Korean J. Chem. Eng., **30**(2), 429-433 (2013)
DOI: 10.1007/s11814-012-0144-7

Inhibition effect of CO_2 on asphaltene precipitation for an Iranian crude oil and comparison with N_2 and CH_4

Mohsen Mohammadi*,*, Mahdi Akbari*, Alireza Bahramian*,**,†, Mahdi Sadeghi Naeeni**, and Zahra Fakhroueian****

*School of Chemical Engineering, University of Tehran, Tehran, Iran
**Institute of Petroleum Engineering, University of Tehran, P. O. Box 11155-4563, Iran
***Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran
(*Received 24 February 2012 • accepted 27 August 2012*)

Abstract−The effects of N_2, CH_4 and CO_2 injection on asphaltene precipitation have been experimentally investigated using a reservoir oil fluid from south of Iran, making use of light transmission method. The results are compared and the effects of injected gases on reducing asphaltene colloidal stability in oil are found in the following order: CH_4> N_2>CO_2. It is observed that CO_2 can act like an inhibitor and can increase the solubility of asphaltene, decreasing the asphaltene precipitation onset. A thermodynamic discussion explains the effect of CO_2 on the solubility of asphaltene based on the solubility parameters of recombined oil and CO_2, calculated from Peng-Robinson equation of state along with an empirical correlation for volumetric properties of CO_2.

Key words: Asphaltene, Asphaltene Precipitation Onset, Light Transmission Method, Gas Injection, Solubility Parameter

INTRODUCTION

Asphaltene is a fraction of crude oil that is insoluble in light alkanes such as n-pentane and n-heptane, but soluble in benzene and toluene at room temperature [1,2]. Asphaltene precipitation that occurs during crude oil production from oil reservoirs, causes many problems such as plugging the wellbore, pipelines and process equipment and wastes time for the expensive and demanding cleanup [3,4]. Asphaltene is composed of hydrogen, carbon and some mineral elements (N, O, S, metals) [5]. In oil reservoirs, there is a thermodynamic equilibrium between asphaltene particles and the other components of crude oil. Variation of temperature, pressure and composition of crude oil can affect this equilibrium and result in the asphaltene precipitation [2,6]. Gas injection, which is one of the oil recovery techniques, is mainly involved with asphaltene precipitation in oil reservoirs. Nitrogen (N_2), natural gas (methane is the main component) and carbon dioxide (CO_2) are the typical gases of the kind.

According to Fig. 1, asphaltene precipitation happens in a specific pressure range [2]. The highest and lowest pressures of this range are called upper and lower asphaltene onset pressure (AOP), respectively. Reducing the pressure, asphaltene precipitation starts at upper AOP and at bubble point reaches a maximum value [2]. If injection of a gas or solvent into the crude oil causes increasing the upper AOP, the injected material will be considered as an asphaltene precipitant.

As already mentioned, CO_2, N_2 and CH_4 are the common gases that are used in EOR processes from oil reservoirs therefore, investigation of the impact of these gases on asphaltene precipitation is an important subject. There are various reports on the effect of gas

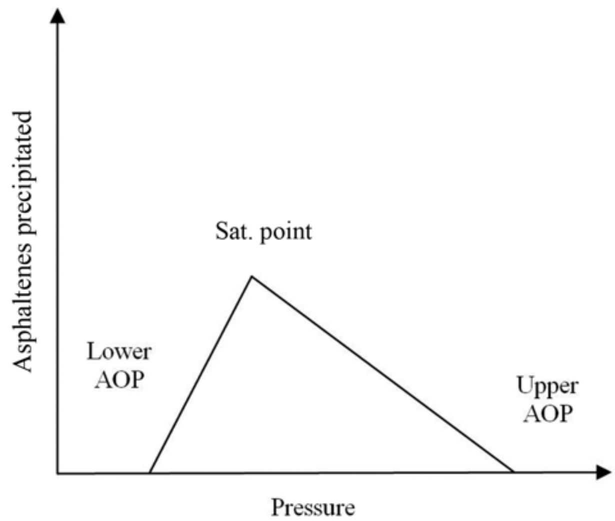

Fig. 1. Asphaltene precipitation versus pressure [2].

injection on asphaltene precipitation and determination of upper AOP. Jamaluddin et al. [7] investigated the effect of various amounts of N_2 on asphaltene precipitation and showed that upper AOP increases with increasing the amount of N_2. Creek et al. [8] compared the impact of light hydrocarbons on upper AOP and indicated that precipitation is more enhanced in presence of CH_4 than when the injected gas is C_2H_6 or C_3H_8. Hu et al. [9] injected carbon dioxide with a fixed rate to a crude oil sample at constant pressures. Results showed that at pressures lower than minimum miscibility pressure there was no precipitation, but at higher pressures, asphaltene precipitated and the amount of precipitated asphaltene increased with increasing the amount of injected CO_2.

There are also some theoretical studies with inconsistent results, comparing the impact of methane, nitrogen, and CO_2 gases on as-

†To whom correspondence should be addressed.
E-mail: abahram@ut.ac.ir

phaltene precipitation. For instance, injection of N_2 and a lean gas (82% CH_4) into four crude oil samples has been modeled with three-phase equilibrium calculation, and it is shown that the lean gas is more effective than N_2 in asphaltene precipitation [10]. Also Gonzalez et al. [11,12] calculated the onset of asphaltene precipitation for a crude oil in the presence of N_2, CH_4 and CO_2 with PC-SAFT equation of state (EOS). The result of this study indicates that among these three gases, the asphaltene precipitation is enhanced in presence of N_2 more than the other two gases. However, no general rule can be stated based on these studies regarding the effects of different gases on asphaltene precipitation. Asphaltene precipitation and the precipitation onset is a thermodynamic property and therefore depends on the system overall composition, temperature, and pressure. Therefore, the impact of injected gas may be case dependent, related to the oil composition.

In this study, the impact of three gases (N_2, CH_4 and CO_2) on upper AOP is investigated, making use of the light transmission method. Doing that, equal molar amounts of these gases are injected into three identical oil samples. The upper AOPs are measured for these samples and also for a sample without injected gas. Various amounts of N_2 also are injected to check the validity of the results, reproducing the trend obtained by Jamaluddin et al. [7]. A theoretical study is conducted to explain the effect of CO_2 on asphaltene stability by using a crossover temperature, where the solubility parameter of CO_2 becomes equal with that of the oil.

EXPERIMENTAL MATERIALS AND METHODS

1. Oil Sample

The oil sample is a dead oil from one of the oil reservoirs in the south of Iran. Table 1 shows the composition of the live oil in this reservoir. The API number of this oil is 19 and asphaltene content of oil is 10 percent, and that of oil and heptanes mixture is 7 percent. The amount of dead oil in each sample is 18.5 cc. Recombination process is carried out by mixing a mixture of 68% (mass based) methane, 14% ethane, and 18% propane with the dead oil. Since the oil is very viscous, recombined oil is diluted with 7.4 gram of n-heptane. The bubble point for recombined oil in presence of added n-heptane is about 1,350 psi and GOR is 368.24 scf/STB. All the processes and the experiments are conducted at 83 °C (temperature of oil reservoir).

Table 1. Reservoir fluid composition

Component	mol%		
N_2	0.04		
CO_2	0.47		
C1	35.70		
C2	7.61		
C3	5.84		
iC4	0.66		
nC4	2.47		
iC5	0.92		
nC5	1.24		
Pseudo components:	mol%	Molwt	Specific gravity
C6+A	3.46	101.55	0.811
C6+B	12.18	162.07	0.868
C6+C	16.84	266.30	0.919
C6+D	10.39	433.60	0.968
C6+E	2.21	710.85	1.020

2. Device Description

DBR-Mercury free PVT is used to determine the upper AOP. This device consists of a cylindrical glass which contains the experimental sample (Fig. 2). There is a movable piston inside the glass in which the studied sample is located on one side of the piston and hydraulic fluid is on the other side, setting the pressure and volume of the sample. The PVT cell is located in the oven to set the experimental temperature. Solid detection system (SDS) is located around the glass to determine formation of solid phase. The device includes a laser transmitter and detector on both sides of the sample, and by diagnosing the amount of detected laser one could determine the onset of solid formation.

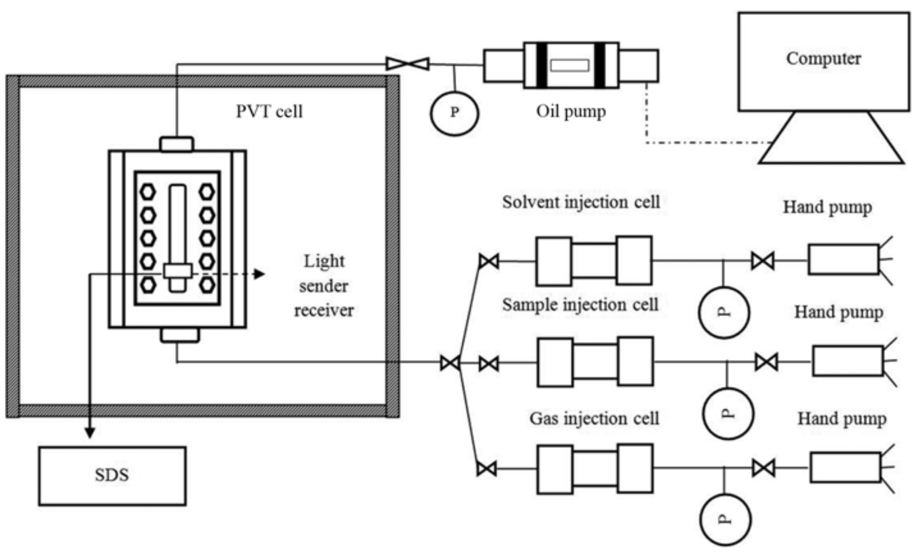

Fig. 2. Schematic diagram of experimental device.

3. Test Method

At first the pressure of prepared sample was adjusted in 9,000 Psi and then depressurized step by step by about 100 Psi. A magnetic stirrer was used to mix the system at all the tested pressures to maintain the equilibrium inside the system. The amount of transmitted light was recorded after mixing for about 15 minutes, when equilibrium was assumed to be reached.

In the primary stages, the amount of transmitted light increases due to decrease in density and reaches a maximum value. When solid phase is formed the light intensity drops sharply. The chart of the transmitted light versus pressure is then plotted and the maximum point is considered as the onset of asphaltene precipitation.

CALCULATION OF RECOMBINED OIL AND CO_2 SOLUBILITY PARAMETERS

The Hildebrand solubility parameter, δ, for nonpolar/nonassociating fluids or polar fluids with a dipole moment lower than 2D (Debye) can be calculated from the volumetric data [13-15], as shown by Eq. (1):

$$\delta^2 \simeq T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad (1)$$

Therefore, one can simply calculate the solubility parameter of fluids making use of an equation of state. Here the empirical equation of Huang et al. has been used [13,16,17] (Eq. (2)) to calculate the solubility parameter of CO_2.

$$\begin{aligned} P = \rho RT[&1 + b_2\rho' + b_3\rho'^2 + b_4\rho'^3 + b_5\rho'^4 + b_6\rho'^5 \\ &+ b_7\rho'^2\exp(-c_{21}\rho'^2) + b_8\rho'^4\exp(-c_{21}\rho'^2) \\ &+ c_{22}\rho'\exp(-c_{27}\Delta T^2) + c_{23}\frac{\Delta\rho}{\rho'}\exp(-c_{25}\Delta\rho^2 - c_{27}\Delta T^2) \\ &+ c_{24}\frac{\Delta\rho}{\rho'}\exp(-c_{26}\Delta\rho^2 - c_{27}\Delta T^2)\Big] \end{aligned} \qquad (2)$$

Where

$$T_r = \frac{T}{T_c};\ \ \Delta T = 1 - T';\ \ \rho' = \frac{\rho}{\rho_c};\ \ \Delta\rho = 1 - \frac{1}{\rho'}$$

And (c_i) are constants and (b_i) are temperature dependent variables as listed in Huang et al. [16]

For calculation of the solubility parameter of the oil, a volume averaging mixing rule method [18,19] (Eq. (3)) has been used.

Table 2. Physical property of component and pseudo component

Component	Tc (K)	Pc (MPa)	ω
CH_4	190.56	4.599	0.0115
C_2H_6	305.32	4.872	0.0995
C_3H_8	369.83	4.248	0.1523
CO_2	304.20	7.382	0.2280
C6+A	574.89	3.586	0.3146
C6+B	690.69	2.66	0.4759
C6+C	803.47	1.738	0.6456
C6+D	931.82	1.028	0.9496
C6+E	1118.68	1.082	2.2206
Stock tank oil	700.661	5.850	0.5229

$$\delta_{Oil} = \Phi_{STO}\delta_{STO} + \Phi_{Methane}\delta_{Methane} + \Phi_{Ethane}\delta_{Ethane} + \Phi_{Propane}\delta_{Propane} \qquad (3)$$

where Φ_{STO}, $\Phi_{Methane}$, Φ_{Ethane} and $\Phi_{Propane}$ are the volume fraction of stock tank oil, methane, ethane, and propane, respectively. Peng-Robinson EOS is used for calculation of δ_i [20] for each fraction [15]. Critical temperature (T_c), critical pressure (P_c) and acentric factor (ω) for pseudo components are calculated from Cavett's method [21], and those of stock tank oil are found from the procedure that is described by Danesh [22]. Acentric factors and critical properties of pseudo components, stock tank oil, and gases are reported in Table 2.

RESULTS AND DISCUSSION

The effect of N_2 quantity on asphaltene precipitation was investigated to confirm the validity of the experimental method. Doing that, different amounts of nitrogen gas (0.043 and 0.056 moles) were injected into the same oil samples (concentrations of injected gases are 16.5 and 20.5 mol%), and the onsets of asphaltene precipitation are measured according to procedure described in the test method section. Table 3 shows the results of these experiments. According to this table, the onset pressure of asphaltene precipitation (Upper AOP) for the sample by 0.056 mole nitrogen, is 6,770 psi and it is higher than upper AOP for sample by 0.043 mole nitrogen (4,903 psi) then the upper AOP increases with increasing the amount of nitrogen. As was mentioned earlier, higher upper AOP means more asphaltene instability. So, with increasing the amount of nitrogen, asphaltene becomes more unstable in oil. These results are in agreement with those of Jamaluddin et al. [7].

To compare the effect of N_2, CH_4 and CO_2 on asphaltene precipitation, four different tests were performed. The upper AOPs were determined for oil sample without injected gas and samples with 0.043 moles of different injected gases (16.5 mol%). Fig. 3 shows the typical plot of transmitted light data versus pressure for the experi-

Table 3. Upper AOP for two different amount of nitrogen

Amount of nitrogen in oil sample (mol)	AOP (psi)
0.043	4903
0.056	6770

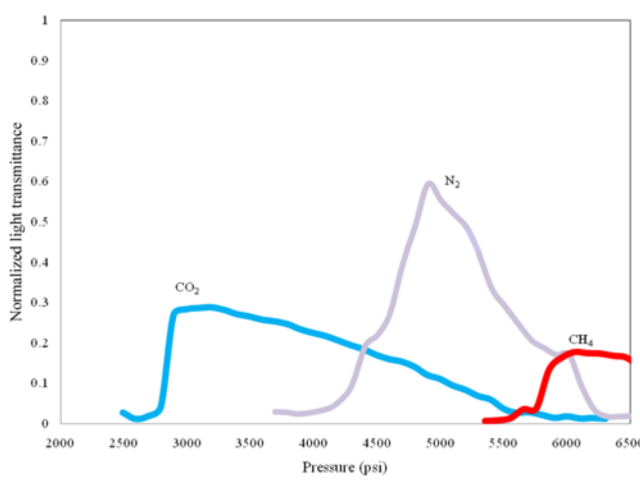

Fig. 3. Typical graphs of transmitted light versus pressure.

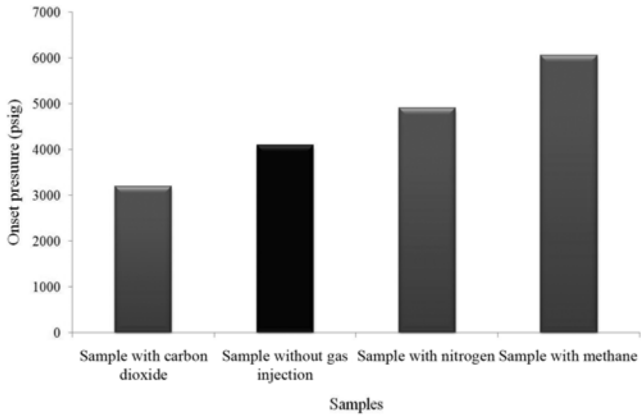

Fig. 4. Amount of upper AOP for different oil samples (Concentration of injected gas is 16.5 mol%).

ments with different gases. As it is obvious from this figure, at high pressures the amount of transmitted light increases with reducing the pressure (due to decrease in density) and reaches a maximum value. After that,the light intensity drops sharply because of solid phase formation. Fig. 4 illustrates the results of Upper AOP measurements. As it is evident from this figure, samples containing N_2 and CH_4 have higher upper AOP in comparison with the original oil sample. Therefore, these gases are asphaltene precipitant and injection of them causes asphaltene precipitation in oil reservoirs. Methane injection increases the upper AOP to 6,061 psi. This is the highest value obtained among the studied gases.

CO_2 has been repeatedly considered as a precipitant in many literatures, contrary to what is evident from Fig. 4. The upper AOP of sample oil with CO_2 injected is 3,190 psi, even lower than the AOP of the oil without injected gas. This procedure was repeated twice and similar results were obtained, suggesting that in our experimental conditions, CO_2 works as an inhibitor for asphaltene precipitation.

As mentioned earlier, Gonzales et al. [12] have calculated the onset pressure of asphaltene precipitation with PC-SAFT equation of state in presence of some gases. According to their calculation, CO_2 in some condition can act as an inhibitor, provided that the temperature is below a certain crossover point, below which the solubility parameter of CO_2 is greater than the solubility parameter of the oil. Therefore, addition of CO_2 below this temperature results in more stable dissolved asphaltene molecules, while above the crossover temperature CO_2 has a reverse effect and its addition decreases the solubility of asphaltene.

To find the crossover temperature we calculated the solubility parameters of CO_2 and the recombined oil as described in previous section. Fig. 5 shows the calculated solubility parameters of CO_2 and oil with respect to the temperature. As it is evident from this figure, the crossover temperature is 395 K and well above the experimental temperature (356 K) in this study. Therefore, according to the theoretical calculation of Gonzales et al. [12], addition of CO_2 at 356 K increases the solubility of asphaltene and results in an upper AOP less than the original sample.

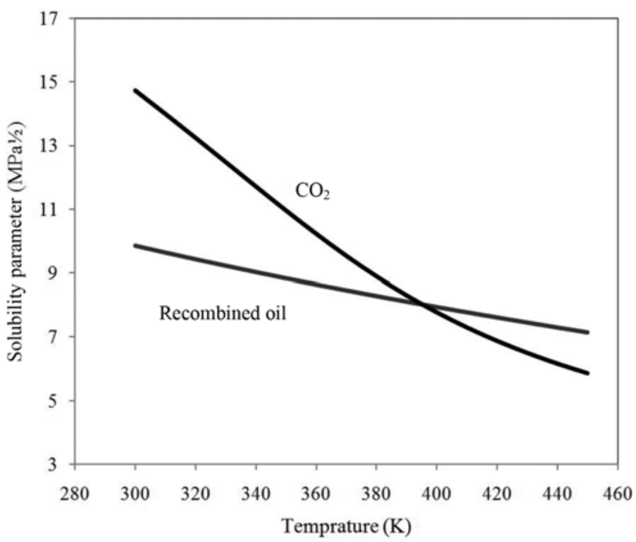

Fig. 5. Solubility parameter for recombined oil and CO_2 versus temperature.

CONCLUSION

A set of experiments have been conducted to investigate the effect of different gases on asphaltene stability and asphaltene precipitation. Both CH_4 and N_2 decrease the solubility of the asphaltene, resulting in precipitation at higher pressures than that of the original oil. The composition of the injected gas also revealed to be in direct relation with the asphaltene instability. So that higher AOP can be seen by increasing the amount of injected gas.

It is also found that, in our experimental conditions, CO_2 acts as inhibitor for asphaltene precipitation. The reason is based on a theoretical discussion related to the CO_2 and the oil solubility parameters and the concept of crossover temperature. It is shown that system temperature is below the crossover temperature, and hence the inhibition role of CO_2.

NOMENCLATURE

a : attraction parameter [$MPa\cdot m^6\cdot kmol^{-2}$]
b : molar co-volume [$m^3\cdot kmol^{-1}$]
b_i : temperature dependent parameter
c_i : Huang equation of state constant
E : cohesive energy [kj]
M : molecular weight
P : pressure [MPa]
R : universal gas constant [$MPa\cdot m^3\cdot K^{-1}\cdot kmol^{-1}$]
T : temperature [K]
v : molar volume [$m^3\cdot kmol^{-1}$]

Greek Letters

ρ : density [$Kg\cdot m^{-3}$]
ω : Pitzer acentric factor
δ : solubility parameter [$MPa^{0.5}$]
Φ : volume fraction

Subscripts

c : critical
r : reduced

STO : stock tank oil

REFERENCES

1. N. Aske, H. Kallevik, E. E. Johnsen and J. Sjöblom, *Energy Fuels*, **16**, 1287 (2002).
2. K. S. Pedersen and P. L. Christensen, *Phase behavior of petroleum reservoir fluids*, CRC Press (2007).
3. R. Thawer, D. C. A. Nicoll and G. Dick, *SPE Prod. Eng.*, **5**, 475 (1990).
4. H. Son, Y. Lee, J. Seo, S. Kim, W. Lee and W. Sung, *Korean J. Chem. Eng*., **28**, 2163 (2011).
5. B. S. Soulgani, D. Rashtchian, B. Tohidi and M. Jamialahmadi, *J. Jpn. Petrol. Inst*., **52**(6), 322 (2009).
6. M. Mohammadi, M. Akbari, Z. Fakhroueian, A. Bahramian, R. Azin and Sh. Arya, *Energy Fuels*, **25**, 3150 (2011).
7. A. K. M. Jamaluddin, N. Joshi, F. Lwere and O. Gurpinar, SPE International Petroleum Conference and Exhibition in Mexico, Villahermosa, February 2002 (SPE Paper 74393).
8. J. L. Creek, J. S. Buckley, J. Wang, SPE 2008 Offshore Technology Conference, Houston, Texas, U.S.A., May 2008 (SPE Paper 19690).
9. Y. F. Hu, S. L. N. Liu, Y. P. Chu, S. J. Park, G. A. Mansoori and T. M. Guo, *J. Pet. Sci. Eng.*, **41**, 199 (2004).
10. A. Hajizadeh, R. R. Ravari and M. Amani, 2009 SPE/EAGE Reservoir Characterization and Simulation Conference, Abu Dhabi, UAE, October (2009) (SPE Paper 123368).
11. D. L. Gonzalez, P. D. Ting, G. J. Hirasaki and W. G. Chapman, *Energy Fuels*, **19**, 1230 (2005).
12. D. L. Gonzalez, F. M. Vargas, G. J. Hirasaki and W. G. Chapman, *Energy Fuels*, **22**, 757 (2008).
13. CH. M. Hansen, *Hansen Solubility Parameters: A User's Handbook*, Second Ed., CRC Press (2007).
14. A. Cipollina, R. Anselmo, O. Scialdone, G. Filardo and A. Galia, *J. Chem. Eng. Data*, **52**, 2291 (2007).
15. M. Nikookar, M. R. Omidkhah and G. R. Pazuki, *Petroleum Sci. Technol.*, **26**, 1904 (2008).
16. F. H. Huang, M. H. Li, L. L. Lee, K. E. Starling and F. T. H. Chung, *J. Chem. Eng. Jpn.*, **18**, 490 (1985).
17. L. L. Williams, J. B. Rubin and H. W. Edwards, *Ind. Eng. Chem. Res.*, **43**, 4967 (2004).
18. K. Kraiwattanawong, H. S. Fogler, S. G. Gharfeh, P. Singh, W. H. Thomason and S. Chavadej, *Energy Fuels*, **21**, 1248 (2007).
19. A. F. M. Barton, *Handbook of solubility parameters and other cohesion parameters*, CRC Press (1983).
20. E. K. Goharshadi and M. Hesabi, *J. Mol. Liquids*, **113**, 125 (2004).
21. R. H. Cavett, *27th API Meeting*, San Francisco (1962).
22. A. Danesh, *PVT and phase behaviour of petroleum reservoir fluids*, Elsevier Science & Technology Books (1998).