Asia Pacific CCUS Conference and Exhibition 2025

Paper Number - **SPE-225819-MS**

Significant Phase Behavior Changes in Chemically Treated Oil During CO_2 Injection

Jerry. Yoeh[1]*, Lei. Shi[2], and Yao. Ge[3]

[1]PES Enterprise Australia Pty Ltd, Sydney, Australia
[2]Karamay Xinyitong Biotechnology Co., Ltd, Karamay, Xinjiang, China
[3]Karamay XianBo Technology Innovation and Incubation Co.,Ltd, Karamay, Xinjiang, China

Abstract

Carbon Capture, Utilization, and Storage (CCUS) has emerged as a critical strategy for reducing greenhouse gas emissions in response to global climate change. Within the fossil fuel industry, CO_2 -Enhanced Oil Recovery (CO_2 -EOR) stands out as a promising dual-purpose technology that not only sequesters CO_2 but also improves oil recovery from mature or challenging reservoirs. The success of CO_2 -EOR largely depends on achieving miscibility between the injected CO_2 and the reservoir crude oil, which enables efficient displacement and maximizes hydrocarbon recovery. However, many reservoirs lack the high pressure and temperature conditions necessary for natural miscibility.

This study explores a chemical-enhancement approach to improve CO_2 miscibility in sub-optimal reservoirs. Specifically, selected oil-based and water-based amphiphilic chemical additives were introduced into a crude oil sample from a reservoir that does not meet miscibility criteria under natural conditions. Through Pressure-Volume-Temperature (PVT) phase behavior experiments, the modified fluids demonstrated significantly reduced saturation pressures and enhanced CO_2 solubility. These findings indicate a favorable shift in phase behavior toward miscibility. Complementary slimtube displacement experiments conducted at reservoir conditions further confirmed that the chemically treated fluids exhibit recovery patterns characteristic of near-miscible or fully miscible displacement.

The results provide compelling evidence that incorporating tailored chemical additives can effectively enhance CO_2 -oil interactions, reduce the minimum miscibility pressure (MMP), and extend the technical feasibility of CO_2 -EOR in reservoirs previously considered unsuitable. This approach offers a cost-effective and scalable solution for improving oil recovery while supporting carbon management goals in various reservoir conditions.

Key words: CCUS, CO_2-EOR, Chemical additives, PVT, Slimtube

Introduction

Enhanced Oil Recovery (EOR) techniques are widely employed to maximize hydrocarbon production from mature or low-permeability reservoirs. Common EOR methods include water flooding, gas injection, and chemical flooding, each targeting the reduction of residual oil saturation through distinct displacement mechanisms. Among these, CO_2-Enhanced Oil Recovery (CO_2-EOR) has gained particular attention due to its unique dual benefits: increasing oil recovery while simultaneously enabling Carbon Capture, Utilization, and Storage (CCUS) to mitigate greenhouse gas emissions.

Under favorable thermodynamic conditions - typically characterized by elevated reservoir pressures and moderate to high temperatures-CO_2 can achieve miscibility with reservoir fluids, particularly crude oil. This miscibility eliminates the interfacial tension between oil and gas, enabling efficient mass transfer and displacement. As a result, miscible CO_2 injection can significantly enhance oil recovery through mechanisms such as oil swelling, viscosity reduction, and extraction of lighter hydrocarbon components. However, in many reservoirs, especially those with lower pressure or complex fluid compositions, miscibility is not naturally attainable, limiting the effectiveness of CO_2 injection and leaving substantial amounts of oil unrecovered [1–4].

Various advanced CO_2 -EOR strategies have been developed to address these limitations. These include [5–7]:

- Increasing CO_2 slug size or utilizing continuous injection to sustain displacement pressure,

- Well pattern optimization to improve sweep efficiency,
- Alternating CO_2 with water (WAG processes) to stabilize mobility ratios,
- And more recently, the incorporation of chemical additives, such as surfactants, polymers, and viscosifiers, which aim to modify fluid properties and enhance CO_2 -oil interactions.

Among chemical approaches, amphiphilic additives - both oil-soluble and water-soluble - have shown promise in reducing minimum miscibility pressure (MMP), increasing CO_2 solubility in oil, and suppressing asphaltene precipitation. These additives can promote pseudo-miscible conditions by facilitating microemulsion formation or by altering interfacial properties, thus improving the efficacy of CO_2 injection in reservoirs that are otherwise thermodynamically unfavorable for miscibility.

This study investigates the potential of integrating chemical additives with CO_2 injection under simulated reservoir conditions. Using a combination of PVT (Pressure-Volume-Temperature) phase behavior analysis and slim tube displacement experiments, we evaluate the effects of oil-based and water-based additives on key performance indicators, including saturation pressure, CO_2 solubility, and minimum miscibility pressure. The objective is to assess whether such additives can effectively lower the miscibility threshold and enhance oil recovery in reservoirs where traditional CO_2 -EOR may fall short. The experimental findings offer practical insights into additive-assisted CO_2 -EOR strategies and their broader implications for coupled EOR-CCUS deployment in the energy transition era.

Experiments

The crude oil sample used in this study, designated as JL2, was sourced from the Karamay Oilfield, Xinjiang, China. Two chemical additives were selected through a preliminary screening process conducted by Karamay Xinyitong Biotechnology Co., Ltd:

- Additive A – an oil-soluble formulation
- Additive B – a water-soluble formulation

Both additives were chosen for their amphiphilic properties and potential to enhance oil-CO_2 interaction during enhanced oil recovery (EOR) operations.

The gas sample used to recombine the live oil was synthetically prepared based on the compositional analysis of the field's original natural gas, thereby simulating reservoir conditions with high fidelity. Commercial-grade carbon dioxide (CO_2) with a purity of 99.5% was utilized in all injection tests to ensure consistency and minimize impurities that might interfere with phase behavior.

All experimental work was conducted at the Karamay XianBo Technology Innovation and Incubation Co., Ltd, where controlled laboratory facilities enabled high-precision testing under reservoir-simulated conditions.

1. PVT and Slimtube Experimental Setup

Phase behavior analysis and displacement experiments were performed using two advanced systems manufactured by PES Enterprise Australia Pty Ltd:

- NIRPVT-1500, Black Oil PVT System
  This system integrates a near-infrared solid particle detection unit for real-time monitoring of phase changes and asphaltene precipitation and a bull's-eye observation window for visual inspection. The high-pressure visual cell features a chamber volume of 250 mL and a volumetric resolution of 0.01 mL, enabling accurate measurement of fluid expansion, gas solubility, and saturation conditions.
- The same system above was used for continuous CO2 injection, testing Asphaltene Onset Concentration (AOC).
- ST-1000, Slimtube Apparatus
  The slim tube device has an inline gas chromatograph for real-time compositional tracking of effluent gases during displacement. The experimental slim tube consists of a coiled stainless-steel tube with an inner diameter of 0.4 cm, a total length of 2000 cm, and a calculated pore volume of 251.2 cm^3. These specifications simulate porous media flow and accurately assess minimum miscibility pressure (MMP) and recovery efficiency.

Both systems are designed to simulate reservoir temperature and pressure conditions and were operated under stringent control to ensure data reliability across all experimental runs.

2. Reservoir and Fluid Properties

Table 1 summarizes the key reservoir parameters relevant to the JL2 oil system, including reservoir temperature, pressure, saturation pressure, and gas-oil ratio (GOR). These parameters define the baseline thermodynamic conditions used in all test procedures.

Table 1. Parameters of reservoir temperature, pressure and gas-oil ratio

	Reservoir Temperature (℃)	Reservoir Pressure (MPa)	Bubble Point (MPa)	GOR (m^3/m^3)
JL2 oil	97	50.12	31.09	130.3

Table 2 provides the detailed composition of the synthetic natural gas used for live oil recombination, including the mole fractions of methane, ethane, propane, and heavier hydrocarbon components. This formulation ensured the recombined oil matched in situ conditions as closely as possible.

Table 2. Composition of Natural Gas

Component	Content (mol%)	Component	Content (mol%)
Methane	93.58	i-pentane	0.16
Ethane	2.57	n-pentane	0.16
Propane	1.04	n-heptane	0.06
i-butane	0.30	N2	1.73
n-butane	0.38	CO2	0.02

3. Infrared Imaging Captures Experiment

An Infrared High-Pressure Optical Cell (IRHPOC) was employed to capture infrared images of CO_2 –crude oil interactions under simulated reservoir conditions. The IRHPOC technique enables in situ visualization of phase behavior and fluid interactions at high pressure and temperature. This method builds upon the High-Pressure Optical Cell (HPOC) system initially developed by Prof. I-Ming Chou [8–9]. In this setup, one end of a fused silica capillary tube is flame-sealed using a hydrogen torch, while the open end is connected to a high-pressure line via a precision valve. This configuration allows fluids of known composition to be loaded into the capillary, with pressure precisely regulated by a Floxlab automatic pump.

Due to crude oil's optical opacity in the visible spectrum, an infrared imaging system is integrated with the HPOC to monitor CO_2 –oil interactions more effectively. Crude oil is introduced into the capillary tube, and CO_2 is injected and pressurized by the pump. A Linkam CAP500 heating stage provides temperature control, ensuring consistent thermal conditions throughout the experiment.

Results and Discussion

The PVT (Pressure-Volume-Temperature) analysis data provided in Tables 3, 4, and 5 offer a comprehensive view of the thermophysical and rheological behavior of the base JL2 crude oil and its chemically treated variants under simulated reservoir conditions. Key parameters - such as saturation pressure, viscosity, and CO_2 solubility - exhibit trends consistent with established industry benchmarks, thereby reinforcing the experimental integrity. However, a more detailed comparison between untreated and chemically modified JL2 oil samples reveals several notable performance improvements attributable to the action of the chemical additives.

Table 3. PVT analysis data of JL2 crude oil under different concentrations of injected CO_2

Concentration of injected CO_2	GOR	Flash oil density	Saturation pressure	Rolling ball viscosity*	Critical temperature Tc	Critical pressure Pc
vol%	m^3/m^3	g/cm^3	MPa	mPa·s	℃	MPa
0.0000	138.50	0.8949	45.80	6.54	333.73	45.71
4.6977	183.20	0.8924	46.20	6.41	324.77	47.10
12.5754	269.70	0.8899	47.90	6.19	295.55	52.70
17.7749	289.00	0.8874	51.90	5.98	274.01	55.33
27.0553	299.70	0.8826	55.20	5.64	234.65	57.83

*Rolling ball viscosity: average viscosity measured above the saturation pressure.

Table 4. PVT analysis results of JL2 crude oil with oil-based chemical additive under different concentrations of injected CO_2

Concentration of injected CO_2	GOR	Flash oil density	Saturation pressure	Rolling ball viscosity*	Critical temperature Tc	Critical pressure Pc
vol%	m³/m³	g/cm³	MPa	mPa·s	℃	MPa
0.0000	117.70	0.8907	33.6000	5.06	338.55	34.42
11.5009	186.50	0.8880	36.2800	3.75#	315.00	45.16
27.2466	366.40	0.8855	48.9000	4.09	227.64	56.68
43.5380	599.80	0.8824	60.2200	3.78	215.18	56.36

*Rolling ball viscosity: average viscosity measured above the saturation pressure.

#Rolling ball viscosity: questionable data.

Table 5. PVT analysis results of JL2 crude oil with water-based chemical additive under different concentrations of injected CO_2

Concentration of injected CO_2	GOR	Flash oil density	Saturation pressure	Rolling ball viscosity*	Critical temperature Tc	Critical pressure Pc
vol%	m³/m³	g/cm³	MPa	mPa·s	℃	MPa
0.0000	110.90	0.8909	31.0000	5.37	365.11	30.86
13.1828	193.80	0.8898	39.8600	3.86	292.10	45.82
27.0373	318.60	0.8864	50.9000	3.91#	245.10	55.08
33.3193	390.90	0.8842	55.4000	3.24	215.96	56.86

*Rolling ball viscosity: average viscosity measured above the saturation pressure.

#Rolling ball viscosity: questionable data.

1. Chemical Additives Alter Crude Oil Properties Prior to CO_2 Injection

Chemically treated crude oils demonstrate significantly reduced saturation pressures and lower viscosities, even before CO_2 is introduced. These changes suggest molecular-level alterations induced by the additives, potentially disrupting asphaltene aggregates and long-chain hydrocarbons that typically elevate viscosity in heavy or waxy crudes. Lower viscosity enhances fluid mobility, which is particularly advantageous under reservoir flow conditions.

Additionally, the treated oils exhibit higher CO_2 solubility at reservoir pressure, as shown in Figure 1. This behavior suggests an enhanced thermodynamic affinity between the oil and CO_2 phases, likely facilitated by amphiphilic additive structures that stabilize CO_2 molecules within the oil matrix. Both oil-based and water-based additives produced similar improvements in solubility, implying a shared functional mechanism - potentially involving polar groups or surfactant-like behavior that reduces interfacial resistance to gas dissolution.

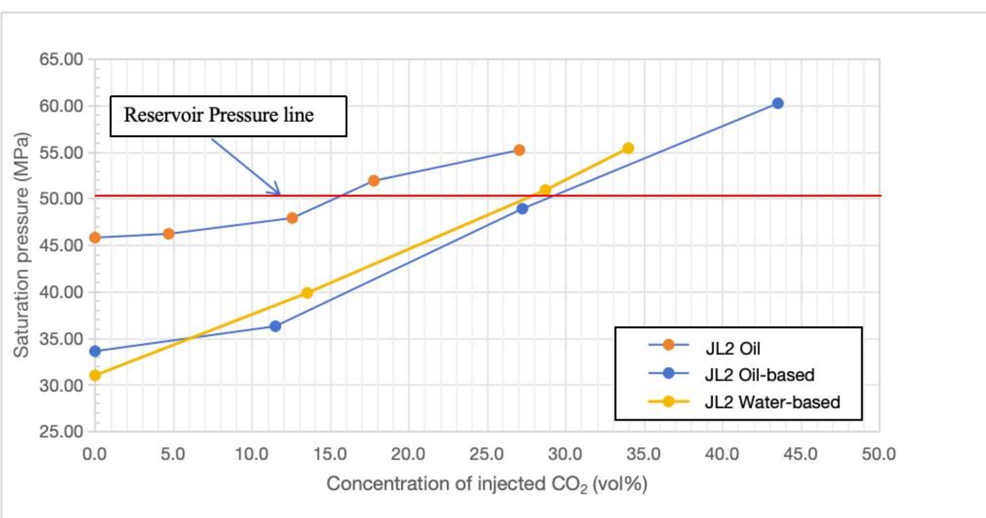

Fig. 1 Relationship of concentration of injected CO_2 with saturation pressure, JL2 oil, and chemically treated JL2 oil.

2. Improved Asphaltene Stability Under CO_2 Exposure

The results from continuous CO_2 injection tests (Table 6, Fig. 2) indicate a 20–35% increase in the Asphaltene Onset Concentration (AOC) for chemically treated oils. A higher AOC reflects delayed asphaltene precipitation, suggesting additives enhance colloidal stability. This stabilization may occur through several mechanisms:

- Competitive adsorption, where additive molecules occupy the surface of asphaltene particles, preventing aggregation.
- Steric hindrance, where the additives form a protective layer that inhibits flocculation.
- Modification of surface energy, altering the dispersion behavior of asphaltene-rich domains.

The consistency between the maximum CO_2 injection volumes predicted by PVT swelling tests and those observed in slim tube experiments reinforces the validity of these observations. The correlation between independent test methods indicates that additive-enhanced stability can be reliably expected during field implementation.

Table 6. Data Comparison of Continuous CO_2 Injection into Oil Without and With Chemical Additives

JL2 Oil	Reservoir Pressure (psi)	Oil vol. (ml)	Injection CO2 vol. (ml)	Injected Vol. (%)	Max Injection Vol. (ml)	Max Vol. (%)
Without chemical additive	7267	33.89	4.65	12.07	7.35	17.82
5% oil-based additive	7267	30.09	9.50	24.00	13.50	30.97
30% water-based additive	7267	30.24	8.60	22.14	10.10	25.04

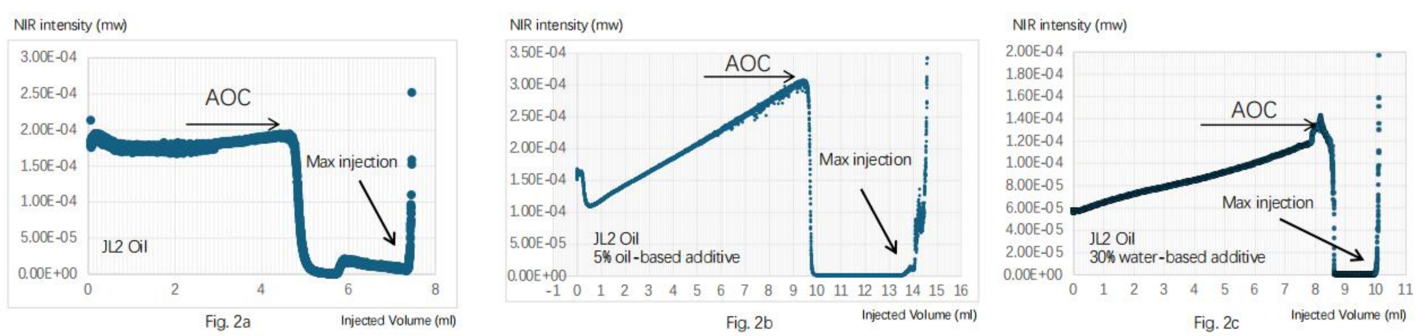

Fig. 2. Continuous CO_2 injection under reservoir conditions (97 ℃ /7267psi) at a flow rate of 0.1 mL/min: (2a) without chemical additive, (2b) with 5% oil-based chemical additive, and (2c) with 30% water-based chemical additive.

3. Enhanced Oil Recovery Efficiency and Favorable Phase Behavior

Slimtube displacement experiments conducted under reservoir temperature and pressure (Figure 3) reveal that chemically treated oils achieve an additional 10–20% increase in recovery compared to untreated samples. This substantial gain surpasses typical CO_2-EOR performance, pointing to the presence of additive-mediated mechanisms such as:

- Reduction in interfacial tension (IFT) to lower levels, promoting CO_2-oil miscibility.
- Formation of microemulsion phases, which enhance sweep efficiency and displace residual oil.
- Improved mobility ratios, resulting in more uniform displacement fronts and reduced viscous fingering.

Distinct phase transitions - observable as turbidity shifts and compositional changes in effluent - support the hypothesis that additives facilitate the formation of CO_2-rich microdomains, which in turn improve phase continuity and oil displacement.

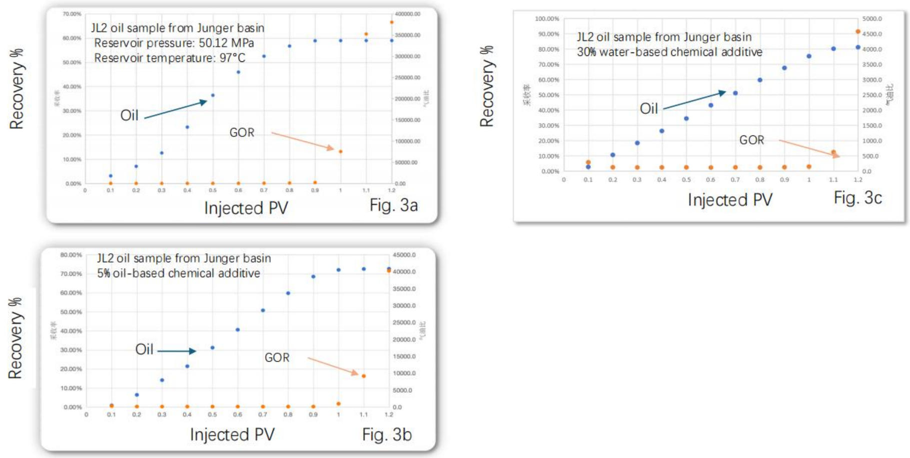

Fig. 3. Effect of various chemical additives—including oil-based and water-based amphiphilic surfactants—on CO_2 injection into oil. These additives significantly enhanced oil recovery (EOR) and increased CO_2 solubility. (3a) without chemical additive, (3b) with 5% oil-based chemical additive, and (3c) with 30% water-based chemical additive.

4. Infrared Imaging Captures Transient Fluid Dynamics

High-pressure infrared imaging (Figure 4) provides valuable visualization of oil-CO_2 interaction dynamics at the pore scale. This method enables real-time observation of:

- Faster CO_2 diffusion rates in treated oils, indicating enhanced gas uptake capacity (Fig. 4b vs. 4a).
- Delayed asphaltene nucleation supports higher AOC values (Fig. 4b and 4c).
- More homogeneous mixing, evidenced by the absence of gas fingering or localized channeling.

Infrared thermography also captures thermal gradients associated with the exothermic nature of CO_2 dissolution, offering insights into mixing energetics not available through standard visual methods. Treated oils displayed smoother, more uniform phase transitions, in contrast to the' chaotic gas channel formation in untreated samples. This suggests that chemical modification improves miscibility and helps regulate gas mobility.

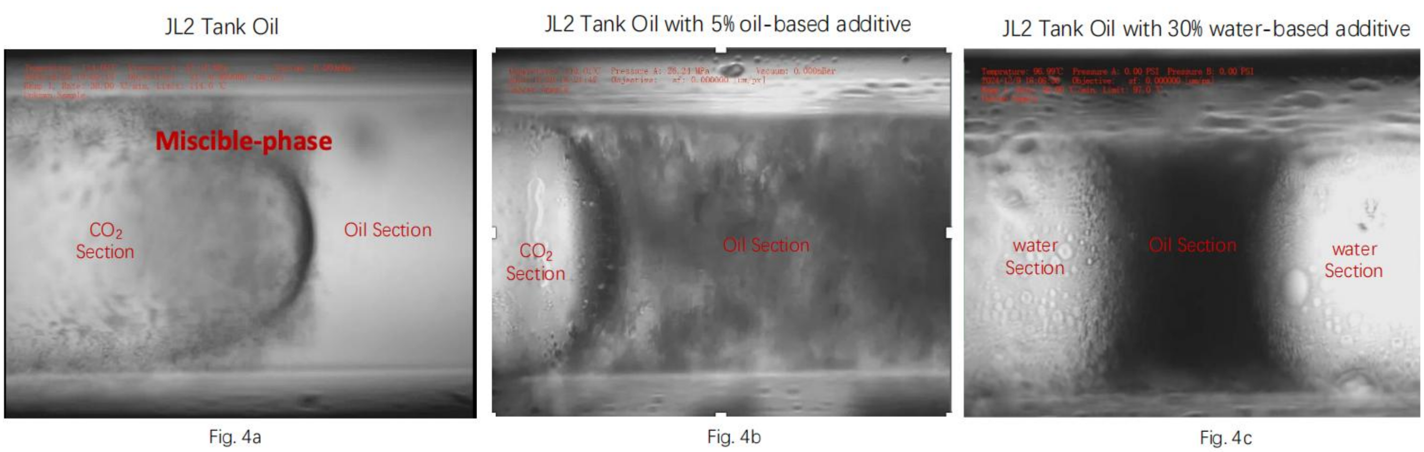

Fig. 4. Interaction between CO_2 and oil under reservoir temperature and pressure observed using the IRHPOC Raman microscope: (a) without chemical additive, (b) with 5% oil-based chemical additive, and (c) with 30% water-based chemical additive.

5. Broader Implications for Field-Scale EOR Strategies

These results suggest that carefully selected chemical additives can serve as powerful enhancers for CO_2 -EOR operations, simultaneously improving oil recovery and mitigating risks such as asphaltene deposition and poor sweep efficiency. The observed behaviors mirror benefits of other enhanced recovery techniques, such as low-salinity waterflooding, surfactant-polymer flooding, and nanoparticle-stabilized CO_2 foams, highlighting the broader relevance of additive-driven phase tuning.

Future work should focus on:

- Evaluating additive retention and reactivity in complex lithologies (e.g., carbonate vs. sandstone).
- Long-term compatibility studies to assess potential interactions with formation water, mineral surfaces, and reservoir brines.
- Upscaling laboratory observations to field-scale pilot projects, incorporating reservoir simulation to quantify economic and operational gains.

Conclusion

This study provides compelling evidence that incorporating chemical additives into CO_2 -EOR (Enhanced Oil Recovery) processes can significantly improve the performance of crude oil under reservoir conditions. The impact of oil- and water-based additives on fluid properties and recovery efficiency was systematically assessed through a comprehensive suite of laboratory evaluations, including PVT phase behavior analysis, continuous CO_2 injection tests, slim tube displacement experiments, and high-pressure infrared imaging.

Key findings include:

- Improved Pre-Injection Fluid Properties: Chemically treated JL2 crude oil exhibited notably lower saturation pressure and reduced viscosity even before CO_2 injection, suggesting structural alterations in the oil phase due to additive interactions. These changes facilitate better CO_2 diffusion and enhanced mobility, which are critical to achieving efficient displacement.
- Enhanced CO_2 Solubility and Miscibility Potential: The treated oils showed increased CO_2 solubility under reservoir pressure, promoting more favorable phase behavior and lowering the threshold for miscibility. This enhances the effectiveness of CO_2 injection in reservoirs where natural miscibility is not attainable.
- Higher Asphaltene Onset Concentration (AOC): Continuous CO_2 injection tests revealed elevated AOC values for chemically modified oils, indicating delayed onset of asphaltene precipitation. This improved stability is essential for minimizing formation damage and maintaining injectivity during long-term CO_2 operations.
- Improved Oil Recovery Efficiency: Slim tube experiments confirmed the performance gains, with chemically treated samples achieving an additional 10% to 20% oil recovery compared to untreated crude. These results demonstrate the additive's ability to enhance sweep efficiency and displacement effectiveness in CO_2 -EOR applications.
- Direct Visualization of Altered Phase Dynamics: High-pressure infrared imaging captured real-time evidence of improved CO_2 -oil interactions, including accelerated CO_2 diffusion, delayed phase separation, and the absence of gas fingering in treated systems. These visual observations support the hypothesized mechanisms behind the improved performance metrics.

Collectively, these results highlight the potential of chemical additives to address two major challenges in CO_2 -EOR: achieving miscibility in sub-optimal reservoirs and mitigating asphaltene-related risks. The ability to tailor fluid properties and control phase behavior offers a promising pathway to improve oil recovery while reducing operational uncertainties.

Future work should investigate long-term additive retention, interactions with reservoir rock and brine, and scale-up feasibility under actual field conditions. The integration of such additives into CO_2 -EOR workflows not only optimizes reservoir performance but also contributes to the broader goals of carbon management and sustainable hydrocarbon production.

References

1. Potential for Additional CO_2-Flood Projects in the US, Dennis Denney, *J Pet Technol* 61 (01): 55–57. Paper Number: SPE-0109-0055-JPT
2. Technologies and practice of CO_2 flooding and sequestration in China, HU Yongle, HAO Mingqiang, CHEN Guoli, SUN Ruiyan, LI Shi, PETROL. EXPLOR. DEVELOP., 2019, 46(4): 753–766.
3. Carbon capture and sequestration technology for environmental remediation: A CO_2 utilization approach through EOR, Narendra Kumar, Amit Verma, Tausif Ahmad, Rajesh Kumar Sahu, Ajay Mandal, Muhammad Mubashir, Muhammad Ali, Nilanjan Pal, Geoenergy Science and Engineering, Volume 234, March 2024, 212619
4. Maximizing CO_2 Sequestration and Utilization Using Viscoelastic Surfactants Alternating Gas: Optimizing Efficiency and Environmental Impact, M Elmuzafar Ahmed, Publisher: Society of Petroleum Engineers (SPE), Paper presented at the Mediterranean Offshore Conference, October 20–22, 2024, Paper Number: SPE-223164-MS
5. Insights from field applications of miscible gases based EOR for unconventional oil reservoirs: A review. Dheiaa Alfargea,b, Ahmed M. Aljarahc, Najeh Alali, Unconventional Resources 5 (2025) 100132
6. Feasibility analysis of China's CO2-EOR project based on a comprehensive economic benefit evaluation across the entire industrial chain, Chuan-wang Liu, Ya-lin Lei, Jing-rui Fu, Journal of Environmental Management, April 2025
7. Multiscale investigation into EOR mechanisms and influencing factors for CO2-WAG injection in heterogeneous sandy conglomerate reservoirs using NMR technology, Jun-Rong Liu, Deng-Feng Zhang, Li Wang, Petroleum Science, April 2025
8. A new optical capillary cell for spectroscopic studies of geologic fluids at pressures up to 100 MPa, I-M. Chou, R.C. Burruss, W.J. Lu, Advances in High-Pressure Technology for Geophysical Applications. Ed. J. Chen, Y. Yang, T.S. Duffy, G. Shen, and L.F. Dobrzhinetskaya, Chapter 24, 2005, 475–485. Elsevier.
9. Optical cells with fused silica windows for the study of geological fluids, I-M. Chou, EMU Notes in Mineral. 2012, 12, Chapter 6, 227–247.