Enhanced Oil Recovery using carbon dioxide directly captured from air does not enable carbon-neutral oil

Antonio Gasós[a], **Ronny Pini**[b], **Viola Becattini**[a], **and Marco Mazzotti**[a,1]

The paper is a non-peer reviewed preprint submitted to EarthArXiv. The paper was submitted to PNAS for peer review.

This study evaluates the feasibility of producing carbon neutral oil via CO_2 Enhanced Oil Recovery (CO_2-EOR) coupled with direct air capture. Existing analyses often provide case-specific insights based on short-term operations that do not encompass the full life cycle of reservoir exploitation. In contrast, we propose a novel, top-down approach based on mass and volume conservation, expanding system boundaries to include emissions from primary, secondary, and tertiary oil recovery phases – the latter being CO_2-EOR. Supported by field data, the analysis demonstrates that CO_2-EOR cannot achieve carbon-neutral oil production. Only 30 % of projects produced carbon-neutral oil during EOR, but all of them were significantly carbon-positive when considering the full reservoir life-time. The volume occupied by the emitted CO_2 exceeded by at least 3 times the pore space freed by reservoir fluids production, namely oil, water and gas. Considering CO_2-EOR in isolation from earlier stages of oil production creates the temporal illusion of carbon-neutral oil, as significant water is co-produced during this phase, freeing storage space without causing direct emissions. The reservoir conditions when CO_2-EOR is carried out, however, are the direct consequence of extensive oil extraction and water injection in earlier exploitation phases. Only residual oil zones may offer potential for carbon-neutral oil due to their low oil saturation and lack of legacy emissions. Although CO_2-EOR may replace conventional oil production methods, potentially reducing carbon emissions, it risks promoting and perpetuating fossil fuel production, thereby undermining critical climate targets.

CO_2-EOR | Direct air capture (DAC) | Oil and gas reservoir | Climate impact assessment | Carbon dioxide utilization and storage (CCUS)

To maximize oil extraction from a reservoir, oil production typically proceeds in three stages (Fig. 1). The first stage, primary recovery, relies on the natural reservoir pressure to produce oil. This is followed by secondary recovery, which involves injecting water, possibly seawater, to maintain the reservoir pressure and displace additional oil. Finally, tertiary recovery, or Enhanced Oil Recovery (EOR), employs miscible fluids such as natural gas or carbon dioxide (CO_2) to mobilize trapped oil and enhance production (1). After oil extraction, depleted reservoirs can serve as sites for permanent CO_2 storage (2, 3). This work focuses specifically on CO_2-EOR, where CO_2 is used as the miscible fluid.

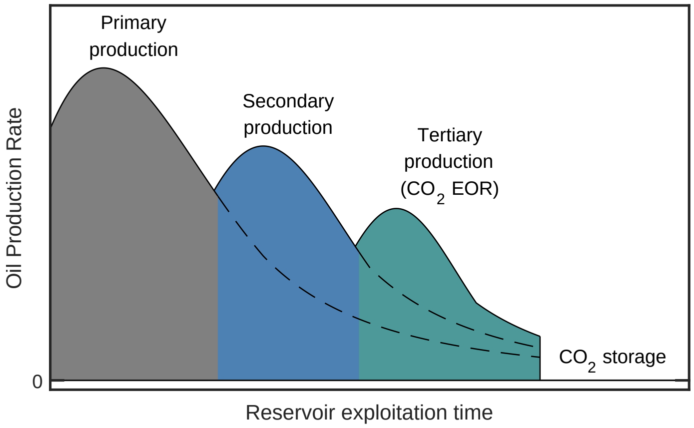

Fig. 1. Qualitative illustration of the oil production phases. Water is injected during secondary production, while CO_2 is injected during tertiary production, i.e., CO_2-EOR, and for storage in the depleted reservoir. Dashed lines represent oil production without transitioning to subsequent production phases.

Significance Statement

Some experts claim that using CO_2 from direct air capture (DAC) in enhanced oil recovery (EOR) can produce carbon-neutral oil by permanently storing more CO_2 than is emitted from the extracted fossil fuels. However, these claims are often poorly evidenced and ignore the carbon-intensive legacy of earlier reservoir exploitation. Using a novel general framework, supported by field data, our analysis reveals that total CO_2 emissions across the entire oil production life cycle far exceed the reservoir's storage capacity. While a few EOR projects appear carbon-neutral in isolation, this perspective overlooks earlier production phases creating a misleading narrative. Producing carbon-neutral oil through CO_2-EOR is not feasible within the reservoir exploitation limits, and achieving net-zero emissions requires transitioning away from fossil fuels.

Author affiliations: [a]ETH Zurich, Institute of Energy and Process Engineering, Sonneggstrasse 3, 8092 Zurich, Switzerland; [b]Imperial College London, Department of Chemical Engineering, Exhibition Road, SW7 2AZ London, UK

A.G. and M.M. designed research; A.G., R.P., and M.M. performed research; A.G. and R.P. analyzed data; and A.G., R.P., V.B., and M.M. wrote the paper.

The authors declare no competing interests.

[1] To whom correspondence should be addressed. E-mail: marcom@ethz.ch

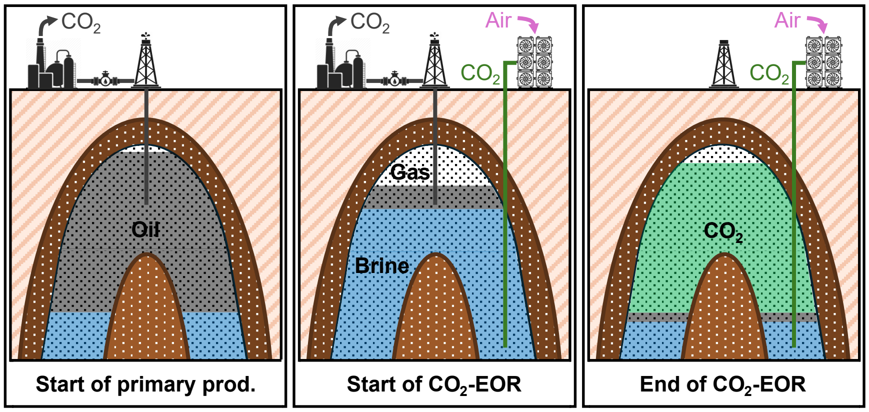

Fig. 2. Schematic representation of an oil and gas reservoir at the start of primary production, at the start of CO_2-EOR (i.e., after water-flooding during secondary production), and at the end of CO_2-EOR.

For decades, the oil industry has employed CO_2 in EOR operations to maximize oil recovery per unit of CO_2 injected, thus minimizing operational costs (4). It is estimated that approximately 180 Gt of oil could be recovered globally through CO_2-EOR in known oil fields (5). As Carbon Capture and Storage (CCS) technologies gained attention for their potential to reduce greenhouse gas (GHG) emissions and mitigate climate change, CO_2-EOR was considered as a possible method for permanently storing CO_2 underground (6, 7). Thus, the goal of CO_2-EOR became that of maximizing the volume of CO_2 stored per unit of oil recovered (8–10). However, using and thus burning the oil produced through EOR results in CO_2 emissions that reduce or annul the climate benefits of CO_2 storage itself. Therefore, CO_2-EOR is now considered a form of CO_2 utilization, whose attractiveness stems from being a profitable business rather than a means of counteracting climate change (11).

In recent years, Direct Air Capture (DAC) has gained significant attention as a Carbon Dioxide Removal (CDR) technology, which enables the direct removal of CO_2 from the atmosphere by technical means (12–16). At least one corporation engaged in hydrocarbon exploration has invested in DAC, viewing DAC as a way to offset the CO_2 emissions generated by its products (17). Proponents of using CO_2 derived from DAC in EOR argue that the oil produced in this manner could be carbon neutral (18, 19). This argument hinges on the claim that the amount of CO_2 ultimately stored in the reservoir exceeds that emitted during the refining and use (i.e., burning) of the extracted oil. If the CO_2 has been captured from the atmosphere, using it for EOR could close the carbon cycle for the oil produced in this manner.

Robust, bottom-up approaches have assessed the climate impact of oil produced through EOR using Life Cycle Analysis (LCA). These methods use operational field data or reservoir fluid dynamics models to estimate the amounts of both CO_2 stored and hydrocarbons produced. The system boundaries are then extended to include factors such as emissions from oil utilization, EOR operation, and the source of CO_2 (20–23). While LCA-based assessments provide detailed insights, they also rely heavily on case-specific data and assumptions, which can limit their ability to support broad conclusions about the feasibility of carbon-neutral oil.

One critical factor in these assessments is the time frame considered. CO_2-EOR starts carbon-negative, meaning that more CO_2 is stored than emitted, as significant volumes of CO_2 are injected to pressurize the reservoir and displace fluids (24). Over time, the operation transitions to a net climate-positive impact, typically after about 10 years, as hydrocarbons are produced and less new CO_2 is injected, with CO_2 produced at the extraction well being re-injected. Given that EOR operations usually last about 20 years, analyses focusing on shorter periods, such as under ten years (22), may be misleading in terms of net climate impact of EOR. Moreover, traditional LCAs typically consider only the EOR phase, which represents a much shorter period than the entire life cycle of reservoir exploitation. Since EOR follows primary and secondary recovery phases (Fig. 1), we argue that assessments must cover the full life cycle of the reservoir to account properly for the overall climate impact.

This paper proposes a novel top-down framework to evaluate the net climate impact of DAC-based CO_2-EOR. This approach enables drawing widely applicable conclusions about CO_2-EOR and the feasibility of producing carbon-neutral oil. Though less detailed than bottom-up models, our analysis remains accurate and expands system boundaries to account for the temporal dimension of reservoir exploitation.

The conceptual framework

The feasibility of carbon neutral oil through CO_2-EOR could be simply dismissed based on two figures: (1) burning one ton of oil generates at least three tons of CO_2 (25), and (2) under reservoir conditions, the density of oil is higher than that of CO_2, with an oil-to-CO_2 density ratio between 1.0 and 1.5 (26). This means that all the CO_2 generated by burning the recovered oil would occupy between 300 % and 450 % of the volume made available by extracting oil; thus, attaining carbon neutrality would be physically impossible given the reservoir's volume constraints.

However, this perspective is incomplete, as it overlooks that injecting CO_2 displaces not only oil but also other fluids present in the reservoir, namely a gas phase and an aqueous phase. In other words, there is an additional fraction of the pore space, previously occupied by less carbon-intensive fluids, that could be occupied by CO_2. Here, we analyze the CO_2-EOR system using a novel top-down approach, based on mass and volume conservation principles, accounting for all reservoir fluids. A schematic of the reservoir before and during exploitation is shown in Fig. 2.

Description of the reservoir. The analysis considers the reservoir as a fixed control volume, namely as a porous rock body with constant pore volume, V_p.

Initially, the pore volume contains fluids at initial temperature and pressure, T_i and P_i. Based on the black-oil model, these fluids are grouped in three phases (see Fig. 2): an aqueous phase (w), a gaseous phase (g), and an oleic phase (o). For the sake of simplicity but without loss of generality, we assume that each phase consists of one pseudo-component only, namely water, methane, and oil. The initial state is described as:

$$V_p = V_o^i + V_g^i + V_w^i \qquad [1]$$

where V_o^i, V_g^i, and V_w^i are the corresponding volumes of oil, gas, and water; these are called in-place volumes by practitioners.

After $\mathrm{CO_2}$-EOR, the pore volume is occupied by the residual fluids, not recovered, and by a dense phase, assumed to consist of pure $\mathrm{CO_2}$ only, at the final reservoir conditions, T_f and P_f. The final state is described as:

$$V_p = V_o^r + V_g^r + V_w^r + V_{\mathrm{CO_2}}^{\mathrm{stored}} \qquad [2]$$

where $V_{\mathrm{CO_2}}^{\mathrm{stored}}$ is the volume of $\mathrm{CO_2}$ stored and V_j^r is the residual volume of phase j remaining in the reservoir.

Equation 2 assumes that all the stored $\mathrm{CO_2}$ exists at its dense phase density, even though it is partially evaporated or dissolved in the liquids. This assumption overestimates the $\mathrm{CO_2}$ storage potential and could be refined by considering a lower $\mathrm{CO_2}$ density that accounts for these phases.

Exploitation of the reservoir. The extraction of in-place fluids results in $\mathrm{CO_2}$ emissions upon their utilization. The emitted $\mathrm{CO_2}$, $V_{\mathrm{CO_2}}^{\mathrm{emit}}$, is calculated using emission factors, f_j, representing the volume of $\mathrm{CO_2}$ emitted, from gate to grave, per unit volume of phase j used (27):

$$V_{\mathrm{CO_2}}^{\mathrm{emit}} = V_o^{\mathrm{prod}} f_o + V_g^{\mathrm{prod}} f_g + V_w^{\mathrm{prod}} f_w \qquad [3]$$

Here, $V_j^{\mathrm{prod}} = (V_j^i - V_j^\mathrm{r}\beta_j)$ is the volume of phase j produced, where β_j is the density ratio after and before exploitation.

DAC and EOR operations have a site-specific carbon footprint, accounted for through an overall $\mathrm{CO_2}$ removal efficiency, $\eta_{\mathrm{CO_2}}$. Thus, the target volume of $\mathrm{CO_2}$ to be stored is given by:

$$V_{\mathrm{CO_2}}^{\mathrm{target}} = \frac{V_{\mathrm{CO_2}}^{\mathrm{emit}}}{\eta_{\mathrm{CO_2}}} \qquad [4]$$

Emission factors. The emission factors are calculated as:

$$f_j = \frac{1}{\eta_j} \frac{\rho_j(T_\mathrm{i}, P_\mathrm{i})}{\rho_{\mathrm{CO_2}}(T_\mathrm{f}, P_\mathrm{f})} \frac{M_{\mathrm{CO_2}}}{M_j} \qquad [5]$$

Here, ρ_j and $\rho_{\mathrm{CO_2}}$ are the densities of phase j and of $\mathrm{CO_2}$ at relevant temperature and pressure levels, respectively, while M_j and $M_{\mathrm{CO_2}}$ are their molar masses, in mass per mole of carbon. We use $M_o = 14$ g/mol (for $\mathrm{CH_2}$, the building block of oil), $M_g = 16$ g/mol (methane), and $M_w = 0$ g/mol (water, being carbon-free).

The densities and molar masses estimate direct emissions from fuel combustion, while the variable η_j denotes the carbon efficiency in the utilization of phase j, accounting for indirect emissions. Such efficiency depends on conditions and events outside the scope of this analysis. Thus, we use a conservative value of 1 in our analysis.

Carbon balance of the reservoir. The production of reservoir fluids may not provide enough pore volume to store the entire quantity of $\mathrm{CO_2}$. The number of displaced fluid volumes needed to store the target amount of $\mathrm{CO_2}$, ξ, is expressed as:

$$\xi = \frac{V_{\mathrm{CO_2}}^{\mathrm{target}}}{V_{\mathrm{CO_2}}^{\mathrm{stored}}} = \frac{1}{\eta_{\mathrm{CO_2}}} \left(\phi_o f_o + \phi_g f_g + \phi_w f_w\right) \qquad [6]$$

where the volume fraction of each phase produced, ϕ_j, can be defined either as a function of the produced volumes, V_j^{prod}, or as a function of the fluid saturations in the reservoir, $S_j = V_j/V_p$, through Equation 2:

$$\phi_j = \frac{V_j^{\mathrm{prod}}}{V_o^{\mathrm{prod}} + V_g^{\mathrm{prod}} + V_w^{\mathrm{prod}}} = \frac{S_j^i - S_j^\mathrm{r}\beta_j}{1 - (S_o^\mathrm{r} + S_g^\mathrm{r} + S_w^\mathrm{r})} \qquad [7]$$

Note that $\phi_j = S_j^i$ if there are no residual fluids remaining.

If $\xi = 1$ the volume of displaced fluids is exactly sufficient to store the target amount of $\mathrm{CO_2}$, enabling carbon-neutral oil production; if $\xi < 1$, there is excess storage capacity, allowing for negative emissions; and if $\xi > 1$, the storage capacity is insufficient, and EOR using DAC-derived $\mathrm{CO_2}$ ultimately emits more $\mathrm{CO_2}$ than it can store.

The climate impact of reservoir exploitation

Case study assumptions. For this analysis, a $\mathrm{CO_2}$ removal efficiency, $\eta_{\mathrm{CO_2}}$, of 0.85 is considered in Equation 4. The efficiency of DAC with storage typically ranges from 0.80 to 0.95 depending on the energy source and geographical location (28, 29). Additionally, $\mathrm{CO_2}$ is co-produced alongside other fluids during EOR, requiring separation and re-injection to ensure effective storage, which further decreases $\eta_{\mathrm{CO_2}}$ (23).

Emissions factors are reported in Table 1, for a typical reservoir at identical initial and final conditions of P = 180 bar and T = 70 °C. Assumed densities for the calculations are 690 kg/m^3 for the oleic phase (30) (including dissolved

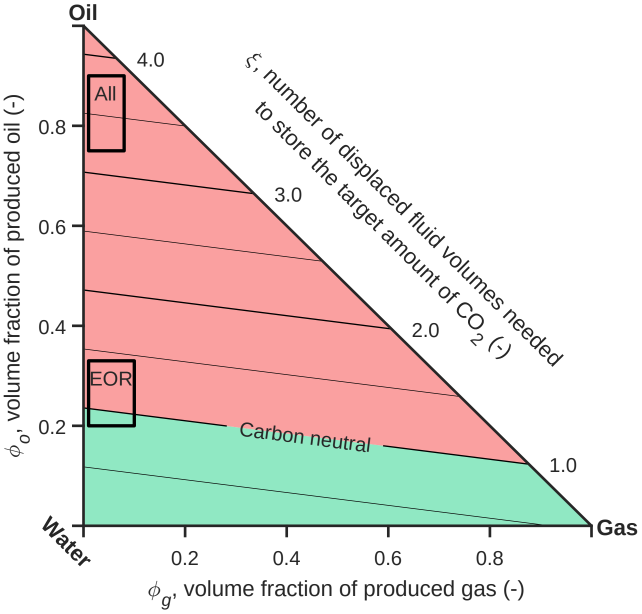

Fig. 3. Ternary diagram of the volume fraction of produced fluids (oil, gas, and water). The squares illustrate typical phase distributions produced during the entire reservoir lifetime (labelled 'All') and during EOR only (labelled 'EOR').

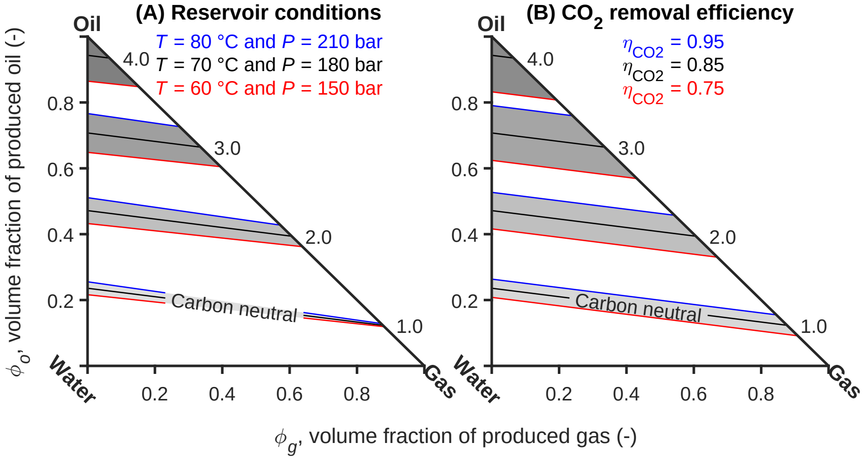

Fig. 4. Sensitivity of the ξ isolines to: **(left)** reservoir conditions, namely T and P within the ranges of 60 to 80 °C and 150 to 210 bar, and **(right)** CO$_2$ removal efficiency of DAC and EOR between 0.75 and 0.95. Black lines are the central values; blue and red lines are the best and worst climate impact scenarios within the ranges.

Table 1. Emissions factors for a reservoir at 180 bar and 70 °C.

Oil (f_o)	Methane (f_g)	Water (f_w)
3.6	0.46	0.0

gas), 600 kg/m^3 for the CO$_2$ dense phase (26), and 101 kg/m^3 for the gas phase (ideal gas law). The oil emission factor is significantly larger than one, primarily due to stoichiometry rather than assumptions: even assuming same CO$_2$ and oil densities, and unitary efficiency, Equation 5 yields $f_o = M_{CO_2}/M_o = 3.14$.

Geometrical representation. The state of any reservoir can be represented as a point on the ternary diagram shown in Fig. 3, where the horizontal and the vertical coordinates are the volume fractions of gas and oil produced – ϕ_g and ϕ_o, respectively. The water fraction is the complement to one. The vertices of the triangle represent reservoirs filled with only one fluid phase, while the edges represent two-phase mixtures, with the excluded phase opposite the edge.

Equation (6) constrains the combination of produced phases, ϕ_j, compatible with a given value of ξ. By varying ξ one obtains straight isolines in the ternary diagram that define loci of points where the volume occupied by the target CO$_2$ to be stored is ξ times the pore volume made available in the reservoir upon extraction of the in-place fluids. The isolines for the case study considered are shown in Fig. 3. Reservoir operations corresponding to points above the $\xi = 1$ isoline (red region) ultimately emit more CO$_2$ than the reservoir can store, while those mapping in points below it (green region) may store more CO$_2$ than they emit.

The ternary diagram may be used to effectively illustrate specific scenarios of interest:

1. **Saline aquifer** (**$\phi_o = \phi_g = 0$**)**:** Only water is displaced, providing CO$_2$ storage capacity without extracting fossil fuels, resulting in $\xi = 0$.

2. **Gas reservoir** (**$\phi_o = 0$**)**:** Only gas and water are produced; since $\eta_{CO_2} > f_g > f_w$, more CO$_2$ is stored than emitted, resulting in $\xi < 1$.

3. **Oil reservoir** (**$\phi_g = 0$**)**:** Only oil and water are produced, with any extracted gas re-injected into the reservoir; since $f_o > \eta_{CO_2} > f_w$, achieving carbon neutrality requires producing more than 70 % water, an economically unattractive proposition for an oil operator.

Sensitivity to assumptions. Fig. 4 illustrates the sensitivity of the ξ-isolines to variations in reservoir conditions, namely temperature and pressure with ranges based on reservoir data from (26) (panel A), and in CO$_2$ removal efficiency (panel B). The blue and red dash-dotted lines represent the best and worst climate impact scenarios within the considered sensitivity range. The effects of pressure and temperature were accounted for by modifying the densities of the dense CO$_2$ phase (from 550 to 650 kg/m^3, according to (26)) and of the gaseous phase (from 87 to 115 kg/m^3, according to the ideal gas law), while the oil density remained unchanged.

It is readily observed that the sensitivity of the position of the ξ-isolines, particularly of the $\xi = 1$ isoline, to reasonable changes of the above parameters is qualitatively and quantitatively rather small. This allows arguing that the conclusions drawn based on the specific scenario considered in Fig. 3 are indeed general.

Existing CO$_2$-EOR projects. Fig. 5 illustrates the carbon balance of reservoir exploitation as a function of the incremental oil recovered for 16 CO$_2$-EOR projects reported in (31), supplemented with additional data from (32, 33) for the box plots (reported in Table S1). The carbon balance is also presented for these projects when accounting for emissions from oil produced before CO$_2$-EOR, assuming a recovery of 35 % of the original oil in place (OOIP) during primary and secondary production; this is considered to be a representative median value for reservoirs globally (1).

Considering only EOR, all projects start carbon negative, as injected CO$_2$ pressurizes the reservoir and displaces fluids before significant incremental oil production. The carbon balance then rises steeply due to increased oil production (effective mobilization) and reduced CO$_2$ retention in the reservoir (down to 40–60 %) as CO$_2$ breaks through at the production well, necessitating separation and re-injection. The curve eventually flattens as the remaining oil becomes increasingly difficult to mobilize, thus requiring more injected CO$_2$ per unit of oil produced. Most projects (11 out of the 16 considered) surpassed the $\xi = 1$ threshold within the temporal boundary of the CO$_2$-EOR operation, typically after 5–10 %

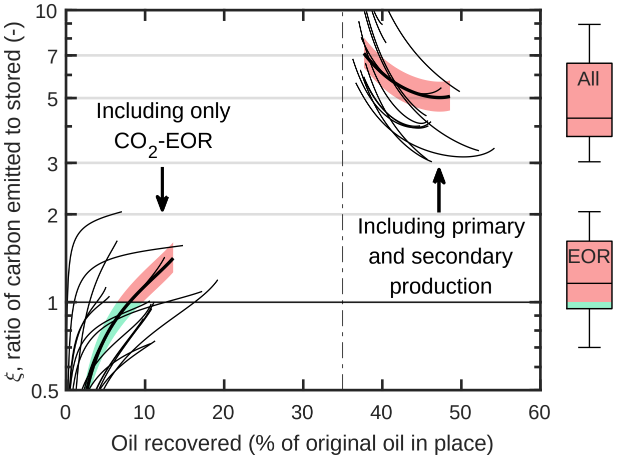

Fig. 5. Ratio of carbon emitted to stored, ξ, as a function of oil recovery for 16 CO_2-EOR projects from (31). The bottom-left lines represent ξ considering only CO_2-EOR, for each project, while the top-right lines include the entire reservoir lifetime, assuming 35 % oil recovery before EOR. Colored areas illustrate the sensitivity to CO_2 removal efficiency between 0.75 and 0.95 for one specific project. Box plots show the final ξ values of each project, supplemented with data from (32, 33).

recovery of OOIP, indicating that the oil produced during EOR ultimately emitted more CO_2 than what was stored.

When emissions from primary and secondary production phases are also accounted for, the overall reservoir exploitation becomes significantly carbon-positive. All projects start with an infinite value of ξ at 35 % OOIP, due to the CO_2 emitted before EOR without associated storage. Then, the value of ξ decreases as more CO_2 is stored, thus progressively reducing the average climate impact of the oil produced. It should be noted that half of the reservoirs emitted between 370 and 660 % of the stored CO_2 over their lifetime.

The temporal delusion of carbon-neutral oil

Two key observations are worth making based on the results presented in Figs. 3 and 5.

First, the exploitation of oil reservoirs during their entire lifetime falls within the region where $\xi > 1$, which makes sense because oil reservoirs are developed and exploited due to the large quantities of recoverable oil. Notably, the maximum allowable volume fraction of oil produced, or oil saturation if all reservoir fluids are recovered, that could enable carbon-neutral oil is only 28 % (with $\eta_{CO_2} = 1$). Such saturation levels are only found naturally, namely without prior exploitation, in residual oil zones, which are deep saline aquifers containing oil at residual saturation levels and are currently unexploited (34, 35). These observations support the argument that oil reservoirs do not have sufficient capacity to store all the CO_2 generated from the refining and combustion of the extracted fossil fuels. Thus, producing carbon-neutral oil is not possible within the reservoir boundaries.

Second, as oil production advances through its various phases, the phase distribution of the reservoir changes. The volume made available by the extracted oil is replaced by gas, which had remained dissolved at higher pressures, and by water injected during secondary recovery. Consequently, the corresponding point in the ternary diagram of Fig. 3 moves downwards, reflecting a decrease in the fraction of oil produced. By the time CO_2-EOR starts, the reservoir composition may fall below the $\xi = 1$ threshold, depending on reservoir conditions, CO_2 removal efficiency, and the extent of EOR exploitation, consistent with previous LCA studies (22, 24). At this stage, the volume of fluids produced when injecting CO_2 may generate less CO_2 than the injected amount, providing arguments to EOR advocates who claim that operational field data demonstrate the potential for carbon-neutral oil.

However, this observation is short-sighted. The carbon negativity of CO_2-EOR operations is quickly exhausted, with only 30 % of EOR projects ultimately achieving $\xi < 1$ (Fig. 5). Moreover, EOR can not be considered in isolation from the earlier stages of oil production. Over the entire life cycle of an oil reservoir, spanning 40 to 80 years, far more CO_2 is emitted than can be stored in the reservoir. In fact, all EOR projects are carbon-positive when the oil recovered during primary and secondary production exceeds just 5 % OOIP (Fig. S2), much lower than typical recovery rates of 25 to 50 % OOIP (1). While DAC-based CO_2-EOR may reduce the carbon footprint of oil by 10 to 32 % (Fig. S2), these findings confirm the unfeasibility of achieving carbon-neutral oil.

The long time frames of oil exploitation, often involving multiple companies and operational phases, lead assessments to artificially decouple the different stages of reservoir exploitation. This practice provides a narrow and potentially misleading perspective, contributing to the false narrative that oil exploitation can achieve carbon neutrality.

Discussion

We developed a general top-down approach that enables to consistently and efficiently assess the climate impact of oil production operations by mapping the produced fluids onto a ternary diagram. Life cycle analyses can provide project-specific insights, which may be used to refine the model parameters of our framework.

Our analysis demonstrates that CO_2-EOR does not enable the production of carbon-neutral oil over the entire reservoir lifetime. While carbon neutrality might be achieved within limited time intervals, such as part of or the whole CO_2-EOR phase, these findings underscore the need for transparent and coherent frameworks to address legacy emissions.

Excess CO_2 that cannot be stored in the reservoir could be stored in alternative sites to offset fossil fuel emissions, such as saline aquifers commonly located beneath oil reservoirs or other suitable geological formations. Our results bring clarity to the debate on the intrinsic feasibility of carbon-neutral oil through CO_2-EOR, directing attention to the broader question of whether fossil fuel emissions should be offset through carbon removals.

CO_2-EOR has the potential to replace part of conventional oil production while financing the development of subsurface CO_2 injection technology (11, 36). However, the prospect of significant oil recovery and CO_2 storage could be misused as a pretext to continue promoting or funding fossil fuel production, which must be phased out to meet critical climate targets (37, 38).

ACKNOWLEDGMENTS. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

1. L Lake, R Johns, B Rossen, G Pope, *Fundamentals of Enhanced Oil Recovery*. (Society of Petroleum Engineers), (2014).
2. S Bachu, Sequestration of CO_2 in geological media: criteria and approach for site selection in response to climate change. *Energy Convers. & Manag.* **41**, 953–970 (2000).
3. MD Aminu, SA Nabavi, CA Rochelle, V Manovic, A review of developments in carbon dioxide storage. *Appl. Energy* **208**, 1389–1419 (2017).
4. M Blunt, FJ Fayers, FM Orr, Carbon dioxide in enhanced oil recovery. *Energy Convers. Manag.* **34**, 1197–1204 (1993).
5. ML Godec, VA Kuuskraa, P Dipietro, Opportunities for using anthropogenic CO_2 for enhanced oil recovery and CO_2 storage. *Energy Fuels* **27**, 4183–4189 (2013).
6. B Metz, O Davidson, H De Coninck, M Loos, L Meyer, *IPCC special report on carbon dioxide capture and storage.* (Cambridge: Cambridge University Press), (2005).
7. F Gozalpour, SR Ren, B Tohidi, CO_2 EOR and Storage in Oil Reservoirs. *Oil & Gas Sci. Technol.* **60**, 537–546 (2005).
8. K Jessen, AR Kovscek, FM Orr, Increasing CO_2 storage in oil recovery. *Energy Convers. Manag.* **46**, 293–311 (2005).
9. AR Kovscek, MD Cakici, Geologic storage of carbon dioxide and enhanced oil recovery. II. Cooptimization of storage and recovery. *Energy Convers. Manag.* **46**, 1941–1956 (2005).
10. A Ettehadtavakkol, LW Lake, SL Bryant, CO_2-EOR and storage design optimization. *Int. J. Greenh. Gas Control.* **25**, 79–92 (2014).
11. N Mac Dowell, PS Fennell, N Shah, GC Maitland, The role of CO_2 capture and utilization in mitigating climate change. *Nat. Clim. Chang.* **7**, 243–249 (2017).
12. R Socolow, et al., Direct Air Capture of CO_2 with Chemicals: A Technology Assessment for the APS Panel on Public Affairs, (American Physical Society), Technical report (2011).
13. C Beuttler, L Charles, J Wurzbacher, The Role of Direct Air Capture in Mitigation of Anthropogenic Greenhouse Gas Emissions. *Front. Clim.* **1** (2019).
14. DW Keith, G Holmes, D St. Angelo, K Heidel, A Process for Capturing CO_2 from the Atmosphere. *Joule* **2**, 1573–1594 (2018).
15. S Fuss, et al., Negative emissions - Part 2: Costs, potentials and side effects. *Environ. Res. Lett.* **13** (2018).
16. M Bui, et al., Carbon capture and storage (CCS): The way forward. *Energy Environ. Sci.* **11**, 1062–1176 (2018).
17. Occidental Petroleum, Occidental enters into agreement to acquire direct air capture technology innovator carbon engineering (https://www.oxy.com/news/news-releases/occidental-enters-into-agreement-to-acquire-direct-air-capture-technology-innovator-carbon-engineering/) (2023) Accessed: 2024-09-17.
18. Occidental Petroleum, Can we use CO_2 in a beneficial way? EOR has the answer (https://www.oxy.com/operations/performance-production/eor/) (2024) Accessed: 2024-09-17.
19. IEA, Can CO_2-EOR really provide carbon-negative oil? (IEA, Paris) (2019).
20. P Jaramillo, WM Griffin, ST McCoy, Life cycle inventory of CO_2 in an enhanced oil recovery system. *Environ. Sci. Technol.* **43**, 8027–8032 (2009).
21. NA Azzolina, et al., How green is my oil? A detailed look at greenhouse gas accounting for CO_2-enhanced oil recovery (CO_2-EOR) sites. *Int. J. Greenh. Gas Control.* **51**, 369–379 (2016).
22. JR Sminchak, S Mawalkar, N Gupta, Large CO_2 Storage Volumes Result in Net Negative Emissions for Greenhouse Gas Life Cycle Analysis Based on Records from 22 Years of CO_2-Enhanced Oil Recovery Operations. *Energy Fuels* **34**, 3566–3577 (2020).
23. J Singh, U Singh, GR Garcia, V Vishal, R Anex, Putting the genie back in the bottle: Decarbonizing petroleum with direct air capture and enhanced oil recovery. *Int. J. Greenh. Gas Control.* **139** (2024).
24. V Núñez-López, R Gil-Egui, SA Hosseini, Environmental and Operational Performance of CO_2-EOR as a CCUS Technology: A Cranfield Example with Dynamic LCA Considerations. *Energies* **12**, 448 (2019).
25. EPA, Greenhouse gas equivalencies calculator - calculations and references (US Environmental Protection Agency) (2024) Accessed: 2024-12-06.
26. LW Holm, VA Josendal, Effect of Oil Composition on Miscible-Type Displacement by Carbon Dioxide. *Soc. Petroleum Eng. J.* **22**, 87–98 (1982).
27. MZ Hauschild, RK Rosenbaum, SI Olsen, *Life cycle assessment.* (Springer), (2018).
28. S Deutz, A Bardow, Life-cycle assessment of an industrial direct air capture process based on temperature–vacuum swing adsorption. *Nat. Energy* **6**, 203–213 (2021).
29. T Terlouw, K Treyer, C Bauer, M Mazzotti, Life Cycle Assessment of Direct Air Carbon Capture and Storage with Low-Carbon Energy Sources. *Environ. Sci. Technol.* **55**, 11397–11411 (2021).
30. R Labedi, Use of production data to estimate volume factor, density and compressibility of reservoir fluids. *J. Petroleum Sci. Eng.* **4**, 375–390 (1990).
31. NA Azzolina, et al., CO_2 storage associated with CO_2 enhanced oil recovery: A statistical analysis of historical operations. *Int. J. Greenh. Gas Control.* **37**, 384–397 (2015).
32. RE Hadlow, Update of Industry Experience With CO_2 Injection. *Soc. Petroleum Eng.* (1992).
33. WR Brock, LA Bryan, Summary results of CO_2 EOR field tests, 1972-1987. *Soc. Petroleum Eng.* (1989).
34. V Kuuskraa, R Petrusak, M Wallace, Residual Oil Zone "fairways" and Discovered Oil Resources: Expanding the Options for Carbon Negative Storage of CO_2. *Energy Procedia* **114**, 5438–5450 (2017).
35. RJ Stewart, G Johnson, N Heinemann, M Wilkinson, RS Haszeldine, Low carbon oil production: Enhanced oil recovery with CO_2 from North Sea residual oil zones. *Int. J. Greenh. Gas Control.* **75**, 235–242 (2018).
36. V Núñez-López, E Moskal, Potential of CO_2-EOR for Near-Term Decarbonization. *Front. Clim.* **1** (2019).
37. IEA, Net zero roadmap: A global pathway to keep the 1.5°C goal in reach (IEA, Paris) (2023).
38. IPCC, Climate change 2023: Synthesis report. contribution of working groups i, ii and iii to the sixth assessment report of the intergovernmental panel on climate change (IPCC, Geneva, Switzerland) (2023).

Supporting Information for preprint submitted to EarthArXiv

Enhanced Oil Recovery using carbon dioxide directly captured from air does not enable carbon-neutral oil

Antonio Gasós, Ronny Pini, Viola Becattini, and Marco Mazzotti

Marco Mazzotti.
E-mail: marcom@ethz.ch

This PDF file includes:

Supporting text
Figs. S1 to S2
Table S1
SI References

Supporting Information Text

Data from existing CO_2-EOR projects. Figure 5 presents the data on reservoir exploitation for 16 CO_2-EOR projects that has been reported by Azzolina et al. (1). The study developed models fitted to the field data for each project, providing key values:

- The net CO_2 utilization, $U_{\mathrm{CO_2}}$, defined as the mass of CO_2 stored per unit mass of oil produced.
- The cumulative incremental oil recovery, R_{EOR}, expressed as % of the original oil in place (OOIP), and defined as the additional oil produced due to CO_2 injection.
- The CO_2 retention, defined as the fraction of injected CO_2 retained in the reservoir.

The net CO_2 utilization and the CO_2 retention are average values calculated from the start of the EOR operation up to a specific point in time during the operation. Fig. reffig:otherParams illustrates the evolution of these values as a function of the total cumulative injected volume of CO_2 and H_2O, expressed as a percentage of the hydrocarbon pore volume (HCPV). The EOR operation progresses over time as the injected volume increases. Based on these parameters, the fraction of carbon emitted relative to stored, ξ, is computed using Equation 6 (the reader is referred to the manuscript for the nomenclature):

$$\xi = \frac{V_{CO_2}^{\mathrm{target}}}{V_{\mathrm{CO_2}}^{\mathrm{stored}}} = \frac{1}{\eta_{\mathrm{CO_2}}} \frac{M_{\mathrm{CO_2}}}{M_o} \left(\frac{1}{U_{\mathrm{CO_2}}} \frac{R_{\mathrm{TOT}}}{R_{\mathrm{EOR}}} \right) \qquad [1]$$

Here, the term in parentheses represents the real net CO_2 utilization. If oil produced before EOR is ignored, then $R_{\mathrm{TOT}} = R_{\mathrm{EOR}}$, and the climate impact is denoted as ξ_{EOR}. Otherwise, $R_{\mathrm{TOT}} = R_{\mathrm{EOR}} + R_{\mathrm{PRE}}$, where R_{PRE} denotes the oil recovered before EOR. A value of 35 % OOIP was assumed for R_{PRE} (2), and the climate impact is referred to as ξ_{TOT}. Table S1 summarizes the operating variables and the calculated ξ_{EOR} and ξ_{TOT} for CO_2-EOR projects from various studies. For data from (1), the field data at the end of operation, i.e., at the maximum injected volume, were utilized.

Carbon footprint of produced oil. Using data from Azzolina et al. (1) and Equation 1, we can estimate the average carbon footprint of the produced oil, C_{oil}, in tons of CO_2 emitted per ton of oil used, as follows:

$$C_{\mathrm{oil}} = \frac{M_{\mathrm{CO_2}}}{M_o} - \eta_{\mathrm{CO2}}\, U_{\mathrm{CO_2}} \frac{R_{\mathrm{EOR}}}{R_{\mathrm{TOT}}} \qquad [2]$$

Fig. S2 illustrates the carbon footprint of the produced oil as a function of the oil recovered before EOR, R_{PRE}, namely during the primary and secondary production phases, for $\eta_{\mathrm{CO2}} = 0.85$. In the United States, where the CO_2-EOR projects were conducted, most oil reservoirs recover 25 to 49% OOIP before EOR (2), as shown by the grey area in Fig. S2. For these recovery rates, most CO_2-EOR projects would have produced oil with a carbon footprint ranging from 2.1 to 2.8 tons of CO_2 per ton of oil, if the stored CO_2 had been captured from the air. Consequently, DAC-based CO_2 EOR reduced the carbon footprint of oil by 10 to 32 %. However, all projects produced carbon-positive oil when the oil recovered before EOR exceeded only 5 % OOIP, highlighting the unfeasibility of achieving carbon-neutral oil within the reservoir's boundaries.

References

1. NA Azzolina, et al., CO_2 storage associated with CO_2 enhanced oil recovery: A statistical analysis of historical operations. *Int. J. Greenh. Gas Control.* **37**, 384–397 (2015).
2. L Lake, R Johns, B Rossen, G Pope, *Fundamentals of Enhanced Oil Recovery.* (Society of Petroleum Engineers), (2014).
3. RE Hadlow, Update of Industry Experience With CO_2 Injection. *Soc. Petroleum Eng.* (1992).
4. WR Brock, LA Bryan, Summary results of CO_2 EOR field tests, 1972-1987. *Soc. Petroleum Eng.* (1989).

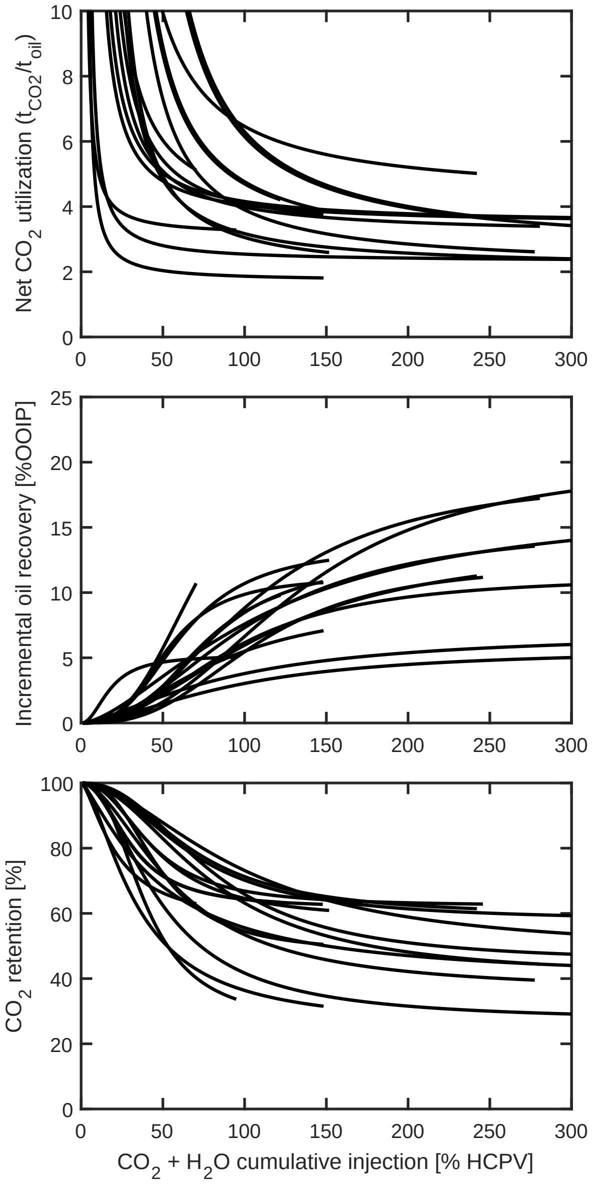

Fig. S1. Evolution of the net CO_2 utilization (top), the incremental oil recovery (middle), and the CO_2 retention (bottom), as a function of the cumulative volume of injected CO_2 and H_2O, expressed as a percentage of the hydrocarbon pore volume (HCPV). Each line represents one of the 16 CO2-EOR projects reported in (1).

Table S1. Data for CO_2-EOR projects used to generate Figure 3 and Figure 5 in the manuscript. Taken from Table 1 in (1), Table 1 in (3), and Table 1 in (4). The value ξ_{TOT} can not be computed for datasets missing an oil recovery value.

Project name (ref.)	Injected volume (% HCPV)[1]	Oil recovery (% OOIP)[2]	Net CO_2 utilization (t_{CO_2}/t_{oil})	ξ_{EOR} (-)	ξ_{TOT} (-)
Site A (1)	246	9.7	11.2	1.0	4.2
Site B (1)	281	8.9	17.2	1.1	3.3
Site C (1)	148	10.2	10.8	1.0	4.0
Site D (1)	450	8.1	19.2	1.2	3.4
Site E (1)	242	13.2	11.3	0.7	3.0
Site F (1)	302	9.6	10.6	1.0	4.3
Site G (1)	148	4.8	7.1	2.0	12.1
Site H (1)	152	6.8	12.5	1.4	5.4
Site I (1)	478	6.0	6.5	1.6	10.4
Site J (1)	70	13.5	10.7	0.7	3.1
Site K (1)	650	9.3	5.5	1.0	7.7
Site L (1)	122	11.0	9.8	0.9	4.0
Site M (1)	95	8.6	5.0	1.1	8.9
Site N (1)	148	9.9	10.8	1.0	4.2
Site R (1)	378	6.2	14.8	1.6	5.3
Site W (1)	278	6.9	13.6	1.4	5.1
Southwest USA average (3)	N/A	N/A	10.0	1.0	N/A
Northwest USA average (3)	N/A	N/A	8.0	1.2	N/A
Oklahoma average (3)	N/A	N/A	7.5	1.3	N/A
Southeast USA average (3)	N/A	N/A	13.3	0.7	N/A
Garber (4)	35	14	6.0	1.6	5.7
Little Creek (4)	160	21	12.6	0.8	2.1
Maljamar (4)	30	8.2	10.7	0.9	4.8
Maljamar (4)	17	0.7	6.1	1.6	N/A
Slaughter Estate (4)	26	20	3.7	2.6	7.2
Weeks Island (4)	24	8.7	3.3	2.9	14.8

[1] Injected fluids include CO_2 and H_2O, and HCPV refers to the to the hydrocarbon pore volume. [2] Oil recovered during CO_2-EOR only, and OOIP refers to the original oil in place.

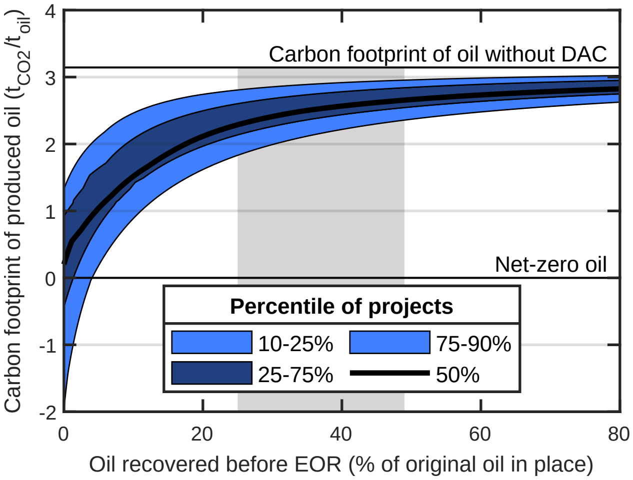

Fig. S2. Carbon footprint of the oil produced, C_{oil}, as a function of oil recovered before EOR, R_{PRE}, for 16 CO_2-EOR projects reported in (1). The black line is the median, the dark blue area indicates the interquartile range (25th to 75th percentiles), and the light blue areas show the 10th to 25th and 75th to 90th percentiles. The grey area represents a typical range of oil produced before EOR for reservoirs in the US (2).