American Journal of Engineering Research (AJER)	2020
American Journal of Engineering Res	earch (AJER)
e-ISSN: 2320-0847 p-ISS	N:2320-0936
Volume-9, Iss	ue-3, pp-60-67
	www.ajer.org
Research Paper	Open Access

# An Experimental and Numerical Study of Asphaltene-Induced Formation Damage during CO<sub>2</sub> Miscible Flooding

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**ABSTRACT:** Asphaltene precipitation, flocculation, and deposition can significantly reduce oil production by impacting wellbores, flowlines, and more importantly, formations' pore space around the well. Any alteration in the temperature, pressure and fluid composition can trigger asphaltene deposition. The ability to predict the occurrence and magnitude of the asphaltene deposition is a majorstep for flow assurance. An accurate prediction of the deposition envelope enables the operator to systematically categorize different cases based on their impact on the production. This critical knowledge can be used to predict the occurrence and magnitude of asphaltene deposition, which could potentially save the expense of installing unnecessary equipment and injecting chemical inhibitors when they are not needed.<sup>1-3</sup>

Predicting asphaltene-related flow assurance issues requiresrobust physically-based modeling capabilities for capturing the asphaltene's deposition tendencies as a function of the prevailing field's operating conditions. Although available simulators are found to be useful for predicting asphaltene's phase behavior, precipitation tendency, and instability curves, they often overlook important physical characteristics of the asphaltenes. These properties may have a detrimental role in obtaining a realistic representation of the asphaltene deposition behavior.

In this paper, the experimental and the numerical investigations are combined to present a comprehensive methodology for studying the thermodynamics of asphaltene precipitation and deposition. A wide range of pressures and  $CO_2$  concentrations are covered that are relevant to actual  $CO_2$  flooding in Middle East oil reservoir. To do so, a series of lab experiments including routine and special PVT analyses where the asphaltene onset points and saturation pressures were measured for different compositions of the reservoir oil and  $CO_2$  mixtures. Furthermore, detailed recommendations are presented in this paper to tune an EOS for running compositional simulations when unstable asphaltene is reported based on the lab experimental measurements. **Keywords**—Asphaltene, EOS Tuning, Asphaltic Fluid &  $CO_2$  field problems

Date of Submission: 25-02-2020 Date of acceptance: 05-03-2020

### I. INTRODUCTION

Asphaltenes are the polar, poly-aromatic and heaviest hydrocarbon fraction of crude oil that are soluble in light aromatic hydrocarbons and solvents such as benzene and toluene but insoluble in low molecular weight paraffin.<sup>4–7</sup>As a result of reservoir fluid depressurization, asphaltene particles may precipitate followed by aggregation and deposition on the rock surfaces and plug pore throatscausing formation damage(i.e., permeability reduction and wettability alteration). This is because asphaltene deposition could potentially alter the surface wettability towards moreoil-wet conditions impacting oil relative permeability for the near-the-wellbore formation. The injection of different displacing fluid during Enhanced Oil Recovery (EOR) processes could change reservoir fluid composition resulting in the asphaltene flocculation and deposition.<sup>8–10</sup> It is worth noting that a higher content of asphaltene in a reservoir fluid is not necessarily problematiculess it becomes thermodynamically unstable and starts precipitation and flocculation form larger molecules that would easily deposit on the rock surface.

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There are several factors that may lead to asphaltene precipitation and deposition. Along with the reservoir fluid properties and composition as well as the rock mineralogy and pore throat size distribution (PTSD), electro-kinetic effects due to streaming potential generation by means of reservoir fluid flow, asphaltene to resin ratio and the amount of formation brine and its composition, etc. are considered as the potential factors to contribute to formation damage due to asphaltene flocculation that easily proceed towards deposition.<sup>11,12</sup>

The injectivity and productivity of wells areoften altered due to the asphaltene deposition in the formation around the wellbore, within the wellbore, and pipelines and processing facilities used at the surface.<sup>13,14</sup>As mentioned, the alteration of fluid composition near agas injection well ora pressure drawdown near aproducer well could trigger asphaltene precipitation and deposition within the pore space of the formation near the wellbore.<sup>13,15,21</sup>

Gas injection is considered as one of the desired secondary and/ or tertiary recovery methods to minimize the residual oil saturation (Sor), increasing oil recoveries especially in light to medium quality oil reservoirs.<sup>13,21</sup>Several researchers, however, concluded that the miscible and/or immiscible gas injection cause changes in the reservoir fluid composition and hence may result inasphaltene precipitation followed byformation damage. Formation damage due to asphaltene deposition may cause serious production losses because of the reduction in well productivity. Most operators adopt the remedial solutions after evidence of asphaltene precipitation (such as chemical treatment and workover operations) rather than its prevention due to late detection of this problem.<sup>14</sup> The dynamic core-flooding experimental analysis is one of the most effective methods that could be utilized to determine the potential of asphaltene precipitation and deposition in the formation'spore space under reservoir conditions. However, it would never be the exact representation of the reservoir in a controlled and limited environment of a laboratory core scale but the closest lab conditions mimicking the reservoir flow and the thermodynamics will definitely give an idea of the possible asphaltene flow dynamics.<sup>1</sup>

For the dynamic aspects of asphaltene precipitation and deposition in the reservoir, there are several experimental measurements that show the precipitation process, whether it is due to pressure depletion or gas injection, is largely reversible. However, there can be significant hysteresis in the re-dissolution process, i.e. the time required for the asphaltene to dissolve back may be considerably longer than the time required for the original precipitate to form especially after being flocculated.<sup>17,18</sup>

It was observed that reservoirs with asphaltene precipitation issues usually have the following characteristics<sup>19</sup>:

- The in situ reservoir fluid is light to medium grade oil with small asphaltene content.
- The initial reservoir pressure is much higher than the bubble point pressure of the reservoir.
- Maximum precipitation occurs around the bubble point pressure.
- Heavier crudes have less asphaltene precipitation problems as they can dissolve more asphaltene.

Reservoir characterization is one of the most important steps in the modeling of asphaltene precipitation and deposition particularly during the splitting of heavier hydrocarbon components. Several different methods are discussed in the literature for the fluid characterization step. Here in this work, we adopt guidelines of Darabi<sup>20</sup> and Khan<sup>19</sup>. We use a wide range of routine and special PVT experimental data (e.g., bubble point pressures and asphaltene onset pressures (AOP) for different concentration of  $CO_2$  and reservoir oil) to tune the EOS. Asphaltene precipitation is a thermodynamic property of hydrocarbon fluid mixture. Hence, the AOP is a dynamic number that is sensitive to the system pressure, temperature and the overall fluid composition.<sup>1,21</sup>

### II. RESERVOIR FLUID CHARACTERIZATION

Before any compositional simulation, the most essential step is to characterize the reservoir fluid by validatingagainst the corresponding laboratory measurements. In this work, the following set of guidelines are utilized for fluid characterizations to minimize the discrepancy between the simulation results and experimental counterparts. The keyfacts to keep in mind is to use the most suitable Equation of State (EOS), considering an accurate fluid description and to have a robust flash algorithm.

The reservoir fluid characterization procedure includes tuning of all the binary parameters of the EOS to match the experimental data including Bubble Point/ Saturation Pressure, Separator Test, Constant Composition Expansion and Liberation Tests, etc. In addition, SARA contents are oftenused for the Asphaltene and the Resin content in the fluid. AOP and asphaltene onset concentration (AOC) measurements for different operating conditions and injected fluid compositions are most importantly used for the asphaltic reservoir fluid characterization. The amount of precipitation at different temperature and pressure conditions can also be used, if available, for the sake of an extended fluid phase diagram.

The specific guidelines for the non-asphaltic and asphaltic reservoir fluid characterization are relatively simpler and commonly available in the literature i.e. also summarized as given below;

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#### 1.1. Non – Asphaltic Fluid Characterization

- First, we use lumping and splitting procedures for different components of the reservoir fluid. The adopted procedure is listed below:
- 1. Lumpall non-hydrocarbons separately.
- 2. Generate separate groups of  $C_1$ - $C_6$  hydrocarbons.
- 3. Split heavier HCs (C7+) in a way that each pseudo component ends up with approximately similar weight percentage.
- 4. Calculate the critical properties of all pseudo componentsbased on the weighted mean average of each carbon number fraction.

Including non-hydrocarbon components, this procedure usually leads to seven to eight pseudo components in general. This lumping method is very general and the following additional, more specific guidelines have been presented by Khan<sup>19</sup>;

- 1. It's highly recommended to ignore the non-hydrocarbon components with the mole fractions less than 0.005, the only exception to this step is when the non-HC external fluid is being injected into the reservoir.
- 2. It was also advised to lump lighter hydrocarbon components i.e.  $C_1$  to  $C_6$  to be lumped as  $C_1$ ,  $C_{2-3}$ , and  $C_{4-6}$ . However, other combinations are also possible depending on their mole fractions.
- 3. It was also recommended using the following Table 1 as a guideline for splitting of the heavier HCs depending on the  $C_{7+}$  mole fraction.

C <sub>7+</sub> Mole Fraction	No. of Pseudo Components
< 0.05	1
0.05 - 0.4	2
0.4 - 0.6	3
0.6-0.8	4
> 0.8	5

Table 1: The recommended number of pseudo-components as a function of C7+ mole fraction

#### **1.2.** Asphaltic Fluid Characterization

The characterization procedure for the asphaltic fluid includes tuning of all the parameters of the phase behavior model to reproduce the experimental data as close as possible to the lab experimental data. Darabi<sup>20</sup> provided detailed instructions for asphaltic fluid characterization:

- 1. Split the heaviest HC component into heavier fractions. As the reservoir fluid PVT data usually reported commercially up to  $C_{7+}$  fractions. However, the average molecular weight of asphaltene is larger than a typical  $C_{7+}$  component in a mixture, so that the HC components between  $C_{30}$  to  $C_{40+}$  could be a good representation of the asphaltene component.
- 2. Further split the heaviest HC component (e.g.  $C_{47+}$ ) into two sub-components, i.e. a non-precipitating component ( $C_{47+A}$ ) and a precipitating component ( $C_{47+B}$ ). The precipitating component will be referred to as asphaltene. Whereas the properties of both the components wouldbe identical, except for their binary interaction coefficients with the lighter components.<sup>22</sup>
- 3. Decide on the EOS tuning parameters to be used as variables for matching the experimental measurements. In the case of asphaltic oils, the tuning parameters include:
- a. Total number of lumping groups
- b. Binary interaction coefficients (BIC)
- *c*. Volume shift parameters
- *d.* Molar volume of asphaltene.
- 4. Reduce the total number of components by lumping some of the middle components.
- 5. Calculate the phase behavior of the mixture.
- 6. Compare model predictions against the experimental measurements.
- 7. Through a trial and error process, keep modifying the EOS tuning parameters such that the calculated EOS phase behavior matches the measured data with the minimum uncertain error differences that shouldn't be more than 10%.
- 8. In case of unacceptable results, modify the middle order lumped components and repeat the stated above until find a good match with an acceptable error band.

### III. EQUATION OF STATE TUNING

The EOS tuning is performed by matching the lab measurements for the following types of data:

- 1. Routine PVT including CCE and DL tests
- 2. Special PVT including CO<sub>2</sub> swelling and MMP measurement tests
- 3. Asphaltene precipitation and saturation pressures for each oil  $-CO_2$  mixtures with different concentrations

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To perform experiments, dead oil and gas samples were collected from the first stage separator sampling point in the field.

The collected samples were analyzed and recombined under average reservoir conditions on the basis of the Gas Oil Ratio (GOR) measured on bottom hole live oil samples i.e. 220scf/bbl. A single flash separation test was conducted on the recombined oil under atmospheric pressure and temperature conditions.

### 3.1 EOS Tuning with Routine PVT Lab Experiments

Based on the procedure described above, the subject reservoir fluid is characterized by using Peng Robinson Volume Translated (PR - VT).A commercial software was used to simulate routine PVT experiments. The resultsare in good agreements with the lab measurements as shown in Figures 1 and 2 where perfect matchesare obtained for the relative volume and liquid density different operating pressures. Figure 3 depicts a good match for the calculated and measured viscosity values. Also, the liquid formation volume factor and the solution gas-oil ratio are in good agreements with the measured data as shown in figures 4 and 5, respectively.



#### 3.2 EOS Tuning with Special PVT Tests

In the second phase, we have conducted special PVT tests to better understand the thermodynamics of reservoir fluid as a function of pressure and composition. In these tests, the saturation pressures and swelling factors are measured at different  $CO_2$  concentrations. Figure 6 shows that the saturation pressures and swelling factors are both directly proportional to the  $CO_2$  concentrations. Adecent simulated match was obtained using the EOS that was generated in the previous step.

The relative volumes and liquid saturationswere measured at different ratios of  $oil - CO_2$  mixtures and pressures.Figures 7 and 8 show decent agreements between the experimental measurements and the simulated results using the tuned EOS. Similarly, we measured the liquid density and viscosity, and subsequently, compared them against the predicted results of tuned EOS model (see figures 9 and 10). The density matches for all mixtures are in good agreement with their experimental counterparts (within 2-5% error). This is contrary to the viscosity predictions. The model's accuracy for predicting liquid viscosity deteriorates at lower concentrations of  $CO_2$ . This discrepancy could be as large as 5-10% which is still acceptable for our purposes.



Comparison of the Fig. 6. measured and the predictedSaturation PressureandSwelling Factor during





Comparison of the measured and the Fig. 9. predictedDensity vs. Pressure for several CO<sub>2</sub> mixtures at T<sub>res</sub>



Comparison of the

Mixtures atTres

Fig. 7.



Comparison of the Fig. 8. measured and the predictedLiquid Saturation vs. Pressure for several Oil-CO<sub>2</sub> Mix. at T<sub>res</sub>



Comparison of the measured and the Fig. 10. predictedViscosity vs. Pressure for several CO<sub>2</sub> mixtures at T<sub>res</sub>

#### 3.3 Tuning of the EOS using Asphaltene Onset Measurements

For an asphaltic fluid, the last phase of the thermodynamic characterizations is to tune the BICs, volume shift parameters, and molar volume of the asphaltene. We consider the fact that the BICs of asphaltene and the lighter hydrocarbon components are oftenhigher due to the larger difference in their molecular structures. All parametersare tuned using atrial-and-error procedure to minimize the discrepancy with the measured experimental data.

Fig. 11 shows an excellent match of the saturation pressure and the asphaltene onset pressures at various CO<sub>2</sub> concentrations under reservoir temperature and pressure conditions.it is worth mentioning that the EOS of this work is only tuned using  $CO_2$  as an injectant fluid so it might not work accurately for other HC or non-HC injectant gases.

The asphaltene precipitation envelops for different concentrations of  $oil - CO_2$  mixtures are shown in Figure 12. For each data set, the lowest pressure represents a sphaltene's onset point. The peaks of the curves correspond to the saturation pressures. The highest pressure for any curve represents the asphaltene offset point. For example, reservoir oil with 50% of  $CO_2$  mole fraction represented by the red curve, shows the asphaltene onset pressure of about 1600 Psi, saturation pressure at 2150 Psi, and the offset pressure at 4400 psi. To put numbers in perspective, the case with 0% CO<sub>2</sub> shows a negligible amount of precipitation which is almost considered as no asphaltene activity, i.e., thermodynamically stable in the absence of CO<sub>2</sub>phase.

A couple of important observations aremade:

- As CO<sub>2</sub> mole fraction increases the saturation pressure rises constantly
- The presence of  $CO_2$ shifts the entire asphaltene precipitation envelop towards higher pressure and at the same time, it expands the asphaltene instability region to a large extent.







Asphaltene Precipitation Envelopat Fig. 12. DifferentCO2 Mole Fractions at Tres

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### IV. PROOF OF EQUATION OF STATE VALIDATION

The tuned EOS was subsequently used to simulate the actual CO<sub>2</sub> core flooding experiment conducted under reservoir conditions. For this experiment, we used a composite core sample consisting of 4 different core plugs with similar rock properties wrapped by a shrinkage tube. The dimensions of the composite core were  $0.716 \times 0.125 \times 0.125$  ft<sup>3</sup>. Table 2 summarizes the properties of the composite core sample and simulationparameters. We measured the porosity and permeability of one of the rock samples (i.e., 25% and 4.725 mD). For simulation, we used these measured values as the mean values of distributions along the main flow direction of the composite core sample (see Figs. 13 and 14). The simulations were done using a nonisothermal dynamic compositional academic reservoir simulator. In the laboratory, CO<sub>2</sub>was injected with a constant flow rate from the inlet. A back pressure regulator was used at the outlet to keep the outlet pressure constant. Same boundary conditions were implemented in our simulation.

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Parameters	Value
No. of grid-blocks	$20 \times 1 \times 1$
Composite Core Dimension	$0.716 \text{ ft.} \times 0.125 \text{ ft.} \times 0.125 \text{ ft.}$
Temperature	212 °F
Pressure	3000 Psi
Initial Water Saturation	0.20
Average Composite Porosity	0.25
Average Composite Permeability	4.725 mD
Injection Fluid	$CO_2$
Inlet Conditions	Fixed Inj. Rate = $0.1 \text{ cc/min}$
Outlet Condition	Fixed Outlet pressure $=$ 3000 Psi



Fig. 13. Porosity Distribution Used for Simulation Purposes



Fig. 14. Permeability Distribution Used for Simulation Purposes

More detail of the core flood design is provided by Syed<sup>1</sup>. In the lab, two different types of data were collected, i.e., total oil recovery versus time and differential pressures along the length of the composite core. The latter was collected by using multiple pressure taps along the core holder. At the end of the experiment, 4 pore volume of  $CO_2$  was injected resulting in an oil recovery of almost 85% (Fig. 15).

We tuned the relative permeability endpoints to match the core-flooding experimental measurements specifically oil recovery and GOR. As shown in Fig. 15, the model successfully captures the experimental measurements of oil recovery as a function of cumulative injected CO<sub>2</sub>. Moreover, the GOR is within  $\pm 10\%$  of the experimental data, as shown in Fig. 16. Figs. 17 through 19 depict the oil saturation distribution at different pore volumes of the injected CO<sub>2</sub>. The inhomogeneity of rock properties along the main flow direction caused a considerable amount of oil to be trapped in the middle of the core. The distributions of asphaltene precipitation and deposition along the core are shown in Figs. 20 and 21 for different PVs of the injected CO<sub>2</sub>. At the beginning ofCO<sub>2</sub> injection, most precipitations occur close to the injector side. As the CO<sub>2</sub> penetrates deeper into the core, it causesdeeper precipitations towards the producer side.

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Fig. 20. The concentration of Precipitated Asphaltene after 1 PV of  $CO_2$  injection

**Fig. 21.** The concentration of Precipitated Asphaltene after 2 PV of CO<sub>2</sub> injection

### V. SUMMARY & CONCLUSION

A complete suite of experimental dataset covering the routine and special PVT analysis as well as asphaltene onset pressure for different compositions of the reservoir oil with  $CO_2$  is presented. A fluid characterization procedure is explained in details for an asphaltic and non-asphaltic reservoir oil; and subsequently, at experimental measurements of a  $CO_2$  flooding experiment performed on a long composite core sample. The predicted results were found to be in a good agreement with the actual core-flooding measurements. This work can be further expanded by designing a 3D sector model to specifically characterize contributions from different parts of the reservoir (i.e., wellbore, near-wellbore, and deep into the reservoir formation).

#### ACKNOWLEDGMENTS

The authors would like to thank ADNOC Offshore, UAE and the Department of Chemical and Petroleum Engineering, University of Kansas, USA for providing their support and permission to publish this work.

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#### NOMENCLATURE

- AOC Asphaltene Onset Concentration
- AOP Asphaltene Onset Pressure
- BICs Binary Interaction Coefficients
- CCE Constant Composition Expansion Test
- DL Differential Liberation Test
- EOS Equation of State
- HCs Hydrocarbons
- PR-VT Peng Robinson Volume Translated
- PTSD Pore Throate Size Distribution
- S<sub>or</sub> Residual Oil Saturation

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Fahad I. Syed, ET. Al " An Experimental and Numerical Study of Asphaltene-Induced Formation Damage during CO<sub>2</sub> Miscible Flooding". *American Journal of Engineering Research* (*AJER*), vol. 9(03), 2020, pp. 60-67.

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