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Asphaltene Precipitation During Solvent Injection at Different Reservoir Conditions and Its Effects on Heavy-Oil Recovery from Oilsands

by

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Everything I am, I owe to my mother

Dedicated to my mother and brother

ABSTRACT

Solvent injection at elevated temperatures (hot solvent or steam-solvent hybrid injection) into heavy-oil/bitumen reservoirs is a promising recovery process. It increases oil mobility via oil dilution, molecular diffusion, and gravity drainage. Meanwhile, injection of light hydrocarbon solvents creates disequilibrium between resins and asphaltene in the oil. Then, asphaltene starts to flocculate and bond to each other in the fluid and on the rock surface. Consequently, permeability reduction due to pore plugging and wettability alteration may take place affecting the underground upgrading and recovery process negatively.

In this thesis, these asphaltene related concerns during solvent injection at different reservoir conditions were investigated through experimental work. A combination of two heavy-oil compositions and four solvent types were tested at different pressure and temperatures to determine the optimal solvent type and operational conditions minimizing the negative effect of asphaltene. The results obtained from visual PVT cell (testing fluid behaviour) and sandpack system (testing heavy-oil recovery) experiments were cross-checked. The roles of solvent type and operation conditions (mainly temperature) on the heavy-oil recovery, wettability alteration, and pore plugging were clarified and presented quantitatively and visually.

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CHAPTER 1: INTRODUCTION

Background

The main challenge to produce oil from large deposits of heavy oil and bitumen resources of Saskatchewan and northern Alberta is the high viscosity of these oils, usually over 10,000 mPa*s at reservoir conditions [26]. Conventional primary, secondary, and chemically enhanced tertiary methods have been inefficient to recover those deposits. There are generally two types of methods to increase oil mobility (viscosity reduction). The first one is to increase oil temperature by injecting a hot fluid, such as steam, into the reservoir or by in-situ generation of heat through the injection of oxygen-containing gases (in-situ combustion, ISC). The second method is to dilute the viscous oil with a light hydrocarbon (solvent).

VAPEX (vapor extraction) process, based on the combination of the aforementioned viscosity reduction methods (by injecting solvents in vapor phase) and horizontal well technology, was proposed to recover heavy oil and bitumen in late 80s [4,5,8,9]. This method is currently at the initial field testing stage. The advantages of the VAPEX technique are low energy consumption, low environmental risks, in-situ upgrading, and lower capital costs compared to thermal processes. However, disadvantages of the method still exist emerging from the solvent cost, asphaltene precipitation, and changes in the surface properties (mainly wettability alteration).

To improve the efficiency of the thermal methods, combination of solvent and steam injection were also proposed [3,14,26]. In this case, temperature comes into play as an additional parameter to alter the behaviour of asphaltene and wettability, which directly affects the efficiency of the recovery process.

Introduction

Solvent-Based Process

The light hydrocarbon solvent injection into the oilsands has established an opportunity to recover a higher amount of heavy oil and bitumen with a better quality than conventional and thermal recovery processes. The full idea about solvent injection into a heavy-oil reservoir was proposed by Butler and Mokrys [4,5,8,9]. In this process, named VAPEX (vapoer extraction), the solvent dilutes the oil and then the distillate hydrocarbon drains down to the production well by gravity. Das and Butler [8] showed that the use of vaporized solvent yields a higher driving force in gravity drainage due to a higher density change between heavy oil-bitumen and solvent vapor. This also guarantees that the remaining amount of solvent in the extracted reservoir will be less than with liquid solvents. The energy requirements for VAPEX are less than thermal methods because VAPEX operates at lower temperatures. Therefore, VAPEX is distinguished as an energy efficient, low operating cost, and high quality oil producing process [20].

Oil dilution (viscosity reduction), molecular diffusion, and gravity drainage are the most important physicochemical mechanisms in the solvent-based process. The mixing of heavy oil and light hydrocarbon solvent destabilize the heaviest and polar compounds from the oilsands. Consequently, asphaltene flocculation and cluster formation take place. On the other hand, tremendous improvement in the oil quality is present such as lower viscosity, density, acid number, and metal elements [3,8,9,18,20,21].

Asphaltenes

Asphaltene constituents are dark brown to black friable solids that have no definite melting point and usually foam and swell on heating, leaving a carbonaceous residue [23,24,25]. Asphaltene flocculates from the petroleum when a nonpolar compound is mixed with the crude oil if the surface tension is lower than 25 dyne cm^{-1} at 25 ˚C [23,24,25]. Asphaltenes are mostly soluble in aromatics (benzene and toluene) and high molecular weight polycyclic organic compounds containing nitrogen, oxygen, and sulfur in their structure [23,24,25]. Other elements such as carbon and hydrogen are also present.

The molecular weight and density of asphaltene is around 500 to 1000 $g.mol^{-1}$ and 1.28 g/cc, respectively. Resins play an important role in the asphaltene dispersion [23,24,25]. The molecular weight of resins is much lower than asphaltenes. The structure of the resins and asphaltene may vary from one reservoir to another. Asphaltene can be dispersed in the oil if sufficient resins are present in the petroleum fluids and their peptizing effect will prevent asphaltene self-association and delay asphaltene deposition [23,24,25].

The solubility parameter or the concept of cohesive energy density is significant in the asphaltene concentration in the fluid [23,24,25]. If the solubility parameter decreases, asphaltene concentration increases or vice versa. This parameter can be calculated using the Scatchard-Hildebrand equation [23,24,25].

Organic Deposition

Asphaltenes and resins are the heaviest compounds of heavy oils and the most common portions of the organic depositions [6,7,23,24,25]. Organic deposition typically affects downstream (refinery) and upstream (oil recovery) processes due to the line plugging and pore blockage. Also organic deposition can vary if inorganic materials are present such as clays, minerals, and debris. For example, illite (Beaver’s bend) and alumina have an adsorption percentage of asphaltene deposition in the reservoirs around 20% to 35% while Berea sandstone, dickite, Ottawa sand, and dolomite have an adsorption percentage of 4% to 5% [6,7]

Asphaltene precipitation has been studied in field and laboratory experiments. Results showed that asphaltene stability is dependent on oil composition, pressure, and temperature [2,10,15,12]. The oil composition and pressure effect are believed to be stronger than the temperature effect. However, the thermodynamic models indicated a strong disagreement with this statement [11,23,24,25].

Statement of the Problem

Solvent injection is a very complex process due to the existence of numerous factors influencing oil production (e.g., temperature, pressure, solvent/crude oil ratio, solvent type, miscibility, rock surface, etc.) as summarized in the above section. Several solvent-based studies in upstream and downstream processes have been conducted during the last decades to better understand this process.

Several studies showed that when the temperature and pressure increase, the concentration of asphaltene in the crude oil decrease [1,2,10,12]. In contrast, Kokal et al. [15] demonstrated that by reducing the pressure, the asphaltene precipitation would not increase. However, all these experiments were conducted at very high operation pressures usually greater than 1000 psig. Consequently, this raises the question whether results can be applied to shallower reservoirs encountered in Alberta, Canada (typically less than 500 m).

Asphaltene has the tendency to precipitate close to the dew point of the fluid, but in some cases, asphaltene precipitation may take place even at different conditions depending on the type of oil composition, temperature, pressure, and the amount/type of n-alkane used [1,10,15]. Thus, the first question to be answered is whether the dew point is the optimal operational condition to apply light hydrocarbon solvent injection processes. This requires a well-designed experimental investigation considering a wide range of temperature, pressure, and solvent type.

The behaviour of asphaltene during oil production under solvent injection at variable pressure and temperatures also needs clarifications. Redford and McKay [22] conducted experiments involving co-injection of steam and different hydrocarbons, such as propane, butane, pentane, and naphtha into Athabasca bitumen. They concluded that contrary to common belief, the injection of solvents, such as propane and pentane, into a reservoir with steam in highly asphaltenic crude such as Alberta bitumen, does not lead to appreciable permeability reduction. Similarly, Das and Butler [8] observed that when deasphalting takes place in the reservoir, it does not affect the production rate. However, Papadimitriou et al. [17], Moghadam et al. [16], and Haghighat and Maini [13] observed significant asphaltene deposition in the porous medium, especially at the injection and production zones. Consequently, they suggested that the VAPEX process is not an effective technology due to the permeability reduction and low rate of oil production. Hence, this appears to be the second question: Under what circumstances did asphaltene flocullation and deposition take place when solvent was injected at elevated temperatures?

Solvent injection is an attractive process to increase the oil production due to in-situ upgrading. This can be a success if the above mentioned asphaltene related -negative- issues are resolved. This requires clarifications on the effect of temperature, pressure, solvent type, and oil composition on the behaviour of asphaltene in the fluid (heavy-oil and solvent mixture) and porous medium during solvent injection. This will lead to identification of optimal operational parameters to prevent or minimize the asphaltene agglomeration and cluster formation in the reservoirs.

Research Objectives

Asphaltene destabilization is one of the main challenges in heavy-oil production by solvent injection. To better understand asphaltene flocculation and cluster formation, experiments were conducted in a pressure, volume, and temperature (PVT) cell and a sandpack -displacement-system. The main objectives from this investigation are as follows:

- To determine the level of asphaltene agglomeration and cluster formation in fluid (liquid, vapor, solid phases) when several parameters, i.e., temperature, pressure, solvent type, and oil composition, are changed. This objective is covered in Chapters 2 and 4. The asphaltene flocculation and cluster formation were evaluated using a phase behaviour apparatus (PVT cell).
- To evaluate the effect of temperature and pressure on oil production when a light hydrocarbon is injected into a porous medium system. This objective is covered in Chapter 3. To determine the effect of temperature and pressure, different types of solvents with different boiling points were injected into a sandpack model.
- To calculate the amount of residual oil saturation and asphaltene deposition in porous medium to determine the optimal operational conditions. This is covered in Chapter 3.
- To calculate and evaluate the organic deposition on the rock surface using several types of light hydrocarbon solvents and to understand its effect on oil production. This is reported in Chapters 3 and 4. High resolution microscopes (scanning electron microscope and focused ion beam dual system) are used for visual analysis.
- To evaluate the organic deposition effect on different wettability (oil- and water-wet) media. This is covered in Chapter 4.

Structure of the Thesis

The thesis is comprised of six main chapters. **Chapter 1** includes a general introduction and background information about the subject the problem description and research objectives. This is a paper-based thesis, the rest of the chapters contain the papers produced. **Chapters 2 through 5** are compilations of papers presented at two conferences and/or submitted to peer-reviewed journals. Each of the chapters includes their own introduction, literature survey, conclusions, and references. Therefore, no separate sections of those (introduction, literature survey, conclusions and references) were presented in the thesis.

Chapter 2 presents a study investigating asphaltene flocculation and cluster formation using the pressure, volume, and temperature (PVT) of an optical cell. In this chapter, three solvents (propane, n-hexane, and n-decane) and heavy oil (8.6˚API) were used to study the fluid behaviour after asphaltene precipitation takes place.

Chapter 3 contains the displacement -porous medium- tests. In this chapter, two heavy oils (8.6 - 10.2˚API) were studied using four types of light hydrocarbon solvents. The experimental results are presented as cumulative oil produced and asphaltene deposition for different types of temperatures and pressure conditions.

Chapter 4 includes pressure, volume, and temperature (PVT) cell experiments combined with porous medium organic deposition (thickness measurements). In this section, two heavy oil samples (8.6 - 10.2˚API) were tested with four different solvents through PVT cell and focused ion beam dual (FIB/SEM) systems to determine the organic deposition from the porous medium.

Chapter 5 investigates the wettability alteration effect after a light hydrocarbon solvent was injected into oil- and water-wet sandpack models. Oil recovery rate and amount of organic deposition were determined using a sandpack model and focused ion beam dual system (FIB/SEM).

Chapter 6 outlines the major contributions from this research and offers recommendations for potential future work on organic deposition during variable pressure and temperature solvent-based processes.

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CHAPTER 2: QUANTITATIVE AND VISUAL CHARACTERIZATION OF ASPHALTENIC COMPONENTS OF HEAVY-OIL AFTER SOLVENT INTERACTION AT DIFFERENT TEMPERATURES AND PRESSURES

This paper is a modified and improved version of SPE 150315, which was presented at the SPE International Symposium on Oilfield Chemistry held in The Woodlands, Texas, USA, 8–10 April 2013. This chapter has been accepted for publication in Fluid Phase Equilibria.

Background

Due to inefficiency of steam injection caused by technical, economic, and operational reasons, solvent methods have received special attention in heavy oil and bitumen recovery recently. Solvent-based recovery processes improves crude oil production and quality because underground in-situ upgrading takes place after heavy oil is diluted with a light hydrocarbon solvent. Consequently, crude oil mobility increases due to significant reduction in viscosity caused by the asphaltene precipitation. However, solvent driven recovery processes are quite complex on account of the ‘‘asphaltene destabilization’’ that takes place due to changes in temperature, pressure, crude oil composition, and solvent dissolved in oil. As a result of this destabilization, the asphaltene particles start to flocculate, and eventually may plug the pores in the reservoir due to larger asphaltene particle agglomeration in the reservoir.

In this paper, the deasphalting of a heavy oil sample [10°API] was carried out using an optical PVT cell. The experiments were undertaken at different temperature ranges [122 F (50 ^{o}C) to 230 °F (110 ^{o}C)] and pressure ranges (30 psig to 500 psig), which are the suggested ranges applicable to typical Canadian oilsands or similar shallow heavy-oil deposits around the world. Three light hydrocarbon solvents (propane, n-hexane, and n-decane) were used to break the stability of the asphaltene in the crude oil. An experimental methodology for “asphaltene precipitation fraction” was developed in order to determine the effect of temperature, pressure, and solvent type on the amount of asphaltene precipitation. The experimental methodology was complemented through visual observations of asphaltene characteristics on the PVT cell as well as using optical microscopy. In addition, the refractive index measurements at the onset of precipitation were used to evaluate the changes in the oil after interacting with the solvent at different temperatures and pressures.

Overall, the results showed that precipitated asphaltene fraction increases when the concentration of the resins goes down after the deasphalting of crude oil with solvent. In addition, the aggregation of asphaltene particles increases with increasing temperature [122 °F (50 ^{o}C) to 230 °F (110 ^{o}C)] and pressure (from 30 psig to 500 psig), and decreasing solvent carbon number (from C10 to C3). At the end, a comparative analysis of the quantitative and qualitative results from the experiments is provided. Based on these observations, the characteristics of asphaltene were classified in terms of their shape, size, and amount for different oil/solvent types, pressure, and temperature.

This study will eventually lead to the identification of the effects of asphaltene characteristics on pore plugging during heavy-oil/bitumen recovery by gravity drainage from oilsands.

Introduction

Solvent based applications of heavy-oil recovery have been proposed as an alternative process due to economical, operational, and environmental concerns of thermal recovery processes. The solvent injection process into the reservoir was proposed initially by Butler and Morkys [1]. They introduced this new process as vapour extraction (VAPEX), which mainly consists of deasphalting of the heaviest components of heavy oil, i.e., asphaltene [2,3,4]. Asphaltene has the highest molecular weight and is the most polar constituent of a crude oil [5,6]. Asphaltenes are insoluble in n-alkanes (e.g. n-heptane and n-pentane) but soluble in aromatics (e.g. benzene and toluene) [5,6]. The asphaltene polydisperse molecules consist mostly of polynuclear aromatic ring systems bearing an alkyl side chain [5,6]. Also, hetero-elements (nitrogen, oxygen, and sulfur) and heavy metals (vanadium, nickel, and iron) were identified in the asphaltene structures [5,7,8].

In addition, asphaltene self-association mainly depends of the resins structure type. Resins structure can vary depending of the oil composition [8-11]. Asphaltenes may partly be dissolved and suspended/peptized by resins in the crude oil. The solubility of the asphalentes in the crude oil can decrease by the injection of the light hydrocarbon solvent [9,11,12]. Consequently, asphaltene may form steric-colloidal particles due to the paraffinic injection, which affects the resins fraction as the dispersing agent. The resin molecules generate the desorption from the asphaltenes surface in order to re-establish the thermodynamic equilibrium [9,13,14]. Subsequently, asphaltene particles start to bond to each other until they create clusters of asphaltene nano-aggregates [8,9,11,15,16]. Asphaltene precipitation can be calculated experimentally using a variety of methods. The most widely used methods are the gravimetric (static) method and filtration (dynamic) method. The gravimetric method is the most commonly used in studies of asphaltene phase behavior in a visual PVT cell [17,18].

Asphaltene precipitation during upstream and downstream processes has been studied for decades. Upstream process has been more challenging as asphaltene agglomeration and cluster formation near the wellbore (and in the reservoir) may significantly affect production rate [19,20]. Chemical treatments have been used in order to increase the dispersion of the asphaltene in the fluid [21,22]. An alternative to this is to control pressure and temperature and remain out of the precipitation point [20,22-24], which requires extensive PVT studies to determine this point for the given oil type.

Studies on asphaltene precipitation envelopes (APE) were determined mostly for natural pressure depletion processes and showed that asphaltene solubility depends on temperature, pressure, and oil composition. However, the relative effects of these parameters on asphaltene behavior are highly controversial. For example, it has been observed that pressure and oil composition effects are more critical than the temperature effect [9,18,25]. As opposed to this, some found the role of temperature in asphaltene deposition process more important. It was reported that increments in the temperature and pressure influence the asphaltene concentration in the crude oil and, as a consequence of this, asphaltene flocculation may decrease [12,17,26,27]. On the other hand, it was demonstrated that by reducing pressure, the asphaltene precipitation does not increase [28]. Moreover, asphaltene has a tendency to precipitate near the bubble point, but in some cases, asphaltene precipitation may take place even at different conditions from the bubble point, depending on the type of oil composition, temperature, and pressure [12,17,28].In addition to the above listed experiences, upstream and downstream processes that are involved in the dilution of crude oil with n-alkanes and the effect of temperature, pressure, and solvent on asphaltene flocculation during this process were also reported. Nielsen, et al. [16] studied the effect of the temperature, pressure, and n-pentane (n-C5) on particle size distribution using different types of oil composition. They found that higher temperature and pressure operational conditions increase the solubility parameter. The solubility parameter can be calculated based on the mixture between crude oil and n-alkane. Other studies found that based on the refractive index of the mixture, higher hydrocarbon number increases the asphaltene dispersion in the crude oil than the lower hydrocarbon number [29,30]. Similarly, Ferwron, et al. [13] and Speight [5] found that lower hydrocarbon solvent decrease the solubility of the mixture due to asphaltene precipitation. Speight [5] concluded that temperature and pressure changes affect the oil composition. Moreover, Akbarzadeh, et al. [17] conducted solvent injection experiments using a pressure, volume, temperature (PVT) cell. They concluded that the amount of asphaltene precipitate decrease as pressure and temperature increase. In short, the natural tendency of asphaltene precipitation is quite complex to understand in the reservoir formation due possible wettability alteration, emulsion formation, asphaltene deposition in porous medium, and oil production [31,32].

Definitely, asphaltene precipitation and deposition into the reservoir is one of the main issues with the solvent injection process. Asphaltene precipitation from the crude oil improves the crude oil quality and mobility due to upgrading; however, asphaltene may be flocculated and agglomerated in the fluid stream and on the rock surface. Das and Butler [33] conducted VAPEX experiments using a Hele-Shaw cell. Three Alberta oil sands (Peace River, Cold Lake, and Lloydminster regions) were diluted with propane at operational conditions near the dew point of propane. They concluded that the asphaltene deposited in the porous medium, and wettability alteration does not stop oil flowing out of the reservoir. Similarly, Das [34] concluded that in a Hele-Shaw cell and high-permeability packed beds did not show that asphaltene precipitation caused any serious problem in the oil production. However, they suggested that the precipitated asphaltene may become a problem in finer sands. Note that these experiments were conducted at ambient temperature (VAPEX) conditions.

Later, Butler and Jiang [35] carried out experiments using butane or propane mixtures with a non-condensible gas (methane) at different temperatures and pressures (69.8 °F – 80.6 ˚C and 30 psig – 300 psig, respectively). They observed more oil production at higher pressure and temperature conditions and better viscosity reduction at higher solvent/oil rate. In addition, they noticed a higher recovery factor with propane compared to butane or mixture of both. In contrast, Papadimitriou et al. [36] observed remarkable asphaltene deposition in Berea sandstone cores when iso-butane was used as solvent, then the oil production declined in the time. They observed asphaltene migration downstream flow, and defined two critical zones of the asphaltenic material deposition close to the injection and production wells [36,37]. Furthermore, after running several experiments using propane and butane, Haghighat and Maini [31] suggested that in-situ upgrading of the oil via asphaltene precipitation in the VAPEX process is not an effective technology due to the permeability reduction and low rate of oil production. In addition, Pathak and Babadagli [38,39] conducted several experiments in an unconsolidated sandpack medium . They concluded that asphaltene deposition on the pore throats promoted reduction of permeability as well as oil production. Earlier studies demonstrated that asphaltene precipitation increases or decreases according to the oil composition, type of paraffin and concentration, pressure and temperature conditions [11,40,43]. These observations indicate that asphaltene deposition, which may cause a negative effect on heavy-oil production due to pore plugging, can be reduced by applying optimal operating conditions.

In this research, the effect of crude composition, temperature, pressure and type/amount of solvent on asphaltene precipitation was investigated. The main objective was to provide a clear understanding of asphaltene precipitation behavior at different pressure and temperature conditions using specific extra heavy oil (87,651 cp at 25 °C) and to substantiate data to be used in asphaltene deposition in porous medium. A visual PVT cell was used to analyze the phase behavior of heavy crude oil and n-alkane solvents for a range of temperature [from 122 °F (50 ˚C) to 176 °F (80 ˚C)] and pressure (from 30 psig to 500 psig). The study was supported by other quantitative and qualitative (visual) measurements (refractive-index analyzer, elementary analyzer, and optical microscopy), and a "map" of asphaltene characteristics with respect to operating conditions and solvent type was provided.

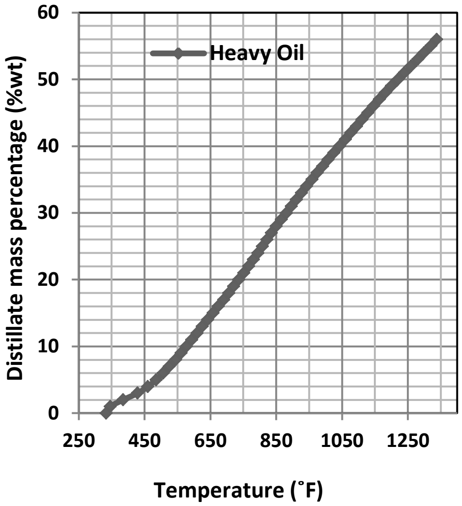
Experimental

Materials

The original crude heavy oil sample was obtained from a field operating in Alberta, Canada. The carbon number distribution of the hydrocarbon is between C_{11} (0.83% wt at 384 °F) to C_{120} (60.1 %wt at 1328 °F). This was measured using the standard test method (ASTM D 5307) by determining the boiling range distribution of the crude oil (**Figure 2-1**). The viscosity and density values were measured at three different temperatures between 77 °F to 158 °F at the atmospheric pressure (**Table 2-1**). Correspondingly, the standard test method for determination of asphaltenes (n-heptane insoluble) in crude petroleum and petroleum products (IP-143) was followed. The asphaltene content of the oil and was measured to be 11.4 wt% (*n*-heptane 99.4% pure) **(Table 2-1)**. In addition, elementary analysis (CHNS) of the crude oil and asphaltene precipitated (*n*-heptane 99.4% pure) were performed using the standard guide for calibration requirements for elemental analysis of petroleum products and lubricants (ASTM D7578). The results of these tests are tabulated in Table 2-1. Experiments were also performed to determine the amount of asphaltenes precipitated with three n-alkane solvents at different temperature and pressure. The purities of n-alkanes ($C_3H_8, C_6H_{14}\ and\ C_{10}H_{22}$) used as precipitants were 99.5%, 99.9% and 99.6%, respectively.

Table 2-1: Heavy Oil Sample Properties

Heavy Oil Properties-ASTM D2007, IP-143 and D2549	
Saturates (wt.%)	17.24
Aromatics (Wt.%)	38.60
Resin (Wt.%)	32.66
Asphaltene (Wt%)	11.40
Heavy Oil Elementary Analysis-ASTM D7578	
Carbon (wt.%)	84.45
Hydrogen (wt.%)	9.731
Sulfur (wt.%)	3.715
Nitrogen (wt.%)	0.553
Asphaltene Elementary Analysis-ASTM D7578	
Carbon (wt.%)	82.06
Hydrogen (wt.%)	7.957
Sulfur (wt.%)	7.431
Nitrogen (wt.%)	0.946
Density [g/cm^3]	
104 ˚F	0.9959
158˚F	0.9774
Viscosity [cP]	
77˚F	87651
104˚F	13298
158˚F	1450



Components	Temperature (°F)	Distillate mass (wt %)
C_{11}	384	0.83
C_{20}	651	14.31
C_{25}	755	21.52
C_{30}	840	28
C_{35}	912	33.03
C_{40}	971	37.24
C_{50}	1067	43
C_{60}	1139	47.18
C_{70}	1196	50.05
C_{80}	1247	51.87
C_{90}	1292	52.88
C_{120}	1328	60.1

Figure 2-1: Boiling range distribution from the heavy oil (ASTM D5307).

Glass System Deasphalting Test

Prior to the phase behavior experiments in the PVT visual cell, the crude oil sample was deasphalted at different n-alkane/oil volume ratios between $\frac{1.2\ Solvent\ cc}{1\ g\ heavy\ oil}$ and $\frac{6\ Solvent\ cc}{1\ g\ heavy\ oil}$. These initial experiments were performed to define the volume ratio to be used in the PVT cell tests. The initial deasphalting experiments were carried out at 122°F and atmospheric pressure using a glass system. The glass deasphalting system consisted in a flask connected at the top with a glass condenser, heating and mixing at the bottom using a stirring hot plate. In these experiments, the IP-143 standard method was followed to precipitate asphaltenes. The volume ratio determined to be used in the PVT cell experiments was 5 cc solvent/1 g oil. After this volume rate, the asphalting mass fraction is almost constant for both n-alkanes (n-hexane and n-decane) (**Figure 2-2**). The third n-alkane (propane) could not be carried out using a glass system due to its phase behaviour at 122 F and atmospheric pressure. Then, the same volume rate calculated for the other two n-alkanes was used in the PVT cell experiments for propane.

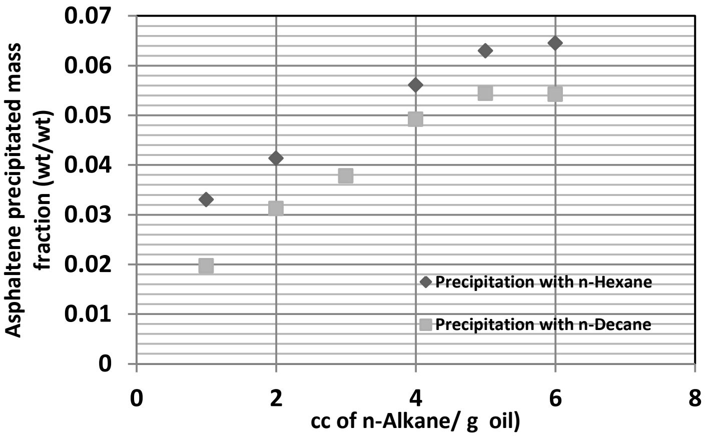


Figure 2-2: Asphaltene precipitation at different volume ratios using n- Alkanes (C_6H_{14} and $C_{10}H_{22}$) at 50 ˚C and at the atmospheric pressure.

Experimental Apparatus

The visual PVT cell was used basically to have quantitative and qualitative information about asphaltene precipitation. In **Figure 2-3**, the experimental apparatus is shown. The experimental setup is composed of mainly four systems:

1. The major part is the visual PVT cell (100cc, 15ksi,H_2S) which can be operated up to 15,000 psi and 392˚F. The PVT cell pressure, temperature and volume are controlled by software. In addition, the PVT cell has a CCD (charge-coupled device) level measurement, long focus which has a high resolution image (NTSC to 768 x 494 pixels). The capture of this visualization was recorded using an AverMedia DVD EZMarker 7. The CCD level measurement was used to calculate the volume, height and sample fluid behaviour inside of the PVT cell glass tube. Moreover, the PVT cell has a magnetic mixer that reduces operating time for establishing phase equilibrium on the sample.
2. The second system is the fluid injection part, which basically consists of two piston-cylinders, one to inject the heavy oil solvent and the other to inject the solvent, and two pumps to put the piston up for heavy oil and solvent injection.
3. The third system is the high pressure and high temperature filter, which primarily makes the separation between the asphaltene and oil phases. This system is connected to a vacuum pump (to achieve a better filtration) and an oil sample container.
4. The fourth piece of the system is the data acquisition unit and an optical microscope.

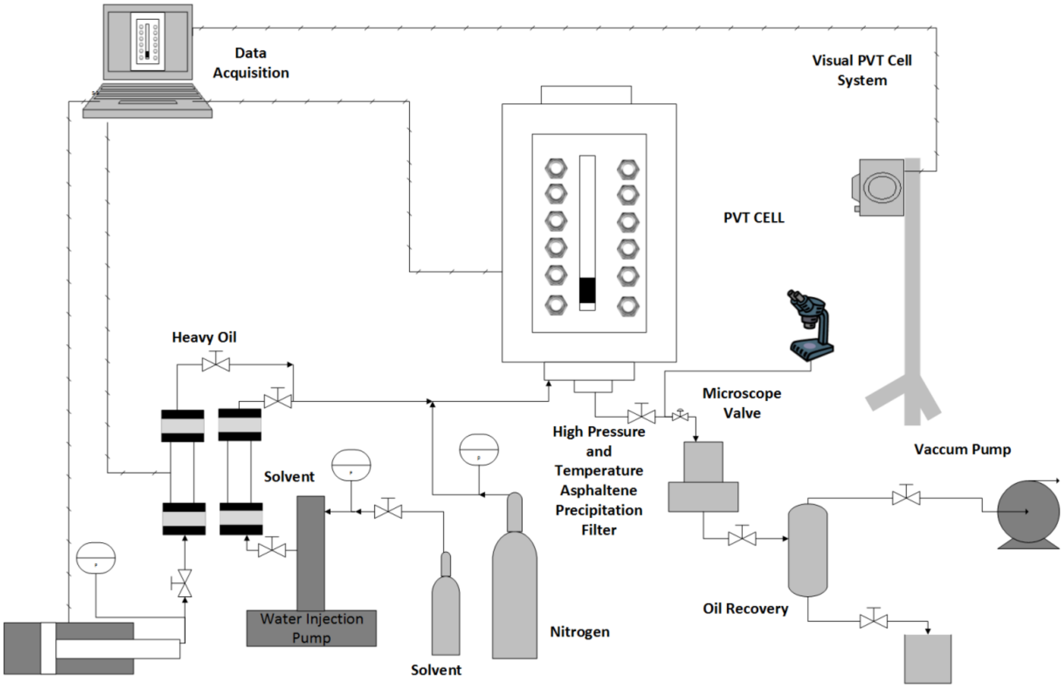


Figure 2-3: Schematic flow diagram of experimental setup.

Experimental Procedure

The PVT visual cell shown in **Figures 2-3** to **2-4** was cleaned with toluene and vacuumed for 0.33 hours. Then, the operating conditions in the PVT cell were stabilized before the sample injection via leaving it over night at the temperature condition of the particular experiment (from 122 F to 230˚F). Also, the heavy oil sample was left over night at 122 F using a heating tape outside of close piston-cylinder in order to reduce the fluid viscosity before injection. Once those temperatures were stable, the mechanical pump, which uses mineral oil, started to pump the heavy oil sample into the PVT cell. After pumping the heavy oil sample, the solvent injection was started. A syringe pump was used to inject the solvent into the PVT cell. Next, using the magnetic mixer, the equilibrium phase was established and pressure, temperature, and volume were monitored and recorded using the existing software package of the PVT system.

The volume percentage of heavy oil and solvent injected was 0.16 v/v% and 0.84 v/v%, respectively. The sample was left at the PVT cell for about 8 hours when n-hexane and n-decane were used as solvent. For propane, this time was extended to 24 hours since propane may need a longer period of time to establish the equilibrium phase. During this operation, the phase behavior of the sample was recorded using the CCD level measurement and Aver Media 7. When the experiment was completed, the multiphase sample was separated using a high pressure and high temperature filter equipment, which contained two Whatman filter grade 42: 2.5μm. A vacuum pump was used for a better filtration **(Figures 2-3 and 2-4)**. When the full separation between the liquid and solid was achieved, pure nitrogen was injected into the production lines to take out the possible asphaltene particles.

After the liquid and solid parts were separated, the analysis of the asphaltene sample was done using the following instruments: Soxhlet extraction, optical microscope, and elementary analyser-CHNS (Varium). Moreover, the analysis of the liquid sample (oil) was done using a digital refractometer, Varium elementary analyser-CHNS, Sim-Distillation- 450 GC, and DV-11+Pro Viscosimeter.

At the end, the PVT cell was cleaned using toluene to dissolve the asphaltene present in the connection lines and glass tube. The toluene-asphaltene solution was separated using rotary vacuum evaporator equipment. The asphaltene separated from the toluene was cleaned using heptane to eliminate the maltenes fraction and this asphaltene was also included in the total mass balance calculations.

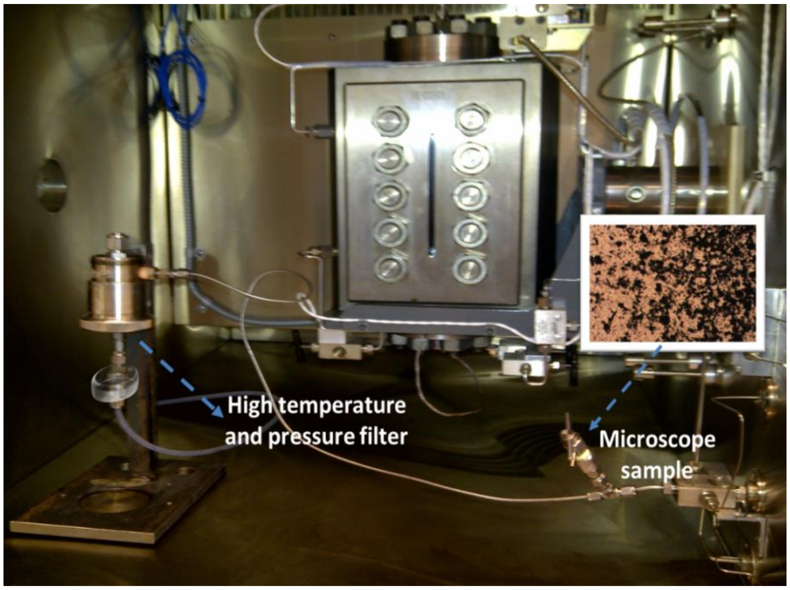


Figure 2-4: PVT visual cell equipment.

Results and Discussion

The quantitative and qualitative analysis of asphaltene precipitation was achieved using three n-alkanes (propane, n-hexane, n-decane) at different temperature ranging from 122 °F to 230 °F and pressure ranging from 30 psig to 500 psig. The respective dew points of the three solvents at 7.348 psi are -70.42 °F (propane), 119 °F (n-hexane) and 298.4 °F (n-decane). The results showed that asphaltene precipitation and deposition increase or decrease if oil composition, the temperature, pressure and type of n-alkane are altered. The sample obtained from the PVT cell was analyzed under the optical microscope to determine the shape and agglomeration of asphaltene particles after the deasphalting with any n-alkane. These asphaltene particles also showed that flocculation, agglomeration and particle size may increase or decrease with alteration in the oil composition, temperature, pressure and solvent type. A detailed analysis is provided below.

Experimental Observation of Asphaltene Precipitation at Different Temperature and at Isobaric Conditions

Asphaltene precipitation studies at different temperatures showed that when the temperature increases from 122 °F to 176 °F, the asphaltene mass fraction decreases gradually for all solvents (propane, n-hexane and n-decane) due to the solubility of the asphaltenes in the crude oil decrease. However, using n-decane as solvent presented different trends in asphaltene precipitation than it did in n-hexane and propane. For example, n-decane yielded a peak asphaltene precipitation at 140 °F. When the temperature continued to increase above 140 °F, the asphaltene concentration started to decrease (**Figure 2-5-a**). This peak value for n-decane may be explained by the effect of low crude oil stability at this particular temperature (140 °F). Subsequently, desorption of the peptizing resins forces the asphaltene micelles to agglomerate. Then asphalting flocculation was observed to be higher at this point. Further, a continuous decline in asphaltene precipitation with temperature was observed for lower carbon number solvents (n-hexane and propane). However, the sample obtained for n-hexane at 230 °F and 30 psig shows an increment on asphaltene mass fraction than the mass fraction achieved at 175 °F **(Figure 2-5-b).** This is likely due to the lower asphaltene solubility is presented near to the boiling point or dew point. This behaviour was also found by Edmonds et al. [12], Kokal et al. [28] and Akbarzadeh et al. [17].

Asphaltene solubility parameter in the crude oil mainly affects asphaltene flocculation and asphaltene dispersion, which can vary depending on the type of oil composition, solvent type, pressure and temperature. Field and laboratory tests have shown that oil composition and pressure have a stronger effect than the temperature effect on asphaltene precipitation [9]. However, there is still a certain disagreement in regards to the temperature effect on asphaltene precipitation [9,12,16,27,44].

In the present research, the extra-heavy oil used showed that the temperature is quite an important parameter to be included and studied when solvent-based process applied. Also the effect of temperature can be significant depending on the solvent type used because the oil composition can cause extreme changes when the deasphalting process take place **(Figures 2-8 to 2-9).** We observed that asphaltene precipitation was higher when the solvent carbon number was lower as also reported by previous researchers [5,7,16,27,44]. Themperature effect is criticla when solvent is used as an enhanced oil recovery material in heavy-oil fields. It may also become a critical factor in asphaltene precipitation in deep wells that shows significant temperature (and pressure) difference between the production formationa and surface.

Experimental Observation of Asphaltene Precipitation at Different Pressure and at Isothermal Conditions

Pressure was also observed to be a critical parameter on asphaltene precipitation at different temperatures. The pressure effect on the amount of asphaltene precipitated for different temperatures are given in **Figure 2-6**. The propane solvent case **(Figure 2-6a)** shows more pressure effect on asphaltene precipitation concentration than n-hexane and n-decane solvents. Propane is a more compressible fluid and the density changes at different conditions unlike n-hexane and n-decane (their densities were almost constant within the pressure and temperature intervals applied in the tests). Moreover, the pressure effect on asphaltene destabilization was less when n-hexane and n-decane were used as precipitating agent. This can be attributed to the incompressible nature of these two solvents, which are almost negligible compared to propane. However, temperature and solvent type were quite important parameters in asphaltene precipitation behavior for those solvents. This behaviour can be attributed to the type of extra heavy oil composition used which has a carbon number distribution between C_{11} (0.83% wt at 384 °F) to C_{120} (60.1 %wt at 1328 °F).

The asphaltene solubility into the crude oil decreases more when pressure increases from 30psig to 200psig for n-hexane **(Figure 2-6b)**. This effects is not as critical in the cases of the other two n-alkanes (propane and decane). Above 200 psig, asphaltene precipitation was almost constant between 158 ˚F to 176 ˚F as similar to n-decane. Overall, pressure increment had a positive effect on the solubility parameter of the asphaltenes.

The behavior of asphaltene precipitation with n-hexane as pressure increases can be attributed to changing crude oil composition due to different thermodynamic equilibrium compared to the other cases. However, the amount of asphaltene precipitation with n-hexane and n-decane were quite close to each other. Note that propane yielded much higher asphaltene precipitation as propane solubility in the resins was much lower compared to that of n-hexane and n-decane. This resulted in less asphaltenes dispersion into the resins when propane was used.

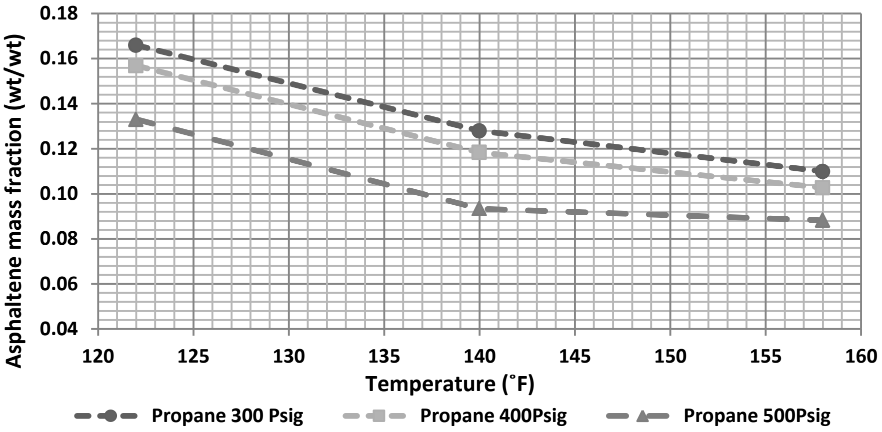
Experimental Observation of Asphaltene Precipitation after Deasphalting with Different Types of Solvent

Figures 2-5 and **2-6** show the mass fraction of asphaltene precipitated calculated for each n-alkane solvent (propane, n-hexane and n-decane). The experimental results indicate that more asphaltene flocculation was achieved using solvent with lower hydrocarbon number. Also, the mass fraction of asphaltene precipitated was higher with propane compared to n-hexane and n-decane. In addition, visualization under the PVT and optical and scanning electron microscope showed that the agglomeration of asphaltene increases when the carbon number decreases.

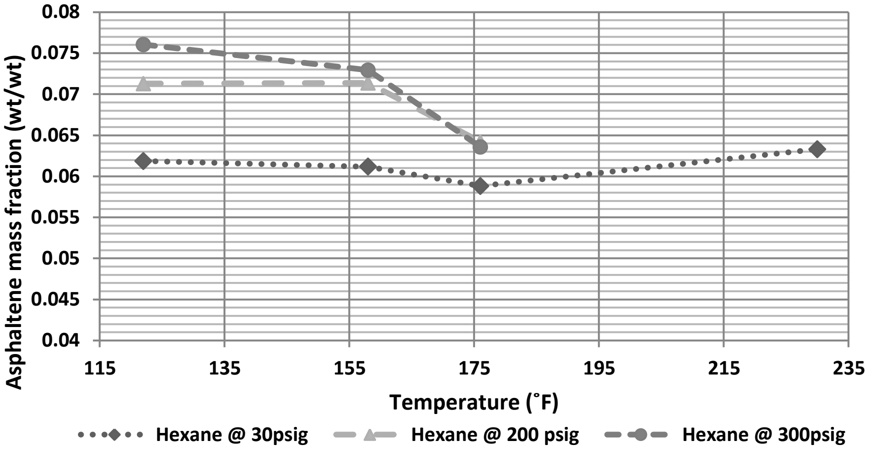
After running several sandpack experiments using propane, n-hexane, and n-decane, it was reported that oil recovery factor increased when a higher hydrocarbon number was used since the solubility of asphaltene increased with increasing carbon number of the solvent [40,41]. They observed that asphaltene deposition on glass beads was higher when propane and n-hexane were used as solvent compared to n-decane (**Figure 2-7**). Note that the qualitative and quantitative characteristics of the asphaltene deposited in the pores (second and third layer of images) are consistent with the visual PVT cell observations (the top layer of images) of the present study.

Moreno and Babadagli [40,41] also concluded that n-decane could be a more proper solvent than propane. In addition, solvent flow rate and operating conditions are two other important parameters. If the flow rate increases, asphaltene concentration increases as asphaltene dispersion into the resins decreases. Moreover, asphaltene concentration decreases with increasing pressure and temperature due to high asphaltene solubility.

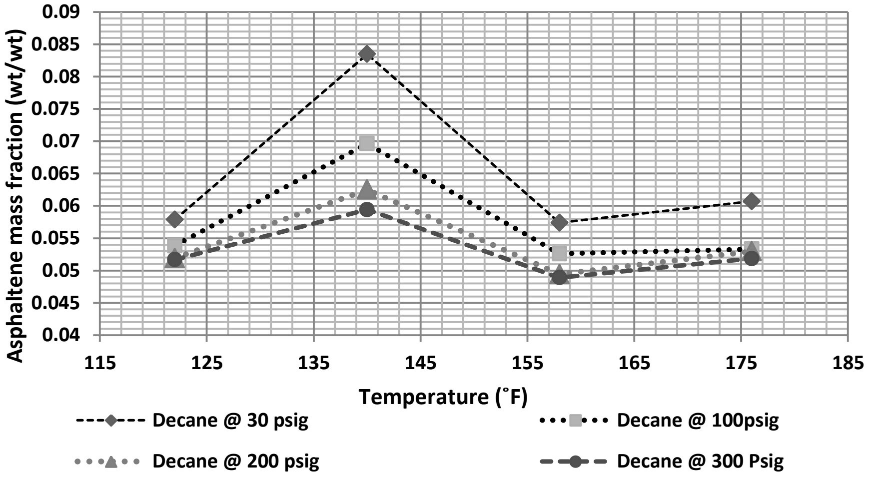
Asphaltene particle size and agglomeration are other important factors on the ultimate oil recovery from sandpacks. When pressure (from 30 psig to 300 psig) and temperature (from 122 ˚F to 230 ˚F) increased, the particle sizes become larger due to adhesion. The same behaviour was reported by Nielsen, et al [16]. They studied the temperature and pressure behaviour on the asphaltene particle sizes using bitumen samples from Cold Lake (Canada) area and Lindberg oil (Canada), which had high asphaltene content (pentane-insoluble 21.8% and 17.6%). They observed that super agglomerates were developed at temperatures around 176 ˚F and higher and this was attributed to the softening and adhesion of asphaltenes particles. They also found that an increase in pressure yielded an increase in the mean asphaltene particle size for the Cold Lake bitumen sample but not for the Lindberg oil.



(a) Asphaltene Precipitated with propane (C_3).

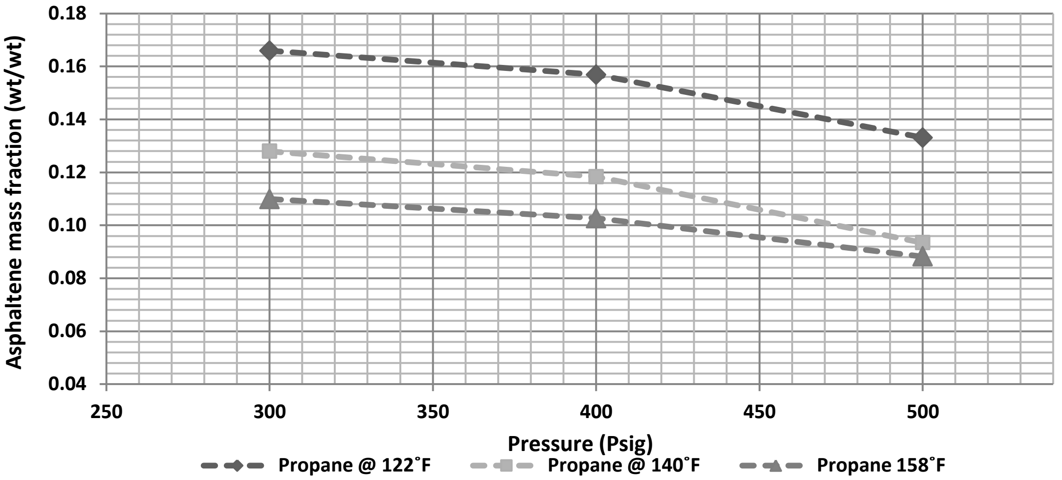


(b) Asphaltene Precipitated with n-hexane (n-C_6).

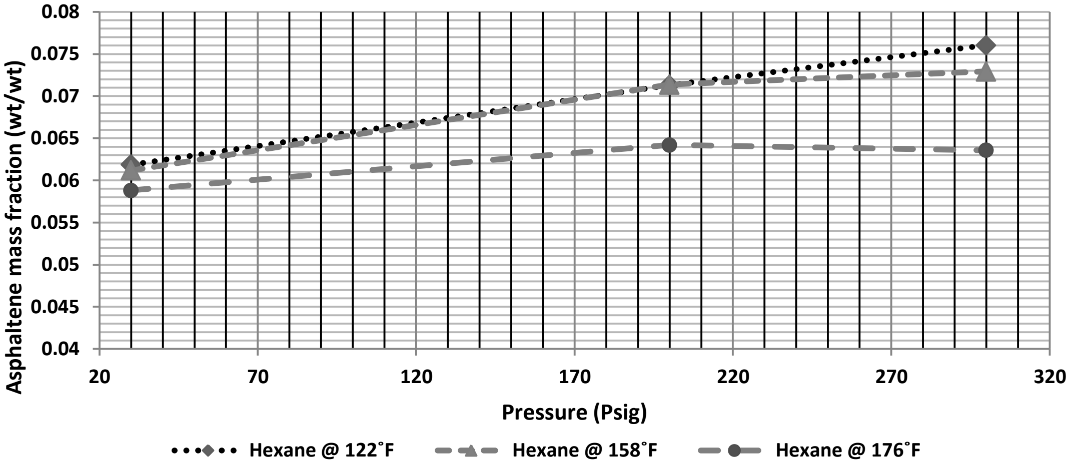


(c) Asphaltene Precipitated with n-decane (n-C_{10}).

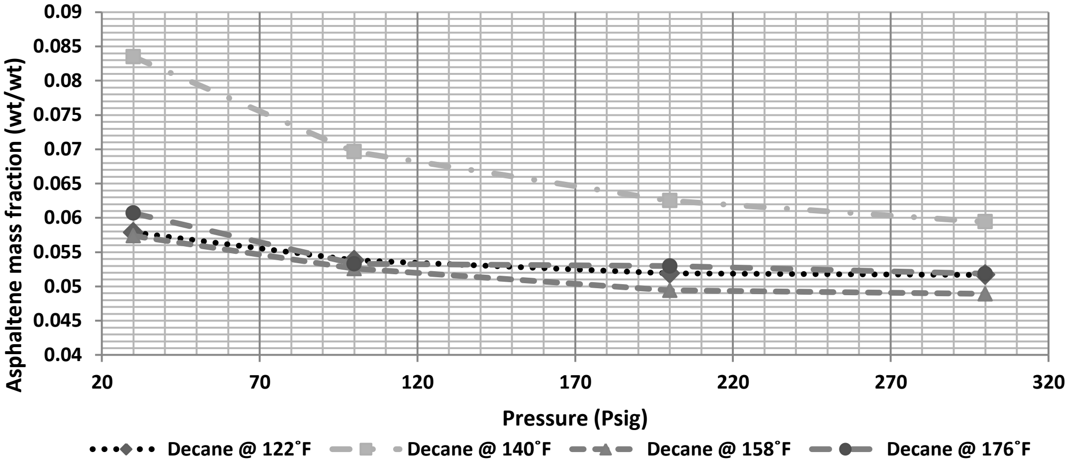
Figure 2-5: Asphaltene precipitation mass fraction at isobaric and several temperature conditions using n-alkanes as precipitating agent at a constant volume ratio determined to be 5 cc solvent/1 g oil: a) propane, b) n-hexane, c) n-decane.



(a) Asphaltene Precipitated with propane (C_3).

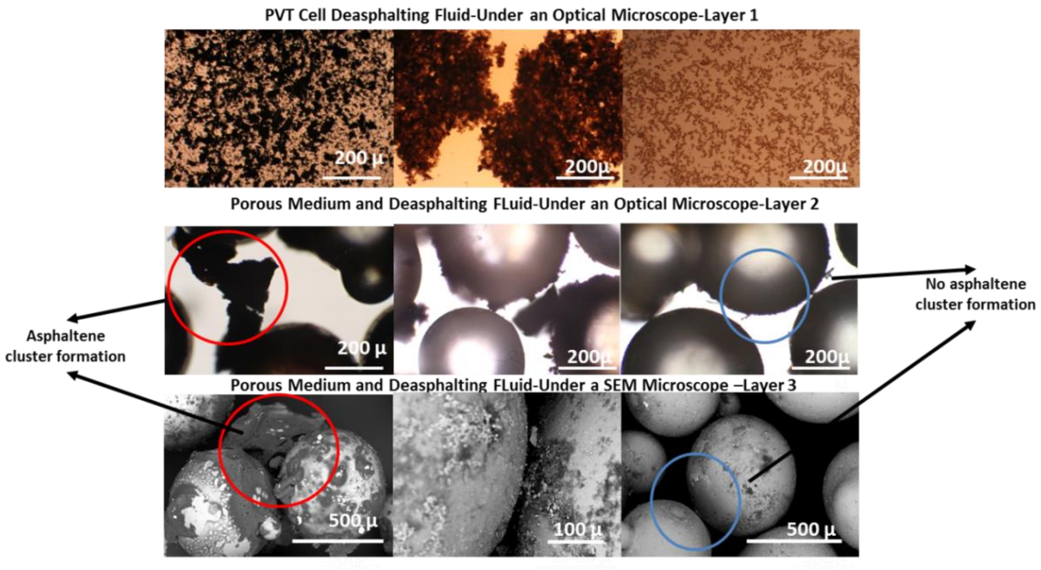


(b) Asphaltene Precipitated with n-hexane (n-C_6).



(c) Asphaltene Precipitated with n-decane (n-C_{10}).

Figure 2-6: Asphaltene precipitation mass fraction at isothermal and several pressure conditions using n-alkanes as precipitating agent at a constant volume ratio determined to be 5 cc solvent/1 g oil: a) propane, b) n-hexane, c) n-decane.



a)propane b) n-hexane c) n-decane

Figure 2-7: Asphaltene deposition on the glass beads (porous medium test) (Moreno and Babadagli [40,41]) and asphaltene precipitation in the fluid (PVT cell experiments) after deasphalting with different n-alkanes: a) C3, b) n-C6 and c) n-C10.

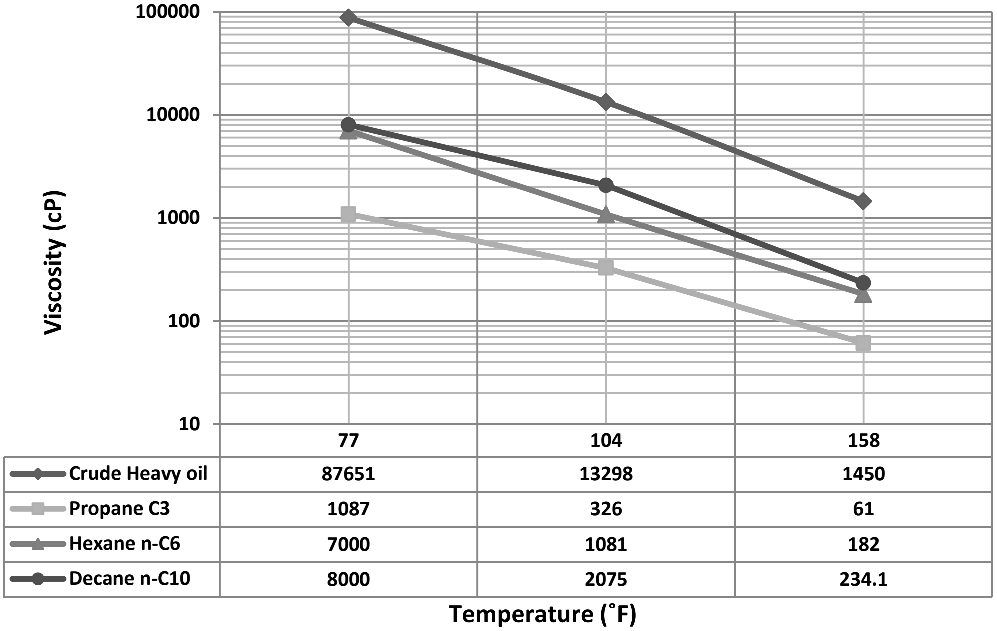
Improvement of Heavy Oil Properties

- **Viscosity Measurements**

The oil sample collected from the vacuum filtration system at the end of the process after each test was exposed to rotary-evaporation which controls the distillation point of each solvent, and left in the oven at 104 ^{o}F for 24 hours in a dark condition to avoid any oil oxidation. As shown in **Figure 2-8**, after that, the viscosities were measured using a DV-11+Pro viscometer apparatus at three different temperatures (77 ˚F, 104 ˚F and 158 ˚F). In general, the viscosity reduction was very dramatic against temperature. At 77 ˚F and atmospheric pressure, viscosity values of 1087 cp, 8076 cp, 8639 cp, were obtained for propane, n-hexane, and n-decane, respectively. Significant reduction was obtained compared to the initial viscosity of the heavy oil sample (87651 cp at 70 ˚F and atmospheric pressure). In addition, less viscosity was obtained using propane as the solvent precipitator, which means that more asphaltene precipitation took place with propane than n-hexane and n-decane. Thus, the viscosity measurement turned out to be a validation of the PVT results given in **Figures 2-5 and 2-6**.

- **Higher Temperature Simulated Distillation of Oil Sample after De-Asphalting**

Simulated distillation was performed to compare the percentage of distilled oil. **Figure 2-9** shows that the oil sample precipitated a higher percentage of residue (23%) with n-decane compared to the lower hydrocarbon number solvents (8% and 14%, with propane and n-hexane, respectively). This was because of the fact that more heavy components from the original heavy oil were precipitated when propane and n-hexane were used compared to n-decane. These results confirmed the data obtained in the asphaltene precipitation concentration experiments given in **Figure 2-5 and 2-6**.



Temperature (˚F)	77	104	158
Crude Heavy oil	87651	13298	1450
Propane C3	1087	326	61
Hexane n-C6	7000	1081	182
Decane n-C10	8000	2075	234.1

Figure 2-8: Viscosity measurements at different temperatures and atmospheric pressure after deasphalting test at 50 ˚C and 300 psig in the PVT cell apparatus using n-Alkanes (propane, n-decane and n-hexane).

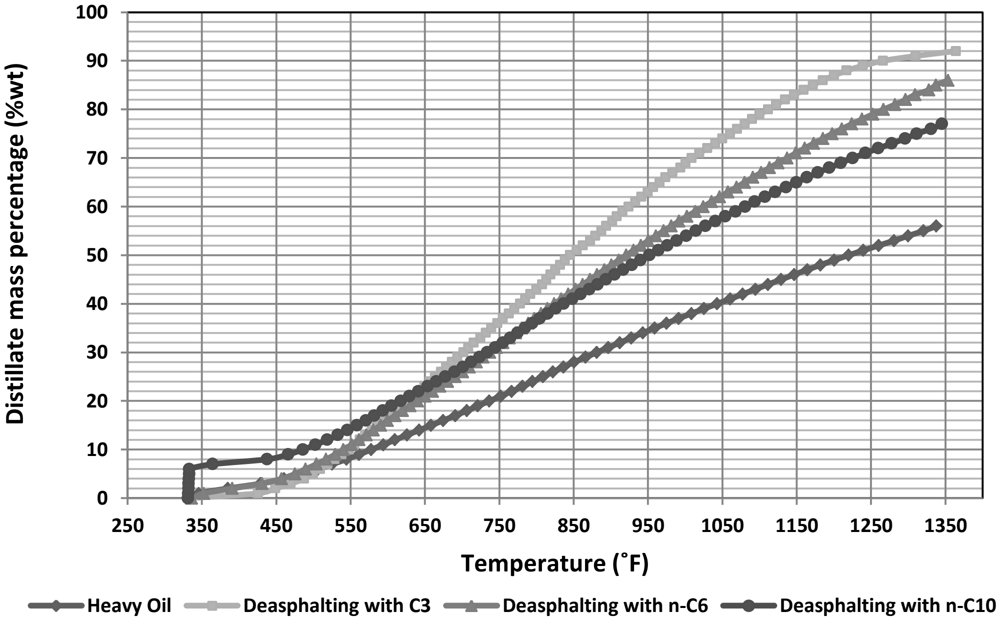


Figure 2-9: Higher temperature simulated distillation (ASTM D5307) of the deasphalting oil samples: using different n-alkanes.

- **Refractive Index**

Refractive index **(**RI) measurements have been commonly used for several reservoir engineering calculations such as PVT behavior and surface tension of reservoir fluids, wetting alterations in reservoirs, and asphaltene content [45]. Moreover, the RI can be an indicator of the solvent concentration in oil and has been used in the past to predict the onset of asphaltene precipitation in addition of solvent to heavy oil [29]. The RI is also a direct indicator of the level of the asphaltene content (at least qualitatively) to be used in comparative analyses between different oil samples for asphaltene content [46].

In this research, the crude oil RI was measured after the deasphalting of the heavy oil sample with three different n-alkanes. The final oil samples were rotary-evaporated to eliminate the n-alkane solvent existing in the sample. The RI values obtained for the Propane case showed lower RI values than n-hexane and n-decane. This means that more asphaltene precipitation was obtained with propane and thus the final oil product after solvent mixing has less asphaltene concentration (**Figure 2-10**). In other words, less asphaltene was precipitated when n-hexane and n-decane were used. As seen, the RI is a direct indicator of the asphaltene content, at least qualitatively.

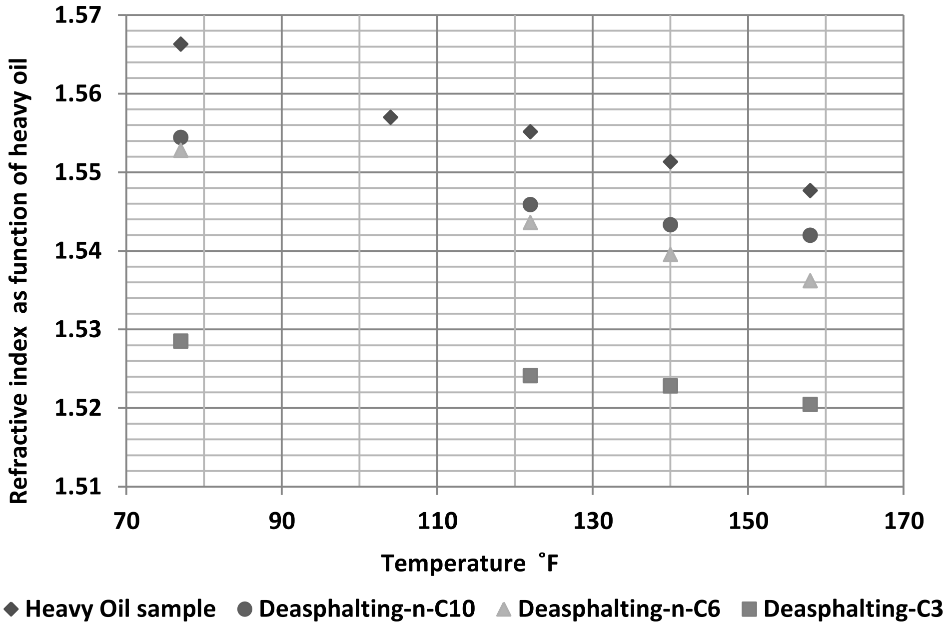


Figure 2-10: Refractive index measurements for original heavy-oil, and heavy-oil after deasphalting with different solvents.

- **Elementary Analysis (CHNS) of Asphaltene Precipitate and Final Oil Sample**

The chemistry composition was measured through the elemental analyzer (Vario Micro Cube) following the ASTM D7578. The aromaticity of the samples was determined indirectly from the atomic ratio of H/C. More aromatic samples yield a low ratio of H/C resulting in the union of several rings. The least aromatic samples are those with a high ratio H/C indicating that they have side chains in the composition [47]. The elementary analysis after the deasphalting is reported in **Table 3**. The results show that the oil quality increases when the asphaltene concentration is less in the oil. The hydrogen percentage is an example of the better quality of the final oil; increasing hydrogen percentage results in more deasphalting. The hydrogen content is higher in propane than n-hexane and n-decane. In addition, the sulfur content decreases in the final oil when the deasphalting was carried out with lower carbon number solvent.

Table 2-3: Elementary analysis of asphaltene precipitate and deasphalting oil samples (DAO)

Elementary composition	Asphaltene precipitate n-C3	Asphaltene precipitate n-C6	Asphaltene precipitate n-C10	DAO n-C3	DAO n-C6	DAO n-C10
C (wt.%)	82.35	82.30	81.55	83.9	82.25	81.3
H (wt.%)	7.38	7.577	7.575	11.670	10.57	10.31
S (wt.%)	7.478	6.944	7.026	0.027	3.468	3.946
N (wt.%)	1.01	0.96	0.85	0.47	0.61	0.77

Asphaltene Precipitation Visualization

Until now, quantitative analysis of asphaltene precipitated at different pressures and temperatures when a heavy crude oil was processed with different n-alkane type solvents. Qualitative observations are also critical as the shape and structure of the asphaltene clusters plays a critical role in pore plugging during solvent injection for enhanced oil recovery.

Furthermore, the original crude heavy oil sample obtained from a field operating in Alberta, Canada was analyzed under the optimal and scanning electron microscope before doing the de-asphalting of heavy oil using different types of solvents. The original crude heavy oil shows some air and water particles in it (white pigmentations) as presented in **Figure 2-11**. In addition, the same asphaltene sample was visualized under the scanning electron microscope (S-3000N-SEM) at different magnifications (between 100 and 250 times). As seen in **Figure 2-12**, the asphaltene particles presented several porous and amorphous structures.

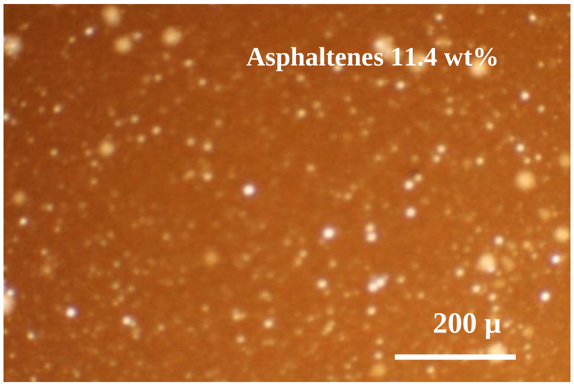


Figure 2-11: Heavy oil sample (the asphalting mass fraction at atmospheric condition was 11.4 wt%) under optical microscopy.

The asphaltene particles flocculation and agglomeration were visualized through the visual PVT cell (**Figure 2-13**) and optical microscope (microscope HBC A/C - Zeiss Axiostar Plus) with high resolution **(Figures 2-12 to 2-16).** The images show that heavier compounds from the heavy oil were broken down when propane and n-hexane were used. As a result, the asphaltene flocculation and agglomeration are considerably higher than those with n-decane **(Figures 2-14 to 2-16)**. Therefore, the asphaltene particles tend to aggregate and create larger agglomerates when propane and n-hexane were used as solvent (**Figures 2-15 to 2-16**). For the n-hexane case at 30psig and 230˚F (close to the dew point), the asphaltene agglomeration is more intensive as well as the size (**Figures 2-15**) due to the temperature and asphaltene concentration increment at this operating conditions. This size and type of clusters are critically important in the pore plugging process and they are obtained at higher temperatures.

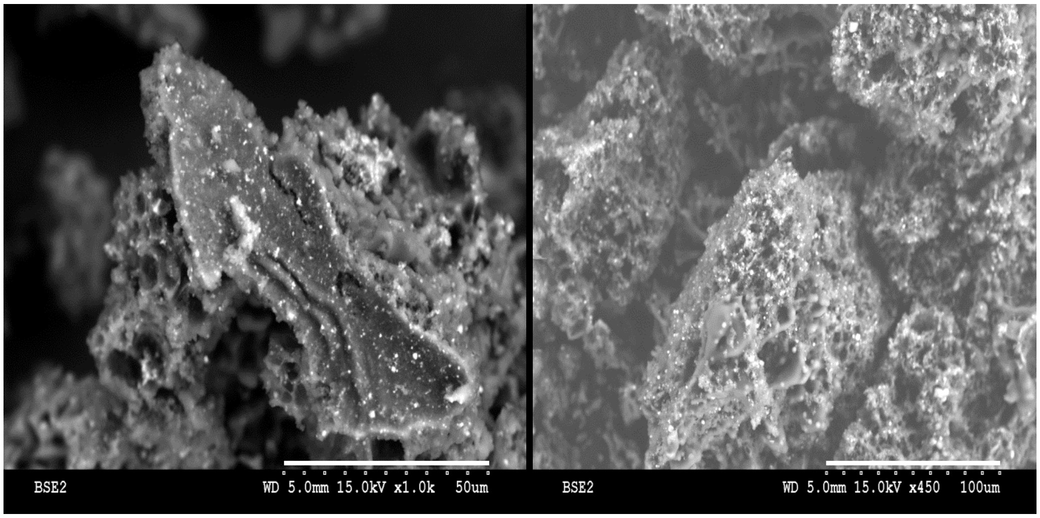
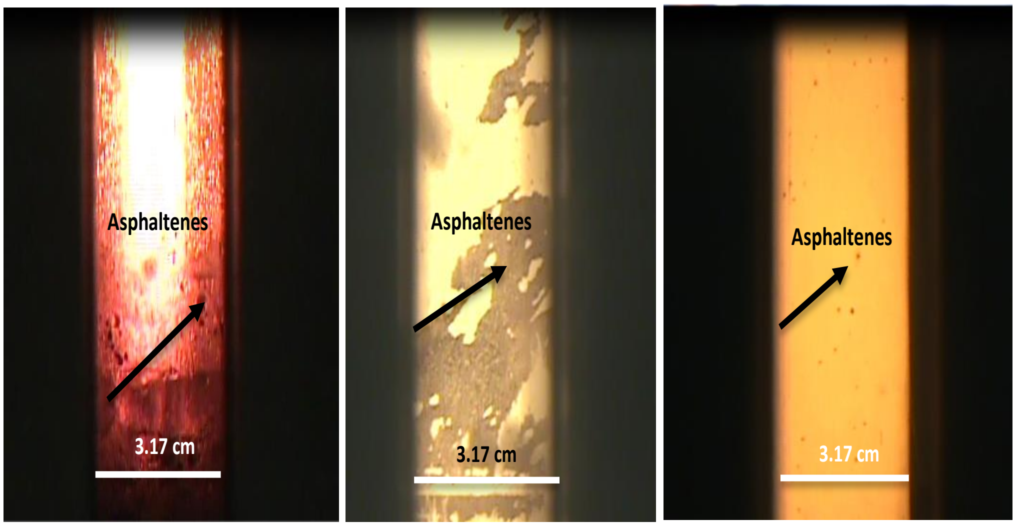


Figure 2-12: Asphaltene sample precipitated with n-heptane at room conditions (visualization under the S-3000N-SEM).

Seifried et al. [48] showed a similar asphaltene particles aggregation structure as the ones provided in **Figures 2-15 to 2-16** for the operation conditions of 100 psig and 158˚F using n-decane, and 30 psig and 230 ˚F using n-hexane (which is close to its dew point). In addition, Akbarzadeh et al. [17] suggested different type of agglomeration sizes and structure of asphaltene particle sizes. They showed that asphaltenes start to form nanoagregates until it has cluster formation. In our study, the asphaltene sample did not show significant nanoagragate type structre forming and formed big particle aggregation due to our operating conditions. The asphaltene floculation and agglomeration were affected by the heavy oil type, nature of n-alkane solvent, and operating conditions. These factors caused the attraction of polar molecules generating larger aggregation (**Figures 2-14 to 2-16**).

The flocculation and agglomeration of the asphaltenes were evaluated under different operating conditions and using several types of solvents. The images of the asphaltene occurrences are given in **Figures 2-14 to 2-16** and it can be inferred from these pictures that when the pressure is between 200 psig and 300 psig and the temperature goes from 1158 ˚F to 176 ˚F, one can observe the most severe asphaltene particles agglomeration and size increase. However, less agglomeration and smaller asphaltene size were created between 30 psig and 100 psig and from 140 ˚F to 158 ˚F (**Figures 2-14 to 2-16**). In other words, when the temperature and pressure increases and the carbon number of the n-alkanes decreases, the asphaltene agglomeration and particle size increase. Similar effects of temperature and pressures were observed by Nielsen, et al. [16]. They studied the effect of the temperature, pressure, and n-pentane (n-C5) on particle size distribution using different type of oil composition. They found that when temperature and pressure increase, the asphaltene particle size also increases due to the softening and adhesion of asphaltene particles. In addition, Evdokimov and Losev [49] measured electrical conductivity and dielectrical properties of solid asphaltenes. They concluded that conductivity increased at higher temperatures. They also found that low-temperature appears to be controlled by interactions between polar side chains of asphaltene particles, while in the high-temperature, interaction involving flat polyaromatic structures in asphaltene became important. Subsequently, higher operational conditions promoted the cluster formation.



a) Propane b) n-hexane c) n-decane

Figure 2-13: Asphaltene concentration visualization in the PVT cell for different n-alkanes as precipitating agent at a constant volume ratio determined to be 5 cc solvent/1 g oil: a) C3 b) n-C6, c) n-C10.

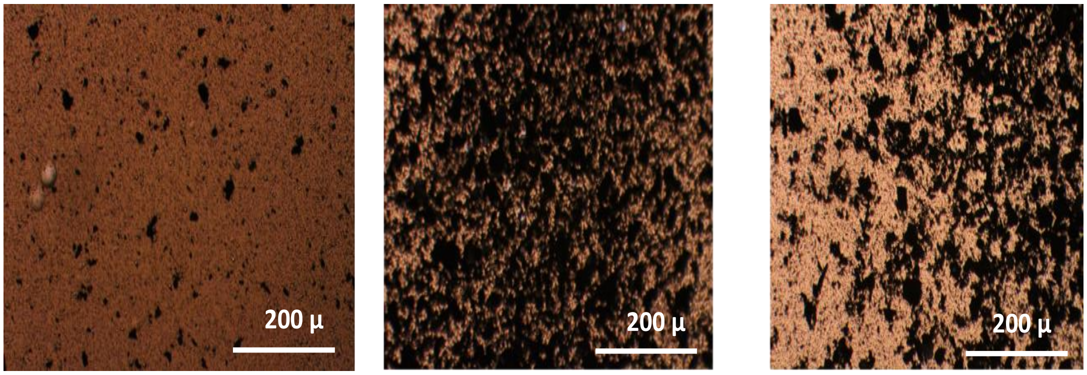


Figure 2-14: Microscope visualization of asphaltene behaviour after PVT cell tests using propane at 122 ˚F and 500 psig and at a constant volume ratio determined to be 5 cc solvent/1 g oil, the asphalting mass fraction at this condition was 12.1630 wt %.

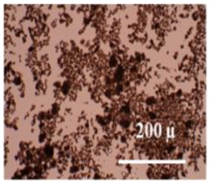
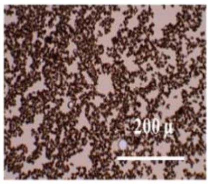
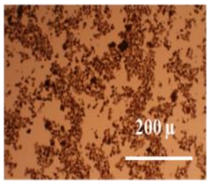
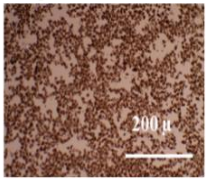
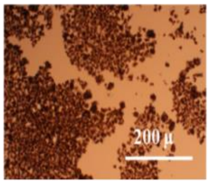
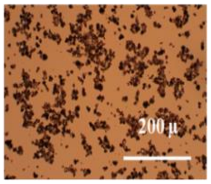
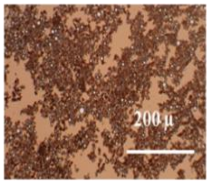
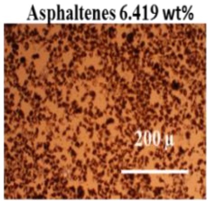
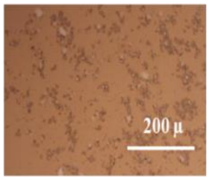
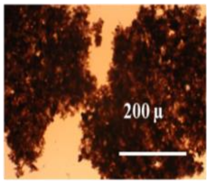
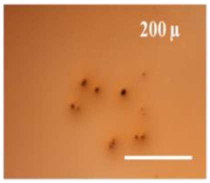
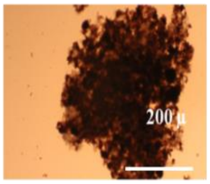
Temperature (˚F)	Pressure (psig)	n-hexane	Pressure (psig)	n-hexane	Pressure (psig)	n-hexane
122	**30**	Asphaltenes 6.186 wt% 	**200**	Asphaltenes 7.129 wt% 	**300**	Asphaltenes 7.604 wt% 
158		Asphaltenes 6.118 wt% 		Asphaltenes 7.137 wt% 		Asphaltenes 7.291 wt% 
176		Asphaltenes 5.882 wt% 		Asphaltenes 6.419 wt% 		Asphaltenes 6.358 wt% 
230	**30**	Asphaltenes 6.330 wt% 				

Figure 2-15: Microscope visualization of asphaltene behaviour after PVT cell tests using n-hexane at several operating conditions and at a constant volume ratio determined to be 5 cc solvent/1 g oil.

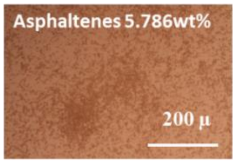
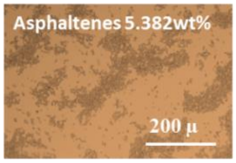
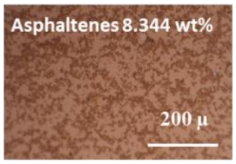
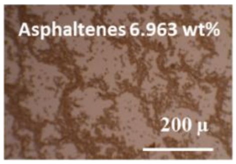
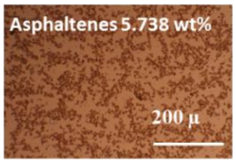
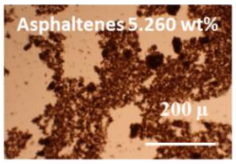
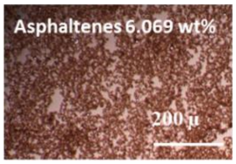
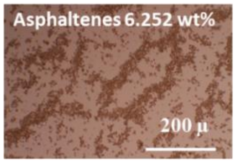
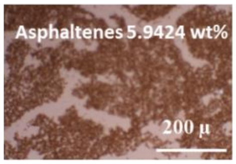
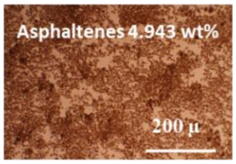
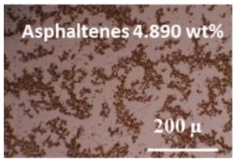
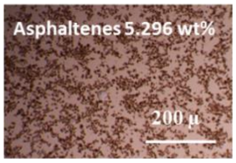
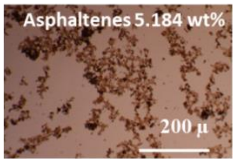
Temperature (˚F)	Pressure (psig)	n-decane	Pressure (psig)	n-decane
122	**30**		**100**	
140				
158				
176				
122	**200**		**300**	
140				
158				
176				

Figure 2-16: Microscope visualization of asphaltene behavior after PVT cell tests using n-decane at several operating conditions and at a constant volume ratio determined to be 5 cc solvent/1 g oil.

Conclusions and Remarks

This paper studied asphaltene precipitation behaviour at different operating conditions qualitatively and quantitatively when a heavy-oil was mixed with three types of n-alkanes (propane, n-hexane, and n-decane). Typical pressure (30-300 psig) and temperature (122-230 ^{o}F) ranges that could be encountered during hot solvent injection in shallow heavy-oil deposits like those found in Canada were applied. The main conclusions reached out of this research are as follows:

1. Experimental observations showed that asphaltene dispersion and solubility increases when temperature increases from 122 ˚F to 230 ˚C at isobaric conditions when a heavy-oil is mixed with three types of solvents (propane, n-hexane, and n-decane).
    a. **In the case of heavy oil diluted with propane**, higher asphaltene concentration was found at the lower limit temperature (122 ˚F) at isobaric conditions (300-500 psig). After this temperature, asphaltene started to disperse in the oil and, consequently, the solubility in the oil increased with temperature and stabilized around the upper point temperature applied in the tests (158 ˚F).
    b. **For the n-hexane case**, asphaltene concentration was higher at the lower limit operational temperature (122 ˚F), like the propane case. However, the change in the solubility of asphaltene with temperature was not as systematic as with propane. At around 175 ^{o}C, a sudden increase in the solubility was observed for all pressure values (between (30 and 300 psig). The solubility change with temperature for the lowest pressure case (30 psig) was almost stable. However, 230 ˚F a slight increment in asphaltene mass fraction compared to 175 °F was observed. This is likely due to the lower asphaltene solubility near the boiling point (or dew point).
    c. **For the n-decane case**, maximum asphaltene concentration was observed at the middle operational point (140 ˚F). This peak value for n-decane may be explained by the effect of low crude oil stability at this particular temperature (140 ˚F). When the temperature continued to increase above 140 ˚F, the asphaltene concentration started to decrease due to the asphaltene dispersion in the oil as well as propane and n-hexane cases.

2. Pressure was also observed to be a critical parameter on asphaltene precipitation at different temperatures.
    a. **Propane** showed more pressure dependency on asphaltene precipitation concentration than n-hexane and n-decane. Propane is more compressible and the density change with pressure is more critical than n-hexane and n-decane. When pressure increased from the lower limit operational pressure (300 psig) to

the upper limit operational pressure (500 psig), the asphaltene solubility in the oil increased due to less asphaltene precipitation.

   b. **For the n-hexane case**, asphaltene concentration increased when pressure was increased from 30 psig to 200 psig. However, after the pressure was increased from 200 psig to 300 psig, the asphaltene dispersion started to occur. Then, asphaltene concentration was almost constant or started to decline. The behavior of asphaltene precipitation with pressure increases may be attributed to changing crude oil composition due to different thermodynamic equilibrium compared to the other cases.

   c. **For the n-decane case**, asphaltene dispersion was present when the pressure started to increase from 30 psig to 200 psig. After the pressure increased to 300 psig, asphaltene precipitation became constant as similar to the n-hexane case.

3. The simulated distillation showed that the oil sample precipitated with n-decane has a higher percentage of residue (23%) than the oil sample precipitated with propane (8%) and n-hexane (14%). This means that more heavy molecules from the original heavy oil were precipitated with propane and n-hexane than n-decane as solvent. The simulated distillate confirmed that a better quality crude oil was obtained after the deasphalting with all solvents (propane, n-hexane, and n-decane).

4. The refractive index (RI) values obtained for the propane case showed lower RI values than n-decane and n-hexane. This means that more asphaltene precipitation was obtained with propane and thus the final crude product had less asphaltene concentration after solvent mixing. In other words, less asphaltene was precipitated when n-hexane and n-decane were used. As seen, the RI is a direct indicator of the asphaltene content, at least qualitatively.

5. The visualization in the optical microscope showed that more heavy components from heavy-oil were broken down with propane and n-hexane. Therefore, the asphaltene concentration and agglomeration are considerably higher than those with n-decane as solvent. In addition, temperature and pressure have a very critical effect on the asphaltene molecular agglomeration and particle size. When temperature and pressure increased and the carbon number of the n-alkanes decreased, the asphaltene agglomeration and particle size increased. This phenomenon can be explained by the attractive forces between asphaltene molecules that are caused by dipole-dipole interaction. In addition, the polyaromatic structures present in the asphaltene became important when temperature and pressure were changed.

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CHAPTER 3: OPTIMAL APPLICATION CONDITIONS OF SOLVENT INJECTION INTO OILSANDS TO MINIMIZE THE EFFECT OF ASPHALTENE DEPOSITION: AN EXPERIMENTAL INVESTIGATION

This paper is a modified and improved version of SPE 165531, which was presented at the SPE held in Calgary, Alberta, Canada, 8–10 June 2013. A version of this chapter has been submitted to Journal of Petroleum Science and Engineering for publication.

Background

Solvent injection into heavy-oil reservoirs is quite complex on account of the asphaltene destabilization that occurs due to the changes in temperature, pressure, and solvent type dissolved in oil. As a result of this destabilization, the asphaltene flocculates agglomerates and eventually plugs the pores in the reservoir due to the formation of asphaltene clusters. In solvent applications, light molecular weight hydrocarbon solvents are preferred because of their high diffusion coefficient; however, as the carbon number of n-alkane solvents decreases, asphaltene precipitation increases. Therefore, the selection of the solvent and application condition is highly critical in cold and thermally-aided solvent applications.

In this research, low carbon number n-alkane (propane, n-hexane and n-decane) and a distillate hydrocarbon (obtained from a heavy oil upgrading facility) injection into sandpack systems saturated with heavy-oil (87651 cp and 20918cp at 25˚C) was evaluated at different pressure conditions that are applicable to typical Canadian oilsands reservoirs (698 kPa-2068 kPa) and temperatures (25-120˚C). First, the asphaltene behavior of different solvents at different pressures and temperatures were studied through deasphalting work in a pressure-volume-temperature (PVT) cell in a previous work by Moreno and Babadagli [13]. Based on the quantitative (amount of asphaltene precipitated) and qualitative (microscopic images of asphaltene clusters) observations, the characteristics of asphaltene were classified in terms of their shape, size, and amount for different oil/solvent types, pressure, and temperature.

Continually, the same n-alkane and the distillate hydrocarbon solvents and heavy-oil were used in gravity drainage recovery experiments on unconsolidated sands. 3-D (cylindrical) sandpack experiments were carried out at the same temperature and pressure conditions used for the PVT experiments. The operational conditions, oil composition, and solvent type showed significant effects on oil recovery rate. Asphaltene deposition and residual oil saturation in the sandpack and the amount of asphaltene in the produced oil were measured, and the standard SARA analysis was applied to determine the optimal operating conditions yielding the highest recoveries with minimal pore plugging. Moreover, the pore plugging process was analyzed through a visual scanning electron microscope and optical microscope in order to find the different organic deposition formation and agglomeration. Oil production was evaluated using microscope visualization, viscosity reduction and refractive index values, respectively. Eventually, optimal application conditions for solvent and thermally-aided solvent injection were listed for a wide range of heavy-oil and solvent types.

Introduction

Injecting light hydrocarbon solvent into oilsands has established an opportunity to recover a higher amount of heavy oil and bitumen with better quality oil than conventional and thermal recovery processes. The full idea about solvent injection into the reservoir was proposed by Butler and Morkys [3,4]. They introduced this new process as a vapor extraction process (VAPEX), which, in general, consists in the deasphalting of high molecules of heavy-oil [17]. The deasphalting phenomenon of heavy-oil showed tremendous viscosity and density reduction, and improvement in heavy oil quality due to the reduction of metals and sulphur content [1,5,6,15,16,18].

In the VAPEX process, ssolvent dilutes the oil and then distillate hydrocarbon drains down to the production well by gravity. Das and Butler [5] suggested that the use of vaporized solvent yields a higher driving force in gravity drainage due to a higher density change between heavy oil bitumen and solvent vapor, and also guarantees that the remaining amount of solvent in the extracted reservoir will be less than with liquid solvents.

Fundamentally, heavy oil and bitumen contain a significant amount of asphaltenes under solubility. This asphaltene solubility is altered from oil when solvent is injected at certain pressure, temperature, type and concentration of the paraffinic solvent used. Then the asphaltenes start to flocculate and bond to each other until they create clusters of asphaltenes due to the polymerization of polynuclear aromatics that are concentrated in asphaltenes [18,13,23]. Asphaltenes are highly aromatic, high in molecular weight, and high in metals, sulphur, and nitrogen [18]. Several studies about the deasphalting process using a PVT cell have shown that when temperature and pressure increase, and carbon number of solvent increases, the asphaltene concentration decreases.

Asphaltenic material deposition in oil reservoirs is one of the main issues involved in solvent injection process. It may take place on the rock surface and can eventually cause pore plugging, permeability reduction, and wettability alteration. Redford and McKay [20] carried out several experiments co-injecting steam and different hydrocarbons, such as ethane, propane, butane, pentane, natural gasoline, synthetic GCOS, and naphtha into Athabasca bitumen. They concluded that, contrary to mostly belief, solvent injection into the reservoir such as propane and pentane with steam in highly asphaltenic crude such as Alberta bitumen does not lead to appreciable permeability reduction. Das and Butler [5] studied the effect of asphaltene deposition on the VAPEX process using a Hele-Shaw cell and three different crude oil samples obtained from the Peace River, Cold Lake, and Lloydminster regions. Propane was injected at a range of 20 ˚C to 35˚C and 862 kPa to 1172 kPa, which is close to the vapor pressure. They observed that when the deasphalting takes place in the reservoir it does not affect the production rate. Moreover, the possible asphaltenic material deposition does not plug the porous medium; therefore, the deasphalting process does not stop oil flowing out of the reservoir. Das and Butler [5] concluded that as the diluted and deasphalted oil flows down, the interface moves away and asphaltenes left behind change the rock wettability. Wettability alteration due to asphaltene deposition on the surface, however, does not affect oil production as the oil has been fully swept from this region.

Later, Butler and Jiang [2] carried out experiments using butane or propane mixtures with a non-condensible gas (methane) at different temperatures and pressures (21 ˚C – 27 ˚C and 206 kPa – 2068 kPa, respectively). The solvent injection rate varied in the range of 0.17 ml/min to 0.7 ml/min. They observed more oil production at higher pressure and temperature conditions and better viscosity reduction at higher solvent/oil rate. In addition, they noticed a higher recovery factor with propane compared to butane or mixture of both.

Papadimitriou et al. [14] observed remarkable asphaltene deposition in Berea sandstone cores when iso-butane was used as solvent. They pointed two critical zones of the asphaltenic material deposition close to the injection and production wells [12,14]. Furthermore, after running several experiments using propane and butane at room temperature and different pressures between 750 kPa and 850 Kpa, Haghighat and Maini [10] suggested that in-situ upgrading of oil via asphaltene precipitation in the VAPEX process is not an effective technology due to the permeability reduction and low rate of oil production. On the other hand, previous experiences showed that using light aromatics as solvent can be an option to improve oil production due to better dilution of oil, higher viscosity reduction and low asphaltene precipitation, and deposition. This means that less or negligible permeability reduction may take place when light aromatic solvents (naphtha or distillate hydrocarbon) are injected [7,8].

As seen, solvent injection definitely increases oil recovery due to the *underground in-situ* upgrading. Several studies demonstrated that asphaltene precipitation increases or decreases according to the amount of solvent/oil rate and operating conditions [1,13,18]. Then, the permeability reduction due to the possible asphaltene deposition can be prevented or minimized using the proper operating conditions and solvent type and concentration in the reservoir.

This study focuses on recovery by solvent injection at different temperatures and pressures. Primary focus is asphaltene precipitation and deposition during this process and their effects on the recovery performance. The two oil samples with the viscosities of 87651 cP and 20918 cP and four different type of solvents as injectant (three pure solvents, i.e., propane, n-hexane and n-decane and the distillate hydrocarbon with a composition of C_4-C_{15}). Warm solvent injection experiments were performed in a sandpack system operated at different temperatures (between 25

˚C to 120 ˚C) and pressures (689 kPa to 2068 kPa). The solvent was injected at the rate of 0.2 ml/min. At the end of each experiment, the sand-pack mixture was analyzed under optical and scanning electron microscope (SEM-3000) to visualize the organic deposition on the grain surface for different type of solvents and operational conditions. Asphaltene deposition and residual oil saturation were calculated to determine the optimal conditions. The study was also supported by quantitative and qualitative (visual) analyses such as refractive-index analyzer, viscosity measurements of produced oil, and carbon number distribution of hydrocarbon (Sim-distilation).

Experimental Set-Up and Procedures

Materials

Heavy oil sample. The original two crude heavy oil samples were obtained from two different fields operating in Alberta, Canada. The viscosity and density values were measured at three different temperatures between 25 ˚C to 70 ˚C at atmospheric pressure (**Table 3-1**). Correspondingly, the standard test method for determination of asphaltenes (n-heptane insoluble) in crude petroleum and petroleum product (IP-143) was followed to determine the asphaltene content from the two oil samples were measured to be 11.5wt% (oil sample A) and 9.6wt% (oil sample B) (*n*-heptane 99.4wt% pure). In addition, the carbon number distribution from both heavy oil samples was determined using the boiling point distribution of crude oil and vacuum residues (ASTM D7169) **(Figure 3-1).** Other important properties of the heavy oil samples including elementary analysis (CHNS), asphaltene precipitation (*n*-heptane 99.4wt% pure), API gravity, and SARA analysis are presented in **Table 3-1**.

Solvent type. The sand-pack experiments were performed to measure recovery (and deasphalting) of heavy oil for four different solvents (three n-alkanes and a distillate hydrocarbon). The purities of n-alkanes (C_3H_8, C_6H_{14} and $C_{10}H_{22}$) used as precipitants were 99.5wt%, 99.9wt% and 99.6wt%, respectively. The characteristics of the distillate hydrocarbon obtained from the heavy oil upgrader are presented in Appendix 3-A.

Table 3-1: Heavy Oil Properties from Two Different Oil Samples A and B

Heavy Oil properties-ASTM D2007, IP 143 and ASTM D2549		
	Oil sample A	**Oil sample B**
Saturates,wt%	17.24	19.45
Aromatics,wt%	38.60	45.60
Resin,wt%	32.66	25.34
Asphaltene,wt%	11.50	9.60
Heavy Oil Elementary Analysis-ASTM D7578		
Carbon,wt%	84.45	81.92
Hydrogen,wt%	9.731	10.31
Sulfur,wt%	3.715	3.536
Nitrogen,wt%	0.553	0.6
Asphaltene Elementary Analysis-ASTM D7578		
Carbon,wt%	82.06	79.6
Hydrogen,wt%	7.957	7.095
Sulfur,wt%	7.431	8.22
Nitrogen,wt%	0.946	1.47
API Gravity at 15.5˚C		
˚API	8.67	10.28
Density [g/cm^3]		
25˚C	1.003	0.9919
40 ˚C	0.9959	0.9767
70˚C	0.9774	0.9503
Viscosity [cP]		
25˚C	87651	20918
40˚C	13298	3571
70˚C	1450	421.3

	Oil sample A	Oil sample B
Components	**Compositions (wt%)**	
C_{10}	0	0.599
C_{11}	0.83	0.732
C_{20}	13.48	20.014
C_{25}	7.21	10.495
C_{30}	6.48	9.271
C_{35}	5.03	7.038
C_{40}	4.21	5.684
C_{50}	5.76	8.062
C_{60}	4.18	5.693
C_{70}	2.87	3.887
C_{80}	1.82	2.596
C_{90}	1.01	1.477
C_{120}	7.22	0.686
C_{120+}	39.9	23.766
Total mass, wt%	100	100

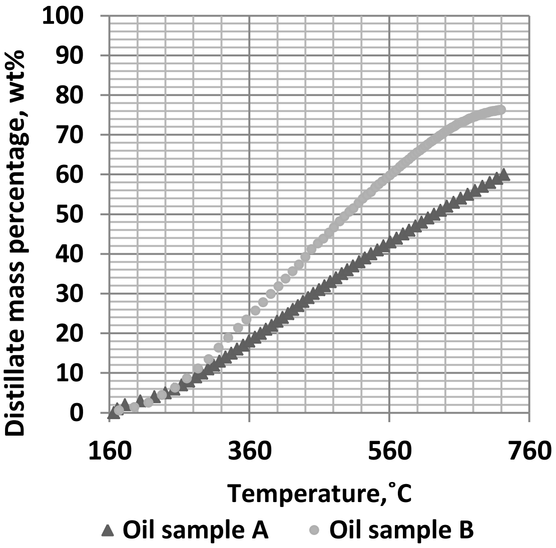

Figure 3-1: Carbon number distribution of the heavy oil samples A and B determined using the boiling point distribution of crude oil and vacuum residues (ASTM D7169).

Preliminary Experimental Procedure

The heavy oil samples were deasphalted at several solvent/heavy oil concentrations in order to determine the volume ratio to apply a during the sandpack experiments. The deasphalting experiments were done at 50 ˚C and atmospheric pressure following the standard test method for determination of asphaltenes in crude petroleum and petroleum product (IP-143) (“asphaltene precipitation”). As a result, the solvent/heavy oil volume ratio to be used in each sandpack experiment was found to be around [2 solvent cm³/1 heavy oil cm³] because the asphaltene precipitation is lower. Asphaltenic flocculation and agglomeration is expected to be lower in the sandpack (**Figure 3-2**), however, the solvent/heavy oil ratios can vary with the operational time. The phase behavior of propane at ambient conditions could not be carried out using the glass deasphalting system designed for liquid solvents. Then, the same volume rate calculated for the other types of solvents were used for the propane case.

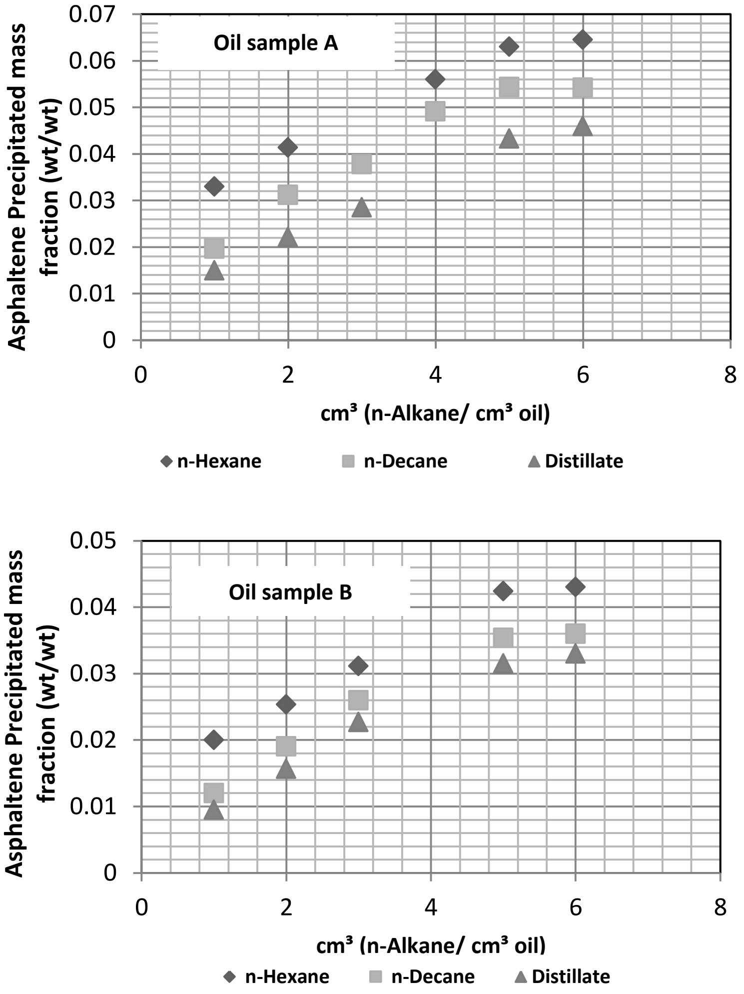

Figure 3-2: Asphaltene precipitation at different volume ratios using n- alkanes (C_6H_{14} and $C_{10}H_{22}$) and distillate hydrocarbon (heavy oil upgrader) at 50 ˚C and at the atmospheric pressure.

Physical Model Type

To propose optimal application conditions minimizing the effect of asphaltene deposition and maximizing the recovery factor, a cylindrical sandpack model with 13.5 cm length and 5 cm diameter, having one injector and one production end, was prepared. The injection point was at the top and the production was at the bottom of the sandpack. The production end was connected to a high pressure and temperature asphaltene precipitation filter and microscope valve. The asphaltene precipitation filter was connected to the oil recovery container (**Figure 3-3**). This sandpack design was a semi-dynamic system. The injection and production pressures were controlled through a pressure transducer. The pressure difference between injector and producer was monitored during the operation to determine if asphaltenic material deposition plugged in the porous medium. In addition, beyond the production point, there exists a back pressure valve, high pressure and temperature asphaltene filter, oil container, and vacuum pump system.

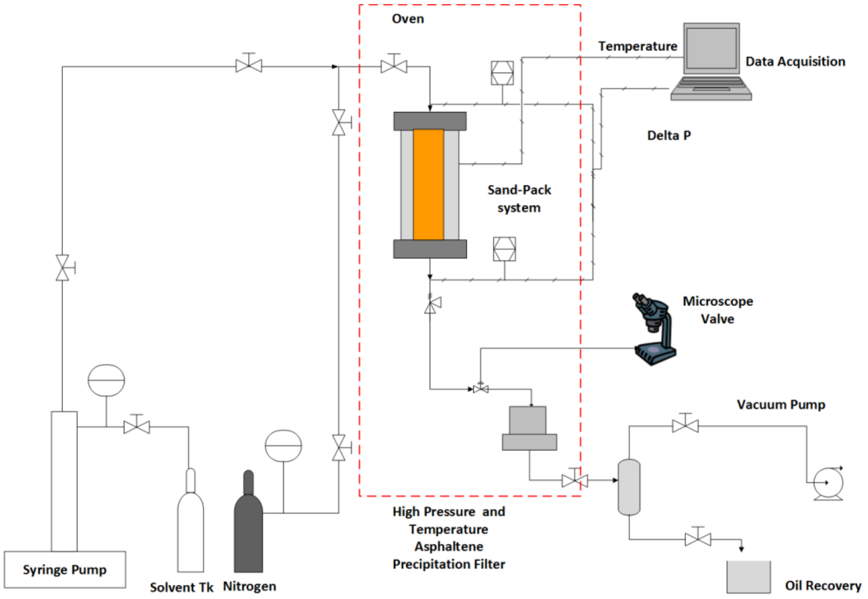

Figure 3-3: Flow diagram of the gravity drainage recovery experiments on unconsolidated sands.

Experimental Methodology

Sandpack System Design to Evaluate the Asphaltene Concentration Effect on the Recovery Factor

The original crude heavy-oil samples were obtained from two different fields operating in Alberta, Canada. Three different n-alkanes and a distillate hydrocarbon were used in the experiments. The type of sandpack particle size was around 0.37 mm to 0.55 mm (370 µm to 550 µm) and porosity was around 38% to 40%. The sandpack model preparation started with mixing 160 ml of glass beads and 38.5 grams of heavy oil. To homogenize the porous medium model the heavy-oil was heated at 40 °C prior to mixing. After that, the sandpack model was placed into the cylindrical core holder. When the operating conditions stabilized, the light solvent injection started and operated at 0.2 ml/min (solvent/ heavy oil "volumetric rate") between 4 to 8 hours. Next, the sandpack was analyzed to determine the quantity and quality of the residual solid (asphaltenes) and the residual oil (maltenes) saturation**.** The quantitative laboratory analysis of asphaltenic material deposition was performed using IP-143, ASTM 2007D and ASTM D2549 standards, and the qualitative analysis was done through Hele-Shaw visualization under the optical and SEM microscopes. In addition, a high pressure and temperature asphaltene precipitation filter and liquid collection system were utilized at vacuum pressure to obtain a better filtration and liquid collection results **(Figure 3-3 to 3-4).** Finally, the sandpack and the system lines were cleaned using toluene and the possible residual maltenes and asphaltenes were collected to be included in the total mass balance.

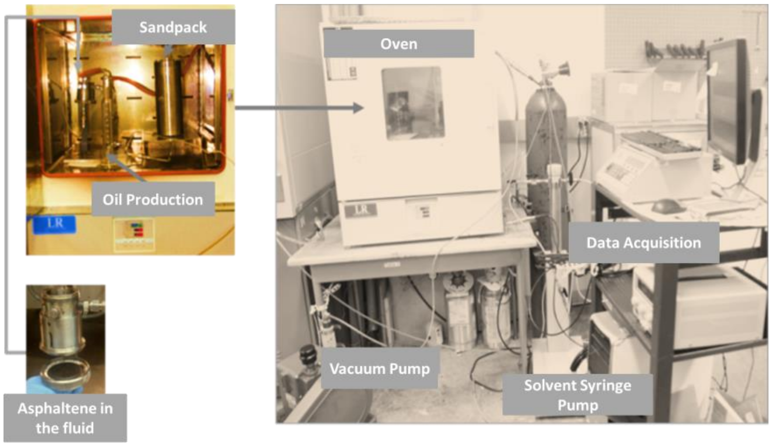

Figure 3-4: Unconsolidated sandpack system setup - Physical model.

Results and Discussion

Oil recovery factor, asphaltene deposition, and residual oil saturation were analyzed for different operating conditions, solvent types, and two different heavy oil types A and B. In all experiments the injection rate of solvent was kept constant at 0.2 ml/min. In agreement with our previous visual PVT cell experiments [13], the results from the unconsolidated sandpacks showed that when the carbon number of the solvent, temperature and pressure increased, the asphaltene precipitation decreased. As a result, asphaltene flocculation and agglomeration (and eventually deposition) are completely dependent on oil composition, solvent type and operating conditions such as temperature, pressure and solvent flow rate.

Effect of Pressure and Temperature on Recovery Factor

The thermodynamic effects on the solvent-based process were analyzed for different types of solvents (propane, n-hexane, n-decane and a distillate hydrocarbon) at different operational conditions. Results showed that heavy-oil recovery from oil samples A and B increase for liquid n-alkanes (C_{10} and C_6) and the distillate hydrocarbon, when temperature and pressure increase (**Figure 3-5 to 3-6**). However, propane showed that when temperature increases further, the solvent phase changes to vapor phase (**Figures 3-6 to 3-7**); consequently, the recovery factor starts to decline as also confirmed by Pathak et al. [15,16]. The phase envelope for each type of solvent with oil recovery factors is shown in **Figure 3-7**. The phase behavior showed a critical effect on final oil recovery especially with the compressible-type solvent (propane and a distillate hydrocarbon).

For the **propane** case, when temperature goes from 25 ˚C to 120 ˚C at 289 kPa, oil production decline from 75.15% to 65.19% and from 82.16% to 61.27% for the oil samples A and B, respectively. The same behavior was also noticed at 2068 kPa. However, higher pressure operations resulted in around 5% increment in oil production compared to lower pressure operations. All these events can be explained by phase behavior (i.e., density and asphaltene solubility) changes. Propane is very sensitive to thermodynamic equilibrium variations when temperature goes from 25 C˚ to 120 ˚C. It goes from the liquid phase (being very close to the dew point) to the vapor phase (**Figure 3-7**), which affects the efficiency of the *dilution* of *heavy* oil. Consequently, the oil recovery factor decreases.

On the other hand, solvents like n-hexane, n-decane, and the distillate hydrocarbon show a strongly positive effect on oil production when temperature increases from 25 ˚C to 120 ˚C. Pressure effect on oil recovery was not as remarkable as temperature (**Figure 3-6**). Oil samples A and B with **n-hexane** yielded oil recovery factors in the range of 81.86% to 89.26%, and 85.3% to 89.56%, at 689 kPa, respectively. The pressure change to 2068kPa shows only 2% increase in oil recovery compared to the experiment at 689kPa for both heavy oil samples.

In addition, heavy oil samples A and B with **n-decane** gave oil recoveries in the range of 84.82% to 92.76% and 85.79% to 90.56% for the oil samples A and B at 689 kPa, respectively. When the pressure was increased to 2068 kPa, the oil production improved only 2%. Moreover, n-hexane and n-decane are incompressible fluids (no density changes), which can explain why temperature increment is more remarkable than pressure effect. Also, in **Figure 3-7**, the phase envelopes show that n-decane and n-hexane do not show any phase change from gas to liquid at the operational conditions applied in the experiments.

Furthermore, the **distillate hydrocarbon** (a mixture of n-alkanes such as butane, n-pentane, n-heptane and mixture of aromatics such as toluene, xylene and benzene) showed oil recoveries of 91.01% to 94.92% and 93.69% to 94.41% for samples A and B at 689 kPa, respectively. The maximum recovery factor was found to be 96% at 50 ˚C for both oil samples. The diluent oil yielded only 1% difference in oil recovery when pressure was increased to 2068 kPa from 689 kPa. This oil recovery effect is due to the fact that lower asphaltene flocculation and agglomerations is present using solvent with aromatics mixture. Toluene, xylene and benzene usually dilute the oil better by increasing the solubility of asphaltene particles in the heavy oil. In other words, aromatics are beneficial in reducing the asphaltene flocculation and agglomeration. As a result, less alteration on the grain surface would occur when a distillate hydrocarbon from C_4 to C_{15} is used.

Effect of Heavy Oil Compositions on Recovery Factor

Two different oil samples with significantly different boiling point distributions (ASTM D7169) and other properties are presented in **Figure 3-1** and **Table 3-1**. Oil sample A, which has a higher viscosity (8761 cP at 25 ˚C) and maximum distillation percent of 60% at 730 ˚C, was tested at two different operational times of 4 and 8 hours. It was observed that the 4-hour test with propane and n-decane yielded significantly lower oil recovery (**Figure 3-5**) compared to the 8-hour test (**Figure 3-6**). Oil recovery increment at 8 hours was ~30% and ~15% higher for the propane and n-decane cases, respectively. This implies that dilution process and molecular diffusion takes more than 4 hours for this particular oil (sample A, which has a composition of C_{11} (0.83wt %) to C_{120+} (39.9wt %) and high asphaltene content -11.5wt %).

Oil sample B showed a quite similar oil recovery factor with a shorter period of time (6 hours test). This effect can be explained by significant lower viscosity and carbon number distribution of this oil than those of oil sample A. Oil sample B had a viscosity and asphaltene content measured to be 20918 cP at 25 ˚C and 9.6wt%, respectively. The boiling point distribution was 76wt% and the carbon number distribution was C_{10} (0.599wt %) to C_{120+} (23.8wt %) (**Figure 3-1** - Sample B). Both oils exhibited a similar response and trends in terms of final oil recovery for different solvent types, pressures, and temperatures. However, asphaltene flocculation and agglomeration, asphaltene deposition and residual oil saturation were different due to significant differences in high end compounds (**Table 3-1**).

SARA analysis results from the heavy oil samples explain the above mentioned differences. For example, oil sample A shows higher resin (32.66wt %) and asphaltene (11.5wt %) percentage compared to oil sample B, which has 7wt % lower resin and 2 wt% lower asphaltene than oil sample A (**Table 3-1**). This resulted in lower asphaltene deposition, flocculation and agglomeration, and residual oil saturation with oil sample B compared to oil sample A **(Figures 3-8 to 3-11)**. Also, the operational time was shorter for oil sample B but a very similar oil production rate was observed for both oils (**Figures 3-5 to 3-7**). In conclusion, oil composition is quite important in selecting the operational parameters, especially solvent injection period.

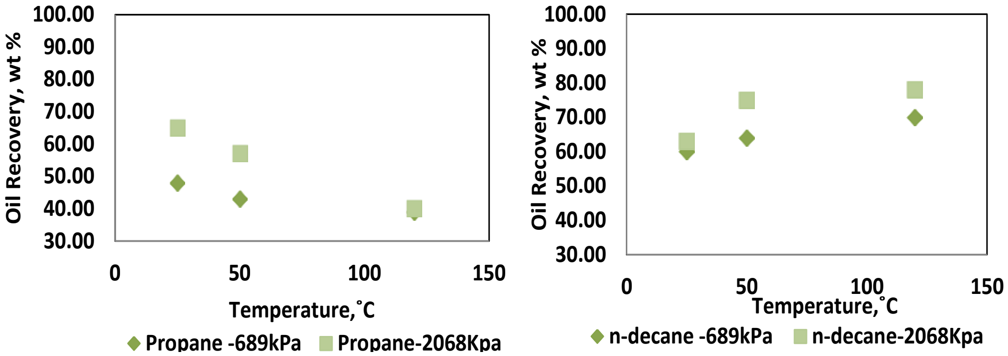

Figure 3-5: Oil recovery (from sample A) after 4-hour test at different operation conditions using two n-alkanes (propane and n-decane).

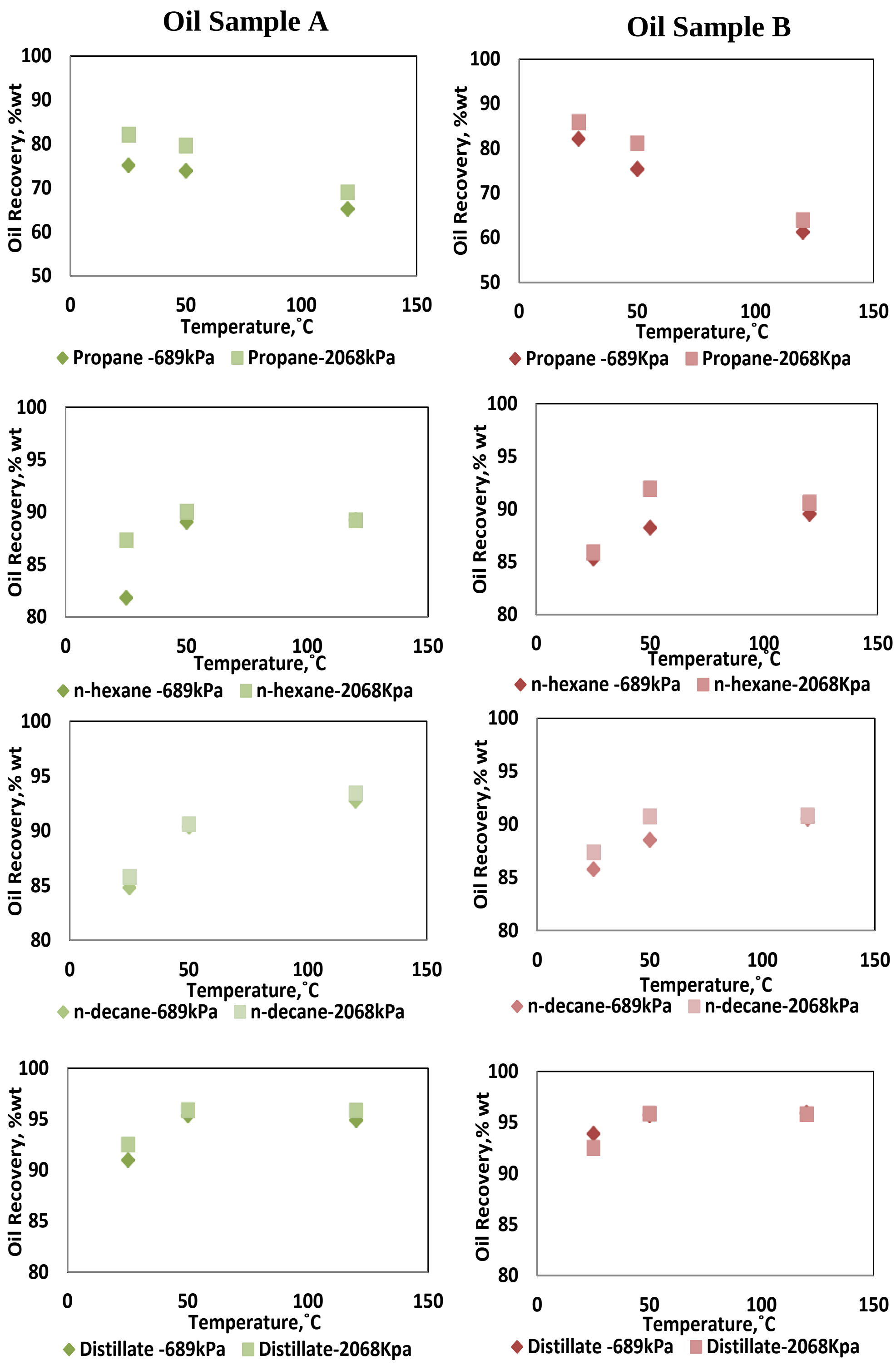

Figure 3-6: Oil recovery at several operating conditions after 6-hour test (oil sample B) and 8-hour test (oil sample A) using n-alkanes and the distillate.

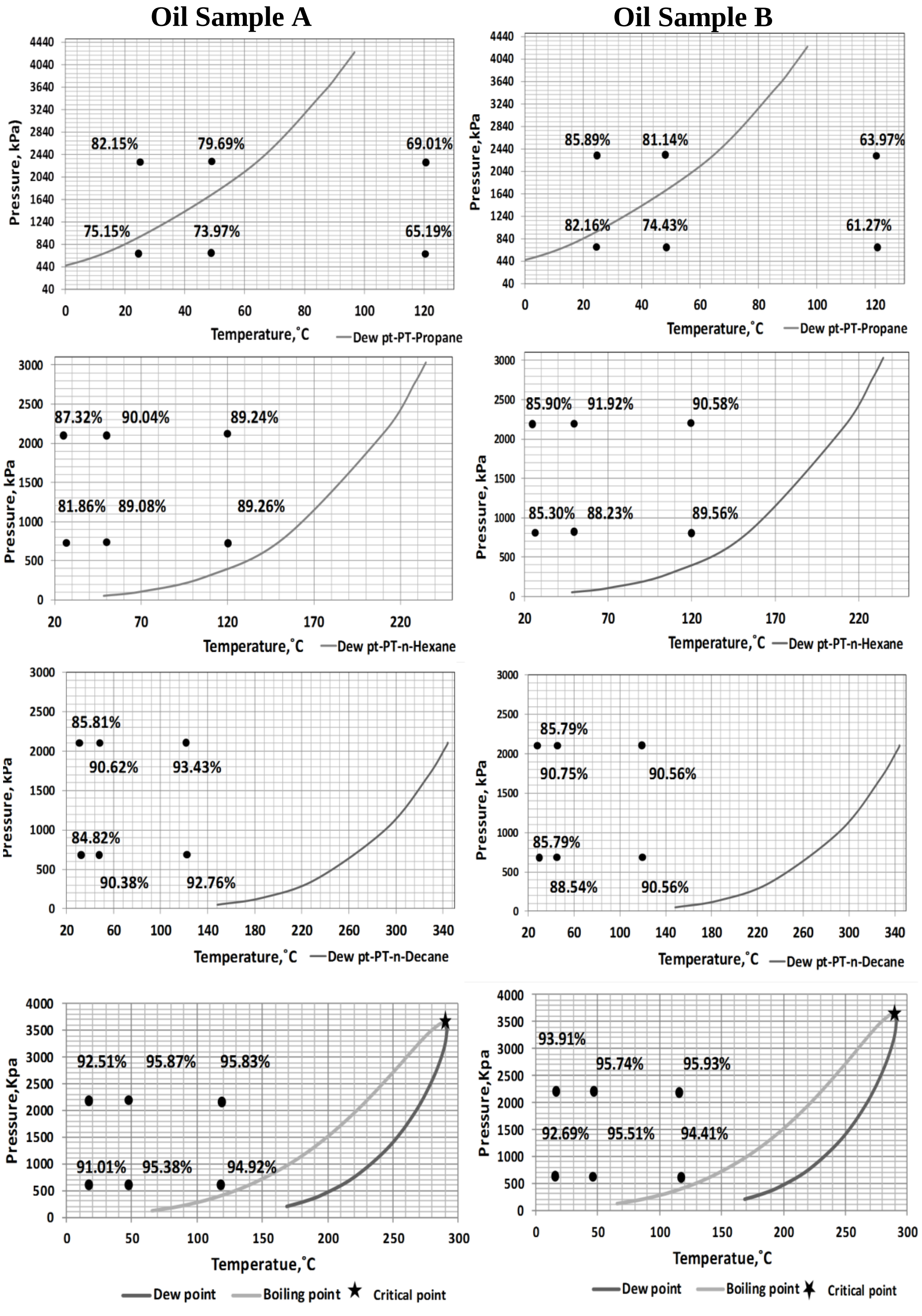

Figure 3-7: Phase envelope for propane, n-hexane, n-decane (pure components) and a distillate hydrocarbon (mixture hydrocarbons).

Residual Oil Saturation in the Sandpack

The residual oil saturation (S_{or}) was obtained after cleaning the sandpack (**Figure 3-8**) in a Soxhlet extraction system with pure n-heptane (99.9 wt %) for about one week. The fluid sample obtained in the flask, which is the mixture of n-heptane and residual oil (maltenes), was distillated using rotary-evaporator equipment, and then the residual oil was calculated based on the final amount left in the flask.

Propane gave higher residual oil in the sandpack compared to n-hexane, n-decane and the distillate hydrocarbon for both oil samples (A and B); however, a higher viscosity reduction was obtained with propane due to high asphaltene precipitation in the core **(Figures 3-10 to 3-13)**. The residual oil saturation is highly sensitive to temperature due to phase changes from liquid to vapor when propane was used as solvent. The residual oil of the heavy oil sample (A) jumped from 8.13% to 21.67% at 689 kPa when temperature was goes from 25 ˚C to 120 ˚C (**Figure 3-8**). The S_{or} for oil sample B shows an increment from 9.75% to 27.57% at 689 kPa for the same temperature change (**Figure 3-8**). As seen, a similar response to temperature change was observed but the residual oil values of oil sample B was slightly higher compared to oil sample A, which can partially be attributed to a shorter operating time of the less viscous oil (sample B), which was two hours less, than that of oil sample A (8-hours).

The S_{or} in the sandpack was also determined for n-hexane, n-decane and the distillate hydrocarbon cases. A significant reduction in the S_{or} was obtained with distillate hydrocarbon compared to propane, n-hexane and n-decane. The characterization of the distillate hydrocarbon (a mixture of hydrocarbons such as butane (1.73%), pentane (15.8%), heptane (3.12) and mixture of aromatics such as toluene (2.01%), xylene (1.62%) and benzene (1%)) indicates its strength in asphaltene dissolution due to high content of aromatics. This is the main reason for lower S_{or} compared to the pure alkanes. The S_{or} obtained for the **distillate hydrocarbon** decreased from 3.83% to 0.41% when temperature was increased from 25 ˚C to 120 ˚C at 689 kPa (oil sample A). Pressure change to 2068 kPa from 689 kPa did not show any significant change in S_{or} (an increase around 0.7%) (**Figure 3-9**). The S_{or} for oil sample B decreased from 2.49% to 0.8% at 689 kPa and did not change when pressure increased to 2068kPa (**Figure 3-9**). **n-Hexane** showed a S_{or} reduction from 6.83% to 3.26% at 689 kPa and from 5.76% to 3.89 at 2068 kPa when temperature was changed from 25 ˚C to 120 ˚C for oil sample A. The S_{or} for oil sample B with n-hexane reduced from 7.44% to 4.52% at 689kPa and from 7.40% to 3.82% at 2068 kPa for the same temperature change. The temperature effect on S_{or} reduction with **n-decane** was more prominent. When temperature increased from 25 ˚C to 120 ˚C, S_{or} of oil sample A decreased from 8.44% to 0.55% at 689kPa and from 8.18% to 0.72% at 2068 kPa. The heavy oil sample B showed a S_{or} reduction of 8.76% to 3.81% at 689 kPa and 6.48% to 3.53% at 2068 kPa for the same temperature range

(**Figure 3-9).** The effect of temperature on S_{or} reduction was more significant for heavier liquid solvents because the higher the asphaltene solubility in the fluid, the lower the asphaltene concentration on the rock surface.

Asphaltene Deposition into the Sandpack

Asphaltene is mainly insoluble in n-heptane but soluble in toluene. To determine the asphaltene deposited in the samples after residual oil calculation process, the sandpack samples were cleaned with toluene for one week. The Soxhlet extraction system was used and the final sample in the flask (toluene and asphaltene) was distillated using the rotary-evaporator. Then, the amount left in the flask was calculated as asphaltene deposited in the sandpack. The asphaltene deposition for four types of solvent and two different types of heavy oil is presented in **Figure 3-10**. Undoubtedly, asphaltene deposition is expected to be higher with oil sample A than oil sample B due to its heavier nature (**Table 3-1 and Figure 3-1**).

In accordance with previous experience, higher asphaltene precipitation is expected with propane than with n-hexane, n-decane and distillate hydrocarbon as can be inferred from **Figure 3-10** [13]. Moreover, distillate hydrocarbon and n-decane showed less asphaltene depositions compared to propane and n-hexane (**Figure 3-10**). All these can be explained by asphaltene solubility increment in the crude oil due to less asphaltene desorption in the cases of n-decane and distillate hydrocarbon. In addition, distillate hydrocarbon contains a degree of aromatics, which improves its strength in asphaltene dissolution (due to high content of aromatics). As a result, the asphaltene deposition for the **distillate hydrocarbon** was just 0.93% at 120 ˚C (oil sample A) and 0.70% at 120 ˚C (oil sample B). For the **n-decane** case, it was 1.13% (oil sample A) and 1.05% (oil sample B) at 120 ˚C. **Propane** yielded 5.27% and 3.39% asphaltene deposition for oil samples A and B at 120 ˚C, respectively. The asphaltene deposition when **n-hexane** was used as solvent was 4.26% for oil sample A and 2.53% for oil sample B at 120 ˚C (**Figure 3-10**). High concentration of asphaltene deposition using propane can be attributed to the resin and asphaltene destabilization power. Resin is soluble in n-hexane, n-decane, and distillate hydrocarbons but insoluble in propane [23].

One may observe that as the molecular weight of the solvent injected increases, asphaltene deposition and precipitation decreases and oil recovery increases. The main reason for the increase in oil recovery is higher asphaltene solubility. Consequently, asphaltene particle size and agglomeration become smaller. Redford and McKay [20] reported similar observations if enough amount of light ends are present in the blend to provide the drive energy during solvent injection. Additionally, asphaltene particle size and agglomeration are other important factors on oil recovery. When pressure (from 206 kPa to 2068 kPa) and temperature (from 50 ˚C to 110 ˚C) increased, the particle size becomes larger [13]. The same behavior was reported by Nielsen et al [11]. They studied temperature and pressure behavior of asphaltene particle sizes using bitumen samples from the Cold Lake (Canada) area and Lindberg oil (Canada), which had high asphaltene content (pentane-insoluble 21.8% and 17.6%). They observed that “super” agglomerates were developed at temperatures around 80 ˚C and higher, which was attributed to the softening and adhesion of asphaltene particles. They also found that an increase in pressure yielded an increase in the mean asphaltene particle size for the Cold Lake bitumen sample but not for the Lindberg oil.

Visual Inspection of Oil Recovery and Asphaltene Deposition

The sandpacks used in the tests were opened and a visual inspection was performed as seen in **Figure 3-8**. The variations in colors from dark to brown indicate higher (dark) or lower (brown) S_{or}. These images are critical in pointing the location of apshaltene deposition as this information cannot be gathered from the production data as analyzed above. Regardless the temperature and pressure, the distribution of remaining oil (in the form of S_{or} or asphaltene) is more uniform for lower carbon number solvents for both oil types. As pressure and, more critically, temperature increase, asphaltene deposition is seen around the production end systematically for higher carbon number solvents like n-decane and distillate. This is more obvious in the heavier (oil sample A) oil case.

In their Hele-Shaw type experiments (no porous media), Pathak et al. [15,16] also observed severe deposition of asphaltene at the first contact point of solvent with the oil. Moghadam et al. [12] and Papadimitriou et al. [14] observed possible asphaltene migration downstream flow and found two critical zones of the asphaltenic material deposition close to the injection and production ends. The location of asphaltene deposition is critical as it eventually effect the permeability and therby the recovery. If this happens near the injection point and throughout the core like in all cases of propane (as also observed in the above mentioned studies), this significantly affects the recovery. Near production wellbore deposition like observed in the cases of high temperature and pressure experiments with higher carbon number solvents (n-decane and distillate) does not affect the recovery in the reservoir but may cause asphaltene deposition in the wellbore, which is a relatively easier problem to deal with.


Oil Sample A (8.67°API)
Operating time: 8hours
Injection
Production
Propane
25°C-100Psig
50°C-100Psig
120°C-100Psig
25°C-300Psig
50°C-300Psig
120°C-300Psig
n-hexane
50°C-100Psig
120°C-100Psig
50°C-300Psig
120°C-300Psig
n-decane
25°C-100Psig
50°C-100Psig
120°C-100Psig
25°C-300Psig
50°C-300Psig
120°C-300Psig
Light Diluted Oil
25°C-100Psig
50°C-100Psig
120°C-100Psig
25°C-300Psig
50°C-300Psig
120°C-300Psig

Figure 3-8: Sandpack after solvent injection (heavy oil A and B) using n-type solvent at different operational conditions and operational time (8-hour, oil A to 6-hour, oil B test). The vertical sandpack system has shown that high residual oil is present at the end of the production well.

Effect of the Type of Solvent on Recovery Factor

The explanation of different effects on the oil recovery such as temperature, pressure, residual oil saturation, and asphaltene deposition are discussed. However, the selection of the solvent type is a critical issue not only for oil recovery and asphaltene deposition but also for the economics and availability of solvents. **Figure 3-12** shows cumulative oil production is presented for one operational condition at 50 ˚C and 689 kPa for oil sample A. The results showed that delayed and lower oil production was obtained with propane as solvent compared to n-hexane, n-decane and distillate hydrocarbon. n-hexane and n-decane, on the other hand, yielded similar oil production, whereas distillate hydrocarbon showed the best recovery among the four solvents.

Another critical factor in the selection of solvent is asphaltene precipitation in the produced fluid and asphaltene deposition in the sandpack. Asphaltene precipitation/flocculation (produced oil) and deposition (sandpack) are presented in **Figures 3-10** and **3-11** for all solvents, respectively. The results show that high asphaltene deposition is obtained for lower carbon number hydrocarbons. SARA analysis revealed that lower asphaltene percent is presented in the final oil production using propane than distillate hydrocarbon (**Table 3-2**). This means that lower asphaltene deposition can be found in the sandpack flushed with distillate hydrocarbon compared to the propane case.

Viscosity Measurements

The viscosity reduction from oil samples A and B were very dramatic against temperature (**Figure 3-13**). At 25 ˚C and atmospheric pressure, the viscosity reduction of oil sample B after solvent injection was 3174 cp, 1505 cp, 1428 cp and 1399 cp for distillate hydrocarbon, n-decane, n-hexane, and propane, respectively. Thus, the viscosity measurement turned out to be a validation of the sandpack results, which explain strong asphaltene precipitation using solvents with lower carbon number such as propane and hexane.

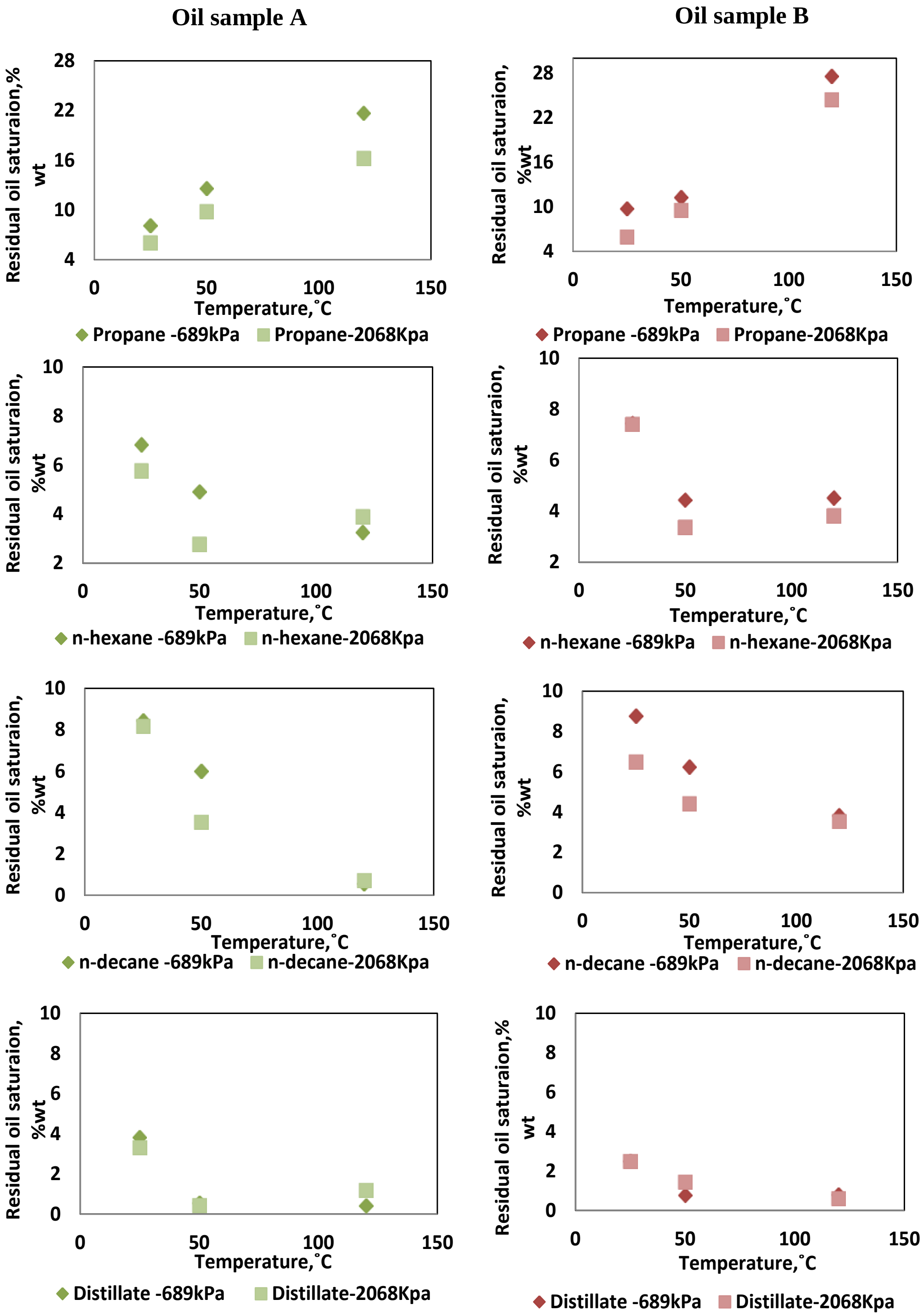

Figure 3-9: Residual oil saturation into the sandpack after 6-hour test (oil B) and 8-hour test (oil A) for different type of solvents.

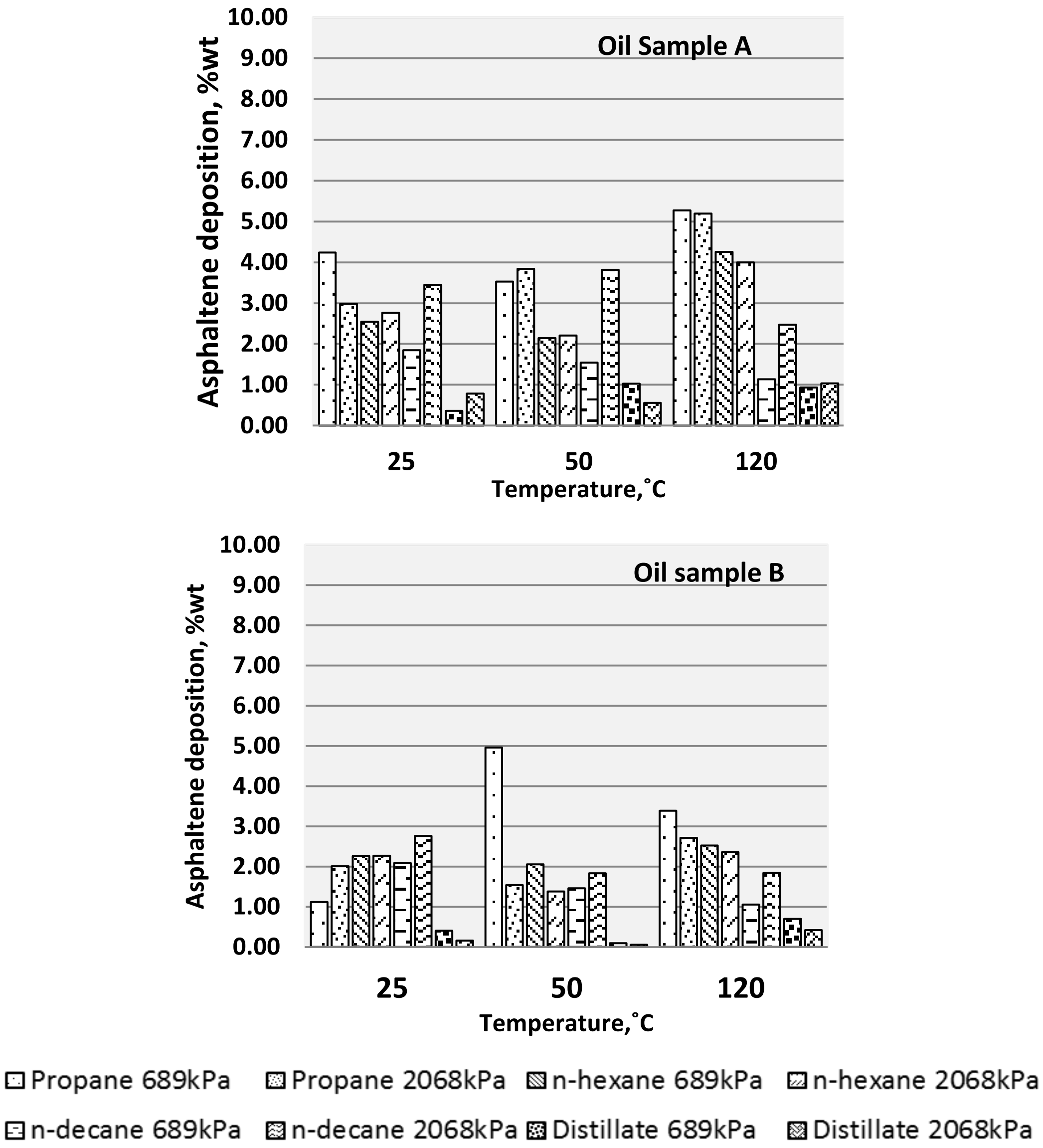

Figure 3-10: Asphaltene deposition on the glass beads surface after 6 (Oil sample B) to 8 (Oil sample A) - hour test using different type of solvent.

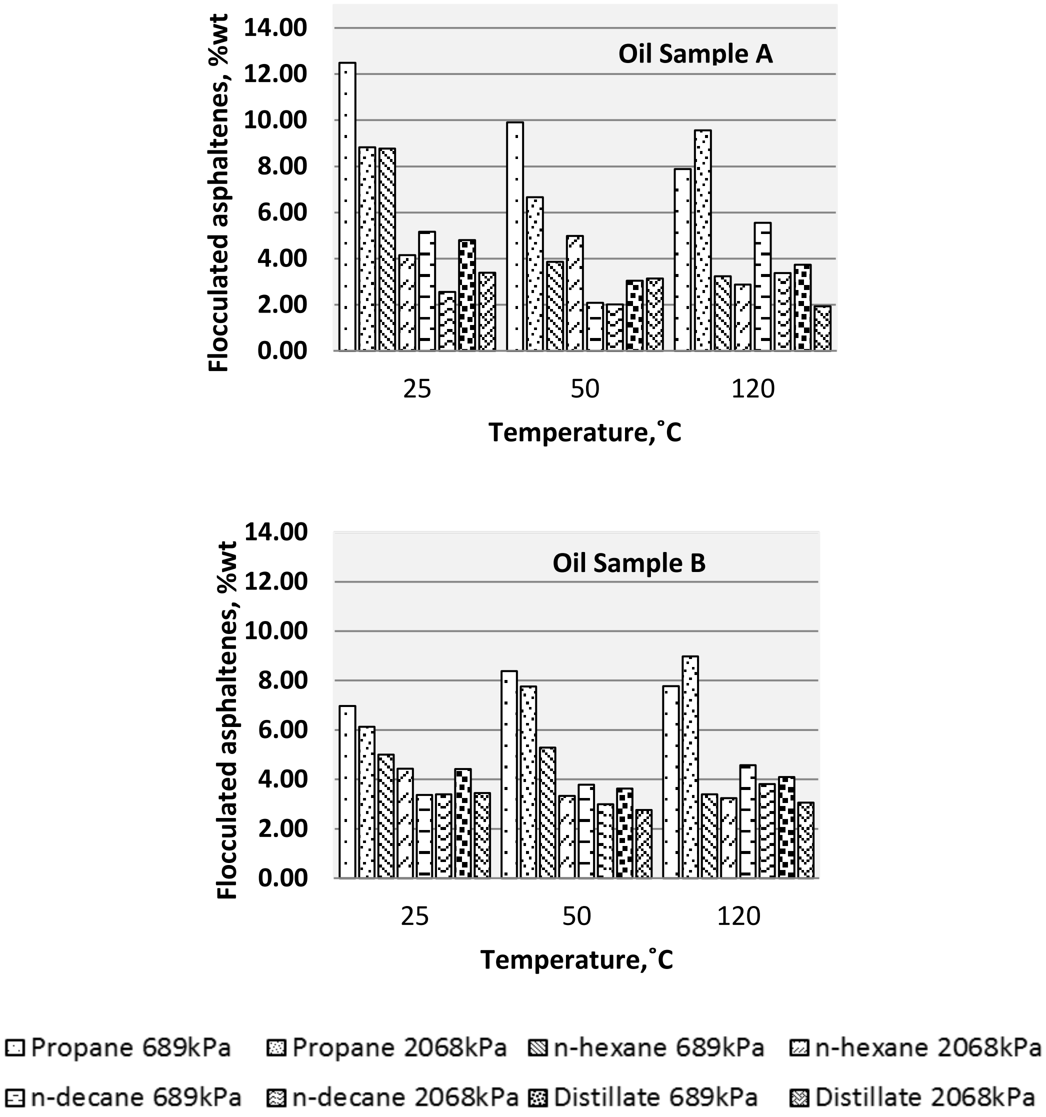

Figure 3-11: Flocculated asphaltenes in the production fluid from oil samples A and B at different operation conditions with n-type of solvent. The asphaltene was collected using a high temperature and pressure filter apparatus.

Table 3-2: SARA analysis from the producer oil after solvent injection into the sandpack (heavy oil –A) with different type of n-alkanes and a distillate hydrocarbon.

Oil production obtained after solvent injection				
Solvent type	**Propane**	**n-hexane**	**n-decane**	**Distillate**
Saturates, wt%	50.19	34.25	34.98	37.12
Aromatics , wt%	29.48	40.72	40.10	36.19
Resin, wt%	13.34	16.53	15.72	15.69
Asphaltene, wt.%	7.00	8.50	9.20	11.00

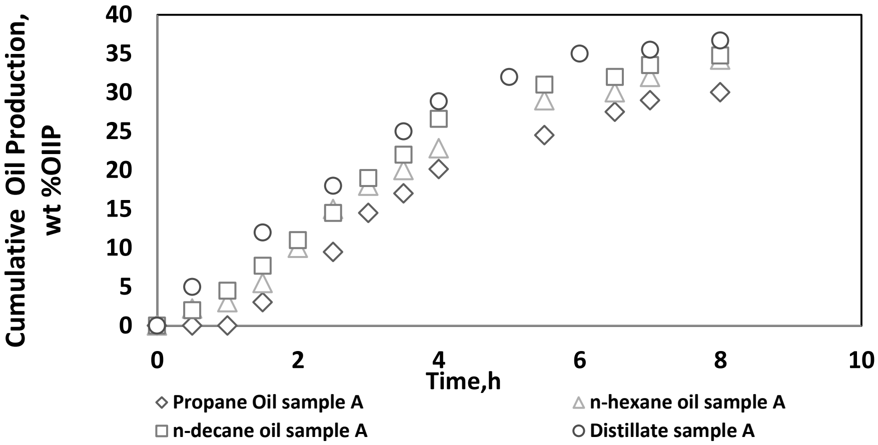

Figure 3-12: Effect on the cumulative oil production (A) using different types of solvents at 50˚C and 689kPa.

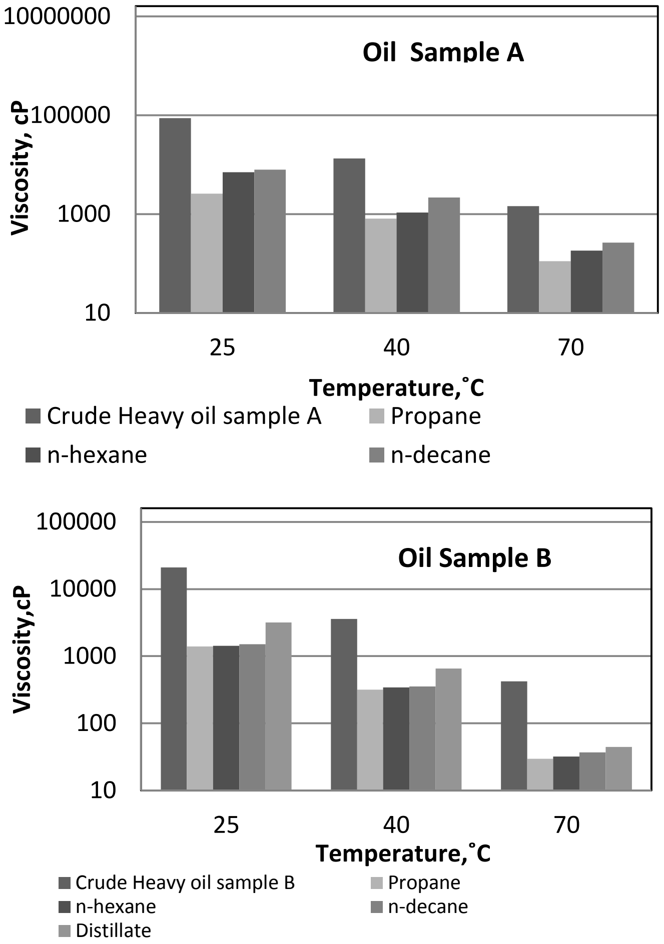

Figure 3-13: Viscosity measurements from the oil samples A and B at different temperatures and atmospheric pressure after solvent injection in the sandpack system using n-alkanes and distillate hydrocarbon.

Quantitative Asphaltene Concentration in the Final Oil Sample

The original crude heavy-oil samples obtained from different fields operating in Alberta, Canada were analyzed under the optimal microscope before doing the deasphalting of heavy-oil using different types of solvents. The original crude oils show some air and water particles in it (white pigmentations) as presented in **Figure 3-14** The standard IP-143 method was followed to determine the asphaltene content of those oils in their original form and were measured to be 11.5 wt% and 9.6 wt% for oil samples A and B, respectively. In addition, the same asphaltene samples were visualized under the scanning electron microscope (S-3000N-SEM) at different magnifications (between 100 and 250 times). As seen in **Figure 3-15**, the asphaltene particles presented several porous and amorphous structures.

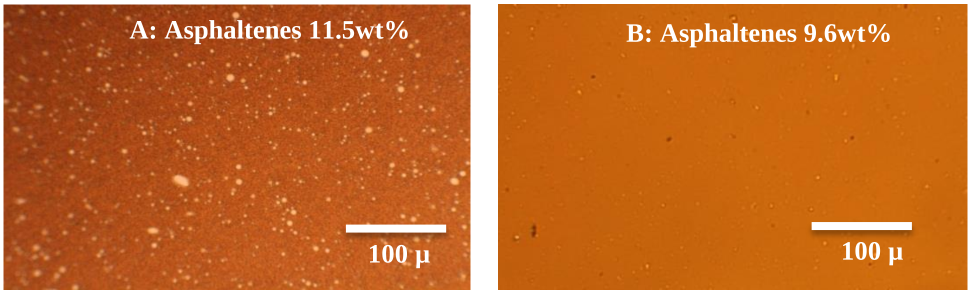

Figure 3-14: Heavy-oil samples A and B under optical microscope.

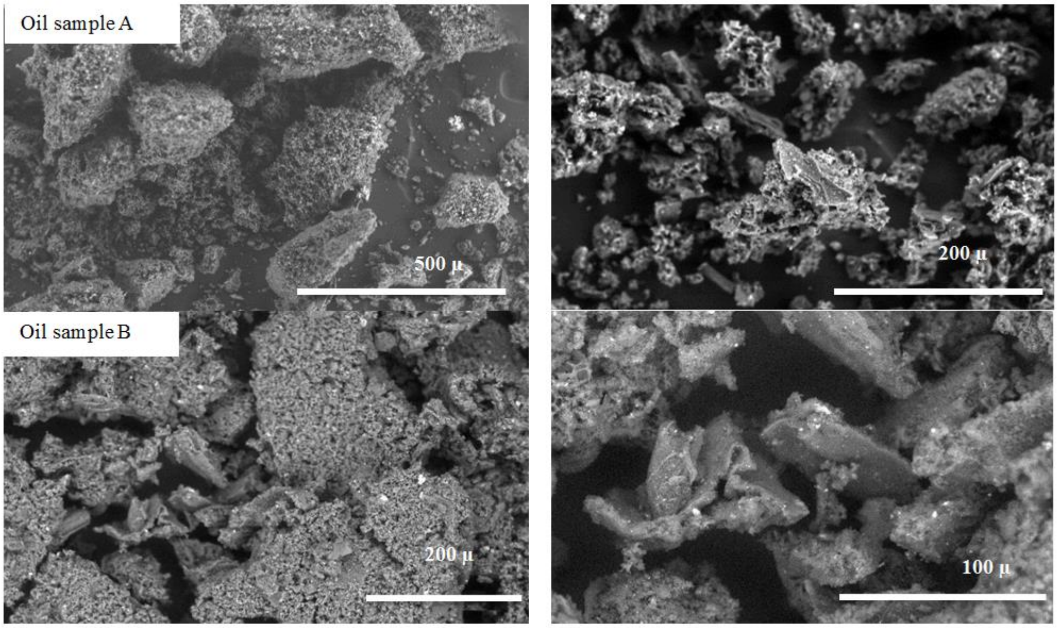

Figure 3-15: Asphaltene sample precipitated with n-heptane at room conditions (visualization under the S-3000N-SEM).

In addition, high resolution scanning electron microscope (SEM) was also used to visualize the organic deposition (maltenes and asphaltenes) and structures developed inside the porous medium after the deasphalting of heavy-oils using several light carbon solvents. Magnifications between 40 to 250 times were used to identify the possible asphaltene structures and deposition on and between the glass beads (**Figures 3-16 to 3-19**). Some of the high resolution pictures showed some bright color, which means that the sample had presented higher atomic number materials such as nickel and vanadium, which are very commonly found in asphaltenes. In **Figures 3-16** through **3-19**, different structure and morphology of the organic deposition on the glass beads showed that a lower carbon number of solvent injected yielded higher deposition on the glass beads. However, the mixture of hydrocarbons (distillate hydrocarbon) showed tremendous reduction in asphaltene deposition and residual oil saturation compare to propane, n-hexane and n-decane due to aromatics compound effect on the asphaltene solubility in the fluid. SEM visualization showed that lower organic deposition was present with heavy oil sample B than with oil sample A. Then the type of heavy oil properties had high influence on the final organic deposition. All these visual observations validate the quantitative data about oil recovery factor and asphaltene depositions given in **Figures 3-5 to 3-10**.

Close-up images in **Figure 3-20** show the organic deposition between the grains (middle and lower images). As the carbon number decreases, asphaltene agglomeration increase (upper images) and results in a more “chain”- like structure. This type of deposition has a tendency to change the wettability of the rock. A recent study conducted by Sayyad Amin et al. [22] concluded that asphaltene precipitation made the surface rougher and also increased the contact angle. Similarly, in the present study, the asphaltene deposition on the grain surface was found to be rougher when propane and n-hexane were used, compared to n-decane and distillate. Consequently, a significant change in the surface properties, especially wettability, can be encountered with lower hydrocarboan solvents (propane and n-hexane). The images given in **Figure 3-20** validate the observed increment or reduction from oil production rate, asphaltene deposition, and residual oil saturation behaviors represented graphically before (**Figures 3-5 to 3-10a-b**). The effect of wettability alteration on the recovery and its relation to asphaltene deposition caused by different solvents will be discussed in that last section of the paper.

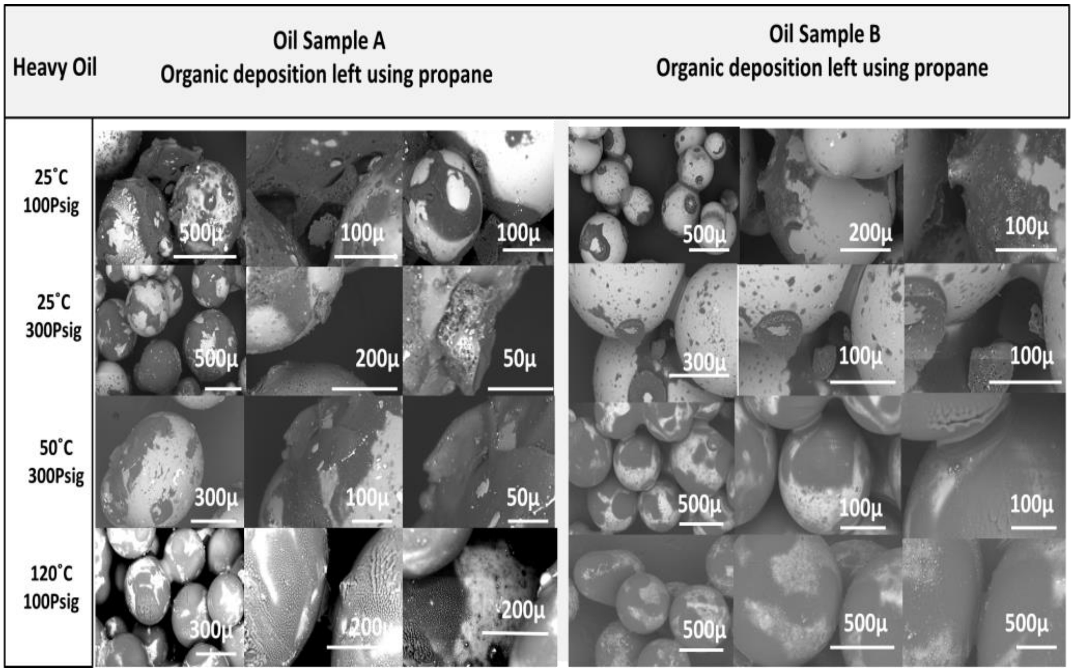

Figure 3-16: Organic deposition: Visualization under the S-3000N-SEM, on the random particles selected from sandpack after solvent injection (propane) at different operating conditions.

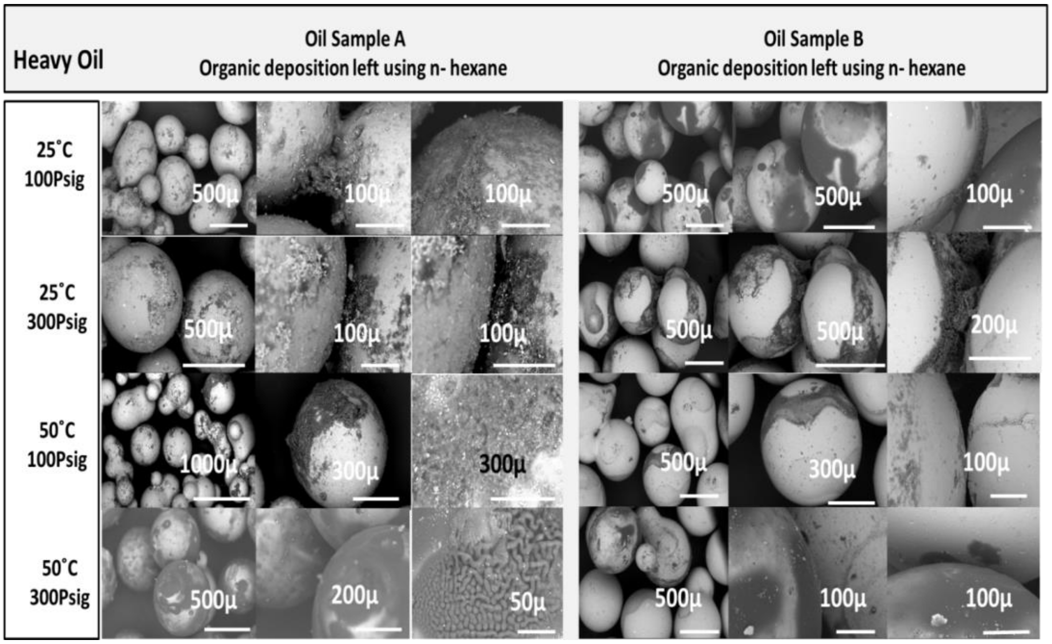

Figure 3-17: Organic deposition: Visualization under the S-3000N-SEM, on the random particles selected from sandpack after solvent injection (n-hexane) at different operating conditions.

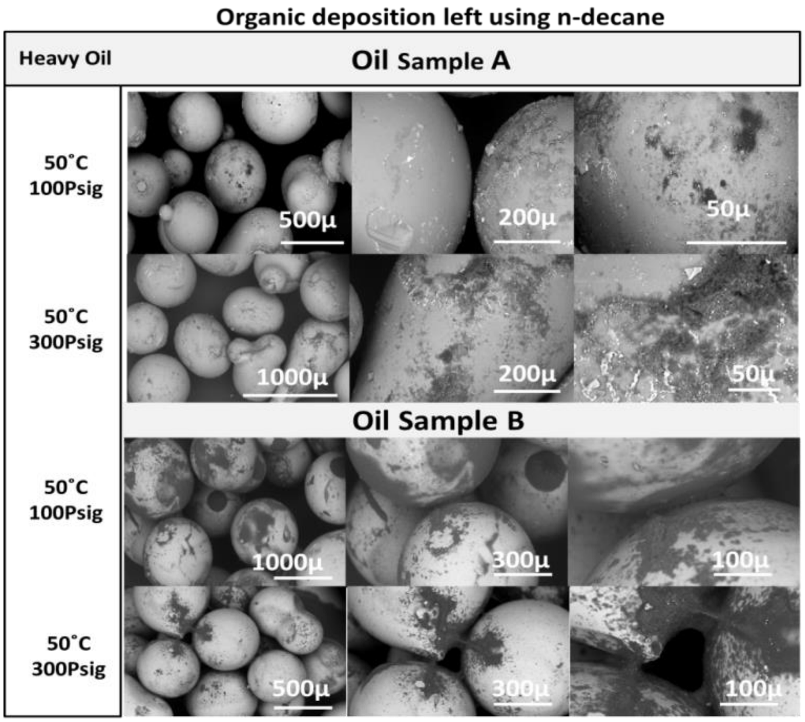

Figure 3-18: Organic deposition: Visualization under the S-3000N-SEM, on the random particles selected from sandpack after solvent injection (n-decane) at operating conditions.

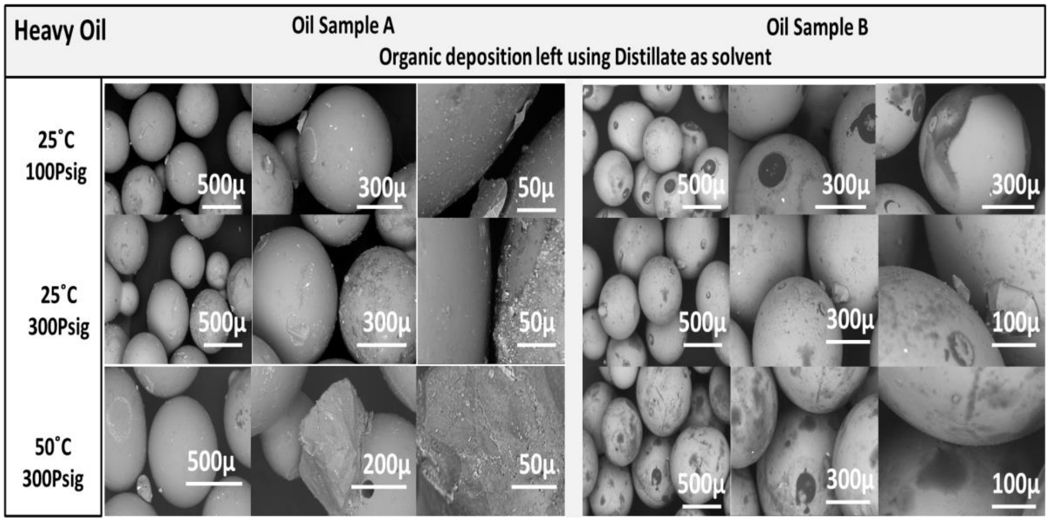

Figure 3-19: Organic deposition: Visualization under the S-3000N-SEM, on the random particles selected from sandpack after solvent injection (distillate hydrocarbon) at operating conditions.

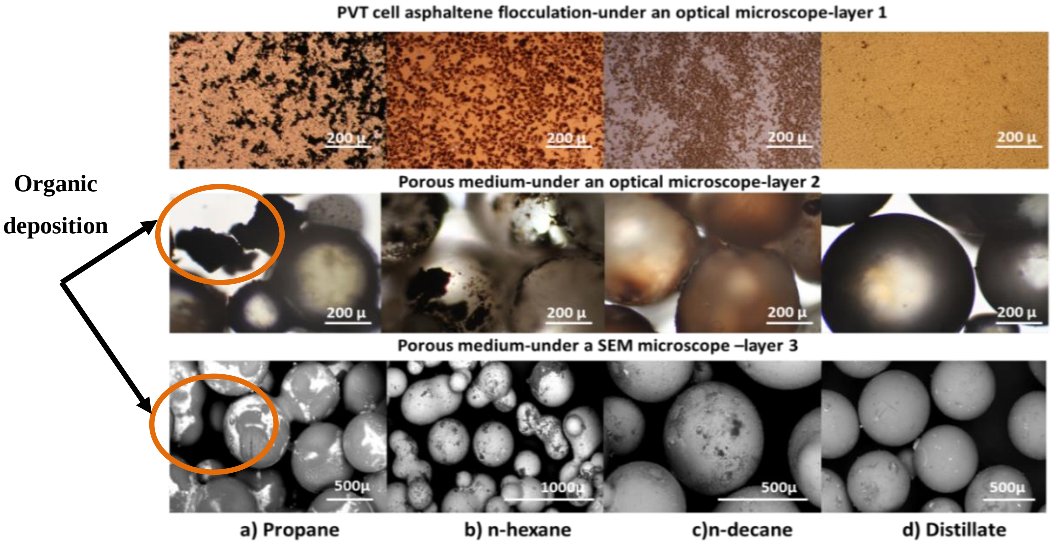

Figure 3-20: Microscope visualization of asphaltene agglomeration in the oil sample and in the sandpack using different n-alkanes in solution with heavy-oil: a) n-decane, b) n-hexane, c) propane and d) distillate hydrocarbon.

Discussion on the Effect of Aspheltene Precipitation and Deposition on Heavy-Oil Recovery Efficiency during Solvent Injection

The data on asphaltene deposition and its effects on oil recovery presented in this paper are summarized schematically in **Figure 3-21.** Asphaltene precipitation/flocculation in the produced oil and its deposition in the sandpacks at different temperature and pressure are quantitatively and qualitatively defined in this diagram. Asphaltene precipitation characteristics can be obtained from a PVT analysis using only oil and solvent [13]. What is more critical, however, is the effect of asphaltene on oil recovery (or residual oil saturation) at different temperature and pressures for a wide range of solvents, which requires experiments in porous media. The trends and quantitative values for the heavy-oil recovery is presented in this diagram as well but the physics of the heavy-oil recovery process in the presence of asphaltene deposited on the rock surface requires further analysis as given below.

As seen throughout this paper and summarized in **Figure 3-21**, lower S_{or} values were obtained with liquid solvents (distillate hydrocarbon, n-decane and n-hexane) than with propane and molecular diffusion coefficient plays a critical role in this process. In theory, molecular diffusion of a gas (propane) solvent is faster than that of liquid solvents (n-hexane, n-decane, and distillate) because the free pathway, gas expansion and molecular driving are faster with gas as solvent. Then, mass transfer between gas solvent and heavy oil is more efficient, which has made vapor solvent injection more favorable historically. However, the solubility of this type of hydrocarbon mixture is more complex and full miscibility between oil and solvent may take quite a long time depending on the molecular weight of the solvent type. In the initial period of solvent injection into heavy-oil reservoirs, the displacement is immiscible in nature until sufficient mass transfer is completed, and thereby infinite solubility is achieved (single phase) [19]. Note, however, that asphaltene flocculation and interfacial tensions caused by this do not allow reaching full miscibility for such a complex mixture of hydrocarbon compounds. Consequently, a partial miscibility is achieved in the cases of low hydrocarbon cases (propane and n-hexane) despite high molecular diffusion coefficient. Lower asphaltene precipitation caused by increasing carbon number of the solvent may result in reaching miscibility conditions quicker with n-decane and distillate [20,23], even if the molecuar diffusion coefficient is low. In other words, asphaltene dispersion into the oil and solvent is a critical parameter in obtaining a complete miscibility and miscibility is controlled by the counter effects of molecular diffusion coefficient and asphaltene precipitation.

On the other hand, interfacial tension and wettability may be a controlling parameter in residual oil saturation during solvent-based process as the recovery is obtained under partially immiscible conditions, at least for a period of time, as emphasized above. Hassan et al. [9] determined the interfacial tensions for normal hydrocarbons (C_1 to C_{10}) at different temperatures and at 5167 kPa. They found that the interfacial tension decreases when the number of carbon atoms increase. Consequently, if the interfacial tension is lower (higher carbon number solvent cases), then the capillary pressure decreases. Capillary forces are important in oil recovery because they control the oil trapping process. Rostami et al. [21] found that the cumulative oil production enhances as a result of solvent-oil relative permeability (Kr) alteration. This alteration in the Kr curves takes place due to surface tension reduction during the process and this is achieved by higher carbon numbers solvents. The relative permeabilities are also affected by wettability. Undoubtedly, wettability alteration from strongly water wet to -partially- oil wet is due to organic deposition. This can be explained by the images given in **Figures 3-16 through 3-19**. A partial coverage of the grain surface by deposited asphaltene could be the reason behind the wettability alteration of the rock to -partially- oil wet or mixed wet. This becomes more obvious in the case of lower carbon number solvents and wettability alteration is more pronounced when propane and n-hexane were used.

The above analysis indicates that oil recovery is controlled by the relative permeability curves, which are governed not only by mixing conditions (molecular diffusion and dispersion rate) but also the interfacial tension and wettability in case of heavy-oil recovery because reaching full miscibility conditions may take a long time, if not never. This leads to a major conclusion that there exists an optimal solvent type that yields technically (and even economically) the highest and fastest recovery of heavy-oil. One option could be to find this optimal solvent through experimental and numerical analyses or to start the heavy-oil recovery process with lower carbon number solvents (due to their higher molecular diffusion coefficient) for a fast -initial- recovery and continue with higher carbon number solvent for more efficient displacement (immiscible initially and fully miscible eventually).

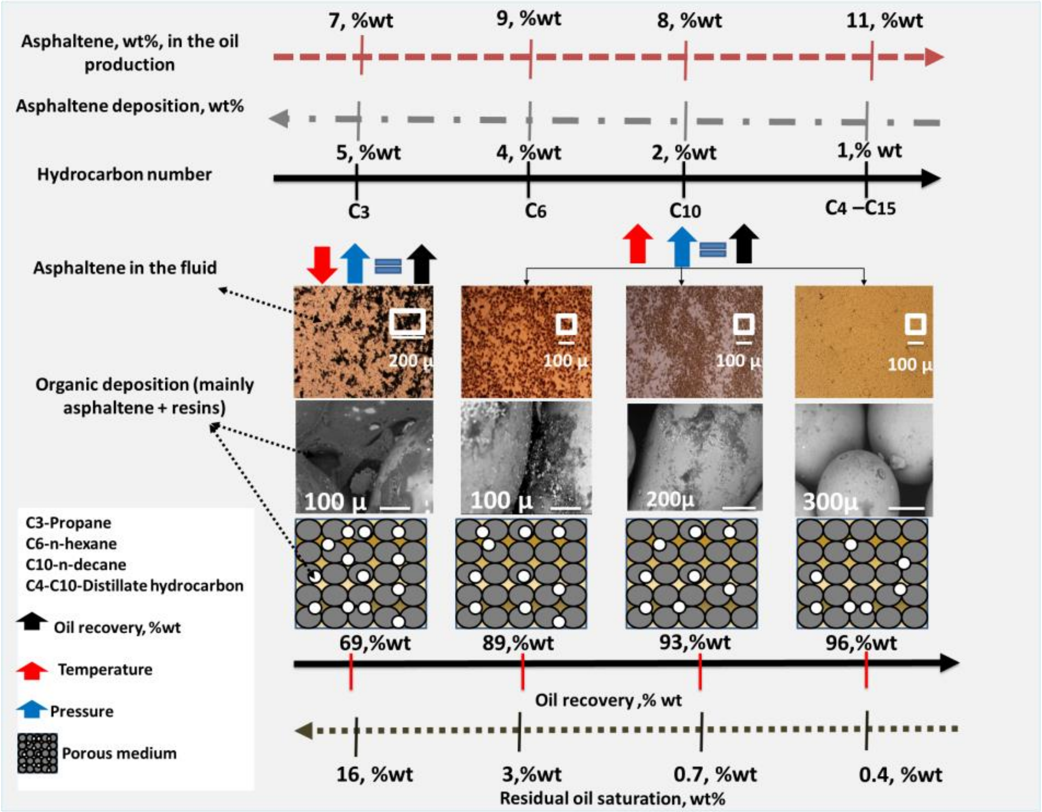

Figure 3-21: A diagram showing the behaviour of solvents as a displacing agent at different temperatures.

Conclusions

Two different types of heavy-oil samples and four different solvents (propane, n-hexane, n-decane, and a distillate hydrocarbon) were used in gravity drainage recovery experiments on unconsolidated sands. The experiments were carried out for the objective to increase oil recovery factor and determine the asphaltene deposition and residual oil saturation in the sandpack model. The major conclusions withdrawn in this study are as follows:

1. The effects of the oil composition and gravity on asphaltene deposition and oil recovery were identified. Two different heavy oil samples with 8.67 ˚API and 10.28 ˚API were

carried out in the sandpacks. Results showed that heavier oil (sample A) requires an 8-hour operational time to achieve oil recovery values as heavy oil sample B reaches in 6-hours. Oil sample A shows a higher asphaltene flocculation and agglomeration than oil sample B. Those effects can be attributed to oil composition; oil sample A has heavier end components (39.9wt %) than oil sample B (23.7wt %).

2. Heavy oil recovery from oil samples A and B by propane showed a decline when temperature increased from 25 °C to 120 °C. This could be attributed to the vapor phase of propane (being far from the dew point), which negatively affects solvent dilution into the oil as temperature increased. On the other hand, higher pressure operations resulted in around 5% increment in oil production compared to lower pressure operations.

3. Heavy oil recovery from oil samples A and B using n-hexane, n-decane, and the distillate hydrocarbon showed a strong positive effect on oil production when temperature increases from 25 ˚C to 120 ˚C. Also, pressure was observed to be an important effect on oil recovery but not as remarkable as temperature.

4. The maximum recovery factor was found to be 96% at 50 ˚C for both oil samples when the distillate hydrocarbon was used as solvent. This could be attributed to lowered asphaltene flocculation and agglomeration caused by the presence of aromatics in the distillate. Toluene, xylene and benzene dilute the oil better by increasing the solubility of the asphaltene particles in the heavy oil.

5. The SARA analysis results of the produced oil showed that the higher the asphaltene concentration in the oil, the lower the asphaltene deposition in the core. For the propane-produced oil, the asphaltene weight percent was 7wt% compared to 11.0wt% obtained from the distillate hydrocarbon.

6. The mixture of hydrocarbons (distillate hydrocarbon) showed tremendous reduction in asphaltene deposition and residual oil saturation compared to propane, n-hexane and n-decane due to the existence of aromatic compounds, which caused higher asphaltene solubility. SEM images showed lower organic deposition in the sandpack with the lighter oil (sample B) than with the heavier oil (sample A).

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CHAPTER 4: ASPHALTENE PRECIPITATION, FLOCCULATION AND DEPOSITION DURING SOLVENT INJECTION AT ELEVATED TEMPERATURES FOR HEAVY OIL RECOVERY

This chapter was submitted as a paper for journal publication and under review.

Background

Solvent-based heavy oil and bitumen recovery has recently become an attractive process. The tendency is to use solvent as an alternate or addition to steam to improve the efficiency of the sole injection steam or solvent. Asphaltene destabilization in the reservoirs during this type of application is a common problem due to continuous changes of temperature, pressure, and oil composition.

In the past, light weight n-alkane type solvents (typically propane and butane, rarely pentane, heptane, and hexane) were considered in the lab and field applications. Asphaltene precipitation and flocculation may increase when a low weight hydrocarbon solvent is used as solvent. Deposition of asphaltene on the rock surface due to asphaltene flocculation in the oil may eventually take place and this could negatively affect oil flow rate due to the possible reduction of permeability and alteration of wettability. Organic flocculation and deposition may change from one reservoir to another because of geology, petrophysics, and oil properties. These characteristics should be investigated for a wide range of solvent and oil types and temperature/pressure conditions.

In this paper, two heavy oil samples from fields in Alberta, Canada were destabilized using three different types of paraffin: propane, n-hexane, and n-decane. The solvent-based process was conducted at different reservoir conditions with alterations made to the temperature, pressure, and oil composition to determine the effect on asphaltene flocculation in the fluid and its deposition on the rock surface. Initially, experiments were carried out using a pressure, volume, and temperature (PVT) cell at different reservoir pressures (1378 kPa to 2068 kPa) and under different temperature conditions (from 40 °C to 120 °C). Next, a Focused Ion Beam (FIB) and Scanning Electron Microscope (SEM) were used to characterize the morphology of the organic deposition on the glass beads surface through core flooding experiments. The results obtained through these two sets of experiments showed that temperature and pressure have a critical influence on asphaltene solubility and temperature effect was more pronounced. Moreover, the asphaltene concentration and optical microscope particle size visualization demonstrated that significantly more asphaltene particle agglomeration was present in oil sample A (8.6 °API and 87,651cp at 25 ˚C) than oil sample B (10.28 °API and 20,918 cP at 25 ˚C). In addition, higher asphaltene destabilization was measured with propane as a solvent compared to the n-hexane and n-decane cases for both oil types. The PVT cell experiments and organic deposition surface roughness calculations were fundamentally important to explain the plugging formation in the reservoir under different operational conditions and with different oil types.

Introduction

The solvent-based injection processes improve heavy-oil production through the reduction of viscosity and capillarity forces, and the segregation of gravity drainage [7,8,9]. Molecular diffusion and oil dilution are two physicochemical mechanisms that take place during this process [7,8,9,26,27]. Viscosity reduction (and thereby oil mobility increase), via in-situ upgrading, mainly occurs due to a decrease in the asphaltene solubility of oil.

Asphaltene has the highest molecular weight and is the most polar constituent from crude oil [26,27]. Asphaltene precipitation takes place due to the injection of light hydrocarbon solvent (e.g., propane, n-heptane, n-pentane, etc.), which usually has a surface tension lower than 25 dyne/cm at 25 ˚C; above this number the asphaltene becomes soluble in fluid (e.g., pyridine, toluene, benzene, etc.) [26,27]. Asphaltene solubility may decrease if resins are preferentially dissolved in the oil or solvent is added [3]. Hence, solvent selection based on application temperature and pressure values is one of the challenges in designing solvent-based processes.

Several studies related to pressure depletion processes showed that asphaltene solubility depends on oil composition, temperature, pressure, and solvent power. At high pressure conditions, the effects of pressure and oil composition are greater than the effect of temperature [14,15,22]. The effect of pressure on asphaltene flocculation is mostly placed at a pressure greater than the fluid saturation pressure and that maximum flocculation takes place at the saturation point [10,14,15,18, 22]. Almehaideb [2] found that the increment of pressure from 101.31 kPa to 19,305 kPa decreases the asphaltene precipitation, however, from 24,131.6 kPa to 37,921.2 kPa the asphaltene precipitation increases because the values are closer to the saturation point of the fluid. On the other hand, Hilderbrand and Scott [16], Hirschberg, et al. [17], and Andersen and Speight [3] showed that asphaltene precipitation depends on the temperature and pressure ranges of operation, not only in the pressure. They concluded that asphaltene solubility parameter decrease when the temperature and pressure start to decline.

Carbon number for the solvent is also an important parameter in this process. The refinery and pipe-line industries investigated on the best carbon number for deasphalting the crude oil for effective heavy oil/bitumen upgrading and transportation, respectively. Ferworn et al. [12], Hammami, et al. [14,15] and Speight [26] observed that when the carbon number of the solvent decreases, the asphaltene flocculation and particle size increases. For example, asphaltenes and resins are insoluble in propane and butane and as a consequence of this, those solvents precipitate the two most polar compounds from crude oil (asphaltene and resin) [3,5,6]. On the contrary, n-heptane has a lower capability in the precipitation of the heavy ends, which results in less viscosity reduction compared to propane and butane [3,6].

Porous medium studies found that organic deposition (asphaltene and resins) takes place in the reservoir. Subsequently, cluster formations from this organic deposition can change the rock surface and permeability of the reservoir. However, it has not been clear until now how organic deposition plugs the porous median and how the organic deposition may be avoided or minimized using optimal operational conditions and different types of solvent. Redford and Mckay [23] concluded that the use of solvents (propane and n-pentane) and steam injection in highly asphaltic crude, such as Albertan bitumen, does not lead to an appreciable loss in permeability. Butler and Jiang [8] studied the oil production effect after injecting solvents at 21˚C to 27 ˚C and 206 kPa to 2068 kPa (butane or propane mixtures with a non-condensible gas, methane) and concluded that a high-temperature, high-pressure, and high-solvent/ oil ratio increases oil production. They also reported a higher recovery factor using propane than butane or a mixture of both. Haghighat and Maini [13] carried out experiments using propane and butane as solvents at room temperature and at a pressure range of 750 kPa to 850 kPa. They concluded that oil production with both solvents was reduced due to asphaltene deposition on the rock surface. Moreno and Babadagli [19,20] observed an increase in heavy-oil production when the carbon number of the solvent increased from C_3 to C_{15} due to the asphaltene solubility effect.

The solvent injection process can be an efficient process if the optimal type of solvent is utilized and ideal operational conditions are created. The solubility of fluid is the key parameter to developing this technology. As seen above, most of the studies on solvent dissolution capability of asphaltenes focused on different pressure conditions. Temperature is also a critical factor, especially in Canadian heavy-oil systems as the pressures in these reservoirs are rather low due to shallowness and solvents had to be used with steam for a more effective and efficient process. Therefore, it is critical to determine the role of pressure and temperatures that are compatible with this kind of heavy-oil reservoirs for different solvent types to determine the ideal solvent for heavy-oil recovery at elevated temperatures.

In order to understand the behaviour of the asphaltene precipitation and flocculation (agglomeration) in the fluid when the operational conditions, solvent type, and oil type are changed, experiments were carried out using an optical pressure, volume, and temperature (PVT) cell at diverse pressures (1,378 kPa to 2,068 kPa), and temperatures (40 °C to 120 °C) for two types of heavy-oil (8.6 ˚API and 10.28 ˚API). The asphaltene flocculation was calculated for the different operational conditions and the agglomeration and cluster formation were evaluated under the optical microscope. In order to establish the optimal injection conditions, the thickness measurements of deposited asphaltene from solvent displacement experiments for the same temperature and pressure ranges and solvent types were carried out under the focused ion beanscanning electron microscope (FIB/SEM). The PVT cell and porous medium experiments were compared and the optimal operational conditions were established. The PVT cell experiment results were observed to be fundamentally important to explain the plugging formation in the reservoir at different operational conditions.

Experimental

Materials

The asphaltene precipitation from two heavy-oil samples, taken from two different fields located in Alberta, Canada was conducted using three n-alkane type solvent (C_3H_8, C_6H_{12} and $C_{10}H_{22}$). The purities of n-alkanes used as precipitants were 99.5wt%, 99.9wt% and 99.6wt%. Correspondingly, the standard test method for the determination of asphaltenes (n-heptane insoluble) in crude petroleum and petroleum products (IP-143) was followed to determine the original asphaltene content of the two oil samples **(Table. 4-1)**. In addition, the carbon number distribution from both heavy oil samples was determined using the boiling point distribution of crude oil and vacuum residues (ASTM D7169) (**Figure 4-1**). The envelopes from the dead oil are also presented in **Figure 4-2**. Other important properties of the heavy oil samples, including elementary analysis (CHNS), asphaltene precipitation (*n*-heptane 99.4wt% pure), API gravity, and SARA analysis, are presented in **Table 4-1**.

Table 4-1: Heavy oil properties from two different oil samples (A and B)

Heavy Oil properties-ASTM D2007, IP 143 and ASTM D2549		
	Oil sample A	**Oil sample B**
Saturates,wt%	17.24	19.45
Aromatics,wt%	38.60	45.60
Resin,wt%	32.66	25.34
Asphaltene,wt%	11.50	9.60
Heavy Oil Elementary Analysis-ASTM D7578		
Carbon,wt%	84.45	81.92
Hydrogen,wt%	9.731	10.31
Sulfur,wt%	3.715	3.536
Nitrogen,wt%	0.553	0.6
Asphaltene Elementary Analysis-ASTM D7578		
Carbon,wt%	82.06	79.6
Hydrogen,wt%	7.957	7.095
Sulfur,wt%	7.431	8.22
Nitrogen,wt%	0.946	1.47
API Gravity at 15.5˚C		
˚API	8.67	10.28
Density [g/cm^3]		
25˚C	1.003	0.9919
40 ˚C	0.9959	0.9767
70˚C	0.9774	0.9503
Viscosity [cP]		
25˚C	87651	20918
40˚C	13298	3571
70˚C	1450	421.3

	Oil sample A	Oil sample B
Components	Compositions (wt%)	
C_{10}	0	0.6
C_{11}	0.83	0.73
C_{20}	13.48	20.01
C_{25}	7.21	10.49
C_{30}	6.48	9.27
C_{35}	5.03	7.03
C_{40}	4.21	5.69
C_{50}	5.76	8.06
C_{60}	4.18	5.69
C_{70}	2.87	3.89
C_{80}	1.82	2.59
C_{90}	1.01	1.47
C_{120}	7.22	0.69
C_{120+}	39.9	23.77
Total mass, wt%	100	100

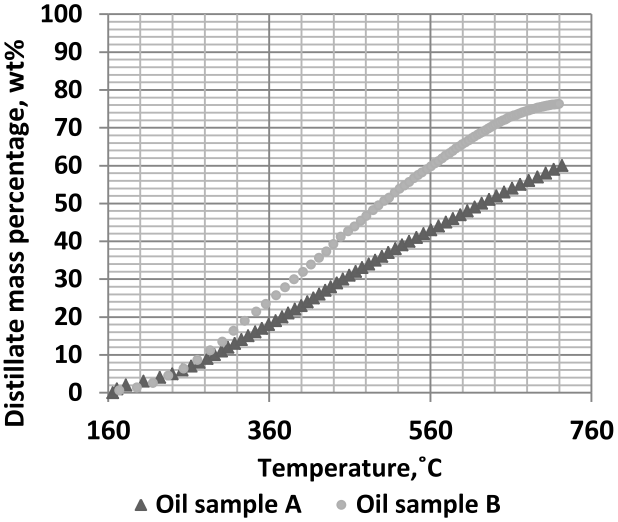

Figure 4-1: Carbon number distribution of the heavy oil samples A and B determined using the boiling point distribution of crude oil and vacuum residues (ASTM D7169).

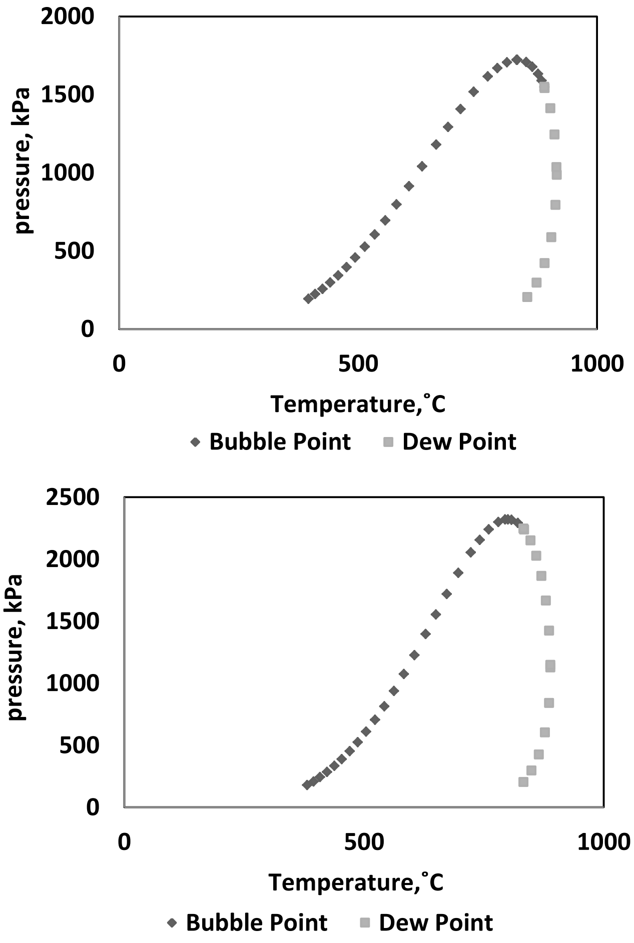

Figure 4-2: Heavy oil A and B envelopes from the dead oil.

Experimental Apparatus

The asphaltene precipitation at different operational conditions was carried out using a high-pressure and high temperature optical PVT cell and high-pressure and high-temperature filter **(Figure 4-3)**. The visual PVT cell (100cc, 15ksi,H_2S) can operate up to 15,000 psi and 200 ˚C. Also, PVT cell pressure, temperature, and volume can be controlled using software. A long focus CCD (charge-coupled device) level measurement device, which has a high resolution image (NTSC to 768 x 494 pixels), was used to for visualizing the experiments. The capture of this visualization was recorded using an Aver-Media DVD EZ-Marker 7. In order to establish higher phase equilibrium, the PVT has a magnetic mixer. The high-pressure and temperature stainless steel filter was incorporated in the PVT cell system in order to do the asphaltene filtration (2.5μm) at each operational condition. In addition, a vacuum pump was connected to the end line of the filter to fluid down the heavy oil sample.

The fluid injection section consists of two piston-cylinders: one from the heavy oil injection and the other from a light hydrocarbon solvent injection. The piston-cylinder from the heavy oil injection was enveloped with a heating tape (the temperature controller was set to 50 ˚C) to increase the heavy oil mobility due to the excessively high viscosity value at atmospheric conditions (Table. 4-1). The pumping of the two fluids was achieved using a mechanical pump for the heavy oil and a syringe pump for the light hydrocarbon.

Experimental Methodology

Optical PVT Cell Experiments

Initially, the optical PVT cell shown in Figure 4-3 was cleaned with toluene and vacuumed for 20 minutes. Then, temperature was stabilized in the PVT cell prior to conducting the heavy oil injection test (from 40 ˚C to 120 ˚C). Meanwhile, the heavy oil sample was heated for five hours at 50 ˚C using heating tape outside of the closed piston-cylinder in order to reduce the fluid viscosity prior to the injection. After the temperature stabilized, the heavy oil was injected and left over night at the test conditions. The next day, the solvent injection was started and the pressure injection was controlled at the operational conditions. The mixing of the fluids was achieved using the PVT magnetic mixer, and then the phase equilibrium was established. The volume percentage of heavy oil and solvent injected was 0.16% v/v and 0.84% v/v, respectively. The sample was left at the PVT cell for about eight hours. During this operation, the phase behavior of the sample was recorded using the CCD level measurement and Aver Media 7. When the experiment was completed, the multiphase sample was separated for approximately one hour using high pressure and high temperature filter equipment, which contained two Whatman filter grade 42: 2.5μm. A vacuum pump was used to improve the filtration of this heavy mixture (Figure 4-3).

When the full separation between the liquid and solid was achieved, the filter was opened and asphaltene in the filter was taken out. The unclean asphalt was cleaned using the Soxhlet extraction technique with n-heptane to eliminate the maltenes present in the sample. The PVT cell and lines were cleaned using an asphaltene soluble solvent (toluene) and then the solvent-asphaltene solution was separated using a rotary-evaporator apparatus. The distilled sample was cleaned with pure n-heptane to extract the maltenes from the sample. The asphaltene collected from the lines was accounted for in the asphaltene mass balance. To finalize the procedure, the upgrading heavy oil without the most polar compounds was analyzed and the asphaltene flocculation in the PVT cell was visualized under the optical microscope (Figure 4-3).

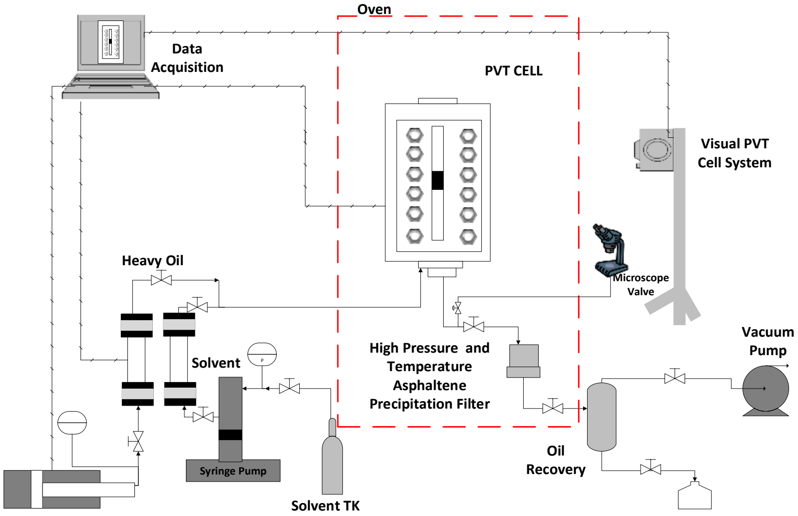

Figure 4-3: Optical PVT cell: Asphaltene flocculation flow diagram setup.

Asphalene Flocculation and Organic Deposition Visualization

The flocculation of asphaltene particles was visualized using a high resolution microscope HBC A/C - Zeiss Axiostar Plus. In addition, cross sectional morphology of coated organic depositions was inspected using a Hitachi NB5000 (FIB/SEM) dual beam system. The glass bead samples from the injection point were coated with about 150 nm Au by sputtering deposition. A protection W layer (about 1 µm thick) was deposited prior to FIB milling. Three cross sections at different locations were milled down to the glass beads by 40 kev Ga beam, and inspected by SEM.

Results and Discussion

Two heavy oil samples obtained from Alberta, Canada with different boiling point distributions, SARA, hydrogen/carbon, and viscosity values were tested in the optical PVT cell at different pressures (1378 kPa to 2068 kPa), and temperatures (40 °C to 120 °C). The asphaltene solubility decreased in the oil samples using propane, n-hexane, and n-decane - all light hydrocarbon solvents (**Figures 4-4 to 4-5**). The solubility was expected to decrease more using propane than the other light hydrocarbons. This is due to the fact that propane decreases the solubility of asphaltene and resin from crude oil as asphaltene and resin are insoluble in liquid propane, but resin is soluble in n-hexane and n-decane.

In the present study, we observed that temperature, pressure, oil composition, and solvent type were the most important factors controlling asphaltene flocculation. However, as explained in the "Introduction" section, disagreement about the temperature factor effect exists. It is generally believed that temperature is negligible with respect to oil composition and pressure effects. It is the fact that previous experience is based on high pressure systems with limited temperature variations. In these types of situations, pressure effect may dominate over the temperature effect. In our systems presented here, temperature range is wider due to involvement of heat injection along with the solvent and pressure range being much lower due to the shallowness of typical Albertan sand depositions.

On the other hand, thermodynamic models used to calculate the asphaltene precipitation points at a fixed saturation pressure showed that temperature effect is critical on the process. The Hildebrand solubility parameter equation explains the important effect of the reversibility of asphaltene flocculation when the temperature increases. Also, the Asphaltene Flory-Huggis-Zue equation state includes the temperature parameter effect. As a result, the present research provides supportive results, which are shared below, to those previous observations.

Asphaltene Flocculation by Temperature and Pressure Influence

The mixture of heavy oil and propane, as a paraffinic solvent, showed that temperatures below the dew point from pure propane give a uniform liquid phase sample between solvent and heavy oil. However, above the dew point, the vapor-liquid equilibrium was observed (Figure 4-4). The optical PVT cell camera showed the two phase separations (V1-heavy oil and V2-light heavy oil compounds plus propane) and the lower mixture between propane and heavy oil at this point was visualized due to the thermal expansion of gas. The Hildebrand solubility parameter equation describes the miscibility of solvents using the solubility parameter, δ $(\mathrm{Mpa})^{1/2}$, which is defined as $(\Delta E^{vm}/V_m)^{1/2}$. As the equation indicates, density (ρ) and molecular weight (Mw) are two important parameters in the solubility parameter calculation ($Vm=Mw/\rho$) (ΔE is the internal energy of vaporization and, V_m is the molar volume of the liquid) [16,17].

Propane is a highly compressible fluid and therefore, when the temperature goes from 40 ˚C to 60 ˚C, the asphaltene solubility increases as lower asphaltene precipitation is present at this point (Figures 4-4 to 4-5). The asphaltene flocculation behaviour, with respect to temperature increments, was similar for both heavy oil samples (8.67˚API and 10.28˚API). Another important effect of using propane on asphaltene flocculation was the pressure increment. Higher pressure gives lower asphaltene flocculation, which indicates that asphaltene dispersion into the oil increases when pressure is increased (Figures 4-4 to 4-5). Earlier studies on asphaltene flocculation at higher pressures and constant temperatures showed that asphaltene solubility increases with increasing higher pressure. Note that our pressure range is much lower, as emphasized before, due to existing reservoir conditions in shallow oilsands in Alberta.

n-Hexane and n-decane experiments were carried out below the boiling point of the pure solvent due to the high temperature required to obtain the vapor phase (Figure 4-4). The two solvents showed a similar influence of temperature and pressure as propane. Due to the complexity of visualization of heavy-oil through the optical PVT cell, the asphaltene particles were further visualized in the glass tube when the fluid sample was pushed down very slowly on the filtration system. As a result, higher agglomerate of asphaltene particles was observed in the glass tube when the temperature and pressure were lower. In addition, asphaltene filtration results showed that lower asphaltene precipitation was obtained at higher temperatures (120 ˚C) and higher pressures (2068 kPa) for both solvents and heavy oils (Figures 4-4 to 4-5). Temperature effect was more notable than the pressure effect on asphaltene flocculation due to the fact that no density change was present. The aforementioned temperature and pressure trends were also observed by Akbarzadeh, et al. (2004) when Athabasca bitumen was diluted with propane, butane, and n-heptane at temperatures from 0 ˚C to 50 ˚C and pressures from 100 kPa to 6900 kPa.

Asphaltene Flocculation by Oil Composition Changes

The solubility parameters for the heavy oils were measured to be 19.85 $\text{MPa}^{1/2}$ (oil sample A) and 19.607 $\text{MPa}^{1/2}$ (oil sample B), which is consistent with the previously reported of 19.1 $\text{MPa}^{1/2}$ [4]. The solubility parameters from the mixture of heavy oil and solvent were calculated in order to explain the asphaltene flocculation results (Figure 4-6). Buckley, et al. [6] solubility parameter correlation (δ=52.042F_{RI} + 2.904) was used to calculate the solubility parameter as a function of the refractive index. The solubility parameter of the mixture of heavy oil with n-hexane and n-decane were calculated (Figure 4-6). As a result, less solubility parameter was calculated for n-hexane than for n-decane because the higher asphaltene flocculation concentration was present in the mixture with n-hexane (n-C_6) than with n-decane (n-C_{10}) (Figure 4-6). This was also confirmed by Wang and Buckley [28] using different types of solvents. They concluded that n-C_{15} has a higher solubility parameter than n-C_7 at 25 ˚C, which supports our observations in the present paper.

The API gravity of the upgraded oil was also measured (**Table. 4-2**). The results confirm that higher asphaltene flocculation was found with propane than n-hexane, and n-decane because, as indicated, lower density of heavy oil treated with propane than of the other two solvents (Table. 4-2). As a result, the solubility mixing parameter is less when propane is used as a solvent rather than n-hexane and n-decane.

Asphaltene agglomeration may change from one oil sample to another. The properties and oil composition of the two typical Canadian oil samples are presented in Table 4-1 and Figures 4-1 and 4-2. The SARA analysis shows that more saturate and aromatic compounds are present in oil sample B than in oil sample A. Consequently, asphaltene destabilization may be more sensible for oil sample B due to the fact that the oil has lighter compounds (Figures 4-1 and 4-2). In Figure 4-5, the asphaltene flocculation concentrations for both oil samples are presented. The results show that asphaltene flocculation has slight similarities in the precipitation trends with respect to temperature, pressure, and solvent type. However, asphaltene flocculation values were lower with oil sample B, which has an original asphaltene content of 9.6 %wt, compared to oil sample A (11.5wt%). Zanganeh, et al. [29] carried out an analysis of asphaltene agglomeration using two types of crude oil. They concluded that heavy oil has more asphaltene precipitation because the bigger molecules with more aromatic rings can aggregate each other and flocculate easily. On the other hand, more rings increase the chance of more contact between the molecules and the likelihood of finally forming a molecular bond.

To cross check the observations obtained from the PVT experiments against the asphaltene deposition porous media, a series of heavy oil displacement experiments were performed using the same oil-solvent pairs at the identical conditions (pressure and temperature). The details of the experimental set-up and the recovery behaviours when different solvents are used can be found in Moreno and Babadagli [19,20]. Here, the images obtained after the experiments (asphaltene in the produced oil and deposited on the surface of glass beads) are included (Figures 4-7 to 4-9). In these experiments, more asphaltene deposition on the glass bead surface was observed with the heaviest oil sample (A), which had a higher end distillation point than oil sample B (Figure 4-1). The images from SEM of the glass beads also showed that more organic deposition would occur with propane than distillate hydrocarbon (a mixture of C_5-C_{13} with 80-20% alkanes-aromatics ration). However, oil viscosity reduction was lower with the distillate hydrocarbon than with propane, while propane improved oil properties (Table 4-2) due to high asphaltene precipitation power (16%wt) (Figure 4-5). Obviously, this left a higher concentration of organic deposition on the rock surface due to the agglomeration and cluster formation into the porous medium (Figures 4-7 to 4-9). **Figure 4-7** shows the asphaltene deposition quantitatively. **Figures 4-7 and 4-8**, display the images of asphaltene flocculation deposition on the rock surfaces with comparison to the PVT observations. Similar to sandpack results, the PVT cell experiments showed that lower asphaltene flocculation and cluster formations were detected with oil sample B (10.2˚API) than oil sample A (8.6˚API) (Figures 4-4 to 4-9). In addition, the PVT cell studies showed less asphaltene flocculation and agglomeration with the heaviest hydrocarbon solvents (Figures 4-7 to 4-8). This also confirms that PVT cell studies integrated with the porous medium experiments can be correlated to understand the pore plugging effect.

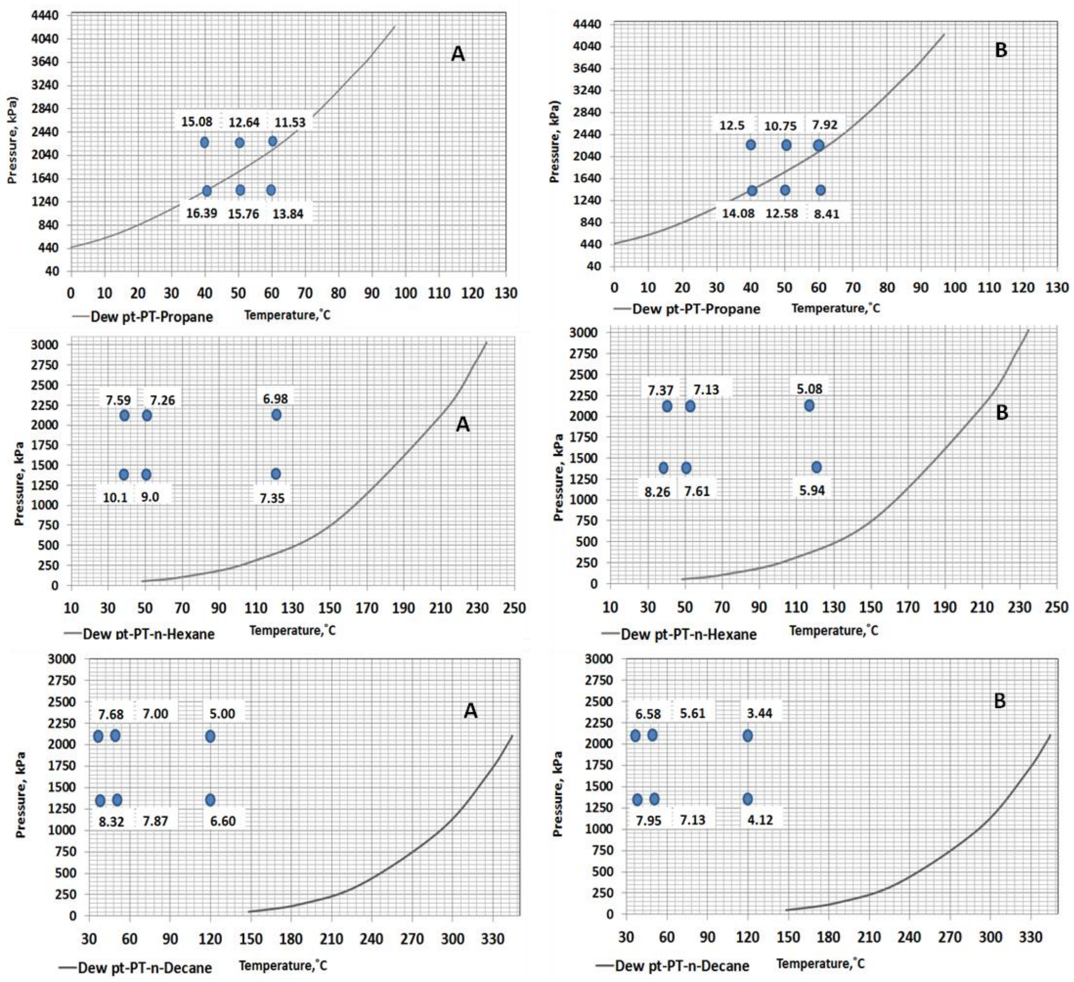

Figure 4-4: Phase envelope for propane, n-hexane, n-decane (pure components): The values below or above the dew point are the asphaltene weight percent precipitated from both heavy oil samples A and B for each solvent type.

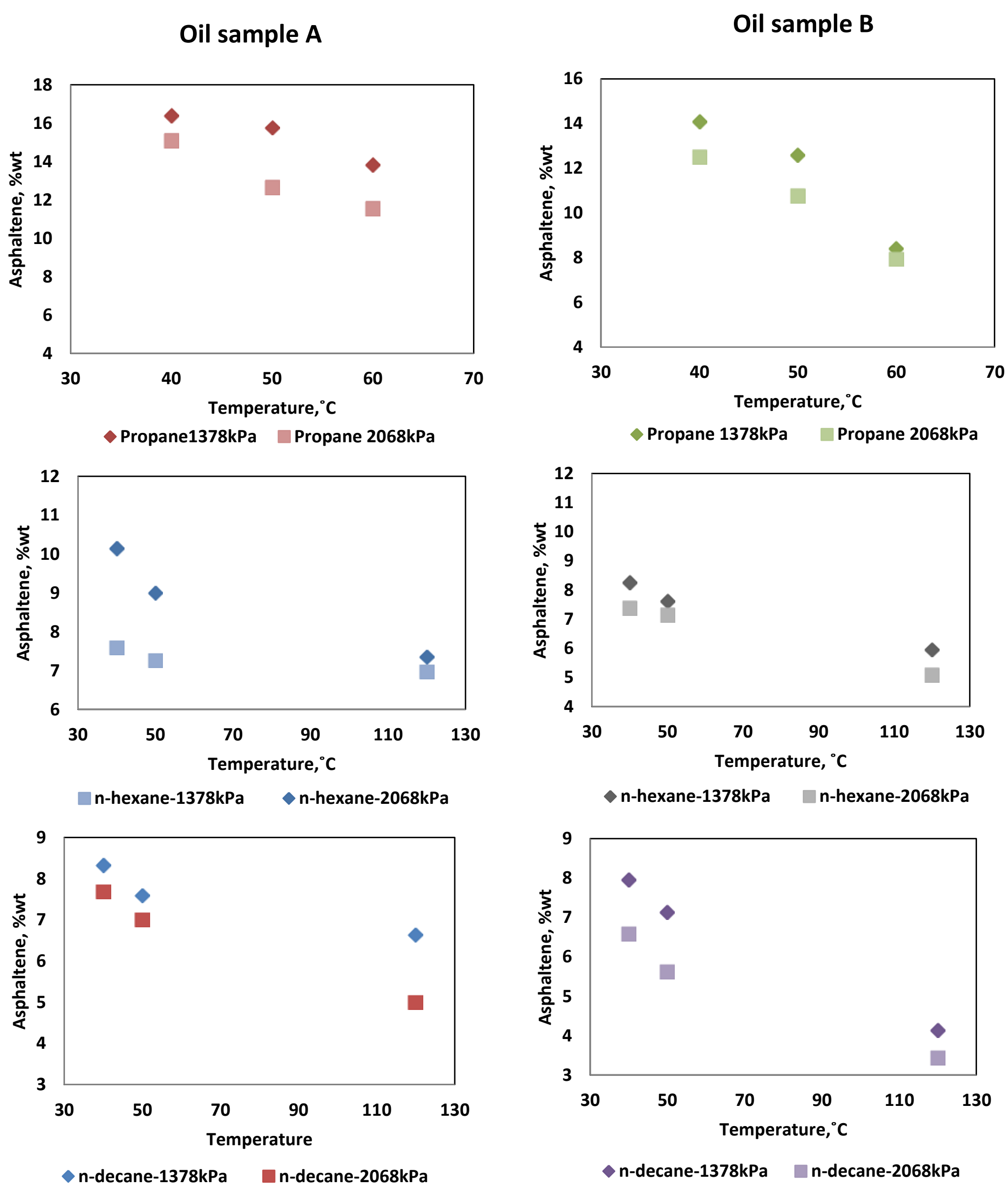

Figure 4-5: Asphaltene precipitation weight percent content at different operational conditions, oil composition types (Oil A and B) and paraffin solvents (propane, n-hexane and n-decane).

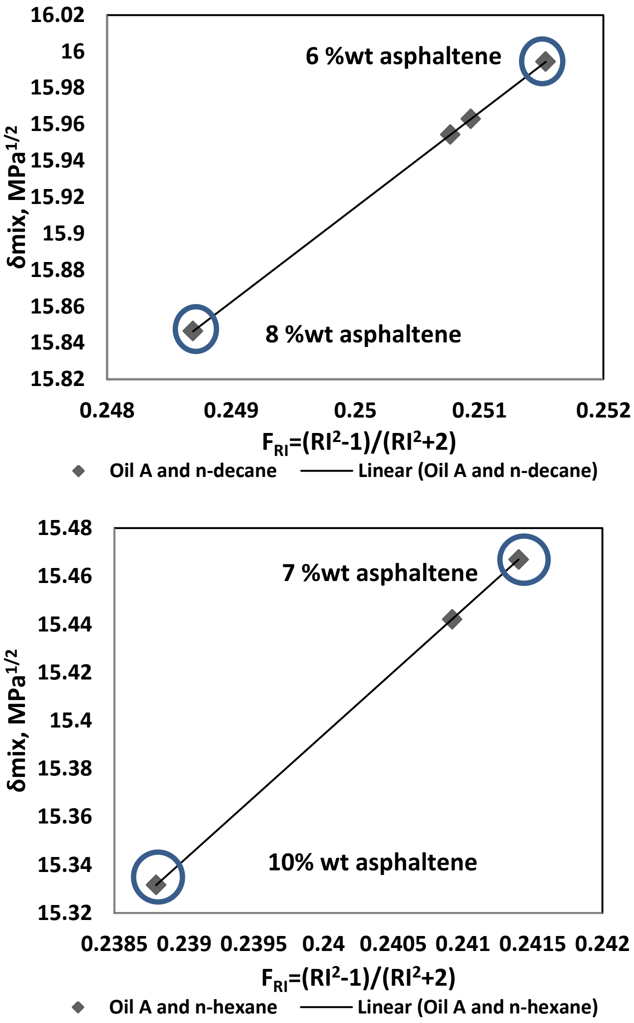

Figure 4-6: Solubility parameter of mixture δmax vs. fractional refractive index FRI for heavy oil and asphaltene in n-hexane and n-decane.

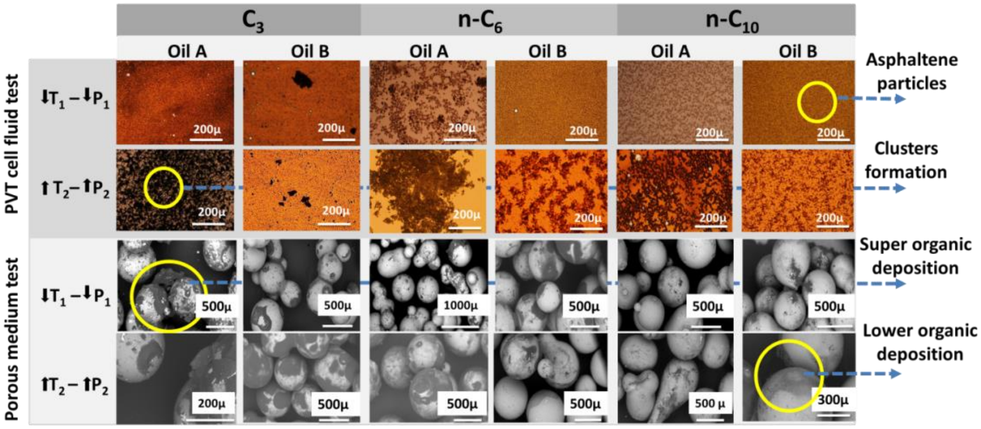

Figure 4-7: Influence of pressure, temperature, oil composition (oil sample A and B) and solvent type on asphaltene agglomeration in the fluid and porous medium.

Table 4-2: Deasphalted oil density after asphaltene has been removed

Solvent type	Propane	n-hexane	n-decane
Deasphalted oil-A (˚API)	14.5	12.53	10.17
Deasphalted Oil-B (˚API)	15.91	15.26	11.24

Asphaltene Cluster Formation in the Fluid and Rock Surface by Temperature and Pressure Influence

Asphaltene flocculation for the two Alberta heavy oil samples is lower at higher temperatures and pressures as discussed above and graphically presented in Figures 4-4 through 4-6. However, cluster formations need to be analyzed qualitatively under several operational conditions. Asphaltene cluster formation on the rock surface is one of the main challenges with the solvent-based process due to permeability reduction and wettability alteration. In addition, asphaltenes are positively charge and may be adsorbed on rock surface depending of the type of clay and minerals from reservoirs [9]. Hence, the fluid liquid sample (heavy oil and solvent) was analyzed under the optical microscope. The sample was taken from a small valve located before the asphaltene filtration point (Figure 4-2) in order to visualize the asphaltene flocculation in the fluids (oil-solvent mixture). The optical microscope image was evaluated instantly to avoid asphaltene agglomeration changes due to room conditions. Results showed that higher temperatures and higher pressures increase the asphaltene cluster formation (Figures 4-7, 4-8 and 4-9). Images from the microscope (Figures 4-7 and 4-8) showed that cluster diameters in the fluid using propane as a solvent with the heaviest oil can randomly vary from 600μm to 200μm. These values are from 500μm to 150μm and 300μm to 50μm for n-hexane and n-decane, respectively, while the cluster diameter was equal/below 100μm for the distillate hydrocarbon.

Similar trends were also reported by Nielsen, et al. [21]. They investigated the temperature and pressure tendencies of asphaltene particle sizes using bitumen sample from the Cold Lake area (Canada), which had high asphaltene content (pentane-insoluble 21.8%). They observed that “super” agglomerates were established at temperatures around 80 ˚C and higher, which was attributed to the softening and adhesion of asphaltene particles. They also found that an increase in pressure yielded an increase in the mean asphaltene particle size for the Cold Lake bitumen sample. On the other hand, Soulgani, et al. [25] carried out experiments modeling the formation and concluded that the surface deposition rate increases with increased temperature and asphaltene concentration. Zanganeh, et al. [29] also concluded that as the temperature increases using carbon dioxide as a solvent, the asphaltene diameter particle increases. All the previous studies also confirmed the formation of asphaltene clusters at high temperatures and pressures, as presented in Figures 4-7, 4-8 and 4-9.

Asphaltenes are very polar compounds; consequently, the most important attractive force between asphaltene molecules is that arising from dipole-dipole interactions [9,12,14]. Asphaltene may be regarded as condensed polynuclear aromatic compounds, which possess semiconductor-type conductivity. Evdokimov and Losev [11] carried out an investigation of the electrical conductivity and dielectric properties of solid asphaltenes. They found that conductivity increased at higher temperatures. They also concluded that the low-temperature “Cold” phase appears to be controlled by interactions between polar side chains of asphaltene molecules, while in the high-temperature “Hot” phase, interaction involving flat polyaromatic structures in asphaltenes became more important. Consequently, higher temperatures and pressures increase the super agglomeration.

Previous experiments conducted by Moreno and Babadagli [19] in a sandpack core holder system showed that organic deposition (mainly asphaltene and resin) affect oil production and the homogeneous rough surface. According to those experiments, organic deposition was found to be lower using hydrocarbons with a higher carbon number. As a result, oil production was increased due to the high asphaltene solubility in the oil sample. In the present study, organic deposition morphology was evaluated under the scanning electron microscope (S-3000N) and the results are displayed in Figures 4-7 and 4-8. As seen, partial organic deposition was present in some beads, while total organic deposition was detected in other beads. Consequently, a wettability mixture is presented from water-wet to partial oil-wet surface as also observed in the earlier works by Civan [9] and Sayyad, et al. [24].

In addition to these images, the peak organic deposition distance for both heavy oil samples and four light hydrocarbon (propane, n-hexane, n-decane and distillate hydrocarbon (C_4 to C_{15}) solvents was calculated using the focused ion beam-scanning electron microscope (FIB/SEM) apparatus (Figure 4-9). For each glass bead sample, three different points were cut using the ion beam and imaged in the SEM (Figure 4-9). A film of 50 nm Au was proved to be enough to protect the asphaltene surface from being modified by the Ga beam. The three cutting points consisted of the lower, middle and higher peaks to ascertain the different levels of surface roughness that could be present on the rock surface after the solvent-based process was applied (Figure 4-9 and Table 4-3). The correction of the tilt ($\theta = 58^\circ$) was done previous to calculating surface parameters (Appendix 4-B). The calculations of surface roughness parameters are shown in **Table 4-3**. The root mean square (RMS) and arithmetic mean square (Ra) of the surface roughness were calculated based on the equation presented in Appendix 4-B. In addition, the confidence interval was 95% (margin error) and the lower limit and upper limit were calculated using the addition or subtraction of the margin error from the arithmetic mean value.

The organic deposition cutting samples are shown in Figure 4-9. Higher thickness distance on the bead surface was observed for the propane case of the heavier oil (sample-A), which was 3.621µm. This value was estimated to be 1.529µm for crude oil B while with n-hexane as solvent, the thickness was 1.936µm for the oil sample A and 1.479 for the oil same B, respectively. Moreover, n-decane and distillate hydrocarbon showed the lowest thickness values. The thickness distances for n-decane were 1.588µm and 1.193µm for oil samples A and B, respectively. The thickness value for the distillate hydrocarbon was 0.546µm (546 nm) (crude oil A) to 0.466µm (466 nm) (crude oil B). The thickness results perfectly explained how a powerful solvent precipitator increases the possibility of pore plugging and permeability reduction. As a result, viscosity reduction can increase oil mobility in the initial production stages, but can no longer maintain a high production rate due to the formation damage. These organic deposition thickness results showed that propane, when used as solvent, can plug the smallest pores of the reservoir (see the circled asphaltene deposition in Figure 4-8).

To summarize, the PVT experimental data and thickness calculations from porous medium experiments were comparatively presented in this paper. Fluid agglomeration experiments concluded that super agglomeration is more likely to take place with propane than using a higher hydrocarbon number as solvent. In addition, asphaltene particle size is higher when using the heaviest oil samples and higher operation conditions due to the polynuclear aromatic in the oil sample. Overall conclusion from PVT studies can be utilized in porous medium solvent-based process studies. Further, solubility parameter can explain how increased asphaltene flocculation can decrease the miscibility of the fluid and cause a decrease in the rate of oil production. In addition, the organic deposition distance measurement was in total agreement with the results of the PVT cell experimental data.

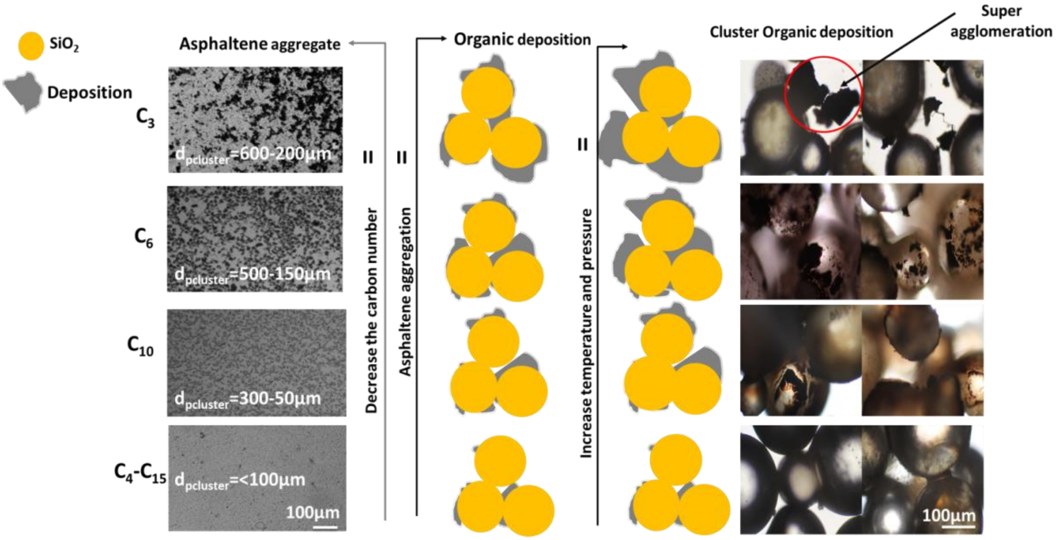

Figure 4-8: General diagram of asphaltene agglomeration in the fluid and porous medium: after solvent-based process with propane, n-hexane, n-decane and distillate hydrocarbon.

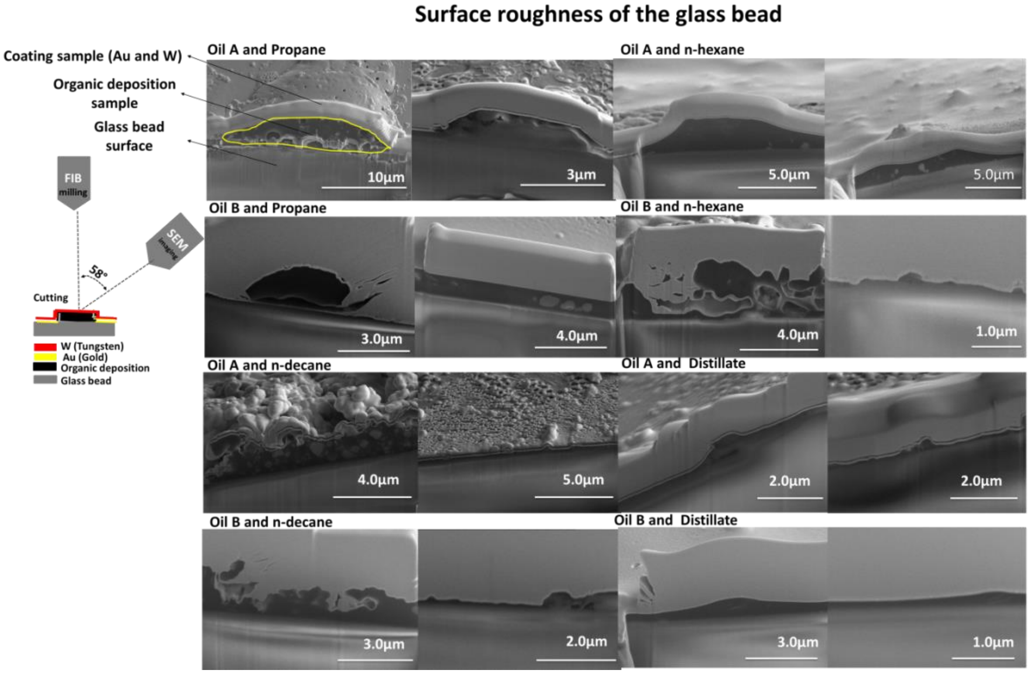

Figure 4-9: Surface roughness determination under the FIB/SEM from organic deposition after solvent based process from heavy oil A and B and four different solvents (propane, n-hexane, n-decane and distillate hydrocarbon).

Table 4-3: Surface roughness of the glass beads after organic deposition: from heavy oil A and B and four different solvents (propane, n-hexane, n-decane and distillate hydrocarbon)

FIB-SEM Cutting Points	Ra	Standard deviation	Margin error	Lower limit	Upper limit	RMS
Oil A and Propane						
Lower Point (µm)	0.140	0.029	0.027	0.113	0.167	0.143
Middle Point (µm)	0.757	0.169	0.142	0.615	0.898	0.773
Upper point (µm)	3.611	0.102	0.095	3.978	4.167	3.621
Oil B and Propane						
Lower Point (µm)	0.837	0.045	0.030	0.807	0.866	0.838
Middle Point (µm)	0.876	0.257	0.238	0.593	1.069	0.866
Upper point (µm)	1.521	0.163	0.136	1.385	1.658	1.529
Oil A and n-hexane						
Lower Point (µm)	0.868	0.058	0.054	0.916	1.024	0.971
Middle Point (µm)	0.888	0.146	0.098	0.790	0.987	0.899
Upper point (µm)	1.924	0.228	0.191	1.734	2.115	1.936
Oil B and n-hexane						
Lower Point (µm)	0.185	0.233	0.156	0.029	0.341	0.289
Middle Point (µm)	0.604	0.223	0.206	0.199	0.612	0.456
Upper point (µm)	1.457	0.265	0.222	1.236	1.679	1.479
Oil A and n-decane						
Lower Point (µm)	0.211	0.080	0.074	0.252	0.400	0.334
Middle Point (µm)	1.313	0.296	0.199	1.114	1.511	1.343
Upper point (µm)	1.578	0.190	0.159	1.418	1.737	1.588
Oil B and n-decane						
Lower Point (µm)	0.128	0.061	0.041	0.087	0.168	0.140
Middle Point (µm)	0.333	0.084	0.077	0.286	0.440	0.372
Upper point (µm)	1.187	0.122	0.102	1.085	1.289	1.193
Oil A and Distillate						
Lower Point (µm)	0.088	0.022	0.015	0.073	0.103	0.090
Middle Point (µm)	0.267	0.064	0.059	0.250	0.367	0.314
Upper point (µm)	0.546	0.010	0.009	0.537	0.554	0.546
Oil B and Distillate						
Lower Point (µm)	0.141	0.022	0.015	0.126	0.155	0.142
Middle Point (µm)	0.273	0.048	0.045	0.235	0.324	0.283
Upper point (µm)	0.460	0.077	0.064	0.396	0.524	0.466

Conclusions

Two different types of heavy oil samples and three different solvents (propane, n-hexane, and n-decane) were used in asphaltene flocculation experiments carried out using an optical pressure, volume, and temperature cell. In addition, calculations regarding the thickness of organic deposition (mainly asphaltene and resins) from porous medium experiments were done using a FIB/SEM apparatus. The experiments were carried out to identify the fluid behaviour of asphaltene agglomeration and organic deposition agglomeration on the rock surface. The main conclusions out of this research are as follows:

1. Asphaltene flocculation and cluster formation with two different oil compositions were determined. Oil sample A, which had a higher viscosity and asphaltene content (87651 cP at 25 ˚C and 11.5 wt%), showed higher asphaltene agglomeration and increased cluster formation when the oil sample was diluted with a n-type of paraffin. On the other hand, oil sample B, which had a lower viscosity and asphaltene content (20918 cP at 25 ˚C and 9.5 wt%) compared to oil sample A, showed significantly less agglomeration and less cluster formation than oil sample A. As a result, asphaltene agglomeration and cluster formation can be determined from the properties of the heavy oil sample.

2. The influence of temperature and pressure was investigated for both heavy oil samples (A and B). The results showed that asphaltene concentration increased at lower temperatures (40 ˚C) and lower pressures (1378 kPa) for both crude oil samples. However, experimental data from the propane case showed that when the temperature was increased to 60 ˚C at 1378kPa or 2068 kPa, asphaltene concentration decreased due to the solubility increment. In addition, the same asphaltene concentration results were noticed for n-hexane and n-decane when used as solvents at 120 ˚C at 1378 kPa or 2068 kPa. The pressure influence also showed remarkable influence at isothermal conditions. Asphaltene dispersion was more at higher pressures (2068 kPs) than at lower pressure (1378 kPa) for all solvent types.

3. The effect of different types of light hydrocarbons as a solvent on asphaltene agglomeration was also studied. Previous studies concluded that asphaltene concentration increases and oil viscosity reduction decreases when lighter hydrocarbons are used. This was also found to be the case in this study when both types of crude oil were combined with propane, n-hexane, and n-decane as solvents. However, higher asphaltene precipitation improves oil properties, creating a higher possibility of porous plugging and permeability reduction. This was confirmed after the thickness calculation distance on the glass bead surface from both heavy oil samples and four different solvents (propane, n-hexane, n-decane, and distillate hydrocarbon (C_4 to C_{15}). The calculated thickness of the organic deposition showed that a thickness of 3.621μm can be present if propane is used as solvent, and 0.466 μm (466 nm) if distillate hydrocarbon is used. Consequently, higher oil mobility may be present at the earliest stages when using propane, but formation damage will likely occur during later stages.

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CHAPTER 5: MULTILAYER ORGANIC DEPOSITION ON THE ROCK SURFACE WITH DIFFERENT WETTABILITIES DURING SOLVENT INJECTION FOR HEAVY-OIL RECOVERY

This chapter was submitted as a paper for journal publication and under review.

Background

The use of a solvent-based recovery process increases heavy-oil production due to underground in-situ upgrading. During this process, viscosity reduction occurs through dilution of oil by mixing process. However, asphaltene precipitation may take place eventually resulting in organic deposition (maltenes and asphaltenes) in the reservoir. This characteristically causes a reduction in permeability through pore plugging and unfavorable wettability reversal. In this paper, two identical porous media (unconsolidated sandpacks) with a significant contrast in wettability were used to investigate these phenomena. The oil-wet and water-wet glass bead models were exposed to constant rate solvent injection (propane, n-hexane, n-decane, and distillate hydrocarbon). The thickness of the multilayer organic deposition was determined using focused ion beam (FIB/SEM) and scanning electron microscope (SEM). Three points from the models were analyzed to determine the level of asphaltene deposition and oil trapping (maltenes) on the surface of the glass beads and pore spaces. The results showed that the asphaltene migration through the sandpack model occurred. As a consequence of this, asphaltene deposition was observed at the middle and production points of the vertically situated sandpacks with an injection point at the top, in addition to accumulated oil trapping at the production -bottom- end. Moreover, elemental mapping from the organic deposition visualization was conducted using the energy dispersive X-Ray (EDX) analysis. Heteroatom elements were found in the sample along with carbon and iron elements.

Introduction

The use of light hydrocarbon solvents is a promising process to improve heavy oil recovery through reduction of its viscosity by in-situ upgrading. Asphaltene—the heaviest and most polar compound—is destabilized and separated from the heavy oil during this process [1-3]. Asphaltenes are insoluble in n-alkanes but soluble in aromatics [4, 5]. The asphaltene polydisperse molecules consist mostly of polynuclear aromatic ring systems bearing an alkyl side chain. Also, hetero-elements (nitrogen, sulfur, oxygen) and heavy metals (vanadium, iron and nickel) were identified in the asphaltene structures [4,5]. Resin constituents prevent asphaltene flocculation because they act as a peptizing agent as well as an aromatic hydrocarbon [1, 4, 5]

On the other hand, the equilibrium between asphaltene and oil can be affected by alterations in oil composition caused by changing temperature and pressure as well as injection of a paraffinic solvent [6-8]. Asphaltene agglomeration may increase as the carbon number of the hydrocarbon solvents is decreased (e.g., propane, butane, and pentane, etc.). Ferwon et al. [6] observed that the particle size becomes larger with n-pentane than with n-hexadecane. As seen, depending on the type of solvent used, asphaltene flocculation may increase or decrease.

Asphaltene flocculation is one of the main concerns when injecting solvents into reservoirs due to the multilayer effect it has on the rock surface. Organic deposition (maltenes and asphaltene) on the rock surface mainly increases the contact angle on the rock surface. Subsequently, the wetting preference of the rock surface can change from water-wet ($\theta<90$) to oil-wet ($\theta>90$) [9, 10]. Moreover, adsorption of the polar compounds may increase depending on the type of clay and minerals on the reservoir rock surface and/or the level of water salinity because the asphaltene is defined as a positively charged material while maltenes are known to be negatively charged materials [11-13]

The deposition of asphaltene on the rock surface will have a critical effect on wettability [14, 15]. In addition, Huang and Holm [16] reported that more oil was retained in core samples after carbon dioxide was injected into water-wet reservoirs than in preferentially oil-wet reservoirs. Yunan [17] and Huang and Holm [16] conducted miscible displacement experiments in water-wet and oil-wet systems. They concluded that residual oil recovery is more efficient in oil-wet rocks than in water-wet rocks. Rezaei et al. [18] carried out vapor extraction experiments in oil- and water-wet glass bead systems. The sandpack was saturated with Cold Lake bitumen, while n-pentane was injected as a solvent. They showed that the oil-wet system increased oil recovery by approximately 40% over the water-wet system. They also compared the fractional wet and oil-wet systems, concluding that the fractional wet system provides the same recovery factor as the oil-wet system. However, these experiments did not include the asphaltene deposition effect on the rock surface. Similarly, Agbalaka et al. [19] attributed a better oil production in the oil- wet system to the absence of water shielding in the oil-wet medium. Subsequently, the mass transfer was more enhanced by the oil-wet surface than the water-wet surface. In contrast, Dehghan et al. [20] concluded that heterogeneous reservoirs provide higher residual oil saturation by reducing the contact area and making it easier for the solvent to bypass the porous medium, causing the oil to be trapped. Consequently, they suggested that surface wettability may increase or decrease displacement efficiency.

Recently, Moreno and Babadagli [7, 8] observed that organic deposition takes place on the glass bead surface after testing different types of solvents. However, the asphaltene layer deposition was higher when propane was used as a solvent than when distillate hydrocarbon was used in an initially water-wet system. They concluded that asphaltene deposition is accompanied by maltenes (saturates, aromatics and resins) compounds on the rock surface, which makes a complex multilayer mixture.

Moreno and Babadagli [7, 8] did not assess the contact angle after organic deposition took place on the rock surface; however, Al-Aulaqi et al. [13] included this measurement in their research. They found that the contact angle was increased from $\theta=60$ to $\theta=140$ when the heaviest oil was used. Nonetheless, their results confirmed the findings of Moreno and Babadagli [7, 8] that more organic deposition was found on the rock surface when the heaviest crude oil was used. Further, temperature, pressure, and solvent type were found to potentially increase the contact angle [7, 8, 13].

In the present study, organic deposition on the rock surface included asphaltene (A) compound and maltenes, which by definition are saturates, aromatics, and resins (SAR) [11,12]. The SARA group type of the crude oil represents the fraction separation [1, 4, 5]. As seen through this literature analysis, asphaltene precipitation as multiple layers on the rock surface and its relation to the wettability state of the rock need further investigations. In the present study, the wettability effect on organic deposition was investigated using unconsolidated sandpack experiments and a multilayer thickness evaluation under a Focused Ion Beam (FIB) and Scanning Electron Microscopy (S-3000N-SEM) dual beam system (NB5000-FIB/SEM). The experiments were carried out using strongly oil-wet and strongly water-wet systems in order to compare the multilayer agglomerate on the glass bead. Residual oil saturation (maltenes) and asphaltene deposition on the bead surface were calculated for four different types of solvents (propane, n-hexane, n-decane, and distillate hydrocarbon). The level of residual oil saturation (maltenes) and asphaltene deposition was determined in three regions from a 13 cm height model. In addition, a scanning electron microscope (S-3000N) was used to visualize three different regions from the model.

Experimental Section

Sandpack Model

The solvent injection experiments were conducted in cylindrical unconsolidated sandpack systems. The physical model consisted of a stainless steel core holder with an internal diameter of 5 cm and a height of 13 cm. The core holder set up was vertical to include the gravity drainage effect. A stainless steel screen (15mesh) was wrapped around the glass beads preventing them from migrating out of the sandpack model. The injection port was installed at the top while the production end was placed at the bottom of the core holder. The production port was connected to a microscope valve and stainless steel filter (2.5 μm) to determine the asphaltene flocculation during oil production. The bottom of the filter was attached to a graduated glass container to collect the oil produced. In addition, a back pressure valve to relieve the pressure from the unconsolidated sandpack was installed in the production line before the filtration point. The injection pressure and production pressure were monitored through a pressure transducer. The pressure signals were connected to a lab-view acquisition data controller (Laboratory Virtual Instrument Engineering).

Alteration of Glass Bead Wettability

The wettability of the glass beads was altered to oil-wet through a surface treatment using SurfaSil fluid. This is a polymeric silicone fluid consisting mainly of dichlorooctamethyltetrasiloxane (C_8-H_{24}-Cl_2-O_3-Si_4), which has no electrical charged (neutral charge) molecular structure [21]. After the surface treatment using the siliconizing agent, the surface became hydrophobic (repelling or beading water) (SurfaSil ^{TM} siliconizing fluid, Thermo Scientific technique-TS-42801). The Surfasil siliconizing process involves HCl as a by-product during the coating of glass beads [22]. The HCl guaranteed that the final results would not be mixed wet. The methodology used to coat the 160 grams of glass beads was as follows: Mix 10v/v% of Surfasil and 90v/v% of toluene, then immerse the glass beads in the mixture and leave them for 12 hours. After that, the sample was cleaned with toluene three times. Subsequently, the glass beads were rinsed with methanol to avoid interaction between the SurfaSil coating and water because this can reverse the siliconization process. Finally, the sample was dried in the oven for two days at 100 ˚C.

A capillary imbibition experiment was carried out to determine that the surface treatment from water-wet to oil-wet was achieved. The water imbibition process was lower for the bead treatment with SurfaSil than for the untreated beads **(Figure 5-A1 - Appendix 5-A)**. As a result, the surface treatment was successful in altering the wettability of the wet glass bead surface. The same surface treatment and imbibition experimental procedure was followed for the four oil-wet bead experiments. The imbibition of the water-wet glass beads also was conducted to compare the water imbibition for the oil-wet beads (Appendix A).

Solvent Injection Experimental Process

The solvent injection experiments were conducted in a core holder cylindrical model as described in **Figure 5-1**. Four different types of light hydrocarbon solvents (propane, n-hexane, n-decane, and distillate hydrocarbon) were used to diffuse and dilute the heavy oil. The heavy oil properties are presented in **Table 5-1**. The composition of the distillate hydrocarbon (C_4-C_{15}) is given in **Figure 5-B1** of Appendix 5-B. The meshed glass beads were selected randomly between 595 and 841μm. The porosity was measured to be 38% to 39%. The literature review related to the permeability for this size of beads is around 210 D to 220 D [18, 20]. The randomly selected glass beads (160 grams) were mixed with the heavy oil (40 grams). The mixture was homogenized by heat at 40 ˚C and the sample for approximately 10 minutes. Then, the 200 gram sample of glass beads and heavy oil were wrapped in a stainless steel screen and compacted together layer by layer. The sample was placed into the cylindrical model and left over night at the operational temperature (50 ˚C). The solvent injection was started at 0.2 cc/min when the operating conditions were stabilized (50 ˚C and 2068 kPa). The solvent was injected during an 8-hour period and the cumulative amount of oil was measured during this time. Furthermore, the fluid was filtrated during the operation time to collect the asphaltene flocculate in the fluid produced. Subsequently, the total amount of oil produced was measured based on its volume and weight. The integrity of the glass bead model (formation damage) was analyzed after each test using the high resolution scanning electron microscope (Hitachi S-3000N).

A Soxhlet extraction apparatus was used to clean the glass bead model (injection, middle, and production points) in order to determine the level of residual oil saturation (maltenes: saturates, aromatic, and resins) and asphaltene deposition. As noted in the literature, asphaltenes are insoluble in n-heptane but soluble in toluene. Hence, the level of residual oil (maltenes) was determined by cleaning the glass bead pack with n-heptane for one week. Afterwards, the glass bead pack without residual oil (maltenes) was cleaned with toluene to dissolve the asphaltene deposited in the glass bead pack. Both the n-heptane with maltenes and asphaltene with toluene solutions were distillated to calculate the residual oil and the asphaltene deposition weight percentages.

The organic layer deposited on the beads surface was visualized in three sections (injection, middle, and production points) of the sandpack model using a high resolution scanning electron microscope S-3000N (SEM) and focused ion beam-scanning electron microscope NB5000 (FIB/SEM from Hitachi). Prior to measuring the thickness of the sample, the cross sectional morphology of organic deposition was coated with about 150 nm Au (gold) by sputtering deposition. A protection W (tungsten) layer (about 1 µm thick) was deposited prior to FIB milling. Three cross sections at different locations were milled down to the glass beads by a 40 kev Ga beam, and inspected using the SEM. In addition, the elementary mapping from the image samples were generated using an energy-dispersive x-ray spectroscopy apparatus (TEM- JEOL 2200 FS-EDX/EELS: Oxford Instruments).

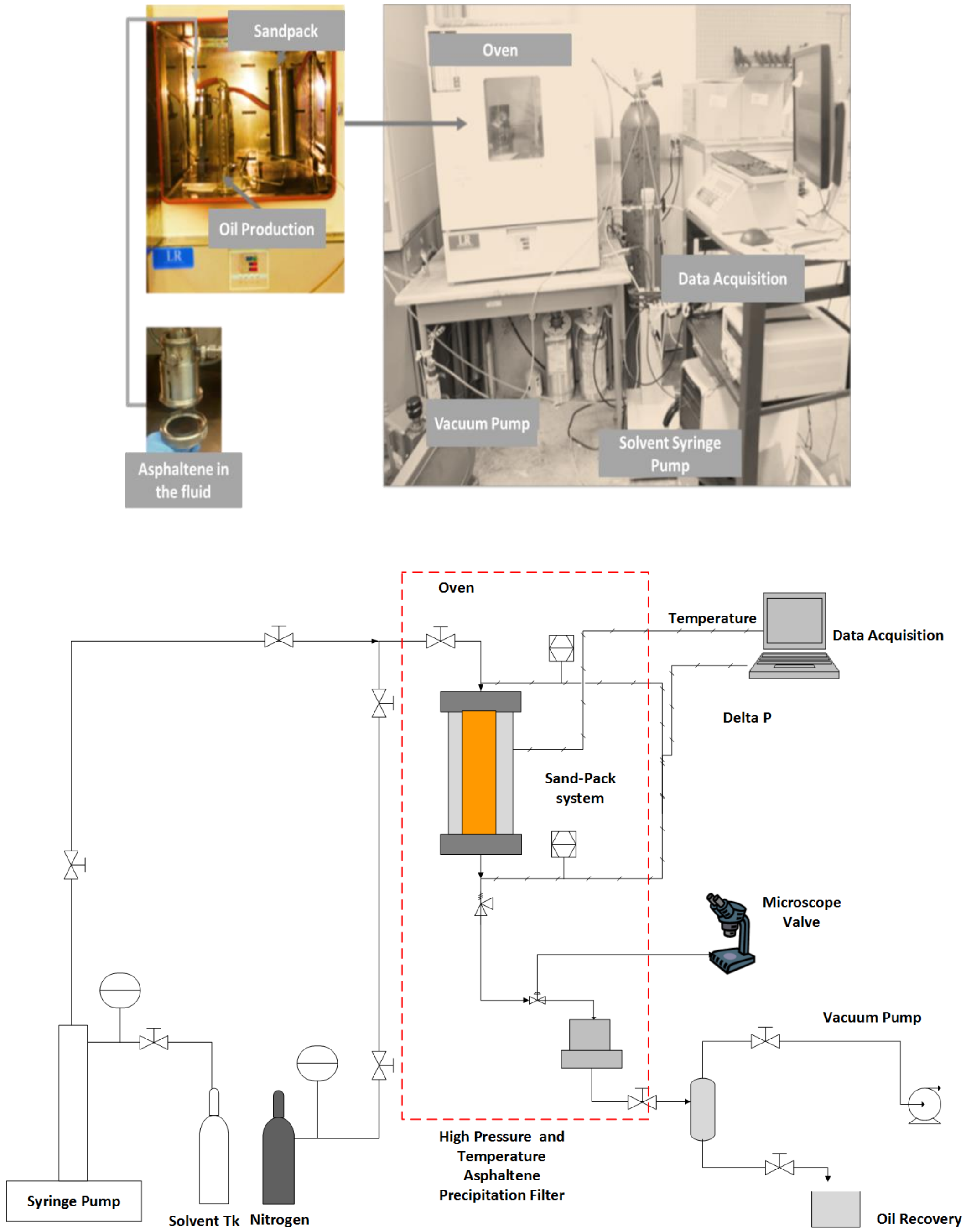
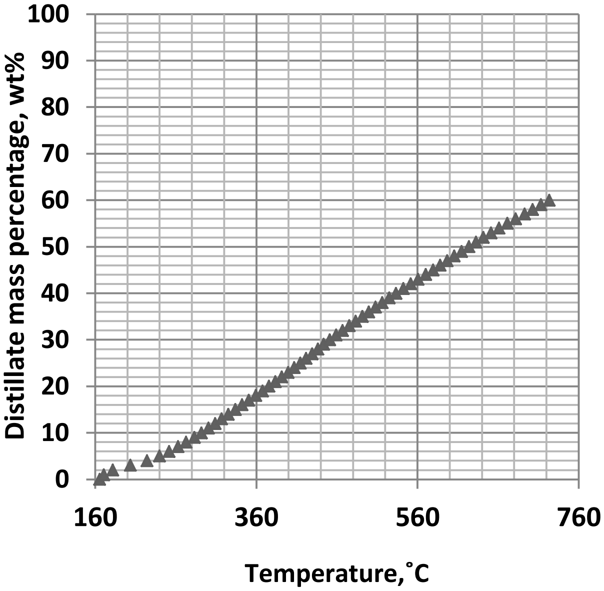


Figure 5-1: Unconsolidated sandpack experimental model.

Table 5-1: Heavy oil properties and accumulate distillation mass percentage (ASTM D7169).

Heavy Oil properties-ASTM D2007, IP 143 and ASTM D2549	
Saturates,wt%	17.24
Aromatics,wt%	38.60
Resin,wt%	32.66
Asphaltene,wt%	11.50
Heavy Oil Elementary Analysis-ASTM D7578	
Carbon,wt%	84.45
Hydrogen,wt%	9.731
Sulfur,wt%	3.715
Nitrogen,wt%	0.553
Asphaltene Elementary Analysis-ASTM D7578	
Carbon,wt%	82.06
Hydrogen,wt%	7.957
Sulfur,wt%	7.431
Nitrogen,wt%	0.946
API Gravity at 15.5˚C	
˚API	8.67
Density [g/cm^3]	
25˚C	1.003
40 ˚C	0.9959
70˚C	0.9774
Viscosity [cP]	
25˚C	87651
40˚C	13298
70˚C	1450



Results and Discussion

Oil-Wet and Water-Wet Oil Production

Oil production after the injection of solvent (propane, n-hexane, n-decane, and distillate hydrocarbon in the heavy oil sandpack model was investigated in two different wet surface systems (strongly water-wet and strongly oil-wet). Four experiments were conducted for each wettability case amounting to a total of eight experiments. Some of the asphaltene flocculated in the fluid left asphaltene deposition on the bead surface after the solvent was injected. Consequently, different types of organic deposition layers were observed on the bead surface through the model. The quantitative and visual representations of these are illustrated in **Figures 5-3 to 5-8**. As a result, alteration of the bead surface with residual oil (maltenes) and asphaltene deposition were present. In contrast, Rezaei et al. [18] reported that pore-scale asphaltene deposition did not have an influence in the oil production rate because asphaltene flocculation was not presented in their experiments. However, Moreno and Babadagli [7,8] found that asphaltene deposition was present on the porous medium surface and increased when a light hydrocarbon solvent (propane) was injected into a heavy oil reservoir. In addition, Al-Aulaqi et al. [13] determined that the surface contact angle increased from θ=60˚ to θ=142˚ when the heaviest crude oil was used due to the higher asphaltene deposition content.

Oil- and water-wet experimental results are presented in **Table 5-2**. The strongly oil-wet surface beads show higher oil production than the strongly water-wet system. This can be explained with the affinity of the solvent with the medium. For example, water flooding in a water-wet reservoir has shown a higher efficiency than in an oil-wet reservoir due to the preferential contact of the fluid on the rock surface [15, 17, 23]. Consequently, the affinity of the hydrocarbon injected in the hydrocarbon surface (oil-wet) increased the displacement of the residual oil through the porous spaces. As a result, the sweep efficiency increased, leading to increased oil production. This was also confirmed by Rezaei et al. [18], who concluded that the crevice flow mechanism encourages better oil recovery in oil-wet reservoirs due to the influence of the contact angle.

Strongly oil-wet beads also showed a higher level of oil recovery depending on the type of hydrocarbon solvent injected (**Table 5-2**). For example, the oil recovery was 7% higher in the oil-wet system than in the water-wet system in the propane case. However, when distillate hydrocarbon **(Figure 5-B1 - Appendix 5-B)** was used, the oil recovery difference was just 1%. Subsequently, asphaltene deposition, which increased more while using propane as a solvent than distillate hydrocarbon, leaves a higher uneven surface (organic layers) with propane than with distillate hydrocarbon (**Table 5-2**). Consequently, a smaller organic deposition layer on the bead surface resulted in no difference between strongly water-wet and strongly oil-wet oil recovery for this particular experiment. Moreno and Babadagli [7, 8] observed that a smaller oil recovery is obtained with propane at higher temperatures (25 ˚C and 120 ˚C) and pressures (689 kPa and 2068 kPa) because miscible displacement is affected by organic deposition on the rock surface. They also concluded that distillate, which has paraffin and aromatic components, increases the miscible displacement, thus improving oil production at higher temperatures (50 ˚C to 120 ˚C).

Temperature and pressure may also intervene in the type of organic layer formed. Al-Aulaqi et al. [13] also confirmed that the surface contact angle increased when the temperature was between 20 ˚C and 60 ˚C using heptane as a solvent.

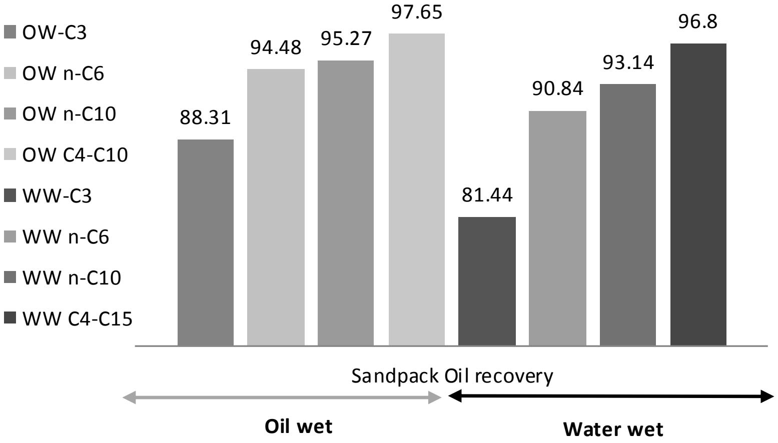


Figure 5-2: Oil recovery (weight percentage) from the water-wet and oil-wet glass surfaces at 50 ˚C and 2068 kPa.

Table 5-2: Water-wet and oil-wet sandpack experimental results after injecting solvents (propane, n-hexane, n-decane, and distillate hydrocarbon) at 50 ˚C and 2068 kPa.

Test	Surface	Solvent	RF, wt%	R_{sor},wt%	d_{asp}, wt%	Total, wt%	Asp-F, wt%
1	OW	Propane	88.31	7.37	4.31	100	10.21
2	OW	n-hexane	94.48	3.33	2.18	100	6.9
3	OW	n-decane	95.27	3.12	1.6	100	5.74
4	OW	Distillate	97.65	1.35	0.99	100	3
5	WW	Propane	81.44	12.2	6.35	100	8.29
6	WW	n-hexane	90.84	5.12	4.03	100	5.07
7	WW	n-decane	93.14	3.58	3.27	100	4.2
8	WW	Distillate	96.8	1.76	1.43	100	2.47

Asphaltene solubility parameters were also involved in alterations to the wettability because lower asphaltene solubility means higher asphaltene deposition on the rock surface. Lower asphaltene solubility in oil was found when solvents with a lower number of hydrocarbons were used (**Table 5-2**). Also, asphaltene aggregate, particle size, and cluster formation increased as the carbon number of the n-alkane type solvent is reduced (**Figures 5-6 to 5-7**). Hence, asphaltene adsorption on the rock surface can increase when light hydrocarbon solvents are injected. On the other hand, temperature, pressure, and oil composition may change the asphaltene solubility parameter. For the same oil used in our experiments, Moreno and Babadagli [7, 8] conducted phase behaviour experiments. They concluded that when temperature and pressure were increased, the asphaltene solubility also increased [7, 8].

As elucidated in **Table 5-2**, asphaltene deposition was higher in the water-wet system than in the oil-wet system. Accordingly, asphaltene precipitation in the fluid was higher in the oil-wet system than in the water-wet system. Thus, it can be concluded that more asphaltene deposition occurred inside the sandpack model in the water-wet system. In other words, asphaltene adsorption became higher on water-wet rock surfaces than on oil-wet surfaces. The reasons of this, which can be explained through attractive-repellant forces, need further analysis. Here, the existence and consequences of this wettability change will be covered.

It has been also noted in the literature that asphaltene adsorption can alter the wettability of the rock surface from water-wet to oil-wet [7,13,14,15]. In agreement with our observations, this directly impacts the oil recovery and efficiency of the displacement process. Other factors, such as capillarity pressure, relative permeability, and interfacial tension may explain the higher oil production in the oil-wet system.

Hassan et al. [24] determined the interfacial tensions for normal hydrocarbons (C_1 to C_{10}) at temperatures from 26.6 ˚C to 59.9 ˚C at 5167 kPa. They found that the interfacial tension decreases when the number of carbon atoms increases. Consequently, if the interfacial tension is lower (meaning the solvent has a higher carbon number), the capillary pressure will decrease. In addition, Rostami et al. [25] found that cumulative oil production is enhanced as a result of the alteration of the solvent-oil relative permeability (Kr). This alteration in the Kr curves takes place due to the reduction of surface tension during the process, which is achieved by solvents with higher carbon numbers. All these changes in capillary pressure and relative permeabilities eventually affect the oil recovery, which is positively affected by increasing solvent carbon number that also yields less wettability alteration.

Residual Oil Saturation and Asphaltene Deposition along the Sandpack

As previously mentioned, organic deposition (maltenes and asphaltenes) is one of the principal factors to increase the contact angle and alter the wettability from water-wet to either intermediate wet or strongly oil-wet. The sandpack model was divided into three dimensionless heights: 0-injection point, 0.5-middle point, and 1- production point **(Figure 5-3)**. Each point was cleaned separately during the Soxhlet extraction process using n-heptane (maltenes separation) followed by toluene (asphaltene dissolution). After the cleaning, the residual oil (maltenes) and asphaltene deposition from each section were calculated **(Figures 5-3 to 5-5)**. As summarized in **Table 5-2**, the water-wet medium presented more residual oil trapping (maltenes) in the sample compared with the oil-wet medium. **Figure 5-3** demonstrates the remaining hydrocarbons throughout the core, opening the sample without disturbing its integrity after the experiments, through colour variations. These eight sandpack model experiments showed two variations in colour - brown (high S_{or}) and light brown (less S_{or}). It can be seen that propane (WW/OW) as a solvent shows higher residual oil saturation compared to distillate hydrocarbon (WW/OW) through the color evaluation. Also, the comparison between each solvent and wet medium **(Figure 5-3)** demonstrates a higher S_{or} in the water-wet model than in the oil-wet model.

As demonstrated in **Figure 5-4**, the change of the residual oil (maltenes) saturation from top (injection point) to bottom (production end) follow a similar systematic in for four solvent types. It is higher at the production regardless the solvent type but average residual oil saturation decreases with increasing carbon number.

Asphaltene adsorption on the glass bead surface was higher mostly at the middle and production points **(Figures 5-5 to 5-7)**, which can be attributed to asphaltene migration and electrical properties. Asphaltene by definition carry electrical charge and it is the most polar compounds of crude oil. The most important attractive forces between asphaltene particles are the dipole-dipole interactions. However, maltenes by definition are non-polar or are relatively low-polarity compounds [1,11,12]. Consequently, higher residual oil (maltenes) in the model resulted in higher asphaltene adsorption on the bead surface due to opposite charges between maltenes (mostly negative charge) and asphaltenes (mostly positive charge) [1,4,5,11-13]. Moreover, the distribution of the asphaltene was more uniform throughout the core in the case of water-wet system, whereas it was more severe at the production and for the oil-wet cases **(Figure 5-5)**. This could be explained by the affinity of the asphaltene to migrate through the oil-wet surface more than the water-wet surface throughout the displacement process, resulting in less tortuous interface between the fluid and porous surface in the oil-wet system, easing the flow of oil downward compared to the water-wet beads.

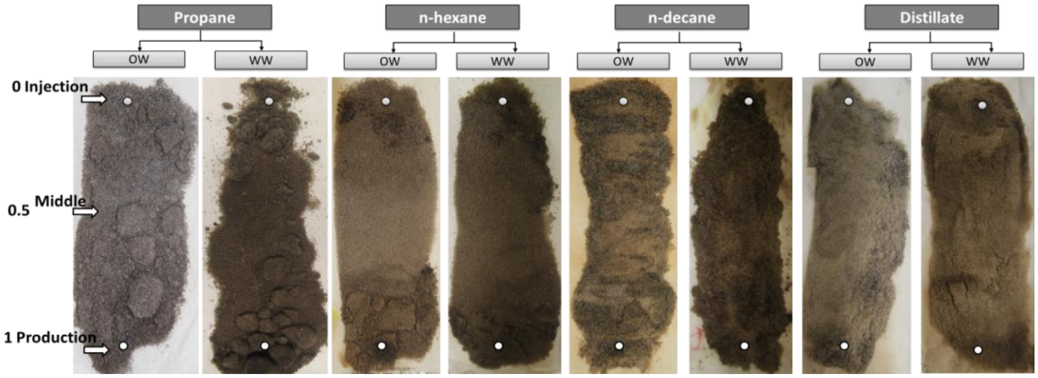


Figure 5-3: Experimental sandpack after testing with different types of solvents and surface wet (water-wet and oil-wet) at 50 ˚C and 2068 kPa.

Hence, the tortuosity (or roughness) of the asphaltene deposited on the surface of the glass beads is a critical issue affecting the flow and wettability alteration. The three dimensionless heights (0-injection point, 0.5-middle point, and 1-production point) of the sandpack model were viewed under the scanning electron microscope (S-3000N) to evaluate the surface roughness **(Figures 5-6 to 5-7)**. The organic deposition (residual oil-maltenes and asphaltenes) showed higher compound adsorption with propane at the middle and production points. However, remarkable organic agglomeration also occurred at the injection point and a higher organic agglomeration was found between the porous spaces in the water-wet beads than in the oil-wet beads **(Figures 5-6 to 5-7)**.

Furthermore, less organic agglomeration was found when n-hexane was used compared to the use of propane as a solvent in the oil-wet and water-wet systems. However, significantly less organic agglomeration occurred when n-hexane was used as a solvent on oil-wet beads rather than the water-wet medium **(Figure 5-6)**. This confirmed that a less tortuous interface was present in the oil-wet medium. The other two hydrocarbons (n-decane and distillate hydrocarbon) demonstrated lower organic deposition from both of the wet mediums **(Figure 5-7)**. The SEM results validated the quantitative oil recovery, residual oil (maltenes), and asphaltene deposition results **(Table 5-2 and Figures 5-3 to 5-5)**.

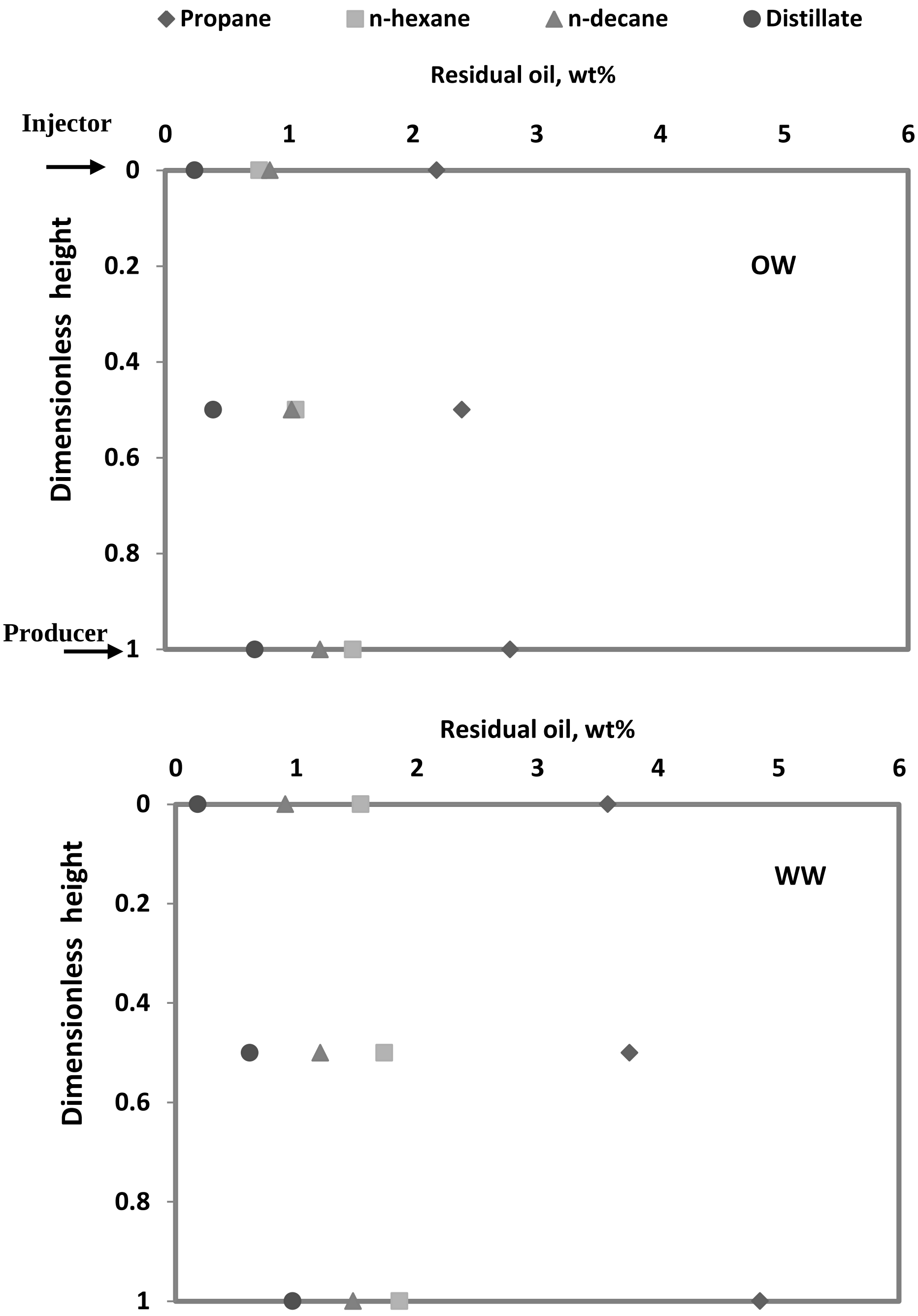


Figure 5-4: Residual oil [maltenes] saturation (weight percentage) from the oil-wet (OW) and water-wet (WW) glass bead surface at 50 ˚C and 2068 kPa.

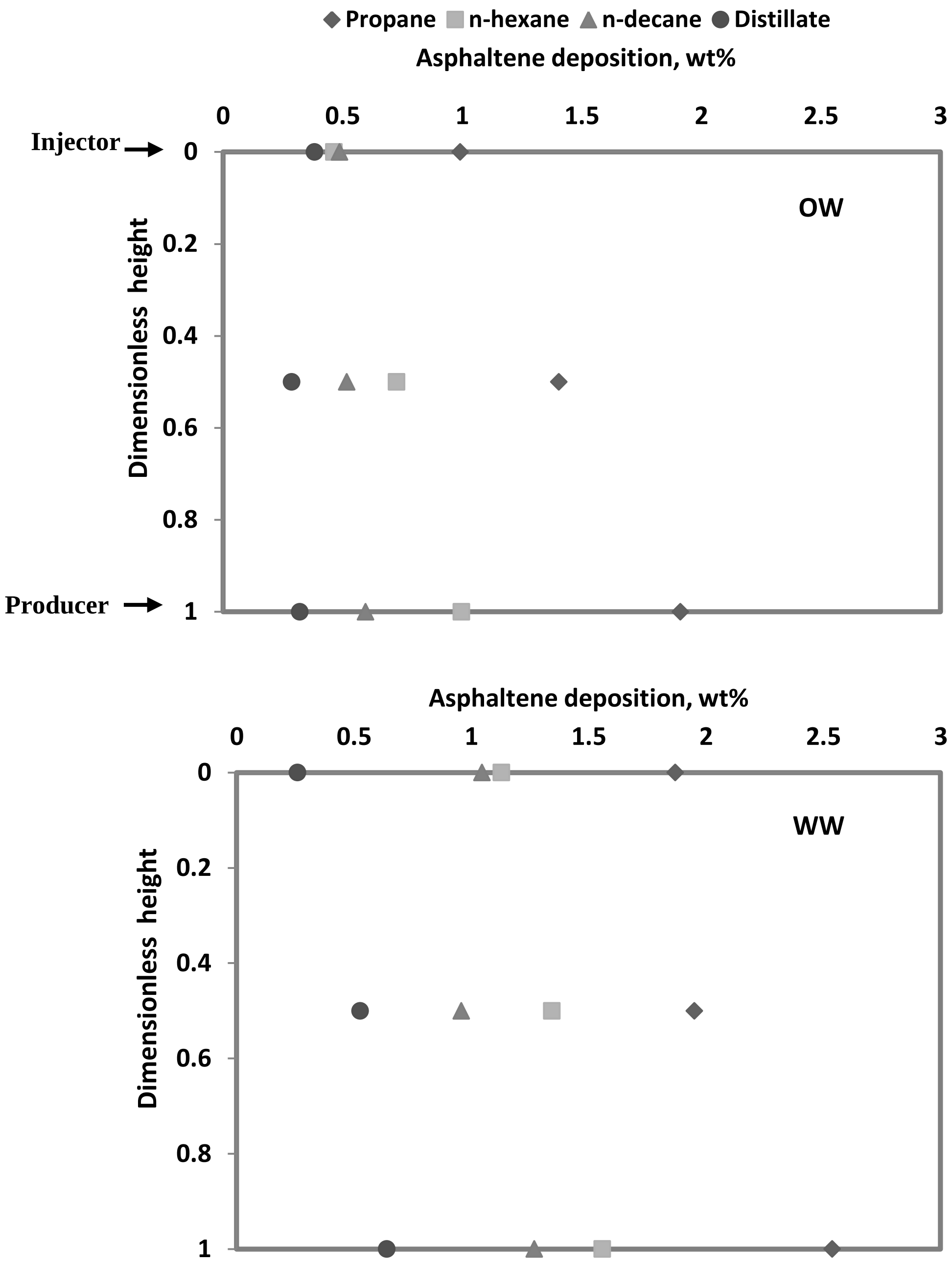


Figure 5-5: Asphaltene deposition (weight percentage) from the oil-wet (OW) and water-wet (WW) glass bead surface at 50 ˚C and 2068 kPa.

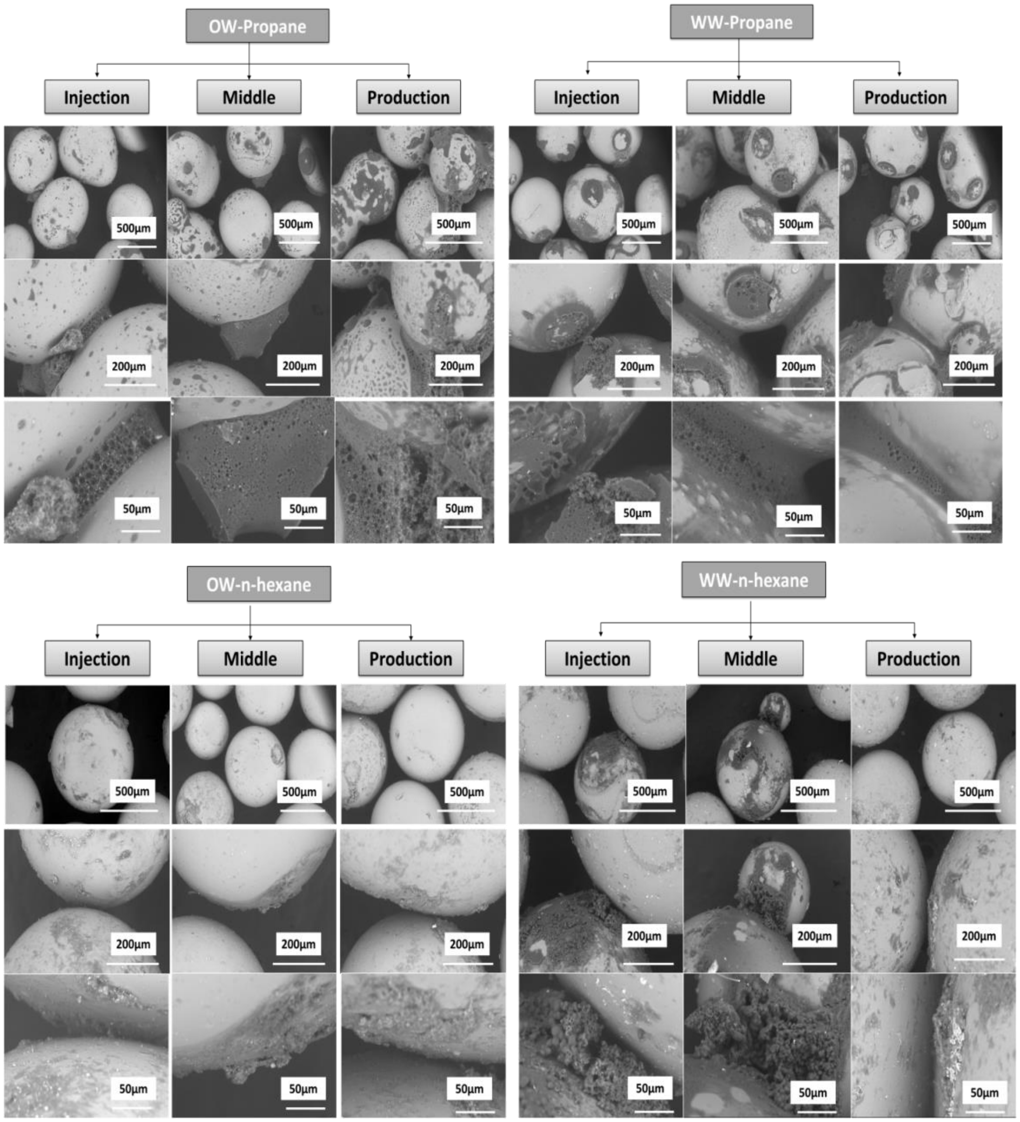


Figure 5-6: Effect of the glass bead surface on the injection, middle, and production points after the injection of solvents (propane and n-hexane) into two different wet glass surfaces (WW and OW) at 50 ˚C and 2068 kPa.

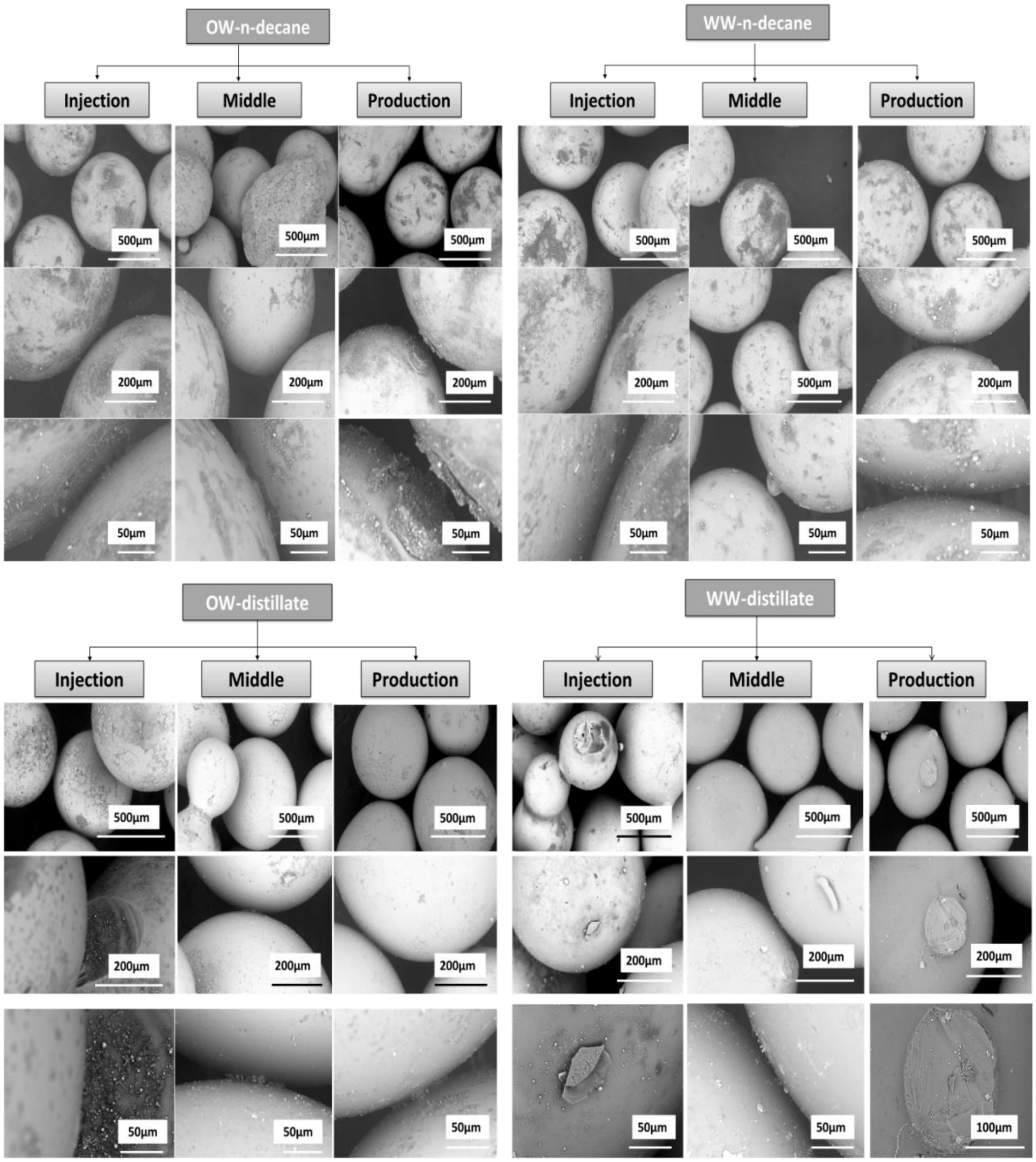


Figure 5-7: Effect of the glass bead surface on the injection, middle, and production points after the injection of solvents (n-decane and distillate) into two different wet glass surfaces (WW and OW) at 50 ˚C and 2068 kPa.

Non-Uniform Wettability Alteration

As previously mentioned, the multilayer organic deposition was studied in two different wettability systems: (1) water-wet beads and (2) oil-wet beads, which were altered using a SurfaSil^{TM} siliconizing process. In the beginning, the wettability for both systems was uniform (homogeneous). However, when the solvent injection was started, asphaltene deposition and residual oil (maltenes) were left in the sandpack model. As a consequence of this, non-uniform changes in wettability were present as can be inferred from **Figures 5-4 and 5-5**. Hence, the results obtained in this research showed that organic layer deposition was not uniform on all bead surfaces. The deposition was thicker on some beads but less thick on other beads depending on the location where the sample was taken from.

Most of the literature related to this topic advocated that if organic deposition occurs on the water-wet rock surface, the wettability changes to oil-wet [9,26]. However, the focused ion beam (FIB) and scanning electron microscope (SEM) showed that the bead surface was heterogeneous (non-uniform) and also highlighted that some surface parts were not covered by organic deposition as visually supported by the images in **Figures 5-6 and 5-7**. Consequently, mixed wettability may be achieved on the bead surface.

Multilayer Organic Deposition

The organic peak deposition distance for each hydrocarbon solvent (propane, n-hexane, n-decane, and distillate hydrocarbon (C_4 to C_{15})) was determined using the focused ion beam-scanning electron microscope (FIB/SEM). Three sections from the organic adsorption were cut to determine the thickness layer. The three cross sectional points were selected to be located on the lower, middle, and higher peaks to ascertain the different levels of surface roughness that could be present on the rock surface after the solvent-based process was applied. The distance (d-image) correction of the $\theta=58^\circ$ angle image was done previously to calculate surface parameters (**Appendix 5-C**). In **Table 5-3**, the calculations of the surface roughness parameters are shown. The root mean squared (RMS) and arithmetic mean square (Ra) of the surface roughness were calculated based on the equation presented in **Appendix 5-C**. In addition, the confidence interval was 95% (margin of error), and the lower limit and upper limit were calculated using the addition or subtraction of the margin of error from the arithmetic mean value.

The organic deposition layers from the oil-wet and water-wet bead surfaces are presented in **Figure 5-8**. The calculated distance shows that a thicker layer of organic material was present on the water-wet rock surface than on the oil-wet surface. The thickness layer using propane from the water-wet system was 3.621μm, while the oil-wet system was 2.824μm. Moreover, n-hexane, when used as a solvent on a water-wet surface, showed a surface thickness of 1.936μm, while on an oil-wet surface the thickness was 1.751μm.

Propane and n-hexane are two powerful solvents that precipitate higher asphaltene content from heavy oil. As a result, the asphaltene deposition left higher heterogeneous layers (asphaltene accompanied by maltenes) on the rock surface compared to n-decane and n-distillate (**Table 5-3**). The thickness values from the water-wet and oil-wet surfaces were similar when distillate hydrocarbon was injected. This can be attributed to less asphaltene flocculation, producing a better recovery factor independent of the rock surface wettability (**Table 5-2 to 5-3**).

The elementary mapping was conducted on a FIB-prepared TEM sample by energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) on a JEOL 2200 FS STEM/TEM microscope in order to determine the elemental compounds in the organic deposition. Also, the substrate (glass bead) and organic deposition were necessary to confirm the measurement of the true organic thickness (**Table 5-3 and Figures 5-8 to 5-10**). As demonstrated in **Figure 5-10**, the organic deposition sample contained carbon, nitrogen, oxygen, sulfur and iron, while the glass bead surface and/or oil field contamination contributed other elements such as sodium, calcium, silicon, and chlorine. Asphaltene heteroatoms (nitrogen, sulfur, and oxygen) and metal elements (nickel, vanadium, and iron) were present in the sample. However, vanadium and nickel elements showed very low intensity. Consequently, EELS was conducted but no nickel or vanadium was found in the area. Iron (Fe) was confirmed by mapping Fe – L edge using the scanning transmission electron microscopy - electron energy loss spectroscopy (EELS) (STEM-EELS) spectrum-imaging, as shown in **Figures 5-9 and 5-10**.

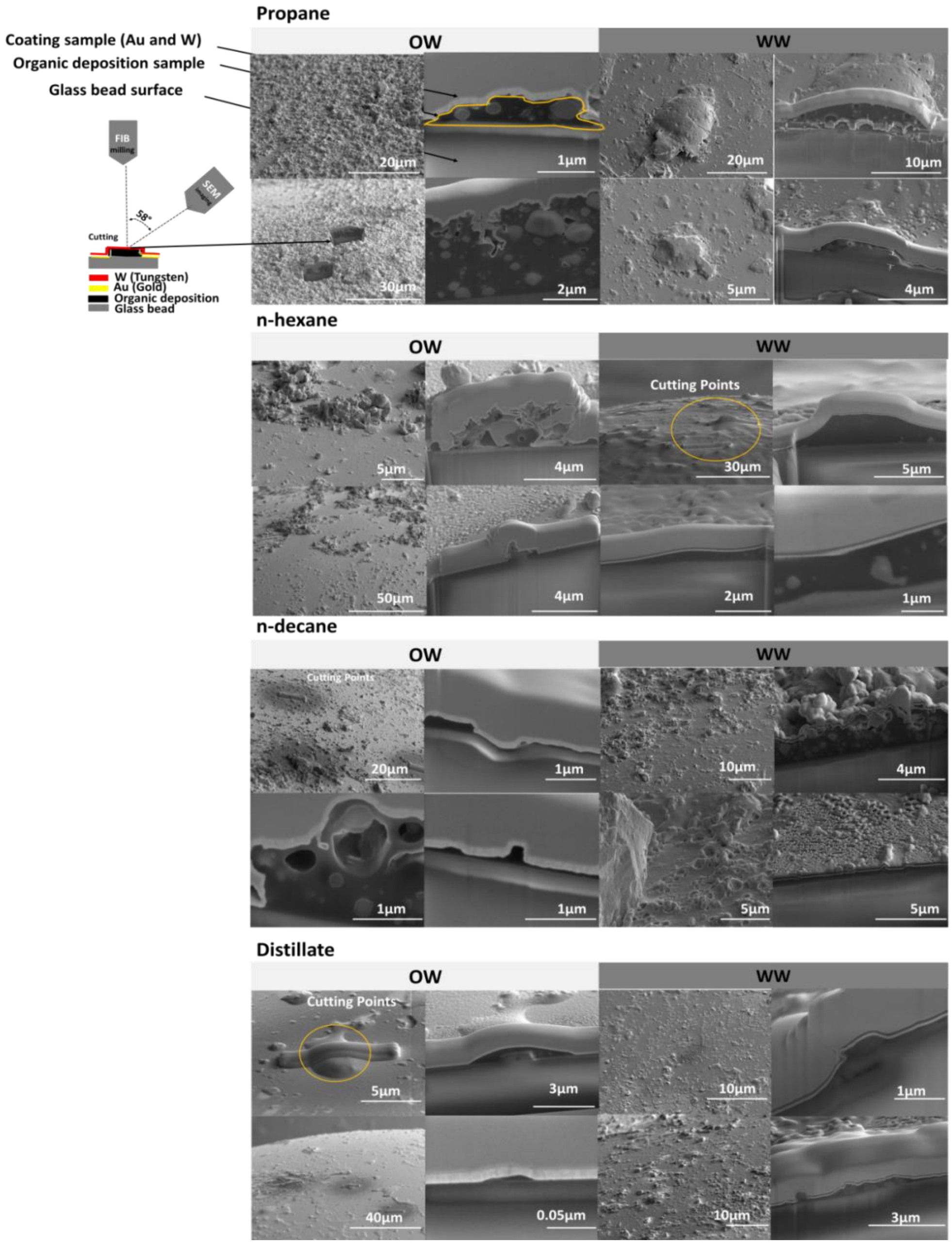


Figure 5-8: Determination of surface roughness under the FIB-SEM from organic deposition after the solvent-based (propane, n-hexane, n-decane and distillate hydrocarbon) process was completed at 50 ˚C and 2068 kPa.

Table 5-3: Organic deposition: Surface roughness parameter calculations from oil-wet and water-wet systems after the injection of a solvent at 50 ˚C and 2068 kPa.

FIB-SEM Cutting Points	Ra	Standard deviation	Margin error	Lower limit	Upper limit	RMS
WW-Propane						
Lower Point (µm)	0.140	0.029	0.027	0.113	0.167	0.143
Middle Point (µm)	0.757	0.169	0.142	0.615	0.898	0.773
Upper point (µm)	3.611	0.102	0.095	3.978	4.167	3.621
OW-Propane						
Lower Point (µm)	0.142	0.012	0.008	0.134	0.150	0.142
Middle Point (µm)	0.499	0.416	0.385	0.248	1.018	0.753
Upper point (µm)	2.805	0.332	0.278	2.527	3.083	2.824
WW-n-hexane						
Lower Point (µm)	0.868	0.058	0.054	0.916	1.024	0.971
Middle Point (µm)	0.888	0.146	0.098	0.790	0.987	0.899
Upper point (µm)	1.924	0.228	0.191	1.734	2.115	1.936
OW-n-hexane						
Lower Point (µm)	0.232	0.231	0.155	0.077	0.387	0.321
Middle Point (µm)	0.954	0.244	0.226	0.412	0.864	0.678
Upper point (µm)	1.726	0.303	0.253	1.473	1.979	1.751
WW-n-decane						
Lower Point (µm)	0.211	0.080	0.074	0.252	0.400	0.334
Middle Point (µm)	1.313	0.296	0.199	1.114	1.511	1.343
Upper point (µm)	1.578	0.190	0.159	1.418	1.737	1.588
OW-n-decane						
Lower Point (µm)	0.059	0.012	0.008	0.051	0.066	0.060
Middle Point (µm)	0.242	0.328	0.304	0.347	0.954	0.720
Upper point (µm)	1.484	0.063	0.053	1.432	1.537	1.486
WW-Distillate						
Lower Point (µm)	0.088	0.022	0.015	0.073	0.103	0.090
Middle Point (µm)	0.267	0.064	0.059	0.250	0.367	0.314
Upper point (µm)	0.546	0.010	0.009	0.537	0.554	0.546
OW-Distillate						
Lower Point (µm)	0.047	0.023	0.015	0.032	0.063	0.052
Middle Point (µm)	0.111	0.074	0.068	0.140	0.276	0.220
Upper point (µm)	0.398	0.069	0.058	0.341	0.456	0.404

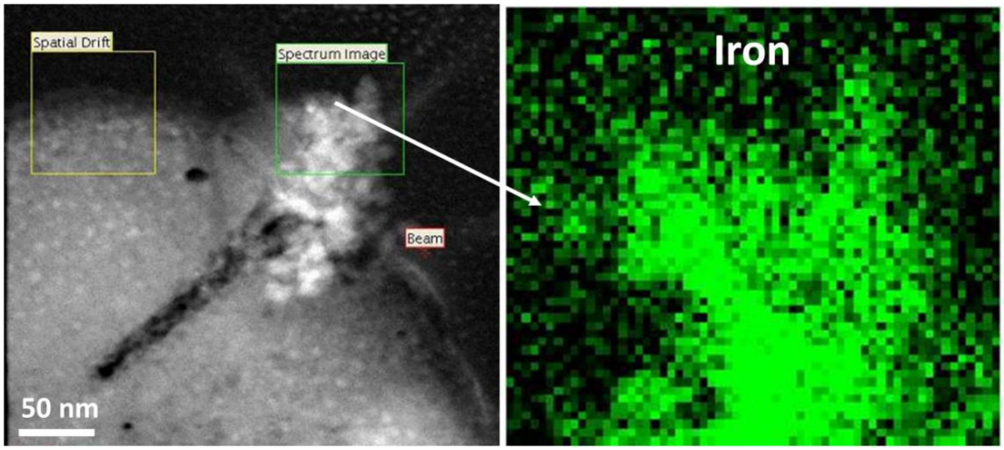


Figure 5-9: Elemental mapping of Iron by STEM-EELS spectrum-imaging of Fe from the oil-wet surface experiment at 50 ˚C and 2068kPa with propane.

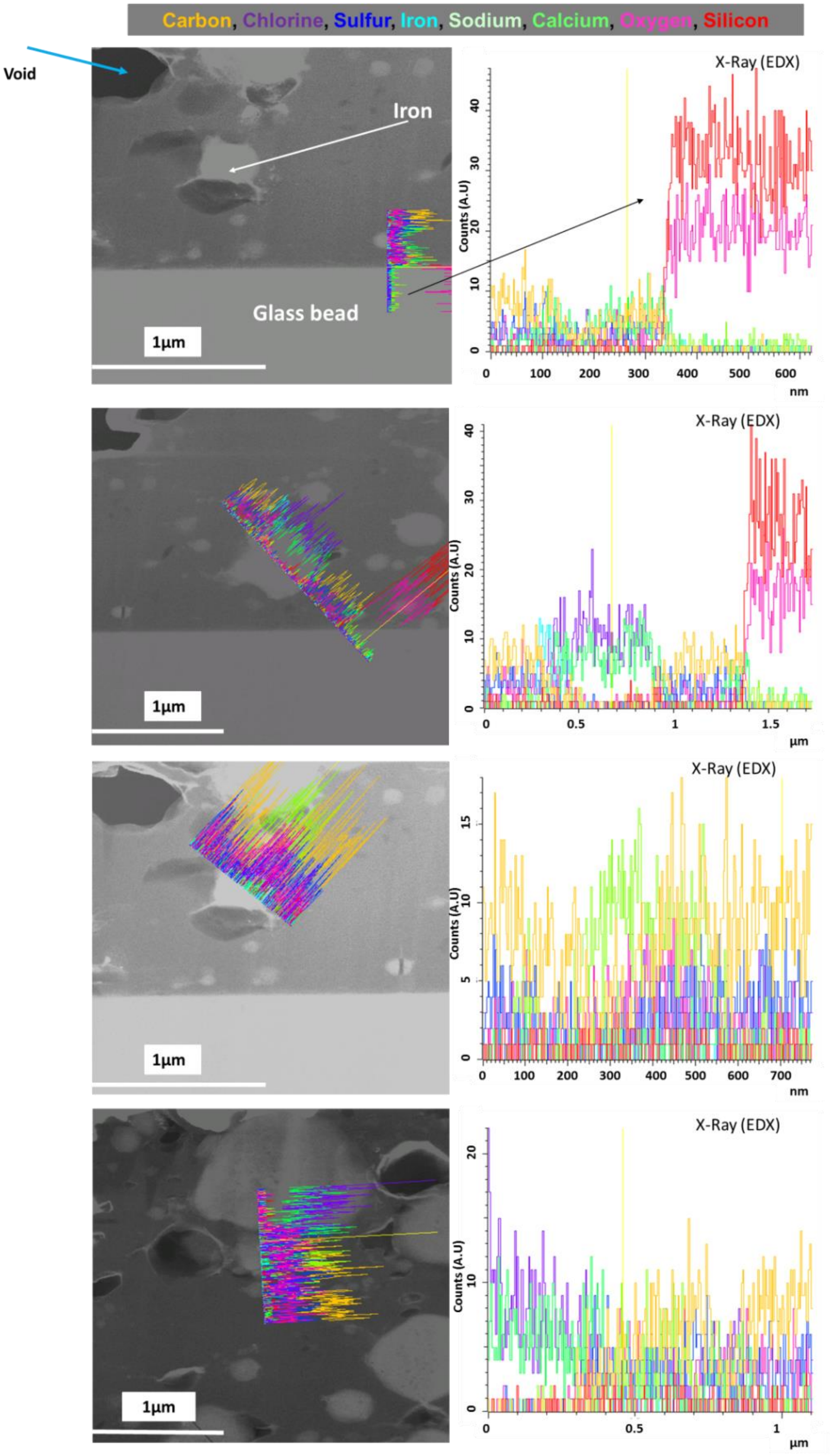


Figure 5-10: Elementary mapping and energy dispersive X-Ray (TEM-FS-EDX-Oxford Instruments) analysis of the bead surface experiment at 50 ˚C and 2068 kPa with propane in the oil-wet surface.

Conclusions

Multilayer organic deposition was evaluated under different surface conditions, such as wettability (oil-wet and water-wet) and the solubility of the fluid (asphaltene flocculation). The asphaltene flocculation was destabilized using four types of light hydrocarbon solvents (propane, n-hexane, n-decane, and distillate hydrocarbon). The level of oil recovery and amount of organic deposition were determined qualitatively and evaluated visually using different apparatuses, such as unconsolidated sandpack experiments, FIB/SEM and EDX/EELS. The most important conclusions in this research are as follows:

1. Wettability surface had a significant effect on the level of heavy-oil production. Oil recovery was demonstrated to increase more when the bead surface was strongly oil-wet than strongly water-wet. The affinity between the hydrocarbon solvent and bead surface may reduce the capillarity forces, leading to less tortuosity in the fluid pathway.
2. Residual oil saturation (maltenes) mainly increased when a lower carbon number solvent was used. As a solvent, propane showed higher residual oil saturation in the water-wet beads than on the oil-wet surface. Higher residual oil saturation was attributed to the increase of organic layer deposition on the bead surface because the electrical charge between maltenes (negative charge) and asphaltene (positive charge). In other words, higher residual oil saturation resulted in higher asphaltene adsorption.
3. Asphaltene deposition and residual oil (maltenes) saturation were determined for the injection, middle, and production points of the unconsolidated sandpack model. The results showed that asphaltene deposition was critical in the three points due to asphaltene migration down the flow. Moreover, residual oil saturation became higher closer to the production point due to the effect of gravity segregation.
4. Thickness peak of the organic deposition for each type of solvent and surface type were calculated using an FIB/SEM microscope and surface roughness equations. As a result, the thickness layer increase when propane and n-hexane were used on a water-wet surface compared to an oil-wet surface. However, the organic layer deposition was significant for both wet systems when propane and n-hexane were used. In contrast, the thickness peak was almost stable when n-decane and distillate hydrocarbon were used for both wet surfaces.
5. The energy dispersive X-Ray (EDX) and electron energy loss spectrometry were used to do the elementary mapping and element identification. Also, the elements revealed in the organic deposition are the heteroatoms (oxygen, and sulfur), carbon and iron (metal).

Nomenclature

Asp-F	Asphaltene filtration from the fluid (g/g)
dasp	Asphaltene deposition [cleaned asphaltene] (g/g)
RF	Oil recovery percentage (g/g)
RS_{or}	Residual oil saturation [maltenes: saturates, aromatics and resins] (g/g)
Φ	Particles porosity (μm)
TEM	*Transmission electron microscopy*
EDX	*Energy-dispersive X*-ray spectroscopy
EELS	*Electron Energy-Loss Spectroscopy*
FIB	Focused ion beam
SEM	Scanning electron microscope

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CHAPTER 6: CONTRIBUTIONS AND RECOMMENDATIONS

Contributions

The main contributions from this thesis are presented below:

- Due to higher molecular diffusion capability, the tendency in the industry was to use lighter hydrocarbon solvents (propane, butane) in low (VAPEX) and high temperature (steam/solvent hybrid or hot solvent) applications. Our study showed the applicability limits of this type of solvent in terms of fluid and rock characteristics alteration that may affect the recovery adversely. Although they are costlier, higher carbon number single component solvents (heptane, decane) as well as distillate oil (naphta) may result in much more efficient recovery due to less significant effects of asphaltene precipitation and deposition. This research showed that the selection of proper solvent for the existing temperature and pressure conditions may maximize the recovery and thereby improve the process efficiency.

- Solvent selection type was conducted using four types of solvents (such as propane, n-hexane, n-decane and distillate hydrocarbon). The results showed that when the carbon number of the solvent decreases (e.g., with propane and n-hexane), more organic deposition and, consequently, formation damage took place. On the other hand, n-decane and distillate hydrocarbon proved to be good solvents to prevent or reduce formation damage. However, distillate hydrocarbon increases asphaltene dispersion in the fluid because of the aromatic compounds present in the solvent.

- It was shown that the optimal operation conditions for all the solvent cases (propane, n-hexane, n-decane and distillate hydrocarbon) and heavy oil samples were 50 ˚C and 2068 kPa (300 psig). These ideal conditions were determined based on the oil recovery factor and organic deposition on the rock surface. Interestingly, these conditions [temperature and pressure] are applicable to oilsands reservoirs in Canada. Also note that the energy required is not as high (only 50 ^{o}C), which indicates that severe steam heating prior to (or together with) steam (or hot water) is not needed.

- Oil composition is very significant in defining the solvent rate needed. It was shown that it is possible to recover almost the same amount of oil in less time when heavy oil with less viscosity is present in the porous medium. In addition, asphaltene deposition on the rock surface and asphaltene flocculation in the fluid was lower when a heavy oil with lower end compounds was used compared to the heavy oil with higher end compounds.
- In the past, the literature had not focused on measuring the thickness of organic deposition from different types of solvents and heavy oils. In the present research, the

thickness measurement was determined for four types of solvents and two heavy oil samples. In addition, the thickness measurement was also performed for the two wet systems—oil-wet and water-wet.. This data is critical in terms of the stability of the organic deposition on the rock surface and wettability alteration.

- Mixed wettability condition was observed after the solvent treatment through the visual analysis of the grains of the porous medium as asphaltene was deposited on the grain surface partially.

Recommendations

- In this thesis work, experiments were carried out in an unconsolidated sandpack. For a future work, different types of core samples need to be tested, such as limestone and consolidated sandstone, containing different types of clays and minerals. This may help identify the effect of electrostatic forces on the asphaltene deposition process as these rock and mineral types have different electrical charges.

- Formation damage due to asphaltene deposition may be identified using different levels of pressure transducers along the core sample, especially for consolidated sandstones and limestone. Subsequently, the absolute pressure at different points can be calculated at any time of the experiment to identify if any formation damage is present.

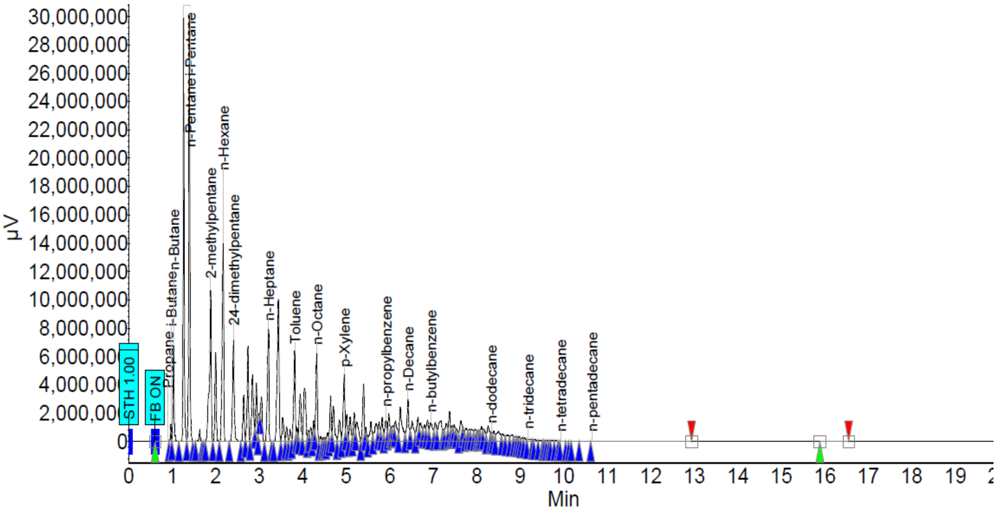
- Miscibility conditions and petro-physical properties are very important in the successfulness of the solvent-based process. Considering the heavy nature of the oils used in this research, a full miscibility may not be achieved effectively, especially at given pressure and temperature ranges. Therefore, determination of surface tension and relative permeabilities may be needed for optimal solvent injection conditions. This is critical as the wettability alteration will cause changes in these parameters.

- One of the main concerns about the solvent injection process is the economic viability. The cost of solvent retrieval using different types of solvents must be studied to determine the economic viability of the process and increase the margin of profit when using the process.

APPENDIXES

Appendix for Chapter 3

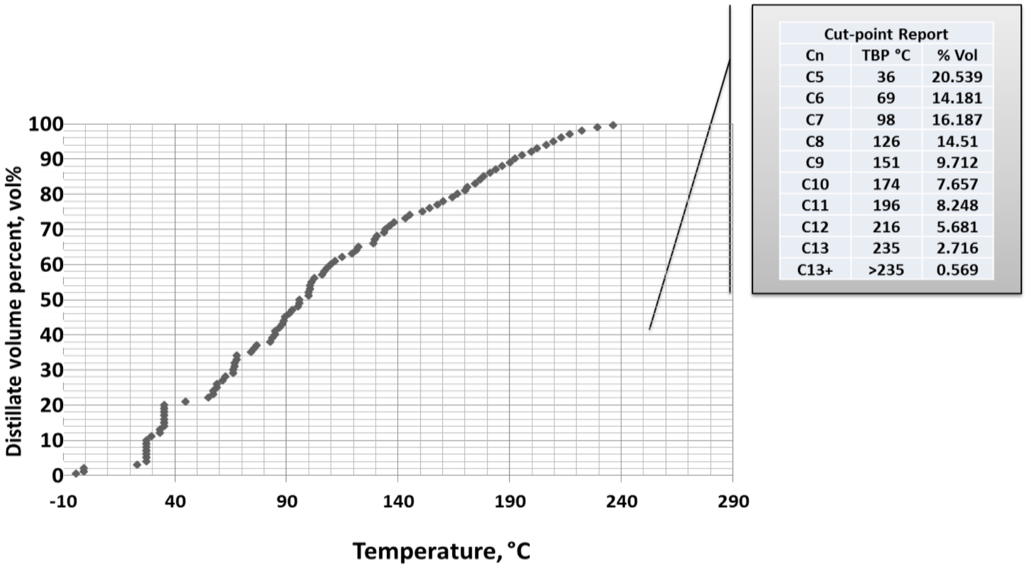
Appendix (3-A) – Characteristics of the distillate used in the experiments as solvent



˚API 62.37

Index	Name	Time (min)	Quantity (%wt)
1	Propane	0.9	0
2	i-Butane	0.97	0.24
3	n-butane	1.03	1.49
4	i-Pentane	1.26	7.52
5	n-pentane	1.39	8.28
10	2-methylpentane	1.88	4.89
12	n-hexane	2.17	5.44
13	24-dimethylpentane	2.41	2.85
20	n-heptane	3.21	3.12
26	Toluene	3.82	2.01
33	n-octane	4.32	2.22
41	p-xylene	4.95	1.62
52	n-propylbenzene	5.91	0.7
58	n-decane	6.42	1.45
64	n-butylbenzene	6.94	0.88
84	n-dodecane	8.33	0.29
95	n-tridecane	9.18	0.17
106	n-tetradecane	9.93	0.03
111	n-pentadecane	10.65	0.02

Figure 3-A1: Quantitative response factor for the distillate using ASTM D7096.10.



Cut-point Report

Cn	TBP °C	% Vol
C5	36	20.539
C6	69	14.181
C7	98	16.187
C8	126	14.51
C9	151	9.712
C10	174	7.657
C11	196	8.248
C12	216	5.681
C13	235	2.716
C13+	>235	0.569

Figure 3-A2: Distillate volume percent of a distillate hydrocarbon using the ASTM D7096-10.

Appendix (3-B) – Error analysis Calculation

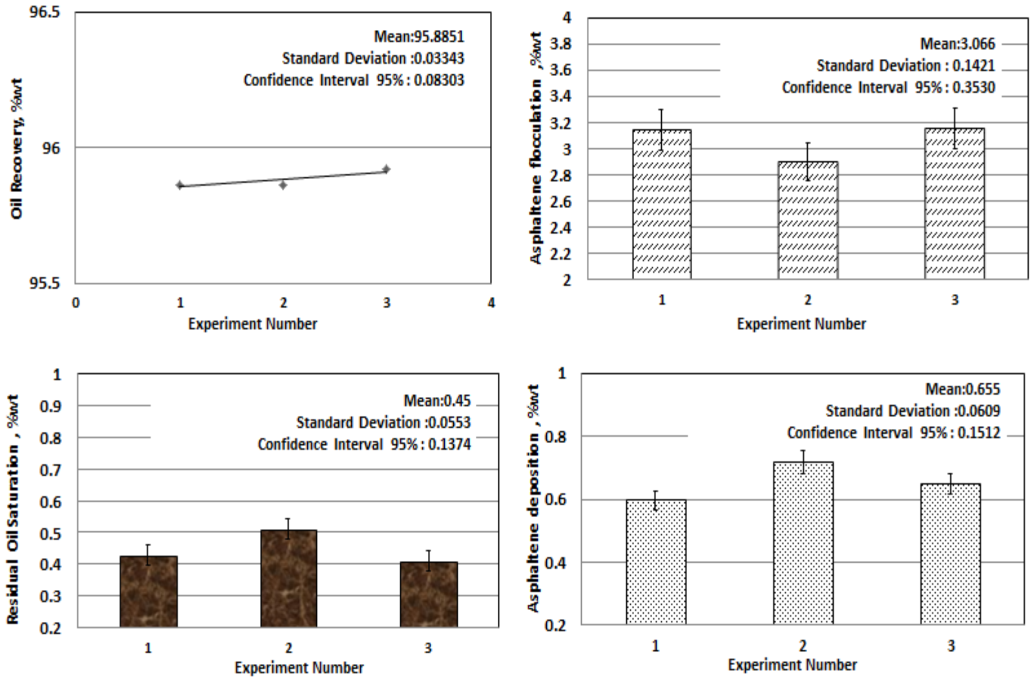


Figure 3-A3: Experimental deviation and *confidence interval* (*CI*) 95% were determined (50˚C and 689kPa) using distillate hydrocarbon as solvent. The error results showed small standard deviation and small confidence interval in the experimental data.

Refractive index measurement

Refractive index **(**RI) measurements have been commonly used for several reservoir engineering calculations such as PVT behavior and surface tension of reservoir fluids, wetting alterations in reservoirs, and asphaltene content. In addition, the RI can be an indicator of the solvent concentration in oil and has been used in the past to predict the onset of asphaltene precipitation in addition of solvent to heavy-oil [3,5]. The RI is also a direct indicator of the level of the asphaltene content (at least qualitatively) to be used in comparative analysis between different oil samples for asphaltene content. In the present study, the refractive index was measured to determine the density reduction in the final heavy-oil sample after the deasphalting process [3,5]. **Figure 3-A4** shows the change in the RI from its original value (original heavy-oil sample) with temperature increment—or the reduction of the refractive index after deasphalting of the heavy-oil using different solvent types. Overall, we observed that propane had a lower refrative index than n-decane, n-hexane and distillate hydrocarbondue to the high asphaltene precipitation (**Figures 3-A4 and 3-A-5**).

Viscosity Measurements

The viscosity reduction was very dramatic against temperature (**Figure 3-A6**). At 25˚C and atmospheric pressure, the viscosity of oil sample B was 3174cp, 1505cp, 1428cp and 1399cp for distillate hydrocarbon, n-decane, n-hexane, and propane, respectively. Thus, the viscosity measurement turned out to be a validation of the sandpack results, which explain strong asphaltene precipitation using solvents with lower carbon number such as propane and hexane.

Higher Temperature Simulated Distillation of Oil Samples. The carbon number distribution is an important parameter in understanding the reasons behind heavy-oil recovery. For this purpose, the two different heavy oil samples (A and B) deasphalting at 50ºC @ 300 psig with different solvent types were analyzed. The distillation percentage shows that higher distillated mass percentage was obtained with propane and n-hexane than with n-decane and distillate hydrocarbon. Lower asphaltene precipitation was obtained with n-decane and distillate hydrocarbon (**Figure 3-A7**), then, less asphaltene deposition and agglomeration can be present in the sandpack. However, oil production has lower quality using n-decane and distillate hydrocarbon than propane and n-hexane as solvent.

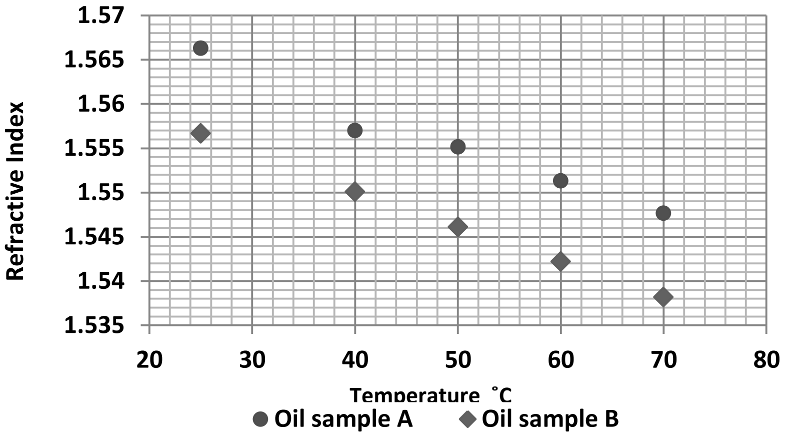


Figure 3-A4: Refractive Index from the heavy oil samples A and B used in the experiments.

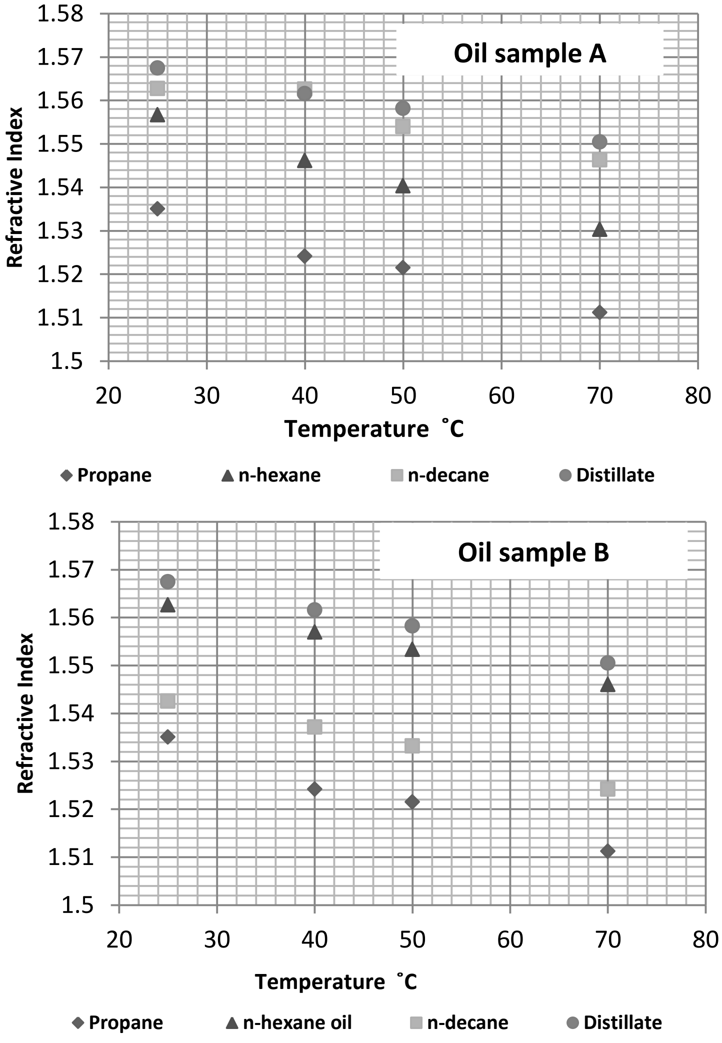
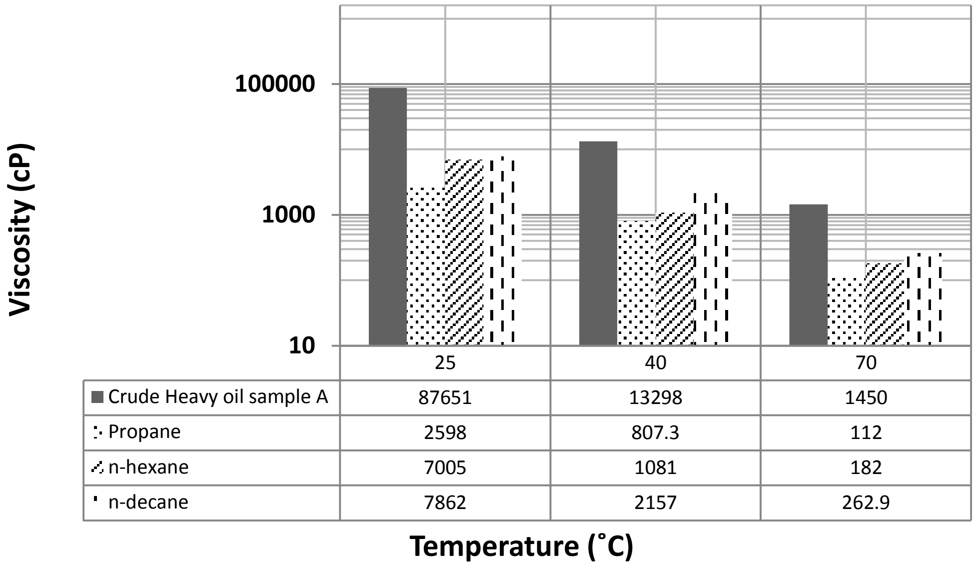
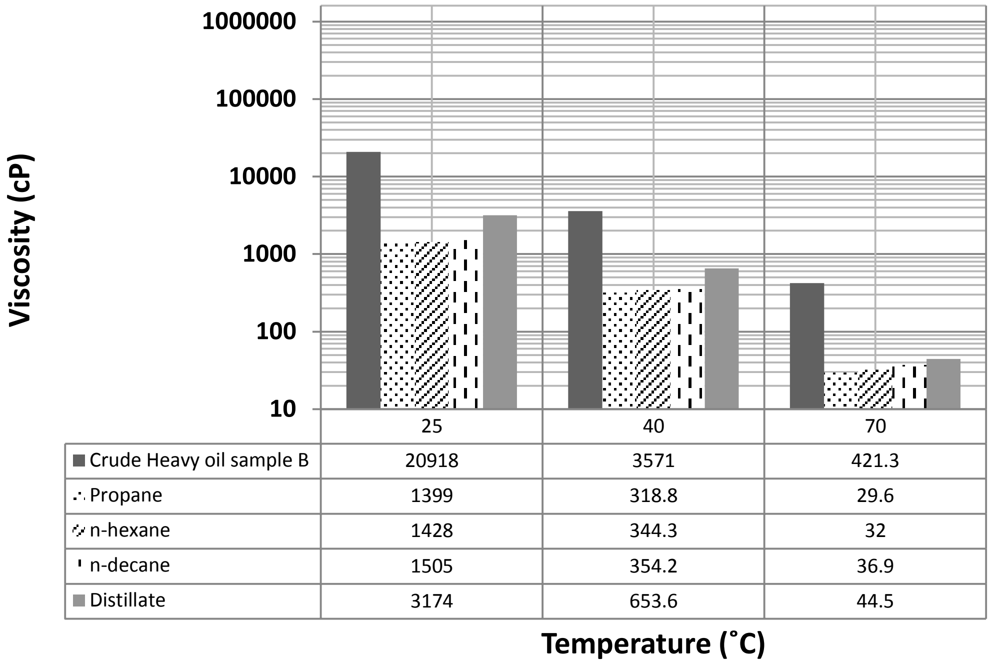


Figure 3-A 5: Refractive Index from the oil production well at different operation conditions and types of solvent.



	25	40	70
■ Crude Heavy oil sample A	87651	13298	1450
⁛ Propane	2598	807.3	112
▨ n-hexane	7005	1081	182
╎ n-decane	7862	2157	262.9

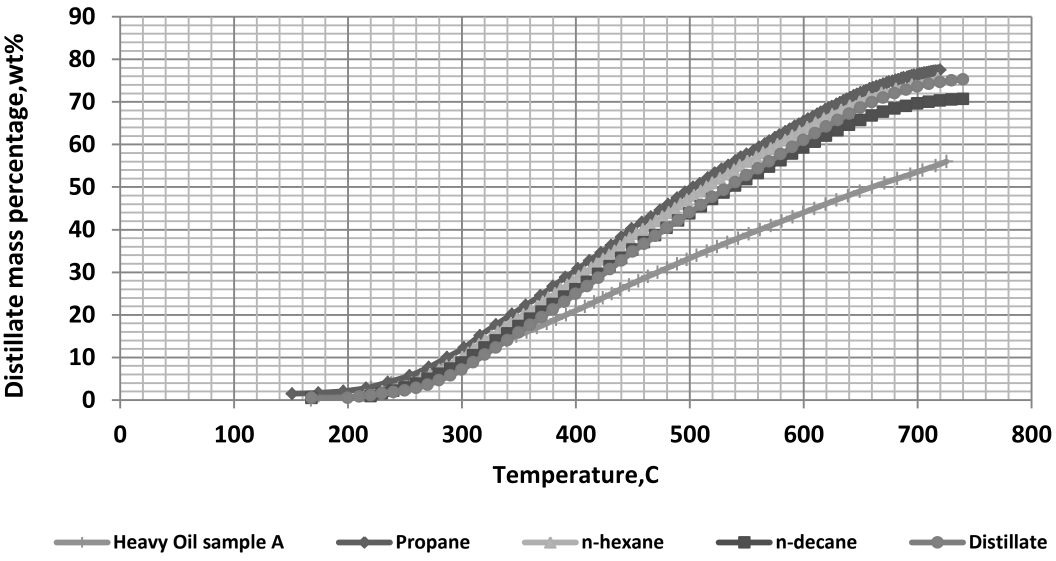
a) Oil sample A



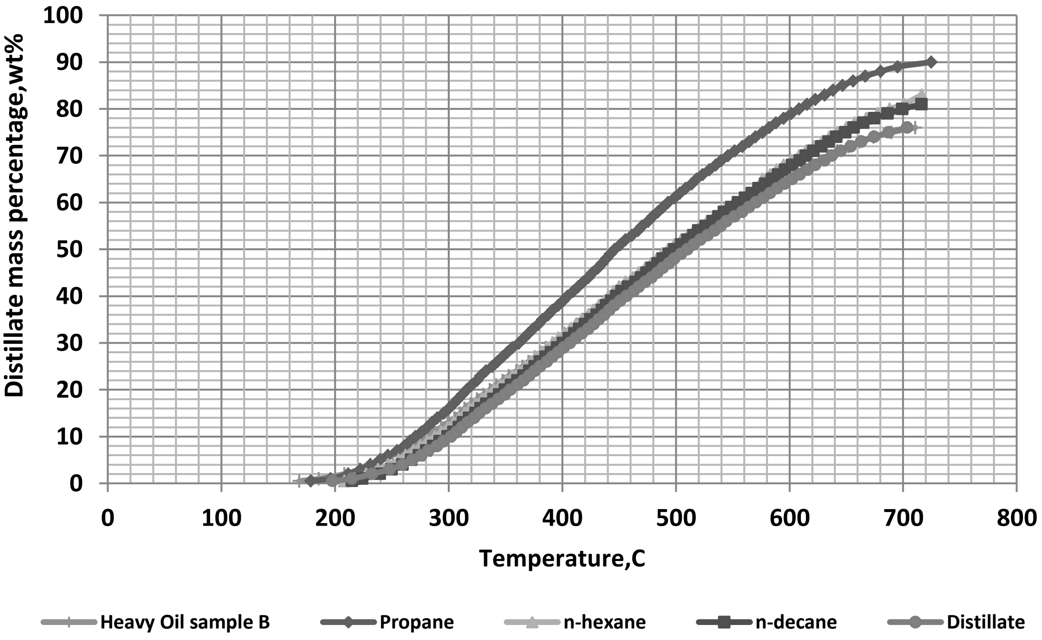
	25	40	70
■ Crude Heavy oil sample B	20918	3571	421.3
⁛ Propane	1399	318.8	29.6
▨ n-hexane	1428	344.3	32
╎ n-decane	1505	354.2	36.9
■ Distillate	3174	653.6	44.5

b) Oil sample B

Figure 3-A6: Viscosity measurements at different temperatures and atmospheric pressure after solvent injection in the sandpack system using n-alkanes and distillate hydrocarbon.



a) Oil sample A



b) Oil sample B

Figure 3-A7: Higher temperature simulated distillation (ASTM D7169) from the oil production well.

Appendix for Chapter 4

Appendix 4-A

Asphaltene precipitation calculation:

$$Asp_{precipitate}(\%wt\ ) = \left[\frac{Asp_{without\ maltenes}}{Initial\ oil\ mass}\right] * 100$$

Appendix 4-B

Organic deposition surface equations:

Equation.4-1 - True distance calculation from the FIB/SEM image distance

$$d_{true} = \left[\frac{d_{image}}{\sin(58)}\right]$$

Equation.4-2 - Arithmetic Mean Square of the surface roughness (µm)

$$R_a = \frac{1}{Number\ of\ the\ peaks}\left[\sum_{i=1}^{n} Z_i\right]$$

Equation.4-3 - Root mean square of the surface roughness (µm)

$$R_{RMS} = \sqrt{\frac{1}{Number\ of\ the\ peaks}\left[\sum_{i=1}^{n} (Z_i)^2\right]}$$

Appendix for Chapter 5

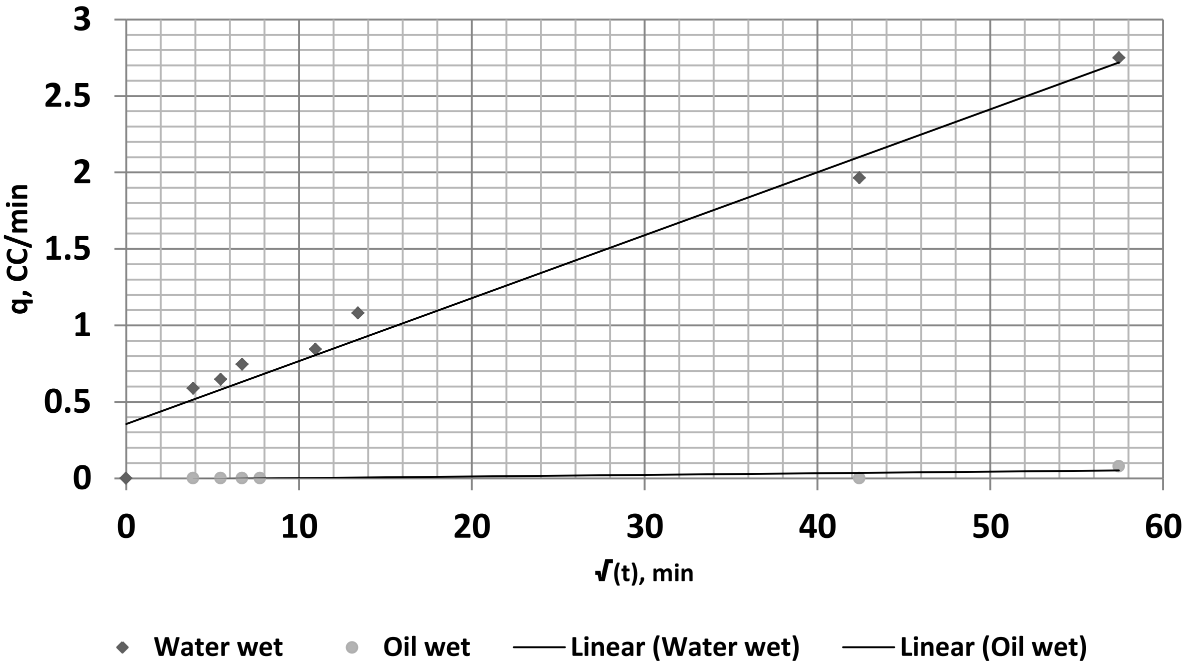


Figure 5-A1: Water imbibition vs. the square root of time in a glass-bead pack: Strongly oil-wet and strongly water-wet systems.

Appendix 5-B - Distillate hydrocarbon

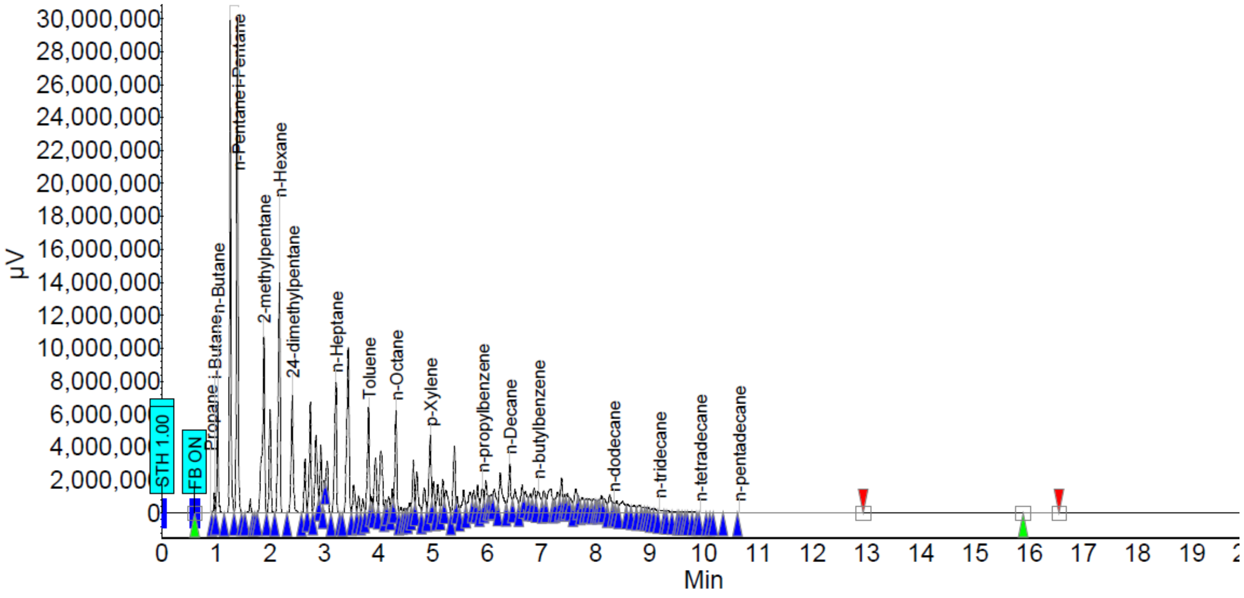


Figure 5-B1: Quantitative response factor for the distillate using ASTM D7096.10.

Appendix 5-C - Organic deposition surface equations

Organic deposition surface equations:

Equation 1 - True distance calculation from the FIB/SEM image distance

$$d_{true} = \left[\frac{d_{image}}{\sin(58)}\right]$$

Equation 2 - Arithmetic mean square of the surface roughness (µm)

$$R_a = \frac{1}{Number\ of\ the\ peaks}\left[\sum_{i=1}^{n} Z_i\right]$$

Equation 3 - Root mean square of the surface roughness (µm)

$$R_{RMS} = \sqrt{\frac{1}{Number\ of\ the\ peaks}\left[\sum_{i=1}^{n} (Z_i)^2\right]}$$