
IOSI PROJECT FINAL REPORT

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EXECUTIVE SUMMARY

This two-year proof-of-concept project was carried out between May 1, 2018 and April 30, 2020 at a total budget of \$182,840, with 50% being contributed by IOSI, and 50% from NSERC through a CRD matching grant. A postdoc and an MSc student were recruited and worked on the project, and the MSc student obtained the MSc degree at the conclusion of the project.

A bitumen froth sample, containing 65% bitumen, 20% water and 15% fine solids was obtained from Kearl Mine of Imperial. Before using the bitumen froth sample in a simulated PFT process with and without CO₂ injection, a solids-free-water-free dry bitumen was prepared from the bitumen froth and used as model bitumen to test the conditions of the CO₂-assisted PFT. Heptane was used as the solvent due to its higher boiling point compared with hexane and pentane.

The first step of the research involved an accurate determination of the solvent/bitumen (S/B) ratio that corresponded to the onset of asphaltene precipitation. This was done by a gravimetric method coupled with microscopic observation. The onset was found to be at S/B = 1.08, or 52 wt% heptane in a heptane-bitumen mixture. At the onset, the asphaltene precipitate yield was 8.3 wt%.

At the onset S/B ratio of 1.08, the injection of 1, 1.4, 1.7 MPa CO₂ at either 21°C or 90°C was found to increase asphaltene precipitate yield. The yield increased with CO₂ pressure, so that at 1.7 MPa CO₂, the asphaltene yield was increased to 12.8 wt%, at both 21°C and 90°C. Control tests in which N₂ was injected indicated that the yield did not change with increasing N₂ pressure.

Tests on the bitumen froth sample indicated the same beneficial effect of CO₂ injection. The 20% water content in the bitumen froth sample was found to further increase asphaltene precipitation (this was observed from testwork in which water was added to the dry bitumen). At S/B = 1.08, 90°C, and 1.7 MPa CO₂, the yield of asphaltene precipitate was found to be 15.2 wt%, which was 7 percentage points higher than without CO₂.

Interestingly, when CO₂ was injected at S/B = 1 (i.e., below onset of asphaltene precipitation), it did not help induce asphaltene precipitation, up to the highest pressure tested (1.7 MPa).

Preliminary study was carried out to characterize the bitumen and asphaltene before and after the PFT treatment involving the use of CO₂. The results were inconclusive although they seem to hint on the removal of a particular sub-fraction of asphaltene, possibly with higher sulfur content, when CO₂ was used.

The practical implication of this proof-of-concept research was that by injecting moderate pressure CO₂, the desired asphaltene precipitation yield could be achieved at the onset S/B of asphaltene precipitation, without the need of adding more solvent. Therefore the potential savings in solvent dosage can be significant. For example, in the tested heptane-bitumen froth sample in this project, to achieve an asphaltene precipitate yield of 15.2 wt% without CO₂, the S/B ratio needed to be 3.3. Therefore, by using 1.7 MPa CO₂, the solvent dosage could be reduced by 67%. ■

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1 INTRODUCTION

1.1 Project Concepts

Warm water extraction of Alberta oil sands produces a bitumen froth that contains about 50 to 60 wt% bitumen with a high concentration of water (as much as 40 wt%) and mineral solids (up to 15 wt%). The mineral solids are the fine-grained minerals with particle size smaller than 44 μm , the majority of which are clay minerals,[1] including kaolinite and illite in addition to small amounts of montmorillonite and chlorite, as well as heavy minerals such as pyrite, zircon, and rutile.[2] The produced bitumen froth needs to be cleaned (by removing water and mineral solids) before the bitumen can either undergo on-site upgrading to convert to synthetic crude oil (SCO) or transport via pipeline to refineries that process the bitumen directly, depending on the froth treatment process used.[3] The final bitumen product has to contain less than 0.5 vol% total mineral solids and water and must have a viscosity of lower than 350 cP (e.g. SCO or bitumen + diluent) to transport via pipeline.[3–5]

In general, the bulk water and the relatively coarse solids can be easily removed from the bitumen froth, but the ultra-fine solids and emulsified water droplets are more difficult to remove.[3,6–8] These need to be removed because the ultra-fine solids can block and damage the catalysts in downstream oil production processes, and the emulsified water contains dissolved salts such as sodium chloride, which can cause corrosion problems.[6]

Current practice in bitumen froth treatment is by adding a light hydrocarbon solvent to dilute the bitumen which reduces the density and viscosity of the bitumen. The diluted bitumen can be separated from water and fine and ultra-fine solids using gravity separation or centrifugation.[3,9]

Depending on the type of solvent being used, there are two bitumen froth treatment techniques. Naphthenic froth treatment (NFT) is a process in which a naphthenic solvent, such as naphtha, is used, whereas, in paraffinic froth treatment (PFT), a paraffinic solvent such as hexane or pentane is used. The final bitumen product from the NFT process is not clean and often contains about 1 to 2 wt% emulsified water and up to 1 wt% mineral solids. Due to the poor quality, the bitumen is required to be upgraded into a higher quality synthetic crude oil (SCO) before selling to open market or refineries. The typical S/B ratio (solvent/bitumen ratio) used in the NFT is about 1:1 or less.[4,10–12]

The paraffinic solvents used in PFT causes precipitation of asphaltene, and the asphaltene precipitates are known to trap the mineral solids and emulsified water so that they settle together. As a result, the PFT process can produce very clean bitumen products with a negligible amount of water and mineral solids. On the other hand, the precipitation of asphaltene results in about 5 to 15% bitumen loss.[3] To induce asphaltene precipitation, the industrial PFT process requires an S/B ratio of 1.2-1.5[13], which is higher than that of NFT. In both NFT and PFT, solvent recovery units are required to remove the large volumes of solvent from the bitumen product, which increases operational costs significantly.[3] Thus, it is desirable to improve the performance of

PFT by using less paraffinic solvent while maintaining the high quality of the bitumen product at as high a bitumen recovery as possible.

To this end, we have attempted to use CO₂ in conjunction with a paraffinic solvent in the PFT process under moderate pressure (up to 1.7 MPa) and temperature (21°C-90°C) to assist paraffinic solvent to lower solvent dosage.

The resulting proposal “Carbon Dioxide-Assisted Paraffinic Froth Treatment” was approved by IOSI Executive Management Committee on June 26, 2017 as a two-year proof-of-concept project (IOSI2017-15). Matching from NSERC as a CRD project was applied subsequently and awarded (CRDPJ516469-17), and the project officially started on May 1, 2018, and ended on April 30, 2020.

1.2 Project Objectives

The objective of this study is to apply CO₂ to assist paraffinic solvent (n-heptane) to precipitate asphaltene under moderate ranges of pressure and temperature. It is important to note that in this study we used CO₂ as a processing aid to promote asphaltene precipitation along with the addition of paraffinic solvent, and we do not attempt to replace the solvent with CO₂ for the PFT process. In PFT operations the best operating temperature is between 70°C to 90°C, while keeping the pressure minimum since pressurizing the system is highly costly. Thus, in this project, we examined the impact of CO₂ at temperatures 21°C and 90°C, while operating at low pressures between 0.1 MPa to 1.7 MPa. Lastly, we ran experiments using n-heptane as a model solvent of paraffinic solvent as it has a higher boiling point compared to n-pentane and n-hexane. This makes n-heptane an ideal solvent to use at relatively high temperature.

The short-term objectives in the proposed two-year proof-of-concept project period are 1) to find suitable parameters for CO₂ assisted asphaltene precipitation in the PFT process including S/B ratio, CO₂ pressure, and temperature; 2) to investigate the influence of CO₂ in bitumen froth in asphaltene precipitation and settling rate of asphaltene precipitation under different conditions; 3) to carry out preliminary investigation regarding the interaction mechanisms of CO₂ and bitumen froth components (bitumen components, water, mineral solids) in the paraffinic solvent.

The long-term objective is to use CO₂ to improve the current PFT process to yield a clean bitumen product with much less solvent usage and possibly also improve bitumen recovery if the CO₂ can help precipitate the “bad” asphaltenes.

1.3 Project Execution

The project period was for 2 years with total funding of \$182,840. The project was officially started from May 1, 2018. Shahrada Khodaei Booran was recruited from July 2018 as a Postdoctoral Fellow, and Xue Wang was recruited from September 1, 2018 as an MSc student to work on the project. Dr. Khodaei will finish his postdoc training as of June 30, 2020 and Xue Wang has

successfully defended her MSc thesis on May 21, 2020. She will received the MSc in November 2020.

Major Findings:

- 1) The onset of asphaltene precipitation was determined by using the gravimetric method and optical microscope observation. The results showed 52 wt% heptane (S/B ratio of 1.08) is the onset of asphaltene precipitation.
- 2) As the CO₂ pressure increased from 0.1 MPa to 1.7 MPa at 21°C, the collected asphaltene increased from 8.3±0.08 wt% to 12.9±0.15 wt% under room temperature. Thus, even at moderate pressure (1.7 MPa), CO₂ injection was effective to assist asphaltene precipitation.
- 3) Control tests were performed using an inert gas (nitrogen). It was shown that an increase in the pressure of N₂ up to 1.7 MPa did not impact on the asphaltene precipitation.
- 4) Asphaltene precipitation is influenced by the operating temperature. The positive benefits of higher temperature are more obvious in control tests (N₂) as asphaltene precipitation yield increased from 8.8±0.09 wt% to 10±0.16 wt% as the temperature increased from 21°C to 90°C. In the case of CO₂, the increasing temperature (21°C to 90°C) at 1.7 MPa did not lead to a further increase in asphaltene precipitation. This was possibly caused by the counterproductive effect of the reduced CO₂ solubility at a higher temperature.
- 5) Water had a significant impact on the asphaltene precipitation in the presence of CO₂. The results showed the asphaltene precipitation yield increased from 12.8±0.09 wt% to 15.2±0.16 wt% in bitumen froth under 1.7 MPa and 90°C due to the presence of 20 wt% water in the bitumen froth. The presence of solids in the bitumen froth did not seem to have any effect.
- 6) At an operating temperature of 90°C, the injection of 1.7 MPa CO₂ increased the yield of asphaltene precipitate to 15.2±0.16 wt% at the onset of 52 wt% heptane (S/B ratio of 1.08). This was a 7 percentage point increase in the yield of asphaltene. To achieve the same asphaltene yield without using CO₂, the S/B ratio needs to be 3.20. Therefore, the potential solvent saving was 66%.
- 7) When tested below the onset of asphaltene precipitation, i.e., 50 wt% heptane or S/B = 1, the injection of CO₂, up to 1.7 MPa, did not have any effect on asphaltene precipitation.
- 8) The practical implication of the research results was that at the onset asphaltene precipitation S/B ratio, the injection of CO₂ under moderate pressure could help achieve desired asphaltene precipitation yield without using additional solvent.

The Relevance of Research Results:

This research showed that at the onset asphaltene precipitation S/B ratio (it was 1.08 in the tested system of heptane/bitumen), injection of up to 1.7 MPa CO₂ could significantly increase the yield of precipitated asphaltene.

However, below the onset S/B (e.g., S/B = 1), the injection of up to 1.7 MPa CO₂ did not have any effect on asphaltene precipitation.

Therefore, if the process is to be used in commercial production, the industry only need to maintain an S/B ratio at the onset of asphaltene precipitation, then inject moderate pressure of CO₂, up to 1.7 MPa, to achieve the desired yield of asphaltene precipitation without the need to add more solvent. This can lead to significant solvent saving and also savings in the capital and operating costs of the solvent recovery units.

However, the economics of CO₂ injection needs to be further studied.

2 BACKGROUND

2.1 Bitumen Froth Generated from Athabasca Oil Sands

Athabasca oil sands consists of a mixture of crude bitumen, silica sand, clay minerals, and water. These oil sand deposits contain about 1.7 trillion barrels of bitumen in place. This makes Athabasca deposit as one of the largest reservoirs of crude bitumen in the world.[6,14]

In general, crude bitumen can be extracted from an oil reservoir using two technologies which are in-situ production and open-pit mining. The selection of the technology depends on how deep the deposits are below the surface. If the deposits lie too deep beneath the surface (greater than 75 metres undergrounds), in-situ extractions have to be used to extract the bitumen. Currently, the most commercial in-situ extraction is Steam Assisted Gravity Drainage (SAGD) which requires drilling two horizontal wells, one marginally on top of the other one. The injection of steam continuously on the top well will result in the reduction of the viscosity of bitumen, and the bitumen flows to the lower well. The bitumen is then pumped to the surface.[13,15]

On the other hand, if the oil sands reservoirs are very close to the surface (less than 75 meters underground), an open-pit mining method is used. Figure 1 presents a detailed flow diagram from oil mining to the bitumen upgrading process. The oil sand ores mined by open pit technology are transported by trucks. After being crushed and sized, the oil sands are mixed with warm water and chemical additives. The slurry is composed of approximately 50 wt% water, 8 wt% bitumen and above 40 wt% mineral solids.[13,14] After a complex process of bitumen liberation and aeration occurring in hydro-transport pipelines, the slurry is discharged to the extraction plants, which are a series of large gravity separation vessels. The bitumen product produced after the extraction process is referred to as bitumen froth.

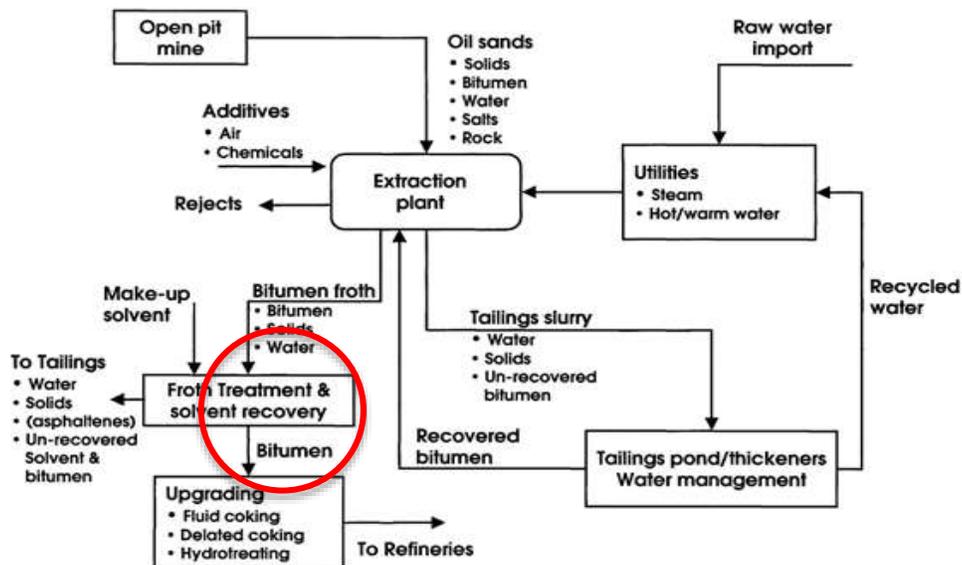


Figure 1 Schematic flowsheet of water-based extraction processes.[14]

A typical overall bitumen recovery in commercial operations is about 88–95%. [14] As an intermediate product, the bitumen froth only contains 60 wt% of bitumen, with about 30 wt% water and 10 wt% mineral solids. [7]

2.1.1 Bitumen

In the Athabasca oil sands region, the unconsolidated sand deposits are impregnated with high molar mass viscous petroleum normally referred to as bitumen. [14] Bitumen is defined as the toluene-soluble constituents in oil sand, [5] which typically has a high density of 1.01 g/mL and high viscosity of the order of 100 Pa·s at ambient conditions. [7]

Molecular weight distribution analysis shows that bitumen is a complex mixture of about 300 to 2000 chemical compounds (medium value 500–700), which makes it extremely challenging to chemically characterize bitumen. [16] For this reason, bitumen is often characterized chemically by its hydrocarbon class compositions such as saturates–aromatics–resins–asphaltene (SARA) contents. The most essential component of bitumen is asphaltene, which is defined as a solubility class of crude oils that precipitate in the presence of aliphatic solvents such as n-pentane or n-heptane but remains solubilized in aromatic solvents such as toluene. [17] On average, the Athabasca bitumen consists of 17 wt% saturates, 40 wt% aromatics, 26 wt% resins, and 17 wt% asphaltene. [3]

2.1.2 Water

Water contained in bitumen froth not only carries mineral solids but also dissolved problematic inorganic salts, such as chlorides which can cause severe corrosion to the downstream facilities. To avoid the further cost of the maintenance of these facilities, it is necessary to remove water during bitumen froth treatment. [3]

Regarding the size distribution, water in diluted bitumen was classified into three types: (a) emulsified water, with water droplet sizes less than 10 μm in diameter, (b) dispersed water, with droplet sizes between 10 and 60 μm, and (c) free water, with droplet sizes larger than 60 μm. [7] The free water can almost instantaneously settle down after contact with the solvent. The dispersed water settles slower than free water and the external force is commonly required to drive the settling. The emulsified water, which is the most challenging one, cannot settle down even with the addition of solvent because of the formation of very stable water-in-diluted bitumen emulsions. [7]

2.1.3 Mineral Solids

In the oil sands industry, the term “fine solids” is adopted to describe the portion, by weight, of mineral solids that are smaller than 44 μm. And clay usually refers to mineral solids smaller than 2 μm. The particle size distribution of mineral solids ore can vary substantially from each other. [1]

The mineral solids in the bitumen froth are mainly minerals with particle sizes smaller than 44 µm. These are predominantly the clay minerals kaolinite and illite. The mineral solids in the bitumen froth also contain significant, but varying, amounts of non-clay minerals, including quartz, dolomite (CaMg(CO₃)₂), calcite (CaCO₃), anatase, and rutile (TiO₂).[1] The mineral solids with clean surfaces are naturally hydrophilic and will not adsorb at an oil-water interface. So, those mineral solids capable of stabilizing water-in-oil (w/o) emulsions are mainly clays whose surface properties have been modified by the adsorption of surfactants present in the oil.[6] Over a long period, the exteriors of these inorganic particles have been rendered hydrophobic as their exposure to highly aromatic, polar organic components such as asphaltene, resin, naphthenic acids and their salts.[18] The interactions between these organic components and inorganic particles impart a bi-wettable character to the solids, allowing them to form solids-water clusters or to stabilize emulsions by forming a rigid barrier between water droplets and the continuous phase.[18] Asphaltenes, when precipitated in a solvent, can also stabilize water-in-oil emulsions.

2.2 Bitumen Froth Treatment

Bitumen froth treatment is a unit operation in the bitumen extraction process aiming to produce clean bitumen from bitumen froth. As explained above, the high contents of water and mineral solids are not accepted by the transportation pipelines, upgrading, and refining facilities. Since they are detrimental to the equipment, they are required to be removed before transportation. The clean bitumen product should contain less than 0.5 vol% total mineral solids and water and the final product must have a viscosity of less than 350 mPa·s for pipeline transportation.[4,5]

Currently, the commercial froth treatment process can be classified into two categories according to the hydrocarbon solvent it utilizes, Naphthenic Froth Treatment (NFT), and Paraffinic Froth Treatment (PFT). The basic role of the hydrocarbon solvent is to lower the density of bitumen froth to facilitate further separation between water and bitumen.[3] In the meantime, a diluent can reduce the density of the hydrocarbon phase so that the water and solids can settle down in gravity settling vessels.[6]

2.2.1 Naphthenic Froth Treatment

In a Naphthenic Froth Treatment (NFT) process, a naphthenic diluent is added to the froth, producing a relatively clean final product. The final bitumen product would still contain 1 to 2% water and up to 1% mineral solids, and it is usually required to be upgraded into a higher quality Synthetic Crude Oil (SCO) before it can be sold to refineries on the open market.[4,10–12]

Naphthenic Froth Treatment was the original technology used to clean bitumen froth for over 30 years. Since naphthenic diluent has a relatively high boiling point at atmospheric pressures, vessels can operate at lower pressures (over 60°C) and makes it easier for equipment maintenance and reduce the risk of ignition.[19] Besides, NFT facilities mostly have a higher bitumen recovery compared to PFT facilities in which NFT facilities can achieve up to 98% bitumen recovery while for PFT is about 90% recovery rate.[19] On the other hand, bitumen/water emulsions formed in

NFT are very stable, NFT facilities require more robust equipment that can generate and withstand high g-forces, such as cyclones and centrifuges.[13] Lastly, since the final bitumen product is not very clean, it is usually required to perform upgrading which is a very expensive and energy-intensive process.[3]

In NFT, the primary solvents are called naphthenic or cycloalkanes. In more detail, naphthenic are a group of hydrocarbon ring compounds (monocyclic saturated hydrocarbons, of the general formula, C_nH_{2n}). Examples of naphthenic are n-cyclopropane, n-cyclobutane, n-cyclopentane, n-cyclohexane, and n-cycloheptane.[3,4,10] The NFT facilities currently served in Suncor, Syncrude, and CNRL are listed below in Table 1.[6]

Table 1 NFT facilities used by different companies.

Operator	Suncor	Syncrude	CNRL
Facilities	IPSSs, cyclones, centrifuges	IPSSs, centrifuges	IPSSs, cyclones

2.2.2 Paraffinic Froth Treatment

In PFT, light hydrocarbons (paraffin or alkane) are added to froth to not only reduce the mineral solid and water contents in the bitumen froth but also precipitate the asphaltene. PFT facilities can produce an extremely clean bitumen product with water and solid contents less than 0.5%. [13]

Paraffinic solvents are predominantly normal and iso-hydrocarbons in the C₄ to C₂₀ range. Solvents used in PFT facilities typically range from n-pentane (C₅H₁₂) to n-heptane (C₇H₁₆) hydrocarbons.[4] Paraffinic solvents dilute the bitumen, reducing the density and viscosity of it and enabling water and solids removal by gravity separation. Plus, paraffinic solvents can precipitate asphaltene. It is important to note that the mechanism beyond PFT is asphaltene precipitation. When paraffinic solvent addition exceeds the onset of asphaltene precipitation, the precipitating asphaltene act as flocculants for emulsified water droplets and mineral solids, breaking the w/o emulsion.[4] The flocs formed contain water droplets, mineral solids, and precipitated asphaltene. Clay solids and water droplets are trapped in the asphaltene flocs, which settle and separate into a sludge layer, leaving a diluted bitumen of less than 0.2% water and virtually free of solids. Additionally, nickel and vanadium, associated with asphaltene, are also reduced.[7]

In general, a lighter solvent (low molecular weight – n-pentane) can produce a larger and denser asphaltene aggregate, as well as, requires a lower S/B ratio to precipitate asphaltene. However, the lighter solvents have a lower boiling point, which requires the process to run at a higher pressure to keep the solvent in the liquid state.[3,13]

In term of advantages of the PFT compare to NFT process, firstly, PFT can produce a very high-quality bitumen that can be sold directly to a refinery without upgrading.[3] This eliminates the need to build upgraders, which are highly complex, energy-intensive and expensive.[6] On the other hand, the PFT process has a lower bitumen recovery compared to NFT. Furthermore, the PFT process requires more solvent (an S/B ratio of 1.2-1.5) compared to NFT process.[13] Thus, the PFT process demands more capacity in the solvent recovery units.

2.3 Asphaltene

The main reason that the PFT process produces a higher quality bitumen product than the NFT process is asphaltene precipitation. Asphaltene, as the most aromatic of the heaviest components of crude oil, is essential to all aspects of petroleum utilization, including reservoir characterization, production, transportation, refining, upgrading, paving, and coating materials.[20] The solid asphaltene always imparts deleterious attributes in fluids such as high viscosity, emulsion stability, low distillate yields, and inopportune phase separation.[20] As asphaltene content of the bitumen for Canadian oil sands is as high as 20% [21], this causes losses of the hydrocarbon. Asphaltene is classified as a fraction of n-alkane-insoluble hydrocarbon, i.e., the addition of n-heptane, n-hexane or n-pentane causes asphaltene precipitation, but it is soluble in aromatic solvents such as toluene or benzene.[22]

Asphaltene is a very complex component made of thousands of molecular species with a distribution of molecular weight in the range of 400 to 2000 g/mol.[22] Besides, asphaltene is mainly composed of carbon, hydrogen, nitrogen, oxygen, and sulfur, as well as trace amounts of vanadium and nickel.[23] The C/H ratio is approximately 1-1.2, depending on the asphaltene source and precipitant used.[22]

2.3.1 Asphaltene Molecular Structure

The chemical structure of asphaltene is still in debate. Two well-known models to describe the structure of asphaltene have been presented in the literature: the archipelago and the continental (island) models, as shown in Figures 2 and 3. The archipelago model is firstly introduced by Strausz et al.[24] In their archipelago model, asphaltene was supposed as a complex molecule which consists of several small polyaromatic parts linked together by aliphatic or naphthenic chains.[24] While the continental (island) model considered asphaltene molecules as a single polyaromatic ring containing about seven condensed aromatic rings with linked aliphatic or naphthenic chains.[20]

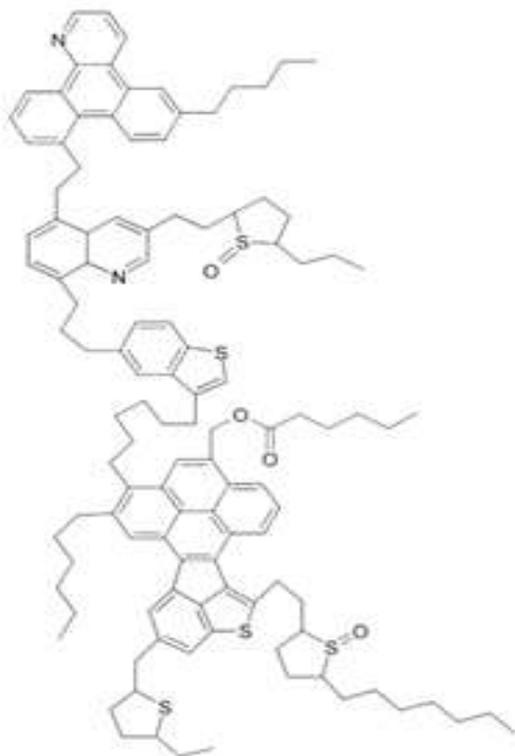


Figure 2 Illustration of the archipelago structure of asphaltene.[24]

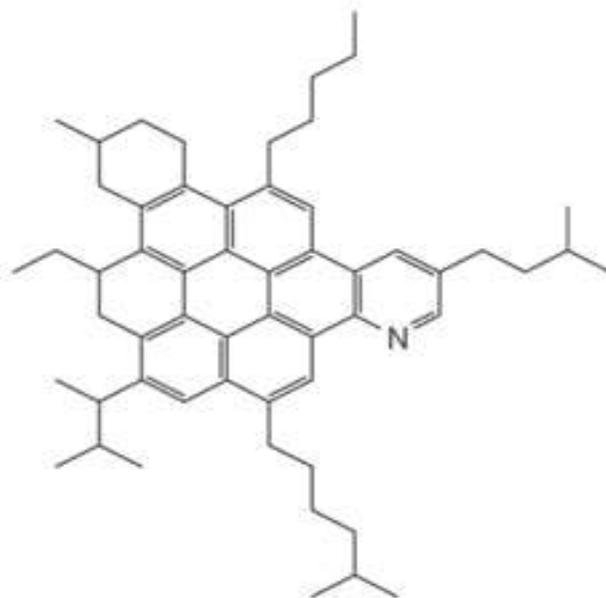


Figure 3 Illustration of the continental structure of asphaltene.[20]

2.4 What Cause Asphaltene to Precipitate

In general, any change in the asphaltene and resins equilibrium will likely cause asphaltene precipitation. The asphaltene/resin equilibrium can be broken by a change in temperature, pressure, and oil composition such as the addition of diluent (e.g., paraffinic solvent) or the dissolution of gases (e.g., CO₂). [25,26] Xu [18] showed that asphaltene content in bitumen started to decrease at temperature range 75°C to 100°C. This agrees with the reports by Zhao and Wei, and Long et al. [11,27] Zhao and Wei [19] measured asphaltene yield versus temperature and showed that the asphaltene yield increased with temperature from 293K to 433K. [27]

Maqbool [20] examined the kinetics of asphaltene precipitation on crude oil at temperatures between 20°C to 50°C using n-heptane as a solvent. The results showed that asphaltene precipitation happened more rapidly at 50°C. The onset time for 20°C was almost 2.5 times longer than at 50°C. Under constant n-heptane concentration (27.25 vol%) and operation time of 200 hrs, the precipitated asphaltene increased from 0.12 wt% to 0.36 wt% when temperature increased from 20°C to 50°C. [28] It is important to note that the increase in the operational temperature decreases the viscosity of bitumen froth/paraffinic solvent and increases the settling rate of the solids/water/asphaltene agglomerates. The higher settling rate means less residence time in the settling stage. [13,29]

Furthermore, many reports showed that increasing S/B ratio increases asphaltene precipitation. [26,29–31] Xu [18] examined the impact of solvent and temperature on asphaltene precipitation in PFT. They conducted autoclave tests MPa and 1.24 MPa. The results showed that the asphaltene content in the bitumen product decreased continuously with increasing S/B. According to the results obtained, the asphaltene content in the bitumen decreased from 18 wt% to 2 wt% as S/B increased from S/B = 1 to S/B = 5.5 using n-pentane as the solvent. [26]

2.5 Mechanism of Asphaltene Precipitation

Understanding asphaltene precipitation mechanisms is both a challenging and urgent objective of many researchers for over decades. Although it seems that precipitation should be the following phase of the asphaltene association, it is still unclear how self-association relates to asphaltene precipitation. [32] The precipitation of asphaltene can be comprehensively viewed in two ways: as a phase separation to form a fluid that is below its glass transition temperature or as coagulation of a colloidal suspension. [33]

From the traditional colloidal point of view, asphaltene is treated as colloidal particles dispersed by resins as stabilizing agents. Precipitation occurs if resins desorb from the particles, leading to an increase in asphaltene aggregate size and eventually precipitation of large asphaltene aggregates. [34]

From the thermodynamic point of view, the aggregates are macromolecules of asphaltene, and precipitation is a conventional liquid or solid phase transition. There are two main types of

thermodynamic models: regular solution models and equations of state models. Regular solution models are usually semi-empirical and predict the effect of solvent addition on asphaltene precipitation with good accuracy. Equations of state-based models are readily applicable for simulation with pressure and temperature effects.[25]

2.6 Application of Carbon Dioxide in the Petroleum Industry

One of the applications of CO₂ injection in the petroleum industry is in enhanced oil recovery (EOR), where CO₂ injection into an oil reservoir would improve the sweep efficiency by increasing the mobility ratio of the oil/injected gas fluid system and reduce the interfacial tension between oil and water which results in enhancing oil displacement efficiency.[35,36]

Fakher and Imqam [37] examined the impact of CO₂ on asphaltene precipitation at different temperatures and pressures. Their results showed that as the CO₂ pressure increased from 1.38 MPa to 4.83 MPa, the amount of precipitated asphaltene increased from 1 to 1.4 wt% as well.[37]

Zanganeha et al. [38] compared the impacts of CH₄, CO₂, and N₂ injection on asphaltene precipitation and deposition for gas-assisted EOR. They found that both CO₂ and CH₄ increased the total asphaltene precipitation in the pressure range from 3 MPa to 14 MPa while N₂ injection (inert gas) had no detectable impact on the amount of asphaltene precipitation.[38] On the other hand, 56% more asphaltene deposition was observed when CO₂ pressure increased from 3 MPa to 14 MPa under the temperature of 90°C representing a change of CO₂ concentration in oil from 5 to 20 mol%.[38]

Dong et.al [39] examined the impact of CO₂ pressure, temperature and CO₂ concentration on asphaltene precipitation using a high-pressure vessel. Their results demonstrated that as the pressure increased from ambient pressure to 20 MPa, the contents of asphaltene in the bitumen decreased from 4.89 wt% to 3.68 wt%. Likewise, as the temperature increased up to 90°C, the contents of asphaltene decreased slightly from 4.89 wt% to 4.82 wt%.[39] Their results were consistent with those of Cruz et al.[27]

In summary, many researchers tested CO₂ application in EOR, and they observed that the injection of CO₂ into the reservoir increases the oil reservoir sweep efficiency and enhances oil recovery.[15,40–43] Also, they observed that CO₂ injection in the oil phase, even at low pressure, has enough solubility to decrease the viscosity of the oil.[37,44,45]

2.7 Onset of Asphaltene Precipitation

In general, the onset of asphaltene precipitation is defined as the minimum volume of solvent required to precipitate asphaltene from the crude oil at a fixed contact time between solvent and bitumen.[46,47] To date, various methods have been proposed to detect asphaltene precipitation, such as gravimetric method, optical microscope observation, Focused Beam Reflectance Measurement Method (FBRM), Acoustic Resonance Technique (ART) Method, and so on.[46,47]

Optical Microscopic Observation

The optical microscopic observation is one of the most accessible approaches to detect the onset of asphaltene precipitation. In this approach, the process of asphaltene aggregates growth is monitored in a high magnification optical microscope equipped with a digital camera. In literature, the size at which asphaltene aggregates become large enough to be distinguished with an optical microscope is about 1 μm . [47] This technique can be used to either monitor the dynamics of asphaltene aggregates growth at a constant precipitant concentration with time intervals or determine the minimum required concentration of a precipitant to precipitate one bitumen sample at constant residence time. [47]

Gravimetric Method

The onset is determined from a series of asphaltene yield measurements in solvent diluted bitumen after a specific contact time. The yield is calculated by the mass of precipitated asphaltene divided by the mass of the bitumen sample. Each time, the known amount of bitumen is added with solvent (e.g. n-heptane) with a specific concentration. After a series of yield measurements, the onset point is then determined by extrapolating the yield data to zero. [47]

Focused Beam Reflectance Measurement Method (FBRM)

The FBRM instrument is a powerful tool as an ‘in-situ’ particle monitoring technique for in-line real-time measurement of particle size. FBRM provides real-time particle size and counts analysis, which can monitor the process of asphaltene aggregates growth by the chord length distribution (CLD) and particle size distribution (PSD). [48]

Acoustic Resonance Technique (ART) Method

Acoustic resonance technique (ART) is based on measuring the response of fluid to applied acoustic stimulation. The change in the pressure, temperature or composition of the system to induce asphaltene precipitation, the variations in the resonance detected will indicate as the onset point. [46,49]

Light Scattering Technique

The light scattering technique (LST) is based on measuring the transmittance of near-infrared (NIR) light through a sample of reservoir fluid undergoing temperature, pressure, or composition changes. For the dark oil, NIR light with 800 to 2200 nm wavelength is specifically used to establish any asphaltene precipitation conditions. [50] The experimental setup is mainly composed of a PVT cell with transparent glass to allow NIR light to transmit. It also contains a magnetic impeller mixer to ensure homogeneity of the sample. On one side of the PVT cell, an NIR light source is mounted across the window to generate light at a specific transmittance power, and process variables (transmitted light power level and time) are detected by a fibre-optic sensor on the opposite side of the NIR source. [50,51] Before asphaltene precipitation, the NIR light can

experience almost a total scattering. When asphaltene starts to precipitate, asphaltene particles appear and cause a partial light scattering. Then, with further particle growth, the NIR light can experience a total scattering causing a drastic drop in the light transmittance.[50]

3 EXPERIMENTAL

This section consists of four parts, (i) the onset of asphaltene precipitation determination, (ii) determination of the impact of pressure, and temperature on asphaltene precipitation using CO₂ assist paraffinic solvent treatment, (iii) determination of settling rate in the CO₂-assist PFT of asphaltene precipitation, and (iv) determination of total acid number (TAN) for the treated and untreated bitumen using CO₂. The asphaltene precipitation tests were repeated two to three times with standard deviations between ± 0.09 to 0.21 wt%.

3.1 Materials

Bitumen froth from Kearnl, Imperial (65.2 wt% bitumen, 20.2 wt% water, and 14.6 wt% mineral solids based on Dean-Stark analysis) was used to separate a clean bitumen sample. To prepare solids-free and water-free bitumen (named as dry bitumen), the bitumen froth was mixed with four volumes of toluene, then centrifuged twice (firstly at 2826 RCF and secondly at 10,000 RCF for 1 hour each) to produce a supernatant of bitumen-in-toluene solution. Then, the supernatant was decanted and toluene in the supernatant was removed with a rotary evaporator, and the resulting bitumen sample was dried in a vacuum oven at 60°C. The produced dry bitumen was used in all the tests for asphaltene precipitation.

The total asphaltene content in the dry bitumen was measured using the standard ASTM D4055 method using n-heptane as the solvent and was found to be 19.1 wt%.

3.2 Experimental Setup

Figure 4 shows an autoclave apparatus, which was used for the asphaltene precipitation experiments. This setup consists of an autoclave (purchased from Parr) with a volume of 450 mL, pressure readout, temperature controller, temperature probe, and mechanical mixer equipped with an impeller shaft stirrer. Also, the head of the autoclave has two dip tubes (1/4 in. inner diameter stainless steel), one for input gas (CO₂ or N₂) and the other for output collection of precipitated asphaltene from the bottom of the autoclave.

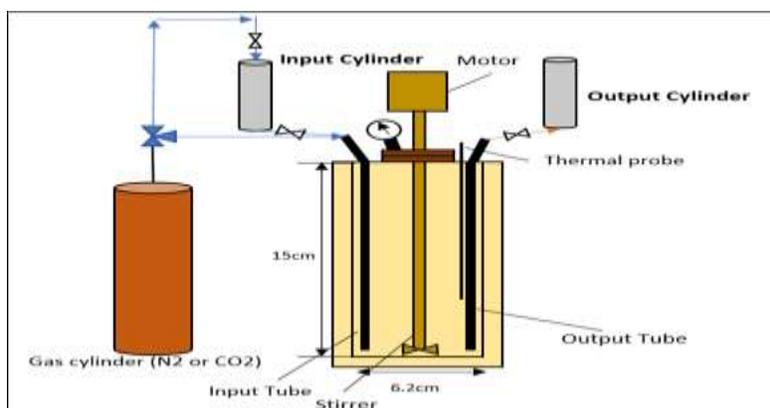


Figure 4 Experimental setup for asphaltene precipitation.

3.3 Test Procedure to Determine the Onset of Asphaltene Precipitation

In this section, we investigated the onset of asphaltene precipitation using the gravimetric method and verified by optical microscope observation. The FBRM measurement was attempted but it did not seem to work due to random fluctuations in the detected chord lengths, possibly caused by the opaque heptane-bitumen solutions.

In a control method, about 20-grams accurately weighed dry bitumen was mixed with n-heptane (30 wt%) in a beaker, followed by 20 min mixing using a magnetic stir bar with the beaker sealed by lab films. This is the premixing stage and it did not count as a part of operational time. The premixing of dry bitumen and n-heptane was necessary because of the high viscosity of the dry bitumen. The premixed bitumen-heptane solution was poured into the autoclave and air was removed by injection of CO₂ gas. After outgassing, the n-heptane solvent was added from the input sampling cylinder at different volumes that could be injected into the autoclave by the regulated CO₂ pressure. It is important to note that in all the experiments, the impact of CO₂ injection was compared with the control tests (N₂ inert gas). Thus, for determination of the onset of asphaltene precipitation under control tests, N₂ gas was injected to remove air or pressurize the autoclave.

To evaluate the onset of asphaltene precipitation at a set time (operational time), different n-heptane concentrations in the bitumen-heptane solution were tested, i.e., 45, 50, 52, 55, 60, 65, 70, 75, and 80 wt%, at 1 atm (0.1 MPa) CO₂ pressure under room temperature (21°C). The tests were performed in the open autoclave to achieve ambient CO₂ pressure. The experimental conditions are shown in Table 2. At the end of the experiment, the treated bitumen product was transferred to a beaker. The asphaltene precipitated from the collected bitumen was determined by filtration using 0.45 µm filter membrane followed by drying at ambient condition and vacuum oven at 50°C till all solvent was removed completely. The weight of the precipitated asphaltene collected on the filter membrane was measured by weighing the filter membrane before and after filtration.

Table 2 Experimental conditions for determination of the onset of asphaltene precipitation.

	Experimental Conditions
n-Heptane Concentration	45, 50, 52, 55, 60, 65, 70, 75, and 80 wt%
Pressure	1 atm (0.1 MPa) CO ₂ or N ₂
Temperature	Room Temperature (21°C)
Operational Time in the autoclave	20 minutes
Mixing Speed	360 RPM

Optical microscopy observation was also used to detect the onset of asphaltene precipitation. In this technique, diluted (or treated) bitumen or crude oil with asphaltene precipitation is monitored in high magnifications with an optical microscope with a digital camera to capture the images of precipitated asphaltene. It is important to note that one of the limitations of the optical microscope is that the size of the asphaltene precipitation may be too small to be detected. In this study, we conducted a similar experiment using autoclave at different n-heptane content ranging from 45 wt% to 80 wt%. At the end of the operational time (20 minutes), we collected a sample with a pipette and used an optical microscope [VWR BA310POL TRINOCULAR] to detect precipitated asphaltene.

3.4 Test Procedure for Asphaltene Precipitation Using CO₂

About 20 g of dry bitumen was mixed with 30 wt% n-heptane in a beaker for 20 min using a magnetic stir bar. The diluted bitumen was transferred to the autoclave. After sealing the autoclave, the air was removed by injection of CO₂ gas. Additional solvent (n-heptane) based on predetermined onset was added to the sampling cylinder that can be injected into the autoclave by the regulated CO₂ pressure.

The experiment proceeded by adding the solvent to reach the set n-heptane concentration (predetermined onset) with the contents fully mixed at maximum stirring (630 rpm). The experiments were conducted at different pressures and temperatures using CO₂ gas or N₂ gas as control tests. The temperature was reached by using a heating element inside the autoclave. It is important to note that at experiments at high pressure and high temperature, the pressure was increased to the set pressure followed by raising the temperature. When the operational time is reached (20 min), the treated diluted bitumen from the bottom of the autoclave was collected into the output cylinder. The collected asphaltene was filtered using 0.45 µm filter paper, then the asphaltene was dried at ambient condition and vacuum oven at 50°C till all solvent was removed completely.

3.5 Test Procedure for Impact of Water on Asphaltene Precipitation Using CO₂

For the examination of the impacts of water on asphaltene precipitation, a series of experiments were conducted based on water addition to bitumen (20.2 wt% H₂O + 79.8 wt% Bitumen) and bitumen froth.

For dry bitumen + distilled water, about 20 g of dry bitumen was added to a beaker. It was followed by adding 20.2 wt% distilled water and 30 wt% n-heptane in the beaker. The solution was premixed using a magnetic stirrer for 20 minutes before transferring to the autoclave. Similar to before, the autoclave was sealed and the air was removed by injection of CO₂ or control test (N₂ injection). Likewise, the experiment was progressed by adding the solvent to reach the set predetermined onset. The experiment was performed for 20 min after reaching the set pressure and temperature. At the end of the test, the treated bitumen was collected using the output tube into the sampling cylinder. The precipitated asphaltene was collected using filtration (0.45 µm filter paper). Lastly,

the asphaltene was dried at ambient condition and vacuum oven at 50°C till all solvent was removed completely.

For bitumen froth testing, 50-gram bitumen froth was premixed with 30 wt% n-heptane (the measurement is based on bitumen content) in the beaker. Likewise, diluted bitumen froth was transferred to the autoclave and the air was removed by injection of CO₂ or N₂. Next additional n-heptane was added to reach the predetermined onset. The bitumen froth treatment was performed at the set pressures and temperatures for 20 minutes.

At the end of the operational time, diluted bitumen froth was collected by depressurizing the autoclave and all the treated bitumen froth was transferred to a beaker. Unlike dry bitumen, bitumen froth contains mineral solids which makes it very difficult to filter it using 0.45 µm filter paper. To measure the precipitated asphaltene, the collected bitumen froth was transferred to a Teflon bottle and centrifuged at 15,000 RCF for 1 hour. The centrifugation allows the settlement of the precipitated asphaltene + mineral solids. After centrifugation, precipitated asphaltene/solid was collected and dried at ambient condition and vacuum oven at 50°C till all solvent is removed completely. To determine the precipitated asphaltene, Dean-Stark analysis was performed, which provided the weight percentage of water, mineral solid and precipitated asphaltene. The precipitated asphaltene was also verified using CHNS Elemental Analyzer. All the tests were conducted at least twice to ensure the precision in the results.

3.6 Determination of Settling Rate of Asphaltene Precipitation

There are numerous ways to measure the settling rate in the PFT process, including optical observation, ashing technique, gravity sedimentation (Tensiometer), X-ray method, experimental sampling, and so on.

Since the bitumen sample is very dark, it was impossible to use visual observation for detection even by applying back-lighting. Thus, we investigated the settling rate using incremental sampling from a fixed depth inside the autoclave. In this method, the treated bitumen samples were collected at different time intervals while the asphaltene was precipitating. The detailed procedure is shown below:

- 1) About 100 g of dry bitumen were premixed with n-heptane (30 wt%) in a beaker for 20 mins. After premixing, the diluted bitumen was transferred to the autoclave. The autoclave was then sealed, and the air was removed by injection of CO₂ gas or N₂ gas (control test).
- 2) The n-heptane was added to reach the predetermined asphaltene onset point (52 wt%) in the autoclave. The solution was mixed inside the autoclave with the maximum speed (632 rpm) for about 2 minutes, and then the mixing was stopped to allow any formed asphaltene precipitate to settle by gravity.

- 3) Next, a small volume of treated bitumen was collected every 5 mins for two hours from a fixed output tube inside the autoclave (1.5 cm from the bottom of the autoclave). The collected samples were filtered with 0.45 μm filter membranes to collect precipitated asphaltene. The precipitated asphaltene was dried at ambient condition and vacuum oven at 50°C until all solvent was removed completely. The weight of asphaltene was lastly measured.

Similarly, for bitumen froth, the settling rate of the asphaltene was measured in the autoclave and the diluted bitumen froth was collected at a different time (0, 10, 20, 30, ..., and 120 minutes). The collected sample was centrifuged 15,000 RCF for 1 hour. After centrifugation, precipitated asphaltene/solid was collected and dried at ambient condition and vacuum oven at 50°C till all solvent is removed completely. To determine the precipitated asphaltene content in the sediments, Dean-Stark analysis was performed, which provided the weight percentage of water, mineral solid and precipitated asphaltene.

3.7 Total Acid Number

The mechanism of how CO₂ assists the asphaltene precipitation was still largely unknown. According to Gabrienko et al.[52], it was a result of Lewis-acid-base-type interactions, resulting in a non-covalent intermolecular complex formation between CO₂ and the substrate molecule. From this perspective, total acid number (TAN) experiments were conducted on the bitumen and asphaltene samples before and after interaction with CO₂. The treated samples were selected under the condition of 21°C and 1.7 MPa CO₂.

The testing samples were 1) dry bitumen, 2) treated bitumen (CO₂-assisted PFT process, without precipitated asphaltene), 3) asphaltene, and 4) treated asphaltene, referring to the precipitated asphaltene after CO₂-assisted PFT process. The procedure was mainly based on ASTM D664, however, some adjustments were required to apply the standard procedure to the bitumen conditions. These adjustments were suggested by The Canadian Crude Quality Technical Association (CCQTA Method Modification of ASTM D664 for Applicability to Heavy Crudes and Bitumen Overview Special note). The detailed dry bitumen experiment is shown below.

- 1) Place a certain amount of bitumen in the vacuum oven and heated up to 60°C to reduce the viscosity for easy handling.
- 2) Test the water contents of the sample and ensure that the water content was below 0.5 wt%. Extra cleaning was required if it exceeded 0.5 wt% since water could significantly impact the results.
- 3) Dissolve a minimum of 10 g of bitumen in toluene, at a 10:1 weight ratio of toluene to sample with 30 mins sonication to ensure complete dissolution.
- 4) Weigh a quantity of sample and add prepared titration solvent (water:2-propanol:toluene=1:99:100), then stirred thoroughly. For the bitumen sample, the size should be restricted to 1 – 2 g/125 mL titration solvent. For the asphaltene sample, the size should be larger than 0.8g/60 mL titration solvent.

- 5) Start the automatic titration with auto-titrator by adding 0.1 mol/L KOH in 2-propanol solution. The titration is terminated when the pH reaches 11.

Each sample was measured at least 4 times to ensure good repeatability.

4 RESULTS AND DISCUSSION

The results reporting is divided into four sections which are 1) determination of the onset of asphaltene precipitation; 2) the impact of CO₂ injection on asphaltene precipitation at different pressures and temperatures under predetermined onset, and the effect of water; 3) settling rate of asphaltene precipitation in different conditions, and 4) Total acid number analysis.

4.1 Determination of the Onset of Asphaltene Precipitation

As previously mentioned, the onset of asphaltene precipitation is based on the minimum volume of solvent (e.g., n-heptane) required to precipitate asphaltene at fixed contact time. In this section, we investigated the onset of asphaltene precipitation using the gravimetric method and verified by an optical microscope. Figure 5 presents the amount of precipitated asphaltene at different n-heptane concentration (wt%). According to the results obtained, no asphaltene was detected at 45 wt% and 50 wt% n-heptane concentration with 0.1 MPa of either CO₂ or N₂. On the other hand, we detected asphaltene precipitation at 52 wt% n-heptane with an asphaltene precipitate yield of 8.3 wt%. As a result, we have conducted all the experiments using the onset of asphaltene precipitation value of 52 wt% n-heptane (S/B = 1.08). At the end of this report, we also presented results when CO₂ was injected at 50 wt% n-heptane, i.e., below the onset.

Figure 5 also demonstrates that as the solvent concentration increased from 52 wt% to 80 wt%, the asphaltene precipitation yield increased as well. Similar results were observed by other researchers.[26,29–31] Lastly, under low pressure (0.1 MPa) there was no difference in the asphaltene precipitation yield between CO₂ and N₂ injection.

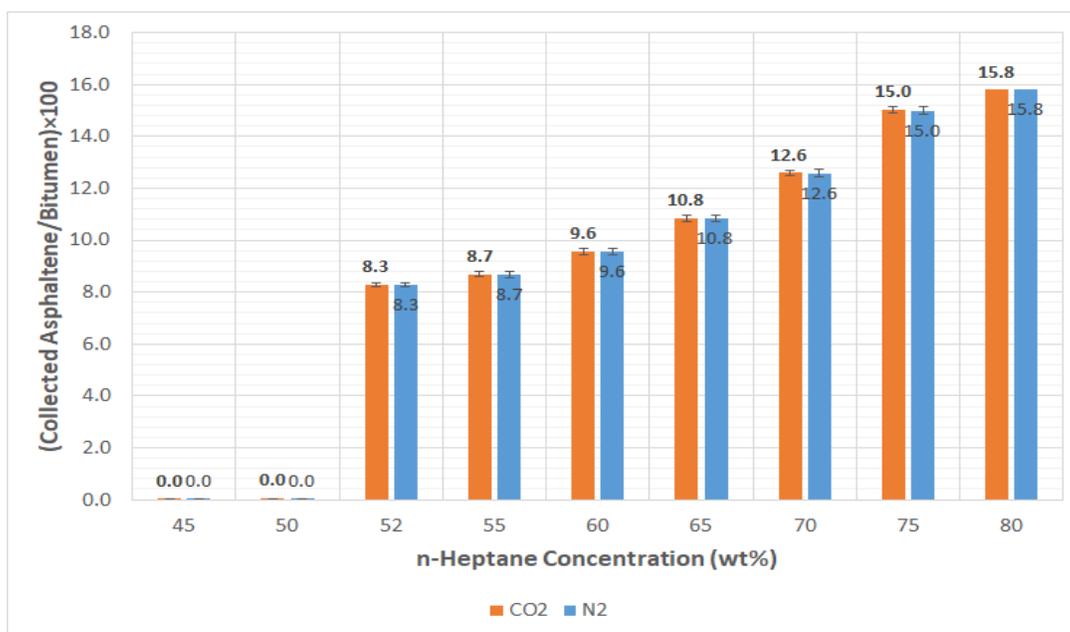


Figure 5 Determination of the onset of asphaltene precipitation using gravimetric method at 20 minutes of operational time at 0.1 MPa pressure and room temperature (21°C).

In the next stage, we have verified the onset using optical microscope technique. Figure 6 shows a series of images for the diluted bitumen after the treatment with CO₂ in the autoclave. According to the pictures obtained, we could not see any precipitated asphaltene at 45 wt% and 50 wt% n-heptane, while asphaltene was detected at 52 wt% n-heptane with a size range between 2 μm to 4 μm. similar results were observed under the control test where N₂ was used. Hence, the onset was 52 wt% which would be used for the rest of the experiments.

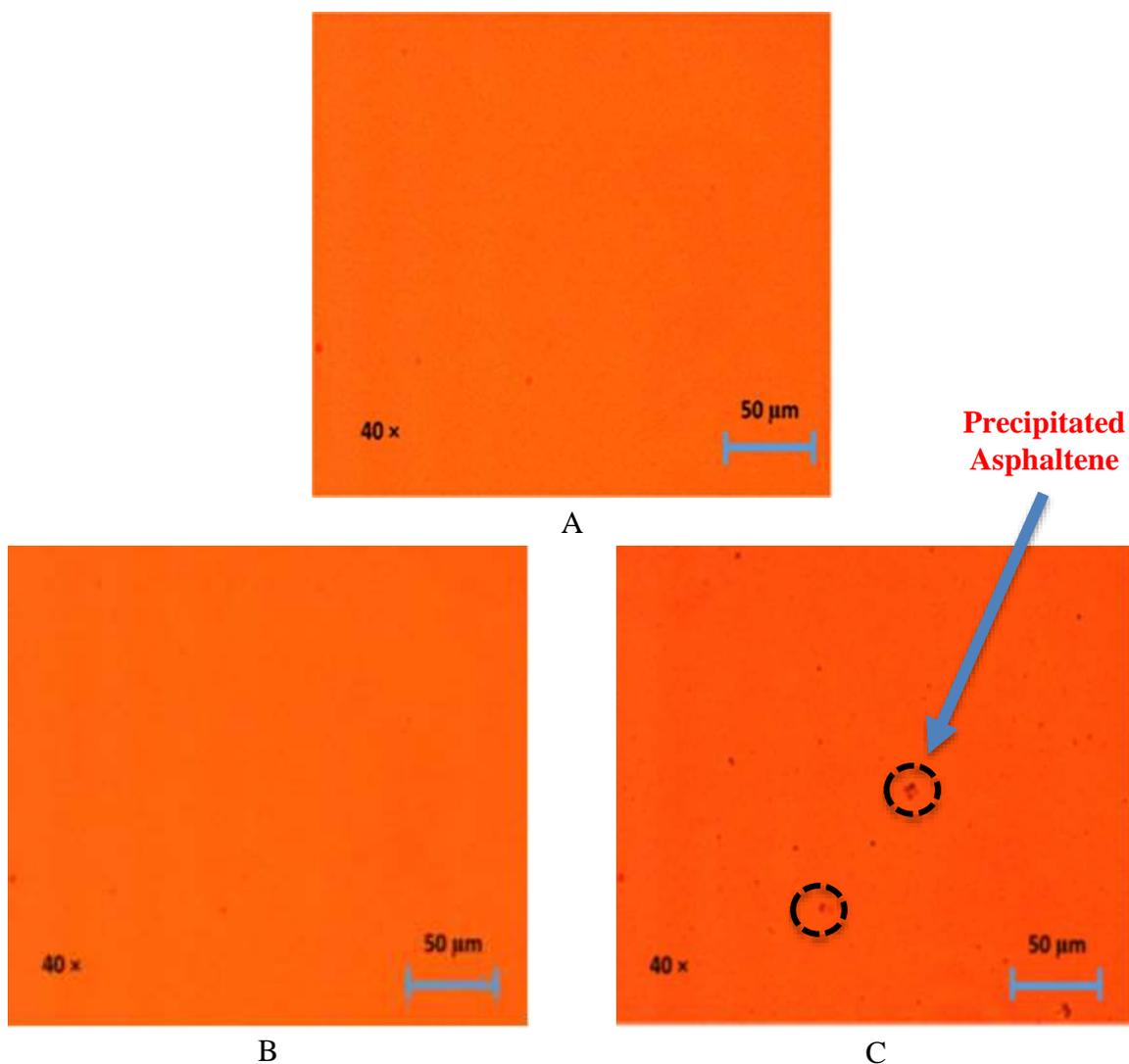


Figure 6 Detection of asphaltene precipitation using an optical microscope at different n-heptane concentrations. A, B, C show optical images at magnification power of 40X under 45 wt%, 50 wt%, and 52 wt% n-heptane, respectively.

4.2 CO₂ Assisted Asphaltene Precipitation

4.2.1 Effect of Carbon Dioxide Pressure on Asphaltene Precipitation

Figure 7 shows the impact of CO₂ pressure (0.1 to 1.7 MPa) on asphaltene precipitation under the predetermined onset condition (i.e., 52 wt% n-heptane) and temperature of 21°C. The results show that as the CO₂ pressure increased from 0.1 MPa to 1.7 MPa, the amount of precipitated asphaltene increased from 8.3±0.08 wt% to 12.9±0.15 wt% (more than 4.6 percentage points, or 55%), which indicate a positive impact of CO₂ injection on asphaltene precipitation. This result agrees with Xu [26] on the significant impact of CO₂ injection on asphaltene precipitation but with a much lower CO₂ pressure used in this study, possibly due to the absence of paraffinic solvent in Xu's study [26].

Lastly, the total asphaltene content in the dry bitumen was measured using the standard ASTM D4055 method using n-heptane as the solvent, and it was found to be 19.1±0.05 wt%. This would be the limit of the precipitated amount of asphaltene.

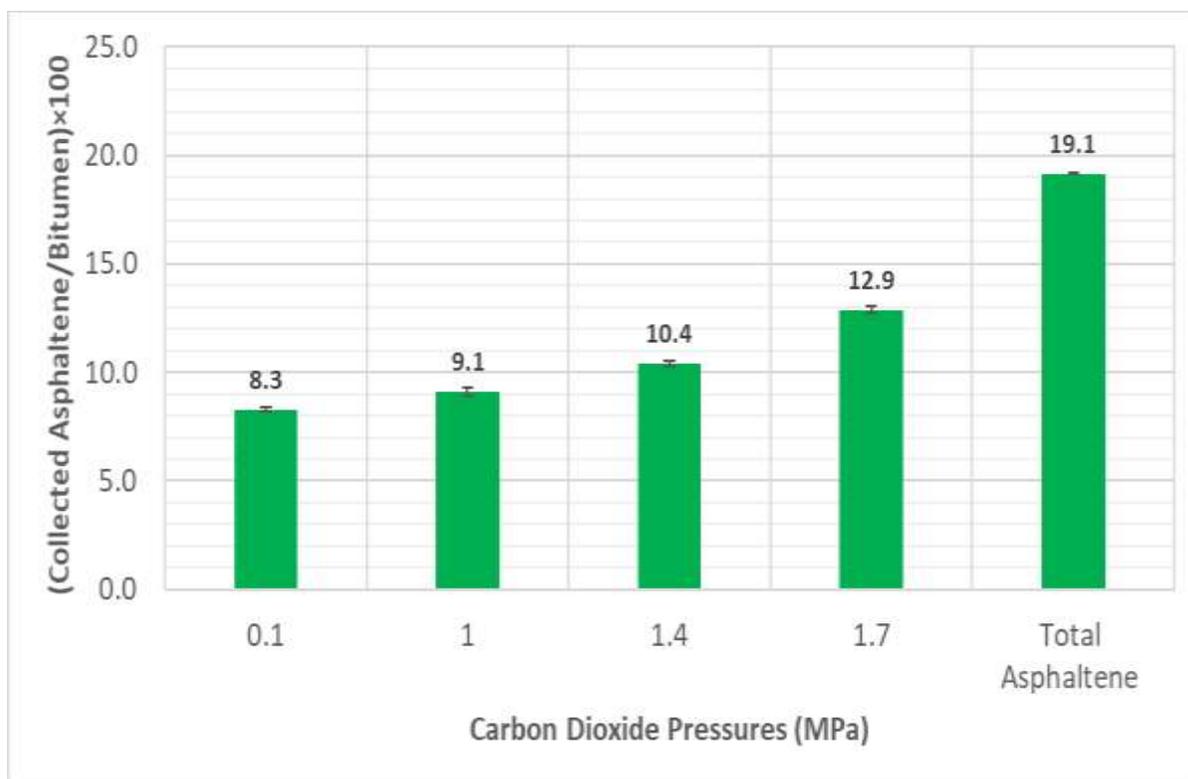


Figure 7 Effect of carbon dioxide pressure on asphaltene precipitation. The concentration of n-heptane was 52 wt%. Total asphaltene content measured using the standard ASTM D4055 method using n-heptane as the solvent was 19.1 wt%.

A question raised was whether the asphaltene precipitation in CO₂ experiments was caused solely by the high pressure, not the CO₂. Figure 8 compares the influence of pressure of both CO₂ and N₂ on asphaltene precipitation. According to the results obtained, the N₂ with the same pressure range with CO₂ did not have any effect on asphaltene precipitation.

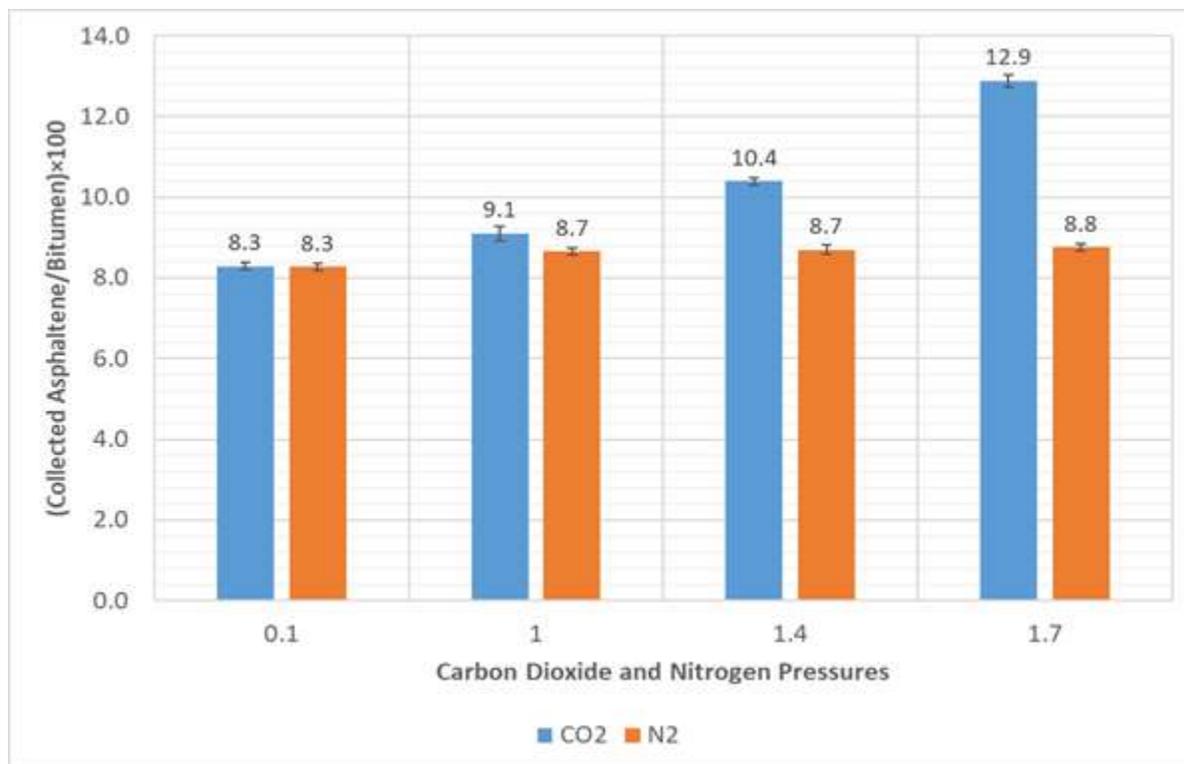


Figure 8 Impact of pressure on asphaltene precipitation in both CO₂ and N₂ gas. The concentration of n-heptane was 52 wt%.

4.2.2 Effect of Temperature on Asphaltene Precipitation

Figure 9 compares the influence of pressure and temperature at ranges 1 MPa-1.7 MPa and 21°C-90°C, respectively, on asphaltene precipitation. By looking at CO₂ at 1 MPa, as the temperature increased from 21°C to 90°C, asphaltene precipitation increased from 9.1±0.18 wt% to 10.1±0.17 wt%, i.e., by 1.0 percentage point (or 10%), which may indicate the significant impact of temperature on asphaltene precipitation even at low pressure.

Next, this study examined the impact of temperature at high pressure. According to the results obtained for CO₂, as the temperature changed from 21°C to 90°C, the asphaltene precipitation did not change, which may be due to a decrease in CO₂ solubility at high temperature. In other words, at high temperature, the CO₂ injection cannot assist paraffinic solvent on asphaltene precipitation. Note that when raising the temperature, the pressure was raised to the desired value first before

raising the temperature, so that the pressure (and available amount) of the gases were the same as at the lower temperature.

Lastly, by looking at the impact of temperature on the control test (N₂), as the temperature increased from 21°C to 90°C the precipitated asphaltene increased. In the case of 1.7 MPa N₂, the precipitated asphaltene increased from 8.8±0.16 wt% to 10±0.16 wt% as the temperature increased from 21°C to 90°C. Thus, our results showed that temperature has a positive impact on asphaltene precipitation, which agrees with other researchers.[11,27,53]

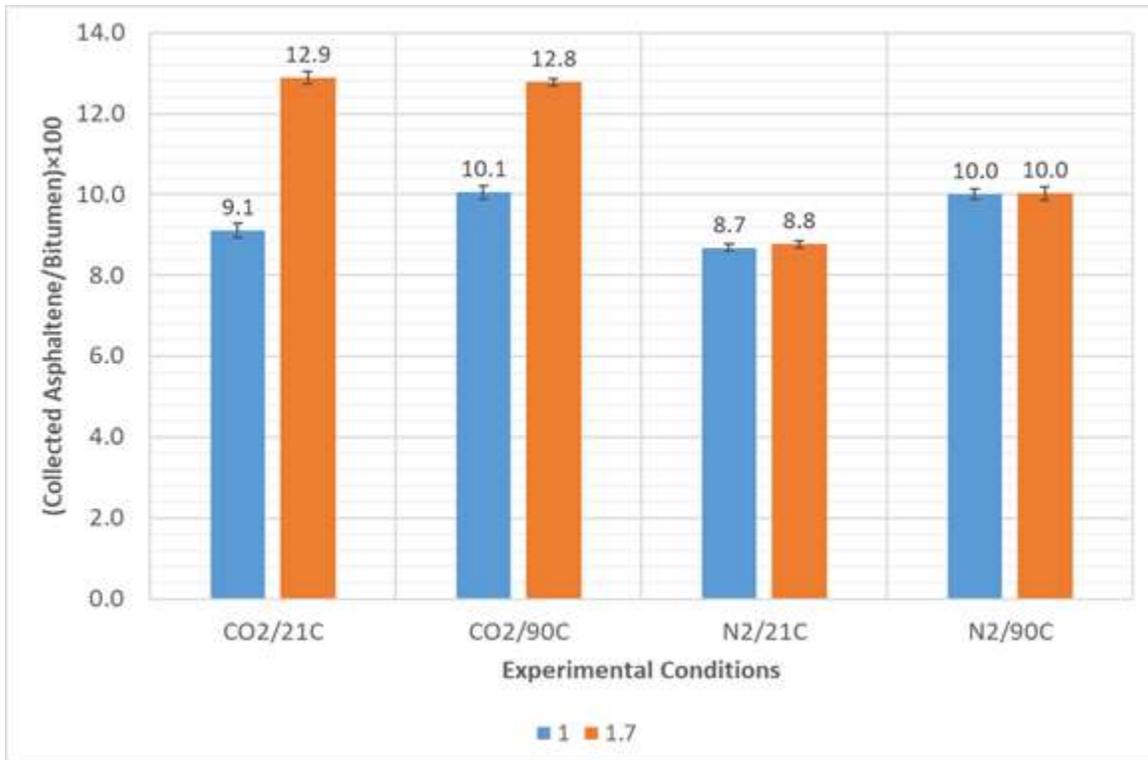


Figure 9 Comparing the influence of pressure and temperature on asphaltene precipitation. The concentration of n-heptane was 52 wt%.

4.2.3 Effect of Water on Asphaltene Precipitation

Thus far, this study was conducted on a high purity dry bitumen sample. In this section, we will discuss the effects of water on CO₂-assisted PFT processes, as well as on commercial bitumen froth samples. In the first case, 20.2 wt% distilled water was added to CO₂-assist bitumen which led to a significant increase in the asphaltene precipitation from 12.8±0.09 to 15.3±0.15 wt% (19.5% increase). On the other hand, the water addition had no impact on asphaltene precipitation yield in the control test with N₂ injection (10.0±0.13 to 10.1±0.14 wt%). Figure 10 demonstrates the influence of water on asphaltene precipitation yield at 1.7 MPa and 90°C.

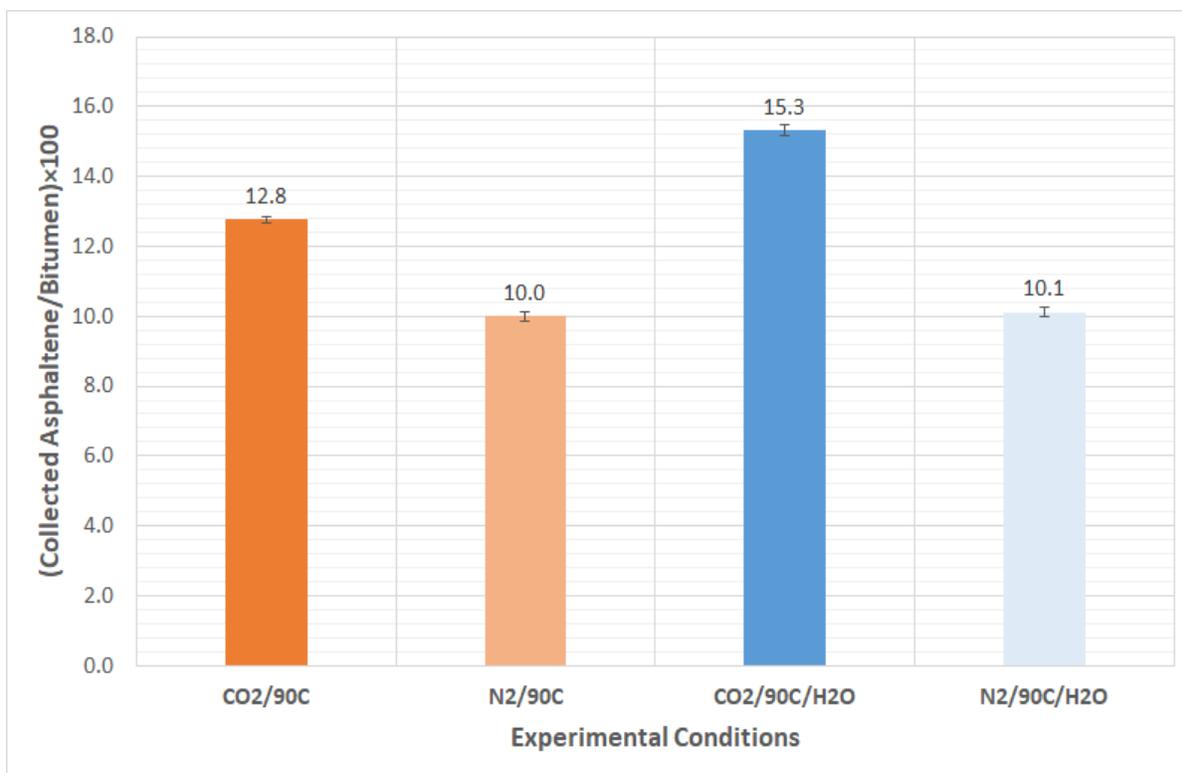


Figure 10 Influence of water on asphaltene precipitate yield. The concentration of n-heptane was 52 wt%.

Zaki [43]'s investigation on the impact of water on asphaltene precipitation indicates that the amount of asphaltene precipitation in the presence of water is higher than in the absence of water.[43] The reason might be that asphaltene adsorbed at the water/oil interface is in a higher degree of association and a higher concentration than the asphaltene present in the bulk phase. It seems that CO₂ preferentially precipitated the most surface-active portion of asphaltene, leading to a substantial weakening of the viscoelastic asphaltenic film built around the dispersed water droplets in the emulsion.[43] Furthermore, Dong [44] examined the impact of low-pressure CO₂ on water-oil emulsion. Their study suggested that at low CO₂ pressure (0.05 MPa to 0.7 MPa), the solubility of CO₂ in the heavy oil is high enough to decrease the viscosity of the heavy oil. Besides, CO₂ dissolved in water would react with heavy oil to generate organic acid to displace the adsorbed film at the oil/water interface and cause more asphaltene precipitation.[44]

4.2.4 Bitumen Froth and Carbon Dioxide Injection

Next, we proceed to investigate the impact of CO₂ in a bitumen froth sample when it was treated with heptane. Unlike dry bitumen, bitumen froth consists of water and solids which makes the operation inside the autoclave more challenging. As a result, the utilization of Dean-Stark and CHNS elemental analyzers are practical options to measure the precipitated asphaltene. Dean-

Stark extraction can separate the precipitated asphaltene from fine sands. Figure 11 shows bitumen froth asphaltene precipitation at the set pressure of 1.7 MPa and the temperature of 90°C.

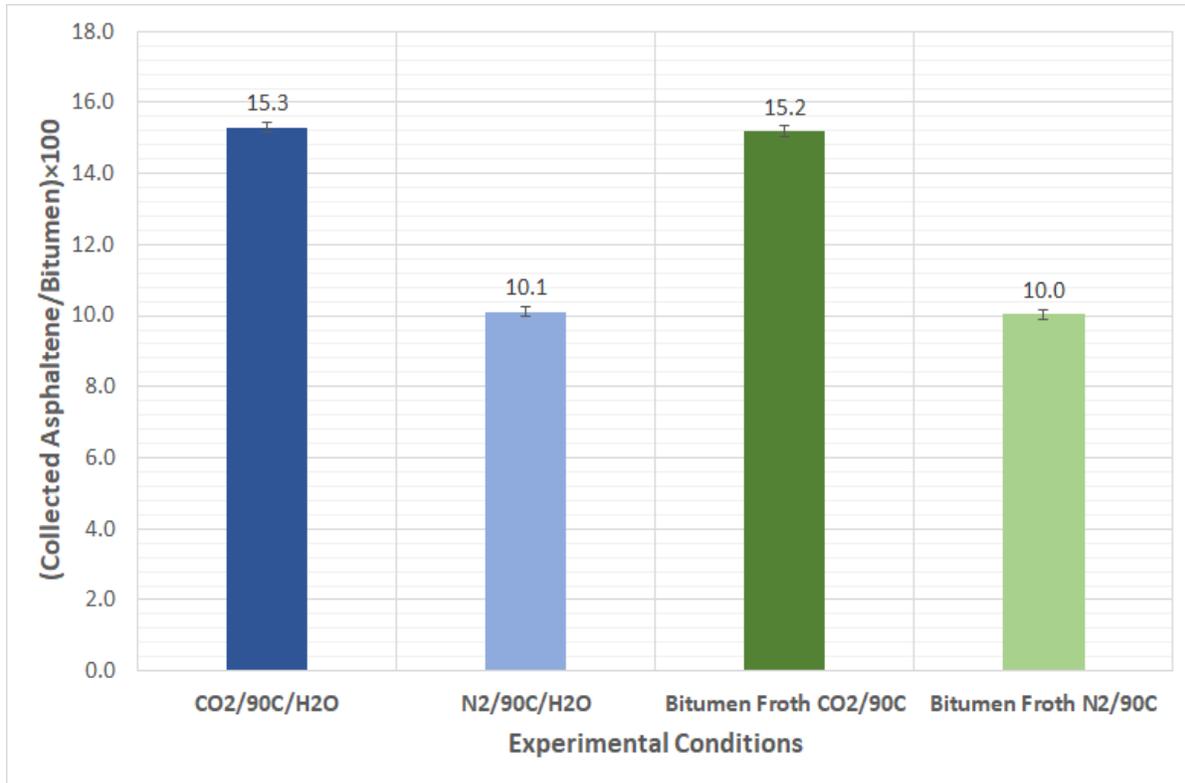


Figure 11 Bitumen froth and asphaltene precipitation in CO₂-assisted PFT. The concentration of n-heptane was 52 wt%.

According to the results obtained CO₂ injection under moderate pressure performed well even by using bitumen froth to assist the paraffinic solvent to generate more asphaltene precipitation.

In the next step, CHNS elemental analysis was performed to verify the positive influence of CO₂ on asphaltene precipitation using bitumen froth. The elemental analysis allows the measurement of carbon, hydrogen, nitrogen, and sulfur of treated bitumen froth. Table 3 shows the elemental composition of CO₂ treated bitumen froth, control tests, and mineral solids.

Table 3 Chemical characterization of CO₂ treated bitumen froth and control tests.

	Nitrogen (wt%)	Carbon (wt%)	Hydrogen (wt%)	Sulfur (wt%)	H/C	N/C
CO₂-PFT	0.29	28.92	2.93	6.79	1.21	0.01
N₂-PFT	0.22	18.36	2.11	4.42	1.38	0.01
Mineral Solids from Dean-Stark	0.21	13.48	1.47	3.33	1.30	0.01

The primary component in asphaltene is carbon. Higher carbon content in the collected sediments indicates higher quantities of precipitated asphaltene. According to the table above, the carbon content increased by 57% by switching from control tests (N₂-PFT) to CO₂ treated bitumen froth (CO₂-PFT), showing that more asphaltene was precipitated.

Interestingly, Table 3 also shows that not only did the 1.7 MPa CO₂ help precipitate more asphaltene, the precipitated asphaltene also had a much higher sulfur content (6.79 wt%) than the control test when N₂ was used (4.42 wt%). Could the CO₂ help precipitate asphaltene with a higher sulfur content? The answer to this question cannot be based on this single data point. More work would need to be conducted to verify this observation.

4.2.5 Solvent Savings

This project demonstrated that CO₂ injection under moderate pressure and temperatures could assist paraffinic solvent to precipitate asphaltene while reducing the solvent usage. To better visualize the importance of CO₂ injection in the PFT process, Figures 12 and 13 show the asphaltene precipitation yields at 21°C and 90°C, respectively, which signify the solvent savings that may be achieved by using CO₂.

The data in these two figures indicate that by injecting CO₂ at a moderate pressure of 1.7 MPa at the onset S/B ratio of 1.08, the amount of precipitated asphaltene was the same as that obtained at much higher S/B ratio without the use of CO₂. These are summarized in Tables 4 and 5.

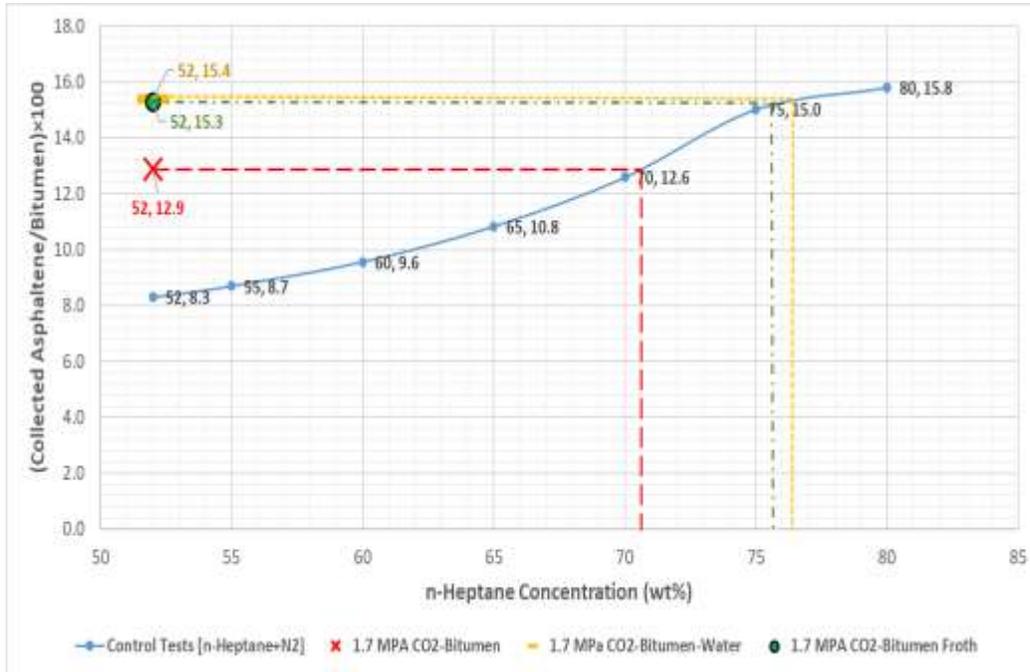


Figure 12 Impact of CO₂ on asphaltene precipitation. “X”, “---“, and “O” show the asphaltene precipitation [S/B 1.08] at 1.7 MPa CO₂ and 21°C for CO₂-bitumen, CO₂-bitumen-water, and CO₂-bitumen froth, respectively. Control test 0.1 MPa and 21°C.

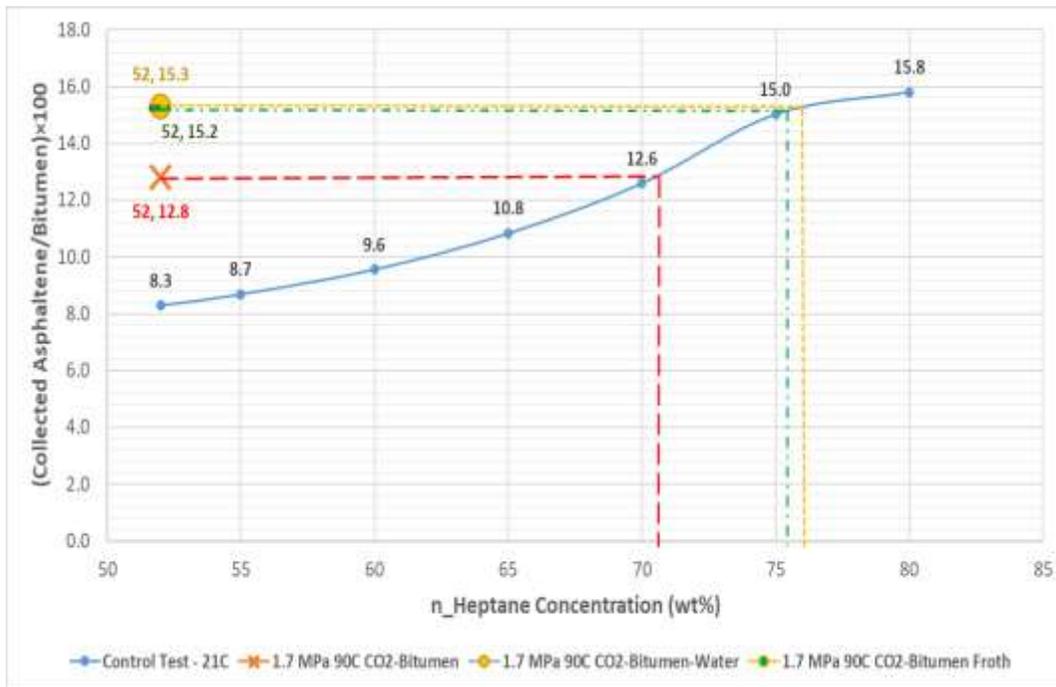


Figure 13 Impact of CO₂ on asphaltene precipitation. “X”, “O“, and “---” show the asphaltene precipitation [S/B 1.08] at 1.7 MPa CO₂ and 90°C for CO₂-bitumen, CO₂-bitumen-water, and CO₂-bitumen froth, respectively. Control test at 0.1 MPa and 21°C.

Table 4 The positive influence of CO₂ treatment to save solvent at 1.7 MPa and 21°C.

	CO ₂ -Bitumen (12.9 wt% asphaltene)	CO ₂ -Bitumen-H ₂ O (15.4 wt% asphaltene)	CO ₂ -Bitumen Froth (15.3 wt% asphaltene)
n-Heptane Concentration, wt%	70.6 (or S/B = 2.40)	77.5 (or S/B = 3.44)	76.9 (or S/B = 3.33)
Solvent Saving (vs. S/B = 1.08)	54.9%	68.5%	67.5%

Table 5 The positive influence of CO₂ treatment to save solvent at 1.7 MPa and 90°C.

	CO ₂ -Bitumen (12.8 wt% asphaltene)	CO ₂ -Bitumen-H ₂ O (15.3 wt% asphaltene)	CO ₂ -Bitumen Froth (15.2 wt% asphaltene)
n-Heptane Concentration, wt%	70.4 (or S/B = 2.38)	76.9 (or S/B = 3.33)	76.2 (or S/B = 3.20)
Solvent Saving (vs. S/B = 1.08)	54.5%	67.5%	66.2%

As can be seen from Figures 12 and 13 and Tables 4 and 5, the reduction in solvent dosage by using 1.7 MPa CO₂ was quite high and could be as much as 70%. This is because the yield of precipitated asphaltene at an S/B ratio of 1.08 when 1.7 MPa CO₂ was used, was the same at much higher S/B ratios (2.4, or 3.4) without the CO₂.

Typical solvent to bitumen ratio in PFT facilities is not that high and is between 1.2-1.5 [13]. Since the commercial PFT process uses a short-chain paraffinic solvent such as n-hexane or n-pentane, even at the lower S/B ratios than used in this work, the commercial PFT process would still precipitate similar quantities of asphaltene. It is anticipated that by injecting CO₂ at moderate pressures, there would still be significant savings of the paraffinic solvent.

For instance, if a hypothetical PFT plant was using a heptane/bitumen ratio of 1.6, then the solvent saving would be 33% because the same result could be achieved at a S/B ratio of 1.08 by injecting 1.7 MPa CO₂.

4.3 Settling Rate of Asphaltene Precipitates in the PFT Process

The settling rate of the mineral solids/asphaltene agglomerates is a critical variable in the design of any PFT facility. A high settling rate translates into less residence time required and smaller settling vessels. According to the results obtained, the settling rate of asphaltene precipitation increased slightly in the presence of CO₂ compared to control experiment.

Figures 14 to 16 show the settling rate of asphaltene precipitates in dry bitumen, bitumen+water, and a bitumen froth sample at 52 wt% n-heptane with and without CO₂. As can be seen, the settling rate of the asphaltene precipitate was higher in CO₂ treatment compared with control (N₂). This was likely caused by the higher mass of precipitated asphaltene when CO₂ was used.

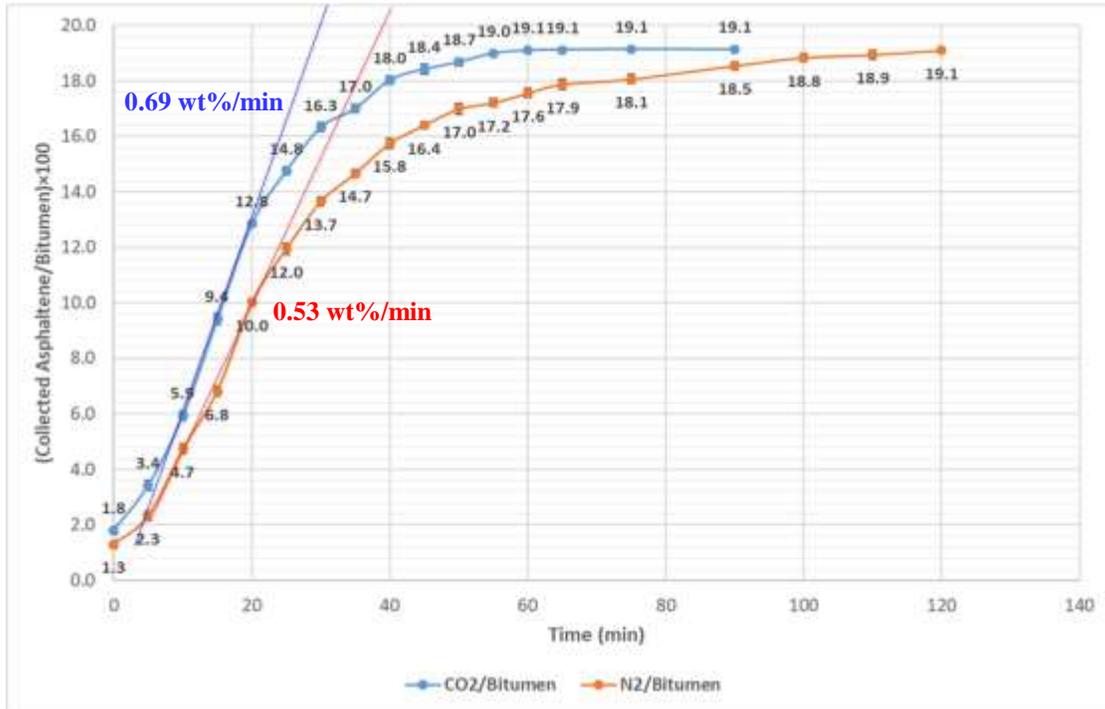


Figure 14 Settling rate of asphaltene precipitate in dry bitumen with CO₂ or N₂. The concentration of n-heptane was 52 wt%.

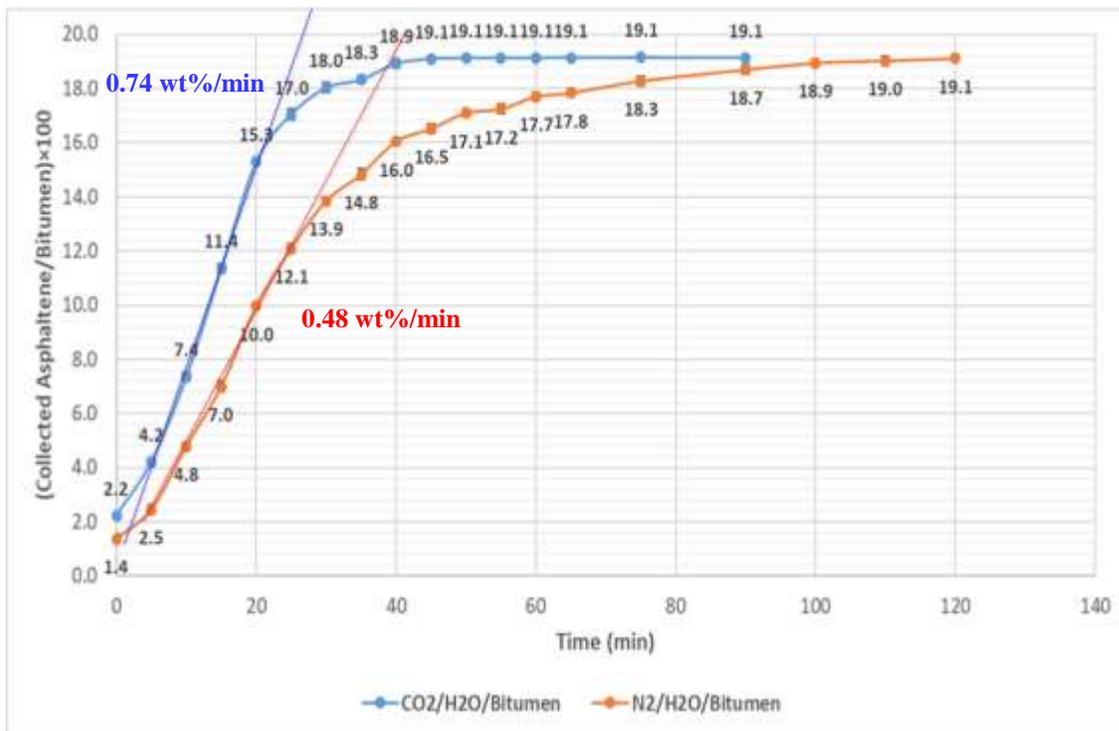


Figure 15 Settling rate of asphaltene precipitate in bitumen+water with CO₂ or N₂. The concentration of n-heptane was 52 wt%.

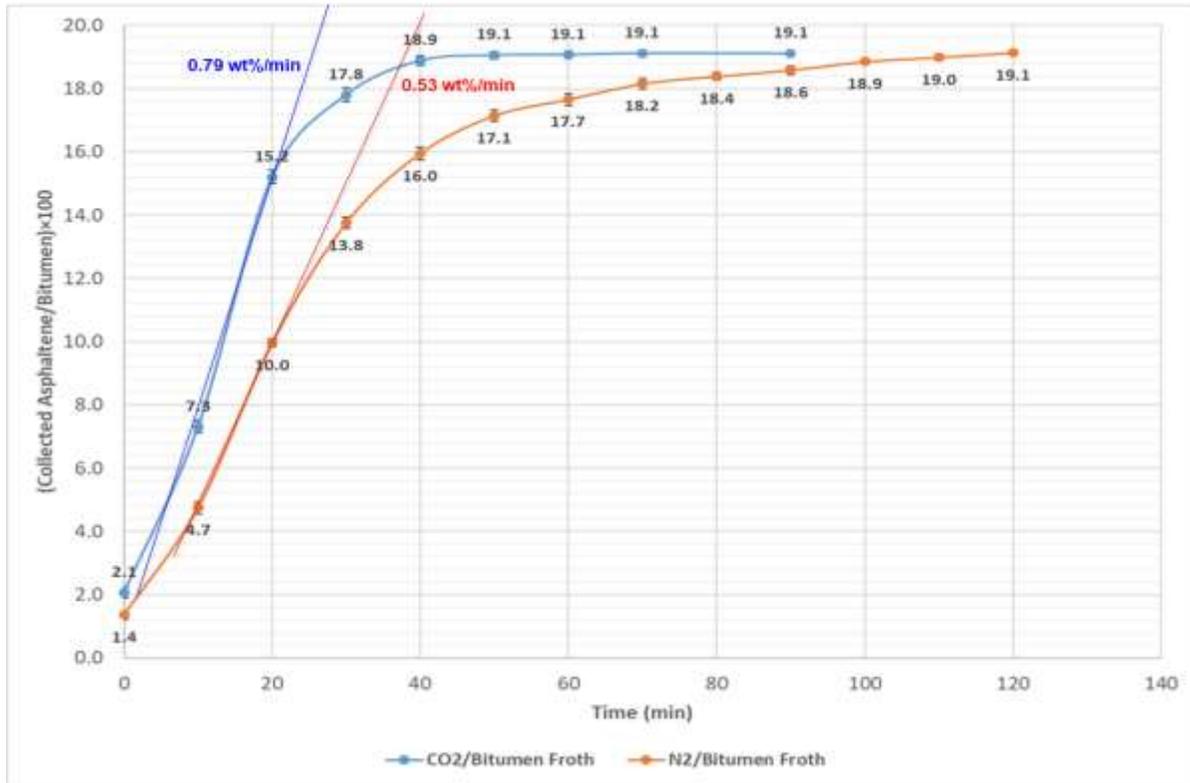


Figure 16 Settling rate of asphaltene precipitate in bitumen froth with CO₂ or N₂. The concentration of n-heptane was 52 wt%.

4.4 Total Acid Number

Table 6 compares the total acid number results of bitumen and asphaltene before and after the CO₂ assisted PFT treatment. There seems no substantial difference between them. Based on the measured TAN, it is inconclusive whether or not CO₂ helped with the precipitation of the “bad” asphaltene, or the most polar asphaltene.

Table 6 The results of Total Acid Number (TAN) experiments.

Total Acid Number (mg KOH/g)	
Untreated Bitumen	4.97±0.39
CO ₂ -Treated Bitumen	4.85±0.35
Total Asphaltene [ASTM D4055 method]	2.27±0.15
CO ₂ -Treated Asphaltene	2.32±0.19

4.5 Effect of CO₂ When S/B was below Onset of Asphaltene Precipitation

Thus far, we observed that CO₂ injection under moderate pressure (1.7 MPa) could assist the solvent (n-heptane) to precipitate more asphaltene at the onset of asphaltene precipitation (52 wt% n-heptane, or S/B=1.08).

The question was what would happen if the S/B ratio was below the onset of asphaltene precipitation? In other words, how effective was CO₂ to assist the solvent if the onset of asphaltene precipitation was not reached?

Several experiments were conducted at different CO₂ and N₂ pressures (0.1 to 1.7 MPa) and 21°C under n-heptane concentration of 50 wt% (S/B=1.0), and the results are shown in Figure 17.

According to Figure 17, if there was a lack of solvent in the PFT process to cause the onset of asphaltene precipitation, the CO₂ injection even under moderate pressure (1.7 MPa) was not sufficient to cause asphaltene precipitation (only 0.2 wt% asphaltene yield).

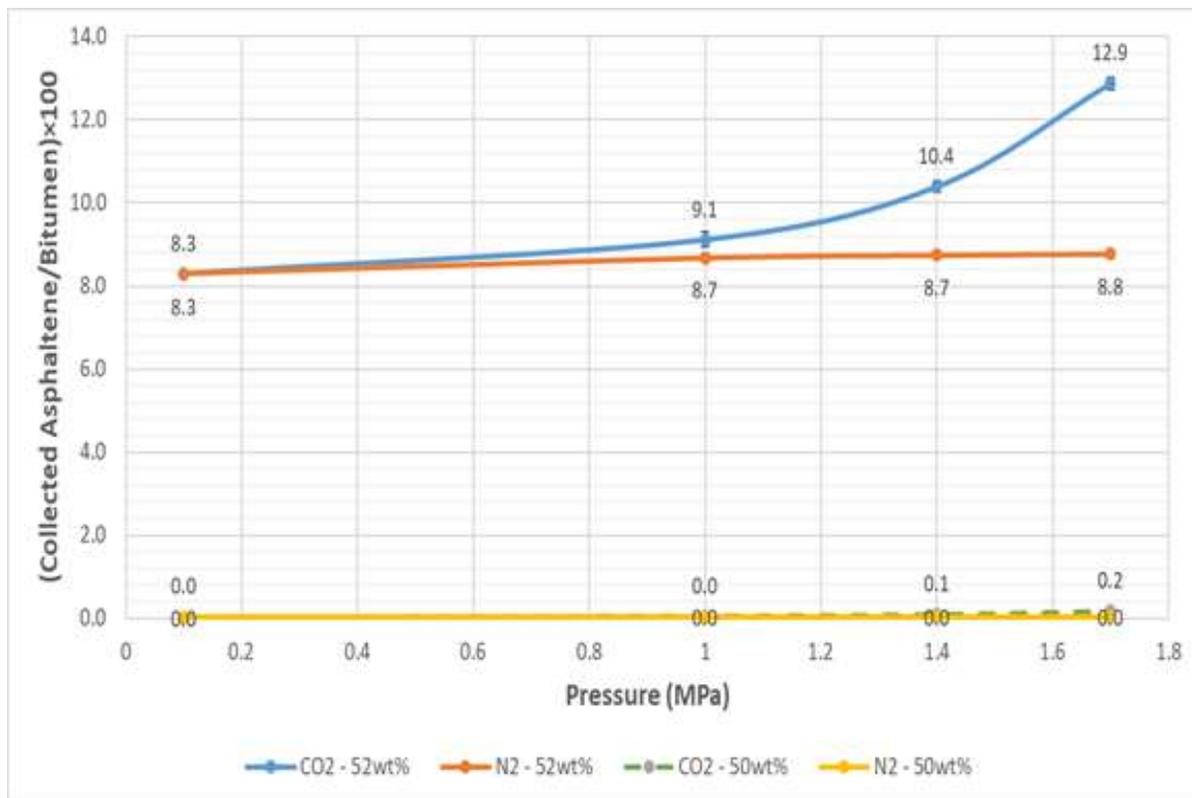


Figure 17 Effect of CO₂ on asphaltene precipitation at n-heptane concentrations of 52 wt% (S/B=1.08, onset) and 50 wt% (S/B=1, below onset).

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this proof-of-concept project, we investigated the effect of CO₂ injection at moderate pressure on paraffinic bitumen froth treatment (PFT), with an objective to lower the dosage of paraffinic solvents required for asphaltene precipitation. CO₂ was injected at two temperatures (21°C or 90°C) and several pressures from 0.1 to 1.7 MPa. The effects of water and fine solids in this process were also studied.

Heptane was used as the paraffinic solvent due to its higher boiling point, although this led to somewhat higher solvent/bitumen ratios in order to precipitate the asphaltene than commercial operations which typically used n-hexane or n-pentane. The test samples included a fine-solids free dry bitumen sample which was used as a model bitumen sample to investigate the conditions of asphaltene precipitation onset, and the effect of water addition. A bitumen froth sample was also used to verify the effect of the CO₂ injection. The main findings are:

- 1) The onset of asphaltene precipitation was determined by using gravimetric method and optical microscope observation. The results showed that 52 wt% (S/B=1.08) n-heptane was the onset of asphaltene precipitation, and at the onset, the yield of asphaltene precipitate was 8.3 wt%. Lowering the n-heptane concentration to 50 wt% or below, asphaltene precipitation ceased.
- 2) At the onset condition of 52 wt% n-heptane, the injection of 1.7 MPa CO₂ increased the collected asphaltene by more than 55% at room temperature (21°C), to 12.9 wt%. Thus, even at moderate pressure (1.7 MPa), CO₂ injection was effective to assist asphaltene precipitation at the onset conditions. On the other hand, when N₂ was injected (up to 1.7 MPa), asphaltene precipitation was not affected.
- 3) Asphaltene precipitation was influenced by the operating temperature. In the case of control tests with N₂ gas injection, precipitated asphaltene increased from 8.8±0.09 wt% to 10±0.16 wt% as the temperature increased from 21°C to 90°C. On the other hand, an increase in temperature when CO₂ was injected did not cause a further increase in asphaltene precipitation. This may be due to a decrease in CO₂ solubility at a high temperature.
- 4) Water exerts a synergistic effect with CO₂ in helping asphaltene precipitation, while the presence of fine solids did not seem to impact asphaltene precipitation. At 90°C, 1.7 MPa CO₂ and n-heptane/bitumen of 1.08, the asphaltene precipitate yield from a bitumen froth sample could reach 15.2±0.16 wt%.
- 5) To achieve a yield of 15.2 wt% asphaltene precipitate using n-heptane alone at 90°C for the same bitumen froth sample, the required n-heptane S/B ratio was 3.2. Therefore, using 1.7 MPa CO₂ at S/B ratio of 1.08 could lead to a solvent saving of 66%.

- 6) Although n-heptane is not the paraffinic solvent used in commercial operation, the practical conclusion of this proof-of-concept project was that the desired degree of asphaltene precipitation could be achieved at the onset S/B ratio when CO₂ was injected at an appropriate pressure without the need to use more solvent. With the tested bitumen froth sample and using n-heptane as the solvent, the onset S/B ratio was 1.08. Higher S/B ratio was unnecessary when 1.7 MPa CO₂ was used.
- 7) The settling rate of precipitated asphaltene as asphaltene/water/mineral solids aggregates in bitumen froth was higher when CO₂ was used to assist the PFT process compared with when N₂ was used. This may be due to the higher yield of the asphaltene precipitates.

Therefore, through this project, the concept of using CO₂ to assist asphaltene precipitation in PFT was proven so that the dosage of the paraffinic solvent could be reduced. This provides a basis for any further investigation if the CO₂-assisted PFT process is deemed attractive.

5.2 Recommendations for Future Work

For further research, there are several directions to consider:

- 1) As n-pentane and n-hexane are used in commercial PFT process, more research should be conducted with n-pentane and n-hexane.
- 2) The mechanism of how CO₂ helps asphaltene precipitation is still unknown. Further investigation of this topic is necessary. A better understanding of the mechanisms will benefit troubleshooting if the process will be used in commercial operations.
- 3) In this proof-of-concept project, water was tested at a fixed concentration of 20 wt% to be in line with the bitumen froth sample. Further research on the impact of water at different concentrations can be conducted to understand its impact.
- 4) The quality of the final bitumen product and the composition and properties of the asphaltene precipitate when CO₂ was used can be systematically investigated to examine if the bad players in the asphaltene fraction could be selectively removed by the use of CO₂.

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7 REFERENCES

- [1] Zhao J, Liu Q, Gray MR. Characterization of Fine Solids in Athabasca Bitumen Froth before and after Hydrothermal Treatment. *Energy Fuels* 2016;30:1965–71. doi:10.1021/acs.energyfuels.5b02325.
- [2] Kosior D, Ngo E, Xu Y. Aggregates in paraffinic froth treatment: settling properties and structure. *Energy Fuels* 2018;32:8268–76. doi:10.1021/acs.energyfuels.8b01656.
- [3] Rao F, Liu Q. Froth treatment in athabasca oil sands bitumen recovery process: A review. *Energy Fuels* 2013;27:7199–207. doi:10.1021/ef4016697.
- [4] Long Y. Stability and settling characteristics of solvent-diluted bitumen emulsions. *Fuel* 2002;81:1945–52. doi:10.1016/S0016-2361(02)00132-1.
- [5] Shelfantook WE. A perspective on the selection of froth treatment processes. *Can J Chem Eng* 2008;82:704–9. doi:10.1002/cjce.5450820409.
- [6] Schramm LL. Book review: Handbook on theory and practice of bitumen recovery from Athabasca oil sands, volume 1: Theoretical basis, J. Masliyah, J. Czarnecki, and Z. Xu, 2011; 468 pp. Kingsley publishing services: Cochrane, AB (ISBN: 978-1-926832-03-6). *Can J Chem Eng* 2012;90:1079–1079. doi:10.1002/cjce.21697.
- [7] Mullins OC, Sheu EY, Hammami A, Marshall AG, editors. *Asphaltenes, heavy oils, and petroleomics*. New York, NY: Springer New York; 2007. doi:10.1007/0-387-68903-6.
- [8] Shafiee Neistanak M. Kinetics of Asphaltene Precipitation and Flocculation from Diluted Bitumen. Master thesis. University of Calgary, 2014.
- [9] Romanova UG, Valinasab M, Stasiuk EN, Yarranton HW, Schramm LL, Shelfantook WE. The effect of oil sands bitumen extraction conditions on froth treatment performance. *Journal of Canadian Petroleum Technology* 2006;45. doi:10.2118/06-09-03.
- [10] Yang X, Czarnecki J. The effect of naphtha to bitumen ratio on properties of water in diluted bitumen emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2002;211:213–22. doi:10.1016/S0927-7757(02)00279-0.
- [11] Long Y, Dabros T, Hamza H. Selective solvent deasphalting for heavy oil emulsion treatment. In: Mullins OC, Sheu EY, Hammami A, Marshall AG, editors. *Asphaltenes, heavy oils, and petroleomics*, New York, NY: Springer New York; 2007, p. 511–47. doi:10.1007/0-387-68903-6_20.
- [12] Ansari NN. Thermogravimetric Analysis of Solvent Interaction with Model TSRU Tailings Components. University of Alberta Libraries 2013. doi:10.7939/r3fh83.
- [13] Oil Sands Magazine Paraffinic Froth Treatment. <https://WwwOilsandsmagazineCom/Technical/Mining/Froth-Treatment/Paraffinic> 2019. <https://www.oilsandsmagazine.com/technical/mining/froth-treatment/paraffinic> (accessed October 2, 2019).

- [14] Masliyah J, Zhou ZJ, Xu Z, Czarnecki J, Hamza H. Understanding Water-Based Bitumen Extraction from Athabasca Oil Sands. *Can J Chem Eng* 2008;82:628–54. doi:10.1002/cjce.5450820403.
- [15] Thomas S. Enhanced Oil Recovery - An Overview. *Oil & Gas Science and Technology - Rev IFP* 2008;63:9–19. doi:10.2516/ogst:2007060.
- [16] Porto M, Caputo P, Loise V, Eskandarsefat S, Teltayev B, Oliviero Rossi C. Bitumen and bitumen modification: A review on latest advances. *Applied Sciences* 2019;9:742. doi:10.3390/app9040742.
- [17] Sztukowski DM, Jafari M, Alboudwarej H, Yarranton HW. Asphaltene self-association and water-in-hydrocarbon emulsions. *J Colloid Interface Sci* 2003;265:179–86. doi:10.1016/S0021-9797(03)00189-9.
- [18] Kotlyar LS, Sparks BD, Woods JR, Chung KH. Solids Associated with the Asphaltene Fraction of Oil Sands Bitumen. *Energy Fuels* 1999;13:346–50. doi:10.1021/ef980204p.
- [19] Oil sand production processes. Elsevier; 2013. doi:10.1016/C2012-0-00595-9.
- [20] Mullins OC. The asphaltenes. *Annu Rev Anal Chem (Palo Alto Calif)* 2011;4:393–418. doi:10.1146/annurev-anchem-061010-113849.
- [21] Rahmani NHG, Dabros T, Masliyah JH. Settling properties of asphaltene aggregates. *Energy Fuels* 2005;19:1099–108. doi:10.1021/ef0496707.
- [22] Podgorski DC, Corilo YE, Nyadong L, Lobodin VV, Bythell BJ, Robbins WK, et al. Heavy petroleum composition. 5. compositional and structural continuum of petroleum revealed. *Energy Fuels* 2013;27:1268–76. doi:10.1021/ef301737f.
- [23] Carnahan NF. Chapter 12 precipitation of asphaltenes in heavy oil and tar sands. *Asphaltenes and asphalts*, 2, vol. 40, Elsevier; 2000, p. 319–33. doi:10.1016/S0376-7361(09)70283-3.
- [24] Strausz OP, Mojelsky TW, Lown EM. The molecular structure of asphaltene: an unfolding story. *Fuel* 1992;71:1355–63. doi:10.1016/0016-2361(92)90206-4.
- [25] Tharanivasan AK. Asphaltene precipitation from crude oil blends, conventional oils, and oils with emulsified water. University of Calgary 2012. doi:10.11575/prism/4677.
- [26] Xu Y. Asphaltene precipitation in paraffinic froth treatment: effects of solvent and temperature. *Energy Fuels* 2017. doi:10.1021/acs.energyfuels.7b03013.
- [27] Zhao Y, Wei F. Simultaneous removal of asphaltenes and water from water-in-bitumen emulsion. *Fuel Processing Technology* 2008;89:933–40. doi:10.1016/j.fuproc.2008.03.008.
- [28] Maqbool T. Understanding the kinetics of asphaltene precipitation from crude oils. Doctoral dissertation. University of Michiga, 2011.
- [29] Casas Y. Settling Rates of Asphaltenes and Solids from Diluted Bitumen. University of Calgary 2017. doi:10.11575/prism/27763.
- [30] Alboudwarej H, Akbarzadeh K, Beck J, Svrcek WY, Yarranton HW. Regular solution model for asphaltene precipitation from bitumens and solvents. *AIChE J* 2003;49:2948–56. doi:10.1002/aic.690491124.

- [31] Wiehe IA, Yarranton HW, Akbarzadeh K, Rahimi PM, Teclemariam A. The Paradox of Asphaltene Precipitation with Normal Paraffins[†]. *Energy Fuels* 2005;19:1261–7. doi:10.1021/ef0496956.
- [32] Yarranton HW, Ortiz DP, Barrera DM, Baydak EN, Barré L, Frot D, et al. On the Size Distribution of Self-Associated Asphaltenes. *Energy Fuels* 2013;27:5083–106. doi:10.1021/ef400729w.
- [33] Gray MR, Tykwinski RR, Stryker JM, Tan X. Supramolecular assembly model for aggregation of petroleum asphaltenes. *Energy Fuels* 2011;25:3125–34. doi:10.1021/ef200654p.
- [34] Sjöblom J, Aske N, Harald Auflem I, Brandal Ø, Erik Havre T, Sæther Ø, et al. Our current understanding of water-in-crude oil emulsions. *Adv Colloid Interface Sci* 2003;100–102:399–473. doi:10.1016/S0001-8686(02)00066-0.
- [35] El-hoshoudy AN, Desouky S. CO₂ miscible flooding for enhanced oil recovery. In: Agarwal RK, editor. *Carbon capture, utilization and sequestration*, InTech; 2018. doi:10.5772/intechopen.79082.
- [36] Mungan N. Interfacial Effects in Immiscible Liquid-Liquid Displacement in Porous Media. *Society of Petroleum Engineers Journal* 1966;6:247–53. doi:10.2118/1442-PA.
- [37] Fakher S, Imqam A. Asphaltene precipitation and deposition during CO₂ injection in nano shale pore structure and its impact on oil recovery. *Fuel* 2019;237:1029–39. doi:10.1016/j.fuel.2018.10.039.
- [38] Zanganeh P, Dashti H, Ayatollahi S. Comparing the effects of CH₄, CO₂, and N₂ injection on asphaltene precipitation and deposition at reservoir condition: A visual and modeling study. *Fuel* 2018;217:633–41. doi:10.1016/j.fuel.2018.01.005.
- [39] Dong Z, Wang J, Liu G, Lin M, Li M. Experimental study on asphaltene precipitation induced by CO₂ flooding. *Pet Sci* 2014;11:174–80. doi:10.1007/s12182-014-0329-2.
- [40] Perera M, Gamage R, Rathnaweera T, Ranathunga A, Koay A, Choi X. A Review of CO₂-Enhanced Oil Recovery with a Simulated Sensitivity Analysis. *Energies* 2016;9:481. doi:10.3390/en9070481.
- [41] Cao M, Gu Y. Oil recovery mechanisms and asphaltene precipitation phenomenon in immiscible and miscible CO₂ flooding processes. *Fuel* 2013;109:157–66. doi:10.1016/j.fuel.2013.01.018.
- [42] Auflem IH, Kallevik H, Westvik A, Sjöblom J. Influence of pressure and solvency on the separation of water-in-crude-oil emulsions from the North Sea. *Journal of Petroleum Science and Engineering* 2001;31:1–12. doi:10.1016/S0920-4105(01)00134-6.
- [43] Zaki NN, Carbonell RG, Kilpatrick PK. A Novel Process for Demulsification of Water-in-Crude Oil Emulsions by Dense Carbon Dioxide. *Ind Eng Chem Res* 2003;42:6661–72. doi:10.1021/ie0303597.
- [44] Dong M, Gong H, Tian W, Li Y. Separation of Water from High pH Water-in-Heavy Oil Emulsions Using Low Pressure CO₂. *Ind Eng Chem Res* 2014;53:12216–23. doi:10.1021/ie501916b.

- [45] Marufuzzaman M, Henni A. Solubility Of CO₂ and C₂H₆ in heavy Oil and its Sara fractions. *Can J Chem Eng* 2015;93:553–64. doi:10.1002/cjce.22150.
- [46] Shadman MM, Saeedi Dehaghani AH, Badizad MH. How much do you know about the methods for determining onset of asphaltene precipitation? *Petroleum* 2016. doi:10.1016/j.petlm.2016.08.011.
- [47] Soleymanzadeh A, Yousefi M, Kord S, Mohammadzadeh O. A review on methods of determining onset of asphaltene precipitation. *J Pet Explor Prod Technol* 2018;9:1–22. doi:10.1007/s13202-018-0533-5.
- [48] Marugán J, Calles JA, Dufour J, Giménez-Aguirre R, Peña JL, Merino-García D. Characterization of the Asphaltene Onset Region by Focused-Beam Laser Reflectance: A Tool for Additives Screening[†]. *Energy Fuels* 2009;23:1155–61. doi:10.1021/ef800626a.
- [49] Sivaraman A, Hu Y, Thomas FB, Bennion DB, Jamaluddin AKM. Acoustic resonance: an emerging technology to identify wax and asphaltene precipitation onset conditions in reservoir fluids. Annual Technical Meeting, Petroleum Society of Canada; 1997. doi:10.2118/97-96.
- [50] Jamaluddin AKM, Creek J, Kabir CS, McFadden JD, D’Cruz D, Manakalathil J, et al. Laboratory techniques to measure thermodynamic asphaltene instability. *Journal of Canadian Petroleum Technology* 2002;41. doi:10.2118/02-07-04.
- [51] Lawal KA, Crawshaw JP, Boek ES, Vesovic V. Experimental investigation of asphaltene deposition in capillary flow. *Energy Fuels* 2012;26:2145–53. doi:10.1021/ef201874m.
- [52] Gabrienko AA, Martyanov ON, Kazarian SG. Behavior of Asphaltenes in Crude Oil at High-Pressure CO₂ Conditions: In Situ Attenuated Total Reflection–Fourier Transform Infrared Spectroscopic Imaging Study. *Energy Fuels* 2016;30:4750–7. doi:10.1021/acs.energyfuels.6b00718.
- [53] Maqbool T, Srikiratiwong P, Fogler HS. Effect of temperature on the precipitation kinetics of asphaltenes. *Energy Fuels* 2011;25:694–700. doi:10.1021/ef101112r.
- [54] Mirmontazeri L. Colloidal Phenomena in Relation to Non-Aqueous Bitumen Extraction. University of Alberta Libraries 2014. doi:10.7939/r3xg9fk3x.
- [55] Karkooti A. Aggregation and Sedimentation of Fine Solids in Non-Aqueous Media. University of Alberta Libraries 2014. doi:10.7939/r3x05xm7r.

APPENDIX: LIST OF PUBLICATIONS AND PATENT FILING/APPLICATION

1. Shahrads Khodaei Booran, Xue Wang, Xiaoli Tan, Qi Liu, 2020. Effect of Carbon Dioxide on Asphaltene Precipitation from Bitumen-Heptane Mixtures, Energy and Fuel, Submitted 2020-05-15.
2. Shahrads Khodaei Booran, Xue Wang, Xiaoli Tan, Qi Liu, 2020. Effect of Carbon Dioxide on Asphaltene Precipitation from a Bitumen Froth Sample Induced by Heptane, In Preparation.