Carbon Dioxide Assisted Paraffinic Froth Treatment

by

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ABSTRACT

In the paraffinic froth treatment (PFT), a large amount of paraffinic solvent is used to produce very clean bitumen products which can be transported directly to market without an upgrading step. However, the high solvent usage demands a large capacity in tailings solvent recovery unit. To solve this problem, CO_2 has been proposed as a processing aid in PFT to assist asphaltene precipitation so that less paraffinic solvents are needed.

In this study, the onset point of asphaltene precipitation was determined by a gravimetric method and confirmed by the optical microscopy method at different solvent-to-bitumen (S/B) ratios. Then, the asphaltene precipitation with the injection of CO_2 was performed at different pressure and temperature conditions. Afterwards, the experiments were extended to test the effect of water addition, and finally to directly test the treatment of bitumen froth with paraffinic solvent addition and CO_2 injection. The bitumen and asphaltene were characterized by the total acid number (TAN) measurements.

All the asphaltene precipitation experiments were also conducted with N_2 as control, in which the asphaltene precipitation was under different pressure and temperature conditions. The impacts of water and solids on asphaltene precipitation were also investigated.

To examine the optimal condition at the industrial operating range, the CO_2-assisted PFT experiments were conducted at low pressure range (0.1-1.7MPa) and low temperatures (21°C, 90°C). At 90°C, with the injection of 1.7 MPa CO_2 and addition of 52 wt% of n-heptane, the asphaltene yield reached 15.3%, which means 80.6% of total asphaltene was precipitated. To reach the same asphaltene yield without CO_2, the n-heptane concentration needed to be 76.9 wt%. Therefore, by using 1.7 MPa CO_2 in PFT, the n-heptane concentration could be reduced by 24.9 percentage point, or 32.4 %.

PREFACE

This thesis is an original work by Xue Wang. The research project, of which this thesis is a part, received research ethics approval from the University of Alberta Research Ethics Board, Project Name "CO_2-ASSISTED PARAFFINIC FROTH TREATMENT", Project number IOSI 2017-15: Extraction Theme, September 01, 2018 to May 31, 2020.

Some of the research conducted for this thesis forms part of a research collaboration, led by Dr. Qi Liu and Dr. Xiaoli Tan at the University of Alberta. The technical apparatus referred to in Chapter 4 was designed by myself, with the assistance of Shahrad Khodaei Booran and Dr. Qi Liu and Dr. Xiaoli Tan. The data analysis in Chapter 5 and concluding analysis in Chapter 6 are my original work, as well as the literature review in Chapter 2.

Chapters 4, 5, 6 of this thesis are planned to be published. I was responsible for experiment execution, data collection, and analysis as well as the manuscript composition. Shahrad Khodaei Booran assisted with the experiments, data collection and contributed to manuscript composition and edits. Dr. Qi Liu and Dr. Xiaoli Tan were the supervisory authors and were involved with concept formation and manuscript composition and revision.

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1. INTRODUCTION

Athabasca is one of the largest known reservoirs of crude bitumen in the world and the largest of three major oil sands deposits located in Alberta, along with the nearby Peace River and Cold Lake deposits. These oil sand deposits lie under 142,000 square kilometers and contain about 2.5 trillion barrels of bitumen in-place. Among these, about 314.5 billion barrels are estimated to be recoverable using current open-pit mining and in-situ technologies (Masliyah et al., 2004).

The first field-scale bitumen extraction test from the Athabasca oil sands was conducted by Karl Clark and his colleagues in the 1920s. Later on, the first commercial application, Clark Hot Water Extraction process (CHWE), was achieved by Great Canadian Oil Sands, GCOS (now Suncor Energy Inc.) in 1967. Figure 1.1 (Rao and Liu, 2013) is a schematic process framework of CHWE. Since then, many operating companies (Syncrude, CNRL, ExxonMobil, etc.) joined the journey and the oil sands industries started thriving.
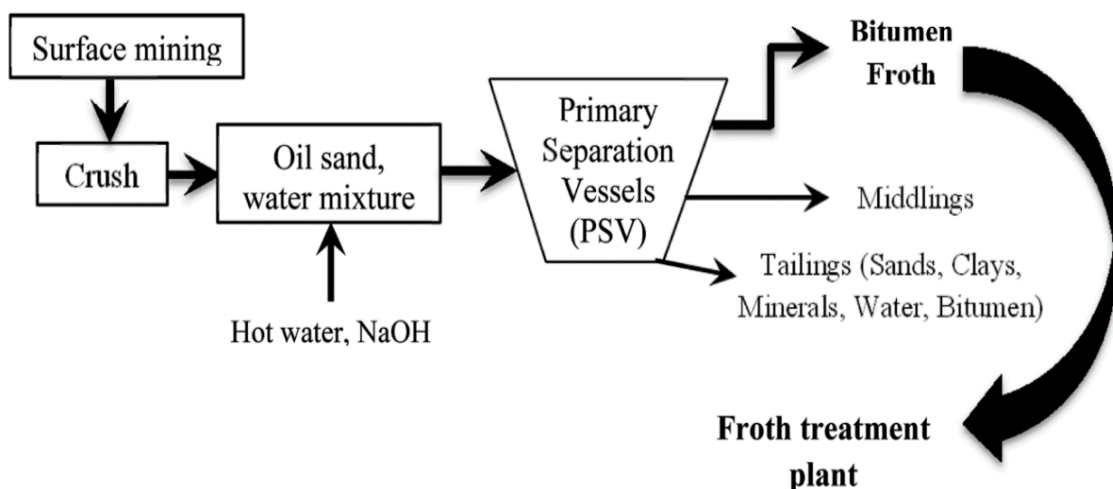
Figure 1.1. Schematic diagram of CHWE process (Rao and Liu, 2013)

As shown in Figure 1.1, the oil sand ores are firstly excavated in an open-pit mine and then crushed into small pieces. After excavation, hot water and NaOH are added to the extracted material. The combination of hot water and agitation releases bitumen from the oil sands and allowed air bubbles to attach to the bitumen droplets. The aerated bitumen floated to the top and then can be skimmed off (Shah et al., 2010). The recovered bitumen froth approximately consists of 60 wt% bitumen, 30 wt% water, and 10 wt% mineral solids. The bitumen froth is then transported to the froth treatment plant to produce a clean diluted bitumen product.

Currently, there are two commercial froth treatment processes available in Alberta oil sands industry, named as the paraffinic froth treatment (PFT) and naphthenic froth treatment (NFT) according to the diluent it uses. The function of diluents is to reduce the bitumen viscosity and to provide sufficient density difference between water and bitumen so that they can be separated by gravity settling (Romanova et al., 2008; Shelfantook, 2004). The NFT process uses naphtha as a solvent to dilute bitumen and remove the solids and water by inclined plate settlers, hydrocyclones, or centrifuges, while the PFT process uses a paraffinic solvent such as hexane or pentane (Rao and Liu, 2013; Romanova et al., 2008; Shelfantook, 2004). The paraffinic solvent at a high S/B ratio in PFT process is used to cause asphaltene precipitation. As asphaltene precipitates, the formed asphaltene aggregates can trap the emulsified water droplets and fine mineral particles so that the water and solids can be efficiently removed.

Since a large amount of paraffinic solvent is required to induce asphaltene precipitation and to maintain the quality of bitumen product, the high solvent usage demands a large capacity in solvent recovery unit (SRU) and tailings solvent recovery unit (TSRU), increasing operation cost significantly. Meanwhile, asphaltene precipitation leads to hydrocarbon loss (Rao and Liu, 2013; Romanova et al., 2008; Shelfantook, 2004), causing

a low overall bitumen recovery compared to NFT. To solve these problems, it is desirable to enhance the PFT process without using large volumes of paraffinic solvent but achieving both high settling rate of asphaltene/water/solids aggregates and high bitumen recovery.

To achieve a high bitumen recovery, less precipitated asphaltene or controlled precipitation of asphaltene from bitumen is required. As the polar asphaltene fractions are typically regarded as the most problematic parts in upgrading and refinery processes, it is preferable for a PFT process to selectively precipitate the more polar asphaltene fractions. The less–polar asphaltene fractions remain in bitumen as the more polar asphaltene is the low-soluble fraction (Evdokimov, 2005). In this study, carbon dioxide (CO_2) is introduced in PFT process to help induce asphaltene precipitation. It is worth mentioning that we are not trying to use CO_2 to eliminate the use of paraffinic solvents in the PFT process conditions. Rather, we intend to use CO_2 as a processing aid dissolved in paraffinic solvent/bitumen/water to achieve the product purification by using much less paraffinic solvent. The detailed objectives include:

1. To obtain suitable parameters for CO_2 assisted PFT process including S/B ratio (onset point concentration), CO_2 pressure, temperature.
2. To investigate the influence of CO_2 on asphaltene precipitation with the presence of water and fine solids.
3. To investigate asphaltene precipitation kinetics under CO_2 injected conditions (i.e. settling rate of asphaltene/water/minerals aggregates under different conditions).
4. To characterize bitumen properties before and after treatment by total acid number (TAN).

This thesis consists of seven chapters. Chapter 1 gives a brief introduction of Alberta oil sands, oil sand processing, and froth treatment, especially on paraffinic froth treatment.

Chapter 2 presents a detailed literature review on bitumen froth components and froth treatment, the science on asphaltene and asphaltene precipitation, as well as the application of CO_2 in the petroleum industry. Chapter 3 describes a series of experiments in detail, including the determination of onset point, the performance of CO_2 at different temperatures and pressures, the application of CO_2 in bitumen with water and bitumen froth, and finally the total acid number experiments. Chapter 4 provides the results and discussion of the experiments conducted. Chapter 5 summarizes the major findings of this study and makes several technical recommendations for future studies.

2. LITERATURE REVIEW

2.1 Bitumen Froth Generated from Athabasca Oil Sands

Figure 2.1 (Masliyah et al., 2004) presents a detailed and comprehensive flow diagram from oil sands mining to the bitumen upgrading process. The oil sand ores mined by open-pit technology are transported by trucks and shovels to crushed. After being crushed and sized, the oil sand ores are mixed with hot water and some chemical additives to make it a wet slurry. The slurry is composed of approximately 40 wt% water, 8 wt% bitumen and above 50 wt% solids (Masliyah et al., 2004). After a complex process of bitumen liberation and aeration, the slurry is then pumped 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.
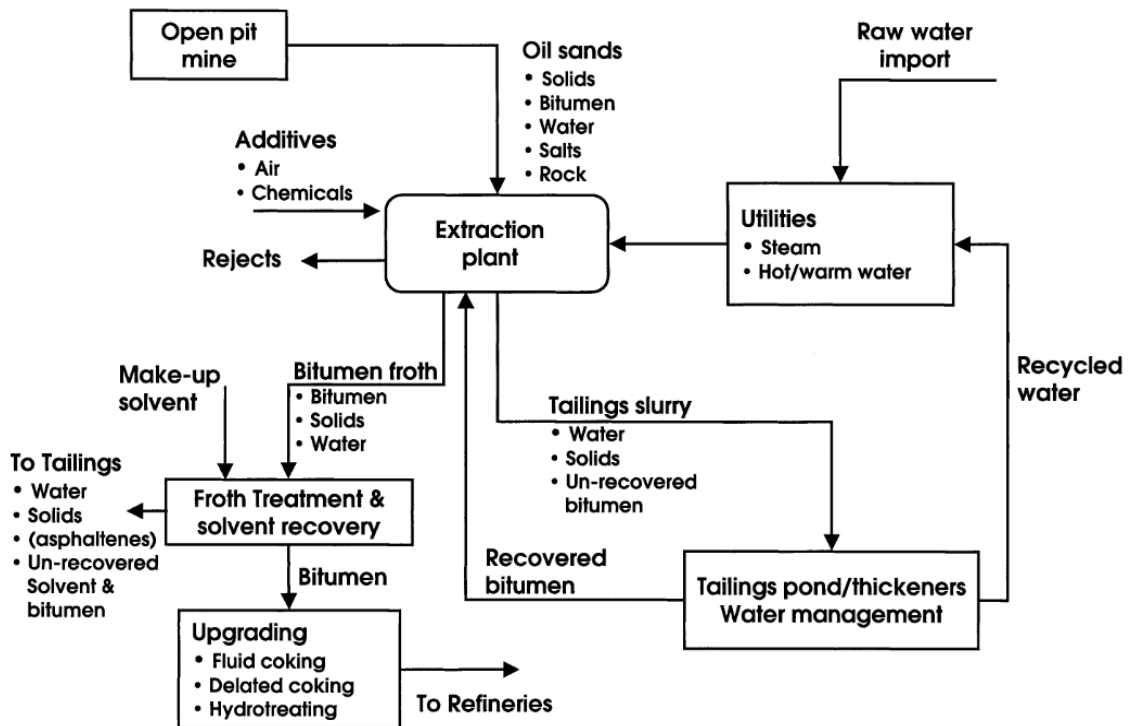
Figure 2.1.Scheme of water-based extraction processes (Masliyah et al., 2004)

A typical overall bitumen recovery in commercial operations is about 88–95% (Masliyah et al., 2004). As an intermediate product, the bitumen froth only contains 60 wt% of bitumen, with about 30 wt% water and 10 wt% mineral solids. Table 2.1 presents some typical compositions of bitumen froth samples (Long et al., 2002).

Table 2.1. Compositions of some typical bitumen froth samples (Long et al., 2002)

Bitumen Froth sample	Bitumen (wt%)	Water(wt%)	Solids(wt%)
Bitumen Froth #1	47.7	39.2	13.1
Bitumen Froth #2	58.8	30.9	10.2
Bitumen Froth #3	44.2	36.5	19.3
Bitumen Froth #4	68.3	20.2	11.5

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 (Masliyah et al., 2004). Bitumen is defined as the toluene-soluble constituents in oil sand (Shelfantook, 2004), which typically has a high density of 1010 kg/m^3 and high viscosity of the order of 100 Pa·s at ambient condition (Mullins et al., 2007).

Molecular weight distribution analysis shows that bitumen is a complex mixture with a molecular weight range of 300 to 2000 g/mol (medium value 500–700 g/mol), which makes bitumen extremely challenging to be chemically characterized (Porto et al., 2019). For such reason, bitumen is often characterized chemically by its hydrocarbon class compositions such as saturates–aromatics–resins–asphaltenes (SARA) contents. The most essential component of bitumen is asphaltene, which is defined as a solubility class of crude

oils that precipitates in the aliphatic solvents such as n-pentane or n-heptane but remains soluble in aromatic solvents such as toluene and xylenes (Sztukowski et al., 2003). On average, the Athabasca bitumen consists of 17 wt% saturates, 40 wt% aromatics, 26 wt% resins, and 17 wt% asphaltenes (Rao and Liu, 2013).

2.1.2 Water

Water contained in bitumen froth carries not only fine solids but also dissolved problematic inorganic salts, such as chlorides, which 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.

Based on droplet size, water in diluted bitumen can be classified into three types: (I) emulsified water, with water droplet sizes less than 10 μm in diameter, (II) dispersed water, with droplet sizes between 10 μm and 60 μm, and (III) free water, with droplet sizes larger than 60 μm (Mullins et al., 2007). 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 (Mullins et al.,2007).

The stabilization mechanism behind the water-in-oil emulsion has been explored for a long time. It is generally accepted that the microscopic water-in-oil emulsions are strongly stabilized by native crude oil surfactants. These surfactants prevent droplet coalescence by creating an insistent steric barrier film on the surfaces of the emulsion droplets (Shelfantook, 2004). Asphaltenes, resins, waxes, and small solid particles are generally identified to be responsible for the stability of water droplets (Sztukowski et al., 2003).

Particularly, asphaltene is perceived as the key component for the stabilization of emulsion (Gu et al. 2002; Yan et al., 1999), especially with the presence of fine solids when the emulsion is in the most steady condition (Yan et al., 1999). The hydrophobic and hydrophilic parts of some asphaltene molecules offer them surfactant properties that enable them to work in concert with mineral solids particles to form an inflexible film at the water-oil interface. This film results in a variety of problems including high stability of the water-in-oil emulsion, the high viscosity of bitumen during pipelining, high-coking propensity and catalyst poisoning during bitumen upgrading and refining (Gu et al., 2002).

2.1.3 Mineral solids

In the bitumen froth treatment process, the presence of mineral solids can contribute to the stabilization of emulsions of water in diluted bitumen, as the solids form a steric barrier for the coalescence of water (Masliyah et al., 2011a). The mineral solids with clean surfaces are naturally hydrophilic and will not adsorb at an oil-water interface. Therefore, those fine solids capable of stabilizing water-in-oil (w/o) emulsions are mainly inorganic clays whose surface properties have been altered by the adsorption of surfactants present in oil (Masliyah et al., 2011a). Over a long period of time, the surface of these inorganic particles have been rendered increasingly hydrophobic due to their exposure to the highly aromatic, polar organic components such as asphaltene, resin, naphthenic acids and their salts (Kotlyar et al., 1999). The interactions between these organic components and inorganic particles endowing a bi-wettable character to the solids, enabling them to form solids-water clusters or to stabilize emulsions by forming rigid barriers between water droplets and the continuous phase (Kotlyar et al., 1999).

2.2 Bitumen Froth Treatment

Bitumen froth treatment is a unit operation in the bitumen extraction process aiming to exact bitumen from bitumen froth. As explained above, the high contents of water and mineral solids are not acceptable by transportation pipelines, upgrading, and refining facilities. As 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 must have a viscosity of less than 350 mPa·s (Long et al., 2002; Shelfantook, 2004). This process is referred to as bitumen froth treatment.

Currently, the commercial froth treatment process can be classified into two categories according to the hydrocarbon solvent used: Naphthenic Froth Treatment (NFT), and Paraffinic Froth Treatment (PFT).

The basic role of the hydrocarbon solvent is to lower the viscosity and density of bitumen froth to facilitate further separation (Rao and Liu, 2013). The high viscosity of bitumen and the similar density with water limit the possibility of successful separation only by gravity settling, even at elevated temperatures. Therefore, it is necessary to increase the density difference between bitumen and water to create the driving force for separation, which can be achieved by the employment of a solvent, or a diluent. A diluent can reduce the viscosity of the hydrocarbon phase so that the water and solids can settle down in gravity settling vessels (Masliyah et al., 2011b).

2.2.1 Naphthenic Froth Treatment

2.2.1.1 Process Overview

In a naphthenic froth treatment (NFT) process, a naphthenic diluent is added to the froth, producing a relatively clean final product. Since the bitumen product still contains 1 to 2 wt% water and 0.5 wt% fine solids, it is required to be upgraded into a higher quality synthetic crude oil (SCO) before transported to refineries on the open market (Long et.al, 2002).

Naphthenic froth treatment is the original technology used to clean bitumen froth for over 30 years. The advantages of NFT have already been commonly accepted. Firstly, since naphthenic diluents have a relatively high boiling point at atmospheric pressures, vessels can operate at lower pressures (Rao and Liu, 2013; Romanova et al., 2008) , which makes it easier for equipment maintenance and reduces the risk of ignition. Besides, because no asphaltene is precipitated, the NFT plants can produce bitumen with a higher recovery than an equivalent PFT process. NFT facilities can recover 98% of the bitumen, while an equivalent PFT facility can only achieve a 90% recovery rate (Shelfantook, 2004). More importantly, in this case, asphaltene handling is not an issue as no asphaltene precipitates.

At the same time, the drawbacks of NFT are very evident as well. First of all, as w/o emulsions formed in NFT are very stable, NFT facilities require more robust equipment that can generate and withstand high g-forces, such as hydrocyclones and centrifuges (Masliyah et al., 2011b). They require more maintenance and usually are more complex than an equivalent PFT facility. Secondly, bitumen product quality is comparatively low, containing at least 1% water and 0.5% solids, which always leads to the severe fouling and corrosion of upgrading equipment (Shelfantook, 2004). Meanwhile, the high water/solids content in the bitumen makes it difficult to transport over long distance without enough dilution. Bitumen upgraders are therefore required to be on-site or in very short distance.

2.2.1.2 Equipment used in NFT

The NFT facilities mainly consist of inclined plate settlers (IPSs), hydrocyclone plants, and centrifuge plants (Masliyah et al., 2011b). Inclined plate settlers usually are employed for the primary cleaning step. They are cone-bottomed gravity separation vessels with internal inclined plates that provide extensive surface area for settling the solids and water fractions (Masliyah et al., 2011b). They can produce a high-quality overflow, with relatively low solids and water contents (less than 2%). But the IPS underflow still contains a significant amount of bitumen and naphtha solvents, which needs to be processed through the centrifuge plants. The centrifuges rotate at very high speeds, applying high g-forces to remove solids from the bitumen product. There are two types of centrifuges: solid-bowl scroll centrifuges which remove coarse sands (larger than 44 µm) and disc nozzle centrifuges which remove fine materials (Masliyah et al., 2011b). Meanwhile, the hydrocyclone can serve as the same function as the centrifuge to clean up the underflow of IPS, while with much less cost. The hydrocyclone can break up emulsions that form in the IPS and facilitate the liberation of diluted bitumen, allowing solids and water to be returned to the underflow (Masliyah et al., 2011b).

More specifically, the facilities currently served in Suncor, Syncrude, and CNRL are listed below in Table 2.2 (Masliyah et al., 2011b), respectively.

Table 2.2. NFT facilities used by the oil sands companies (Masliyah et al., 2011b)

Operator	Suncor	Syncrude	CNRL
Facilities	IPSs, hydrocyclones, centrifuges	IPSs, centrifuges	IPSs, hydrocyclones

2.2.1.3 Naphthenic diluents

The naphthenic diluents used in NFT are a mixture of naphthenic hydrocarbons in the C_5 to C_{10} range. The S/B ratio used in NFT is 0.6-0.7 (Masliyah et al., 2011b; Shelfantook, 2004). At this ratio range, all the asphaltenes contained in the bitumen remain in solution. In other words, there is no asphaltene precipitation.

Since the naphtha-based process operates below critical dilution ratio, the oil-water interface is flexible, and emulsions are easily formed (Rao and Liu, 2013). To break up the stubborn emulsions in the diluent, some demulsifiers and demineralizers are commonly used as process aids. Demulsifiers used in the oil sands are blends of surfactants, such as amines, copolymers of ethylene oxide and propylene oxide (Al-Sabagh et al., 2011). Adding demulsifiers to the process can reduce bitumen loss to the underflow of the separation units.

2.2.2 Paraffinic Froth Treatment

2.2.2.1 Process Overview

Paraffinic froth treatment (PFT) is now the preferred technology for those operators who do not have a upgrader nearby since it can produce a clean product with water and solid contents less than 0.1 wt% (Long et al, 2002, 2004), which can be transported to a high conversion refinery directly.

Paraffinic solvents are predominantly aliphatic hydrocarbons in the C_4 to C_{20} range. Solvents used in PFT facilities typically include n-pentane (C_5H_{12}) to n-heptane (C_7H_{16}) hydrocarbons (Maqbool et.al, 2011; Rao and Liu, 2013). On one hand, paraffinic

solvents dilute the bitumen, reducing the viscosity of bitumen and enabling water and solids removal by gravity separation. On the other hand, paraffinic solvents can precipitate asphaltene. When paraffinic solvent addition exceeds the onset of asphaltene precipitation, the precipitated asphaltene acts as flocculants for emulsified water droplets and fine solids, and thus breaks the w/o emulsion (Long et al., 2002). The flocs formed contain water droplets, fine solids, and precipitated asphaltene. Clay solids and water droplets are entrapped in the asphaltene flocs, which separate from the hydrocarbon phase and settle to the bottom, leaving a diluted bitumen of less than 0.2 wt% water that is nearly free of solids. Additionally, nickel and vanadium, associated with asphaltene, are also reduced (Mullins et al., 2007).

The advantages and disadvantages of paraffinic froth treatment are also very evident. In terms of advantages, firstly, PFT produces a very high-quality bitumen that can be sold directly to a refinery without upgrading. This eliminates the need to build upgraders, which are highly complex, expensive, and labor-intensive. In the meantime, as asphaltene precipitation breaks most of the emulsions, hydrocyclones, centrifuges, and filters are not required, making the process simpler, lower maintenance and less power-consuming. Moreover, since the paraffinic solvent has a relatively low boiling point, solvent recovery requires less heat and steam, making the process less energy-demanding and largely eliminating the GHG emission produced (Cao and Gu, 2013).

However, the precipitated asphaltene can cause fouling, plugging and foaming issues in the vessels (Alves et al., 2019; Wiehe et al., 2005). Meanwhile, some of the solvents are captured within the precipitated asphaltene agglomerates, making it challenging to recover all the solvent from the tailings stream without applying external forces and leading to the considerable bitumen loss (Rao and Liu, 2013). Besides, to keep the light solvent in liquid form, PFT typically runs at high pressures, which requires more expensive pressurized

equipment and more energy. Furthermore, twice as much paraffinic solvent is required compared to NFT, and consequently the PFT process demands more capacity in the solvent recovery unit (SRU) and tailings solvent recovery units (TSRU).

2.2.2.2 Equipment used in PFT

The key equipment in PFT includes froth settling units (FSU), solvent recovery units (SRU), and tailings solvent recovery units (TSRU) (Esmaeili et al., 2012). The froth settling units are some gravity settling vessels to separate the clean diluted bitumen from the solids, water and asphaltenes. There are two types of settling vessels: the original lower temperature (30°C-40°C) paraffinic froth treatment (LTPFT) settlers, which are large, modified clarifiers with a shallow-sloped bottom and internal rakes; and the new high temperature (70°C-90°C) paraffinic froth treatment (HTPFT) units, which are smaller vessels with a steep cone bottom and no internal rakes (Esmaeili et al., 2012). The FSUs produce an overflow mixture of solvent and bitumen, relatively free of water and fine solids, containing as much as 60% solvent by volume (Sharma and Raterman, 2012). The SRUs are flash columns that can recycle some or all of the solvent (Stevens and Reipas, 2014). This minimizes the volume of solvent transported in the pipelines and largely saves cost. However, the tailing stream produced from FSUs still contains some residual bitumen and solvent. The residual solvent can be recovered and recycled in TSRUs before the disposal processes of the tailings in the tailings ponds via a tailings flow line (Sharma and Raterman, 2012).

2.2.2.3 Paraffinic diluents

Generally speaking, a lighter solvent can produce a larger and denser asphaltene aggregate, and requires a lower S/B ratio to precipitate asphaltene at the same time (Long et al., 2004; Yang et al., 2016). 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. Practically, the solvents used in the PFT process are mainly in the C_5 to C_7 range. The S/B ratio is normally between 1.5 to 2.0, which is necessary to achieve at least 50% asphaltene precipitation as required by the product specifications (Long et al., 2013; Rao and Liu, 2013).

2.3 Asphaltene

2.3.1 Asphaltene chemistry

Asphaltene, as the most aromatic of the heavy components of crude oil, is essential to all aspects of petroleum utilization, including reservoir characterization, production, transportation, refining, upgrading, paving, and coating materials (Mullins, 2011). The solid asphaltene contributes to some of the detrimental properties of fluids such as high viscosity, emulsion stability, low distillate yields, and unwanted phase separation (Mullins, 2011). The fundamental nature of asphaltene has been investigated over hundreds of years, since it can form dense precipitation and deposition in reservoirs, wellbores, and transportation pipelines and thus generate severe operational and production problems.

Asphaltene is defined as the component of crude oil or carbonaceous material insoluble in light n-alkanes such as n-heptane (C_7H_{16}) but soluble in aromatic solvents as toluene ($C_6H_5CH_3$). Two of the more accurate definitions are ASTM standard D 3279-97 and IP standard IP 143/01 (identical to ASTM D6560-00) defining asphaltene as the n-heptane insoluble and toluene soluble fraction in oils and bitumen. A different definition is found in ASTM D2007 which defines asphaltene as the n-pentane insoluble fractions (Redelius, 2009). These different standards led to terminologies such as C5 asphaltene, and C7 asphaltene.

The average molecular weight of petroleum asphaltene is 750 Da, with the range of 500 and 2000 Da (Andrews et al., 2011; Guerra et al., 2007; Morgan et al., 2010). The asphaltene molecule is a basic structure of carbon and hydrogen atoms, with smaller amounts of nitrogen, oxygen, sulfur and some transition metals, e.g. nickel and vanadium (Shi et al., 2010).

2.3.2 Asphaltene molecular structure

The chemical structure of asphaltene is still on debate. There are two well-known models to describe the structure of asphaltene in the literature: the archipelago and the continental (island) models, as shown in Figures 2.2 and 2.3. The archipelago model is firstly introduced by Strausz et al. (1992). In their archipelago model, asphaltene was proposed as a complex hydrocarbon molecule, which consists of several small polyaromatic parts linked together by aliphatic or naphthenic chains. 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 (Mullins, 2011).
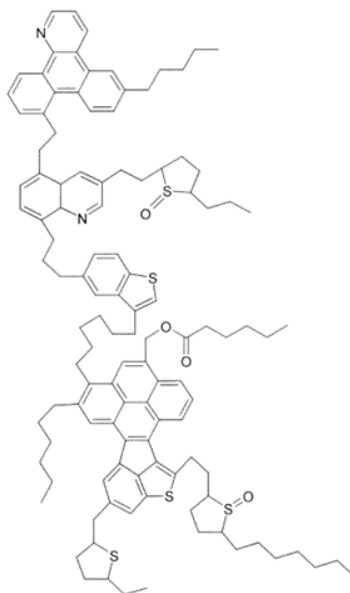
Figure 2.2. Illustration of the archipelago structure of asphaltene (Strausz et al., 1992)
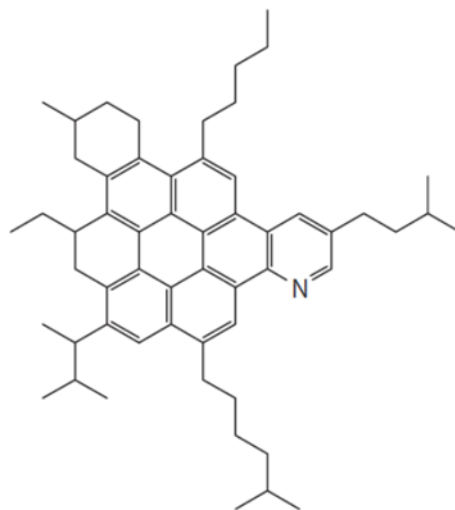
Figure 2.3. Illustration of the continental structure of asphaltene (Mullins, 2011).

There has been a considerable consensus that continental (island) model is a favorable model of asphaltene considering its molecular and colloidal nature (Rashid et al., 2019), but more evidences from most recently studies support the archipelago model. The time-resolved fluorescence depolarization (TRDF) study confirmed chemical configuration of petroleum asphaltene as the island structure (Badre et al., 2006; Buch et al., 2003). The number of hydrocarbon rings condensed in asphaltene polycyclic aromatic hydrocarbons (PAHs) has been supported by optical imaging (Daaou et al., 2016; Schneider et al., 2007), electronic absorption study combined with quantum calculations (Ruiz-Morales et al., 2007), Raman spectroscopy (Ruiz-Morales and Mullins, 2009) and nuclear magnetic resonance (NMR) investigations (Majumdar et al., 2017). However, the island model hardly interprets many properties including the presence of abundant benzene, naphthalene, and anthracene derivatives from thermally modified asphaltene (Chacón-Patiño et al., 2018). Podgorski et al. (2013) showed evidence of archipelago structures by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The infrared multiphoton dissociation (IRMPD) results from Chacón-Patiño et al. (2017) illustrate that island and archipelago structures coexist in petroleum asphaltene.

2.3.3 Asphaltene aggregation

Asphaltene tends to form aggregation clusters in nature. Although considerable progress has been made in establishing the theory on explaining the asphaltene aggregation mechanism, it is still challenging for researchers to reach a consensus and the debate is still continuing. Based on the previous research, there are some well-accepted models and their brief descriptions are outlined below.

2.2.3.1 Yen model and Yen-Mullins model

The dominant conceptual models for aggregation of asphaltene are from the colloidal point of view. The early concept that asphaltic bitumen should be considered as colloid systems developed by Pfeiffer and Saal (1940) has been further researched by Dickie and Yen (1967) as the Yen model (Mullins, 2010). The asphaltene molecules consist of individual sheets which are combined together to create unit cells and larger associated micelles (Dickie and Yen, 1967). Later on, the modified Yen model, the same as the Yen-Mullins model, was proposed to describe the fact of asphaltene aggregation since it is consistent with the recent studies which confirm the configuration of asphaltene as island structure and size of its nano aggregates.

As shown in Figure 2.4 (Mullins, 2010), the predominant asphaltene molecular architecture has a single, moderately large polycyclic aromatic hydrocarbon (PAH) ring system with peripheral alkane substituents. Several asphaltene molecules can form asphaltene nanoaggregates with aggregation numbers of around 6 and with a single disordered stack in the interior with peripheral alkanes. Then, the asphaltene nanoaggregates can form fractal clusters and the aggregation numbers estimated to be around 8 according to their size (Mullins, 2010).
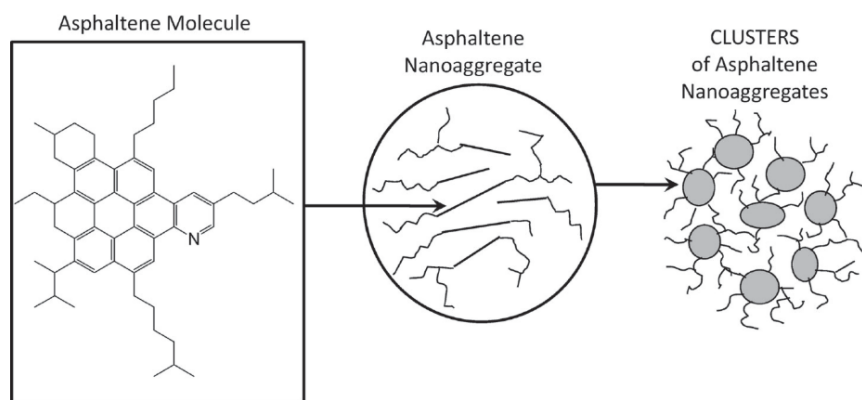
Figure 2.4. The illustration of the modified Yen model. (Mullins, 2010)

The asphaltene aggregation tendency is driven by the PAH. The PAH itself is a major site of intermolecular attraction, particularly π-π stacking (Mullins, 2010). Due to its polarization, it also causes dipole-induced dipole interaction. Meanwhile, the external alkane substituents generate steric hindrance, which prevents the approaching of the attractive PAHs inside the asphaltene molecules. Thus, there is a balance of attractive and repulsive forces between and among asphaltene molecules. After several asphaltene molecules aggregate, their alkanes start to deform and occupy the reduced remaining volume, so the nanoaggregates only repelled alkanes from the outer world and the other asphaltenes are not able to access the inner PAHs. Instead of adhering to the existing nanoaggregates, the asphaltene molecules tend to form new nanoaggregates. Normally, the dimension of asphaltene nanoaggregates is around 2 nm. Then, the asphaltene

nanoaggregates can form fractal clusters, and the smallest type of clusters is approximately 6 nm. Moreover, it is worth noting that the classic view of the "surfactant resin" for asphaltene nanoaggregates is incompatible with the modified Yen model since the Yen model treats the formation of asphaltene nanoaggregates and nanoaggregate clusters without initiating any resin interaction. The Yen model states the resin is not necessary for asphaltene stabilization and the role of resin has been overstated.

2.2.3.2 Yarranton model

This model was formulated by Agrawala and Yarranton (2001). Here, asphaltene self-association was modelled in a manner similar to linear polymerization. Asphaltene is treated as the archipelago structure, a molecule consists of several polyaromatic ring clusters with attached aliphatic chains. The links between asphaltene molecules can be formed through aromatic stacking, acid-base interactions, hydrogen bonding or van der Waals interactions. Also, the number of potential links that can form depends on the solvent and temperature conditions. High temperature and good solvent conditions make asphaltene monomers dispersed in crude oil, while low temperature and poor conditions let monomers flocculate and even form linear or branched aggregations, as depicted in Figure 2.5 (Agrawala and Yarranton, 2001).
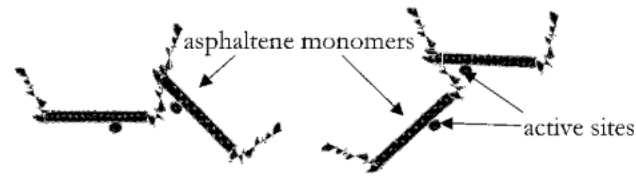
(a)   High temperature, good solvent

(b)   Low temperature, poor solvent (linear aggregation)

(c)   Low temperature, poor solvent (random, branched aggregation)

Figure 2.5. Oligomerization-like asphaltene association (Agrawala and Yarranton, 2001).

The key concept in the model is that asphaltene molecules may contain single or multiple active sites (functional groups) which are capable of linking with other asphaltenes. This linear polymerization model is described in terms of propagators and terminators. Molecules with multiple active sites act as propagators and molecules with single active sites act as terminators in these polymerization-like association "reactions". In this theory, asphaltenes are treated as free molecules in solution that contain multiple active sites (heteroatoms or aromatic clusters) and can interact with other similar molecules to form aggregates. Thus, asphaltenes can be treated as propagators. Resins have a single active site and can link up with just one other molecule so that they can be treated as terminators.

A propagator monomer can link up with another monomer or with an existing aggregate to start propagation until a terminator monomer link up with them and terminating association. The model was tested on existing molar mass data for asphaltene in different solvents and at different temperatures, as well as new molar mass measurements of mixtures of asphaltene and resins. However, the model has too many oversimplified assumptions.

2.3.3.3 Gray model

The model nominated by Gray et al. (2011) challenges the perspective of asphaltene behavior from the molecular to the macroscopic scale. The proposed supramolecular assembly of molecular mechanism provides a brand-new perspective to understand, model and predict asphaltene molecules behaviors. The model is consistent with the asphaltene archipelago structure. The supramolecular assembly results in a wide range of structures, while the extraordinarily complex mixture of diverse components gives rise to the very limited length scale of the structure. The driving forces of supramolecular assembly include acid-base interactions, hydrogen bonding, metal coordination, a hydrophobic pocket, van der Waals interactions, aromatic π–π stacking. Each of these interactions is relatively weak in isolation, but multi-component assemblies are strong in total. Notably, there is no dominant force in asphaltene aggregation (Gray et al., 2011).

2.3.4 Asphaltene precipitation

Precipitation refers to the aggregation of solid particles into a semi-solid phase (Mullins et al., 2007). The precipitation of asphaltene occurs due to the change in pressure, temperature, or the chemical composition of crude oils. Asphaltene precipitation is the initial stage of asphaltene deposition. After that, precipitated asphaltene flocculate together and deposit on the surface. The process is shown in Figure 2.6. In oil sands industry, asphaltene

precipitation and subsequent deposition during bitumen production and transport are recognized as a severe problem since it can lead to formation damage, plugging of wellbores and production facilities (Subramanian et al., 2016). As one of the costliest technical problems which the petroleum industry currently faces, asphaltene precipitation has been blamed for causing significant interference in hydrocarbon production (Zanganeh et al., 2012). Many field conditions including normal pressure depletion, acid stimulation, gas-lift operations, and miscible flooding and enhanced oil recovery (EOR) process can conduce to precipitation (Buenrostro-Gonzalez et al., 2004).
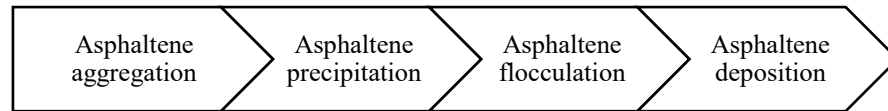
Figure 2.6. Schematic of asphaltene precipitation to deposition process

For paraffinic froth treatment particularly, asphaltene precipitation is beneficial as it removes the emulsified water, fine solids, and asphaltene at the same time. The light alkanes, such as n-heptane, n-hexane or n-pentane, not only dilute the bitumen but also cause the precipitation of some asphaltene. The precipitated asphaltenes form agglomerates with the fine solids and water, and these agglomerates quickly settle, producing very clean diluted bitumen (Xu, 2018).

2.3.4.1 Mechanism of asphaltene precipitation

Understanding asphaltene precipitation mechanisms is both 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 (Yarranton et al., 2013). The precipitation of asphaltene can be fully understood 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 (Gray et al., 2011). From the traditional colloidal point of view, asphaltene are treated as colloidal particles dispersed by resins as stabilizing agents. If the resin falls off from the colloidal particles, precipitation occurs resulting from an increase in asphaltene aggregate size and eventually the large asphaltene aggregates precipitate out (Sjöblom et al., 2003). 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 (Akbarzadeh, 2005). Equations of state-based models are readily applicable for simulation with pressure and temperature effects (Tharanivasan, 2012).

2.3.4.2 Onset of precipitation

The definition of the onset of precipitation is the solvent (precipitant) content at which asphaltene molecules are assumed to precipitate. The onset of precipitation is defined as the precipitant content at which the solid particles are first detected after a fixed contact time (Duran et al., 2019).

Approaches to determine the onset of precipitation

There are several different approaches to determine the onset point of asphaltene precipitation, such as viscosity measurement, filtration technique, visual microscopic

observation, particle size distribution, fluorescence spectroscopy, acoustic methods, light scattering, and so forth (Shadman et al., 2017).

Optical microscopic observation. 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 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 most commonly regarded as the threshold at which asphaltene precipitation onset occurs (Soleymanzadeh et al., 2019). The threshold asphaltene particle size is usually around 0.5–1.0 µm. This method 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 a constant residence time.

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, a known amount of bitumen is added with solvent (e.g. n-heptane) with a specific concentration. Then the precipitated asphaltene is collected by high-speed centrifugation after a fixed time reaction and the mass can be measured. After a series of yield measurements, the onset point is then determined by extrapolating the yield data to zero.

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. Pioneer research on the determination of the onset point of

asphaltene by using focused-beam laser reflectance measurements (FBRMs) was conducted by Marugán et al. (2009). 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).

Acoustic Resonance Technique (ART) Method. Acoustic resonance technique (ART) is based on measuring the response of fluid to applied acoustic stimulation (Buriro et al., 2016). Thus, by monitoring the state and time evolution of the resonance response of the fluid with changes in pressure, volume, or temperature, phase behavior or phase transition can be detected. By changing the pressure, temperature or composition of the system to induce asphaltene precipitation, the variations in the resonance detected will indicate as the onset point (Sivaraman et al., 1997).

Near Infrared Technique. The near infrared (NIR) technique is based on measuring the transmittance of near-infrared light through a sample of reservoir fluid undergoing temperature, pressure, or composition changes (Buriro et al., 2016). For the dark oil, NIR light with 800 to 2200 nm wavelength is specifically used to establish any asphaltene precipitation conditions (Jamaluddin et al., 2001). 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 (e.g. transmitted light power level and time) are detected by a fiber-optic sensor on the opposite side of the NIR source (Khaleel et al., 2016; Jamaluddin et al., 2001). 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

(Jamaluddin et al., 2001).

2.3.4.3 Factors affecting asphaltene precipitation

Many factors are affecting the asphaltene precipitation process, including temperature, pressure, and composition. Any changes in pressure, temperature, and composition may disturb the initial equilibrium state and cause asphaltene precipitation. The effect of composition and pressure on asphaltene precipitation is generally believed to be stronger than the effect of temperature (Buenrostro-Gonzalez et al., 2004).

Temperature

The effect of temperature on asphaltene precipitation is still controversial. On one hand, the influence of temperature depends on the temperature range. Leontaritis (1996) concluded that as long as the operating temperature was less than the reservoir temperature, the solubility of asphaltene increased with increasing temperature. In contrast, the solubility of asphaltene decreased with increasing the temperature, if the operating temperature was higher than the reservoir temperature.

On the other hand, the promotion or hindrance effect of temperature depends on the physical quantities people choose for judgment. Maqbool et al. (2011) have demonstrated that at higher temperatures, the yield of asphaltene precipitation was lower, but the precipitation onset time was shorter, due to the effect of viscosity on the aggregation of asphaltene. However, Bjoroy et al. (2012) stated that the increase in temperature led to higher asphaltene onset values, while the precipitation yields decreased.

Pressure

Regarding the pressure effect, inconsistent observations have also been reported. Likewise, the effect of pressure also depends on the pressure range. The asphaltene phase behavior under reservoir conditions can be represented in a phase stability diagram of pressure versus temperature, which is called the asphaltene phase envelope (APE). Above the bubble point, any decrease of pressure increases the asphaltene precipitation as it reduces the density of the reservoir fluid. At the bubble point, the precipitation has a maximum value because the medium density has a minimum. In contrast, any pressure decreases below the bubble point decrease the asphaltene precipitation (Buenrostro-Gonzalez et al., 2004b).

Pressure depletion is also a common inducement for asphaltene precipitation. When producing oil from oil reservoirs, the reservoir pressure will begin to drop as the oil moves from the formation to the wellbore. This pressure drop can result in asphaltene precipitation and deposition (de Boer et al., 1995). If the reservoir pressure is initially above bubble point, asphaltene precipitation will be much more severe once the reservoir falls beneath the bubble point. If the reservoir is initially below bubble point, asphaltene precipitation may still occur if the production rate is high enough to result in a reduction in reservoir pressure (Fakher, 2019).

Akbarzadeh et al. (2004) investigated the onset point and amount of asphaltene precipitation from Athabasca bitumen over a range of temperatures and pressures by diluting with n-alkanes. Their result demonstrated that the amount of precipitation decreased slightly with increasing pressure while the mass ratios of solvent-to-bitumen at onset point remained approximately the same.

Composition

Any compositional changes including dilute bitumen with paraffinic solvents or with gas injection could lead to asphaltene precipitation.
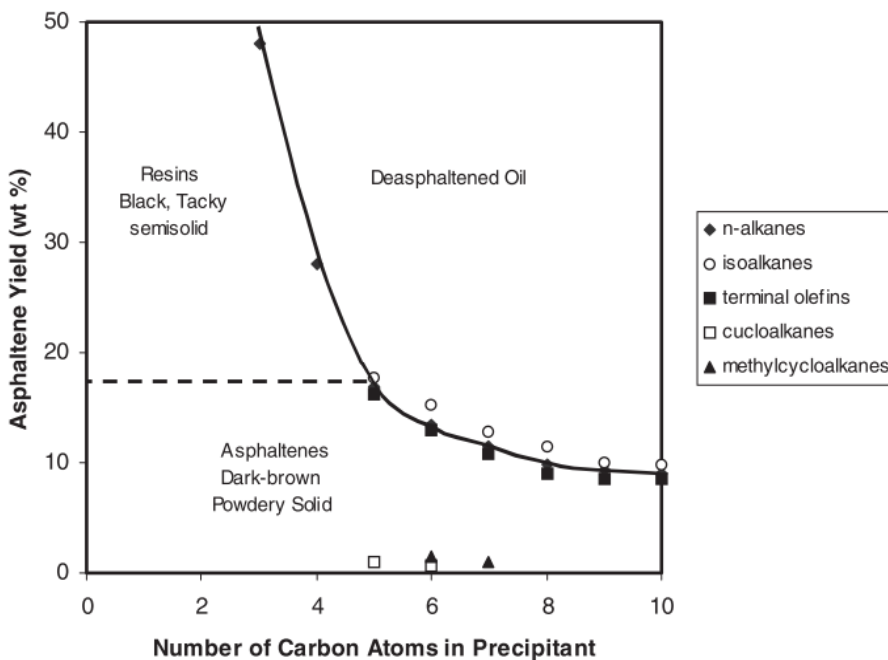
Figure 2.7. Asphaltene yield as a function of carbon number of precipitants.

Figure 2.7. presents the amount of asphaltene precipitated versus the carbon number of precipitants, which illustrates the asphaltene yield decreases with the carbon number of precipitants increase. There is also a paradox of asphaltene precipitation with the normal paraffin, according to Wiehe et al. (2005). They found that the onset point of asphaltene precipitation increased as the carbon number of n-paraffin solvent increased, reaching a maximum at a carbon number of 9 or 10, and then decreased. It was also established that at high concentrations of paraffin, short-chain n-alkanes behaved as stronger precipitants than long-chain ones. While at low precipitant concentrations, alkanes with longer chain length (ranging from 7 to 10 carbon molecules) increased the asphaltene precipitation onset to a maximum.

A detailed explanation of how gas injection, for example, CO_2, impacts the asphaltene precipitation will be discussed in the next part.

2.4 Application of CO_2 in the petroleum industry

2.4.1 CO_2 on asphaltene precipitation–EOR

Now CO_2 flooding has been widely used in enhanced oil recovery, in which CO_2 has already been proven to successfully reduce the oil viscosity and cause asphaltene precipitation (Cao, 2012; Chukwudeme and Hamouda, 2009; Dong et al., 2014; Srivastava and Huang, 1997). Among the three primary EOR techniques, gas injection or miscible flooding, especially the CO_2-EOR, is the most attractive one to the market. Research on CO_2 injection for EOR has been carried out since 1950 in both laboratory and field studies. Subsequently, CO_2 for EOR processes has been injected since the early 1970s (Seifried, 2016). For decades, EOR-CO_2 miscible flooding process has been widely employed in the United States and Canada as it not only significantly increases the reservoir productivity but also reduces the greenhouse gas emission.

When CO_2 comes into contact with crude oil for the first time, it will expand the oil and lower the viscosity, then the light hydrocarbon components of crude oil can transfer to the CO_2, developing a more hydrocarbon-rich mixture and replacing the original CO_2. If the pressure is higher than MMP (minimum miscible pressure), then the exchange process will continue until the enriched CO_2 mixture is completely miscible with the crude oil. This developed miscibility process produces a miscible fluid that can replace all the oil when it contacts in the reservoir, and thus has the potential to recover a large fraction of the ROS (remaining oil saturation) after the complete conventional recovery (Bondor, 1992).

However, it is well-known that one of the most troublesome problems in CO_2-EOR is asphaltene precipitation. The injection of CO_2 leads to severe asphaltene precipitation in the reservoir and other production equipment. From this perspective, CO_2 can work as the same function as a paraffinic solvent, changing the composition of oil and inducing asphaltene to precipitate in a good way.

Up to the present, there was a wide range of researchers working on CO_2 and asphaltene precipitation. Srivastava and Huang (1997) reported that asphaltene could start to flocculate[*] with 39-46 mol% of CO_2 at Weyburn reservoir condition. Cruz et al. (2019) studied the onset of CO_2-induced asphaltene precipitation, and evaluated the effects of pressure, temperature, asphaltene concentration, and system composition. Gonzalez et al. (2008) used thermodynamics to show that CO_2 could act as an inhibitor or a promoter of asphaltene precipitation depending upon the range of temperature, pressure, and composition. Verdier et al. (2006) reported that less asphaltene was precipitated when the temperature was decreased and when pressure was increased because of the change of solubility parameter of the liquid medium. Alian et al. (2011) concluded that by increasing the injection pressure of CO_2, less asphaltene would deposit. Wang (2017) focused on the main factors (temperature, pressure, and mass fraction of CO_2) affecting the state of asphaltene in the crude oil during CO_2 flooding, and showed that high pressure and high mass fraction of CO_2 could increase asphaltene precipitation while temperature did not have an effect.

Gabrienko et al. (2016) used an ATR−FTIR spectroscopic imaging approach to study CO_2-induced precipitation of asphaltene from crude oil on a molecular level. They proposed that

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[*] The authors used the term "flocculation" in their paper. It is understood that flocculation typically follows precipitation, although it is often difficult to distinguish the two processes.

CO_2 could reduce the number of resins molecules adsorbed on the asphaltene surface and acted as a peptizing agent, by competing with resin molecules for the interaction with asphaltene. The asphaltene with oxygen-containing functional groups had been previously demonstrated to be capable of forming specific interactions with CO_2 molecules. This was a Lewis-acid−base-type interaction, resulting in a non-covalent intermolecular complex formation between CO_2 and the substrate molecule. When the number of CO_2 molecules interacting with the asphaltene molecule became large enough to change the asphaltene/resin ratio to a critical value, the asphaltene molecule could be destabilized, followed by flocculation and aggregation with other asphaltene molecules.

2.4.2 CO_2 for emulsion breaking

Likewise, considerable attention has been attracted to CO_2 in the oil-water demulsification process, as CO_2 can be employed to break emulsions. Sun et al. (2018) found that the stability of the crude oil emulsions was reduced with the increasing pressure of CO_2. Zaki et al. (2003) successfully used dense CO_2 (6.8 MPa-31.3 MPa) to break water-in-crude oil emulsions and resolve bulk water. More importantly, their analysis indicated that CO_2 can preferentially precipitate the most polar asphaltene, leading to a substantial weakening of the viscoelastic asphaltenic film built at interfaces of water and oil in the emulsion.

Dong et al. (2014) designed a novel demulsification treatment process for high pH water-in-oil (w/o) emulsions, using both low-pressure CO_2 (0−700 kPa) and demulsifier, and they reported an increase in the demulsification efficiency with the increase of CO_2 pressure. It implied that the solubility of CO_2 even in the low-pressure range was enough for inducing asphaltene precipitation. The mechanism they proposed for the demulsifying process was that CO_2 can transfer from the oil phase to the water phase, and dissolve in water to generate carbonic acid, which can neutralize the alkali and convert the in-situ surfactants to organic

acids. The generated organic acid could easily dissolve into the oil phase from the oil/water interface, which could damage the adsorption film at the oil/water interface and enlarged the oil/water interface. Meanwhile, CO_2 could dissolve in the oil phase and decrease the viscosity of heavy oil, which could also accelerate the coalescence progress of water droplets.

2.4.3 Feasibility of using CO_2 for asphaltene precipitation

Considering the satisfying performance of CO_2 in EOR and in w/o emulsion breaking, we thought it should be a practical idea to use CO_2 as a process aid to promote asphaltene precipitation in PFT. Firstly, as mentioned above, when CO_2 is dissolved in oil, it swells oil and reduces oil's viscosity, and it tends to be completely miscible with the crude oil (Bondor, 1992). The study (Dong et al., 2014) suggests that even at relatively low-pressure range, the solubility of CO_2 in the oil phase is high enough to decrease the viscosity of the heavy oil. Secondly, the dissolved CO_2 changes the chemical composition of crude oil and functions similarly as paraffinic solvents to induce asphaltene precipitation. CO_2 can preferentially precipitate the most polar asphaltene, leading to a substantial weakening of the viscoelastic asphaltenic film built at interfaces of water and oil in the emulsion (Zaki et al., 2003). Lastly, the CO_2 can dissolve in oil and interact with some specific asphaltene and generate non-covalent intermolecular complex molecules, which makes CO_2 competitive with resins and capable of reducing the asphaltene/resin ratio to a critical amount, resulting in asphaltene precipitation (Gabrienko et al., 2016). When there is water present, such as in the bitumen froth, CO_2 can dissolve in water to generate carbonic acid. The generated organic acids easily dissolve into the oil phase from the oil/water interface, destroying the adsorbed film at the oil/water interface, so that the aggregates settling process can be accelerated (Dong et al., 2014).

3. EXPERIMENTAL

3.1 Materials

Bitumen froth. Bitumen froth used in this work was from Kearl, Imperial. Its composition was 65.2 wt% bitumen, 20.2 wt% water, and 12.6 wt% fine solids based on Dean-Stark analysis. The asphaltene content in the bitumen phase of the froth was 19.1±0.05 wt% as well.

Solvents. Both n-heptane and toluene (ACS grade) were obtained from Fisher Scientific Canada.

Dry bitumen. The dry bitumen was separated from the bitumen froth collected from Kearl, Imperial. The bitumen froth was mixed with four volumes of toluene and then centrifuged at 2,826 RCF for 1 h to separate the supernatant (i.e., bitumen in toluene). To remove fine solids as much as possible, the supernatant was centrifuged again at 10,000 RCF for 1 h. Then, to remove toluene, the diluted bitumen was dried in a rotary evaporator at 60°C and 1 kPa vacuum pressure for at least 5 h, followed by vacuum oven drying for 1 week. The asphaltene content in the dry bitumen was 19.1±0.05 wt%, measured by the standard ASTM D3279-12 method using n-heptane as the solvent.

Bitumen and water mixture. The mixture was composed of 79.8 wt% bitumen and 20.2 wt% tap water. The water content was chosen to be the same as the bitumen froth sample.

Asphaltene. The pure asphaltene was precipitated from the dry bitumen sample following the procedures of ASTM D3279-12 using n-heptane as precipitant.

3.2 Experimental Setup

The CO_2-assisted asphaltene precipitation process was conducted in an autoclave apparatus, illustrated in Figure 3.1. The setup consists of an autoclave (Series 4560 Bench Top Reactor System, Parr Instrument company) with a volume of 450 mL, pressure gauge, automatic temperature controller, mantle hear jacket with a thermal probe, and mechanical mixer equipped with a two impeller shaft stirrer, a solvent reservoir for loading solvent, a sampling container, and a gas cylinder for gas supply. Additionally, the head of the autoclave has two dip tubes, one for injecting gas and solvent, and another for collecting the output of precipitated asphaltene from the bottom of the autoclave.
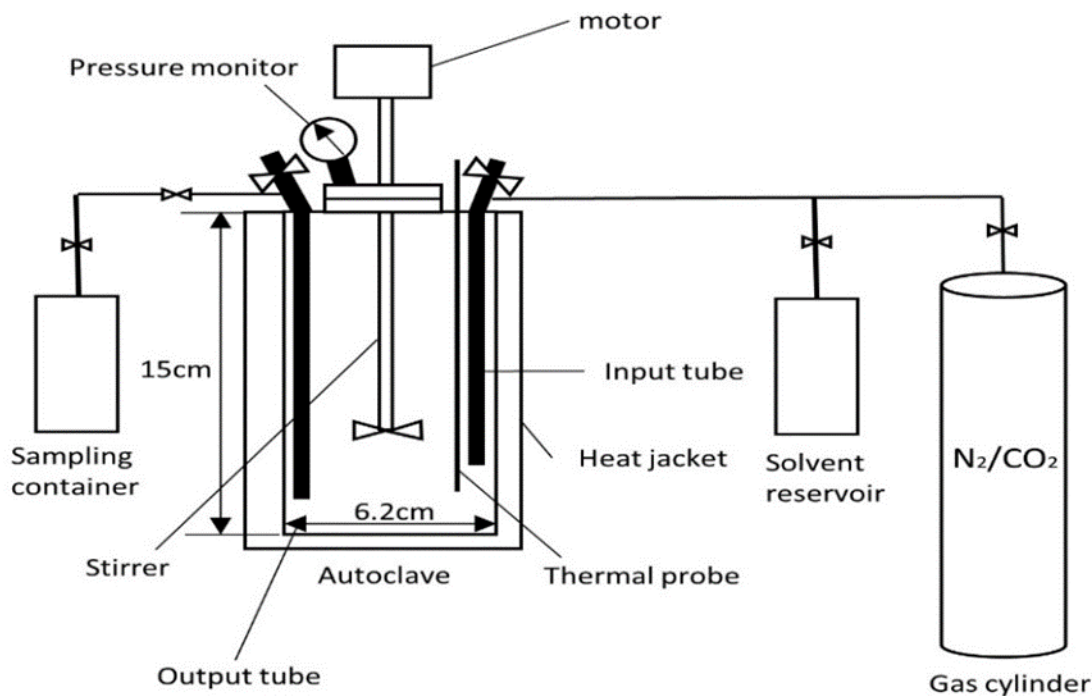
Figure 3.1. Experimental setup for CO_2-assisted asphaltene precipitation.

3.3 Experimental method

3.3.1 Determination of onset of asphaltene precipitation

The onset of asphaltene precipitation is one of the most important parameters of studying asphaltene precipitation. The onset of asphaltene precipitation is defined as the minimum volume of solvent (e.g., n-heptane) to precipitate asphaltene at a fixed contact time. In this study, the onset point was determined with the condition of CO_2 injection, and the N_2 injection was also conducted as control. To ensure the accuracy of the result, two methods were employed to determine and cross-check the onset of asphaltene precipitation: the gravimetric method was employed for determination and the optical microscopy method was employed for verification.

3.3.1.1 Gravimetric method

About 20 g of dry bitumen was mixed with n-heptane at a concentration of 30 wt% n-heptane in a beaker followed by 20 min mixing using a magnetic stir bar. This was the premixing stage and it did not count as a part of operational time. The pre-mixing of dry bitumen and n-heptane was necessary because of the high viscosity of the dry bitumen, and the precipitation of asphaltene was not occurred even with a prolong contact time. The premixed bitumen-heptane solution was poured into the autoclave, and air trapped in solution and autoclave was removed by injection of CO_2 (or N_2). After outgassing, the n-heptane solvent was added from the input sampling cylinder at a specific volume to the autoclave by the regulated CO_2 (or N_2) pressure.

To evaluate the onset of asphaltene precipitation at a set time, a series of n-heptane concentrations were tested, i.e., 45, 50, 52, 55, 60, 65, 70, 75 and 80 wt%, at 1 atm (0.1 MPa) CO_2 (or N_2) pressure under room temperature (21°C) for 20 min. The operational

time was fixed at 20 min as it is relevant to the PFT process in field operation. The tests were performed in an autoclave to achieve ambient pressure. The experimental conditions are shown in Table 3.1. 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℃ till all solvent was removed completely. The weight of the asphaltene collected on the filter membrane was measured by weighing the filter membrane before and after filtration was measured after the drying procedure.

Table 3.1. Experimental conditions for determining asphaltene precipitation onset point

Experimental Conditions	
Gas	CO_2, N_2
n-Heptane Concentration (wt%)	45, 50, 52, 55, 60, 65 ,70,75, 80
Pressure (MPa)	0.1
Temperature (℃)	21℃
Mixing speed (rpm)	632
Operational Time (min)	20
Centrifuge speed (RCF)	10,000

3.3.1.2 Optical microscopy method

Optical microscopy was also used to detect the onset of asphaltene precipitation. In this method, the treated bitumen with asphaltene precipitation was monitored in high magnifications optical microscope with a digital camera to capture the images of precipitated asphaltene. After the autoclave experiment, about 1 mL sample was collected by pipettes and the detection of precipitated asphaltene was accomplished with an VWR BA310POL Trinocular optical microscope with 40-fold magnification.

3.3.2 The effect of CO_2 on asphaltene precipitation under different conditions

It is well-known that bitumen froth consists of bitumen, water and, fine solids. To accurately assess and decouple the effect of different compositional factors, this study was conducted on three samples: dry bitumen, bitumen with water, and bitumen froth. There were four main factors to evaluate: pressure, temperature, water content, and solid content, thus the experiments were conducted at elevated pressures, elevated temperatures, with the presence of water, and with bitumen froth (presence of both water and fine solids), respectively.

The experiments were carried out under different conditions. N_2 gas was used as a control inert gas to compare with CO_2 injection. The detailed conditions are shown in Table 3.2.

Table 3.2. The conditions for CO_2-assisted PFT experiments.

Experimental conditions	
Gas	CO_2, N_2
Pressure (MPa)	0.1, 1, 1.4,1.7
Temperature (°C)	21, 90
n-Heptane concentration (wt %)	52
Mixing speed (rpm)	632 (maximum)
Operational time (min)	20

All experiments were performed following the same procedure to compare the results. The procedure was as follows:

1. About 20 g accurately weighed bitumen was diluted with n-heptane (30 wt%) for pre-mixing. The pre-mixing included manual mixing and mixing by a magnetic stirrer for

20 min. (For bitumen with water, the total mass was about 25 g. For bitumen froth, the total mass was about 31 g. In all cases, the amount of bitumen was about 20 g)

2. The diluted bitumen mixture above was transferred to the autoclave. Air was removed by injecting CO_2 (or N_2), and the required amount of additional n-heptane was loaded to the autoclave to reach the desired concentration. The autoclave was pressurized with CO_2 or N_2 to the desired pressure, and then the desired temperature was obtained by the heating mantel if needed. A timer was started when the desired temperature was reached.

3. After 20 min operational time, the autoclave was depressurized, and the treated diluted bitumen at the bottom with precipitated asphaltene was withdrawn by output tube to the sample container.

4. The collected samples were filtered with 0.45 µm filter membranes to collect precipitated asphaltene. The precipitated asphaltene were dried at ambient condition and vacuum oven at 50°C until n-heptane was removed completely. The weight of asphaltene were measured.

A similar procedure was applied to the bitumen with water and bitumen froth samples. However, for those tests with bitumen froth, the precipitated asphaltene was collected by centrifugation, as the presence of solids in bitumen froth affects the gravimetric determination of precipitated asphaltene. Step 4 was changed to centrifugation of the treated bitumen froth sample at 15,000 RCF for 1 hour. The centrifuge cake was a mixture of precipitated asphaltene, solids and water. To determine the amount of the precipitated asphaltene, both Dean-Stark extraction and CHNS elemental analyses were employed.

To ensure accuracy and repeatability, the experiments were repeated three times and average values and standard deviation were calculated and reported.

3.4 Total acid number

The mechanism of CO_2 assists the asphaltene precipitation was still unknown. According to Gabrienko et al. (2016), it was a result of Lewis-acid-base-type interactions, resulting in a non-covalent intermolecular complex formation between CO_2 and the asphaltene or resins molecules. From this perspective, total acid number (TAN) measurement experiments were conducted on the bitumen and asphaltene samples before and after treatment with CO_2. The treated samples were selected under the reaction condition of 21°C and 1.7 MPa CO_2, in the presence of 52 wt% n-heptane.

The testing samples were 1) dry bitumen described in 3.1; 2) treated bitumen, referring to the bitumen and n-heptane mixture after CO_2-assisted PFT process and after the precipitated asphaltene was removed; 3) asphaltene described in 3.1; 4) treated asphaltene, referring to the precipitated asphaltene after CO_2-assisted PFT process.

The procedure on TAN measurement was mainly based on ASTM D664; however, some adjustments were required. These adjustments were suggested by The Canadian Crude Quality Technical Association (Fuhr et al. 2007). The details are shown below.

1. Placed the bitumen samples in a vacuum oven and heated to 60ºC for 5 hours and thoroughly mixed bitumen samples before subsampling to obtain a representative sample.
2. Tested the water contents of the bitumen sample and ensured the water contents were below 0.5 wt%. Extra cleaning (e.g. higher-speed centrifugation) was required if water content exceeded 0.5 wt% since water could significantly impact the results.
3. Dissolved 10 g of bitumen in toluene, at a toluene : bitumen mass ratio of 10:1, with 30 min sonication to ensure complete dissolution.

4. Weighed a quantity of the toluene diluted bitumen (or asphaltene) and added prepared titration solvent (water: propan-2-ol: toluene = 1:99:100), then stirred thoroughly with proper rate. 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 0.8 g/60 mL titration solvent.

5. Started the automatic titration with auto-titrator by adding 0.1 mol/L KOH in 2-propanol solution. The titration should be terminated when the pH value reached pH 11.

The tests were repeated at least 4 times to ensure repeatability.

4 RESULTS AND DISCUSSION

In this study, the performance of CO_2 assisted paraffinic froth treatment (PFT) was evaluated by several approaches. First, different solvent-to-bitumen (S/B) ratios were tested to gravimetrically determine the onset of asphaltene precipitation. Yields of precipitated asphaltene at different CO_2 or N_2 pressures and temperatures were determined using the dry bitumen sample at the onset S/B ratio. Second, CO_2 and N_2 was applied to bitumen+water mixtures as well as bitumen froth. Last, the acidity changes of both bitumen and asphaltene before and after the treatment were characterized by the total acid number (TAN) measurements.

4.1 Onset point of asphaltene precipitation

As previously mentioned, the onset of asphaltene precipitation was based on the minimum volume of solvent (e.g., n-heptane) required to precipitate asphaltene at a fixed contact time (or operational time in this study). In this section, we investigated the onset of asphaltene precipitation using the gravimetric method and verified by the optical microscopy method.

4.1.1 Gravimetric result

Figure 4.1 illustrates the asphaltene yield vs the n-heptane concentration (wt%) from 45 wt% to 80 wt%. The asphaltene yield in this study was defined as follows:

$$Asphaltene\ yield\ (\%) = \frac{the\ amount\ of\ precipiated\ asphaltene\ (g)}{the\ amonut\ of\ bitumen(g)} \times 100\% \qquad (1)$$

In other words, the asphaltene yield represented the extent of asphaltene precipitation.
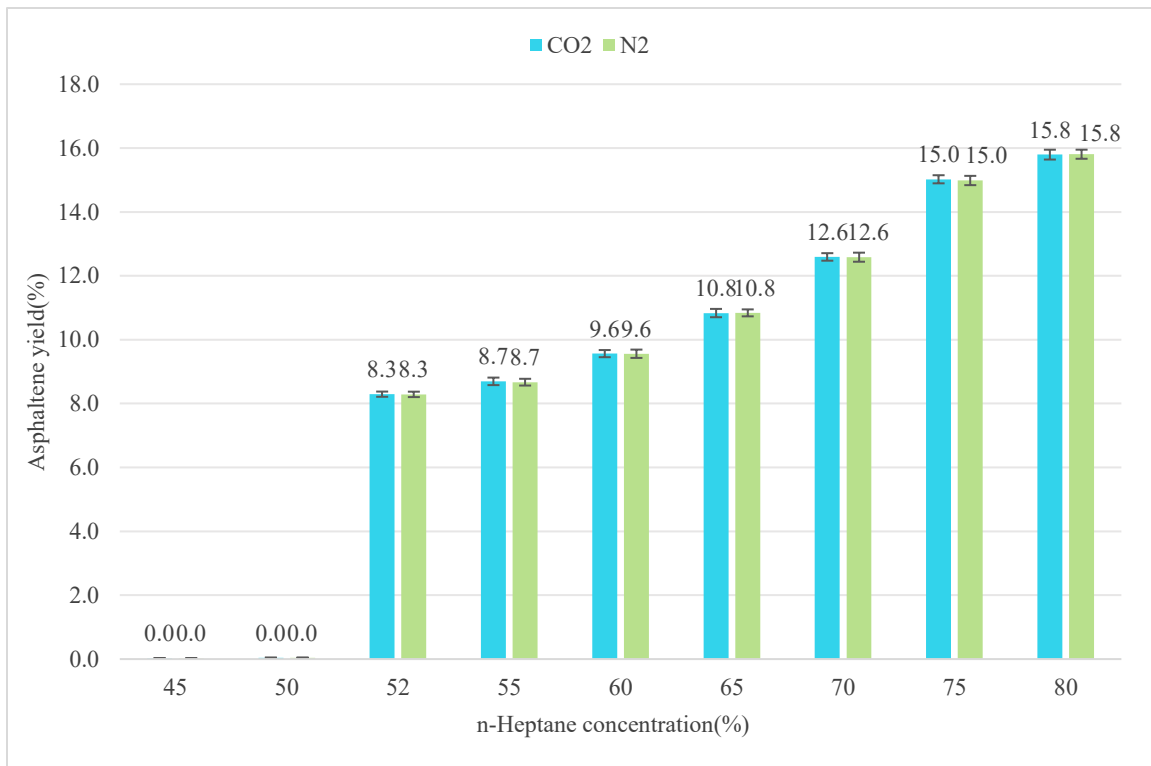
Figure 4.1. Asphaltene precipitation yield as a function of n-heptane concentration. 21°C, 0.1 MPa CO_2 or N_2, 20 min operational time.

According to the results obtained (Figure 4.1), no asphaltene was detected at 45 wt% and 50 wt% n-heptane concentrations. The asphaltene precipitation was detected at 52 wt% n-heptane with the precipitated asphaltene yield of 8.3 wt%. Based on this result, it can be stated that 52 wt% n-heptane concentration was the asphaltene precipitation onset point at 20 min operational time. In the subsequent experiments, we have conducted all the experiments using the onset of asphaltene precipitation value of 52 wt% n-heptane (i.e., S/B = 1.08). The same experiments were also conducted with N_2. It was also worth mentioning that, at low pressure (0.1 MPa), there was no difference in the asphaltene precipitation yield between CO_2 and N_2 injections at all measured S/B ratios, while a high

S/B ratio yields a high amount of precipitated asphaltene as expected.

4.1.2 Optical microscope results

In the next stage, optical microscope was used to verify the presence or absence of asphaltene precipitates. Figure 4.2 shows a series of images of the diluted bitumen after the treatment in the autoclave. As can be seen from Figure 4.2, no asphaltene precipitates were observed at 45 wt% and 50 wt% n-heptane, but asphaltene precipitates were detected at 52 wt% with a size range between 2 µm to 4 µm.

A   B   C
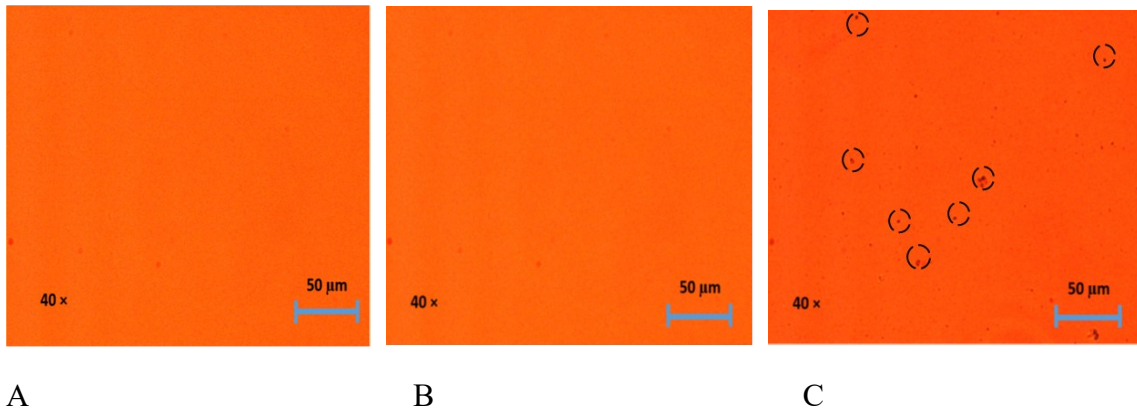
Figure 4.2. Detection of asphaltene precipitation using an optical microscope at different n-heptane concentrations. A, B, C show optical images at 40x magnification on 45 wt%, 50 wt%, and 52 wt% n-heptane, respectively.

4.2 The effect of CO_2 at different pressures and temperatures

4.2.1 Pressure effect

Figure 4.3 shows the effect of CO_2 pressure on asphaltene precipitation at the temperature of 21°C and n-heptane onset concentration of 52 wt%. The CO_2 pressure range was from 0.1 MPa to 1.7 MPa. The result showed that asphaltene yield increased from 8.3±0.1% at 0.1 MPa to 12.9± 0.2% at 1.7 MPa, which was a 55% increase caused by the pressure change.
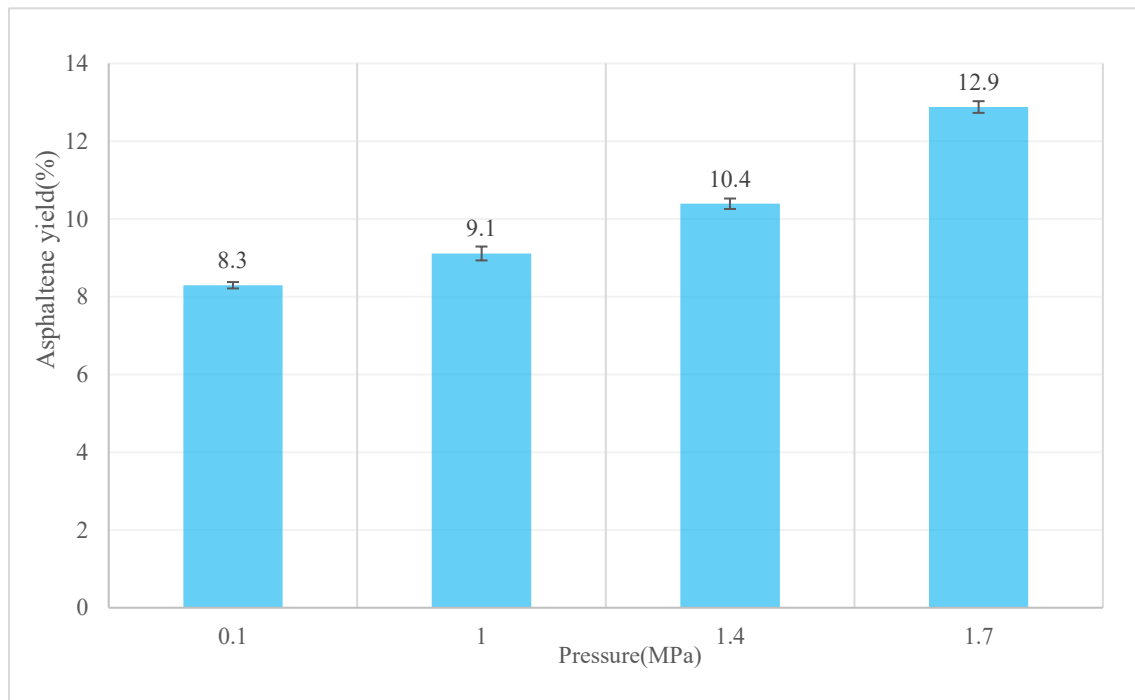
Figure 4.3. Effect of CO_2 pressure on asphaltene precipitation at 21°C and with n-heptane concentration of 52 wt%. Dry bitumen was used in the experiments.

To be more exact, the increase in asphaltene yield varies with applied CO_2 pressure. Asphaltene yields were increased from 8.3% to 9.1% when CO_2 pressure was increased from 0.1 MPa to 1 MPa, i.e., when the CO_2 pressure was increased ten times, the asphaltene yield increased by 0.8 percentage points. When the CO_2 pressure was increased from 1

MPa to 1.4 MPa and from 1.4 MPa to 1.7 MPa, the asphaltene yield increased by 1.3 and 2.5 percentage points, respectively. In other words, high CO_2 pressure had a beneficial effect on asphaltene precipitation induced by n-heptane.

The results discussed above was consistent with the results of many other researchers although the pressures used in this study were much lower. Zanganeh et al. (2012) performed tests with two synthetic crude oils with CO_2 injection at the pressure range from 3 MPa to 14 MPa, and their results showed that asphaltene precipitation and deposition both increased by increasing pressure. Fakher and Imqam (2019) investigated the impact of CO_2 on asphaltene precipitation, and confirmed that the asphaltene weight percentage for the produced oil increased with the increase in CO_2 injection pressure. Moreover, Behbahani et al. (2014) experimentally demonstrated that during CO_2 flooding, as pressure increased, more asphaltene tended to be precipitated. Wang et al. (2017) found that the degree of asphaltene precipitation significantly increased with an increase in the CO_2 injection pressure from 4 MPa to 36 MPa.

However, since there were two factors involved in this experiment, the injection of CO_2 and the increase in pressure, a question came up here as whether the promotional effect was caused by CO_2 or by a high pressure. To decouple the effects, N_2 was introduced as the control experiment. Figure 4.4 compares the influence of pressure of CO_2 and N_2 on asphaltene precipitation. From the figure, it can be seen that CO_2 injection was the main factor for increased asphaltene precipitation because N_2 did not present any considerable effect on asphaltene precipitation at the same pressure range as CO_2. The biggest difference between asphaltene yields for N_2 cases was only 0.5 percentage points, which seemed reasonable to be considered as within experimental error. That was to say, high pressure did not really help asphaltene precipitation itself (within the tested range). By calculating the relative increase in asphaltene yields that CO_2 induced (the orange line), it confirmed

that CO_2 worked more efficiently at higher pressure. The most likely reason was the increased CO_2 solubility at the high pressure (Haddadnia et al., 2017; Marufuzzaman and Henni, 2015; Mutelet et al., 2005; Zirrahi et al., 2015).
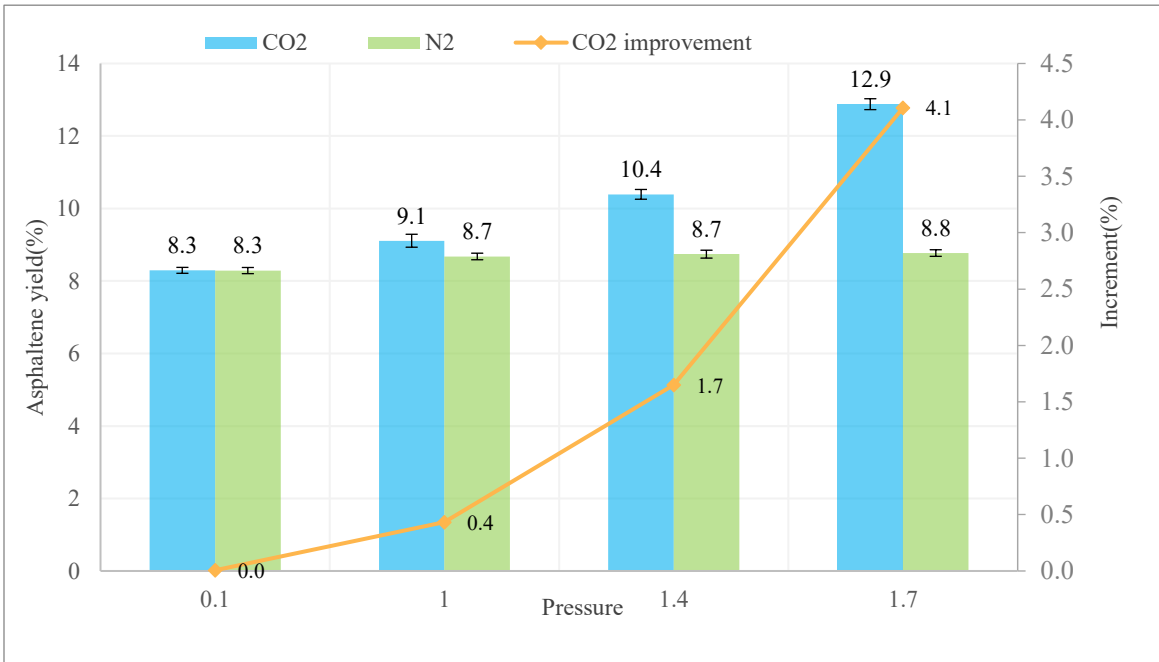
Figure 4.4. Impact of CO_2 or N_2 pressure on asphaltene precipitation at 21℃ and with n-heptane concentration of 52 wt%.

4.2.2 Temperature effect

Figures 4.5 and 4.6 illustrate the influence of temperature on asphaltene precipitation at 21℃ and 90℃ and the pressure of 1 MPa and 1.7 MPa respectively. Generally speaking, the high temperature had a favorable effect on asphaltene precipitation.
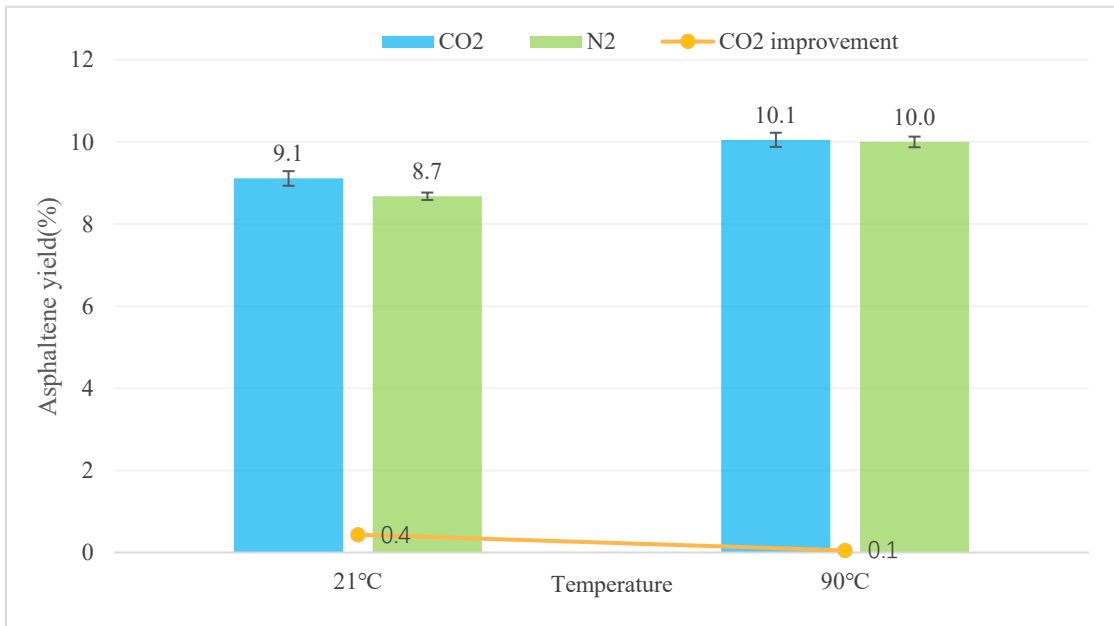
Figure 4.5. The influence of temperature on asphaltene precipitation in N_2 or CO_2 at 1 MPa and with n-heptane concentration of 52 wt%.
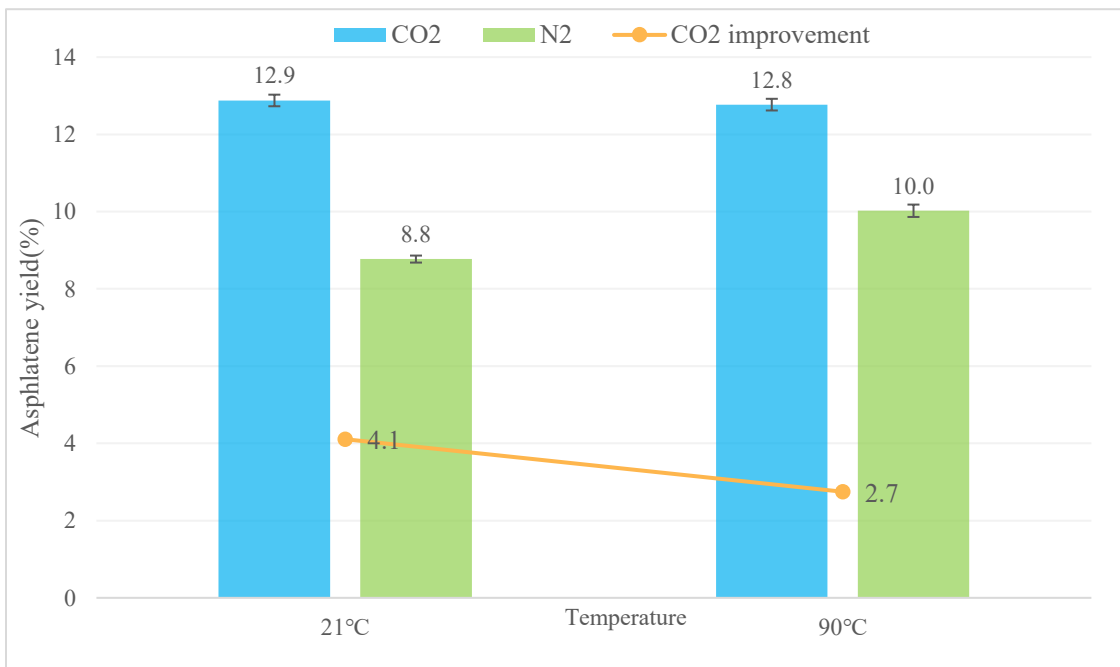

Figure 4.6. The influence of temperature on asphaltene precipitation in N_2 and CO_2 at 1.7 MPa and with n-heptane concentration of 52 wt%.

To be more exact, at the pressure of 1 MPa, by increasing temperature from 21°C to 90°C,

the asphaltene yield increased from 9.1±0.2% to 10.1±0.2% with CO_2 injection. As a comparison, the control experiment conducted by N_2 exhibited the same trend. The asphaltene yield rose from 8.7±0.1% to 10.0±0.1%. At this comparatively low pressure, the experimental data obtained from both CO_2 and N_2 inferred that high temperature had a promotional effect on asphaltene precipitation. Moreover, it was worth mentioning that CO_2 still favored the asphaltene precipitation, especially at the low temperature of 21℃.

At the pressure of 1.7 MPa, the results were mixed. On one hand, comparing the performance of CO_2 on asphaltene precipitation at 21℃ and 90℃, it was obvious that the temperature increase did not increase asphaltene precipitation, and it stayed at around 12.9% when CO_2 was injected. This may be due to a decrease in CO_2 solubility at high temperature. While as the control, the experiment results gained by N_2 still showed a similar increasing trend, which meant an increase in temperature still benefited asphaltene precipitation, increasing the asphaltene yield from 8.8±0.1% to 10±0.2% when N_2 was used. On the other hand, CO_2 had a distinctively positive effect at both 21℃ and 90℃, especially at 21℃. From this perspective, the amount of precipitated asphaltene was higher at the high temperature while the efficiency of CO_2 is higher at the low temperature. In other words, at the high temperature, the CO_2 injection cannot easily assist the paraffinic solvent on asphaltene precipitation.

As discussed above, it can be proposed that the solubility of asphaltene and CO_2 might both change with increasing temperature. The solubility of asphaltene decreased with increasing temperature since the asphaltene yield increased at higher temperature in N_2 under both tested pressures. The orange lines in Figure 4.5 and 4.6 demonstrated the asphaltene yield improvement induced by CO_2 injection, and they both decreased with increasing temperature. This was likely due to the decreasing solubility of CO_2 with increasing temperature (Haddadnia et al., 2017; Mutelet et al., 2005).

4.3 The effect of CO_2 on asphaltene precipitation in the presence of water

Figure 4.7 shows the effect of water on asphaltene yield at 21℃ or 90℃ and 1.7 MPa of CO_2 or N_2. Clearly, the presence of water promoted asphaltene precipitation when CO_2 was used, while it did not make a difference when N_2 was used. As can be seen from Figure 4.7, by adding water and CO_2 together, the asphaltene yield increased from 12.9±0.2% to 15.4± 0.1% at 21℃, and from 12.8±0.2% to 15.3±0.2% at 90℃. The improvement of asphaltene yield brought about by the co-existence of water and CO_2 were 2.5 percentage points at both 21℃ and 90℃.
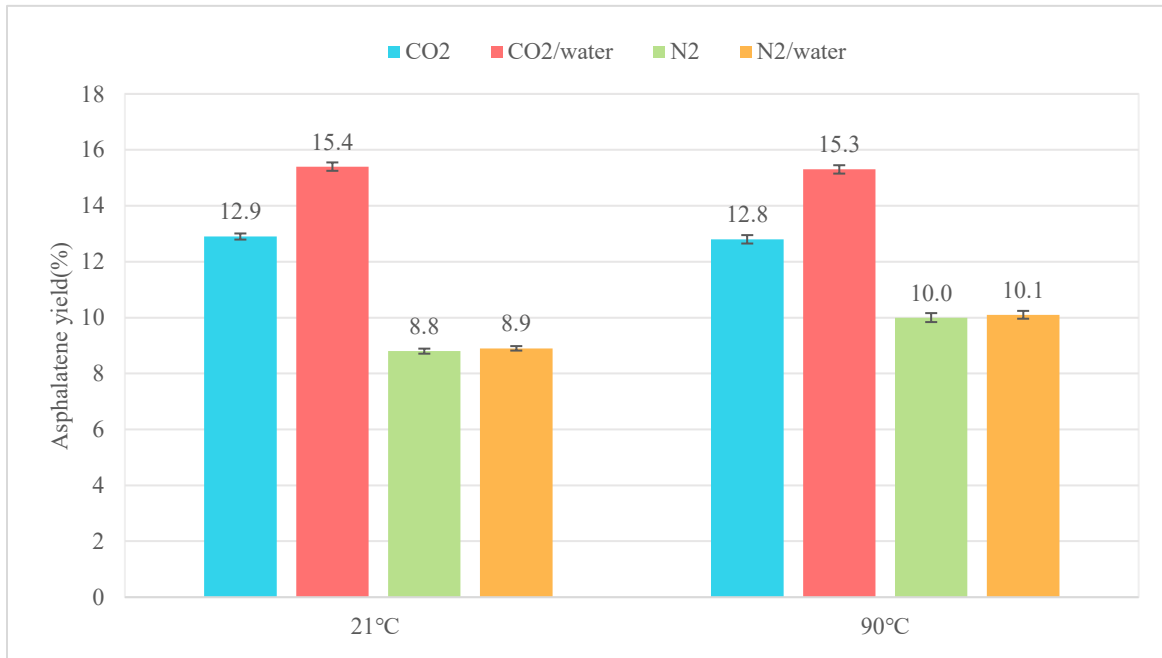
Figure 4.7. Asphaltene yields for bitumen/bitumen with water in N_2 or CO_2 at 1.7 MPa pressure and with n-heptane concentration of 52 wt%. The concentration of water in the bitumen+water mixture was 20.2 wt%.

The result was consistent with the work of Zaki et al. (2003), who showed that the amount of asphaltene precipitation in the presence of water was higher than in the absence of water,

by comparing the asphaltene yields inducing by only CO_2 (without n-heptane) at 25 ℃ and 0.007MPa. The main reason behind this observation was likely due to the fact that asphaltene molecules were concentrated at w/o interface and were thus in a higher degree of association than the asphaltene in the bulk phase. Another possibility was the dissolved CO_2 in water promote the coalescence of water droplets along with accumulated asphaltene at w/o interface.

4.4 The effect of CO_2 on asphaltene precipitation from bitumen froth

In this section, the effect of CO_2 on the yield of asphaltene precipitated from a bitumen froth sample was studied. The experiments were carried out at 21℃ and 90 ℃ and at pressure of 1.7 MPa N_2 or CO_2.

From Figure 4.8 and Figure 4.9, it can be seen that the injection of CO_2 in the bitumen froth with 52 wt% n-heptane had a similar influence on asphaltene precipitation compared to the addition of water (20.2 wt%) to CO_2 and n-heptane treated bitumen. The solids in bitumen froth did not have any impact on asphaltene yield.
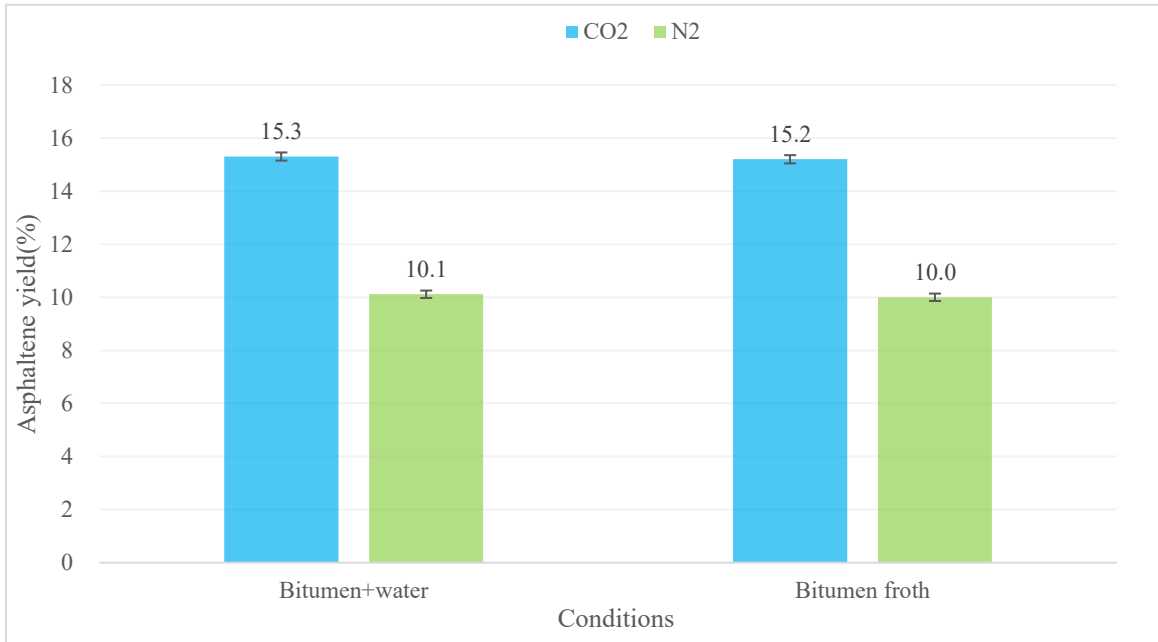
Figure 4.8. Asphaltene yield from a mixture of bitumen+water and a bitumen froth sample, 90ºC, 1.7 MPa of N_2 or CO_2. The concentration of n-heptane was 52 wt%.
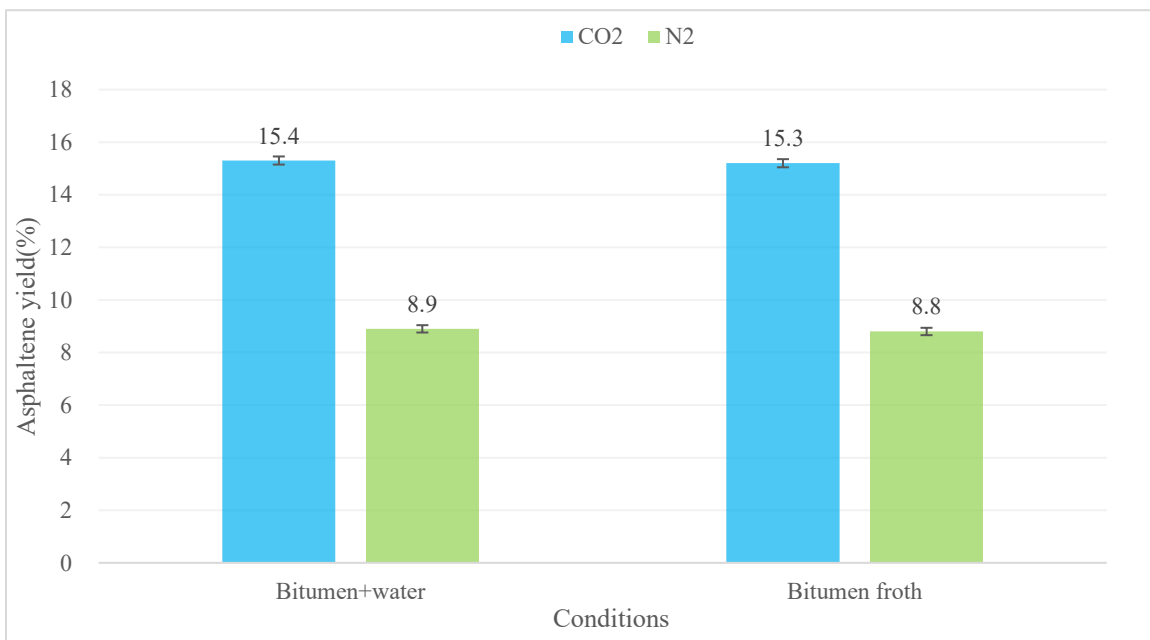
Figure 4.9. Asphaltene yield from a mixture of bitumen+water and a bitumen froth sample, 21ºC, 1.7 MPa of N_2 or CO_2. The concentration of n-heptane was 52 wt%.

It is worth mentioning that the total asphaltene content in the dry bitumen was measured

using the standard ASTM D3279-12 method using n-heptane as the solvent and was found to be 19.1± 0.05 wt%. This value was the same in the bitumen froth as the dry bitumen sample was extracted from the same bitumen froth. This would be the limit of the precipitated amount of asphaltene. The results shown in Fig. 4.8 and Fig. 4.9 indicated that under the tested industrial operating conditions, 79.5% and 80.1% of total asphaltene were precipitated respectively.
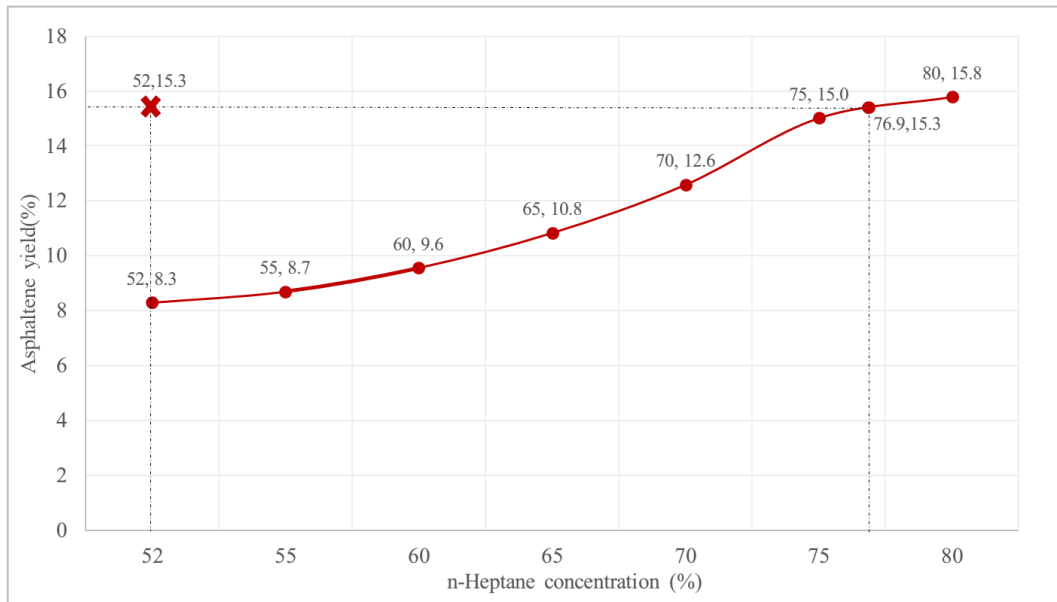
Figure 4.10. Asphaltene precipitation as a function of n-heptane concentration with or without CO_2 treatment. The cross "x" shows the condition with injection of 1.7 MPa CO_2.

As mentioned above, at 21 °C, 1.7 MPa CO_2, with a n-heptane concentration of 52 wt%, the asphaltene yield was 15.3 % for the bitumen froth. To achieve the same asphaltene yield with n-heptane only, Figure 4.10 shows that the n-heptane concentration should be about 76.9 wt%. In other words, by applying CO_2 in PFT, we could reduce the n-heptane concentration by 24.9 percentage points, which was a 32.4% decrease of solvent usage.

4.5 Total Acid number (TAN)

Table 4.1 compares the total acid number results of bitumen and asphaltene before and after CO_2 assisted PFT treatment. There seems no substantial difference between them. Based on the measured TAN, it is inconclusive whether or not CO_2 helped with the precipitation of the "bad" asphaltene, or the most polar asphaltene.

Table 4.1. The result of total acid number measurements.

Total Acid Number (mg KOH/g)	
Bitumen	4.97 ± 0.39
Treated bitumen	4.85 ± 0.35
Asphaltene	2.27 ± 0.15
Treated asphaltene	2.32 ± 0.19

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, the possible beneficial role of carbon dioxide (CO_2) in paraffinic bitumen froth treatment was investigated. This study firstly examined the performance of CO_2 on asphaltene precipitation by injecting CO_2 to the mixture of n-heptane and dry bitumen at different pressures and temperatures. Then, in order to test the performance of CO_2 under industrial conditions, the mixture of dry bitumen and water were tested under CO_2 injection followed by bitumen froth under PFT conditions. The major conclusions are:

1. Under low pressure (0.1 MPa), there was no difference in asphaltene precipitation onset whether CO_2 or N_2 was used. The asphaltene precipitation onset for the tested bitumen sample was at n-heptane solvent concentration of 52 wt% (S/B = 1.08) at 20 min operational time. Under this condition, the weight of precipitated asphaltene from a dry bitumen sample was 8.3 wt%, while the dry bitumen had a total asphaltene content of 19.1 wt%.

2. At the asphaltene precipitation onset (i.e., 52 wt% n-heptane), CO_2 could enhance asphaltene precipitation at the tested pressure of 1-1.7MPa and temperature of 21℃ or 90℃. The best condition was at the temperature of 21℃ and pressure of 1.7 MPa CO_2, where the weight of precipitated asphaltene from the dry bitumen reached 12.8 wt%, i.e., a 55% increase from the test where no CO_2 was used.

3. Pressurizing the PFT system with an inert gas such as nitrogen did not enhance asphaltene precipitation. However, pressurizing the PFT system with CO_2 increased the asphaltene precipitation yield, and the enhanced precipitation was more pronounced at high pressure.

4. Higher temperature in general benefits asphaltene precipitation, and the temperature

effect was most obvious with an inert gas such as nitrogen. When CO_2 was used, increasing temperature from 21ºC to 90ºC did not lead to further increase in asphaltene precipitation. This was attributed to the counterproductive effect of the reduced CO_2 solubility at the higher temperature.

5. The presence of water further enhanced the asphaltene precipitation when CO_2 was used in a PFT process of dry bitumen. In the presence of 20 wt% water in the bitumen, and at the onset of asphaltene precipitation (i.e., 52 wt% n-heptane), the injection of 1.7 MPa CO_2 at 90 ºC increased the weight of precipitated asphaltene to 15.4 wt%.

6. Testwork performed on a bitumen froth sample indicated that under 21 °C and 1.7 MPa CO_2, and 52 wt% n-heptane, the yield of asphaltene precipitate reached 15.3 wt%, a full 7 percentage points higher than without CO_2. To achieve 15.3 wt% asphaltene precipitation without CO_2, the required n-heptane concentration was 76.9 wt%. Therefore, the use of the moderate pressure of CO_2, at 1.7 MPa, could lower solvent dosage by 32.4%.

7. The total acid number of bitumen and asphaltene before and after CO_2 and n-heptane treatment did not demonstrate any significant difference. It is therefore not possible to tell if the precipitated asphaltene with and without the use of CO_2 had different properties.

5.2 Recommendations

For further research, there are several directions to consider:

1. The scaled-up experiments are recommended. This project only tested in laboratory conditions. While applying the parameters to the large vessels, there might be some difficulty and uncertainties.

2. The solubility of CO_2 in these working conditions can be tested. In literature, there is

no particular data of the solubility of CO_2 in water, paraffinic solvent, and bitumen phase under the test conditions in this work.

3. As n-pentane and n-hexane are widely used in PFT process, the same research can be conducted with n-pentane and n-hexane as well and the optimal process parameters for these solvents can be studied.

The mechanism of how CO_2 helps asphaltene precipitation remains unclear, further investigation on this topic is highly recommended.

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