CARBON MANAGEMENT TECHNOLOGY CONFERENCE

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# Carbon Dioxide in Situ Generation for Enhanced Oil Recovery

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## Abstract

Carbon dioxide flooding of oil fields around the world is proven as a successfully adopted practice in increasing oil production particularly in marginal wells with low production rates. However, the limitations of this technology lie in the limited supply of carbon dioxide, high capital cost, and infrastructure corrosion. In this work, we present an alternative CO2 flooding method which generates CO2 inside the reservoir to increase oil recovery. The process involves the injection of a concentrated CO2 producing solution of ammonium carbamate (AC). Chemical solvent CO2 capture technology was widely used for years. Carbamates were formed when aqueous amines absorbed CO2. The new proposed in situ CO2 generation EOR technique provides a way to directly apply the product of the CO2 capture technology for outstanding tertiary recovery.

Ammonium carbamate (CH6N2O2), highly water-soluble chemicals, can dissociate at reservoir temperature producing carbon dioxide and ammonia. The carbon dioxide migrates to the oil phase, causing oil phase swelling and reducing oil viscosity, and therefore increasing oil production. The ammonia dissolves in the water, and the ammonia-water solution increases the water wettability of the rock.

Flow experiments were conducted using 6" Ottawa sand packs. The experiments demonstrated that the decomposition of a 35% AC solution injected to the sand packs resulted in further lowering of the residual oil saturation following a standard water flood. The tertiary recovery in the high-pressure sand pack experiments was found to average 27%.

In the proposed process, AC can be dissolved in produced reservoir fluids or seawater and injected into the reservoir to generate CO2 in situ and increase oil production as it decomposes. The benefits of this process compared to CO2 flooding lie in the simplicity of adapting this technology to an existing waterflood, and the lack of the complicated infrastructure needed in a typical CO2 project, such as compression and gas handling facilities. An additional advantage lies in the ability to deliver the CO2 in the form of a room temperature solid, alleviating the need for a pipeline. In situ CO2 generation by injecting CO2 producers has the potential to bring many inshore and offshore oil fields into the economic

production landscape by making them amenable to CO2 flooding without needing to be near a traditional source of CO2.

## Introduction

To address excessive conformance control issues of Water Alternating CO2(Han and Gu 2014, Lei et al. 2016) and CO2 solubility limitation of Carbonated Water Injection (CWI)(Dong et al. 2011, Mosavat and Torabi 2014, Fathollahi and Rostami 2015), i.e., injecting water with dissolved CO2, In situ CO2 generation EOR method(Gumersky et al. 2000, Bakhtiyarov 2008, Li et al. 2013, Wang, Hou, and Tang 2016, Abdelgawad and Mahmoud 2015, Chen et al. 2016) was proposed as an alternative approach in the past few years.

Among these efforts, to achieve reasonable oil recovery, quite a few rather complex formulations were used, involving a combination of elevated concentrations of surfactant, polymer, plus additives like alkali or acids. Our target is to develop a new in situ CO2 generation approach. The potential benefits of this improved formulation may include:

I. Not relying on the natural CO2 sources and installation of CO2 transportation pipeline.
II. Better sweep efficiency than CO2 WAG process.
III. Several folds increase of GWR (Gas Water Ratio) comparing to CWI.
IV. Simple and cheap (directly link CO2 capture and CO2 EOR).
V. Desirable tertiary recovery performance at both above and below minimum miscibility pressure conditions.

CO2 capture applications by using Amine scrubbing technique were studied for years. (Bonenfant, Mimeault, and Hausler 2003, McCann, Maeder, and Attalla 2008, Rochelle 2009). Aqueous amines solution could absorb CO2 from flue gas and form carbamates by the following reaction(Khatri et al. 2006):

$$2R_1R_2 + CO_2 \leftrightarrow R_1R_2NH_2^+ + R_1R_2NCOO^- \quad \cdots\cdots(1)$$

At elevated temperature condition, the carbamates could decompose and release the absorbed CO2 along with the ammonia. In the meantime, the benefits of CO2 and ammonia(van den Pol et al. 2014) on enhanced oil recovery were extensively proved. Therefore, delivering of these EOR chemicals could be done by injecting carbamate solution. To be able to do lab scale experiments, ammonium carbamate was chosen to be the simplest representative of the solute compounds in typical CO2 captured carbamate solution. It could decompose in aqueous solution at elevated temperature.

$$NH_2CO_2NH_4 \rightarrow 2NH_3 + CO_2 \quad \cdots\cdots(2)$$

Batch experiments conducted in our labs have shown that AC in aqueous solution dissociates to release CO2 and ammonia either with elevated temperature (above 95℃) or by the titration with acids such as hydrochloric acid or citric acid(Shiau et al. 2010). The acid lowers the decomposition temperature down to room temperature. In the previously proposed technique, the in situ CO2 generation was not the main EOR mechanism. The gas generating agent was used in low concentration with low generated gas volume. The outstanding tertiary recovery was the synergistic effect from low inter facial tension flooding and in situ CO2 generation.

In the current work, the mechanism of in situ CO2 generation EOR was isolated and studied closely without surfactants or polymers. The involved EOR mechanisms were oil swelling and viscosity reduction caused by CO2. Moreover, the generated ammonia could provide the benefits form alkali flooding. Other than an EOR method, it also had the potential for CO2 sequestration(Shen, Moghanloo, and Tian 2015).

## Material & Apparatus

Ammonium carbamate (99 wt.%) NaCl (99.5 wt.%) and Dodecane (99.5 wt.%) were purchased from Sigma-Aldrich. Besides pure normal alkane, two more crude oil were tested. Crude oil with 40 API and 27 API had a viscosity at 4.6 cP and 22 cP respectively. F-95 Ottawa sand was purchased from U.S. silica. F-95 Ottawa sand size distribution was between 0.075mm and 0.3 mm with d50 at 0.145mm. The F-95 Ottawa sand packed stainless steel had a porosity at 34.5% and permeability at 4 D. The length and the diameter of the porous media in the sand pack test were 6'' and 0.834'' respectively.

To test the in situ CO2 generation system as a tertiary recovery method, all the tests were conducted in high-pressure sand pack flooding system.

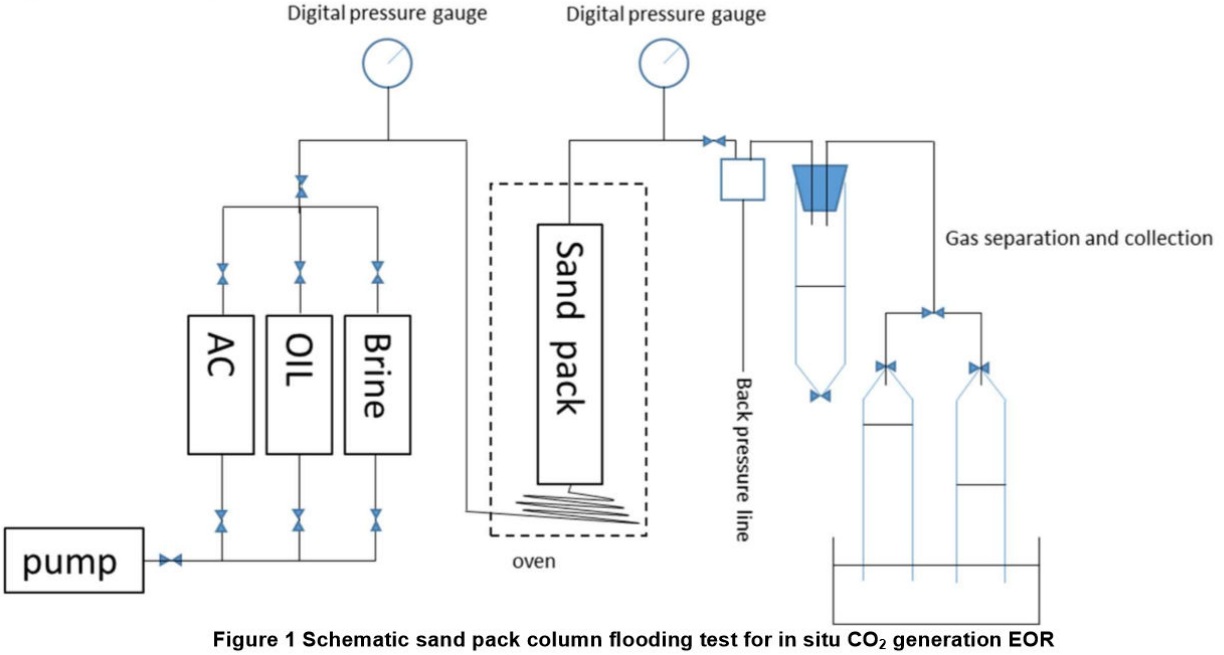


**Figure 1 Schematic sand pack column flooding test for in situ $CO_2$ generation EOR**

**Figure 1** is a schematic of the flooding system. It consisted of three accumulators for different fluids, two syringe pumps (Teledyne Isco 260D), digital pressure gauges, a high-pressure stainless-steel column as a sand pack or a core holder for core flooding test, back pressure regulator, oven and sample collector (gas separating and liquid/gas collecting). The coiled tubing was used to heat the chemical slug before it reached the porous media.
The PH meter was ORION model 420A.

## Experiment Procedure

Sand packs were pre-saturated by injecting a known amount of crude oil. The sand pack and core were aged at 80℃ for two months to reach a higher residual oil saturation value. The temperature and back pressure of the system were set to 120℃ and 1500 psi through the whole sand pack flooding experiment. Injection rate of all the slugs were 0.03 mL/min. Then all the sand packs were flooded in the same sequence. In the beginning, water flooding was done till oil cut reached zero. Then it was followed by two

pore volumes injection of gas generating agent slug. After the gas generating agent injection, water flooding was resumed till no more oil produced. Once the oil cut reached zero again, two more pore volumes of the gas generating agent slug were injected. Following the injection, the flow stopped for 48 hrs (shut-in cycle). After the shut-in, the water flooding resumed till oil cut reached zero again. Pressure and temperature were automatically recorded. The recovered liquid and gas were recorded manually at certain injected pore volume. The oil produced by water flooding and in situ CO2 generation was collected separately. Then Gas chromatography analyzed the compositional differences of these crude oils.

The Brine used in this work was 5 wt. % NaCl solution. The gas generating agent slug was 35 wt.% ammonium carbamate and 5 wt. % NaCl solution.
For the PH measurement solution, the concentration of the NaCl was fixed at 5 wt. %. The concentration of AC was from 0.5 wt. % to 30 wt. %.

## Experiment Result

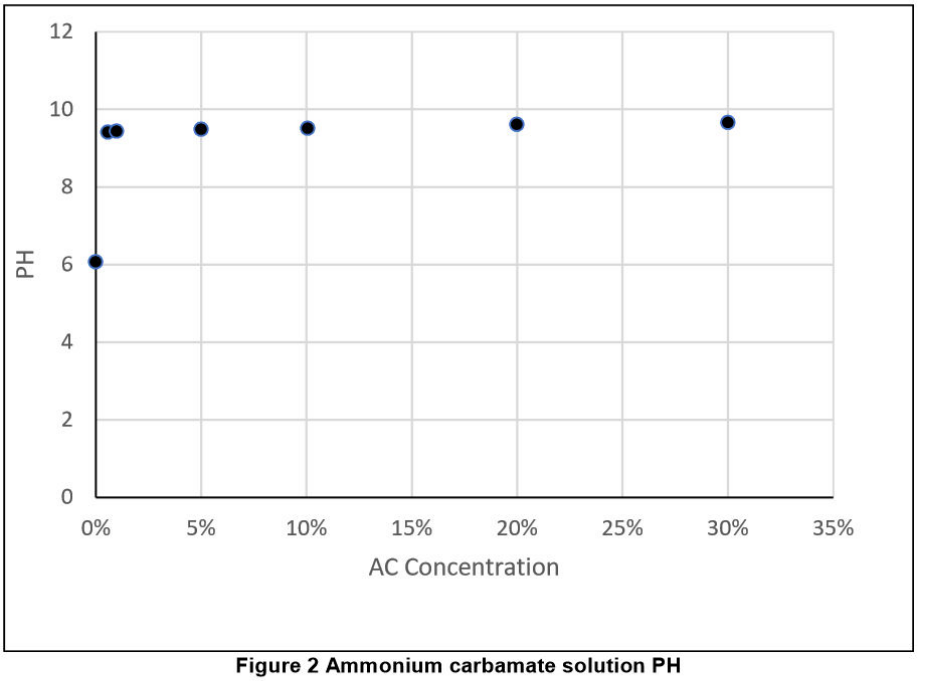


**Figure 2 Ammonium carbamate solution PH**

Figure 2 showed the PH measurement of ammonium carbamate brine solutions. The PH of 5 wt. % NaCl solution was around 6. After adding a small amount of ammonium carbamate, the 0.5 wt. % ammonium carbamate solution showed a high PH at 9.4. Then the PH of the solution reached its plateau (PH=9.5) when the concentration of ammonium carbamate was higher than 1 wt. %. The gas generating solution in the in situ CO2 generation EOR test was acting as a PH buffer. An alkaline solution containing ammonium could help produce crude oil in tertiary recovery stages(van den Pol et al. 2014).

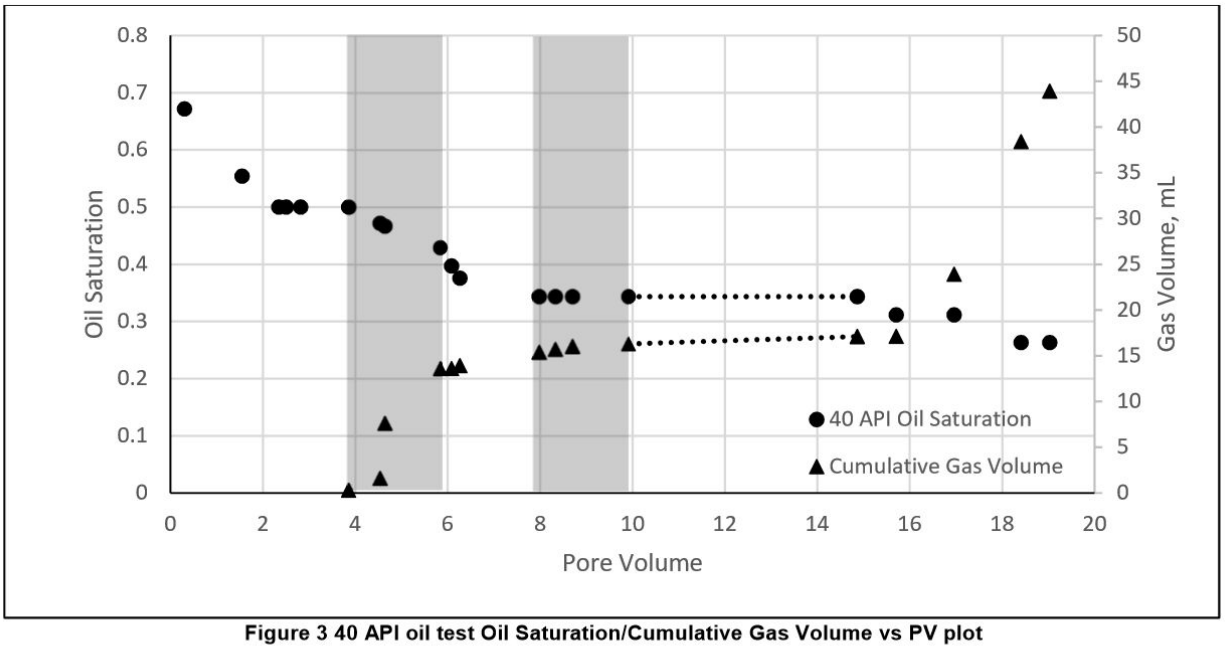


**Figure 3 40 API oil test Oil Saturation/Cumulative Gas Volume vs PV plot**

Figure 3 showed the oil saturation, and cumulative gas volume results from the 40 API crude oil in-situ CO2 generation test. The shaded area indicated the injection of the gas generating agent. The dashed line indicated the flow stoppage. At the first water flooding stage, the oil cut reached zero within 4 pore volumes brine injection. The oil saturation stopped changing at 50% after water flooding. The oil breakthrough happened at about half pore volume gas generating agent injection. CO2 gas breakthrough time was the same as the oil breakthrough. Oil was continuously produced during gas generating agent injection stage. Then the oil cut reached zero within 2 pore volume brine injection. In the second gas generating agent slug injection, oil collector did not receive more crude oil. However, gas production did not stop after the gas generating agent injection. After 2 days shut-in, water flooding produced more crude oil. Moreover, the gas production was at the similar rate as stages before shut-in.

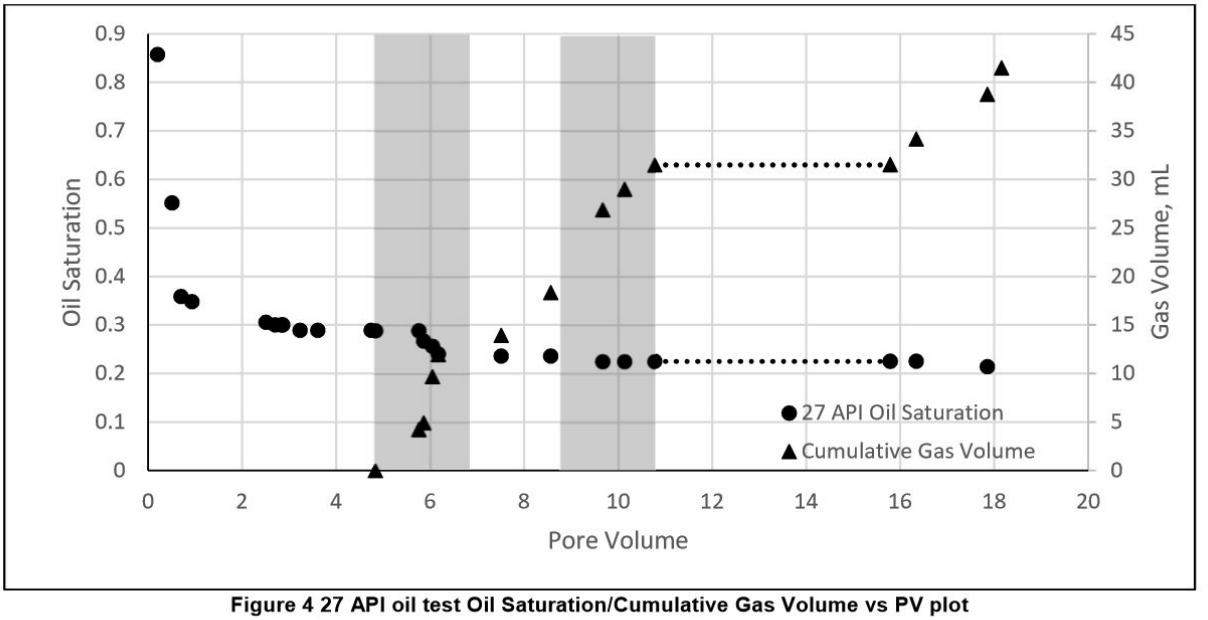


**Figure 4 27 API oil test Oil Saturation/Cumulative Gas Volume vs PV plot**

Figure 4 showed the test result of a heavier oil. The viscosity of this oil was 20 cP. Because of the difference between crude oils. The aging process was not helping on increasing the residual oil saturation of this sand pack. After the water flooding, the oil saturation dropped to 30%. At the first gas generating

agent injection stage, no oil breakthrough was observed after 1 pore volume injection. However, gas collector observed CO2 breakthrough at 1 pore volume injection. The oil breakthrough happened right after the gas breakthrough. The high crude oil viscosity did affect the mobility ratio of the flowing system. And the oil cut reached zero during the injection of the gas generating agent. Part of the reason would be that the residual oil was too low to see an extended oil production stage. The gas production rate was constant after the breakthrough till the system shut-in. The produced oil volume by 2 days shut-in was small. The gas production rate was the same as the rate before the shut-in.

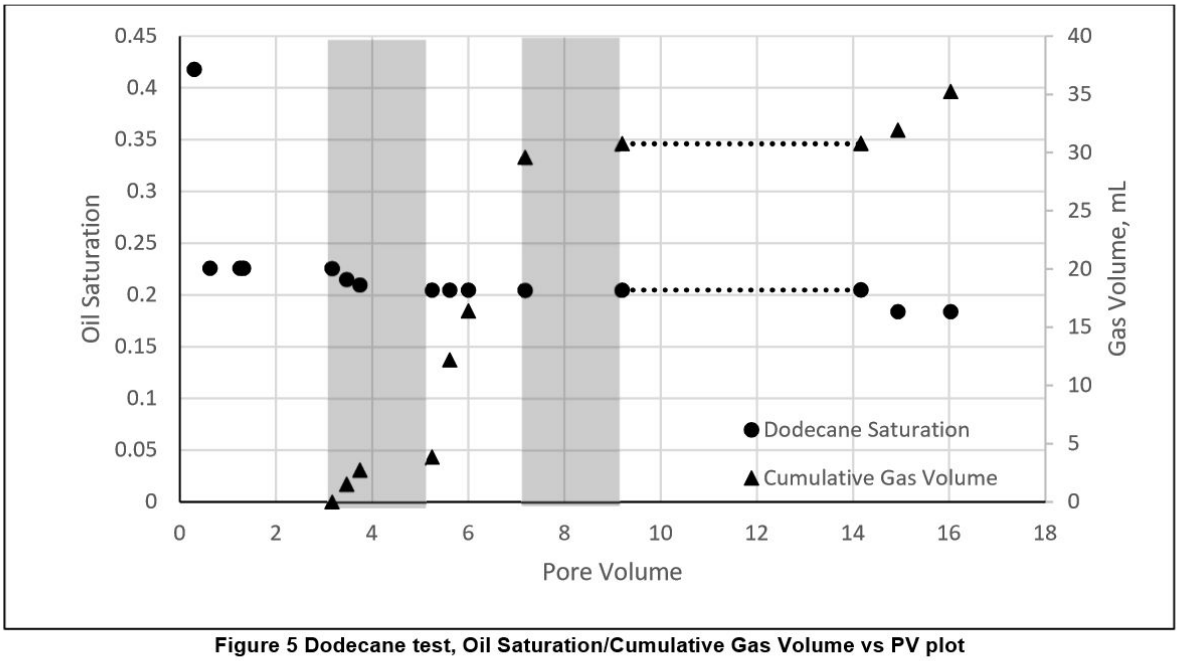


**Figure 5 Dodecane test, Oil Saturation/Cumulative Gas Volume vs PV plot**

Figure 5 showed the Dodecane flooding case. Dodecane was a pure normal alkane. Therefore, the aging process was designed to keep consistency between this test and previous tests. The aging would not help on the residual oil saturation. Because the viscosity of Dodecane was lower than the brine in the water flooding, the sand pack reached its residual oil saturation at the first 0.5 pore volume brine injection. In the gas generating agent flooding stages, the oil breakthrough was at 0.5 pore volume along with the gas breakthrough. The shut-in treatment produced a small amount of oil. However, considering the low volume of residual oil, it is still a significant production. The gas rate is still the same constant before and after the shut-in reaction.

From all the tests, the oil breakthrough was dependent on the oil viscosity. The collected CO2 volume was corresponding to the volume of collected liquid. All the tests showed the tertiary recovery ability of the in situ CO2 generation technique.

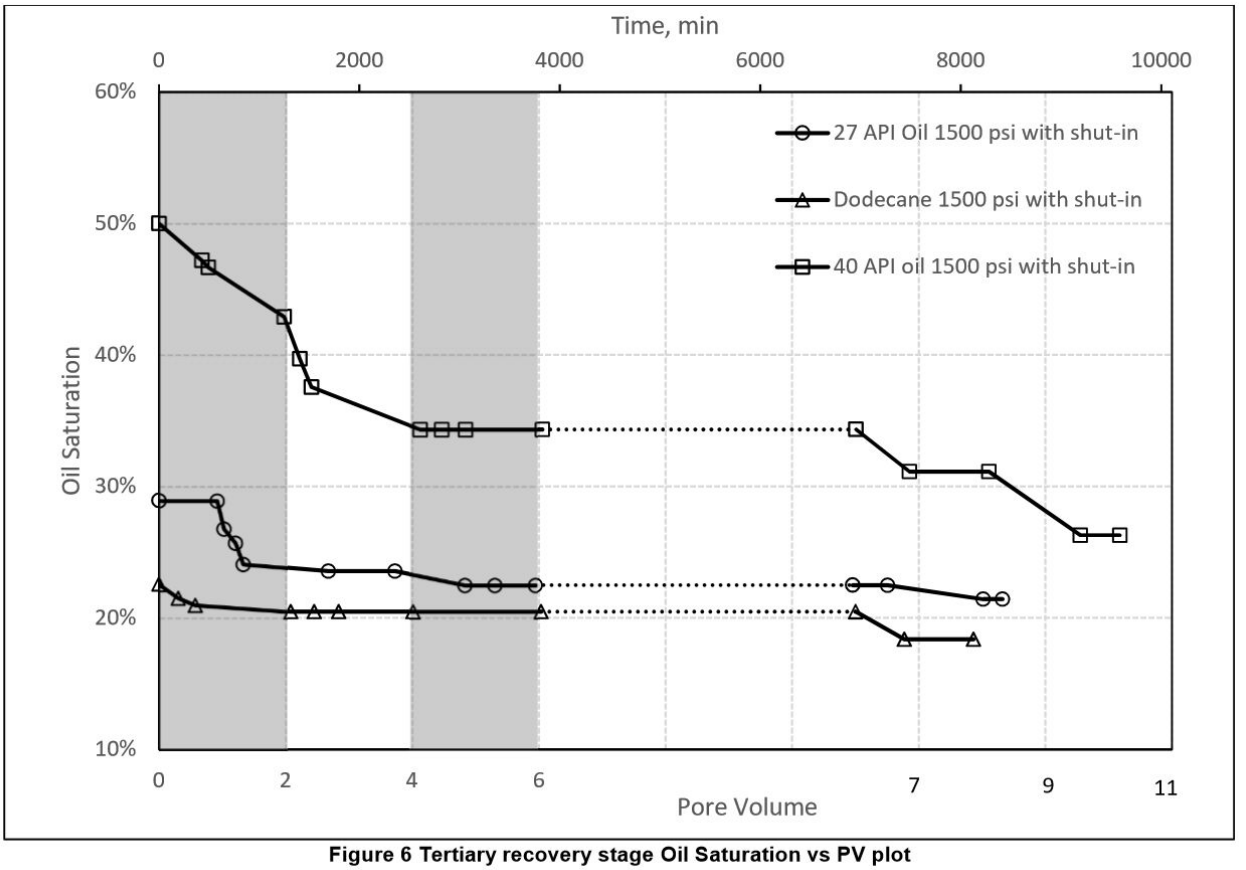


**Figure 6 Tertiary recovery stage Oil Saturation vs PV plot**

Figure 6 compared the oil saturation changing of all the tests during the tertiary recovery stage.

For 40 API oil test, the residual oil saturation after water flooding was 50%. After the tertiary recovery by in situ CO2 generation, the final oil saturations was 26.41%. The tertiary recovery was 47.19%.

For 27 API oil test, the residual oil saturation after water flooding was 28.93%. After the tertiary recovery by in situ CO2 generation, the final oil saturations was 20.66%. The tertiary recovery was 28.6%.

For 40 API oil test, the residual oil saturation after water flooding was 22.57%. After the tertiary recovery by in situ CO2 generation, the final oil saturations was 18.37% The tertiary recovery was 18.6%.

Light oil with high residual oil saturation showed best tertiary recovery. Because all the tests were run at below minimum miscibility pressure condition for all the oil, the CO2 oil solubility was the only parameter that controlled the CO2 partition between the aqueous phase and oil phase when the CO2 water solubility was fixed at certain pressure and temperature. CO2 oil solubility was higher in light oil than it in heavy oil. Therefore, more generated CO2 from the gas generating agent slug could transfer to the oil phase. This phenomenon would lead to better swelling factor and viscosity reduction in light oil test. Dodecane was the lightest oil among all the tested oil. However, the low residual oil saturation limited its performance. Therefore, 40 API oil showed the best tertiary recovery.

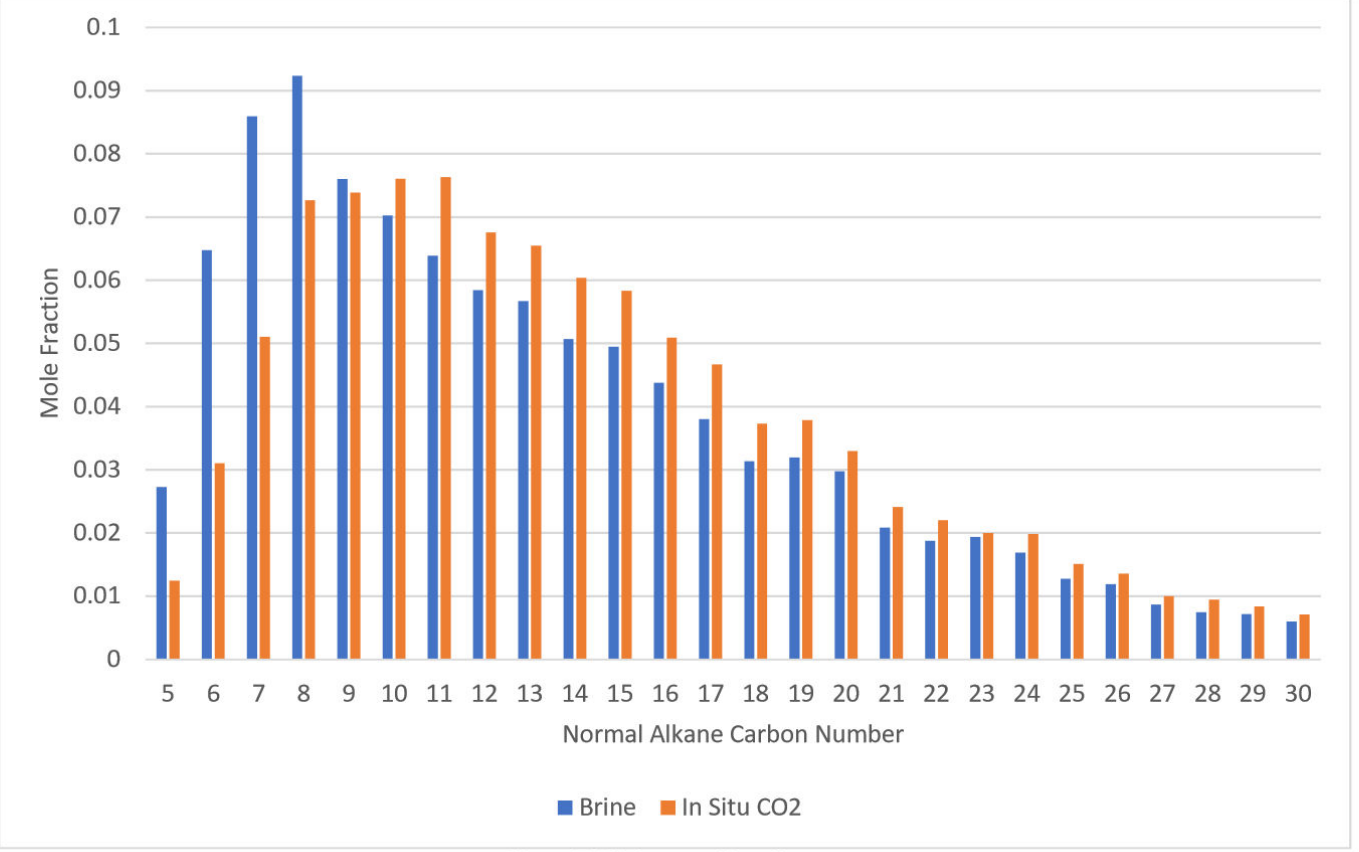


**Figure 7 Oil Composition Change**

Figure 7 was the oil compositional analysis of the 27 API oil test. The recovered oil from secondary recovery (water flooding) and tertiary recovery (in situ CO2 generation) was collected separately. Therefore, the changing of the oil composition caused by in situ CO2 generation EOR could be detected by gas chromatography analysis. In water flooding produced oil sample, the mole fraction of lighter components below C9 was higher than them in in situ CO2 generation produced sample. Comparing to water flooding sample, in situ CO2 generation produced oil sample contained more components heavier than C9.

This measurement indicated that this test did not have a multiple contact miscibility process since it could make the produced oil lighter. There was no separate gas phase in the flooding system, which was consistent with our visual observation. Asphaltene liberation caused by ammonium(Flury et al. 2013) was the reason of more heavy components in the tertiary recovered oil sample.

## Conclusion

1. Single chemical ammonium carbamate system can be used to deliver CO2 to the oil reservoir and generate a significant amount of CO2 to enhance oil recovery.
2. The new proposed in situ CO2 generation system shows comparable tertiary recovery efficiency to previously proposed complex in situ CO2 generation system.

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