Evaluation of Asphaltene Stability During CO₂ Flooding at Different Miscible Conditions and Presence of Light Components

Vahid Alipour Tabrizy¹ & Aly A. Hamouda²

¹ Department of Reserve Replacement, ASG PTC, Statoil ASA, Norway
² Department of Petroleum Engineering, University of Stavanger, 4036 Stavanger, Norway

Correspondence: Vahid Alipour Tabrizy, Department of Reserve Replacement, ASG PTC, Statoil ASA, Norway. Tel: 47-90-039-846. E-mail: vtab@statoil.com

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Abstract
The negative side effect of the flooding with CO₂ is asphaltene deposition; while little work was reported in the literature on asphaltene precipitation due to CO₂ flooding in presence of light components. The main objective in this paper is to address asphaltene precipitation for oil containing methane and propane due to CO₂ flooding at different miscibility conditions. Experimental measured asphaltene deposition due to miscible CO₂ injection is compared with corresponding values estimated by proposed model. It is shown that there is a critical concentration of CO₂, where below it; solubility parameter of the liquid is enhanced, hence preventing asphaltene from depositing. The first objective of the paper is to address an approach which is based on solubility parameters/CO₂ fraction in the liquid to qualitatively assess stability/instability region for the asphaltene. The second objective is to quantitatively compare the predicted and experimental results. It is shown that the higher CO₂ flooding pressure and temperature, the more deposited asphaltene. It was also shown that a higher risk for asphaltene deposition in case of chalk cores than for sandstone cores.

Keywords: miscible CO₂ flooding, asphaltene, solubility parameter, light components

1. Introduction
Carbon dioxide flooding in Enhanced Oil Recovery (EOR) processes has been encouraging; however it may result to asphaltene deposition which it turns affect reservoir rock and fluid properties (Moritis, 2006; Chukwudeme & Hamouda, 2009; Hamouda et al., 2008; Idem & Ibrahim, 2002; Simon et al., 1978; De Boer et al., 1995; Burke et al., 1990; Haskett & Tartera, 1965). Haskett and Tartera (1965) reported that crude oils with low asphaltene percentage could experience asphaltene precipitation/deposition due to pressure reduction in early stage recovery, as well as reservoir fluid composition variations during enhanced recovery by gas/chemical injection.

Different models have been reported in the literature to describe the behaviour of asphaltene deposition using different approaches. Hirschberg (1984) described a method based on solubility model using the Flory-Huggins theory with thermodynamic model considering temperature and pressure effects on asphaltene precipitation. Kawanaka et al. (1991) extended Hirschberg et al. (1984) approach considering asphaltene is a large nonhomogeneous polymers providing better fitting though increasing, the number of parameters to be adjusted. Thomas et al. (1992) derived an empirical correlation including the precipitated asphaltene as a multicomponent system using liquid-solid wax theory. Yang et al. (1992) described a modified Hirschberg solubility model and pointed that the oil phase should be modelled as a multicomponent system. Nghiem (1999) documented a thermodynamic solid model to see the dynamic description of asphaltene precipitation/deposited using a compositional simulator during miscible CO₂ injection. Paricaud et al. (2002) used statistical association fluid (SAFT) theory of the thermodynamics of large chain polymers used to model the onset of stability of polymer-colloid mixtures. Updated Statistical association fluid theory (SAFT) Equation of State derived by Chapman et al. (2004) was described providing the influence of polymer shape, Van der Waals interaction and aggregation of molecules. Kirangkrai et al. (2007) showed an empirical correlation between the solubility parameter limit and the molar volume of precipitants to observe the effect of dissolved gas on the onset solubility parameter of live oils. Gonzalez et al. (2008) demonstrated that CO₂ can be an inhibitor or a promoter of asphaltene precipitation depending on temperature, pressure, and composition studied. They have shown that at
specific pressure and for specific live oil, CO₂ addition increases the asphaltene stability less than the crossover
temperature, while above this point, the asphaltene is more unstable when the CO₂ concentration is increased.
Hamouda et al. (2009) derived a modified solubility equation to take into account the effect of dissolved CO₂
fraction on asphaltene precipitation. The model considers the volume occupied by one mole of CO₂ and fluid as
a function of the solubility parameter of the fluid. They have proved that below an onset CO₂ fraction (mol%) in
fluid, asphaltene is stabilized, while asphaltene precipitates based on the model and observed experimental
asphaltene solubility as a function of temperature and pressure. Verdier et al. (2006) considered the effect of
pressure and temperature on asphaltene instability in presence of gas components. They observed experimentally
and verified with the thermodynamic model, the solubility of asphaltene in oil increases with increasing pressure
and decreasing temperature.

Compositional models considering oil as multicomponents system and asphaltene molecular shape and size can
have a more robust estimation of asphaltene solubility/precipitation. Hamouda et al. (2009) reported higher oil
recovery due to better sweep efficiency in cores with higher deposited asphaltene. Among proposed models,
none of them can predict asphaltene precipitation which could results to divergence of CO₂ streamlines and
higher sweep efficiency.

In spite of the fact that there are many literatures describing asphaltene solubility in oil and associated proposed
thermodynamical models, few works can link the measured experimental asphaltene deposition in rocks and
estimated values predicted by model. Within them, the influence of light components in oil (e.g., methane and
propane) on asphaltene precipitation during CO₂ miscible flooding is even not addressed individually. The main
objective in this paper is to address asphaltene precipitation due to CO₂ miscible flooding of oil containing
methane and propane at different miscibility conditions. A comparison is made in the paper between asphaltene
precipitated and estimated.

2. Experiments

2.1 Cores

Outcrop chalks and outcrop Benthiemer sandstones are used in this study. The chalks have porosity of forty up to
forty eight percentages and absolute permeability of two to six mili Darcy. Sandstone cores have porosity near
twenty to twenty five percentage and permeability range between six to nine hundreds mili Darcy. Both types of
cores are in macro scale homogenous while sandstone cores are in micro scale heterogeneous.

2.1.1 Preparation of Fluids Containing Asphaltene and Light Components

The synthetic oil system is composed of asphaltene from crude oil in addition of n-C₇ (with the ratio of 1 to 40).
Mixture of crude oil and heptane was shaken for at least two times a day and left for two days to reach
equilibrium conditions, and then the solution was centrifuged and filtered through a 0.22 micrometre filter and
dried for 1 day using a vacuum at room temperature. 0.25 g asphaltene was dissolved in toluene (22 ml) and
mixed with 0.01 M stearic acid (CH₃(CH₂)₁₆CO₂H) dissolved in n-decane (42 ml) and then filtered for chalk
cores, and 0.01 M N, N-dimethyldodecylamine (CH₃(CH₂)₁₁N(CH₃)₂) dissolved in n-decane (42 ml) and after
filtration is used for sandstone cores. The live oils are made by mixing of methane and propane with the dead oil
at a constant gas oil solubility ratio (GOR = 280 ft³/bbl at standard conditions). The methane or propane was
supported from cylinder at Pb to the dead oil cell containing dead oil by pump to make the live oil, and then the
live oil cell was rotated by the rotating mixer with the speed of 50 rpm. The pressure of the cell was observed
twice per hour. Then, the pressure was set as required using a pump, to keep a pressure higher than the calculated
Pₛ of the fluid. Stable pressure was reached by mixing process for at least one day.

2.2 Experimental Procedure

Experimental apparatus is demonstrated in Figure 1. The CO₂ is injected after aging for cores by dead oil using
core holder that consists of Hassler core holder and rubber/nylon sleeve to prevent from any corrosion by
Carbone dioxide. For CO₂ injection of saturated cores with live oil, first the dead oil is removed by live oil near 1
PV with injection pressure of at least 20 bar higher than the Pₛ live oil. The oil saturated core (with live or dead
doil) was flooded with CO₂ at pressure equal to MMP. CO₂ was flooded into the core at constant pressures of 90
± 0.2, 120 ± 0.2 and 140 ± 0.2 bar for corresponding temperatures of 50, 70 and 80 °C. The pressure of gas is
providing by injection pump. Mass flow meter one measures the inlet flow properties of Carbone dioxide (mass
flow rate, density and total mass). A back pressure regulator is attached to the core to control the pressure during
CO₂ flooding. The outlet flow properties (mass flow rate, density and total mass) of the produced gas/effluent
were determined using flow meter two connected to the separator. The CO₂ injection continued for at least 4 PV
until steady state condition that no extra oil is produced. Finally core was dried using vacuum at a temperature of
120 °C until a constant weight was reached. Flooded cores by CO$_2$ were crushed as powder and dried in oven under vacuum. The asphaltenes precipitated is obtained from the weight of the dried core before the experiments and after the flooding from powdered cores at high temperature and under vacuum. The experimental errors of selected repeated crush cores are within ten percent. It is worth mentioning that the variations of observed asphaltenes precipitation weights are more than this limit.

3. Main Results and Analysis

3.1 Effect of Miscible CO$_2$ Flooding on Asphaltenes Deposition

As CO$_2$ dissolves in the oil, the oil expands and the interfacial tension between oil and CO$_2$ reduces. Light hydrocarbon components can also be vaporized/extracted by Carbon dioxide. Oil composition gradients are developed from the injection inlet until production outlet depending on the mole percentage of injected Carbon dioxide and flooding conditions. To address the effect of the miscible CO$_2$ flooding on the asphaltenes precipitation, it is important to determine the solubility parameter for different oil compositions (live and dead oils) and different flooding conditions. There are a wide spread definition of the solubility parameter (Verdirer & Anderson, 2005). The definition where the cohesive energy is equal to the residual internal energy is used by applying the equation below for liquid solubility parameter. This is adapted in this work to account for pressure and temperature effects.

$$
\delta_L = \left( \frac{U_{vap}(T, P = 0) - U_{liq}(T, P)}{V_{liq}(T, P)} \right)^{1/2}
$$

(1)

Where $U_{vap}$ and $U_{liq}$ are internal energy of vapour and liquid phases respectively and $V_{liq}$ demonstrate the volume of the one mole of mixture and are obtained from Redlich–Kwong equation of state -Peneloux Equation of State, using PVT simulator version Seventeen (2007).

The definition of asphaltene solubility parameter ($\delta_A$) as a function of temperature, by Hirschberg et al. (1984) is used in this work.
At miscible flooding condition of 90 bar and 50°C, a comparison of liquid solubility parameters for dead and live oils is shown in Figure 2 for the different mol% of CO₂ in the liquid. At this flooding condition, asphaltene precipitation is probable. The probability increases with the CO₂ content for both dead and live oil. Live oil #1 (methane with dead oil), shows slightly less difference between δₐ and δₖ at all CO₂ contents compared to live oil #2 (recombined methane and propane with dead oil recombined at same gas oil ratio), indicating asphaltene instability. Kirangkrai et al. (2007) observed similar trend in their study of asphaltene instability in live crude oils. Verdier et al. (2006) reported same observation, where solubility parameter of the liquids decreases with dissolved gas in the liquid. The effect of temperature and pressure is shown for model oil and live oils. The combined temperatures and pressures for miscible flooding of model oil are 50°C/90 bar, 70°C/120 bar and 80°C/140 bar, however, for the live oil, the temperature is kept at 50°C and the pressure changed similar to that for model oil. This is done in order to be within minimum miscibility pressure. The results obtained for the model oil at 50, 70 and 80°C and pressures of 90, 120 and 140 bar are shown in Figure 3 to Figure 5, respectively. For a same CO₂ content, it is shown that the higher the pressure, the higher δₖ is. As CO₂ content less than 10% mole, the asphaltene is stable for combined miscible conditions of 50°C and pressures of 140 and 120 bar (Figure 3). When the temperature is then increased, for CO₂ content less than 10% mole, to 70 and 80°C with pressures 120 and 140 bar, the asphaltene became in the unstable region (Figure 4). However, Figure 5 indicates that asphaltene is in the unstable region for the combined miscibility conditions of 50°C/90 bar, 70°C/120 bar and 80°C/140 bar. On the other hand for the live oil #1 and #2 as shown in Figure 6a and Figure 6b, respectively, in general, same trend as for the model oil is observed. However at all temperature/pressure combinations, the oil lay in the unstable region. It can also be seen that in all cases, increasing pressure increases the asphaltene stability while increasing the temperature reduces the asphaltene stability. The asphaltene stability is related qualitatively to the solubility parameter. This is in agreement with the findings by Verdier et al. (2006).

\[ \delta_x = 20.04 \times (1 - 1.07 \times 10^{-3} \times T(C)) \]  

Figure 2. Comparison between liquid solubility parameter and asphaltene solubility parameter for different types of oil at flooding temperature of 50°C and flooding pressure of 90 bar
Figure 3. Comparison between liquid solubility parameters and asphaltene solubility parameter for model oil at flooding temperature of 50 °C and different flooding pressures.

Figure 4. Comparison between liquid solubility parameters and asphaltene solubility parameter for model oil at flooding pressure of 140 bar and different flooding temperatures.
Figure 5. Comparison between liquid solubility parameters and asphaltene solubility parameter for model oil at different miscibility conditions (T=50 °C/P=90 bar, T=70 °C/P=120 bar, T=80 °C/P=140 bar)

Figure 6. Comparison of liquid solubility parameter and asphaltene solubility parameter at flooding temperature of 50 °C and different flooding pressures for a) live oil #1 and b) live oil #2
3.2. Comparison Between Precipitated and Estimated Asphaltene

Asphaltene deposition is estimated using the model developed by Hamouda et al. (2009) defined by Equation (3). Figure 7a and Figure 7b compare the estimated asphaltene from flooded cores, saturated with different dead and live oil types, at different miscibility conditions.

\[
W_{\text{Model}}(\%) = \frac{W_{\text{TAL}} - W_{\text{AL}}}{V_{\text{TL}} - V_{\text{L}} \cdot \exp \left( \frac{V_{\text{L}}}{V_{\text{L}}} - 1 - \frac{V_{\text{L}}}{RT} (\delta_{\text{A}} - \delta_{\text{L}})^2 \right)} \cdot \rho_{\text{d}} + W_{\text{AL}} \times 100
\]

Where, \( W_{\text{TAL}} \) shows the total asphaltene in the liquid (g), \( W_{\text{AL}} \) is the mass of asphaltene in the liquid phase (g), \( \rho_{\text{A}} \) and \( V_{\text{TL}} \) represents the asphaltene density (g/cm\(^3\)) and the total volume of solution (cm\(^3\)), A and L shows respectively to asphaltene and liquid phase, \( V \) (cm\(^3\)/mol) and \( T \) (K) shows volume of one mole and temperature, \( R \) (MPa.cm\(^3\).mol\(^{-1}\) K\(^{-1}\)) is the gas constant and \( \delta_{\text{A}} \) and \( \delta_{\text{L}} \) (MPa\(^{1/2}\)) are solubility parameters for asphaltene and liquid, respectively. The experimental results for the different cases are shown in Figure 8a and Figure 8b, for sandstone and chalk, respectively. Higher asphaltene deposition corresponds to the higher miscible flooding conditions and presence of the light components (methane and propane), for both types of the cores. This is in line with the indicated results from the solubility parameter curves, where at the aforementioned conditions and presence of light components, the more the risk for precipitation as the difference between \( \delta_{\text{A}} \) and \( \delta_{\text{L}} \) increases. It can also be seen that the amount of asphaltene deposition is higher in the case of chalk compared to sandstone for the same oil type and flooding conditions. This may be due to the difference in the surface area for the two cores. Kozeny-Carman correlation demonstrated that chalk cores have tighter pore throats and larger surface areas compared to that for sandstone cores, where, the surface area changes between one and two m\(^2\)/g while for sandstone cores, the surface area varies between 0.02 and 0.04 m\(^2\)/g. It is attempted here to relate asphaltene deposition induced by miscible CO\(_2\) flooding mechanism to the mixing zone index (I) defined by Equation (4).

\[
I = 3.625 \sqrt{\frac{K_L}{v x}}
\]

In this equation, \( K_L \) is longitudinal dispersion coefficient (m\(^2\)/sec), \( v \) is the one dimensional velocity of the injected CO\(_2\) through core and \( x \) is the length of core.
Figure 7. Comparison between predicted amount of asphaltene deposition for different types of oil at different miscibility conditions ($T=50^\circ C/P=90$ bar, $T=70^\circ C/P=120$ bar, $T=80^\circ C/P=140$ bar) in a) chalk core and b) sandstone core.

Figure 8. Comparison between experimental measured asphaltene deposition for different types of oil at different miscibility conditions ($T=50^\circ C/P=90$ bar, $T=70^\circ C/P=120$ bar, $T=80^\circ C/P=140$ bar) in a) chalk core and b) sandstone core.
Figure 9 compares the mixing zone index at three miscible flooding conditions for both sandstone and chalk cores. The figure shows that miscible bank zone increases as the miscible flooding conditions increase. In other words, surface area and the mixing zone enhance the contact efficiency between the flooding and flooded fluids.

Figure 9. Comparison of mixing zone index for a) chalk and sandstone cores saturated with dead oil b) cores saturated with live oil #1 (with methane and gas oil ratio as 280 ft³/bbl at standard conditions and c) cores saturated with live oil #2 with methane and propane and gas oil ratio as 280 ft³/bbl at standard conditions)
4. Conclusions
An approach to assess the process for asphaltene deposition during the miscible CO\textsubscript{2} flooding is developed. The approach is based on solubility parameters/CO\textsubscript{2} fraction in the liquid. The used solubility parameter of the liquid is defined when cohesive energy is equal to the residual internal energy. The adapted equation accounts for pressure and temperature effects. This approach enables the determination of the critical CO\textsubscript{2} fraction that below it the asphaltene is stable.

Solubility parameters increases with pressure and decreases with temperature. In general, the presence of light components enhances the risk for the asphaltene instability. The comparison between predicted and experimental asphaltene deposition, is in agreement with the trend of the results obtained from the solubility parameters/CO\textsubscript{2} content, where the light components and the higher the miscible flooding conditions, induced asphaltene instability.

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