Microfluidics and Nanofluidics for Unconventional Resources in Micropores and Nanopores

by

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Abstract

Unconventional resources play a crucial role in meeting the current global energy demand, however, production from these formations is challenging. The challenge mainly stems from either the extreme fluid properties (oil sands) or extreme rock properties (shale and tight sandstone). Primary production from unconventional reservoirs is very low which motivates testing and developing recovery strategies to improve the reservoir production. Micro/nanofluidic technologies have shown to be a promising tool to quantify the pore-scale recovery efficiency of different methods with a tight control over the operating conditions, i.e. pressure, temperature, and composition. In this work, we designed and developed two distinct micro/nanofluidic platforms to test some of the recovery methods for both bitumen and tight oil systems. This work highlights the unique potential of microfluidic and nanofluidic methods in resolving the pore-scale behavior of enhanced oil recovery processes under relevant reservoir conditions.
Dedication

I would like to dedicate my thesis to my wife, Cassey Wang, who unconditionally supported my decision to pursue my MASc degree at the University of Toronto.
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Chapter 1

1 Introduction

The 2018 BP Energy Outlook reports that the global energy resource demand is shifting from fossil fuel to cleaner energy resources with less GHG (greenhouse gas) emissions, with associated environmental benefits [1]. While recent advances in renewable energy are to be celebrated and further encouraged, annual oil consumption continues to increase each year due to even faster growth of total energy demand [1]. In addition, coal-powered electricity production is being replaced in many regions with less GHG-intensive natural gas produced from hydraulic fracturing, however oil demand is generally more difficult to satisfy with natural gas. For these reasons it is likely that substantial oil demand will continue in the coming few decades.

To satisfy the high demand in the near future, the world’s oil production rate must be maintained at or higher-than the current level; a demand that will be satisfied largely through the development of unconventional resources [2]. As two major unconventional resources, bitumen and tight oil account for 30% of the global recoverable unconventional oil resources [3]. However, production from these reservoirs is challenging and associated with economic and environmental issues [4], [5]. Therefore, various Enhanced Oil Recovery (EOR) methods need to be tested to understand their overall efficacy and impact on the environment.
1.1 Oil Sands Recovery

1.1.1 Background and Motivation

Canada is one of the largest bitumen producers in the world [6]. With 174 billion barrels of proven bitumen reserves, the province of Alberta (Canada) is ranked as the third largest oil reserve in the world [4]. The major challenge in bitumen production is its extremely high viscosity. The bitumen viscosity is over one million mPas under reservoir conditions, resulting in a severely low bitumen mobility [7]. Surface mining method is used to extract shallow bitumen reserves with a depth less than 75 meter. However for deeper bitumen reserves, which account for 80% of the total bitumen reserve in Alberta, viscosity plays a significant role in recovery process [7], [8]. Thermal recovery is currently the most effective method for viscosity reduction. When the temperature is increased to around 200 °C, the viscosity can be reduced to around 10 mPas, which greatly increases the flow of bitumen [9].
Steam Assisted Gravity Drainage (SAGD) is the most practical method for thermal bitumen extraction where two parallel horizontal wells are drilled at a vertical separation distance of 5 to 7 meters. Saturated steam carrying significant latent heat energy is injected into the top well at a pressure in a range of 1~2MPa. Steam condenses at the bitumen interface, transferring heat (thermal energy) to the bitumen phase which reduces the bitumen viscosity, making it mobile towards the lower production well (Figure 1-1). A steam chamber is gradually developed and continuously growing as the extraction continues until the heatloss to the surrounding formation reaches a balance with the energy of the injected steam, known as the end of the SAGD lifecycle [11]. The SAGD process is very energy intensive due to the demand of continuous steam generation which is powered by burning natural gas. When compared to recovery processes of
different oil reserves, the bitumen extraction process releases more CO$_2$ (Figure 1-2b), which accounts for about 10% of the total annual GHG emission in Canada [12]. Among the factors that drive up emissions, natural gas powered steam generation accounts for the majority (Figure 1-2a). In SAGD, the most important objective is to achieve a lower Steam-Oil-Ratio (SOR) which is a measure of the energy usage per barrel of oil produced. Therefore, to minimize the impact on the environment, a reduction in SOR is needed to either reduce steam usage or increase bitumen production.
One of the methods to decrease SOR is to use organic solvents, such as propane and butane, as a steam additive to provide additional bitumen dilution at the bitumen/steam interface. This strategy can improve the mobility of bitumen and, if successful, translates into enhanced oil production and lower SOR. However, the addition of solvents both increases the cost of the injection fluid, and complicates the already complex multicomponent thermal-chemical process [15]. To study and optimize the factors that affect the oil production, a set of experiments were conducted on a glass micromodel with both pure solvents and industrial mixtures (full details in Chapter 2).

1.1.2 SAGD Literature Review

After the proven success of SAGD bitumen recovery method, many similar methods have been derived to accommodate variations in reservoir conditions or reduce the SOR.

For thinner bitumen reservoirs, such as the oil reserve in Lloydminster (Canada), overloss of thermal energy to overburden formation make traditional SAGD uneconomic. To reduce the cost, Butler and Mokrys developed a Vapor Extraction (VAPEX) method that can recover the viscous bitumen at a lower temperature (T~80 C) [16,17]. The process is very similar to SAGD method, but the injected fluid is replaced by the mixture of hot water and saturated vapor of lighter hydrocarbon solvent (propane). It was found that the saturated solvent vapor condensed at the bitumen interface which further lowered the bitumen viscosity and eased its flow. It was also found that with the presence of a solvent, the asphalting deposition occurs in the reservoir, which improved the quality of produced oil [18]. VAPEX has been proved to be a technically and economically feasible thermal recovery method for thinner bitumen reserves. For extremely thin
reservoirs, a single well SAGD (SW-SAGD) is more suitable. The single well is completed with long tubing to the toe and annulus to the heel, where the steam is injected to the toe through the long tubing and heated bitumen is produced at the heel through annulus [19]. Thermal energy can be transferred from steam to the liquid flowing outside of tubing to reduce the viscosity and ease the flow of bitumen.

During SAGD production, bitumen can be recovered through steam chamber growth, however, the oil between two nearby chambers is very hard to extract. A Fast-SAGD method was developed to solve this issue. During the Fast-SAGD operation, an infill well is drilled between two nearby chambers to perform cyclic steam stimulation, which can heat the cold bitumen between nearby well-pairs and accelerate the thermal communication of the two chambers. Once the thermal communication is established, the infill well can be converted to a production well to recovery the heated bitumen, which not only can accelerate the bitumen production process but also result in additional oil production compared to conventional SAGD method [20,21].

Bitumen extraction from mature SAGD steam chamber usually requires more steam to maintain the pressure of the large chamber, which is not economic due to the higher SOR ratio. A non-condensable gas (NCG) injection method can be used, where gas is injected with steam to maintain the pressure and free up more steam for chamber edge development, which can significantly reduce the steam usage and lower SOR [22]. Suncor Energy Inc. has implemented this technology in a field pilot which has shown encouraging results [23].

Due to the economic and environmental issues associated with steam generation, researchers have long looked to improve on the current SAGD method. One approach to improve performance is to replace steam with saturated solvent vapor (e.g. propane). The bitumen is heated and then diluted by large amounts of condensed solvent, which can greatly reduce the viscosity and ease the flow
This process eliminates water usage and requires a relatively low reservoir temperature (T~60°C), which can reduce 80% of the energy consumed in SAGD process. However, the recycle efficiency of the solvent remains unknown.

Solvent-Assisted SAGD is another new method, where only a small amount of solvent is injected with steam to provide the additional benefit of bitumen viscosity reduction due the dissolving of the solvent in bitumen at steam/bitumen interface, which results in higher recovery rate and lower SOR [25]. Due to the addition of solvents, the underground thermal-chemical process becomes very complex where more research studies are needed to analyze factors that potentially affect the performance.

1.2 Tight Oil Recovery

1.2.1 Background and Motivation

Tight oil refers to light crude oil from a sandstone and shale formations having very low matrix permeability. There is a tendency to refer to tight oil as shale oil, which is confusing because the latter one also refers to the distillate produced from oil shale by thermal decomposition [26]. In the thesis, tight oil is used instead of shale oil to eliminate the confusion. Tight oil was originally considered an unrecoverable resource due to the extremely tightness of these formations, until the emergence of horizontal drilling and hydraulic fracturing technologies. The advancement of these two technologies have unlocked substantial tight oil reserves and boosted the oil production in the U.S. (Figure 1-3) [27,28]. Since 2010, the U.S. oil production rate have increased from 5.5 million barrels per day (MB/d) to 9.6 MB/d in five years, which resulted in a drop of oil imports of 2 MB/d and greatly reduced the dependence on imported oil [27,29].
Unlike conventional vertical wells, the well for tight oil recovery is drilled horizontally, which is followed by a stimulation fluid injection at extremely high pressure to frack the shale rock and ease the flow of surrounding oil towards the wellbore (Figure 1-4a).

Although the advancement in technologies has gradually increased the oil production rate of newly drilled wells since 2008, the extremely low permeability still restricts the flow in the non-fractured shale formation around the wellbore (Figure 1-4c). The result is low primary recovery, commonly
only 5~10% of the original oil in place (OOIP) [32]. This forces shale operators to drill more new wells at a higher frequency and higher surface density which consumes a huge amount of energy and water (hydraulic fluid) and also results in significant surface disturbance [33,34]. To operate the tight oil resource in an economic and less damaging manner, a variety of effective tight oil enhanced oil recovery (EOR) methods are needed. The analogy with conventional oil is that tight oil is still in primary production, and a wide range of EOR technologies awaits for secondary and tertiary production strategies. Perhaps more critically, methods to test new strategies in these intensely tight formations are critically needed. In chapter 3, CO₂ and N₂ floodings and CO₂ huff-and-puff methods are studied on a nanomodel platform that is representative of the tight oil recovery process.

1.2.2 Literature Review of Tight Oil EOR

Water and gas flooding are the two most mature EOR methods for conventional oil recovery. However, in the shale formation, waterflooding may result in an injectivity issue due to the low permeability and porosity. A simulation study compared gas and water injection in a shale reservoir simulation model with results showing a low oil recovery rate for the water injection case [32]. However, another study pointed out that water injection can reduce the reservoir temperature and increase the pressure, both of which can result in more fractures in the shale formation [35]. Such additional fractures can provide additional hydrocarbon recovery not considered in the previous simulation model.

Gas injection has been proven to be effective in some cases. CO₂, for instance, can easily reach supercritical point (T~ 31 °C, P~7.3 MPa) where the density is 70% that of water but the viscosity is only 0.1~0.25 that of water. This low viscosity greatly eases the flow of supercritical CO₂ (ScCO₂) in a tight shale formation [36]. When the injection pressure is above minimum miscible
pressure (MMP), the interface between ScCO$_2$ and oil disappears, which also reduces any capillary effects during displacement and further contribute to recovery. For extremely tight shale reservoirs, it may take great amount of time for the injection pressure to propagate to the production well. In such cases the huff-and-puff method is more suitable since it does not require communication between two wells. The huff-and-puff process usually involves gas injection, soaking, and production from the same well[36]. An experimental study was conducted on shale core plugs to study the effect of CO$_2$ soaking pressure and time to the oil recovery rate [37]. It was found that oil recovery does not increase at a longer soaking time when the pressure is lower than the MMP, but it increases when pressure is above MMP. As expected, with subsequent huff and puff cycles, it was found that the incremental oil production decreases - a result also confirmed by Song and Yang’s simulation and experiments related to the Bakken shale formation [38]. A field-scale simulation based on the geophysical properties of Bakken Shale was conducted to compare CO$_2$ injection and huff-and-puff methods [39]. The simulations show that the CO$_2$ injection expressed better recovery than the huff-and-puff method. However, the continuous CO$_2$ injection makes the process less economic.

Based on the literature review, most research in this area to date has focused on simulations and shale core plugs, neither of which can provide a direct visualization of the recovery dynamics in nanopores. In chapter 3, a nanofluidic platform is developed to study and compare N$_2$, CO$_2$ flooding and CO$_2$ huff-and-puff to provide a better understanding of those EOR methods in nanopore oil recovery.

1.3 Application of Microfluidics in Petroleum Industry

Microfluidic platforms are becoming more popular in the oil and gas sector because they can provide quick and accurate analysis while providing precise control over the operating conditions
(temperature and pressure) of the system [40,41]. The platform reduces both the operating time and the volume of testing samples for experiments, which lower the material and operating cost (cost per test result).

Oil property measurement is one of the most popular applications for oil and gas microfluidics. Phong et al. measured minimum miscible point (MMP) of CO$_2$/crude oil on a microfluidic device, where native fluorescence of the crude oil phase was used to detect miscibility with the non-fluorescent CO$_2$ phase. The experiment achieved very accurate results while reducing the testing time from a few days to 30 mins. Based on Phong’s experiments, Sharbatian et al. designed a new microfluidic chip with closed-ended channels which can be considered as micro-Pressure-Volume-Temperature (micro-PVT) channels. This chip was used to measure many CO$_2$–oil mutual properties such as solubility, diffusivity, and contact angle in addition to MMP [42]. The micro-PVT channels allowed the measurement of oil swelling/extraction in response to CO$_2$ at various pressure and the results were very close to previous studies but required a fraction of the time compared to traditional PVT cells. Microfluidic devices have also been used to measure the whole phase diagram of CO$_2$ [43], asphaltene deposition [44], and the wax appearance temperature of reservoir fluids [45].

Another major application of microfluidics in the oil and gas industry is in the screening of enhanced oil recovery (EOR) strategies in physical models of the reservoir – commonly called micromodels. These systems can provide unprecedented direct visualization of real-time pore scale dynamics and instantaneous oil recovery rates during extraction. This level of resolution is not available through traditional experiments conducted on core plugs or sand packs. He et al. fabricated a microfluidic chip with random network of channels, which was used to simulate porethroats in the reservoir, for studying the non-emulsifying (NES) and weakly-emulsifying
(WES) surfactants flooding [46]. Their results indicated that the WES-based injection fluid has a higher recovery rate, which was also confirmed by the results of large-scale field pilots. To study foam flooding in a reservoir with varying permeabilities, Ma et al. fabricated a PDMS microfluidic chip with both high and low permeability porous medium region [47]. Their experiments demonstrated that surfactant-stabilized foams can greatly enhance the sweep efficiency of the system, which in turn indicated the potential application of this tool for foam optimization. De Hass et al. designed a glass micromodel to study bitumen extraction in the SAGD process [48]. In their experiment, steam propagation and bitumen emulsification are studied to compare the steam and steam additive runs. It was found that the alkaline steam injection enhanced the emulsification and improved the stability of the emulsion, which resulted in a higher oil recovery. Using similar micromodel, Qi studied pure solvent injection as an alternative to steam in the recovery of bitumen at low temperature. They found that strong bitumen dilution and vapor fingering at the condensing edge was essential for bitumen production using this approach [49].

1.4 Thesis Overview

The main objective of the thesis is to develop and apply microfluidics and nanofluidics to analyze and screen EOR strategies for both bitumen (oil sands) and tight oil (shale) recovery.

In Chapter 2, four different solvents were tested as steam additives to boost oil recovery. As compared to pure solvents and an alternate blend, naphtha was found to provide the highest oil recovery. This performance was due to the combination of (1) bitumen dilution at the edge of steam chamber, (2) the delivery of higher thermal energy to bitumen/steam interface, and (3) less asphaltene deposition at the condensation zone. This process insight was uniquely accessible with the micromodel system.
In Chapter 3, gas flooding (CO\textsubscript{2}, N\textsubscript{2}) and huff-and-puff (CO\textsubscript{2}) were studied to find the most effective method for oil recovery in a nano porous medium. CO\textsubscript{2} flooding with injection pressure higher than MMP was found to have the best recovery results due to (1) the lack of interfacial tension easing the displacement process, (2) the higher mobility ratio (still less than one) resulting from the higher density of supercritical CO\textsubscript{2} (ScCO\textsubscript{2}), and (3) the larger solubility of CO\textsubscript{2} (compared to N\textsubscript{2}), which enhances the extraction of lighter oil components.
2 Pore-Scale Analysis of Steam-Solvent Co-injection: Azeotropic Temperature, Dilution and Asphaltene Deposition

A large portion of this chapter was published in Fuel [15] – and parts here have been reprinted with permission from publisher. The applicant was the primary author for this work and played the primary role in experimental design, data collection and analysis, and write-up. The efforts of Dr. Ali Abedini, ZhenBang Qi, Mira Kim, Adriana Guerrero and Professor David Sinton are gratefully recognized.

2.1 Introduction

Steam-assisted gravity drainage (SAGD) is the main commercial in situ thermal recovery for bitumen extraction. SAGD includes injecting steam and producing bitumen via a pair of parallel horizontal wells drilled in the bitumen formation [50–54]. Saturated steam is injected from the upper well and condenses at the steam boundary, which in turn, delivering the latent heat to the bitumen. The bitumen viscosity significantly reduces as a result of heat transfer; allowing bitumen to flow toward the lower well (i.e., producer) under gravity force. While SAGD is effective for high production rate, it has significant economic and environmental challenges. Natural gas powered steam generation and associated CO₂ emissions are the major economic and environmental costs [55,56]. Some alternatives have been proposed to increase the performance of SAGD on both fronts, including steam-solvent co-injection, steam-additive co-injection, and pure solvent injection [57–59]. Among the aforementioned scenarios, steam-solvent co-injection is a hybrid approach that is attracting the most current interest [60–64]. This approach combines the advantages of steam in terms of delivering intense latent heat at the oil interface, with solvent dilution, and promises a reduction in steam-oil-ratio (SOR) with and associated cost and emission
reductions. It has been reported that small addition of solvent into the steam improves the recovery efficiency by ~25% and reduces the SOR by ~40% [61]. The addition of solvent, however, complicates an already complex multicomponent thermal-chemical process, necessitating careful planning and analysis.

Steam-solvent co-injection involves complex flow dynamics with a complex multi-component phase behavior that occurs under extreme operational conditions. A variety of methods have been used to assess the performance of steam-solvent processes, including large 3-D physical modeling [62,65–68] and numerical simulations [61,67,69]. With steam as the major component of the injected mixture, the challenge is to select a solvent whereby the solvent-steam condensation temperature - the azeotropic point – is matched that of pure steam. In this way the solvent travels effectively through the vapor chamber, and then condenses at the oil interface where it can provide bitumen dilution. While solvents with phase transitions close to that of pure steam (such as hexane) have been recommended for this process, recent numerical simulations have shown heavier hydrocarbon solvents (e.g., C8s–C10s) perform more effectively due to better match between the steam-solvent azeotrophic temperature and the steam saturation temperature [60,70].

Large sand pack models also provide insight into overall effectiveness, showing for instance cumulative oil production as a function of total pore volume of injected phase, and overall size of steam chamber with some local temperature measurements [62]. While insightful, past experimental and simulation methods cannot resolve the full combination of condensation, dissolution, asphaltene precipitation and recovery at the oil interface – insight essential for this complex process.

Microfluidics-based approaches have been developed to probe the details of fluid interactions in various chemical and petroleum processes [40,71]. One important application is the measurement
of phase properties of solvent–oil systems at relevant reservoir conditions [43,72–77]. There is also precedent for the application of microfluidics in phase measurement and recovery assessment of bitumen extraction processes. A T-junction pattern was employed to measure the diffusivity of a toluene-bitumen mixture using the variation of fluorescence intensity at the interface [78]. A similar chip was developed to measure the diffusion coefficient of CO2 in Athabasca bitumen at pressures up to 5.0 MPa [79]. The solubility and diffusivity of propane in bitumen were measured using a microchannel version of a conventional PVT cell [80]. Likewise rheology of heavy oil during capillary driven flow has been studied on-chip [81]. An associated body of work involves micromodels – microfluidic chips designed to mimic the reservoir rock pore geometries – to analyze the pore-scale dynamics of enhanced oil recovery processes [15,82–86]. Relevant micromodel studies of bitumen recovery include (i) pure steam and steam injections with alcohol- and alkaline-based additives [48,87], (ii) condensing solvent injection [15], and (iii) steam-solvent co-injection [88]. The latter one visualized the steam-solvent condensation at the bitumen interface with associated asphaltene precipitation and phase entrapments at atmospheric pressure using n-pentane and n-hexane as injected solvents with steam. The variety of previous micromodel applications points to the importance of pore-scale investigation of recovery processes. In addition to the direct observation of the fluid transport, micromodels provide a tight control over operating conditions (i.e., pressure, temperature, and saturation) with fast quantification, ease of operation, and low experimental cost; all stemming from small volume of fluid samples required for experiments.

In this chapter, the pore-scale mechanisms of steam-solvent co-injection for bitumen extraction are quantified through optical and thermal imaging of a micromodel. Series of tests (i.e., pure steam and steam-solvent co-injection tests) were conducted with different pure and industrial solvents under relevant reservoir conditions. A suite of optical, thermal, and pore-scale microscopy
tools is employed to capture the real-time process-critical data and resolve the complex pore-scale behavior at the heart of steam-solvent co-injection strategies. Imaging both the fluid phases and the thermal field enables thorough analysis of the steam-solvent condensation zone with both pure and industrial solvents.

2.2 Experimental

2.2.1 Fluids

Athabasca bitumen processed to remove sands and water, was used for micromodel experiments. The molecular weight and density of the bitumen were 588.8 gram/mole and 1.02 gram/cm$^3$, respectively – with composition of light components ranging from $C_1$–$C_{10s}$ ($C_{10s}$, a name for hydrocarbons with ten carbon atoms) is less than 0.1 wt%. The viscosity of the bitumen was measured using a capillary viscometer over a wide range of temperature and determined to be $\sim 10^6$ mPas at the room temperature. The compositional analysis and measured viscosity-temperature data of the bitumen are presented in the appendix. Two pure hydrocarbon solvents, n-butane and n-hexane, and two industrially practiced diluents namely condensate and naphtha were used for steam-solvent tests. The condensate sample was more volatile compared to the naphtha sample. The condensate was composed of $\sim 70$ wt% of $C_{5s}$ and $C_{6s}$ fractions while the naphtha contained $\sim 77$ wt% of $C_{7s}$ – $C_{10s}$. The compositional analysis and fluid properties of the condensate and naphtha samples are presented in the appendix.
2.2.2 Microfluidic Apparatus

**Figure 2-1.** Schematic diagram of the micromodel apparatus used for pore-scale analysis of steam-solvent co-injection, with the imaging system shown expanded on top. The red shading indicates the heating elements covered by insulations.

The schematic of the experimental setup used for solvent-solvent co-injection experiments is shown in Fig. 2-1. A 2-D glass micromodel with 10 cm x 10 cm dimensions was designed and fabricated by photolithography and wet-etching methods with hydrofluoric acid solution to a depth of 57 µm on a 2.25 mm borosilicate glass (Schott BF33).
Figure 2-2. (a) Unit cell of pore network pattern after etching micromodel; (b) pattern depth profile obtained by an optical profilometer; (c) Grain size distribution of the pattern; (d) Pore throat size distribution of the pattern; (e) Pore body size distribution of the pattern. In Figure 2-2a: The red text signifies the grain diameters; the white text signifies the pore throat sizes (dimensions all in µm) and the blue circles show the pore body areas.

The physical dimensions and pore characteristics of the micromodel are presented in Fig.2-2. A peek manifold was designed and machined to firmly hold the micromodel and to connect injection and production lines to the micromodel. Two distinct syringe pumps (Teledyne-Isco 260D) were used to injected deionized water and solvent into a coil type steam generator. The steam generator contained three cartridge heaters (McMaster-Carr, 3618K413) and was used to generate a uniform mixture of steam-solvent vapor at the required temperature prior injecting into the micromodel. A by-pass line was used to stabilize the temperature and pressure of the steam-solvent mixture prior to injection. The inlet and outlet lines (1/16” stainless steel tubing) of the system were wrapped and heated with heating ropes (McMaster-Carr, 3641K24) and well insulated to prevent heat loss to the external environment. Three separate, dedicated temperature controller systems (Omega,
CNI3222) with the accuracy of ±1 °C were also used to control the temperature of all heating elements including the steam generator, inlet and outlet lines. The micromodel outlet was connected to a back pressure regulator (Equilibar, EB1ZF1) to control the outlet pressure – resembling the well-bore pressure in field-scale SAGD operations. A combination of imaging tools was employed to capture the real-time process data. A digital single-lens reflex (DSLR) camera (Canon, D60) was used to capture the model-scale progression of the steam chamber development and overall sweep efficiency. In parallel with optical imaging of the micromodel, an infrared camera (Razir, RAZ-IR Nano) was also used to obtain the temperature map of the process. For pore-scale observation, a USB microscope camera (Dinolite, AD-4013TL) captured the displacement at the pore-level of the micromodel.

2.2.3 Experimental Procedure

The micromodel was first filled with deionized (DI) water followed by bitumen injection using a glass syringe to establish the initial fluid saturation. The bitumen is injected into the micromodel at 85 °C, allowing easier and uniform filling due to less bitumen viscosity at a higher temperature. The saturated micromodel was then embedded in the manifold with all the ports connected to the injection and production lines. A rim of LED lights was also used to provide a proper light for imaging. All the cameras were also aligned with the micromodel for high-quality imaging.

The solvent and deionized water were injected into the system through a by-pass line with the volumetric ratio of 1:10 and volumetric flow rate of 90 and 900 µl/min, respectively. A relatively high flow rate of steam in the side channel was required to set the thermal boundary condition for the test, and to produce reservoir-relevant steam-bitumen interface advancement velocities (~100 µm/min) in the chip [89]. The steam generator and all the heating elements were also set at desired temperatures to achieve a steam-solvent mixture with 185–195 °C. The back-pressure regulator
was adjusted at 1.0 MPa to obtain a uniform fluid flow through the system. Once all the operational parameters (i.e., steam-solvent temperature, injection flow rate, and pressure) reached an equilibrium condition, the injection was switched from the by-pass line into the inlet of the micromodel. The DSLR and IR-thermal cameras were set to take optical and thermal images of the micromodel every 30 s during the experiments. The USB camera also captured the pore-scale images of different regions for multiple times during the experiments. To calculate the oil recovery, optical images are first converted to B/W and then ImageJ (image processing software) is used to calculate the recovered area at each time frame. The recovered area can be converted to cumulative recovery and instantaneous recovery rate.

After the termination each test, the entire injection and production lines were sequentially cleaned by toluene, IPA, and DI water. The micromodel was also completely cleaned with toluene and IPA at ~90 °C. Thereafter, the chip was placed in a vacuum oven at ~150 °C for ~1 hr to vaporize remaining fluid in the micromodel. The inlet and outlet ports of the manifold was also cleaned with toluene to remove any blockage. Over the course of several preliminary runs, loading and cleaning with bitumen and hydrocarbon solvents, the micromodel becomes preferentially oil-wet, as reported in previous studies [49,90]. This condition was the standard starting condition for all test results here.
2.3 Results and Discussion

2.3.1 Steam Chamber and Condensing Zone Development
Figure 2-3. Compiled micromodel results from steam and steam-solvent runs. a) Stacked optical-thermal images of micromodel runs indicating the steam chamber and condensing zone advancements; b) cumulative recovery factor of all steam-solvent runs with time-lapsed chamber growth shown in inset; c) final recovery factor of all steam-solvent runs with recovery improvement over steam case shown in inset.

Fig. 2-3a shows the time-lapsed images (optical and thermal images are stacked) of all micromodel runs with the temperature scale shown in the right. The maximum temperature on the scale is set at 180 °C which corresponds to the steam saturation temperature at 1.0 MPa. Three distinct regions were formed during all steam-solvent co-injection tests (from left to right) including steam chamber, condensation zone, and untouched bitumen zone. The steam chamber holds steam and vapor-phase solvent, while the condensing zone consists of steam and solvent in both vapor and liquid form. The temperature is very uniform in the steam chamber and then declines sharply in the condensing zone. It is noteworthy that the IR-thermal camera records the temperature of the external surface of the micromodel, which through calibration tests has been verified to be within 1–2 °C of the internal surface of the micromodel when the experimental temperature is in the range of 25–200 °C. Thus, the temperature contours marking the pure steam condensation boundary are likely biased leftward a distance less than 1 mm (~1% of the model width), a relatively small deviation due to the high temperature gradients in the chip.

Fig. 2-3b compares the time-lapsed cumulative recovery factor for all micromodel runs with the time-lapsed steam chamber growth shown in inset. For all steam-solvent runs, the steam chamber grew faster at initial times of the process mainly due to thinner condensing zone and relatively low heat loss to the surroundings. The steam chamber slowed after ~30 min of the experiments which consequently resulted in decline of recovery rate. Fig. 2-3c shows the final bitumen recovery factor.
of all micromodel runs with the recovery improvement over the pure steam case shown in inset.

The recovery improvement over the steam case is the ratio of additional recovery factor obtained by steam-solvent to the base case steam recovery factor. In contrast with all solvents, steam-naphtha showed the highest bitumen recovery (RF = 60%) compared with the corresponding steam run (RF = 46%), improving the total recovery by ~30% over the pure steam. The condensate and hexane also showed recovery improvement over pure steam and increased the final bitumen recovery factor to 52%, and 50%, respectively. Unlike the aforementioned solvents, butane had a minimal improvement on the bitumen production with a final recovery factor close to that of steam run.

**Figure 2-4.** Final profile of a) steam chamber border, and b) bitumen front interface for all micromodel runs. The area between these two profiles is condensing zone. The steam chamber border is taken by IR-thermal data and the bitumen front profile is directly taken from optical images.

Fig. 2-4a shows the final profile of steam chamber border as determined from the thermal imaging (i.e., the line where the steam starts to condense, T = 180 °C). The position and profile of the steam
border compares the final extent of the steam chamber for all micromodel runs. In general, addition of solvent enlarged the chamber, and this improvement is most pronounced for the steam-naphtha case. The final profile for steam-hexane is very similar to that of steam-condensate case, and both advanced further than the corresponding steam case. However, butane had a minimal impact on the progression of the steam border with the profile very close to that of steam case. Fig. 2-4b compares the bitumen front interface as determined from the optical camera (i.e., the line along the condensed steam/solvent-bitumen interface) for all runs. Similar to the isothermal analysis of Fig. 2-4a, the bitumen interface profile of butane-steam case was overlapped with that of pure steam run. However, the bitumen front interface for both steam-naphtha and steam-condensate runs were more advanced, indicating more effective recovery, especially in the steam-naphtha case.

2.3.2 Thermal Analysis of The Steam-Solvent Condensation Zone

Steam-solvent phase behavior and condensation dynamics are critical to the recovery performance of the steam-solvent co-injection process. The condensation zone here is defined as the region between the steam saturation line and bitumen interface, where the condensation of injected fluid mixture (i.e., steam and vapor solvent) occurs. Co-condensation of steam-solvent mixtures depends strongly on the composition of the solvent. For a given steam-solvent mixture, the solvent condenses with steam at a temperature lower than steam saturation temperature which is known as steam-solvent azeotropic temperature.
As an example, the azeotropic point of steam-hexane mixture with low hexane content is 182 °C at 2.5 MPa, which is lower than the corresponding steam saturation temperature (224 °C) [60]. Above this temperature, the condensed phase is largely steam. The implication is that at 182 °C, a steam-hexane mixture will condense together giving a liquid mixture which is more hexane rich.

In general, the azeotropic temperature of steam-solvent mixtures is lower than the steam saturation temperature and approaches the steam saturation temperature as the hydrocarbon solvents become heavier. Azeotropic temperatures of steam-solvent mixtures for a wide range of hydrocarbon solvents have been calculated elsewhere and summarized in appendix [60].

**Figure 2-5.** T-xy diagram for n-hexane-steam system, azeotropic temperature at 2.5 MPa [60]. *Figure reproduced with permission of the rights holder, Society of Petroleum Engineers.*
Figure 2-6. Azeotropic temperature analysis of bitumen interface, at t = 10 min, for a) steam-butane, b) steam-hexane, c) steam-condensate, and d) steam-naphtha cases. The black solid line shows the steam saturation temperature boundary obtained by IR-thermal data and the black dash line shows the temperature at bitumen interface obtained by overlapping the optical and thermal images. The white line shows the azeotropic temperature of solvents at 1.0 MPa.

Fig. 2-6a shows the thermal analysis of the condensing zone of the steam-butane run. The steam saturation temperature at 1.0 MPa and bitumen interface temperature are profiled by black solid and dashed lines, respectively. The steam saturation temperature was directly taken from IR-thermal data and the bitumen interface temperature was obtained by overlapping the optical and thermal images. The azeotropic temperature of steam-butane mixture is ≈77 °C at 1.0 MPa [60],
which is significantly lower than the steam saturation temperature (The azeotropic temperature profile of steam-butane case is shown by white line). The temperature at the bitumen front interface in steam-butane experiment was ~132 °C which is far higher than the azeotropic temperature of steam-butane mixture. As a result, butane remained in vapor phase at the bitumen interface with no noticeable bitumen-dilution effects. Due to the lack of condensed solvent and the corresponding lack of dilution for steam-butane case, the bitumen recovery performance is close to that of pure steam with no detectable improvement, as shown in Fig. 2-6b.

Fig. 2-6b shows the temperature profile of bitumen interface for the steam-hexane co-injection test with a measured value of ~142 °C. The azeotropic temperature of the steam-hexane mixture at 1.0 MPa is ~140 °C, which is very close to the temperature at the bitumen front. This observation is in agreement with previous steam-hexane simulation studies [60]. The hexane concentration in the vapor phase increased by progressive steam condensation in the condensing zone and reached a concentration corresponding to the azeotropic temperature at which hexane condensed with steam. In contrast to the butane case, the bitumen-solvent dilution at the interface in steam-hexane test indicated significant hexane condensation. It is noted that the mixing of bitumen into the condensed steam-solvent mixture will, in principle alter the azeotropic temperature locally, the expectation is to have negligible impact overall, consistent with findings elsewhere [60].

The condensation zone for steam-condensate and steam-naphtha is more complex as the solvents themselves are mixtures. There is no single azeotropic point for condensate and naphtha as both of these solvents are in the form of multi-component systems with different hydrocarbon fractions. The condensate sample contained a significant amount of pentane (~40 wt%), while the naphtha was in general heavier, starting with hexane (~8wt%) (see appendix for detailed compositional information). Fig. 2-6c and 2-6d show the thermal analysis of the condensation zone inset for
steam-condensate and steam-naphtha runs, respectively. For the steam-condensate case, the condensate components started to condense after the steam saturation line with heavier compounds condensing first (the azeotropic temperature for major condensate components are plotted inset). The pentane is the lightest fraction in the condensate and thus condensed closer to the bitumen interface. The temperature at the bitumen front for the steam-condensate run is \( \sim 124 \, ^\circ C \), which is relatively close to the azeotropic temperature of the pentane (\( \sim 120 \, ^\circ C \)). For the steam-naphtha case (Fig. 2-6d), the condensation followed the same trend with the lightest component (C6s here), condensing close to the bitumen interface. The inset shows the azeotropic temperature of major naphtha components. The bitumen interface temperature for steam-naphtha case was \( \sim 145 \, ^\circ C \), close to the azeotropic temperature of hexane (\( \sim 140 \, ^\circ C \)). In both cases, the condensation zone is largely spread across the azeotropic lines of the mixture components. A key difference, however, is the higher interfacial temperature with naphtha - an example of solvent-mixture properties influencing the thermal recovery mechanism, as well as the solvency recovery mechanism.

The condensation zone thickness during steam-solvent co-injection was influenced by solvent composition. The condensate contained lighter fractions (i.e., \( \sim 70 \, \text{wt}\% \) of C5s and C6s), requiring lower temperatures to reach the azeotropic temperature of lighter hydrocarbon compounds. The lower temperature corresponds to a thicker condensation zone for the steam-condensate case. In contrast, naphtha was rich in heavier fractions (i.e., \( \sim 77 \, \text{wt}\% \) of C7s – C10s) and condensed at higher temperature, resulting in a thinner steam-solvent condensation zone.

### 2.3.3 Pore-scale of Condensation Zone

The residue percentage in the condensation zone is very important to the oil recovery. Fig. 2-7 compares the pore-scale dynamics at the condensing zone for all micromodel runs.
Figure 2-7. Pore-scale dynamics of the condensing zone for a) steam-butane, b) steam-hexane, c) steam-condensate, and d) steam-naphtha cases; f) comparison of final residual percentage in condensing zone for all micromodel runs.

Fig. 2-7a shows pore-scale detail of pure steam run, with long connected bitumen ganglia and well-defined, round bitumen-water interfaces within the pores. The steam-butane run (Fig. 2-7b) showed smaller bitumen ganglia and some vapor-in-oil emulsions, with no obvious bitumen...
dilution at the interface (negligible butane condensation). In contrast with butane, hexane condensation at the bitumen interface resulted in significant solvent-bitumen dilution, together with severe asphaltene precipitation and deposition in the porous medium. It is known that asphaltene precipitation requires large amount of solvent to occur, which indicate that, in our cases, the low solvent concentration in steam may restrict the deposition of asphaltene. However, due to the azeotropic effect, majority of the solvent (except butane) condenses at the interface with high concentration, which together with continuous solvent injection can generate a high concentration of solvent at the bitumen interface and result in asphaltene precipitation. It is expected that asphaltene precipitation resulted in some additional bitumen viscosity reduction which in turn contributed to more efficient bitumen displacement in the condensing zone, as compared with pure steam case. Both of condensate and naphtha also condensed at the bitumen interface, however they show distinct pore-scale dynamics. Similar to hexane, the condensate sample resulted in bitumen dilution with asphaltene deposition due to presence of a large amount of light fractions (Fig. 2-7d). Unlike condensate, naphtha produced a uniform bitumen dilution at the interface with no noticeable asphaltene deposition in the porous medium (Fig. 2-7e). Less asphaltene precipitation is consistent with the presence of aromatic/naphthenic fractions and heavier components in the naphtha [44].

The residual percentage in the condensing zone for all micromodel runs is compared in Fig. 2-7f. Image processing software (ImageJ) was used to quantify the residual percentage in the condensing zone. Images were first converted into black and white format based on the color intensity. The regions that were fully cleared during recovery present as white pixels and pore spaces occupied by residues present as fully-black pixels. The ratio of black area to the total pore area gives the residual percentage in the condensing zone. The percentage of residues in the condensing zone was almost uniform from top to bottom and the data reported here is an average value obtained by
image analysis on several pore-scale images taken from the entire condensing zone. As expected, the residual percentage in the steam-butane case (47%) is close to that of the steam case (51%) due to minimal butane condensation at the interface. Hexane and condensate produced a similar amount of residue (25% and 27%, respectively) in the condensing zone since both resulted in bitumen dilution with asphaltene deposition, however, the asphaltene deposition was found to be more prominent in steam-hexane case. In contrast with all solvents, the condensing zone of the steam-naphtha case contained remarkably less residues trapped in the porous medium (16%), an effect attributed here to more effective dilution, higher interfacial temperature, and minimal asphaltene deposition.

2.4 Conclusion

In this chapter, a series of micromodel experiments combined with optical and thermal imaging were conducted to quantify the efficacy and pore-scale dynamics in steam-solvent co-injection at relevant reservoir temperature and pressure. Two pure solvents (i.e., butane and hexane) and two industrial solvents (i.e., condensate and naphtha) were assessed. The performance of steam-solvent co-injection critically depends on the difference between the azeotropic temperature of the steam-solvent mixture and steam saturation temperature, the bitumen-solvent dilution at the interface, and the resulting asphaltene deposition in the condensing zone. Butane did not condense at the interface with no dilution effect since the steam-butane azeotropic temperature was much lower than the steam saturation temperature. However, hexane condensed with steam at the bitumen interface with an azeotropic temperature much closer to steam saturation temperature and resulted in bitumen dilution with sever asphaltene deposition. While both condensate and naphtha condensed with steam at the bitumen interface, the temperature at the bitumen interface was higher for naphtha due to the presence of heavier fractions in its composition which condensed at higher
temperatures, closer to steam saturation temperature. In addition, there was minimal asphaltene deposition in the steam-naphtha co-injection compared to steam-condensate case which resulted in less residual percentage and effective sweep efficiency in the condensing zone.

2.5 Additional Comments Not Included in the Paper

This section mainly discusses the subtleties and challenges not included in the published paper.

During oil filling, the micromodel and the syringe for oil injection must be heated to around 60 °C to lower the viscosity and ease the injection. Once the filling is completed, the model is left to cool down. But it was found that the oil shrinks and can entrain air into the chip during cooling, which ruins the whole experiment. To avoid the issue, many methods were tried. It was found that if we leave small amount of oil to seal the inlet and outlet of the chip, the additional oil fills the void, instead of outside air, which greatly improved the oil filling.

Prior to the experiment, the IR camera was calibrated by pointing to the hot plate that was set at a specific temperature. During the experiment, steam was injected into the micromodel and the IR camera measures the temperature of the surface which was assumed to be the temperature of the injected steam. However, the analysis of few early runs showed that the temperature obtained from IR camera was about 20 °C lower than the expected temperature. Through analysis, it is found that the surface temperature of the micromodel is about 20 °C lower than the heating source temperature (when steam temperature is at 180 °C). The issue was a calibration error, and recalibration of the IR camera solved the problem. It is recommended that the IR camera be calibrated using both hotplate and thermocouple attached to the outer surface of the micromodel.
A very important thing for each run is to ensure that the steam is superheated prior to entering the chip at the start of the experiment. The heat loss for the system is highest at the beginning of the experiment. If the temperature of steam is low or steam is saturated, the high initial heat loss will condense all the steam, which will turn steam injection effectively into hot water flooding. After few rounds of failed runs, a bypass line was added to the setup to bypass the steam from the chip at the beginning of the experiment – effectively warming the setup components upstream of the chip prior to injection. After 40 min, when the steam temperature is very high and stable, steam is redirected to the chip to start the experiment.

It was also found that after the naphtha experiment, the micromodel was severely contaminated. This is because the naphtha is directly collected from the field without refining and has many extremely small solid particles within the liquid that can damage both the micromodel and the inlet part of the setup. Therefore, after the naphtha run, both the micromodel and the inlet part of the setup is replaced to avoid contamination with next experiment. In terms of costs, producing the micromodels is expensive and not being able to reuse the micromodels used with naptha would limit such testing in a commercial setting.
Chapter 3

3  Nanomodel: A Window into Enhanced Oil Recovery Strategies for Tight Oil Reservoir

This is an ongoing collaborative project in which I have made significant contributions to experimental design, data collection, and analysis. These aspects are detailed in this chapter.

3.1 Introduction

Unconventional tight oil, a light oil resource trapped in shale formations with low Sulphur content, is continuously reshaping the global energy market. Compared to conventional reservoirs, shale reservoirs typically have extremely low porosity and permeability [91,92]. The mean pore size in shale formations is usually less than 100 nm, which is significantly different from that in conventional oil reservoirs (micrometer), and significantly limits well productivity [93,94]. As a result, the primary production of unconventional oil is estimated to be less than 10% of that in the entire reservoir [32], motivating the development and implementation of enhanced oil recovery (EOR) techniques to improve oil production. In a typical EOR process for a conventional reservoir, a secondary fluid is injected into the formation to extract more of the remaining oil by modifying rock surface characteristics and/or fluid properties. Conventional EOR strategies mainly include water/chemical flooding [95,96] [97,98], water-alternating-gas (WAG) flooding [99,100], and immiscible/miscible gas flooding [101,102]. However, these strategies do not necessarily translate to unconventional oil formations due in large part to the complexity of multicomponent fluids in nanoscale confinement. Assessing existing EOR strategies, as well as developing new ones for unconventional reservoirs is thus of both academic and commercial interests.
Numerical simulations [103,104], core plug tests [105,106] and pilot tests in the field are currently the main means of studying EOR processes in unconventional reservoirs. Although they have provided some insights into tight oil EOR strategies, there are limitations for these approaches. For the numerical simulation, a fundamental challenge is the applicability of classical fluid mechanics and thermodynamics at nanoscale. While for the core test, the resolution of the experimental results is very limited by the size and opacity of the system, lacking access to the fluid behavior at the nanopore scale – key phenomena for understanding as well as improving the EOR processes. The pilot test can capture all necessary variables, but it is highly time consuming and not economic, and not particularly informative regarding directions for improvement. Recent progress in micro/nanofluidic platforms has allowed a researcher to perform fluid analysis at the nanometer scale in petroleum/chemical engineering, such as hydrocarbon phase behavior measurements [107] [108,109]. While these studies provide a fundamental insight into the primary production in unconventional reservoirs, these methods have not in general been applied to the critical challenge of assessing EOR strategies in unconventional oil recovery – a system with complex fluid mixture transport and interactions under nanoconfinement.

Here, a nanofluidic approach targeting rapid screening of EOR strategies for unconventional tight oil recovery is proposed. A nanomodel with $10^6$ 2-D nanopore arrays are fabricated with a pore size of 60-nm (close to the major pore size in many unconventional oil formations), meanwhile matching the low porosity (~10%) and permeability (~10 µD) of shale. The nanomodel allows direct and in-situ observation of nanopore-scale complex fluid behaviors, enabling fast detection of the effect for different EOR strategies with much less cost and time (a few hours) compared to core (days) or filed pilot tests (weeks or months). For demonstration, we perform (1) gas flooding of N$_2$ and CO$_2$ and (2) huff-and-puff of CO$_2$ to recover trapped light oil in the nanomodel. We directly prove the feasibility of these EOR strategies, as well as study their performance as affected
by fluid parameters that are relevant to field operations. Importantly, the developed nanomodel is not only limited to the EOR strategies tested here but is also expected to be powerful in probing other unconventional reservoir relevant technologies, such as injection water additives to reduce fracture fluid trapping in the reservoir. The oil used in the experiment is West Texas Crude with a density of 867.4 kg/m$^3$ at 15°C. The composition of the oil is listed in table below.

**Table 1.** Compositional analysis of representative West Texas crude oil under atmospheric condition (stock tank condition) [110].

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition (mole%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_1$</td>
<td>0</td>
</tr>
<tr>
<td>C$_2$</td>
<td>0</td>
</tr>
<tr>
<td>C$_3$</td>
<td>0</td>
</tr>
<tr>
<td>C$_4$</td>
<td>0</td>
</tr>
<tr>
<td>C$_5$</td>
<td>0.0587</td>
</tr>
<tr>
<td>C$_6$</td>
<td>0.0909</td>
</tr>
<tr>
<td>C$_7$</td>
<td>0.0933</td>
</tr>
<tr>
<td>C$_8$</td>
<td>0.1030</td>
</tr>
<tr>
<td>C$_9$</td>
<td>0.0849</td>
</tr>
<tr>
<td>C$_{10}$</td>
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</tr>
<tr>
<td>C$_{11}$</td>
<td>0.0560</td>
</tr>
<tr>
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</tr>
<tr>
<td>C$_{13}$</td>
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</tr>
<tr>
<td>C$_{14}$</td>
<td>0.0405</td>
</tr>
<tr>
<td>C$_{15+}$</td>
<td>0.325</td>
</tr>
</tbody>
</table>

![Average molecular weight: 199.3 g/mol](image)

3.2 Nanomodel and Image Processing

For tight oil recovery (Fig. 3-1A), nanopores in shale rock are connected through bulk hydraulic fractures and horizontal wells. To simulate such a scenario, a fluidic device is fabricated with a nanoporous media (1 mm × 1mm, Fig. 3-1B) connecting two microchannels (hydraulic diameter at 300 μm). The hydraulic diameter of the nanopore is ~70 nm, representing the oil-richest pore size (sub-100 nm) in shale (Fig. 3-1 C). The porosity and permeability of the nanoporous media is ~14% and ~10 μD, respectively (Fig. 3-1C), which are close to the actual shale rock properties. Due to the extremely low permeability in shale, water-based flooding is less likely to be technically
feasible. However, gas-based flooding and huff-and-puff are potentially more applicable in enhanced tight oil recovery. In the gas-based flooding (Fig. 3-1D), high-pressure gas is injected into the reservoir from a horizontal well, and oil is expected to be pushed to and recovered from the neighboring well. While in the huff-and-puff case (Fig. 3-1E), high-pressure gas is firstly injected into the reservoir from multiple wells (huff) and sealed for weeks (soaking). After reaching equilibrium, wells are reopened to produce oil at a high rate resulted by the high reservoir pressure (puff). To directly verify and quantify the efficiency, both methods were tested in the nanomodel.

For the flooding test, the fabricated nanoporous media was initially filled with light crude oil (Texas Crude) through one microchannel (right one, namely oil channel). The oil pressure in the porous media was controlled through the oil channel pressure during the test. By injecting gas from another microchannel (gas channel on the left) at a pressure higher than the oil reservoir pressure, the pressure gradient drives the oil towards the oil channel.

During the huff-and-puff test, the nano porous media was also first saturated with light oil. Then two microchannels were cleaned with air, ensuring that the fluorescence signals vanished. Afterwards, gas at the test pressure was injected into both microchannels. The entire system was sealed long enough to reach diffusive equilibrium. By reducing gas pressure from the microchannels, oil is recovered due to the pressure difference and the release of the dissolved gas into the oil. For all tests, the nanofluidic chip was under isothermal conditions (323 K). The time-lapsed images were captured using an optical microscope and analyzed for the displacement dynamics of oil (darker brown) and gas phases (lighter brown, Fig. 3-1F). The images were processed to track the gas-oil interactions with time and to provide a measure of recovery efficiency as a function of operating conditions and treatment (Fig. 3-1F).
Figure 3-1. Potential enhanced oil recovery strategy for tight oil formation: (A) Schematic of horizontal wells drilled for primary production. (B) On-chip physical nanomodel of shale formations connecting two fractures. The scale bar represents 500 µm. (C) SEM and AFM characterization of the nanomodel. The nanopore dimension is characterized to be ~100 nm × 50 nm and the nanomodel permeability is ~12 µD. (D) Principle of gas flooding with an injection well and a production well. (E) Principle of huff-and-puff where a gas is first injected into the reservoir (i.e., huff cycle) followed by production cycle from the same well (i.e., puff cycle). (F) Example of image processing from original experimental results to recovery history plot. The images are first converted to black/white and then stacked together with respect to time. Blue is the initially developed finger and red is the finger developed later. This is to describe how gradually the finger is developed.
3.3 Results and Discussion

3.3.1 Immiscible Nitrogen Flooding

Figure 3-2. Demonstration of immiscible gas flooding (N\textsubscript{2}) for shale reservoir at 5 MPa and 323 K. (A)-(C) Oil recovery history of immiscible N\textsubscript{2} flooding at 7, 9 and 11 MPa, with (D) Accumulative oil recovery changes with time. The inset figure shows the final oil recovery percentage (FOR) at different N\textsubscript{2} pressures. The error bar is from three independent on-chip reservoirs. The oil reservoir pressure on chip was set at 5 MPa.

Nitrogen injection is a commonly applied EOR strategy for conventional oil operations, with a track record of good performance. In shale, the performance, or potential, of N\textsubscript{2} injection is largely unknown. Here, after oil filling, the oil reservoir pressure was set at 5 MPa (simulating depleted reservoir pressure after primary recovery). Then, N\textsubscript{2} was injected at three different pressures (7MPa, 9MPa, 11MPa) in three runs. Due to a high N\textsubscript{2}–oil minimum miscibility pressure (~40
MPa), the experiments involved immiscible flooding for all runs, in keeping with the expected conditions in many shale reservoirs [111,112]. It was noticed that the initiation of N₂ flooding happens at 7 MPa, indicating a significant threshold that is not present in conventional gas flooding. This threshold is a product of the strong capillarity effects in nanoconfinement. In this case, the capillary pressure of oil is estimated to be at ~1-2 MPa (calculation provided in appendix). When the pressure difference between N₂ and oil is below this threshold, the system simply reaches a pressure equilibrium at the liquid-gas interface – a barrier to oil recovery.

Fig. 3-2a-c presents spatio-temporal advancement of nitrogen into the oil phase with the color bands showing the relative time during the injection process (that is, the colour reflects the first instant that a given pore was cleared), at 7, 9 and 11 MPa. At all pressures, the fingering of nitrogen into the oil phase mainly impacted the oil displacement, leaving noticeable residual oil in the nanoporous media. The fingering was classic capillary fingering as detailed by Lenormand phase diagram [113], among others. As described in section F of appendix, when pressure was increased from 7 to 11MPa, the location in the Lenormand diagram move up but remains in the capillary fingering region. As the gas pressure increases, the gas fingers become smaller and exhibit a higher spatial density. While the fingering effect is generally unfavorable for flooding, increasing the injection pressure can significantly improve EOR productivity. In this test, the ultimate oil recovery in the nanomodel increases from 48% to 86% by increasing the injection pressure from 7 to 11 MPa (Fig. 3-2d), which also confirms with previous studies by Lenormand that increasing the capillary number within the capillary fingering region results in a larger recovered area [114].

While it is typical for micro- and nanomodel results to overestimate recovery, the difference here in the side-by-side comparison of nanomodels indicates the significance of the initial gas pressure on the performance of immiscible gas flooding in these reservoirs.
3.3.2 Miscible Carbon Dioxide Flooding

**Figure 3-3.** Demonstration of miscible gas flooding (11 MPa – CO₂ injection pressure) for tight oil reservoir at 323 K, and (A) relatively low pressure reservoir (5 MPa – oil side pressure) and (B) high pressure reservoir (10 MPa – oil side pressure). The scale bar represents 200 µm. The black/white graphs show the recovery dynamics at different time frame to help the understanding of the stacked color images representing the whole recovery process. (C) Cumulative oil recovery
changes with time. The inset figure shows the final oil recovery percentage (FOR) at different reservoir pressures. The error bar is from three independent on-chip reservoirs.

CO₂ is another candidate injection gas for enhanced oil recovery. CO₂ can not only improve oil recovery efficiency, enhanced oil recovery using CO₂ can also serve a carbon sequestration goal. Compared to nitrogen, the minimum miscible pressure of CO₂ in light oil is very low. The minimum miscibility pressure of CO₂ with the light oil in this study (i.e., West Texas crude) at 323 K has been reported elsewhere at bulk scale (~10 MPa). Here, we found the minimum miscibility pressure in the nanomodel was close to that bulk value. The miscible CO₂ flooding experiments were conducted under two cases, at (A) low initial oil reservoir pressure below the minimum miscibility pressure (i.e., 5 MPa) and (B) high initial oil reservoir pressure at minimum miscibility pressure (i.e., 10 MPa), simulating two potential cases of unconventional formations with low and high depleted reservoir pressure after primary production, respectively. The CO₂ was injected at 11 MPa to maintain the initial miscible flooding conditions for both cases.

The spatio-temporal advancement of the CO₂ phase into the oil phase for both the low and high initial reservoir pressures is depicted in Fig. 3-3A and 3-3B, respectively. For the low reservoir pressure case (5 MPa), oil displacement was first triggered as immiscible flooding close to the oil reservoir side (right), with significant fingering effect. It was then followed by a significant film-wise displacement initiating from the gas channel (left), resulting a clean sweeping of the oil in the nanoporous media. It is also observed that oil displacement in the nanoporous media close to the gas injection side is better than that the oil side. This effect is mainly caused by a pressure drop across the nanoporous media, resulting in miscible (gas side, where the system pressure is above the minimum miscibility pressure), and immiscible (oil side, where the system pressure is below the minimum miscibility pressure) displacement. The overall flooding result in terms of oil
recovery percentage (93%, Fig. 3-3c) is notably better than that in the immiscible N\textsubscript{2} flooding case (86%), under the same gas pressure condition (11 MPa).

For the high pressure reservoir case (10 MPa), the oil displacement process is uniformly film-wise through the entire process, exhibiting highly efficient oil recovery (~100% cumulative oil recovery percentage, Fig. 3-3c). For miscible flooding, the interfacial tension between gas (here CO\textsubscript{2}) and oil is much less than that in immiscible gas flooding. The capillarity for oil in nanoporous media is thus minimized, with benefits in terms of both flooding and ultimately recovery. In the experiments, it was found that the minimum pressure difference required to achieve miscible flooding was ~1 MPa, which was less than the 2 MPa required for recovery with immiscible nitrogen flooding. For complete comparison, the efficiency of N\textsubscript{2} flooding was also tested for a 10-MPa oil reservoir condition. When the N\textsubscript{2} was injected at 11MPa, which was the same injection pressure as the CO\textsubscript{2} case, there was no flooding phenomenon observed, further proving our discussion on the higher capillarity for N\textsubscript{2}. When N\textsubscript{2} injection pressure was increased to 12 MPa, the displacement was initiated but the cumulative oil recovery percentage was only 31%, which is much lower than the CO\textsubscript{2} miscible flooding results (approaching ~100%) shown here. Although capillary pressure reduction is a major factor for a higher recovery factor at the miscible pressure, there are many other benefits at miscible pressure injection case. At such a high pressure, CO\textsubscript{2} is miscible with oil and significant mass transfer occurs at the interface, which result in a uniform CO\textsubscript{2} and oil phase. In this process, significant CO\textsubscript{2} diffuse into the oil phase which greatly reduces the viscosity of oil. Importantly, miscible diffusion of the CO\textsubscript{2} into the oil phase removes the sharp discontinuity between the phases which otherwise could give rise to viscous fingering. The smooth miscible transition zone avoids fingering and promotes piston-like recovery. The diffusion of CO\textsubscript{2} into the oil phase greatly ease the flow of crude oil and the displacement process [42]. To conclude, these experimental results together indicate that by selecting a gas or gas mixture with low
minimum miscibility pressure in unconventional light oil (e.g., CO\textsubscript{2}), the overall recovery efficiency can be significantly improved even in the relatively extreme nanoconfinement of shale reservoirs. The bulk scale minimum miscibility pressure seems reasonably representative at the nanopore scale and provides a useful guide to understanding EOR performance in these systems.

3.3.3 Carbon Dioxide Huff-And-Puff

![Image of CO\textsubscript{2} Huff-n-Puff test on-chip. CO\textsubscript{2} was initially injected into the nanomodel (filled with oil) at (A) 7, (B) 9 and (C) 11 MPa, respectively (Huff). The scale bar represents 200 µm. After soaking for one hour, the system pressure was directly reduced to 1 MPa (Puff). Oil was produced from the nanomodel during the Puff process, with (D) accumulative oil recovery changing with time plotted. The inset figure shows the final oil recovery percentage (FOR) at different injecting CO\textsubscript{2} pressures. The error bar is from three independent on-chip reservoirs.]

As flooding requires continuous gas injection into the reservoir, it will introduce relatively high cost in both power supply of facilities (especially pump) and gas usage. As an alternative solution,
gas huff-and-puff injection has gained interest for tight oil recovery. However, the fundamental understanding of the huff-and-puff process in nanopores still remains largely unknown and requires experimental investigation to both improve understanding and ultimately efficacy of these processes. Here, the CO$_2$ huff-and-puff experiment is conducted on the nanomodel with geometry shown in Figure 3-1b. After filling the nanoporous media with oil followed by cleaning the microchannels with air, CO$_2$ was injected into the microchannel at the target pressure (5-11 MPa, 2 MPa as interval). After sealing the system at high pressure for 1 hr to allow sufficient CO$_2$ to diffuse into the oil, the system was fast depressurized to 1 MPa to produce oil from the nanomodel.

The test CO$_2$ pressures were ranging from immiscible (5-9 MPa) to miscible CO$_2$ (11 MPa) huff-and-puff conditions. Huff-and-puff in the nanomodel initiated at 7 MPa (Fig. 3-4a). While at 5 MPa, no oil was produced. This result indicates that for the huff-and-puff in nanopores, there is a significant threshold for the initiation of oil displacement under immiscible conditions, which is similar to the immiscible gas flooding case noted earlier – and a departure from conventional EOR understanding. The potential reason for this threshold is the limited dissolved gas in the oil at relatively low gas pressures. When system pressure is further reduced, gas solubility in oil is not significantly changed. Thus, in these cases the amount of the released gas is not enough to accumulate and form bubble phase. The low pressure drop is also unable to overcome the capillary pressure at the oil-gas interface. As a result, released gas is unable to push oil out from the nanoporous media, but instead slowly diffuses to the microchannel.

When initial CO$_2$ injection pressure was above the threshold, it was observed that the initiation of oil sweep was from the center of the nanoporous media instead of the edge. Such a phenomenon indicates that, oil extraction through huff-and-puff in nanoporous media depends on significant CO$_2$ solubility change and CO$_2$ release resulting from sudden pressure change. While the released
CO₂ close to the entrance of the nanoporous media can diffuse to the microchannel, CO₂ in the center of the nanoporous media will accumulate and form high pressure bubble phase, and then push the tapped oil out from the nanoporous media. An additional effect for huff-and-puff is oil swelling as a result of CO₂ dissolving into the oil phase in the soaking phase. The swelled oil in the nanoporous media can expand into the microchannel, which can be further produced during pressure reduction.

The experimental results are shown in Fig. 3-4a-c for injected CO₂ pressure at 7, 9 and 11 MPa. The spatio-temporal profiles show that the recovery performance significantly varies by increasing the pressure, from immiscible to miscible conditions. At 7 MPa (immiscible condition), the sweep efficiency was lowest with a few disperse CO₂ fingers. By increasing the CO₂ pressure to 9 MPa (near-miscible condition), the oil displacement was improved through more interconnected and dense fingering phenomena. While at 11 MPa (miscible condition), the CO₂ huff-and-puff exhibits a more film-wise oil recovery process, further improving the recovery efficiency. The cumulative oil recovery percentage (Fig. 3-4d) is increase from 17% at 7 MPa (i.e., immiscible injection) to 77% at 11 MPa (i.e., miscible injection) during the test. These results indicate that miscible huff-and-puff injection could significantly enhance the oil production compared to immiscible huff-and-puff injection, which agrees with previous core test findings [115]. Fundamentally it is relevant to a much higher CO₂ solubility at a pressure above the minimum miscibility pressure, as well as a larger pressure drop providing higher oil displacement momentum.

While the ‘huff’ injection pressures (~ 7-11 MPa) applied here are potentially relevant to various reservoirs and well conditions in shale oil operations, the ‘puff’ draw-down pressure (~ 1 MPa) was setting very low. This condition was required to generate a huge pressure drawdown gradient to produce trapped oil from the nanomodel. At more moderate drawdown pressures (e.g., 5 MPa),
no trapped oil was produced from the nanomodel. This result indicates that without a significant pressure disturbance on the equilibrium saturated oil-gas system in shale after “huff”, gas is unlikely to gather and generate bubble phase to further replace liquid oil in nanopores. Instead, it will slowly diffuse out from the shale nanoporous media, which cannot help with oil recovery. From an engineering perspective, the results indicate the necessity in leveraging a fast pressure drawdown from gas injection wells during the “puff” stage of tight oil production.

### 3.4 Conclusion

In this work, a nanofluidic approach is proposed in directly probing the effectiveness of enhanced oil recovery strategies for unconventional oil reservoirs. A 2-D nanoporous media was fabricated matching the main pore size, permeability, and porosity in unconventional formations. To demonstrate the ability of nanomodel in screening the enhanced unconventional oil recovery process, two potential applicable strategies were tested: gas flooding and huff-and-puff. For the gas flooding case, the immiscible gas flooding (e.g., N\textsubscript{2}) required a high injection pressure to overcome the pressure threshold governed by the strong oil capillarity in nanopores, which is not expected in conventional reservoirs with micro/millimeter pores. Immiscible gas flooding generates capillary fingers in nanoporous media (shale reservoir) similar to that in macroporous media (conventional reservoir). While by selecting gas species with low minimum miscibility point in oil (e.g., CO\textsubscript{2}), at the same gas pressure condition one can achieve miscible gas flooding with a much lower initiation pressure threshold, and meanwhile significantly improve the recovery efficiency through a stable film-wise displacement. In the field operation, when selecting the appropriate gases and injection pressure, Lenormand diagram can be used to optimize the capillary number and mobility ratio to achieve a more stable displacement process. In this study, we have demonstrated that with the increase of capillary number in the capillary fingering region (nitrogen
flooding), the recovery improves. However, to obtain significant improvement, it is better to increase the capillary number to a positive number which can change the displacement process to stable displacement instead of capillary fingering displacement.

In the huff-and-puff case, it is noticed that the initiation of oil displacement also requires a high soaking pressure and a large pressure drawdown. Due to the high capillary pressure, the oil pressure is lower than the gas injection pressure, which result in lower CO$_2$ solubility in oil. The purpose of higher soaking pressure is to overcome the capillary pressure and increase the oil pressure and subsequently increase the CO$_2$ solubility in oil. Therefore, more gas bubble can be generated to push the oil out during depletion stage. A large pressure drawdown is also needed to create a large solubility change to release more gas and to push more oil out of the nanomodel.

With the gas injection pressure increasing from the immiscible condition to the miscible condition in the nanomodel, more CO$_2$ is absorbed. Due to the large amount of released gas at the pressure drawdown, oil displacement is shifting from obvious capillary fingering to a more film-wise displacement, leading to an increase in oil recovery. The result also informs field operators that it is necessary to study the pore throat size and calculate the capillary pressure. Therefore, a relatively higher injection pressure can be used to overcome the capillary pressure and increase the CO$_2$ solubility in oil. However, for gas with low miscible pressure it is also necessary to have a large drawdown pressure to generate gas bubbles and increase oil production.

### 3.5 Additional Comments Not Included in the Paper

This chapter described the development and testing of an EOR nanomodel – a challenging technology that is still very much under test. While fabrication and bonding are always a challenge, the most difficult part of running this experiment is filling the oil into the nanomodel,
that is, establishing the initial condition. Due to the extremely small nano-confinement, the entire system needs to be vacuumed for at least three hours to ensure the system is free of air. Trapped air is extremely hard to be remove once oil is filled in the system due to strong capillarity inside nanochannel. The system was also pressure tested with high pressure nitrogen in order to ensure high pressure operating condition during the experiment.
Chapter 4

4 Conclusions

4.1 Summary

To meet the increasing oil and gas demand in the next few decades, effective EOR methods are needed to unlock the huge reserve of unconventional oil, such as bitumen and tight oil. This thesis describes the application of microfluidics and nanofluidics in screening EOR strategies for bitumen (oil sands) and tight oil (shale) recovery respectively.

In the bitumen EOR analysis, a series of micromodel experiments combined with optical and thermal imaging were conducted to quantify the efficacy and pore-scale dynamics of steam-solvent co-injection at relevant reservoir temperature and pressure. Both pure and industrial solvents were assessed. Butane did not condense at the interface because the steam-butane azeotropic temperature was much lower than the bitumen interface temperature. Hexane condensed with steam at the bitumen interface with an azeotropic temperature much closer to steam saturation temperature and resulted in bitumen dilution with severe asphaltene deposition. While both condensate and naphtha condensed with steam at the bitumen interface, the temperature at the bitumen interface was higher for naphtha. This is because of the presence of heavier fractions in its composition which condensed at higher temperatures, closer to steam saturation temperature. In addition, there was minimal asphaltene deposition in the steam-naphtha co-injection compared to steam-condensate case. This resulted in effective sweep efficiency in the condensing zone.

In the tight oil experiments, a series of nanomodel experiments were conducted to compare the gas flooding (N₂ and CO₂) and huff-and-puff (CO₂) EOR recovery methods. It was found that miscible
CO₂ flooding provided the highest recovery due to the disappearance of the gas-liquid interface at miscible pressure, which greatly increased the capillary number and thus resulted in stable displacement as indicated in the Lenormand diagram. The solubility of CO₂ is also larger than N₂, in oil which enhances the dilution effect and subsequently reduces oil viscosity.

4.2 Outlook and Future Work

The current system for both micromodel and nanomodel are indeed successful, but they are still subjected to many future improvements. Also, both models can be potentially applied in various applications outside of the oil and gas industry.

For the bitumen thermal recovery experiments discussed in Chapter 2, a detailed temperature analysis was conducted and the azeotropic temperature for each component was identified which was highlighted in Fig. 2-6c-d. However, the condensation temperature of each component in a multicomponent (more than one hydrocarbon) mixture was still unclear. For future work, the micromodel can be made with packed glass beads which can be removed after each experiment to perform composition analysis of the residues on the glass beads. Depending on the composition of the residues, the condensation location of each component of the mixture can be identified in the micromodel which can then be correlated to the associated temperature on the recorded temperature profile. Heat loss to the environment through the glass micromodel is another issue which can be addressed in the future. Currently, to overcome the heat loss to the surrounding and maintain desired temperature, the steam flow rate is relatively higher than the actual SAGD operation in the field. For future experiments, the micromodel can be placed entirely in a hot air bath to minimize the heat loss to the surrounding from the micromodel. In terms of potential applications, the micromodel can be used in fundamental studies, such as viscous fingering effect
in two phase displacements. With the precise control of temperature and pressure of our micromodel system, the application of micromodel can be extended to many industries that need visualization of high-temperature and high-pressure processes inside micro porous media.

One future improvements that can be done for the nanomodel is the pore size variation of the porous media. In actual shale reservoir, the sub-100nm nanosized pores are connected by even smaller sub-10nm pore throats. The pore throat may restrict the flow of oil and mass transfer of the displacing fluid. In the future, sub-10nm pore throats can be added into the model to match closely with the shale reservoir. In this study, the effect of surface wettability was also not considered. However, in the real process, hydraulic liquid from hydraulic fracturing can change the regional surface wettability of the porous media. In the future studies, the hydraulic liquid can be injected into the nano porous media to partially fill the model prior to the experiment to setup the reservoir relevant initial condition. As a future study, the nanomodel can also be used to study hydraulic liquid retention during production to select the optimal liquid with the least retention effect. Besides oil recovery, the nanomodel can be used in many other areas. For example, researchers found that nanomembrane can effectively reduce the invaded air bubble to nanobubbles which can effective prevent hydraulic failure during long-distance water transport in plants under negative pressure. A nanomodel can be developed to verify this phenomenon and explain the fundamental mechanism. In general, nanofluidics have the potential to be used in wide-range of areas to enhance researcher’s understanding to the behavior of fluids in nanoscale porous media.
Bibliography


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Appendix

A) Compositional analysis and fluid properties of the bitumen sample

Figure 4-1. a) Compositional analysis and fluid properties of the Athabasca bitumen sample (the weight percent of all components lighter than C$_7$ is zero; the molecular weight and density of the bitumen were 588.8 g/mol and 1.02 g/cm$^3$, respectively), and b) bitumen viscosity as a function of temperature.

B) Compositional analysis and fluid properties of industrial solvents

Figure 4-2. Compositional analysis of condensate and naphtha samples (The condensate was composed of $\sim$70 wt% of C$_5$s and C$_6$s fractions while the naphtha contained $\sim$77 wt% of C$_7$s –
C\textsubscript{10}s). C\textsubscript{5}s here refers to all hydrocarbon components with five carbon atoms in their structure, such as n-C\textsubscript{5} and i-C\textsubscript{5}. The same for other components.

C) Physical dimensions and pore characteristics of the micromodel

Table 2. Physical dimensions and pore characteristics of the micromodel.

<table>
<thead>
<tr>
<th>Physical dimensions</th>
<th>Pore characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimension (cm × cm)</td>
<td>Depth of etching (µm)</td>
</tr>
<tr>
<td>Pore area (cm\textsuperscript{2})</td>
<td>Pore throat size (µm)</td>
</tr>
<tr>
<td>Pore volume (cm\textsuperscript{3})</td>
<td>Pore body size (µm)</td>
</tr>
<tr>
<td>Porosity</td>
<td>Particle size (µm)</td>
</tr>
<tr>
<td>Permeability (Darcy\textsuperscript{*})</td>
<td>149.4</td>
</tr>
</tbody>
</table>

\* 1 Darcy = 9.87 × 10\textsuperscript{-13} m\textsuperscript{2}

D) Steam-solvent mixture azeotropic temperature for a wide range of hydrocarbon solvents (Khaledi et al., 2015)

Figure 4-3. Steam-solvent mixture azeotropic temperature for a wide range of hydrocarbon solvents (Khaledi et al., 2015).
E) Instantaneous oil recovery rate

![Figure 4-4. Instantaneous oil recovery rate](image)

F) Capillary pressure calculation

\[ P_{\text{oil}} = P_{\text{CO}_2} - P_c \]

\[ P_{\text{CO}_2} < P_{\text{oil}} + P_{\text{capillary}}, \text{ Stationary} \]

\[ P_{\text{CO}_2} > P_{\text{oil}} + P_{\text{capillary}}, \text{ Moving} \]

Interfacial tension of CO2-crude oil \( \sim 20\text{mN/m} \)
Hydraulic diameter ~ 60nm

\[ P_{\text{capillary}} = \frac{2\gamma}{r_{\text{hydraulic}}} = \frac{2 \times 20 \text{mN/m}}{30 \text{nm}} \approx 1.3 \text{MPa} \]

G) Lenormand’s diagram for nitrogen flooding

At 7MPa and 323K, the viscosity of nitrogen is \( \sim 2 \times 10^{-5} \text{ Pas} \) [116], the estimated velocity is \( 1 \times 10^{-5} \text{m/s} \)

At 11MPa and 323K, the viscosity of nitrogen is \( \sim 2.1 \times 10^{-5} \text{ Pas} \) [116], the estimated velocity is \( 4 \times 10^{-5} \text{m/s} \)

\[
M(\text{mobility ratio}) = \frac{k_{\text{nitro}}}{k_{\text{oil}}} = \frac{\mu_{\text{nitro}}}{\mu_{\text{oil}}} = \frac{1}{\mu_{\text{oil}}} \times \frac{1}{2 \times 10^{-5}} = 100
\]

\[ \log(M) \sim 2 \text{ for both cases due to the small difference of nitrogen viscosity at different pressure} \]

\[
Ca(\text{capillary number}) = \frac{\mu_{\text{oil}} V}{\sigma} = \frac{2 \times 10^{-3} (\text{Pa.s}) \times V}{20 \times 10^{-3} \left(\frac{N}{m}\right)}
\]

At 7MPa, \( \log(Ca) = -6 \)

At 10MPa, \( \log(Ca) = -5.4 \)
Figure 4-5. Location of two nitrogen injection cases on Lenormand diagram [113].

**H) Lenormand’s diagram for carbon dioxide flooding**

At 5MPa and 323K (immiscible flooding), the viscosity of carbon dioxide is \( \sim 1.7 \times 10^{-5} \) Pa.s, the estimated velocity is \( 3 \times 10^{-5} \) m/s, the interfacial tension is similar to nitrogen case \( \sim 20 \times 10^{-3} \) N/m

\[
M(\text{mobility ratio}) = \frac{k_{\text{CO}_2}}{k_{\text{oil}}} \frac{\mu_{\text{CO}_2}}{\mu_{\text{oil}}} = \frac{1}{\frac{\mu_{\text{CO}_2}}{\mu_{\text{oil}}}} = \frac{1}{\frac{1.7 \times 10^{-5}}{2 \times 10^{-3}}} = 118
\]

\[
\log(M) \sim 2.1 \text{ for immiscible flooding}
\]

\[
Ca(\text{capillary number}) = \frac{\mu_{\text{oil}} V}{\sigma} = \frac{2 \times 10^{-3} (\text{Pa.s}) \times V}{20 \times 10^{-3} (\text{N/m})}
\]

At 5MPa, \( \log(Ca) = -5.5 \)

For case A, where the injection pressure is 11MPa and the oil pressure is 5MPa, flooding occurs close to the oil side is immiscible flowing and is capillary fingering displacement shown on the
Lenormand diagram below. At 11MPa, the miscible pressure, interfacial tension is minimized and resulted in an extremely large capillary number. In this case, the displacement process becomes stable displacement.

**Figure 4-6.** Location of carbon dioxide injection cases on Lenormand diagram [113]