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Viscosified CO_2 Widens the Application Window for CO_2 Frac and EOR

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ABSTRACT

Optimized utilization of CO_2 for Fracturing and EOR alongside CCS will not only make a positive contribution to the climate account; it can overhaul the future of the oil and gas sector. Our study has been focused on modifying rheological properties of CO_2 (liquid and super critical phase) to provide favorable fluid systems in the application of CO_2 EOR in combination with CO_2 fracturing that would widen the operation window of CO_2 Utilization.

This paper discusses the development of CO_2 viscosifier systems that would allow the development of simplified CO_2 fracturing technology and wider application to improve the efficiency of CO_2 EOR.

Numerous successful field tests of the simplified CO_2 fracturing and an ongoing viscosified CO_2 EOR field test are shown in the paper. Potential applications of the viscosified CO_2 systems to achieve optimized asset values in the oil industry is discussed at the end of the paper.

Keywords: Viscosified CO_2, CO_2 Frac, CO_2 EOR, CCUS

1. INTRODUCTION

The application of CO_2 plays an important role in adding value to the CCUS process. As discussed by Rassenfoss[1], the tax credit is not in favor of CO_2 EOR compared to CO_2 storage. Making CO_2 EOR economically viable depends on the added value created by CO_2 EOR. CO_2 EOR has been conducted in the US[2,3] and North Sea for quite a long time. Currently, most of the CO_2 EOR is through the Huff-n-Puff methodology in unconventional resources. In conventional reservoirs, CO_2 flooding is still the dominant procedure[2]. Due to the very low viscosity of liquid CO_2 (0.1 mPa.s), (in most reservoir conditions CO_2 may reach critical state where its viscosity would be close to gas – 0.01 mPa.s), swipe efficiency becomes very low because of the low mobility ratio. Having a good control of mobility ratio to increase swipe efficiency has become a key technology for engineers in the business.

Advanced technologies have been developed with the successful shale gas/oil revolution. Horizontal drilling and multiple-stage hydraulic fracturing are the key technologies among them. They have provided more options for the development of future conventional and unconventional resources with higher efficiency and more economical values. Utilizing CO_2 as a flowback energizer in horizontal well fracturing is very common4. For some water sensitive formations, dry CO_2 (pure CO_2 without water) fracturing has been conducted with necessary equipment such as pressurized blenders[5]. The unique operational requirements make dry CO_2 fracturing complex and costly.

There are key values possessed by the oil and gas industry: 1. Pore space; 2. Access to the target (land and pore space including wells); 3. Already built infrastructure and facilities and 4. Well-developed technologies and personnel who are familiar with the assets and the technologies. It is the industry's mission to take advantage of the values in hands to realize the maximum value in the process of CCUS.

2. OBJECTIVES OF THE STUDY

In the area of CO_2 EOR, the challenges are:

- CO_2 has very low viscosity (0.01 – 0.1 mPa.s). The occurrence of finger through and CO_2 break through is very high.
- The critical point of CO_2 (31.26 ℃ & 7.38 MPa) in most cases is below the formation condition. Under critical conditions, the density of CO_2 is close to liquid,

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but its viscosity is close to that of gas. Early gas break-through is very likely.

Increasing the viscosity of CO_2 and its critical point has become a key task. Even though there are efforts to find proper CO_2 viscosifyers[6], to our knowledge, there is no commercial product in the market to meet the needs especially for CO_2 EOR.

The challenges in dry CO_2 fracturing include the requirement of pressurized blender and increase CO_2 viscosity at low temperatures in the pressurized blender for proppant carrying capacity.

This study has been focused on modifying rheological properties of CO_2 (liquid and super critical phase) to provide favorable fluid systems in the application of CO_2 EOR in combination with CO_2 fracturing that would widen the operation window of CO_2 utilization making use of the well-developed technology without requiring more complicated procedures and cost effective.

The developed technology covers the following areas:

1. Develop viscosified fluid chemicals for CO_2 fracturing and EOR.
2. Simplify CO_2 fracturing.
3. Field testing for both EOR and fracturing.
4. Explore the utilization window.

3. METHODOLOGY

Temperature controlled rheometer and phase balance evaluation apparatus were the main instruments for the development of the rheology modifiers for both CO_2 EOR and fracturing.

Fracture and reservoir simulators are the main tools in exploring the optimized application of CO_2 EOR including potential application of horizontal wells and fracturing technology in addition to currently applied CO_2 EOR practices.

3.1 CO_2 Phase Balance Tester

Fit-for-purpose equipment for evaluating CO_2 viscosifyers has been designed and constructed in house. It includes:

- Pressurizing section to create liquid CO_2.
- Agitating capability to dissolve viscosifyers and observe the results through a see-through cell.
- Heating section to control the temperature of the testing cell.
- Proppant suspension test capability.

A picture of the apparatus is shown in Figure 1.

Figure 1. CO2 phase balance tester

3.2 Liquid CO_2 Rheology Measurement

Rheological measurements were conducted under controlled temperatures and pressures with the use of a Haake RS6000 Rheometer as shown in Figure 2. At pressures beyond the rheometer's limit, a falling-ball viscometer was used to measure the viscosity of the test fluids.

Haake RS6000 Rhometer

HTHP System

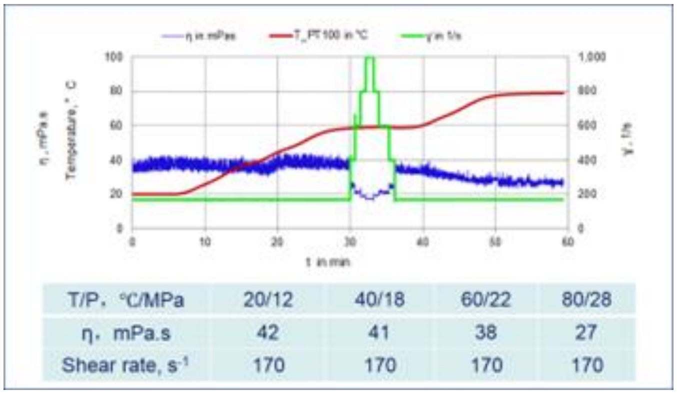
Figure 2. Haake RS6000 for rheological measurements

4. RESULTS OF PRODUCT DEVELOPMENT

Through a series of chemical design and development followed by evaluation lab testing, two patented synthetic polymers have been developed for field applications. They are APFR-2 for CO_2 fracturing and APFR-4 for CO_2 EOR respectively.

APFR-2 is a polymeric liquid CO_2 viscosifier. It is 100% CO_2 soluble and not water soluble. However, it can be dispersed in water. It has the features of fast dissolving in liquid CO_2 to create viscosity (50-150 mPa.s) for creating desired fracture geometry; shear thinning with high friction reduction (70% reduction compared to water); and viscoelastic property that would provide good proppant transport. When it is mixed with a certain percentage of water and a water-soluble polymer, its rheological properties will be enhanced. The application will be discussed in detail in the next session.

Figure 3 (a) shows the viscosity versus time at various shear rate and temperature conditions of a fluid mixed with APFR-2. Figure 3 (b) shows a perfect proppant suspension under high pressure (20 MPa) and high temperature (89.1 °C).



T/P，°C/MPa	20/12	40/18	60/22	80/28
η，mPa.s	42	41	38	27
Shear rate, s^{-1}	170	170	170	170

Figure 3(a) Viscosity of a mixed fluid （30% H2O + 70% CO2）vs. temperature and shear rate.

Figure 3(b) See-through cell showing a perfect proppant suspension (30 minutes without proppant settling).

APFR-4 is also a polymer that dissolves completely in liquid CO_2 and super-critical CO_2 with no residue. It is not water soluble but can be dispersed in water. At high concentrations (1-2%), dissolution rate is very high (1-3 minutes) at ambient temperature. At low temperature, a cosolvent would help to enhance the process. In reality, formation temperature would help the dissolution process. Viscosified CO_2 has a much higher critical point making CO_2 EOR process in the liquid drive condition.

Figure 4 illustrates that at 90 °C and 20.69 MPa, the viscosified CO_2 is still in liquid state meaning that the critical point has been shifted.

Figure 4. CO_2 mixed with APFR-4：0.5%, APFR-R (cosolvent)：0.5%. Temperature：90℃, Pressure：20.69 MPa, Viscosity：~20 mPa.s, State: homogeneous liquid phase

Viscosity stability tests for CO_2 mixed with 1% and 2% of APFR-4 at different pressures and temperatures are shown in Figure 5a and 5b.

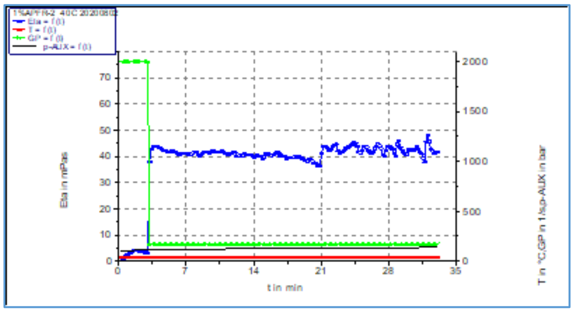


Figure 5a – Stability of CO_2 with 1.0%APFR-4 at 40 ℃. The viscosity is 41.67 mPa.s.

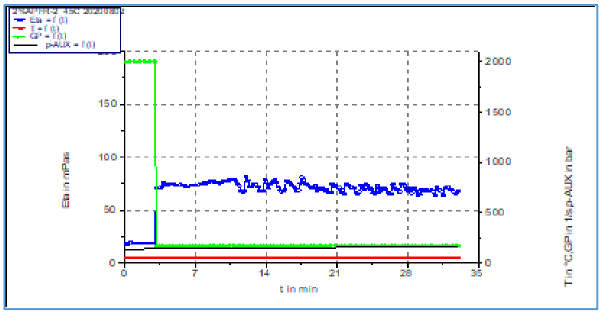


Figure 5b – Stability of CO_2 with 2.0%APFR-4 at 45 °C. The viscosity is 67.86 mPa.s.

Core flow tests have been conducted to evaluate the viscosified CO_2 recovery improvement potential. We used a HPHT core flow system to compare the effectiveness between viscosified CO_2 (with 0.3%APFR-4+cosolvant) injection to pure CO_2 injection.

Results indicate that the recovery factor of pure CO_2 displacement is around 40% while the recovery factor of viscosified CO_2 is 50-53%. A 10% recovery improvement is achieved. The following table provides the tests results.

Core #	Porosity %	Water saturation %	Residual oil saturation %	Differential pressure MPa	Displacement efficiency %	Injected pore volume #	Injecting fluid
1	12.7	56.88	25.61	0.50	40.60	5.97	Pure CO_2
2	12.5	54.77	22.05	0.50	51.25	5.94	Viscosified CO_2
3	12.8	52.58	22.93	0.50	51.65	6.04	
4	12.3	53.26	21.63	0.50	53.72	6.05	
5	12.9	55.32	22.07	0.50	50.60	8.27	

Challenges in numerical simulations for viscosified CO_2 in liquid CO_2 fracturing and EOR have been identified. Work to provide solutions to build applicable tools has been initiated with software developers.

Initial field testing of CO_2 fracturing and EOR have been conducted and are ongoing. Simulation work has been initiated and some potential advantages have been identified.

5. FIELD APPLICATIONS

5.1 CO_2 fracturing

A simplified liquid CO_2 fracturing (quasi-dry) procedure has been developed and applied in the field successfully.

The challenges in liquid CO_2 fracturing (dry) include:

- Viscosifying liquid CO_2 at low temperature is difficult.
- The low viscosity results in poor proppant carrying capacity, and high friction, leading to less desired fracture geometry with poor proppant placement.
- Requires pressurized mixing system – meaning operational complexity.
- Fracture scope is limited by the capacity of the pressurized mixing system.
- High cost.

The unique feature of APFR-2 is that it can be dispersed in water and joint thickening the CO_2 and water mixture with a water-soluble polymer. This has led us to consider whether we can overcome the above-mentioned challenges: 1. Whether we can avoid the use of pressurized mixing system? 2. Can we improve fracture geometry and proppant placement by pumping fluid with desired rheology and proppant concentration? 3. Can the volume of liquid CO_2 be reduced to lower the total cost?

Through the work with operators and service providers, a simplified procedure has been developed. In practice, two groups of pumps are working together in a fracture operation.

Group A – Using a blender to mix proppant with water (10 to 30% of the total fluid volume) viscosified by

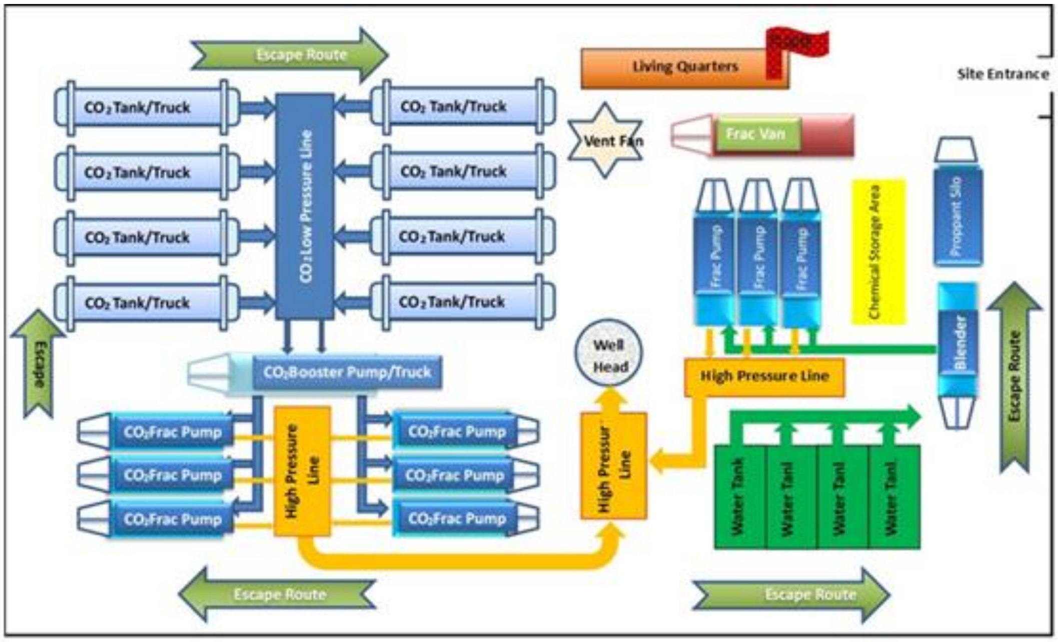


Figure 6 – Wellsite layout of a quasi-dry CO_2 fracturing operation.

a water-soluble polymer to form a highly viscoelastic high proppant concentration (up to 15.9 ppg) slurry. APFR-2 is dispersed in the mixture. The mixing is at ambient condition. The proppant laden slurry is pumped to the wellhead by a group of fracture pumps.

Group B - Pump liquid CO_2 at high pumping rate and mix it with the high proppant concentration slurry at the wellhead. At turbulent flow in the pipe, liquid CO_2 immediately increase its viscosity and form a multi-phase proppant slurry. The viscoelastic behavior of the combined slurry has high proppant carrying capacity. The effective proppant (high density ceramic proppant) concentration of the combined slurry can reach up to 6.3 ppg (8 ppg was achieved during field trial).

Since the process involves a certain amount of water, we call it quasi-dry CO_2 fracturing. Pressurized blenders are not needed, and the proppant volume is not limited by the pressurized blenders. Figure 6 is a wellsite layout for a quasi-dry CO_2 fracturing operation.

Figure 7 is the treatment curve for a real field pumping operation. The maximum proppant loading has reached 8 ppg.

To date, there have been 9 wells fractured with quasi-dry fracturing technology using APFR-2 as CO_2 viscosifier. All the wells performed much better than offset wells using conventional hydraulic fracturing

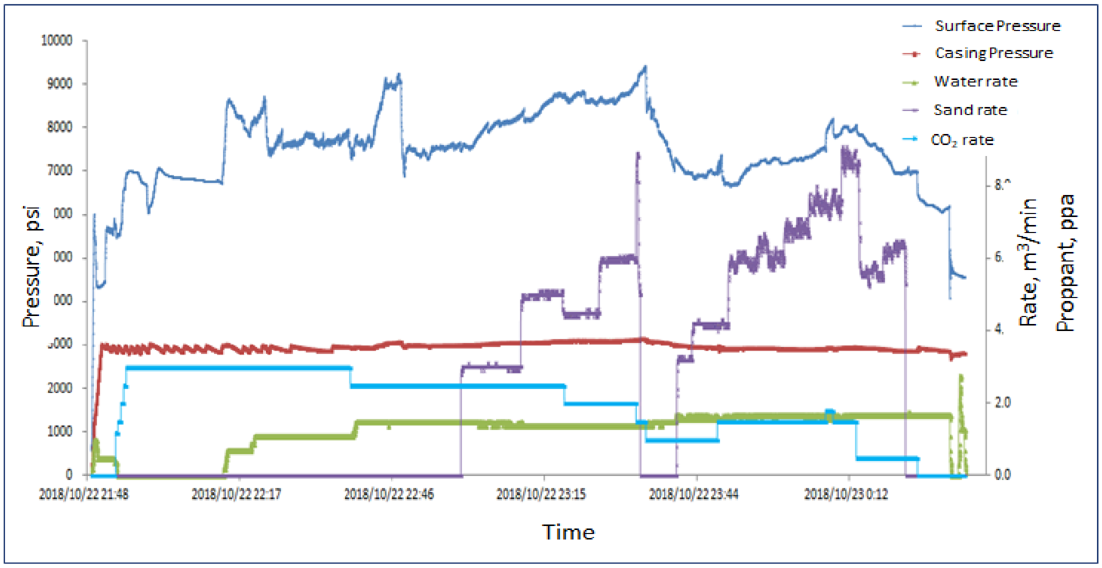


Figure 7 – The treatment curves of a real quasi-dry CO_2 fracture operation.

technology (slick water fracturing). Two wells were fractured with dry CO_2 fracture technology using APFR-2 as CO_2 viscosifier. They also performed above expectations.

5.2 CO_2 EOR

An EOR field trial using APFR-4 as viscosifier has been started recently. Initial results indicate that the viscosified CO_2 as injection fluid has performed positively. The following table illustrates a comparison.

Comparison of viscosified CO_2 EOR with offset well in Yanchang Oil Field

Well	APFR-4 concentration, %	Injection pressure, MPa	Injected CO_2, m^3	CO_2 concentration in producer, %
Test well 2#	0.2	10.45	1300	1.3
Offset well 5#	0	7.65	1300	76.0

The viscosified CO_2 has shown an obvious advantage in increasing the injection pressure and reducing the break-through occurrence. The test is ongoing.

6. SUMMARY

Viscosifying CO_2 and viscosifyer's solubility have been the roadblock for oil field chemistry industry. Two patented CO_2 viscosifiers have been developed for CO_2 fracturing and EOR respectively. The new systems significantly improve the mobility ratio for the EOR and has very good temperature stability. It also increased the supercritical point that is in favor to the EOR process.

In addition, the viscosifiers have helped in developing a simplified CO_2 fracturing technique – quasi-dry CO_2 fracturing. Successful field testing on multiple wells have been achieved indicating that the technique is ready for future applications.

The viscosifiers provided a means of CO_2 rheology control showing a wide application potential in improving CO_2 EOR effectiveness. The ongoing first field indicated the differences between procedures with mobility control and without.

More work needs to be done in finding applications in CCUS in the oil and gas industry utilizing already developed technology. Developing numerical tools for CO_2 fracturing and EOR will be our next step.

7. LOOKING FORWARD

Mobility controllable CO_2 EOR and quasi-dry CO_2 fracturing have provided tools for the industry to widen the application window in maximizing the value of CCUS. For example, finding ways to best utilize pore space and recovery factor simultaneously.

In addition to huff-n-puff and traditional injector/produce pattern, more injection options could be explored.

Wells stimulated with CO_2 can provide better reservoir pressure maintenance than stimulated with slick water as shown in Figure 8.

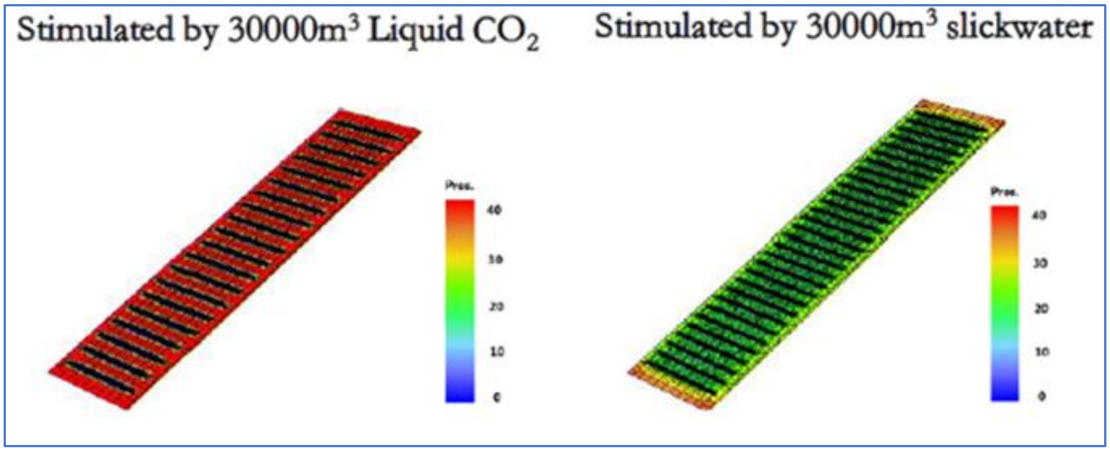


Figure 8 - Simulation results illustrating better pressure maintenance for wells stimulated with CO_2. Courtesy of Fan Yuelong, 2022.

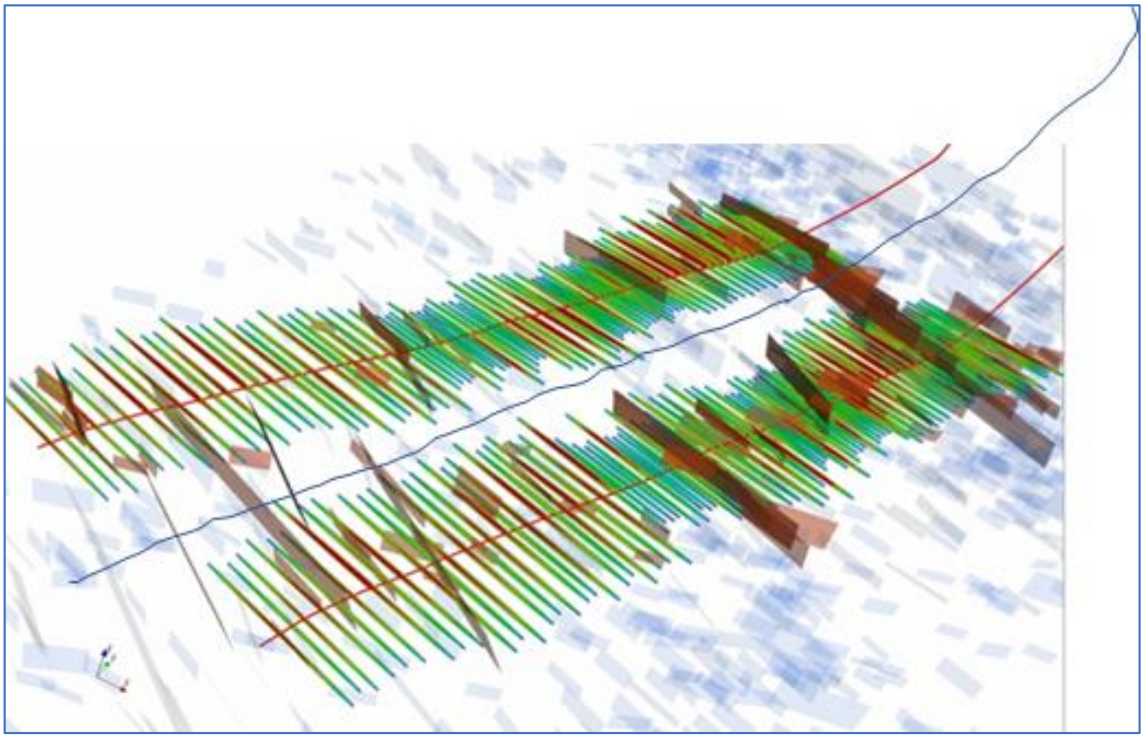


Figure 9 – Imaginary scenario of CO_2 fracturing and injection.

One can imagine a scenario where two horizontal wells have been hydraulically stimulated. To enhance their production and utilize the pore space for CO_2 storage, an injection well can be drilled and fractured by CO_2, the number and location of stages and whether to frac-hit depends on the design, then utilize the well to inject CO_2 as shown in Figure 9. If done properly, the recovery would be higher, and the pore space will eventually be occupied to a large percentage by CO_2.

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