B. A. and Meyers, J. G., Influence of temperature and pressure on asphaltene flocculation. Paper SPE 11202 presented at the SPE 57th Annual Technical Conference and Exhibition, New Orleans, LA, September 26-29 (1988).
- Hu, Y. F., Chen, G. J., Yang, J. T. and Guo, T. M., A study on the application of scaling equation for asphaltene precipitation. Fluid Phase Equilibria, 171, 181-95 (2000).
- Hu, Y. F., Lib, S., Liub, N., Chuna, Y. P., Park, S. J., Mansoori, G. A. and Guoa, T. M., measurement and corresponding states modeling of asphaltene precipitation in Jilin Reservoir oils. Journal of Petroleum Science and Engineering, 41, 169-182 (2004).
- Huang, S. S. and Dyer, S., Miscible displacement in the Weyburn Reservoir: A laboratory study. Journal of Canadian Petroleum Technology, 32, 42-52 (1993).

- Idem, R. O. and Ibrahim, H. H., Kinetics of CO₂induced asphaltene precipitation from various Saskatchewan crude oils during CO₂ miscible flooding. J. Pet. Sci. and Eng., 35, 233-246 (2002).
- IP-143/90-ASTM D3279-90, Standards for Petroleum and its Products. Institute of Petroleum, London, 143.1-143.7 (1985).
- Jamaluddin, A. K. M., Joshi, N., Iwere, F. and Gurpinar, O., An investigation of asphaltene instability under nitrogen injection. Paper SPE 74393 presented at the SPE International Petroleum Conference and Exhibition, Mexico, February 10-12 (2002).
- Kohse, B. F., Nghiem, L. X., Maeda, H. and Ohno, K., Modeling phase behavior including the effect of pressure and temperature on asphaltene precipitation. Paper SPE 64465 presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition, Australia, October 16-18 (2000).
- Leontaritis, K. J. and Mansoori, G. A., Asphaltene flocculation during oil production and processing: A thermodynamic colloidal model. Paper SPE 16258 presented at the SPE International Symposium on Oil Field Chemistry, San Antonio, TX, January (1987).
- Monteagudo, J. P., Lage, P. L. C. and Rajagopal, K., Towards a polydisperse molecular thermodynamic model for asphaltene precipitation in live oil. Fluid Phase Equilibria, 187-188, 443-471 (2001).
- Mousavi-Dehghani, S. A., Mirzayi, B. and Vafaie-Sefti, M., Polymer solution and lattice theory applications for modeling of asphaltene precipitation in petroleum mixtures. Brazilian Journal of Chemical Engineering, 25, (3), 523-534 (2008).
- Negahban, S., Bahamaish, J. N. M., Joshi, N., Nighswander, J. and Jamaluddin, A. K. M., An experimental study at an Abu Dhabi Reservoir of aspaltene precipitation caused by gas injection. SPE Production & Facilities, 115-125, May (2005).
- Nghiem, L. X. and Li, Y. K., Computation of multiphase equilibrium phenomena with an equation of state. Fluid Phase Equilibria 17, 77-95 (1984).
- Nghiem, L. X. and Coombe, D. A., Modeling asphaltene precipitation during primary depletion. SPE Journal, 2, 170-176 (1997).
- Novasad, Z. and Costain, T., Experimental and modeling studies of asphaltene equilibria for a reservoir under CO₂ injection. Paper SPE 20530 presented at the 65th Annual Technical Conference and Exhibition, New Orleans, LA, September 23-28 (1990).

- Pan, H. and Firoozabadi, A., Thermodynamic micellization model for asphaltene aggregation and precipitation in petroleum fluids. SPE Production & Facilities, 13, 118-127 (1998).
- Pan, H. and Firoozabadi, A., Thermodynamic micellization model for asphaltene precipitation inhibition. AIChE Journal, 46, 416-426 (2000).
- Pazuki, G. R. and Nikookar, M., A Modified Flory-Huggins model for prediction of asphaltenes precipitation in crude oil. Fuel, 85, 1083-1086 (2006).
- Pazuki, G. R., Nikookar, M. and Omidkhah, M. R., Application of a new cubic equation of state to computation of phase behavior of fluids and asphaltene precipitation in crude oil. Fluid Phase Equilibria, 254, 42-48 (2007).
- Rassamdana, H., Dabir, B., Nematy, M., Farhani, M. and Sahimi, M., Asphalt flocculation and deposition. I. Then onset of precipitation. AIChE Journal, 42, 10-22 (1996).
- Rassamdana, H. and Sahimi, M., Asphalt flocculation and deposition: II. Formation and growth of fractal aggregates. AIChE Journal, 42, 3318-3332 (1996).
- Sahimi, M., Rassamdana, H. and Dabir, B., Asphaltene formation and precipitation experimental studies and theoretical modeling. SPE Journal, 2, 157-169 (1997).
- Speight, J. G., Wernick, D. L., Gould, K. A., Overfield, R. E., Rao, B. M. L. and Savage, D. W., Molecular weight and association of asphaltenes: A critical review. Revue de L'Institut Français du Pétrole, 40, 51-56 (1985).
- Srivastava, R. K., Huang, S. S. and Dong, M., Asphaltene deposition during CO₂ flooding. SPE Production & Facilities, Vol. 14, No. 4, 235-245 (1999).
- Takahashi, S., Hayashi, Y., Yazawa, N. and Sarma, H., Characteristics and impact of asphaltene precipitation during CO₂ injection sandstone and carbonate cores: An investigative analysis through laboratory tests and compositional simulation. Paper SPE 84895 presented at the SPE International Improved Oil Recovery Conference, Kuala Lumpur, October 20-21 (2003).

- Vafaie-Sefti, M., Mousavai-Dehghani, S. A. and Mohammad-Zadeh, M., A simple model for asphaltene deposition in petroleum mixtures. Fluid Phase Equilibria, 206, 1-11 (2003).
- Vafaie-Sefti, M. and Mousavai-Dehghani, S. A., Application of association theory to the prediction of asphaltene deposition: Deposition due to natural depletion and miscible gas injection processes in petroleum reservoirs. Fluid Phase Equilibria, 247, 182-189 (2006).
- Vargas, F. M., Gonzalez, D. L., Hirasaki, G. J. and Chapman W. G., Modeling asphaltene phase behavior in crude oil systems using the perturbed chain form of the statistical associating fluid theory (PC-SAFT) equation of state. Energy Fuels, 23, 1140-1146 (2009).
- Vargas, F. M., Gonzalez, D. L., Creek, J. L., Wang, J., Buckley, J., Hirasaki, G. J. and Chapman, W. G., Development of a general method for modeling asphaltene stability. Energy Fuels, 23, 1147-1154 (2009).
- Vargas, F. M., Creek, J. L. and Chapman, W. G., On the development of an asphaltene deposition simulator. Energy & Fuels, 24, (4), 2294-2299 (2010).
- Vargas, F. M. and Chapman, W. G., Application of the one-third rule in hydrocarbon and petroleum systems. Fluid Phase Equilibria, 290, 103-108 (2010).
- Verdier, S., Experimental study and modeling of asphaltene precipitation caused by gas injection. Ph.D. Thesis, Technical University of Denmark (2006).
- Wang, S. and Civan, F., Productivity decline of vertical and horizontal wells by asphaltene deposition in petroleum reservoirs. Paper SPE 64991, presented at the SPE International Symposium on Oilfield Chemistry, Houston, Texas, February 13-16 (2001).
- Yang, Z., Ma, C. F., Lin, X. S., Yang, J. T. and Guo, T. M., Experimental and modeling studies on the asphaltene precipitation in degassed and gasinjected reservoir oils. Fluid Phase Equilibria, 157, 143-58 (1999).