



OPEN Mechanistic analysis of flow functions in tertiary enriched gas injection following secondary lean gas injection

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Significant amounts of residual oil can remain trapped after primary and secondary recovery stages, which can be effectively recovered using tertiary gas injection processes. While tertiary gas injection in water-swept reservoirs has been widely studied, the characterization of tertiary enriched gas injection following secondary lean gas injection remains underexplored. One critical challenge is the lack of gas–oil relative permeability and capillary pressure functions specific to this process, which play a key role in controlling multiphase flow behavior and oil mobilization. To address this gap, a series of coreflood experiments was performed by injecting lean gas followed by enriched gas into a low-permeability carbonate core. The CMG/GEM compositional simulator, coupled with the Design Exploration Controlled Evolution (DECE) history-matching algorithm, was used to match experimental data, including oil recovery, cumulative gas production, and pressure drop. Relative permeability and capillary pressure curves for tertiary enriched gas injection were derived from these simulations. Results showed the ultimate oil recovery increased by 12%. Analysis of ternary diagrams and produced fluid composition indicated that residual oil was mobilized primarily through a combined vaporizing–condensing mechanism. This study demonstrates the potential of tertiary enriched gas injection as an effective recovery strategy for reservoirs subjected to prior lean gas flooding.

Keywords Tertiary enriched-gas injection, Flow functions, History matching, Experimental, Compositional simulations, Residual oil recovery

List of symbols

B_o	Formation volume factor, res. cc/sc. cc
GOR	Gas–oil ratio, sc. cc/ sc. cc
S_{wi}	Initial water saturation, %
S_{oD}	Normalized oil saturation, –
S_o	Oil saturation, –
S_{org}	Residual oil saturation, –
S_{wcon}	Connate water saturation, –
S_{gcon}	Connate gas saturation, –
L_{gog}	Empirical parameter for gas phase in LET relative permeability model, –
E_{gog}	Empirical parameter for gas phase in LET relative permeability model, –
T_{gog}	Empirical parameter for gas phase in LET relative permeability model, –
k_{rgcl}	Gas relative permeability at connate liquid (Water + Oil) saturation, –
k_{rgo}	Gas relative permeability, –
L_{goo}	Empirical parameter for oil phase in LET relative permeability model, –
E_{goo}	Empirical parameter for oil phase in LET relative permeability model, –
T_{goo}	Empirical parameter for oil phase in LET relative permeability model, –
k_{rogcg}	Oil relative permeability at connate gas saturation
k_{rog}	Oil relative permeability, –
a_g	Exponent of the oil–gas capillary pressure equation, –
p_d	Oil–gas capillary pressure at $S_o = 1 - S_{wcon}$, psi

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p_{cog}	Oil–gas capillary pressure, psi
k_{rh}	Miscible hydrocarbon relative permeabilities, –
f_{k_r}	Weighting factor for including IFT effects in oil–gas relative permeabilities, –
n_{k_r}	Exponent of the oil–gas relative permeability weighting factor, –
k_{rgt}	Gas relative permeability including IFT effects, –
k_{rot}	Oil relative permeability including IFT effects, –
f_{p_c}	Weighting factor for including IFT effects in oil–gas capillary pressure, –
n_{p_c}	Exponent of the oil–gas capillary pressure weighting factor, –
p_{cogt}	Oil–gas capillary pressure including IFT effects, psi

Greek symbols

σ_{go}	Gas–oil interfacial tension, mN/m
σ_{go}^*	Threshold gas–oil interfacial tension below which IFT effects are triggered, mN/m

Abbreviations

BPR	Back-pressure regulator
TV	Transfer vessel
CMG	Computer modelling group
GEM	CMG's GEM module
CMOST	CMG's CMOST module
DECE	Designed exploration controlled evolution
DG	Dry gas
EOS	Equation of state
EOR	Enhanced oil recovery
GHG	Greenhouse gases
HPHT	High-pressure, high-temperature
IFT	Interfacial tension
IOIP	Initial oil in place
LET	Lomeland–Ebeltoft–Thomas relative permeability model
LPG	Liquefied petroleum gas
MMP	Minimum miscibility pressure
NGL	Natural gas liquid
SAGD	Steam-assisted gravity drainage

Tertiary injection processes can potentially recover significant amounts of the initial oil in place (IOIP) left unrecovered after natural drive and secondary waterflooding or gas injection^{1–5}. Numerous experimental and simulation studies have explored the impacts of wettability status, miscibility conditions, vertical heterogeneity, and specifically operational parameters, such as injection pressure, injectant composition, injection rate, well constraints (completion), and injector location, on the performance of tertiary gas injection following secondary waterflooding^{6–17}. However, limited research has focused on tertiary gas injection into reservoirs previously subjected to secondary gas injection, despite the frequent use of lean gaseous solvents in field operations to mobilize residual oil recovery after secondary recovery¹⁸.

Gas injection offers distinct advantages, particularly in fractured systems, where mass transfer between the fracture and matrix would occur because of molecular diffusion, and in dipping reservoirs with a relatively high vertical permeability, where gravity-assisted gas injection would enhance oil recovery^{19–22}. Furthermore, carbonate reservoirs, which are typically oil-wet and yield low oil production during conventional recovery processes such as waterflooding, benefit significantly from gas injection, making it a crucial strategy for enhancing oil recovery^{23–25}. Importantly, tertiary enriched gas injection after secondary gas injection could not only target residual oil within gas-invaded zones but also might mobilize oil in areas that secondary gas injection may fail to reach effectively.

Laboratory experiments and field observations show that the ultimate displacement efficiency of a gas injection process is highly dependent on the amount of mass transfer/crossflow, capillarity, gas–oil phase behavior, as well as the injection conditions^{26–31}. As a hydrocarbon gas mixture is injected into a porous medium containing another mixture of hydrocarbons, a series of complex interactions starts to occur. For instance, during gas–oil displacement, components in the gas dissolve in the oil, and components in the oil are extracted into the gas as local chemical equilibrium is achieved^{6,32,33}. This component exchange is referred to as “compositional effects”. At the same time, interfacial tension between gas and oil can also be substantially lowered because of the component exchange. There are many experimental observations and theoretical evidence representing a significant hydrocarbon film/layer flow at gas/oil interfacial tension (IFT) around 1–3 mN/m, which reflects itself as an increase in hydrocarbon relative permeability^{34–36}. As the system achieves miscibility, “compositional effects” and “IFT effects” become the key mechanisms^{37,38}.

Several studies have demonstrated that near-miscible processes yield significantly higher oil recovery than immiscible displacements. Most of this research achieved near-miscibility conditions by increasing the injection pressure^{7,8}, which can reactivate existing natural fractures/faults³⁹, compensate for caprock integrity⁴⁰, and initiate man-made flow paths, leading to induced seismicity⁴¹.

Approaching near miscibility by either (1) choosing an injectant that is strongly soluble in oil, e.g., CO₂, which would be highly effective in mobilizing oil through swelling and viscosity reduction^{23,24,42} or (2) enriching the injected gas with intermediate components, e.g., liquefied petroleum gas (LPG) or natural gas liquid (NGL), is rather more attractive compared to pressurizing the injectant from both operational and economical perspectives⁴³. In fact, the process of gas injection at a lower pressure reduces the operational risks associated with the compression of injected gas and lowers the cost associated with delivering a high-density injectant.

In addition, some reservoirs are at a pressure lower than the minimum miscibility pressure (MMP) or are experiencing pressure decline, in which a lower-pressure operation may be more feasible^{37,43–45}.

Several researchers have conducted coreflood experiments to investigate the influence of gas types and, in turn, miscibility conditions on tertiary oil recovery after waterflooding. Karimaie, et al.^{23,24}, using a fractured carbonate rock core, found that secondary CO₂ injection recovered over 70% of the oil, while N₂ injection only recovered 15%. This difference was attributed to compositional effects, lower IFT, and potentially oil swelling from CO₂. In tertiary injection, CO₂ recovered an additional 15.7% of the remaining oil after waterflooding, compared to 11% from N₂. Norouzi et al.⁴² confirmed that water shielding is a major obstacle to tertiary recovery through experiments with CO₂ and CH₄. They highlighted that miscible gas injection, especially with highly soluble gases like CO₂, is crucial for breaking through the water film and achieving effective oil swelling.

Grigg et al.⁴⁶ conducted several gas-injection corefloods to analyze the effect of pressure on tertiary oil recovery and suggested that the recovery efficiency of gas injection processes can still be high at pressure below the MMP, and observed that CO₂, due to its drastic density change when pressure falls below the MMP, is not feasible for near-miscible oil recovery efficiency compared to hydrocarbon gases, which maintain a relatively consistent extraction efficiency even at pressures below the MMP, leading to more sustained oil recovery^{46,47}. They also found that enriching the hydrocarbon gas with intermediate components crucially enhanced oil recovery, especially in near-miscible conditions. Recent experimental studies have highlighted the strong impact of gas composition on tertiary recovery. Coreflood experiments by Ge et al.⁴⁸ and Xian et al.⁴⁹ showed that modest enrichment with intermediate hydrocarbons can substantially enhance oil recovery compared to lean gases such as N₂ and CH₄, with hydrocarbon-enriched gases often outperforming conventional injectants. Complementary carbonate coreflooding and molecular simulation studies have further confirmed that enriched-gas injection induces composition-driven shifts in displacement behavior under near-miscible conditions⁴⁵. Zick⁵⁰ also provided experimental observations, supported by equation-of-state predictions, indicating that a combined condensing/vaporizing gas drive makes displacements of oil by enriched gases highly efficient, even though true miscibility is not quite developed^{46,47}. Although the need for further research, including compositional simulations, to fully understand the complex interplay of different recovery mechanisms involved in these processes was also underscored throughout all the aforementioned studies.

Additionally, the use of well-representative gas-oil relative permeability and capillary pressure functions is crucial for accurately modeling fluid displacements^{11,16,51}. Especially in near-miscible tertiary enriched gas injections, the well-established flow functions can play a crucial role in accurately modeling complex fluid displacement. This leads to better predictions of recovery performance, optimization of injection strategies and operational parameters, and a more comprehensive understanding of the complex interplay of different recovery mechanisms. Pratama and Babadagli^{14,18} focused on improving heavy oil recovery while reducing the environmental impact of tertiary recovery methods by performing a series of Hele-Shaw cell and 2-D porous media experiments using pure and enriched solvents as low greenhouse gas (GHG) and high-efficiency tertiary recovery options in post-steam-assisted gravity drainage (SAGD) applications. Although both studies provide valuable insights into tertiary recovery methods, they lack a discussion on determining gas-oil relative permeability and capillary pressure, especially in tertiary enriched gas injection following a secondary lean gas injection.

This study aims to address these key challenges by experimentally and numerically investigating the gas-oil relative permeability and capillary pressure functions associated with tertiary enriched gas injection, while also evaluating its effectiveness as a recovery strategy after secondary lean gas injection by examining the impacts of key mechanisms—compositional effects and IFT effects—on flow behavior at the core scale. By generating reliable flow function data and demonstrating the enhanced oil recovery potential of this tertiary process, the study fills a vital gap in the literature and provides practical insights into improving recovery from gas-invaded reservoirs.

Methodology

In this study, a sample of live oil was prepared by combining crude oil and gas samples from the separator based on the gas-oil ratio (GOR) and formation volume factor (B_o) at reservoir conditions. Table 1 summarizes key properties of the recombined oil. Two gases were synthesized for injection scenarios: (1) lean gas for secondary injection and (2) lean gas enriched with intermediate hydrocarbons for tertiary injection. These gases were synthesized by blending pure components according to the target composition percentages. Detailed compositions of the injection gases are provided in Table 2. In comparison to the lean gas, the enriched gas shows a clear compositional shift, with methane decreasing from 91.58% to 83.20% and the cumulative C₃–C₇ fraction increasing from about 2% to nearly 10%. This enrichment in intermediate hydrocarbons significantly alters the phase behavior by enhancing gas–oil miscibility, strengthening the vaporizing–condensing mechanism, and reducing interfacial tension, thereby improving interface mass transfer and oil recovery efficiency.

To simulate formation water, synthetic brine was prepared by dissolving a mixture of salts, including sodium chloride (NaCl), magnesium chloride (MgCl₂), calcium chloride (CaCl₂), sodium sulfate (Na₂SO₄), sodium bicarbonate (NaHCO₃), and potassium chloride (KCl), in deionized water. At room temperature, the density

Temperature (°C)	Pressure (psia)	Viscosity (cp.)	GOR (Sc/Sc)	Bo (res. cc/sc. cc)	Density (gr/cc)
107	4100	0.6	164.7	1.4	0.71

Table 1. Properties of live oil at test conditions.

Component	N2	CO2	C1	C2	C3	i-C4	n-C4	i-C5	n-C5	C6	C7	C8
Lean gas	0.27	0.12	91.58	6.07	1.14	0.24	0.31	0.07	0.07	0.11	0.02	0
Enriched gas	0.24	0.11	83.20	6.86	3.39	0.92	0.99	0.95	1.09	1.19	0.26	0.8

Table 2. Lean and enriched gas composition used in coreflooding experiments.

Component	K ⁺ , Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Total
Concentration (ppm)	60,535	13,000	1633	121,063	536	268	197,035

Table 3. Ionic composition of synthetic formation brine.

Length (cm)	Diameter (cm)	Pore volume (cm ³)	Porosity (%)	Permeability (md)	S _{wi} (%)
20.11	3.73	39.90	18.15	1.82	37.10

Table 4. Petrophysical properties of the composite core used in the study.

and viscosity of the prepared brine were 1.1396 g/cm³ and 1.0 cp., respectively. The experiments were conducted in the presence of connate water to replicate in-situ reservoir conditions, acknowledging the ubiquitous presence of water in oil reservoirs. Detailed compositional data for the synthetic brine are provided in Table 3.

Four reservoir core samples from a carbonate reservoir in southern Iran were used for the coreflood experiment. The cores, homogeneous and uniform limestone without fractures, were combined into a composite core following the Huppler criterion to minimize capillary end effects. The cores were cleaned using a Soxhlet apparatus with toluene and a methanol/chloroform mixture, then dried and weighed. Porosity was measured with a helium porosimeter and validated via brine saturation. Irreducible water saturation was achieved using the centrifuge technique with brine and dead crude oil, incrementally increasing the rotational speed to 13,000 RPM. Reservoir wettability was restored by aging the cores in dead crude oil at reservoir temperature (107 °C) for four weeks. The properties of the composite core are summarized in Table 4.

Experimental setup

The coreflood experiments were conducted using a high-pressure, high-temperature (HPHT) coreflood setup designed to replicate reservoir conditions. The apparatus featured a temperature-controlled air oven housing the core holder, injection fluids, and associated components to ensure uniform temperature. Four transfer vessels (TVs) contained the injection fluids: dead crude oil, live oil, dry gas, and enriched gas. Fluid injection was performed using a high-precision double-cylinder pump, with separate cylinders for live oil and other fluids. The core was oriented vertically, with an overburden pressure of 750 psia above the pore pressure applied via a manual hand pump to ensure proper confinement. Differential pressure across the core was measured using two high-accuracy pressure transmitters at the inlet and outlet. A back-pressure regulator (BPR) maintained the outlet pressure and directed the effluent to a separator, where the liquid phase was collected in a graduated cylinder and the gas phase was measured using a gas-metering system. A data acquisition system recorded pressures through a host computer, while gauges monitored transfer vessel pressures. Prior to experimentation, inlet lines and connections were evacuated using a vacuum pump. A schematic of the HPHT coreflood setup is shown in Fig. 1.

Experimental procedure

The coreflood experiment was conducted under simulated reservoir conditions (107 °C, 4100 psia) using carbonate core samples. The composite core was assembled by weighing and mounting the cores into a sleeve within the core holder. To prevent trapped air, dead crude oil was dripped onto the cores, and inlet lines were evacuated using a vacuum pump. The injection rate was set at 0.25 cc/min, with a back-pressure regulator maintaining a constant outlet pressure of 4100 psia. Dead crude oil was first injected at 0.1 cc/min, gradually raising the pressure and temperature to reservoir conditions while maintaining a net stress of 750 psia. Once thermal equilibrium was achieved and the pressure drop stabilized after injecting two pore volumes, the injection rate was increased incrementally, and the composite core permeability was calculated using Darcy's law. Subsequently, live oil was injected at 0.25 cc/min to displace the dead crude oil, with the effluent GOR monitored to confirm full displacement of the dead oil by the live oil. Injection continued until the pressure drop stabilized after three pore volumes. Lean gas was then injected as a secondary recovery agent at a rate of 0.25 cc/min, with pressure drop and production data recorded until oil production ceased. Finally, enriched gas was injected under tertiary recovery conditions at the same rate until additional oil production became negligible. The step-by-step workflow of the experimental procedure is illustrated in Fig. 2.

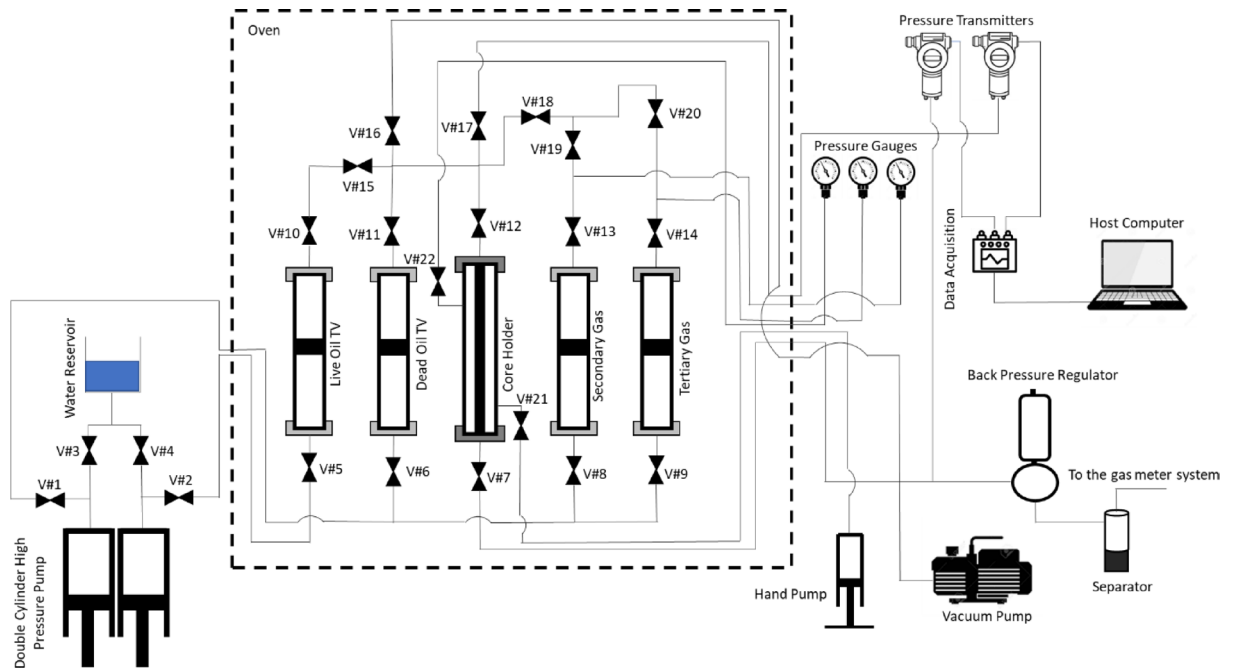


Fig. 1. Schematic of the coreflooding setup used in the study.

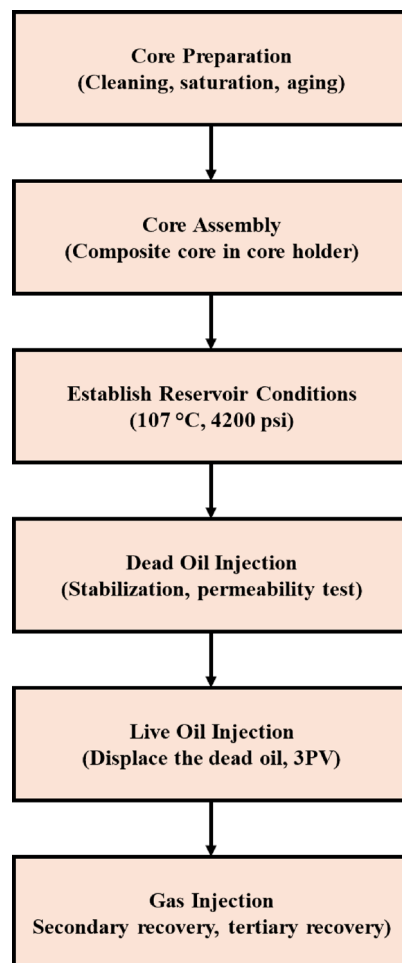


Fig. 2. The flowchart summarizing the experimental procedure used in this study.

Simulation model

The experimental processes of lean gas as well as enriched gas (10% NGL + 90% LG) secondary and tertiary injection into a volatile oil-saturated core sample of low permeability were simulated using the CMG/GEM module (CMG 2020). The commercial simulator uses the correlations proposed by Jossi, et al.⁵² and Macleod-Sugden⁵³ to calculate viscosity and gas-oil interfacial tension, respectively, throughout the processes, and the PVT behavior of gas and liquid phases during gas injection processes was predicted by the Peng-Robinson EOS⁵⁴.

Given the shortcomings of analytical and semi-analytical methods—such as not accounting for fluid compressibility, capillary pressure, component exchange, and phase changes—the flow functions (gas-oil relative permeability and capillary pressure) for various injection processes were history matched according to the experimental gas injection data obtained in the laboratory using CMG's CMOST module (CMG 2020) with the DECE history-matching approach that has been proved to be a reliable and efficient method when it comes to history matching the reservoir engineering problems⁵⁵.

In this study, experimental data on oil recovery, cumulative gas production, and pressure drop along the core plug were used to simultaneously estimate the gas-oil relative permeability and capillary pressure functions. The pre-defined forms of flow functions are adopted from the LET relative permeability and Gang-Kelkar capillary pressure models^{56,57}, respectively, as outlined below:

$$S_{oD} = \left(\frac{S_o - S_{org}}{1 - S_{wcon} - S_{gcon}} \right) \quad (1)$$

$$k_{rgo} = k_{rgcl} \left(\frac{(1 - S_{oD})^{L_{gog}}}{(1 - S_{oD})^{L_{gog}} + E_{gog} S_{oD}^{T_{gog}}} \right) \quad (2)$$

$$k_{rog} = k_{rogcg} \left(\frac{S_{oD}^{L_{goo}}}{S_{oD}^{L_{goo}} + E_{go} ((1 - S_{oD})^{T_{go}})} \right) \quad (3)$$

$$p_{cog} = p_d^* \times \left(\frac{1 - S_g - S_{org} - S_{wcon}}{1 - S_{org} - S_{wcon} - S_{gcon}} \right)^{-a_g} \quad (4)$$

where S_{org} , L , E , T , k_{rgcl} , k_{rogcg} , p_d^* , a_g are the parameters used in the history matching processes. Additionally, S_{wcon} is assumed to remain constant at the irreducible water saturation level, while S_{gcon} and S_{gcrit} are set to zero. In addition, it is noteworthy that the ignorance of water-oil flow functions in the study is because the processes of gas injection were conducted at irreducible water saturation, where the water phase is totally immobile. The LET relative permeability model was adopted due to its versatility and proven suitability for history matching. With three tuning parameters, this correlation allows independent control over curve shape across different saturation ranges, making it highly flexible for accurately reproducing displacement behavior⁵³. For capillary pressure, the Gang-Kelkar model was selected because of its ability to capture both spontaneous and forced imbibition characteristics and to reliably represent capillary pressure curves derived from production data during history matching^{56,57}.

Furthermore, the Betté' model (Coats⁵⁸; Betté et al.⁵⁹) available in CMG/GEM was employed to account for the mechanism of IFT effects by interpolating between immiscible (initial k_{rog} and k_{rgo}) and miscible hydrocarbon relative permeabilities (k_{rh}) using a weighting function (f_{kr}), detailed in the Eqs. (5–9). When the gas/oil IFT (σ_{go}) drops below the threshold IFT (σ_{go}^*), the oil and gas relative permeabilities, k_{rot} and k_{rgt} respectively, are adjusted, otherwise they remain the same as their initial values. According to the Eq. (8), smaller values of the weighting factor f_{kr} strengthens the influence of IFT on relative permeabilities. A similar approach was taken to adjust oil/gas capillary pressure values when ($\sigma_{go} \leq \sigma_{go}^*$), although the exponent (n_{pc}) used in weighting factor (f_{pc}) is different, leading to independent adjustment of capillary pressure due to the IFT effects, as can be seen in the Eq. (9).

$$k_{rh} = 0.5(k_{rogcg} + k_{rgcl}) \quad (5)$$

$$k_{rgt} = f_{kr} k_{rgo} + (1 - f_{kr}) k_{rh} \left(\frac{S_o}{1 - S_w} \right) \quad (6)$$

$$k_{rot} = f_{kr} k_{rog} + (1 - f_{kr}) k_{rh} \left(\frac{S_o}{1 - S_w} \right) \quad (7)$$

$$f_{kr} = \begin{cases} 1, & \sigma_{go} > \sigma_{go}^* \\ \left(\frac{\sigma_{go}}{\sigma_{go}^*} \right)^{n_{kr}}, & \sigma_{go} \leq \sigma_{go}^* \end{cases}, \quad f_{pc} = \begin{cases} 1, & \sigma_{go} > \sigma_{go}^* \\ \left(\frac{\sigma_{go}}{\sigma_{go}^*} \right)^{n_{pc}}, & \sigma_{go} \leq \sigma_{go}^* \end{cases} \quad (8)$$

$$p_{cogt} = f_{pc} p_{cog} \quad (9)$$

Results and discussion

This section presents the results of cumulative gas production, oil recovery, and pressure drop from compositional simulations of the coreflooding experiments, and history-matched gas-oil relative permeability and capillary pressure functions, along with their adjusted parameters, are also provided. Additionally, to comprehensively

evaluate the prevailing oil mobilization mechanisms during the tertiary gas injection, the ternary diagrams and pseudo-component production throughout the coreflooding experiments are analyzed.

Production results and the history-matched flow functions

The experimental as well as compositional simulation results of cumulative gas production, oil recovery, and pressure drop from coreflooding experiments, including secondary lean gas injection, secondary continuous enriched gas injection (10% NGL + 90% DG), and secondary lean gas injection followed by tertiary enriched gas injection (10% NGL + 90% DG) are illustrated in Figs. 3 and 4. A comparison of the ultimate oil recovery factors indicates that tertiary enriched gas injection increases the oil recovery from 73% at the end of secondary lean gas injection to 85%, aligning closely with the recovery achieved through secondary enriched gas injection. This improvement is attributed to both compositional and IFT effects, which become more active upon the initiation of tertiary enriched gas injection. The detailed analyses of the reasons behind how tertiary enriched gas injection would trigger the rigorous interplay of these mechanisms, leading to a significant enhanced oil recovery, are provided in sections 3.2 and 3.3.

As shown in Figs. 3 and 4, the DECE history matching technique achieved a strong alignment with the experimental production and pressure drop data. The history-matched gas-oil relative permeability and capillary pressure, used by the compositional simulator to accurately predict experimental production and pressure drop data for secondary lean gas injection, secondary continuous enriched gas injection, and tertiary enriched gas injection following secondary lean gas injection, are presented in Figs. 5 and 6, and Fig. 7 respectively. Additionally, the history-matched parameters for gas-oil relative permeability, capillary pressure, and IFT effects models are detailed in Table 5. The comparison of flow functions across various injection schemes reveals that enriching the injectant with intermediate components results in more linear gas-oil relative permeabilities, a reduction in gas-oil capillary pressure, as well as S_{org} . Although the injectant composition in tertiary enriched gas injection matches that of secondary enriched gas injection, the resulting flow functions differ significantly due to variations in saturation history and oil mobilization mechanisms, which will be discussed in detail in sections 3.2 and 3.3. These differences highlight the inadequacy of flow functions from secondary gas injection for simulating tertiary enriched gas injection, underscoring the need for re-determination of relative permeability and capillary pressure functions tailored to tertiary gas injection processes.

Ternary diagrams

As shown in Fig. 8, the composition paths of the gas phase, oil phase, and overall mixture at a specified grid block ($0.5 \times L$ away from the injector grid, where L is the length of the porous medium) throughout the processes of secondary lean gas injection, secondary continuous enriched gas (10% NGL + 90% DG) injection, and secondary lean gas followed by tertiary enriched gas (10% NGL + 90% DG) injection are analyzed.

During secondary lean gas injection, the oil phase composition evolves primarily parallel to ($CH_4 = 0$) axis, with intermediate components (C_2-C_{12}) being evaporated into the gas phase, and heavy components (C_{13}^+) contributing more to the oil phase. The ultimate overall fluid composition indicates that a significant portion

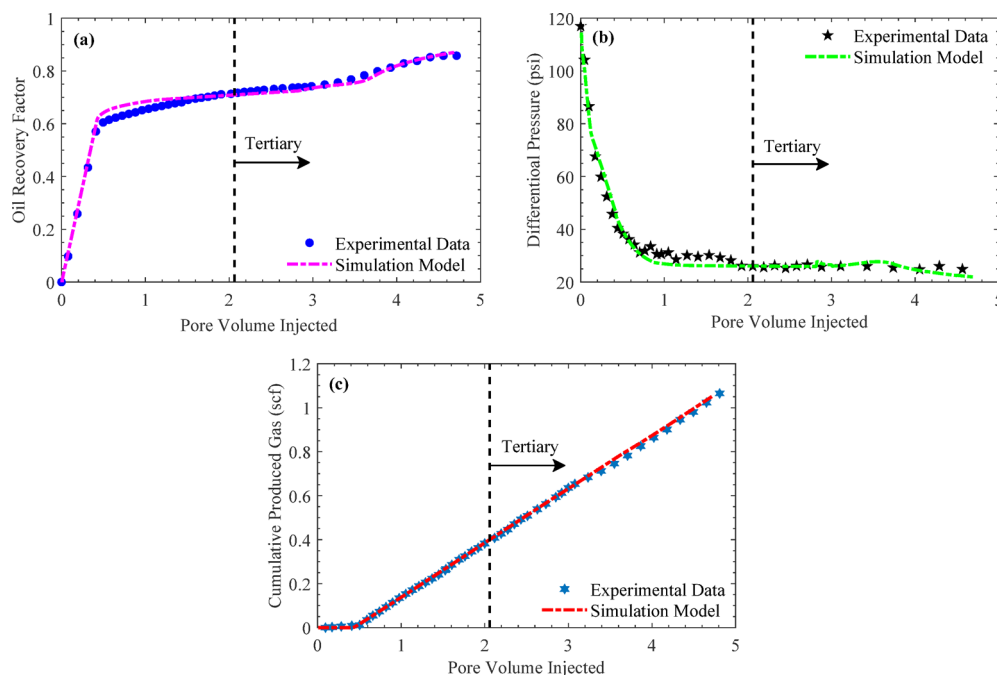


Fig. 3. Comparison of experimental and history-matched (a) oil recovery, (b) pressure drop along the core, and (c) cumulative gas production for secondary lean gas injection followed by tertiary enriched gas (10% NGL + 90% DG) injection.

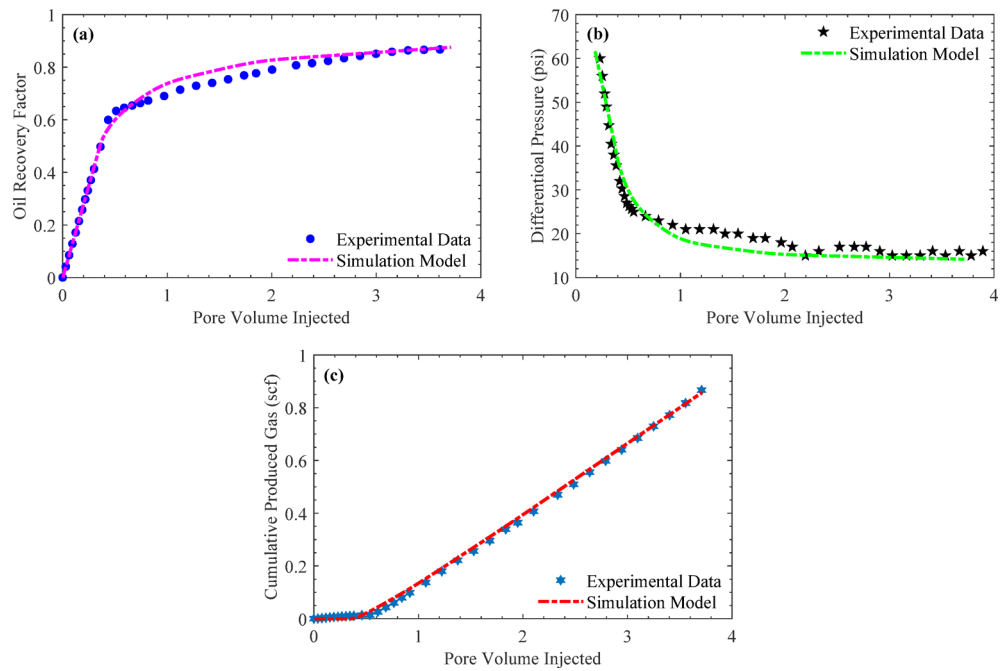


Fig. 4. Comparison of experimental and history-matched (a) oil recovery, (b) pressure drop along the core, and (c) cumulative gas production for secondary continuous enriched gas (10% NGL + 90% DG) injection .

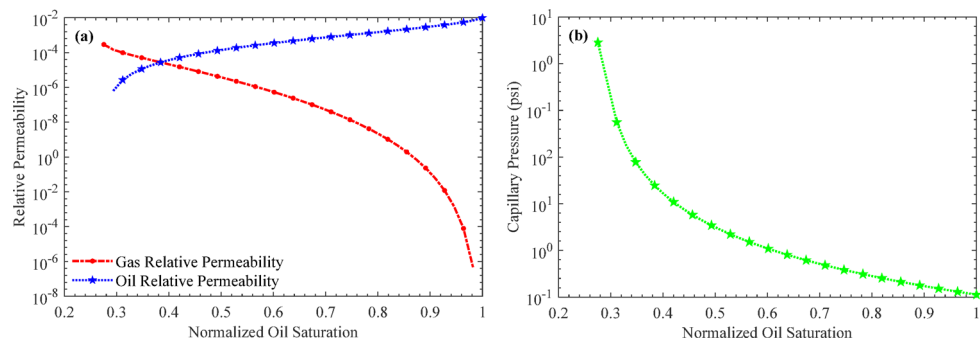


Fig. 5. Comparison of history-matched (a) gas-oil relative permeabilities and (b) capillary pressure functions for secondary lean gas injection.

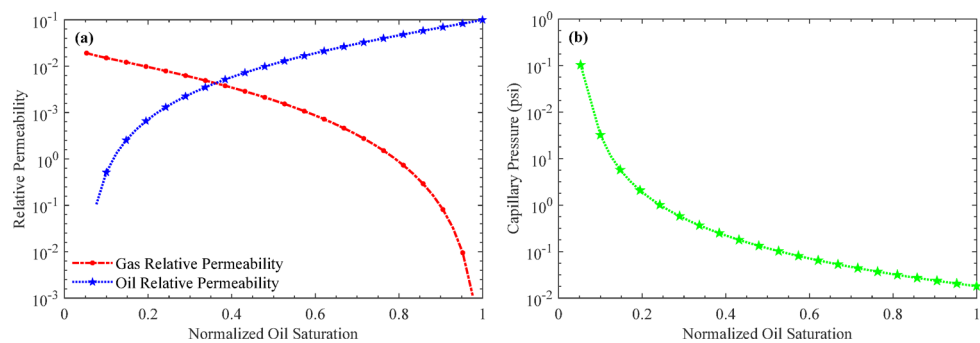


Fig. 6. Comparison of history-matched (a) gas-oil relative permeabilities and (b) capillary pressure functions for enriched gas (10% NGL + 90% DG) injection.

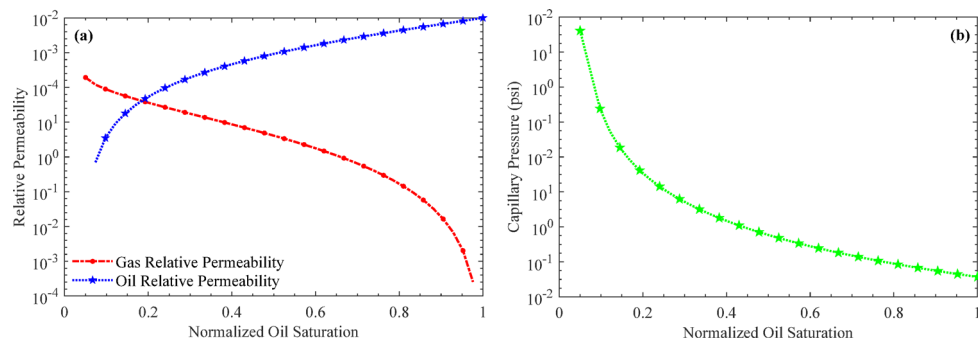


Fig. 7. Comparison of history-matched (a) gas-oil relative permeabilities and (b) capillary pressure functions for tertiary enriched gas (10% NGL + 90% DG) injection following secondary lean gas injection.

	Secondary lean gas injection	Secondary enriched (10% NGL + 90% DG) gas injection	Tertiary enriched (10% NGL + 90% DG) following secondary lean gas injection
S_{org}	0.186	0.037	0.03385
k_{rogc}	0.292	0.48	0.828
L_{gog}	1.015	1.12	1.135
E_{gog}	2.98	1.58	1.8375
T_{gog}	0.7425	0.95	0.975
k_{rgcl}	0.05	0.21	0.115
L_{goo}	3.565	1.5	1.465
E_{goo}	4.575	1.65	3.975
T_{goo}	0.6775	0.8825	0.74
a_g	1.42	0.5	0.74
P_d (psi)	0.1061	0.071	0.082
σ_{go}^*	–	1.08	1.3
n_{kr}	–	0.12	0.495
n_{pc}	–	0.59	0.84

Table 5. History matched parameters of the relative permeability (LET), capillary pressure, and IFT effects models in secondary and tertiary gas injection processes.

of the oil remains, highlighting the limited efficiency of the lean gas injection process. However, throughout the secondary continuous enriched gas injection, the overall fluid composition predominantly approaches gas phase composition, implying that the overall mixture contains a negligible amount of the oil phase, suggesting a satisfactory efficiency for the secondary continuous enriched gas injection process. More interestingly, as can be seen in Fig. 8, despite the processes in which miscibility conditions are achieved by pressurizing, in the core-plug compositional simulations in which miscibility is approached by enrichment of the injectant, the miscibility conditions are not immediately achieved in the early stage of the process^{46,47}.

Following the compositional paths in tertiary enriched gas injection shows that the onset of tertiary flooding causes compositional paths to change course as the oil phase composition mainly progresses parallel to the axis ($CH_4^- = 0$) with an increase in intermediate components (C_2 to C_{12}), signifying the dissolution of intermediate components from the gas phase into the oil phase. Therefore, a combined condensing/vaporizing gas drive makes the displacement of oil by the enriched gas highly efficient⁴⁷. Ultimately, the trajectory of the overall fluid composition toward the gas phase indicates that the final mixture contains only a negligible fraction of the oil phase. This outcome reflects the high efficiency of the tertiary enriched gas injection process in recovering residual oil after secondary gas drive.

Component production

In order to compare the relative dominance of the prevailing oil mobilization mechanisms and the extent to which near-miscibility is achieved, the production of a heavy pseudo-component throughout the processes of secondary lean gas, followed by tertiary enriched gas (10% NGL + 90% DG) injection, and secondary continuous enriched gas (10% NGL + 90% DG) injection is displayed in Figs. 9 and 10, respectively. The left, middle, and right columns represent the moles of the pseudo-component in the injector well, whole core, and producer well,

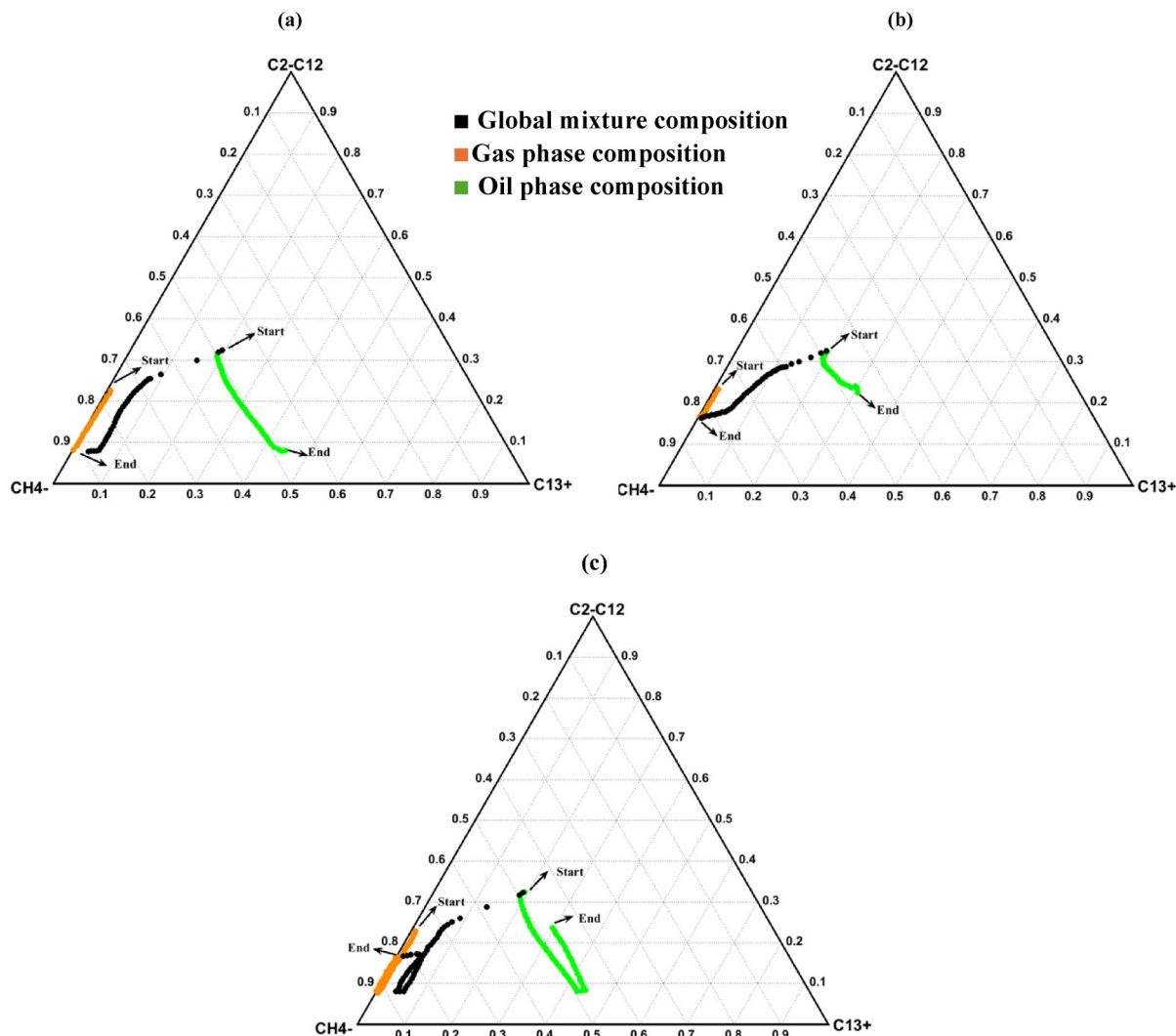


Fig. 8. Composition paths of the gas phase, oil phase, and overall mixture at midlength (0.5 L) throughout (a) secondary lean gas injection, (b) enriched gas (10% NGL + 90% DG) injection, and (c) secondary lean gas injection followed by tertiary enriched gas (10% NGL + 90% DG) injection. (The start and end points of the processes are marked in the figures).

respectively. It should also be noted that all the processes were conducted at a constant rate with the pressure of 4200 psi and temperature of 107 °C, and the moles of the pseudo-component are calculated under standard conditions for the left and right columns and under reservoir conditions for the middle column.

C_{12}^+ heavy pseudo-component

As illustrated in Figs. 9 and 10, in the left column, due to the absence of the C_{13}^+ in the composition of injectants, the molar amount of the pseudo-heavy component remains consistently zero; therefore, the C_{13}^+ pseudo-component appearing in the gas phase, either in the core or the producer sector, has to be traced back to the oil phase. In the middle column, comparing secondary injection processes, as near-miscibility is approached by enrichment, more component exchange due to compositional effects as well and IFT effects causes the ultimate moles of C_{13}^+ in the oil phase to decrease and the molar content of C_{13}^+ in the gas phase to increase, suggesting more C_{13}^+ of the oil phase is vaporized into the gas phase and eventually is produced, manifesting itself through a greater production of the pseudo-component in the right column.

Interestingly, switching the injection scheme from secondary lean gas to tertiary enriched gas injection enhances component exchange due to compositional effects. This shift can also reduce the IFT to values below the critical threshold, leading to a decrease in residual oil saturation. Consequently, more target oil becomes available for component exchange, extraction from volatile oil, and eventual recovery under near-miscible conditions. Following the onset of tertiary enriched gas injection after secondary lean gas injection, the C_{13}^+ content in the oil decreases more rapidly, transitioning into the gas phase. Consequently, a comparison of the ultimate recovery reveals that tertiary enriched gas injection following secondary lean injection achieves a

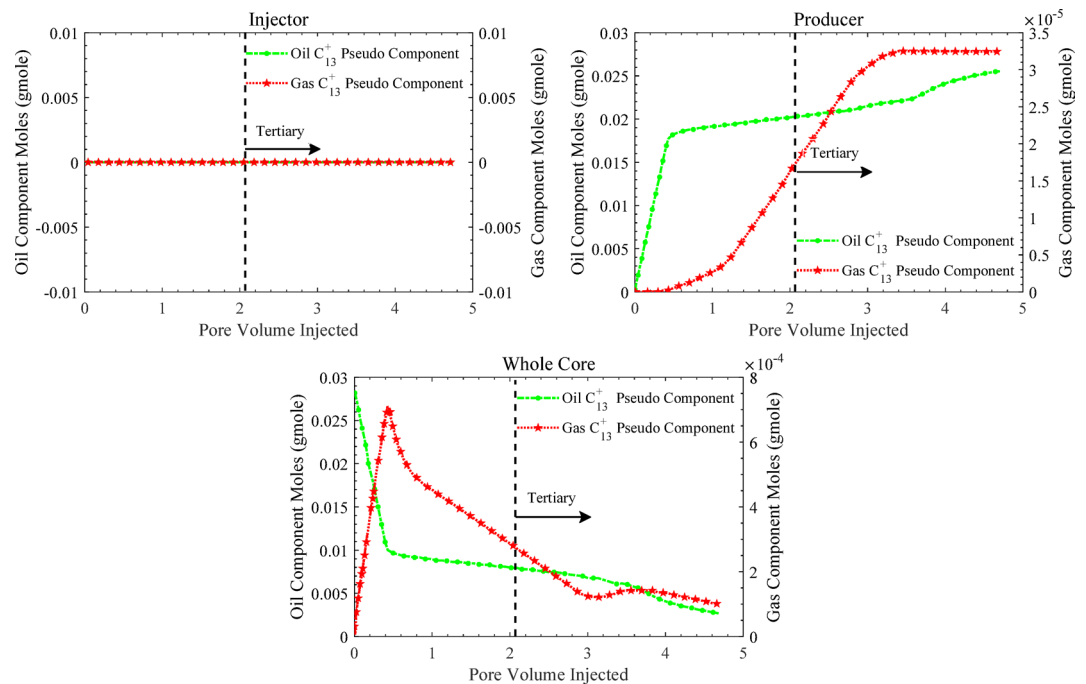


Fig. 9. C_{13}^+ pseudo-component molar content in the injector, core, and producer sectors throughout secondary lean gas injection followed by tertiary enriched gas (10% NGL + 90% DG) injection.

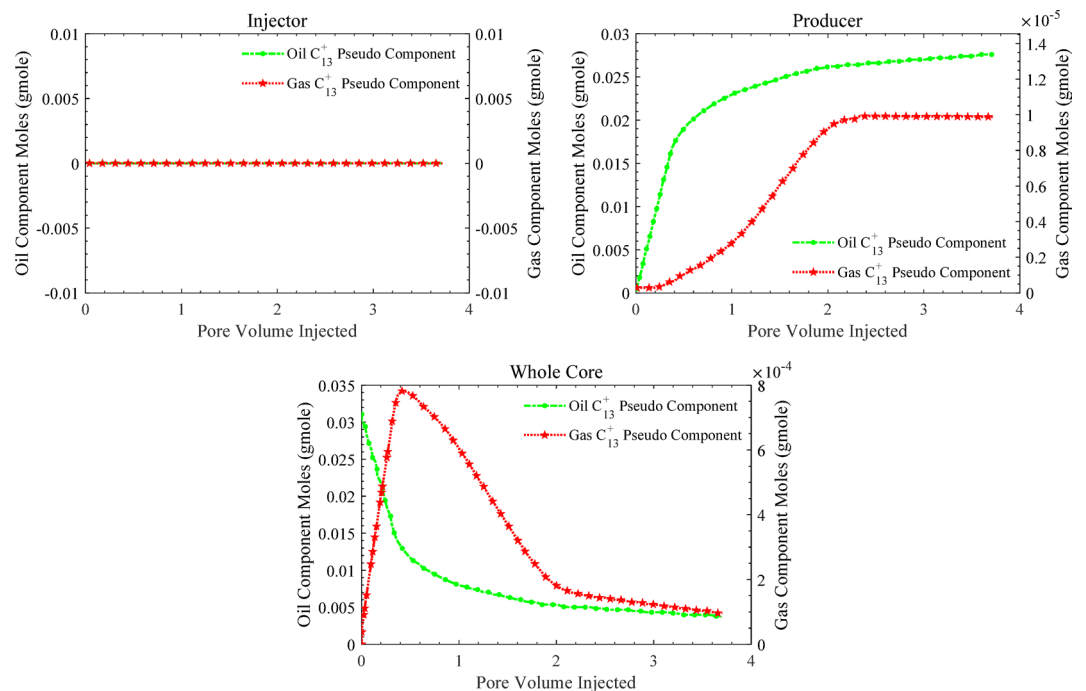


Fig. 10. C_{13}^+ pseudo-component molar content in the injector, core, producer sectors throughout secondary continuous enriched gas (10% NGL + 90% DG) injection.

comparable recovery of C_{13}^+ compared to secondary continuous enriched gas injection, suggesting a reliable, efficient enhanced oil recovery (EOR) method.

Summary and conclusions

This study investigates the effectiveness of tertiary enriched gas injection following secondary lean gas injection for residual oil recovery as a relatively unexplored enhanced oil recovery method in previous research. To

address this, a series of experiments involving injecting lean gas followed by enriched gas in volatile oil-saturated carbonate core samples was conducted. The CMG/GEM compositional module was employed to simulate the experiments, and the DECE history matching technique was applied to match experimental data on oil recovery, cumulative gas production, and pressure drop. For the first time, gas-oil relative permeability and capillary pressure functions for the tertiary enriched gas injection following secondary lean gas injection were simultaneously determined. The following conclusions can be drawn,

- Tertiary enriched-gas injection increased the ultimate oil recovery factor from 73% (after secondary lean-gas flooding) to 85%, representing a significant increase in oil recovery. This demonstrates that enrichment can effectively mobilize residual oil left behind after secondary lean-gas injection.
- Compositional and interfacial tension (IFT) effects were found to strongly influence flow behavior and relative permeability during tertiary enriched-gas injection. The derived gas-oil relative permeability and capillary pressure functions for tertiary enriched-gas injection differ substantially from those obtained in secondary gas floods, reflecting the impact of saturation history and altered fluid interactions. As a result, flow functions from secondary gas injection are inadequate for accurately simulating tertiary processes.
- This study demonstrates, for the first time, the simultaneous derivation of gas-oil relative permeability and capillary pressure functions for tertiary enriched-gas injection following secondary lean-gas injection, and highlights the need for dedicated experimental characterization or model calibration to capture history-dependent multiphase flow behavior in tertiary injection scenarios.
- Ternary diagram trajectories and component production analyses revealed that the dominant recovery mechanism during tertiary enriched-gas injection is a combined vaporizing-condensing gas drive, enhanced by increased intermediate hydrocarbon transfer and interfacial tension reduction.
- These findings show that tertiary enriched-gas injection could be a technically promising strategy for enhancing residual oil recovery in reservoirs that have previously undergone secondary lean-gas injection, particularly under reservoir conditions where increasing injection pressure to achieve miscibility is not operationally or economically feasible. This approach is best suited for reservoirs containing volatile to intermediate oils, where the addition of intermediate hydrocarbon components to the injection gas can significantly enhance mass transfer and reduce interfacial tension. In contrast, its effectiveness diminishes for heavy oils with limited volatile fractions.
- Overall, this work fills a key gap in the literature by providing experimental cases and history-matched flow functions for tertiary enriched-gas injections and by illustrating the underlying oil-mobilization mechanisms under these specific reservoir and operational constraints. These insights provide a stronger basis for reliable modeling and design of tertiary hydrocarbon-gas recovery strategies.

Data availability

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

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Author contributions

All authors contributed to the conception, design and analysis of the results of this research, and also to the writing of the manuscript. The experiments were performed by Z. Adak, and the numerical modeling and simulation was done by M. Rahmani. M.H. Ghazanfari and M. Fatemi supervised the research. All authors read and approved the final manuscript.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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