Effect of Carbon Dioxide on Paraffinic Bitumen Froth Treatment: Asphaltene Precipitation from a Commercial Bitumen Froth Sample

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ABSTRACT: In this study, the effect of carbon dioxide in assisting paraffinic bitumen froth treatment was investigated. The work was divided into two parts, the effect of water addition on CO2-assisted asphaltene precipitation from a dry and clean bitumen sample by n-heptane and the effect of CO2 injection to a mixture of n-heptane and a commercial bitumen froth sample. It was found that water addition to the dry and clean bitumen improved the beneficial effect of CO2 on promoting asphaltene precipitation by n-heptane, where asphaltene precipitation increased by 2.5 percentage points (or 19%) with the presence of water and CO2. The asphaltene precipitation enhancement may be due to chemical reactions between injected CO2 and water in the formation of carbonic acid in the aqueous phase, which destabilized asphaltene. On the other hand, no improvement was detected under the control tests (N2). Similar results were observed in the case of CO2 injection to paraffinic solvent (n-heptane) treatment of the commercial bitumen froth sample. The results indicated that when the commercial bitumen froth sample was mixed with n-heptane at a solvent/bitumen ratio of 1.08, the injection of 1.7 MPa CO2 increased the amount of precipitated asphaltene from 10.0 ± 0.1% (without CO2) to 15.2 ± 0.2% (with 1.7 MPa CO2) at 90 °C, indicating a potential reduction of solvent usage by about 66%.

KEYWORDS: carbon dioxide, bitumen froth treatment, paraffinic solvents, asphaltene precipitation, bitumen, water, mechanism

1. INTRODUCTION

The objective of this study was to prove the concept of using CO2 to assist in paraffinic bitumen froth treatment (PFT) to improve the performance of PFT and to decrease the usage of the paraffinic solvent. In our previous publication,1 we studied the effect of CO2 on asphaltene precipitation from a dry and clean bitumen–heptane mixture under moderate pressures (0.1 to 1.7 MPa) and temperatures (21 and 90 °C) at 52 wt % n-heptane concentration. The 52 wt % n-heptane in the n-heptane–bitumen mixture represented a solvent/bitumen ratio of 1.08, which was found to be the onset of asphaltene precipitation from the tested dry and clean bitumen sample that was free of water and mineral solids.1 To ensure the accuracy of the onset of asphaltene precipitation, two different techniques were used for validation, (1) the gravimetric method (inside an autoclave) and (2) optical microscopy.1 Asphaltene precipitation was detected at 52 wt % n-heptane concentration or a solvent/bitumen ratio of 1.08.1 Furthermore, no asphaltene precipitation was spotted at 45 and 50 wt % n-heptane concentration for both CO2 injection and the control test (N2) at 0.1 MPa. The initial asphaltene precipitation at 52 wt % n-heptane concentration was detected for 8.3 wt % of the mass of bitumen with no difference between CO2 and N2 injection.1 The increase in the concentration of the paraffinic solvent (n-heptane) from 52 to 80 wt % increased asphaltene precipitation. Similar results were observed by other researchers.2–5 For example, our results
indicated that participation of 10 wt % of asphaltene requires a solvent to bitumen ratio of 1.6 at 0.1 MPa. In general, asphaltene is a complex component of bitumen and its chemical structure is still in debate, and many factors can cause or influence asphaltene precipitation, including temperature, pressure, and even the chemical composition of oil.2,5

The results showed that at 21 °C and 52 wt % n-heptane concentration, CO2 injection at 1.7 MPa pressure increased the collected precipitated asphaltene by 55%, from 8.3 ± 0.1 to 12.9 ± 0.2 wt %. In control tests where N2 was injected instead of CO2, asphaltene precipitation yield remained unchanged at 8.3 wt %.6 Our results indicated that even at low CO2 pressure, CO2 injection could assist the paraffinic solvent (n-heptane) to enhance asphaltene precipitation in paraffinic froth treatment. The mechanism of CO2 and asphaltene precipitation is still a bit unclear.2,6,7 Some of the mechanisms beyond CO2 that could disturb the equilibrium conditions of bitumen to cause asphaltene precipitation are as follows:2,6 (1) even a small amount of CO2 in bitumen could change the solubility parameter of the liquid media and lead to asphaltene precipitation,6 (2) a similar role to the paraffinic solvent removes resins from the asphaltene surface, and CO2 injection can remove resins as well,6 (3) the increase in the interfacial energy between liquid/gas interfaces during CO2 injection, which the system needs to decrease the interfacial energy, thus causes asphaltene molecules to precipitate,8 and (4) the formation of amide functional groups upon CO2 injection, which may lead to asphaltene precipitation.11 The study by Dong et al. suggested that even at a relatively low-pressure range, the solubility of CO2 in the oil phase is high enough to decrease the viscosity of the heavy oil.10 Second, CO2 can precipitate the most polar asphaltene in diluted bitumen, leading to a significant weakening of the viscoelastic asphaltene film built at interfaces between water and oil in the emulsion.12 Finally, the CO2 can dissolve in oil and interact with asphaltenes and cause noncovalent intermolecular complex molecules, leading CO2 to compete with resins and follow-on asphaltene precipitation.8

Commercial bitumen froth differs from the dry and clean bitumen in that it contains water and mineral solids. It is desirable to understand how these components in bitumen froth affect the process. In general, the stability of asphaltene in crude oil depends on pressure, temperature, and the composition of the crude oil.6 Any changes in these parameters in the crude oil could disturb the stability of asphaltene, leading to asphaltene aggregation, precipitation, and deposition.13,14

The application of CO2 in the petroleum industry has gained considerable interest especially in enhanced oil recovery (EOR).9,10,13,17 It has been shown that when CO2 is dissolved in oil, it reduces oil’s viscosity, and it tends to be completely miscible with crude oil.18 However, one of the most troublesome problems in CO2-EOR is asphaltene precipitation. The injection of CO2 leads to severe asphaltene precipitation in the reservoir and other production equipment.19–21 From this perspective, CO2 can assist paraffinic solvents, changing the composition of oil and inducing asphaltene to precipitate in a good way. In more detail, the whole idea beyond paraffinic froth treatment causes asphaltene to precipitate using paraffinic solvents (i.e., n-heptane) to produce a very clean bitumen product. When CO2 is dissolved in crude oil, even at low concentration, the crude oil swells and its viscosity is reduced while causing asphaltene to precipitate.18 Dong et al. designed a novel demulsification treatment process for high pH water-in-oil (w/o) emulsions, using both low-pressure CO2 (0–700 kPa) and demulsifiers, and they reported an increase in the demulsification efficiency with the increase of CO2 pressure.22 This implied that the solubility of CO2 even in the low-pressure range was good enough for causing asphaltene precipitation.23 Considering the satisfactory performance of CO2 in EOR and w/o emulsion breaking, we thought that it should be a practical idea to use CO2 as a processing aid to promote asphaltene precipitation in PFT.17,23,24

In both CO2-EOR and PFT systems, a noticeable amount of water is present. For example, bitumen froth contains a high concentration of water (up to 40 wt %) and mineral solids (up to 15 wt %).7,25 Research has been reported on the impact of water addition on asphaltene precipitation in crude oil. As water comes into contact with the crude oil, a fraction of asphaltene tends to move from the bulk of the crude oil to the oil/water interface, changing the interfacial tension and causing asphaltene to precipitate. On the other hand, the results from Tharanivasan et al. showed that the presence of water had no detectable effect on the solubility of asphaltene in crude oil, and no impact on asphaltene precipitation in the presence of water was detected.26

Research conducted by Zaki et al. on the impact of water on asphaltene precipitation for CO2-EOR indicated that the amount of asphaltene precipitates in the presence of water was higher than that in the absence of water.27 Similarly, Dong et al. suggested that even in the low-pressure range, the solubility of CO2 in the oil phase is sufficiently high to decrease the viscosity of the heavy oil, resulting in the accelerated coalescence of water droplets.28 Moreover, CO2 dissolved in water reacts with heavy oil to generate organic acid to displace the adsorbed film at the oil/water interface.29 The dissolution of CO2 in water under moderate pressure and temperature causes the formation of carbonic acid, and the carbonic acid ionizes into a proton and bicarbonate ions, lowering pH in the aqueous phase.29,30

\[ \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \] (1)

The decrease in pH in the aqueous medium may cause a decrease in asphaltene stability at the oil/water interface leading to asphaltene precipitation.

Other possibilities have also been reported in the literature regarding the influence of water on asphaltene aggregation.31,32 First, solubilized water in heavy oil may affect asphaltene precipitation by affecting asphaltene self-association.33 Andersen et al. performed calorimetric measurements of asphaltene association and found that the amount of water contained in asphaltene solution changed the amount of heat absorbed, indicating that water could interact with asphaltene, which may impact their aggregation.33 Second, water molecules can promote asphaltene association due to their small size and high intrinsic polarity.34 Murghich et al. demonstrated this effect by conducting molecular simulation studies of asphaltene aggregation with and without trace amounts of water.35 They showed that water may form bridging hydrogen bonds between the heteroatoms of asphaltene molecules.

There has been a lack of research on the impact of CO2 injection on asphaltene precipitation in PFT. The objective of this study was to investigate the impact of water on asphaltene precipitation in CO2-assisted paraffinic froth treatment. All the experiments were conducted using n-heptane at a set n-heptane/bitumen weight ratio = 1.08. The impact of CO2
injection on asphaltene precipitation was compared with nitrogen (N$_2$) injection as control.

2. RESULTS AND DISCUSSION

In this section, the influence of water addition on CO$_2$-assisted PFT using a dry and clean bitumen sample and the effect of CO$_2$ injection in a mixture of $n$-heptane and a commercial bitumen froth sample were discussed. Furthermore, to validate the results of asphaltene precipitation, two sets of tests were performed (Section 3.3.1).

2.1. Effect of Water on Asphaltene Precipitation from $n$-Heptane–Bitumen Solution. Figure 1 shows the effect of water addition (to 20.2 wt % water in the bitumen + water mixture) on the asphaltene precipitation at an $n$-heptane/bitumen ratio of 1.08, with an injection of 1.7 MPa of either CO$_2$ or N$_2$ at 90 °C. As can be seen, with the injection of N$_2$, the addition of water did not cause any difference in the weight yield of the precipitated asphaltene, which remained at 10–10.1 wt % with or without water. However, with the injection of CO$_2$, the weight yield of asphaltene precipitates was increased from 12.8 ± 0.1 wt % in the absence of water to 15.3 ± 0.2 wt % in the presence of the 20.2 wt % water. This indicates that the presence of water had a positive effect on asphaltene precipitation with an increase of 2.5 percentage points of precipitated asphaltene (or 19%). Although the mechanisms behind this phenomenon were still unclear, the result was consistent with the work of Zaki et al.,$^{12}$ who showed that the amount of asphaltene precipitation in the presence of water was higher than that in the absence of water, by comparing the precipitated asphaltene yields induced by the only CO$_2$ (without $n$-heptane) at 25 °C and 1000 psi (6.9 MPa).$^{12}$ The main reason behind this observation was likely
because asphaltene molecules were concentrated at the w/o interface and were thus in a higher degree of association than the asphaltene in the bulk phase. Another possibility was that the dissolved CO₂ in water promotes the coalescence of water droplets along with accumulated asphaltene at the w/o interface, as proposed by Zaki et al. The presence of water may also affect the asphaltene precipitation by impacting the aggregation behavior and generating bridging hydrogen bonds with asphaltene molecules. Finally, the enhancement in asphaltene precipitation in the presence of CO₂ and water may due to the formation of carbonic acid that decreases the pH of the aqueous media, leading to asphaltene destabilization at the oil/water interface and asphaltene precipitation.

2.2. Commercial Bitumen Froth Sample. Figure 2 shows the weight yield of asphaltene from the commercial bitumen froth sample when it was treated with n-heptane at an n-heptane/bitumen ratio of 1.08 at 90 °C with or without the injection of 1.7 MPa CO₂. Unlike the dry and clean bitumen, bitumen froth consisted of water and mineral solids so that the amount of the precipitated asphaltene could not be determined by the filtration method. As a result, Dean–Stark analysis was used to determine the quantity of precipitated asphaltene. Figure 2 shows asphaltene precipitation determined by Dean–Stark analysis, and the precipitates were obtained by reacting the bitumen froth sample at the set pressure of 1.7 MPa CO₂ or N₂ and a temperature of 90 °C in the presence of n-heptane. The toluene extraction in the Dean–Stark procedure treatment of the dried sediments (a mixture of precipitated asphaltene + mineral solids) allowed the separation of precipitated asphaltene from mineral solids.

The results show that the injection of CO₂ to bitumen froth had a similar influence on asphaltene precipitation by n-heptane as the addition of water (20.2 wt %) to the dry and clean bitumen. On the other hand, tests under an N₂ atmosphere (control tests) showed no impact of the nitrogen gas on asphaltene precipitation from the bitumen froth at an n-heptane/bitumen ratio of 1.08. The results also seemed to indicate that mineral solids in the bitumen froth samples had no impact on asphaltene precipitation yield.

Finally, to validate the experimental results, the second set of tests was performed on the asphaltene content in the bitumen remaining in the supernatant phase (un-precipitated asphaltene). The difference between the total asphaltene (ASTM D3279–12 method using n-heptane) and asphaltene content in the supernatant phase bitumen was equal to the precipitated asphaltene presented in this paper (results not shown).

2.3. CO₂-Assisted Asphaltene Precipitation and Solvent Saving in PFT. The foregoing description showed that CO₂ injection under moderate pressure (1.7 MPa) and temperature (90 °C) can be used effectively as an additive in PFT to lower the amount of paraffinic solvents required to induce asphaltene precipitation. Figure 3 shows the positive influence of CO₂ to reduce paraffinic solvent usage in PFT. The control tests (N₂ + n-heptane) were performed at 0.1 MPa and 21 °C.

Figure 3 shows that under the control experiment (N₂ + n-heptane), to precipitate 12.8 wt % asphaltene, the n-heptane concentration needed to be 70.4 wt % (i.e., an n-heptane/bitumen ratio of 2.38). The same asphaltene precipitation yield (12.8 wt %) could be achieved by using only 52 wt % n-heptane (i.e., n-heptane/bitumen ratio of 1.08) with the injection of CO₂ at 1.7 MPa.

In the case of the commercial bitumen froth sample, the asphaltene precipitation yield in the CO₂-assisted process was 15.2 wt % at an n-heptane/bitumen ratio of 1.08 at 1.7 MPa CO₂ and 90 °C. To achieve a similar result under control tests (when N₂ was used instead of CO₂), the n-heptane concentration needed to be raised to 76.9 wt % (n-heptane/bitumen ratio of 3.20). Thus, by using CO₂ in the n-heptane treatment of the bitumen froth, the solvent usage could be reduced by 66.2%.

The typical industrial PFT process uses a solvent/bitumen ratio of 1.2–1.6. This paper showed that by using 1.7 MPa CO₂, asphaltene precipitation could be achieved at an n-heptane/bitumen ratio of 1.08, much lower than the high n-heptane/bitumen ratios that were required without CO₂. Therefore, if a hypothetical PFT plant was using an n-heptane/bitumen ratio of 1.6, then the solvent saving would be about 33% because the same amount of asphaltene precipitation could be achieved at a solvent/bitumen ratio of 1.08 by injecting 1.7 MPa CO₂.

Figure 3. Positive impact of CO₂ on asphaltene precipitation. The (X), (O), and (—) show the asphaltene precipitation achieved at an n-heptane/bitumen ratio of 1.08 at 1.7 MPa CO₂ and 90 °C for CO₂—Bitumen, CO₂—Bitumen—Water, and CO₂—Bitumen Froth, respectively.
3. EXPERIMENTAL SECTION

In this section, the experimental procedures were described to study the impact of water on the amount of precipitated asphaltenes in CO2-assisted asphaltene precipitation in paraffinic solvent–clean bitumen mixtures and on a commercial bitumen froth sample. The tests were repeated at least three times, and the standard deviations of the precipitated asphaltenes were observed to be between ±0.09 and ±0.16 wt %.

3.1. Materials. The bitumen froth sample was collected from an oil sands mine in Fort McMurray in northern Alberta, Canada. The sample contained 65.2 wt % bitumen, 20.2 wt % water, and 14.6 wt % mineral solids, determined by Dean–Stark analysis. The paraffinic solvent (n-heptane) was purchased from Fisher Scientific with 99 + % purity. The nitrogen gas (99.9% purity) and carbon dioxide (99.9% purity) were purchased from Praxair. The total asphaltene content in the bitumen was measured by using the standard ASTM D3279–12 method using n-heptane as the solvent.

3.2. Experimental Setup. The same autoclave setup from our previous publication for the asphaltene precipitation tests was used in this work.1 It consisted of a Parr autoclave (4560 Mini Bench Top Reactor, Parr Instrument Company), temperature controller, and pressure readout. The autoclave had two sampling tubes (1/4 in. inner diameter stainless steel), one for injecting the solvent n-heptane by pressurized CO2 or N2 and the other for output collection (i.e., precipitated samples). The total volume of the autoclave was 450 mL, and it was equipped with a mechanical impeller.

3.3. Bitumen or Bitumen Froth Treatment Using CO2. To study the effect of water on asphaltene precipitation, experiments were conducted by adding water to a dry and clean bitumen (20.2 wt % distilled water +79.8 wt % dry and clean bitumen) or testing directly on the commercial bitumen froth sample. In all the experiments, the impact of CO2 injection on asphaltene precipitation was compared with the control test (N2 + n-heptane).

To prepare the dry and clean bitumen, the commercial bitumen froth sample was mixed with four volumes of toluene and centrifuged at 2826 relative centrifugal force (RCF) for 1 h to separate the supernatant (i.e., bitumen in toluene). To remove mineral solids, the supernatant was centrifuged again at 10,000 RCF for 1 h. The toluene-diluted bitumen was then dried in a rotary evaporator at 50 °C and 1 kPa vacuum pressure for 5 h followed by vacuum oven drying for 7 days to remove toluene. The total asphaltene content in the dry bitumen and bitumen froth was measured using the standard ASTM D3279–12 method using n-heptane; the total asphaltene was equal to 19.1 ± 0.05 wt %.

3.3.1. CO2-Assisted Asphaltene Precipitation from Dry and Clean Bitumen in the Presence of Water. For experiments on mixtures of the dry and clean bitumen and distilled water, about 20 g of accurately weighed (NewClassic ME Analytical Balance, Mettler Toledo, accuracy 0.0001 g) bitumen was added to a beaker followed by the addition of distilled water (to a concentration of 20.2 wt % water in the bitumen–water mixture) and n-heptane (to an n-heptane/bitumen ratio of 0.43). The solution was then premixed with a magnetic stirrer for 20 min before transferring to the autoclave. After transferring the diluted bitumen into the autoclave, the autoclave was sealed, and the air inside the autoclave was removed by purging with CO2 or N2. After outgassing, more n-heptane was added from the input sampling cylinder into the autoclave by the regulated CO2 (or N2) pressure to reach the set n-heptane/bitumen ratio of 1.08. The diluted solution was mixed at the maximum stirring speed (630 rpm) in the autoclave for the duration of the experiment.

The experiments were conducted at moderate pressure (1.7 MPa) and temperature (90 °C) for 20 min. The autoclave was pressurized first with CO2 (or N2); then, the temperature was increased by using heating elements incorporated in the autoclave. The final pressure after increasing the temperature was higher than the stated value (1.7 MPa), but the partial pressure of the CO2 or N2 remained unchanged at the stated value of 1.7 MPa. The increased pressure (higher than the stated value—the total pressure at 90 °C was 2.1 MPa) was contributed by the vapor pressures of the solvent and water. At the end of the experiment, the precipitated asphaltenes at the bottom of the autoclave were collected into the output cylinder. The collected sample was filtered using a 0.45 μm pore size filter paper and dried in a vacuum oven at 50 °C till all solvent was removed completely. The weight of the asphaltene was recorded. It is important to note that the second set of tests was also performed on the measurement of remaining asphaltenes (un-precipitated asphaltene) in the bitumen (the supernatant phase). At the end of the experiment, the supernatant bitumen was collected from the top of the autoclave. n-Heptane was added to cause the remaining asphaltene (un-precipitated asphaltene) to precipitate (the standard ASTM D3279–12 method). Similar to before, the precipitated asphaltene was measured by performing filtration (using a 0.45 μm pore size filter paper—Millipore .45 Micron Mixed Esters of Cellulose Filter Paper) and dried in a vacuum oven at 50 °C till all solvent was removed completely. The difference between total asphaltene and remaining asphaltene (second set tests) in the supernatant bitumen was equal to the recorded precipitated asphaltene after CO2-assisted PFT.

3.3.2. CO2-Assisted Asphaltene Precipitation from Commercial Bitumen Froth. About 50 g of accurately weighed commercial bitumen froth samples was premixed with n-heptane (at an n-heptane/bitumen ratio of 0.43) in a beaker. The change in the initial weight from 20 g (bitumen) to 50 g (bitumen froth) is because bitumen froth contains about 65.2 wt % bitumen. In addition, handling bitumen froth is much more difficult compared to dry bitumen. Thus, more commercial bitumen froth samples were used to represent the experimental results. The diluted bitumen froth was transferred to the autoclave, and air was removed by purging with CO2 or N2. Afterwards, more n-heptane was added to reach the set n-heptane concentration (S/B = 1.08). The bitumen froth treatment was performed at the set pressure (1.7 MPa) and temperature (90 °C) for 20 min. Since the commercial bitumen froth sample contained mineral solids, the filtration method to determine the amount of precipitated asphaltene in the dry and clean bitumen case would not work. Thus, at the end of the autoclave run, a sample from the bottom of the autoclave was collected by depressurizing the autoclave and transferring the sample to a beaker. To determine the amount of precipitated asphaltene, the collected sample was transferred to a Teflon bottle (centrifuge bottles made with Teflon, Nalgene, 250 mL) and centrifuged at 15,000 RCF for 1 h. The centrifugation allowed the sedimentation of the precipitated asphaltene together with mineral solids. After centrifugation, the sediments were...
collected and dried in a vacuum oven at 50 °C until all solvent was evaporated.

As the dried sediments were a mixture of precipitated asphaltene and mineral solids, Dean–Stark analysis was performed to separate the precipitated asphaltene from mineral solids to determine the weight of precipitated asphaltene.

4. CONCLUSIONS
In this research, the effect of CO₂ injection in PFT was studied to reduce the amount of paraffinic solvent (i.e., n-heptane). The experiments were conducted at moderate pressure (1.7 MPa) and temperature (90 °C).

(1) Mixing water to a dry and clean bitumen sample (to 20.2 wt % water) increased the amount of precipitated asphaltenes when CO₂ was used. At an n-heptane/bitumen ratio of 1.08, 90 °C, and a CO₂ pressure of 1.7 MPa, the addition of 20.2 wt % water increased the collected asphaltene precipitates from 12.8 w% (without water) to 15.3 wt % (with water).

(2) Similarly, at 90 °C and 1.7 MPa, CO₂ injection into a commercial bitumen froth sample, which contained 20.2 wt % water, increased the amount of precipitated asphaltene from 8.3 to 15.2 wt %. Control tests in which 1.7 MPa N₂ was injected had no impact on asphaltene precipitation. Note that the dry and clean bitumen mentioned in (1) was generated from the commercial bitumen froth sample.

(3) To achieve 15.2 wt % asphaltene precipitation using n-heptane alone at 90 °C from the same bitumen froth sample without CO₂, the required n-heptane concentration would be 76 wt % (solvent/bitumen ratio of 3.20). Therefore, using 1.7 MPa CO₂ could lead to a solvent saving of 66%.

(4) The practical conclusion was that the desired degree of asphaltene precipitation could be achieved at the onset solvent/bitumen ratio when CO₂ was used. With the tested bitumen froth sample and using n-heptane as the solvent, the onset solvent/bitumen ratio was found to be 1.08. To achieve the desired amount of asphaltene precipitation, a higher solvent/bitumen ratio was likely not necessary, and it could be kept at 1.08 by varying the pressure of injected CO₂.

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Notes
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