SPE-204294-MS

An Experimental Study Investigating the Impact of Miscible and Immiscible Nitrogen Injection on Asphaltene Instability in Nano Shale Pore Structure

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This paper was prepared for presentation at the SPE International Conference on Oilfield Chemistry held in The Woodlands, Texas, USA, 6 – 7 December, 2021.

Abstract

Miscible gas injection has become the most used enhanced oil recovery (EOR) method in the oil and gas industry. The deposition and precipitation of aspahltene during the gas injection process is one of the problems during the oil production process. The asphaltene can deposit and plug the pores, which reduces the permeability in a reservoir; thus, decreasing the oil recovery and increasing the production costs. This research investigates the nitrogen (N_2) miscible and immiscible pressure injections on asphaltene instability in shale pore structures. First, a slim-tube was used to determine the minimum miscibility pressure (MMP) of N_2 to ensure that the effect of both miscible and immiscible gas injection was achievable. Second, filtration experiments were conducted using a specially designed filtration apparatus to investigate the effect of nano pore sizes on asphaltene deposition. Heterogeneous distribution of the filter paper membranes was used in all experiments. The factors studied include miscible/immiscible N_2 injection and pore size distribution. Visualization tests were conducted to highlight the asphaltene precipitation process over time. The results showed that increasing the pressure increased the asphaltene weight percentage. The miscible N_2 injection pressure had a significant effect on asphaltene instability. However, the immiscible N_2 injection pressure had a lower effect on the asphaltene deposition, which resulted in less asphaltene weight percentage. For both miscible/immiscible N_2 injection pressures, the asphaltene weight percentage increased as the pore size of the filter membranes decreased. Visualization tests showed that after one hour the asphaltene clusters were clearly noticed and suspended in the solvent of heptane, and the asphaltene was fully deposited after 12 hours. Microscopy imaging of filter membranes indicated significant pore plugging from asphaltene, especially for smaller pore sizes.

Introduction

Gas injection was widely implemented in the oil industry to increase oil recovery. The main mechanisms increased by gas injection technique include a reduction in the oil viscosity, oil swelling effect, and gas-oil properties, such as decreased interfacial tension (Shuker et al., 2012; Godec et al., 2013; Liu et al., 2017). Although horizontal wells can use hydraulic fracturing techniques to extract trapped oil, only 4 to 6 % can be recovered (Unal et al., 2019; Eltaleb et al., 2020; 2021; Awad et al., 2020; Biheri, 2017; Biheri et al., 2020; 2021a; 2021b; 2021c; Elturki et al., 2021a). Asphaltene precipitation and deposition cause severe issues during oil production and processing. Asphaltene can be defined as a high molecular weight substance from crude oil that is soluble in toluene, but insoluble in alkanes. The high molecular weight components in the crude oil, such as asphaltenes, can be precipitated from the oil phase during gas injection because mobility was achieved; thus, it deposited into the pores, which lead to reduced oil recovery (Escobedo and Mansoori, 1997; Wang et al. 2016; Elturki et al., 2020a). Asphaltenes were stabilized in the crude oil by resins, and maltenes, which surrounded the molecules of asphaltene (Punase et al. 2016; Groenzin and Mullins, 2000). Any change in the reservoir conditions that affect the equilibrium conditions, such as changes in temperature or pressure, changes the asphaltene stability, and lead to deposition in the pores (Rassamdana et al., 1996; Zendehboudi et al., 2014).

The effect of asphaltene precipitation in reservoir pores and its impact on reducing the oil recovery has gained attention in the last few years. Many researchers have investigated the effect of high molecular weight components mainly, asphaltene precipitation and deposition in conventional reservoirs during carbon dioxide (CO_2) and N_2 injections, but fewer studies were implemented for unconventional reservoirs (Buriro et al., 2012; 2013; Luo et al., 2017; Elturki and Imqam, 2021b; 2021c; Elwegaa and Emadi, 2018). Jamaluddin et al. (2002) used N_2 injections to study the impact on asphaltene instability, and they stated that the bulk precipitation amount of asphaltene was increased when the concentration of N_2 in the reservoir fluids increased. Moradi et al. (2012) conducted experiments using a filter membrane with a 0.2 μm pore size, methane, and N_2; they reported that asphaltene precipitation was much higher when using methane compared to N_2. Mohammed et al. (2017) modeled the asphaltene precipitation in low permeability reservoirs during CO_2 flooding with simulation software and suggested the use of brine with cyclic CO_2 flooding. Shen et al. (2018) used cyclic gas injection to study the asphaltene precipitation in the Eagle Ford shale reservoir. They used various filter membranes of 30 nm, 100 nm, and 200 nm to mimic real reservoir pores and stated that decreasing the pore size of the filter membrane increased the asphaltene precipitation. Elwegaa et al. (2019) used cold N_2 during the cyclic gas injection process in shale cores. They concluded that increased the pressure increased the oil recovery. Fakher and Imqam (2019) conduced an experimental study to investigate the effect of the CO_2 flow mechanism on nano-pores and the impact on asphaltene precipitation. They used nano-composite filter membranes to study the effect of various factors such as pressure, temperature, and CO_2 soaking time. They concluded that high pressure and temperature resulted in higher asphaltene precipitation. Altawati et al. (2020) conducted experiments using cyclic CO_2 and N_2 injection methods to investigate the effect of water on the shale recovery factor (RF). Their results revealed that higher RF was observed when the soaking time was increased and they concluded that the presence of water in shale cores had a negative impact on RF. Elturki and Imqam (2020b) used an immiscible N_2 injection process to investigate the effect of gas on asphaltene deposition using nano filter membranes. Their results demonstrated that more asphaltene precipitated at higher pressure, especially using filter membranes with small pore size.

Based on the aforementioned literature review, limited research has been conducted to study and compare the effects of miscible and immiscible N_2 on asphaltene instability in crude oil. This research performed multiple experiments to evaluate the asphaltene stability in nano-pores and quantifies the asphaltene weight percent during miscible and immiscible N_2 injection processes and its impact on pore plugging. Better understating of the asphaltene behavior by changing different factors such as pressure, and soaking time will add much knowledge to the literature and the topic of N_2 injections in unconventional reservoirs.

Asphaltene Precipitation and Deposition

The main components of crude oil are saturates, aromatics, resins, and asphaltenes (Mullins, 2008). All of these components are holds together by resins. In the equilibrium of the reservoir conditions such as pressure and temperature, the asphaltene is stabilized and soluble in the oil. Once the reservoir conditions changed, the resins become weaker and the stability of asphaltene in the crude oil will change and it starts to form clusters. When the precipitation and deposition process of asphaltene starts, pore plugging occurs. The common conditions that may affect the stability of asphaltene in the oil include pressure, temperature, solvent injections such as N_2 and high oil production flowrate (Bahman et al., 2017). The asphaltene deposition can cause a decrease in oil recovery, and it leads to production facilities' ineffectiveness. Figure 1 shows the asphaltene life cycle and its impact on oil recovery.

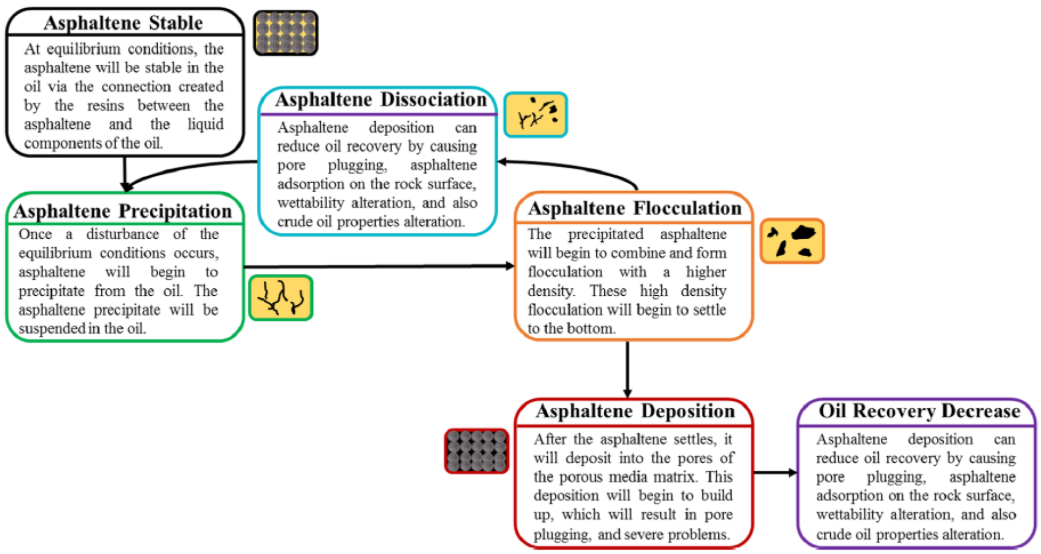

Figure 1—Asphaltene life cycle (Fakher, 2020)

Experimental Apparatus and Materials Description

Three sets of experiments were conducted in this research. First, the MMP of N_2 was determined using slim-tube. Then, the filtration experiments were conducted using miscible and immiscible pressures. The process of aspahltene deposition and precipitation was captured in the visualization experiments. Figure 2 shows the flow chart summary of the experiments conducted in this research.

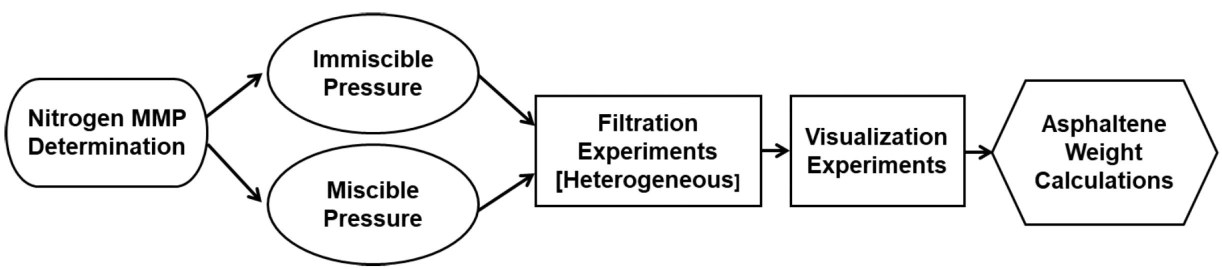

Figure 2—Research experiments design flow chart

MMP Experiment

MMP experiment was conducted in order to ensure that all subsequent filtration experiments were intended to be below the MMP.The minimum miscibility pressure is the lowest pressure at which a gas can mix with the storage oil at the reservoir temperature. MMP is the minimal pressure at which the miscibility between the injected gas and the reservoir oil is attained when the interfacial tension between oil and gas disappears after multiple contacts (Elturki and Imqam, 2021d). Figure 3 shows the significant parts of the slim-test tube, which include a syringe pump, three accumulators, gas cylinders, a stainless-steel slim-tube full of sand, and a pack pressure controller. There were several steps in the slim-tube tests, beginning with the preparation for a pre-test where the slim tube was filled with water at a rate of 1.5 PV water. This phase is essential in calculating the weight of water-saturated slim-tube after filling with sand and calculating the volume of pores. The second phase was filling the slim-tube with crude oil at a low rate of 0.5 PV to ensure a 100 % saturation of the crude oil after pumping. The final phase was experimenting by controlling the temperature to the predetermined level, fill the gas into the gas cylinder, and pump the gas at the rate of 1.2 PV during the injection. A regulator for backpressure was installed at the outlet for the slim-tube and used to control the pressure by using a different water pump as the back-up reservoir for pressure. Figure 4 shows the results of MMP experiments. It was found that the MMP of N_2 at 30˚C was 1600 psi when using 19 cp viscous oil.

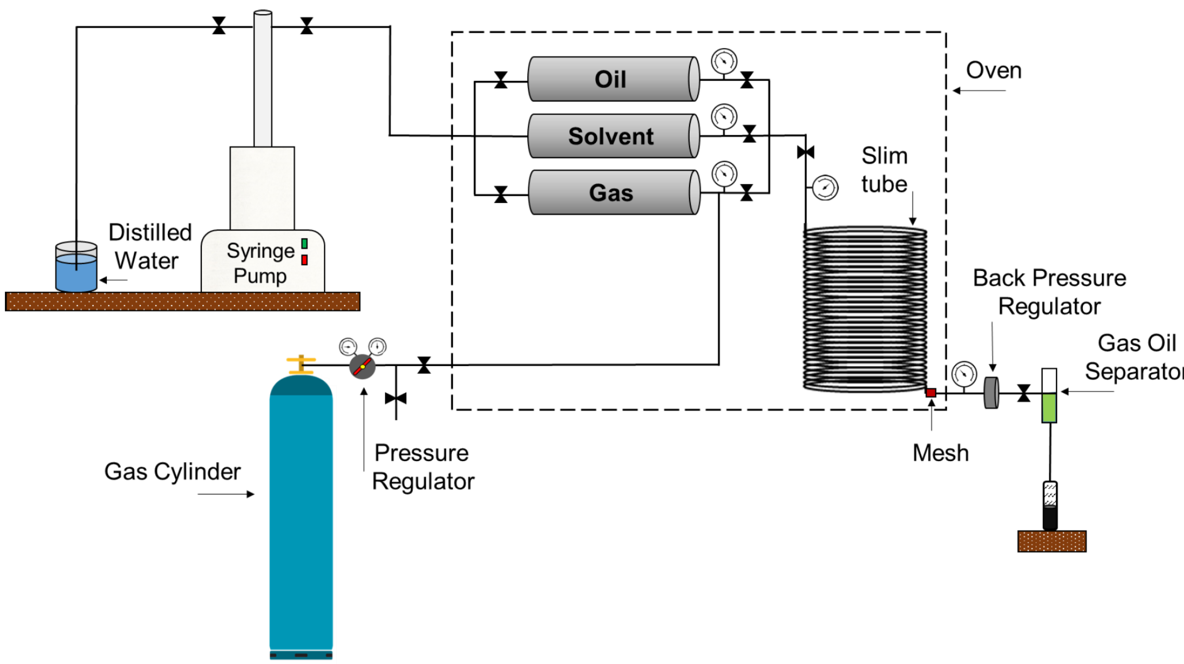

Figure 3—Schematic diagram of the slim-tube apparatus.

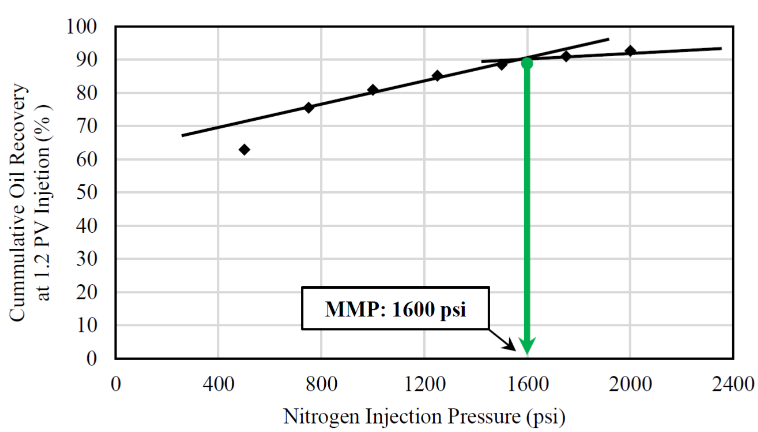

Figure 4—N_2 MMP determination using slim-tube apparatus

Filtration Experiments Apparatus:

The essential parts included a high purity N_2 cylinder with a pressure regulator to control the cylinder pressure. The vessel of filtration was made to accommodate three mesh screens to prevent the filter membranes from folding at high pressure. The mesh screens were made with small pores to allow natural percolation of oil. Spacers were placed between each mech screens as support to maintain them in place.

Rubber O-rings were used above and below each spacer to prevent any possible leakage and to guarantee the passage of the oil through the filter paper membranes. A regulator for backpressure was installed at the filtration vessel outlet and used to control the pressure using a syringe pump. The produced oil from the outlet was collected for asphaltene analysis. An oven was utilized to control the temperature of the filtration vessel and investigate the impact of various temperatures. Last, two transducers were placed at the inlet and outlet of the filtration vessel and linked to a computer to monitor the pressure differences. Figure 5 shows all the parts of the apparatus used in conducting the investigation. A crude oil with viscosity of 19 cp was used in all the experiments and Gas Chromatography-Mass Spectrometry was used to determine the composition of the crude oil, as shown in Table 1.

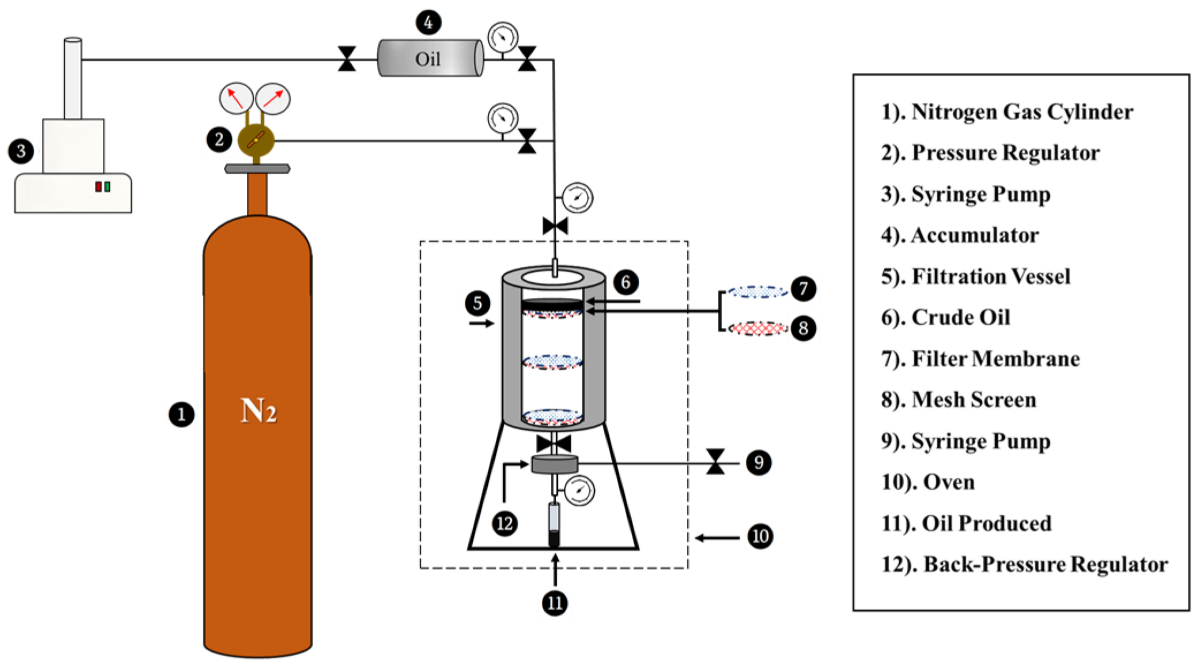

Figure 5—Specially designed filtration setup

Table 1—Crude oil composition

Component	Weight percentage (%)
C_8 -C_{14}	65.14
C_{15}-C_{19}	6.06
C_{20}-C_{24}	9.16
C_{25}-C_{29}	14.48
C_{30+}	5.17
Total	**100.00**

The asphaltene percentage weight was calculated using the following equation:

$$\text{Asphaltene wt\%} = \frac{\text{wt asphaltene}}{\text{wt oil}} * 100$$

Where:

Asphaltene wt% Asphaltene weight percentage

Wt asphaltene	Asphaltene weight on the filter paper
Wt oil	Oil sample weight

Filtration Experimental Procedure

The following steps were followed for all filtration experiments:

1. The first set of mesh screens, filter membrane papers, rubber O-rings, and spacers were placed inside the filtration vessel, respectively. This step was repeated for the next two sets.
2. The vessel was closed tightly using a specially designed cap to tighten all the sets together and prevent any possible leakage during the experiment.
3. A crude oil of 30 ml was poured into the accumulator. A syringe pump was used to inject the oil into the vessel.
4. N_2 was injected into the vessel to reach the desired level (500 psi for immiscible conditions or 2000 psi for miscible conditions). The crude oil was then exposed to the gas for a predetermined soaking time which is 2 hours.
5. The syringe pump at the outlet was turned on to a constant pressure (500 psi for immiscible conditions or 2000 psi for miscible conditions) to let the crude oil pass through the membranes.
6. The produced oil was collected. The experiment was stopped when no further oil production was observed.
7. The inlet and outlet pressures were observed and recorded using transducers that connected to a computer. The difference between the two pressures was designed not to exceed 50 psi.
8. After gas injection was completed, the vessel was opened, and the remaining crude oil was collected from each filter membrane for asphaltene analysis.

Results and Discussion

Effect of Filter Membrane Pore Size

Three sets of filter membranes (450, 100, and 50 nanometers) were used in this research with a heterogeneous distribution to investigate the effect of the pore size on asphaltene deposition. All the experiments were carried out at a temperature of 32 °C. The filter membranes were fitted inside the vessel in a heterogeneous manner beginning with 450 nm in the upper mesh screen, followed by 100 nm in the middle, and then 50 nm in the lower mech screen. Two pressures were selected to study the effect of miscible pressure (2000 psi) and immiscible pressure (500 psi) on the asphaltene instability. Figure 6 shows the results for the asphaltene weight percentage in all the filter membranes. The results showed that the asphaltene weight percentage increased when using the miscible injection pressure compared to the immiscible injection pressure. The results demonstrated an increase in the percentage of asphaltene weight from 2.00% in 450 nm paper to 3.12% in 50 nm using immiscible pressure. There was a significant observation of higher asphaltene weight percentages at pressures above the MMP (2000 psi) of 13.55% and 21.42% in 450 nm and 50 nm, respectively. The results showed that the miscibility had a significant impact on the asphaltene deposition due to the higher pressure. At higher pressure, the miscibility was achieved and the bonds between the asphaltene and resins became weaker, and thus it led to more asphaltene precipitation.This can be explained as a decrease in the pore size of the filter membrane, the asphaltene particles did not percolate easily, which led to more deposition of asphaltene. For example, asphaltene particles with sizes larger than 450 nm will not permeate through a filter membrane of 450nm. There was precipitation of asphaltene particles with sizes exceeding 50nm but less than 100nm on a 50nm filter membrane. The asphaltene molecules less than 50nm will percolate and gathered produced oil. Therefore, the precipitated Asphaltene on the 450 nm, 100 nm, and 50nm filter membranes, respectively, had sizes of >450 nm, 450-100 nm, and >100 nm.

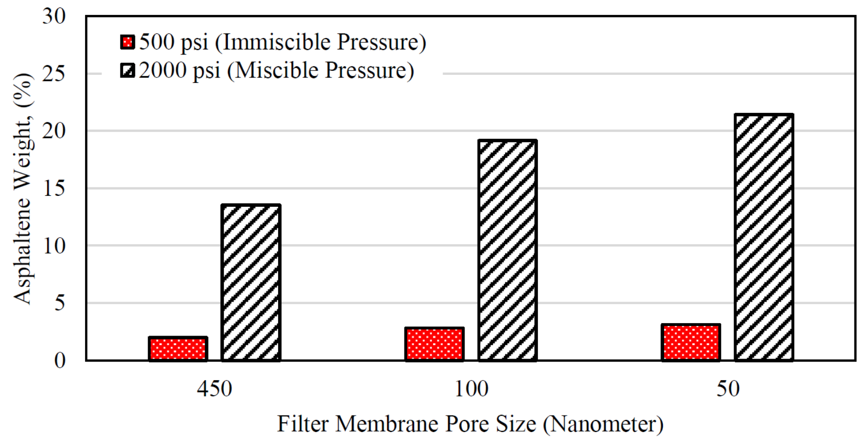

Figure 6—Asphaltene weight percent using a heterogenous filter paper membranes distribution during 500 and 2000 psi of N_2 injection

Effect of Miscible/Immiscible Pressure

Two N_2 injection pressures were investigated in this section, including the immiscible pressure (500 psi) and miscible pressure (2000 psi). The percent of asphaltene weight for the remaining oil above the 450 nm filter membrane and the produced oil is shown in Figure 7. The remaining oil is the oil that remained above the upper filter membrane after the experiment. The produced oil is the oil that passed through all the filter membranes (450, 100, and 50 nm) and reached the outlet of the vessel. The experiments were conducted using heterogeneous filter membrane distribution, 32 °C, and 2 hours of soaking time. The oil remaining had a higher aspahltene weight compared to the oil produced when using immiscible injection pressure. This was mainly due to the lower pressure and the immiscible condition of N_2 injected. Similarrly, the same observation was seen when using miscible conditions. The asphaltene weight percent of the oil produced was lower than the oil remaining due to the pore size of filter membranes being plugged by asphaltene particles. These observations revealed that the miscibility conditions had a significant impact on asphaltene stability in crude oil compared to the immiscible ones.

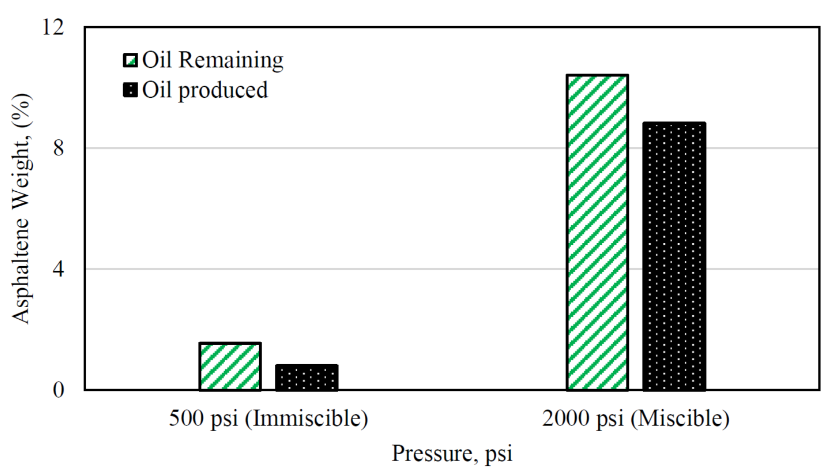

Figure 7—Asphaltene weight percent in remaining and produced oil at 500 and 2000 N_2 injection pressures.

Visualization Results of Asphaltene Deposition Process

The remaining oil was collected after each experiment and dissolved in heptane at a ratio of 1:40. The pictures were captured at various times including 0, 2, 4, and 12 hours to examine and visually capture the asphaltene deposition process. Figure 8 indicates the process of visualizing asphaltene of the oil remaining for both miscible and immiscible experiments. The experiments were conducted to observe the process of depositing asphaltene from the remaining oil. At first, no clear asphaltene could be seen. The dark color was observed in both experiments with a slightly darker color with miscible pressure at zero duration. For the immiscible pressure, the deposition of asphaltene occurred slightly after an hour, and the lighter color appeared after 12 hours. For the miscible pressure, the deposition of asphaltene was seen after an hour and was similar to the immiscible pressure with a slightly higher concentration. Although the observations were almost identical, the final observation of miscible pressure had higher asphaltene deposition after 12 hours. With the progression of time, the heptane had a suspension of some asphaltene and much settled at the bottom of the tube after 4 hours. Lastly, a high deposition of asphaltene was seen on many bases of test tubes, which indicated the deposition of asphaltene. These observations gave more indications of how the asphaltene precipitated in a real reservoir.

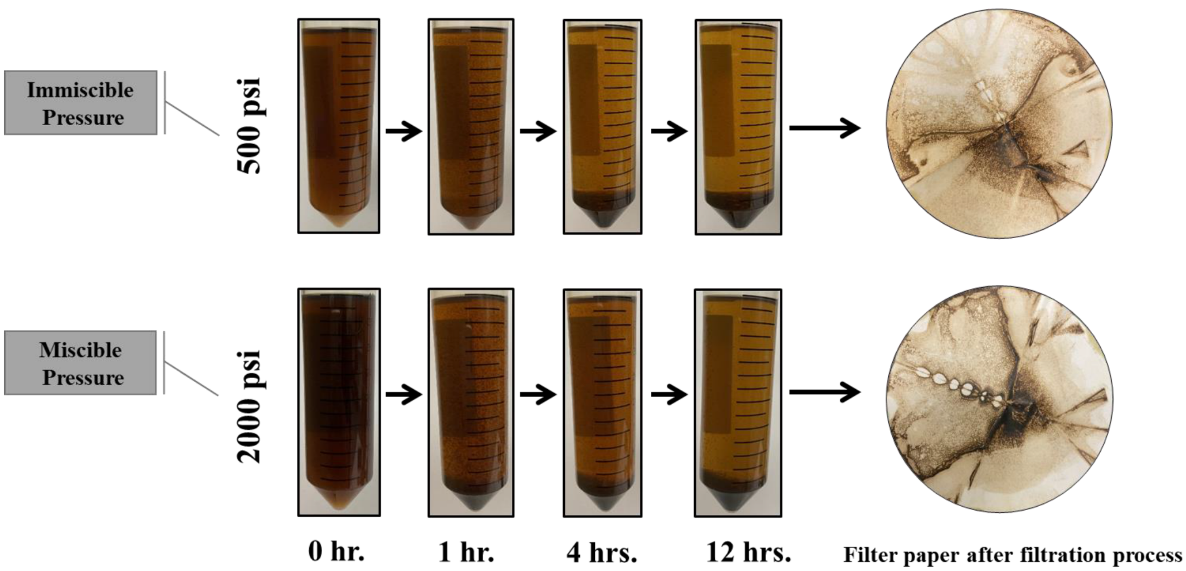

Figure 8—Asphaltene precipitation and deposition visualization process using miscible and immiscible N_2 injection pressures.

Asphaltene Pore Plugging

The asphaltene particles is induced by gas injection, and large asphaltene clusters can be formed leading to asphaltene holdup in a reservoir. Asphaltene can plug the pores and cause severe problems including a reduction in oil relative permeability, altering the wettability of the rock, and an overall reduction in oil production (Amin et al., 2010; Roshan et al., 2016; Siddiqui et al., 2018; Pan et al., 2020; Mohammed et al., 2021; Arif et al., 2021). The filter paper membrane of 450 nm with 2000 psi gas injection was cleaned by the solvent of heptane to highlight the pore plugging in the filter paper. Figure 9 shows the filter membrane before conducting the experiment, after conducting the filtration experiments, and after cleaning the crude oil from the filter membrane. The photo shows the asphaltene deposited in the filter membrane pores and plugged path for the crude oil to move.

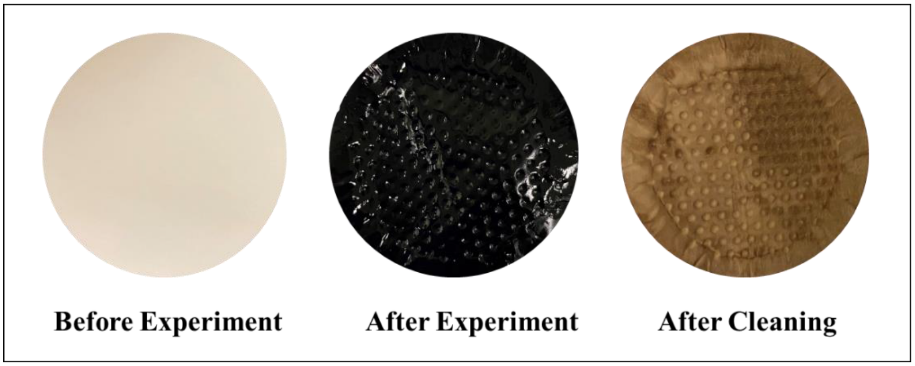

Figure 9—Illustration of filter membrane (450nm) before and after the experiment, and after cleaning

Microscopy Imaging Analysis

A HIROX digital microscope was used to identify the plugging pores and asphaltene clusters in the filter membranes. Figure 10 shows the microscopic images (50um) of the filter membrane's pore structure of 450, 100, and 50 nm using N_2 injection pressure of 500, and 2000 psi at 30 °C. The images highlight the severity of asphaltene pore plugging and gives indications on how the pore size impact the asphaltene precipitation. The microscopy imaging was implemented after cleaning the filter membranes with the solvent of heptane for 24 hours. The images revealed that the immiscible injection pressure had lower impacts on the pore plugging caused by asphaltene deposition. The smaller the pore size, the darker the pore structure image. The miscible gas injection images showed a higher indication of asphaltene deposition due to the miscibility conditions. The dark color is clearly visible in the images, especially in 50 nm filter membrane.

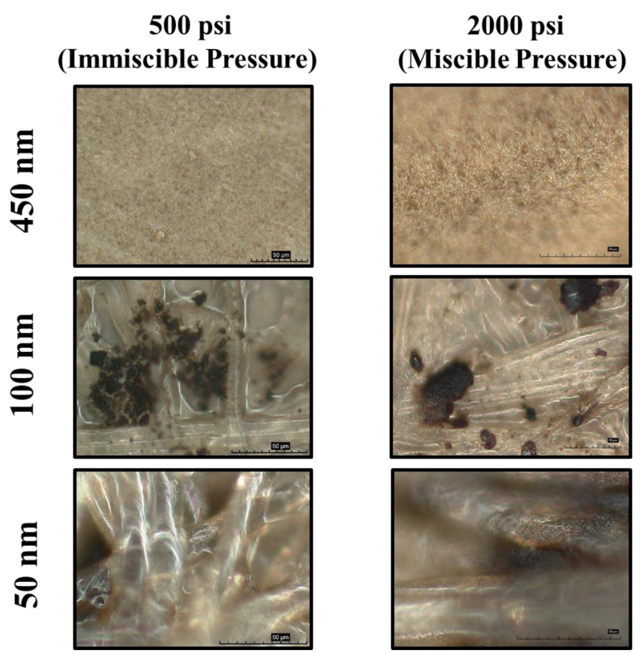

Figure 10—Digital microscopic images (50um) of 450, 100, and 50 nanometer filter membranes using miscible and immiscible N_2 injection pressures

Conclusions

This research performed laboratory work to investigate the effect of miscible and immiscible nitrogen pressure injection on asphaltene deposition in nanopores. Given our results, we suggest the following conclusions:

- The results demonstrated that as the nitrogen injection pressure in miscible conditions (2000 psi), the asphaltene weight percentage increased. The immiscible nitrogen injection pressure (500 psi) resulted in lower asphaltene weight percentage.
- The results showed that as the pore size decreased of membranes, asphaltene clusters were unable to pass. As a result, an increase in asphaltene precipitation and deposition was observed.
- Asphaltene visualization tests demonstrated that asphaltene particles started to precipitate after 1 hour. At zero time collapse, a darker color was observed with miscible conditions. After 12 hours, the colloidal asphaltenes were fully precipitated.
- Microscopy imaging analysis showed a noticeable asphaltene clusters inside the structure of the filter membranes, which the miscibility showed more asphaltene deposition, especially in smaller pore sizes, compared to immiscible conditions.

Acknowledgements

The authors would like to acknowledge the National Science Foundation, Chemical, Biological, Environmental, and Transport systems for funding the work under grant no. CBET-1932965.

Nomenclature

MMP	Minimum Miscibility Pressure
PV	Pore Volume
ml	Milliliter
cp	Centipoise
nm	Nanometer
°C	Celsius Degree

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