The Effect of CO₂ Phase on Oil Displacement in a Sandstone Core Sample

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Abstract: CO₂ sequestration in saline aquifers and hydrocarbon reservoirs is a promising strategy to reduce CO₂ concentration in the atmosphere and/or enhance hydrocarbon production. Change in subsurface conditions of pressure and temperature and CO₂ state is likely to have a significant impact on capillary and viscous forces, which, in turn, will have a considerable influence on the injection, migration, displacement, and storage capacity and integrity of CO₂ processes. In this study, an experimental investigation has been performed to explore the impact of fluid pressure, temperature, and injection rate, as a function of CO₂ phase, on the dynamic pressure evolution and the oil recovery performance of CO₂ during oil displacement in a Berea sandstone core sample. The results reveal a considerable impact of the fluid pressure, temperature, and injection rate on the differential pressure profile, cumulative produced volumes, endpoint CO₂ relative permeability, and oil recovery; the trend and the size of the changes depend on the CO₂ phase as well as the pressure range for gaseous CO₂–oil displacement. The residual oil saturation was in the range of around 0.44–0.7; liquid CO₂ gave the lowest, and low-fluid-pressure gaseous CO₂ gave the highest. The endpoint CO₂ relative permeability was in the range of about 0.015–0.657; supercritical CO₂ gave the highest, and low-pressure gaseous CO₂ gave the lowest. As for increasing fluid pressure, the results indicate that viscous forces were dominant in subcritical CO₂ displacements, while capillary forces were dominant in supercritical CO₂ displacements. As temperature and CO₂ injection rates increase, the viscous forces become more dominant than capillary forces.

Keywords: CO₂ sequestration; CO₂-EOR; CO₂ phase; differential pressure; capillary forces; viscous forces

1. Introduction

The amounts of oil produced during primary and secondary oil recoveries are around one-third of the original oil in place. The growing world energy demand, decline in the exploration of new oil reservoirs, and maturity of oil fields that produce most of the hydrocarbons are motivating oil companies to develop new enhanced oil recovery techniques [1]. Generally, enhanced oil recovery techniques are categorized into three main methods: thermal, chemical, and gas recovery methods. Thermal recovery methods have their limitations; they are not suitable for heavy oil reservoirs if the formations are thin (<10 m) or too deep (>1000 m) due to heat loss to surrounding formations [2]; they are also not suitable for reservoirs with low permeability and low oil saturation [3]. Chemical flooding methods are a good candidate, but they are generally not implemented because of their high cost.

Recently, application of CO₂ for CO₂ enhanced oil recovery (CO₂-EOR) has gained much momentum as it can be used to enhance oil recovery with the added benefit of reducing CO₂ emissions.
into the atmosphere [4] via CO₂ sequestration processes [5]. It is estimated that about 80% of oil reservoirs around the world are good candidates for CO₂-EOR processes [6]. The injection of CO₂ can increase oil recovery through a number of different mechanisms, firstly by displacing oil that is left behind during water displacement. Moreover, it can enhance oil recovery gradually over years through a number of different mechanisms, including oil swelling, viscosity reduction, capillary impact reduction via CO₂–oil interfacial tension (IFT) reduction [7], oil extraction [2,8–10], permeability alteration [11], mass transfer through diffusion and dispersion, and miscibility [12]. Oil viscosity can drop significantly by about 90% of its original value upon mixing with the injected CO₂ [13,14], increasing its mobility. Oil swelling due to CO₂ dissolution can enhance oil recovery by expelling oil out of the matrix and increasing oil volume above the residual saturation, leading more oil to flow. Reduction in residual oil saturation can also be achieved by oil extraction upon exposing the oil to a sufficient flow of CO₂-rich gas [7]. However, the evaporation of light components of the oil into CO₂ may cause oil to increase in density [7]. It is worth mentioning that the extraction mechanism is inversely related to oil density. Thus, the heavy crude oils are less influenced by this mechanism in comparison to light crude oils [2]. The contribution of each aforementioned mechanism to oil recovery is controlled by the pressure, temperature, and CO₂ solubility.

The injected CO₂ can displace oils through miscible, near miscible, and immiscible CO₂ flooding depending on the pressure and temperature conditions and oil reservoir characteristics [15]. Miscible CO₂ processes are the most attractive scenario for oil recovery due to their high displacement efficiency [2]. The dissolution of CO₂ in the oil phase can substantially improve oil recovery [2] by avoiding the adverse effect of gas–oil interfacial tension, i.e., eliminating trapping forces [2,14]. However, miscible displacements can only be achieved when the reservoir pressure is higher than the minimum miscibility pressure (MMP), which is not the case for the mature oil fields due to the depletion of energy and the low permeability formations due to the high-differential pressure drop between injector and producer wells [15]. The MMP depends on CO₂ purity, temperature, and oil composition [16]; the MMP decreases when the reservoir pressure increases or the reservoir temperature decreases [13]; Yellig and Metcalf observed that increasing CO₂ temperature by 1 °F (≈0.56 °C) over a temperature range from 95 to 192 °F (35–89 °C) caused the MMP to increase by approximately 15 psi (1 bar) [13]. Near miscible flooding refers to the process of not having a full miscibility and occurs when CO₂ is injected at a pressure slightly below the MMP [15,17]. The main displacement mechanisms are oil swelling, oil viscosity reduction, oil extraction, and IFT reduction that leads to favourable conditions [17,18]. On the other hand, immiscible CO₂ flooding is a promising and a field-proven method [19] that occurs when reservoir pressure is less than the MMP. Maximum oil recovery can be achieved with this method when the injected CO₂ is sufficient to saturate the oil and water. The key factor that governs the success of the CO₂ immiscible displacement is the availability of enough resources of CO₂ at low cost [19]. This technique can be used for low-pressure reservoirs (≤1000 m depth) and thin and heavy oil reservoirs (10–25° API and >3000 m depth [20]) where thermal recovery processes are generally unsuitable [3,20]), with moderately viscous oils [8], and for some shallow-light oil reservoirs where the pressure needed for miscibility cannot be achieved [19]. This technique can also be deployed with gravity-assisted injection into the top of a reservoir [21].

Due to great variations in subsurface conditions of pressure and temperature, the injected CO₂ can exist in a gaseous state in warm coal seams (e.g., Alabama Black Warrior Basin: ∼70 bar, 22.85 °C), a liquid state in permafrosts and marine sediments (e.g., West Sak reservoir: ∼110–125 bar, 23.9 °C), and a supercritical state in deep hot rocks (e.g., Weyburn oil field: ∼140 bar, 49.85 °C) [22–27], as shown in Figure 1. An example where the injected CO₂ can exist in both gaseous and liquid CO₂ state is the mature oil fields of the Illinois Basin (USA) that have underground reservoir temperature close to the critical temperature (31.1 °C) [27].
were conducted under more than one CO₂ state. Sankur [44] performed reservoir condition-gaseous 
CO₂ displacements to study the performance of CO₂ miscible flooding in tight oil reservoirs. The average oil recovery 
ranged by around 3.9% and 8.59%, respectively. Arshad [46] performed supercritical CO₂ displacements to 
study the performance of CO₂ miscible flooding in tight oil reservoirs. The average oil recovery 
behaviour during its injection into an oil-saturated porous system.

Since CO₂ has been in use for several decades, extensive laboratory studies [38,39], numerical 
simulations, and field applications of CO₂ flooding have been conducted in various light, medium, [40] 
and heavy oil reservoirs [41]. A review of current literature showed that CO₂–oil displacements have 
been conducted to investigate different topics such as (a) oil displacement efficiency and mechanisms, 
especially in relation to phase behaviour [10], (b) oil displacement efficiency and mechanisms associated 
with the injection of liquid CO₂ and CO₂-foam in heavy crude oil [2], (c) the relation between oil 
recovery and viscosity [42], (d) the effect of viscous forces, diffusive, and gravitational forces on the 
CO₂ slug (20% hydrocarbon pore volume (HCPV)) for heavy oil recovery processes [20], and (e) the 
phenomena of reservoir blockage and oil production drop [43].

However, the literature review also revealed that CO₂–oil displacements were conducted either 
under gaseous, liquid, or supercritical CO₂ conditions with the exception of a few experiments that 
were conducted under more than one CO₂ state. Sankur [44] performed reservoir condition-gaseous 
displacements of oil by CO₂ and refinery gas for the Wilmington Tar zone CO₂ injection project. 
Their results showed that the injection of CO₂ enhances the recovery to a greater extent than that 
of the refinery gas for continuous or low water alternating gas (WAG). Moradi [45] conducted a 
umerical simulation to investigate the impact of liquid CO₂ injection on oil recovery. Liquid CO₂ 
 injection yielded 14.79% oil recovery, which was higher than water flooding and natural depletion 
by around 3.9% and 8.59%, respectively. Arshad [46] performed supercritical CO₂ displacements to 
study the performance of CO₂ miscible flooding in tight oil reservoirs. The average oil recovery ranged

Figure 1. The pressure and temperature ranges at which saline aquifers are found underground adopted from Saraji et al. [24].
from 87 to 96%. Chung [47] performed supercritical CO$_2$ core flooding experiments to examine the technical feasibility of the use of CO$_2$ flooding to enhance the recovery of viscous oil under immiscible displacements conditions. They found that CO$_2$ injection resulted in a higher recovery (66% of original oil in place (OOIP)) in comparison to waterflood (44% of OOIP). In addition, the CO$_2$-alternate-brine injection significantly delayed the breakthrough of gas, produced slightly more oil and was a more efficient in CO$_2$ utilization than continuous injection [47]. Huang [10] performed continuous immiscible supercritical CO$_2$ flooding, at 90 °F (32.2 °C) and 1250 psi (86.2 bar), into Texas oil (36° API) saturated watered-out cores to determine the oil recovery efficiency and improve the understanding of oil recovery mechanisms, especially in relation to phase behaviour. The data showed an oil recovery of 69% and 66% of residual oil from a 6 ft Berea and 20 ft sand-packed core sample, respectively. They attributed the oil recovery mainly to the CO$_2$ swelling and CO$_2$ extraction of oil.

On the other hand, Wang [40] carried out both gaseous and liquid CO$_2$ oil recovery displacements under immiscible and miscible conditions to examine oil recovery and permeability reduction in a tight sandstone reservoir. They noticed that during immiscible flooding, the oil recovery was higher when the fluid pressure was between the onset pressure of asphaltenic precipitation and the MMP; nonetheless, the effective permeability reduction of the oil was greater at higher fluid pressure. Cao [48] conducted both immiscible and miscible CO$_2$ floodings into light crude oil saturated tight sandstone core plugs at gaseous and supercritical CO$_2$ conditions. The oil recovery increased monotonically as pressure increased during the immiscible flooding. Liu [5] conducted gaseous and supercritical near-miscible CO$_2$ floodings to examine the displacement front characteristics. The supercritical CO$_2$ displacements gave higher oil recovery in comparison to gaseous displacements. Lashkarbolooki [49] and Bayat [50] investigated the recovery efficiency during the injection of supercritical CO$_2$ and supercritical N$_2$ into a live crude oil. The core-flood experiments showed that supercritical CO$_2$ injection, compared with supercritical N$_2$ injection (8.7% of OOIP), could result in a higher recovery (15.8% of OOIP).

Despite the extensive research on CO$_2$–oil displacements, the analysis of the pressure data in core flooding has been widely overlooked despite its high importance [51]. To the best of the authors’ knowledge, there is no study that has been conducted to investigate the effect of CO$_2$ phase on the dynamic pressure evolution and the oil recovery performance during CO$_2$–oil drainage core floodings. In this study, drainage experiments were performed by injecting pure CO$_2$ into an oil-saturated Berea sandstone core sample to investigate the effect of fluid pressure, temperature, and injection rate on the pressure and production behaviour under gaseous, liquid, and supercritical CO$_2$ conditions, especially focusing on the differential pressure profile, cumulative produced volumes, residual oil saturation, and endpoint effective and relative permeabilities of CO$_2$. The results of this study will provide deep insights into the impact of CO$_2$ phase on the injectivity, displacement efficiency, storage capacity, and integrity of CO$_2$ flooding.

2. Materials and Experimental Setup

A Berea sandstone core sample with a diameter of 2.54 cm and a length of 7.62 cm was used for the unsteady state dynamic drainage experiments (CO$_2$–oil displacements). The average porosity and absolute water permeability of the core sample were about 20% and 28.9 mD, respectively. To calculate the core sample pore volume and porosity, the weight difference between the dry and the wet core sample was used. To calculate the absolute water permeability, the steady differential pressure and the water injection rate was used. To alter the core sample wettability to an oil-wet state, the core sample was aged inside the oil at 80 °C for more than eight months.

2.1. Experimental Setup

The schematic of the experimental core flooding setup for this study is shown in Figure 2. It consists of two high-pressure syringe pumps (Teledyne ISCO, Lincoln, NE, USA) with flow rates ranging from 0.0001 to 25 mL/min for the CO$_2$ injection and the CO$_2$ and oil collection, a water bath
When the experiment was finished, the produced volumes were measured to calculate the residual oil saturation with mass balance. Later, the weight of the core sample was measured using a Sartorius weighing scale with a resolution of 0.0001 g to confirm the residual oil saturation measurements.

2.2. CO₂–Oil Displacement Procedure

The three phases (G, L, and Sc) CO₂–oil drainage displacements were performed on an oil-wet Berea sandstone core sample with the following steps:

1. The core sample was wrapped into a shrinkable Teflon tube followed by a rubber sleeve and then fixed inside the core holder. The core holder was mounted horizontally inside the water bath.

2. To prevent fluid bypassing, a confining pressure of about 135 bar, which is always higher than the pore pressure, was applied to the core with the confining pump. The temperature was controlled by the heater.

3. The vacuum pump was connected to the system to remove the trapped gas.

4. To fully saturate the core sample with oil, about 40–60 pore volumes (PVs) of oil were injected at a high-differential pressure of 80–90 bar.

5. To obtain heat equilibrium, the water bath temperature was set to the required temperature and the system was left overnight for the temperature to stabilize.

6. Prior to each flooding experiment, a constant pressure was applied to the entire system using the syringe pump at each end.

7. After reaching the experimental pressure, the system was left for about 20 min to ensure that temperature stabilization had been achieved throughout the system.

8. The mode of the injected pump (ISCO pump CO₂) was changed from a constant pressure mode to a constant flow rate mode to inject CO₂ into the core at a constant injection rate to displace the saturated oil. The injected CO₂ volumes and the collected volumes were recorded every 30 s.

9. During the experiment, the inlet and outlet pressure transducer readings were recorded every 6 s, using the LabVIEW software, in order to calculate the differential pressure across the core sample.

10. When the experiment was finished, the produced volumes were measured to calculate the residual oil saturation with mass balance. Later, the weight of the core sample was measured using a Sartorius weighing scale with a resolution of 0.0001 g to confirm the residual oil saturation measurements.
3. Results and Discussion

To gain a deep understanding of the effect of CO\(_2\) phase on the two-phase flow characteristics of CO\(_2\)–oil drainage displacements, the inlet and outlet pressure, the outlet CO\(_2\) and oil flow rates, the differential pressure profile, the cumulative injected and cumulative produced volumes, the residual oil saturation, and the endpoint effective and relative permeabilities of CO\(_2\) were measured and analysed.

The differential pressure profile was obtained by taking the difference between the readings of the pressure transducers at the inlet and outlet sides of the core sample. The most influential forces that govern the differential pressure of a drainage displacement during horizontal injection are the capillary forces and the viscous forces [20]. The capillary forces are governed by the CO\(_2\)–oil interfacial tension, contact angle, and pore diameter and geometry [52–55] as well as the saturation of the displacing and displaced fluids. The capillary forces arise from the presence of the interface between the immiscible fluids [53]; they are responsible for the entrapment of one phase by another during immiscible displacements in porous media [54,56]; and they govern the multiphase flow in low permeability rocks and fractured reservoirs [57]. The viscous forces are controlled by the viscosity contrast between the displacing and displaced fluids, injection rate of the injected fluid, the permeability and length of the invaded porous media.

In the literature, various formulations have been suggested to account for the impact of the capillary and viscous forces on the differential pressure profile. Recently, Espinoza and Santamarina [22] proposed the following equation to account for these forces:

\[
\Delta P = P_{CO_2} - P_{Oil} = 4 \frac{\sigma_{CO_2-Oil} \cos \theta}{d} + v \frac{32 l}{d^2} \left( \frac{l_{CO_2} \mu_{CO_2} + l_{Oil} \mu_{Oil}}{L} \right)
\]

where \(\Delta P\) is the differential pressure across the core sample (Pa). \(P_{CO_2}\) and \(P_{Oil}\) are the CO\(_2\) and bulk oil pressures, respectively. \(\sigma_{CO_2-Oil}\) is the CO\(_2\)–oil interfacial tension (mN/m), \(d\) (m) is the diameter of the largest effective pore [58–61], \(L\) (m) is the length of the core sample, \(l\) (m) is the length of the CO\(_2\) or oil phase inside the core sample, \(v\) (m/s) is the fluid velocity in the pores, and \(\mu\) (Pa\cdot s) is the viscosity of the fluids. The first and second terms on the right-hand side of Equation (1) refers to the Young–Laplace equation and Poiseuille’s equation, respectively [22,62]. The Young–Laplace equation can be used to determine the critical pressure point, which is the excess pressure required for the displacing fluid to invade the core sample for the first time. The non-wetting fluid cannot invade the core sample unless its differential pressure exceeds the critical pressure point [61].

In addition to the Young–Laplace equation, a number of analytical capillary pressure formulations have been used to explain laboratory results [63,64]. Among them, the Leverett’s J-function has been intensively used to convert all the capillary pressure \((P_c)\) data, as a function of the invaded fluid saturation, to a universal curve.

\[
J(S_{g}^*) = \frac{P_c}{\sigma \cos \theta} \sqrt{\frac{k}{\phi}} = a(S_{g}^*)^{-b}
\]

where

\[
S_{g}^* = \frac{S_g - S_{gr}}{1 - S_{gr}}
\]

where \(S_{g}^*\) is the effective or normalized gas saturation. \(a\) and \(b\) are coefficients. \(\sqrt{\frac{k}{\phi}}\) is the pore geometry factor or (hydraulic radius), which has a similar dimension to the pore radius and is used to correlate petrophysical properties such as relative permeability and saturation.

In this study, the quasi-differential pressure refers to the differential pressure measured at the end of the displacement experiment. The corresponding time represents the time required to achieve the maximum-differential pressure at the start of the experiment. The data are categorized into three main sections. The first main section deals with the impact of fluid pressure, experimental temperature,
and injection rate on the differential pressure profile as a function of CO\textsubscript{2} phase. The second and the third sections deal with their impact on the production data profiles including the endpoint effective and relative permeabilities of CO\textsubscript{2} and the residual oil saturation as a function of CO\textsubscript{2} phase, respectively.

3.1. The Pressure Behavior of CO\textsubscript{2}–Oil Displacements as a Function of CO\textsubscript{2} Phase

This section deals with the impact of fluid pressure, experimental temperature, and injection rate on the differential pressure profile of gaseous, liquid, and supercritical CO\textsubscript{2} displacements.

3.1.1. The Effect of Fluid Pressure on the Differential Pressure Profile of CO\textsubscript{2}–Oil Displacements

Figures 3–6 present the impact of increasing fluid pressure on the differential pressure profile of gaseous, liquid, and supercritical CO\textsubscript{2} drainage displacements. During the experiments, the experimental temperature and CO\textsubscript{2} fluid rate were held constant. The data from Figures 3–6 reveal three important observations (A, B, and C) that can be identified as follows:

(A) For all fluid pressures, the differential pressure profile is characterized by a high increase followed by a sharp decline; the rate and the magnitude of the increase in the differential pressure profile are dependent on the CO\textsubscript{2} phase as well as the fluid pressure for gaseous CO\textsubscript{2} displacements. The slope of the reduction in the differential pressure profile decreased over time and is dependent on the CO\textsubscript{2} phase and the fluid pressure for the gaseous CO\textsubscript{2} displacements. Based on the shape of the differential pressure profile, the data is discussed and analysed in two groups. The first group deals with the low-fluid-pressure GCO\textsubscript{2}–oil displacements (fluid pressure \(\leq 60\) bar), while the second group deals with the high-fluid-pressure GCO\textsubscript{2}–oil displacements, LCO\textsubscript{2}–oil displacements, and ScCO\textsubscript{2}–oil displacements.

(A.1) Figure 3 shows the differential pressure profile of the low-fluid-pressure GCO\textsubscript{2} displacements. The differential pressure profile is characterized by a slow but significant increase until its maximum value is reached, after around 1.2 pore volumes (PV) of CO\textsubscript{2} was injected; then, it is characterized by a slow and slight reduction over time; with the slope of the reduction decreasing over time. Increasing fluid pressure reduced the magnitude of the entry pressure and its associated time before CO\textsubscript{2} breakthrough. For illustration, as the fluid pressure increased from 40 to 60 bar, the entry pressure decreased from 1.196 to 0.883 bar and the associated time reduced from around 12.5 to 7.2 min.

The initial increase in the differential pressure profile was to overcome the fluid entry pressure. The reduction in the entry pressure and the associated time as fluid pressure increases can be related to the reduction in the capillary forces due to the reduction in the interfacial tension, as shown in Figure 7, and the increase in the contact angle, respectively. The slow and slight reduction in the differential pressure over time might indicate a slight and slow change in the effective permeability of CO\textsubscript{2} and oil due to the low-efficiency displacement of the CO\textsubscript{2}–oil experiments performed at low-pressure conditions. The low-efficiency displacement might arise from high capillary forces due to high interfacial tension [65] and high mobility contrast at these conditions.

(A.2) Figures 4–6 presents the differential pressure profile of the high-fluid-pressure gaseous, liquid, and supercritical CO\textsubscript{2}–oil displacements. For all displacements, the differential pressure profile is characterized by a high increase until its maximum-differential pressure value is reached, after the injection of around 0.08–0.155 PVs of CO\textsubscript{2}, and a steep reduction is then experienced until its quasi-differential pressure value is achieved, after around 0.08–0.155 PVs. The maximum-differential pressure varied with the phase of the injected CO\textsubscript{2}. Liquid CO\textsubscript{2} phase gave the highest magnitudes, while gaseous CO\textsubscript{2} phase gave the lowest. The highest maximum differential pressure profile of the LCO\textsubscript{2} displacements might be attributed to the fact that liquid CO\textsubscript{2} phase is less miscible with oil [2] in comparison to gaseous and supercritical CO\textsubscript{2} phases. The result of less miscibility of the liquid CO\textsubscript{2} was a lower reduction in the CO\textsubscript{2}–oil interfacial tension and the oil viscosity when the liquid CO\textsubscript{2} phase was injected; thereby, the highest differential pressure was obtained. Nonetheless, it might
be proposed that the highest differential pressure of the LCO\textsubscript{2}–oil displacements was because LCO\textsubscript{2} displacements were conducted at 20 °C, while GCO\textsubscript{2} and ScCO\textsubscript{2} displacements were performed at 33 °C; thus, the large temperature difference, 13 °C, which caused a sharp reduction in oil viscosity, could be responsible for the difference in the differential pressure. However, we believe this is not the reason because the LCO\textsubscript{2} displacements performed at 29 °C, as shown in Figure 11, also show much higher differential pressure profile than that of GCO\textsubscript{2} and ScCO\textsubscript{2} displacements performed at 33 °C, despite the smaller temperature difference between these, which was only 4 °C.

The observed high increase in the differential pressure after the injection of CO\textsubscript{2} into the core sample can be associated with the increase in pore pressure due to CO\textsubscript{2} invasion [66]. According to Equations (1) and (2), the reduction in the differential pressure can be related to both capillary forces and viscous forces. The reduction in the viscous forces can be related to the combined effect of the relative permeability of CO\textsubscript{2} and oil and the replacement of a highly viscous fluid (CO\textsubscript{2}) with a less viscous one (CO\textsubscript{2}) [66,67]. The reduction in the capillary forces can be associated with the number of pores that were opened to flow by CO\textsubscript{2}, as CO\textsubscript{2} flooding continued after its breakthrough. This agrees with the findings of Kwelle [68], who found that the resistance of capillary pore to two-phase flow (CO\textsubscript{2} and water) is much greater than its resistance to single-phase flow (water or CO\textsubscript{2}). Thus, as the number of the opened pores increased, the two-phase flow is significantly reduced, and the pore resistance to the injection of CO\textsubscript{2} flow is significantly reduced. Therefore, the differential pressure is sharply reduced [68].

(B) The differential pressure profile of the low-fluid-pressure GCO\textsubscript{2} displacement is characterized by oscillations that increased with increased fluid pressure; for illustration, as the fluid pressure increased from 40 to 60 bar, the oscillations increased from one to three times over the duration of the experiment, as shown in Figure 3. The appearance of the oscillations in the differential pressure profile can be related to the impact of the capillary forces at the trailing end of the CO\textsubscript{2}–oil slug [67]. According to Nutt, the impact of capillary forces at the trailing end of a CO\textsubscript{2}–oil slug is dependent on whether a non-wetting or a wetting fluid is flooded. If a non-wetting fluid (e.g., CO\textsubscript{2}) is flooded, then the capillary forces will oppose the applied viscous forces. Later, with the diminishing of the viscous pressure drop across the core sample due to the progress of oil depletion, it is possible to reach a point at which the flow of CO\textsubscript{2} through non-depleted capillaries is prevented by the capillary forces [67]. Hildenbrand et al. observed that the reduction in the excess pressure in the non-wetting phase after gas breakthrough will ultimately lead to a re-imbibition process for the wetting phase [69]. This re-imbibition process begins with the smallest pores and continues progressively to the larger pores. Consequently, it causes a progressive reduction in the relative permeability of the non-wetting phase because of the successive loss of the interconnected flow paths. In the end, when the last interconnected flow path for the non-wetting phase is closed, the permeability of the non-wetting phase will drop to zero [69]. Figure 8 exhibits this re-imbibition process.

The observed oscillations, in Figure 3 as an example, indicate that as the interconnected flow paths for the non-wetting phase (CO\textsubscript{2}) were closed, the inlet pressure and hence the differential pressure increased due to the continuous injection of CO\textsubscript{2}. Once the differential pressure became high enough to overcome the capillary forces, the blocked pores opened to flow, leading to the quick release of accumulated CO\textsubscript{2}, which, in turn, caused a quick reduction in the differential pressure.

However, increasing the frequency of differential pressure oscillations can be attributed to the reduction in the capillary forces and the increase in gas density. An increasing gas density and decreasing capillary forces mean less time was needed to reach a pressure value that is sufficient to overcome the capillary forces, thus pushing the oil that blocks production out of the sample and in turn increasing the differential pressure oscillation frequency.

Nonetheless, since the CO\textsubscript{2}–oil displacements can be strongly affected by the capillary end effect and viscous instabilities [35], the appearance of the oscillations might be related to the impact of the capillary retention due to the discontinuity of the capillary pressure [51]. The capillary end effect arises at both the inlet and outlet faces of the core sample, but its severances increase at the outlet face.
Müller [35] concluded that the impact of the capillary end effect can never be entirely prevented but can be corrected for it. Rapoport and Leas [70] proposed a scaling coefficient for the minimization of the capillary retention and viscous instabilities effects. According to their formula, the capillary retention can be minimized if the scaling coefficient is greater than one:

\[ \mu \geq 1 \]  

(C) Increasing fluid pressure led to an increase in the differential pressure profile for the displacements conducted under subcritical conditions but caused a reduction for the displacements performed at supercritical conditions; the magnitude of the change depends on the CO\(_2\) phase and the pressure range for GCO\(_2\) displacements. The highest percentage increase occurred in the low-fluid-pressure GCO\(_2\) displacements, whilst the lowest occurred in LCO\(_2\) displacements.

For low-fluid-pressure GCO\(_2\) displacements, increasing the fluid pressure from 40 to 60 bar caused the maximum-differential pressure to increase by around 93% (from 1.196 to 2.306 bar), and the differential pressure at the end of the displacements to rise by around 155% (from 0.411 to 1.049 bar), as shown in Figure 3. However, for high-fluid-pressure GCO\(_2\) displacements, increasing the pressure from 65 to 70 bar caused the maximum-differential pressure to increase by around 6% (from 3.248 to 3.438 bar), the quasi-differential pressure to rise by about 30% (from 0.536 to 0.699 bar), and the corresponding time to increase by around 27% (from 1.5 to 1.9 min). For LCO\(_2\) displacements, as the pressure increased from 70 to 90 bar, the maximum-differential pressure increased by around 49% (from 3.533 to 5.26 bar), the quasi-differential pressure increased by 37.5% (from 0.272 to 0.374 bar), and the corresponding time increased by around 6.7% from (3 to 3.2 min). On the other hand, increasing pressure from 75 to 90 bar for ScCO\(_2\) displacements caused the maximum-differential pressure to decrease by 33.3% (from 2.345 to 1.564 bar), the quasi-differential pressure to decline by around 56% (from 0.134 to 0.059 bar), and the corresponding time to decrease by 36% (from 2.5 to 1.6 min).

According to Equation (1), the observed increase in the differential pressure of the subcritical displacements as fluid pressure increased means that the impact of viscous forces was higher than that of capillary forces. The observed increase in the differential pressure is a combination of the increase in the viscous forces and the reduction in the capillary forces. The increase in the fluid pressure leads to an increase in the viscous forces owing to the increase in the CO\(_2\) and oil viscosities and the injection rate inside the core sample due to the expansion effect. The reduction in the capillary forces with increasing fluid pressure is because of the reduction in the CO\(_2\)–oil interfacial tension [65] and the increase in contact angle [71] due to increasing CO\(_2\) solubility [41,72,73]. The highest increase in the differential pressure as pressure increases can be related mainly to the increase in the CO\(_2\) injection rate due to expansion. The gas expansion occurs due to the temperature difference between the inside and outside of the water bath [74,75]. The change in density leads to a change in the injection rate inside the core sample. The density ratio \((d_r)\) [74] has been used to explain gas expansion and to calculate the injection rate inside core samples. For instance, at an experimental pressure of 40 bar, an injection rate of 1 cm\(^3\)/min at 20 °C becomes 1.108 cm\(^3\)/min at 33 °C.

\[ d_r = \frac{d_{\text{CO}_2 20 \, ^\circ\text{C}, 40 \, \text{bar}}}{d_{\text{CO}_2 33 \, ^\circ\text{C}, 40 \, \text{bar}}} \]  

On the other hand, the reduction in the differential pressure of the supercritical CO\(_2\) displacements as fluid pressure increased means that the reduction in capillary forces was higher than the increase in viscous forces. According to the J-function (Equation (2)), the reduction in the capillary forces can be related to the reduction in the IFT, the increase in contact angle, and the reduction of CO\(_2\) saturation, i.e., increase residual oil recovery. The data from Section 3.3 show that, as pressure increased, the residual oil saturation decreased; therefore, CO\(_2\) saturation was not responsible for the reduction in the differential pressure. The interfacial tension decreases with the increase in pressure and the reduction in temperature [41], as shown in Figure 7. No reduction in the differential pressure was
observed during the subcritical displacements, despite the reduction in their interfacial tension as pressure increased. This indicates that the reduction in the IFT is not the main factor responsible for the observed reduction in the differential pressure profiles of supercritical CO₂ displacements. The only possible factor that causes the reduction in the differential pressure is the contact angle. This agrees with the findings by Yang [30], Liu [76], and Jung and Wan [77]. Yang [30] and Liu [76] observed that supercritical CO₂ has a higher ability than gaseous and liquid CO₂ to alter reservoir rocks towards less water-wetting. Jung and Wan [77] found that, at a pressure higher than the CO₂ critical pressure (larger than 73.8 bar), the contact angle increases sharply with a pressure rise up to 100 bar. Below the critical pressure, or above 100 bar, the contact angle remained fairly constant.

**Figure 3.** Effect of fluid pressure on the differential pressure profile of low-pressure GCO₂–oil displacements conducted at 0.4 mL/min and 33 °C.

**Figure 4.** Effect of fluid pressure on the differential pressure profile of high-pressure GCO₂–oil displacements conducted at 0.4 mL/min and 33 °C.
3.1.2. The Effect of Temperature on the Differential Pressure Profile of CO₂–Oil Displacements

Figures 9–12 show the effect of increasing experimental temperature on the differential pressure profile of gaseous, liquid, and supercritical CO₂–oil drainage displacements. The results reveal that increasing temperature led to a reduction in the differential pressure for both subcritical and supercritical displacements. The increase in temperature resulted in the appearance of differential pressure (PD) oscillations for the gaseous and supercritical CO₂ displacements but not for the liquid CO₂ displacements. The highest reduction in the differential pressure profile as temperature increased occurred in the high-fluid-pressure and then low-fluid-pressure gaseous CO₂ displacements, followed by supercritical CO₂ and then finally by liquid CO₂ displacements.

**Figure 5.** Effect of fluid pressure on the differential pressure profile of LCO₂–oil displacements conducted at 0.4 mL/min and 20 °C.

**Figure 6.** Effect of fluid pressure on the differential pressure profile of ScCO₂–oil displacements conducted at 0.4 mL/min and 33 °C.

**Figure 7.** Interfacial tension (IFT) tension for CO₂-crude oils (WO = Weyburn crude oil-CO₂ system against equilibrium pressure data at T = 27 °C [78]; A-0 and B-0 = Iranian crude oils at 49.85 °C [79]; BGA-13 = Iranian crude oil at 48.85 °C [80].
Figure 7. Interfacial tension (IFT) tension for CO$_2$-crude oils (WO = Weyburn crude oil-CO$_2$ system against equilibrium pressure data at T = 27 °C [78]; A-0 and B-0 = Iranian crude oils at 49.85 °C [79]; BGA-13 = Iranian crude oil at 48.85 °C [80].

Figure 8. Re-imbibition process in fine-grained rocks (schematic re-imbibition): (A) drainage, (B) an initially water-saturated sample, (C) gas breakthrough, and (D) re-imbibition [69].

3.1.2. The Effect of Temperature on the Differential Pressure Profile of CO$_2$–Oil Displacements

Figures 9–12 show the effect of increasing experimental temperature on the differential pressure profile of gaseous, liquid, and supercritical CO$_2$–oil drainage displacements. The results reveal that increasing temperature led to a reduction in the differential pressure for both subcritical and supercritical displacements. The increase in temperature resulted in the appearance of differential pressure (PD) oscillations for the gaseous and supercritical CO$_2$ displacements but not for the liquid CO$_2$ displacements. The highest reduction in the differential pressure profile as temperature increased occurred in the high-fluid-pressure and then low-fluid-pressure gaseous CO$_2$ displacements, followed by supercritical CO$_2$ and then finally by liquid CO$_2$ displacements.

Figure 9. Effect of experimental temperature on the differential pressure profile of low-fluid-pressure GCO$_2$–oil displacements conducted at 0.4 mL/min and 40 bar.

![Diagram of re-imbibition process in fine-grained rocks](image-url)
For low-fluid-pressure GCO₂ displacements conducted at 40 bar, increasing the temperature from 33 to 55 °C caused the maximum-differential pressure to decrease by around 69% (from 1.196 to 0.371 bar), the quasi-differential pressure to drop by around 81% (from 0.406 to 0.076 bar), and the corresponding time to decline by 67.5% (from 12.3 to 4 min). However, for high-fluid-pressure GCO₂ displacements performed at 70 bar, increasing the temperature from 33 to 55 °C caused the maximum-differential pressure to decrease by around 70.6% (from 3.438 to 1.01 bar), the quasi-differential pressure to decline by 88% (from 0.684 to 0.082 bar), the corresponding time to decrease by about 76% (from 2.9 to 0.7 min), and the differential pressure oscillations to appear for the first time. It should be noted that, as the temperature increased from 45 to 55 °C, the quasi-differential pressure increased slightly by around 17% (from 0.082 to 0.096 bar). This increase might be associated with the appearance of the differential pressure oscillations. The appearance of the oscillations indicates that the 55 °C displacement is characterized by a stronger impact of the capillary forces than the 45 °C displacement; thereby, a high quasi-differential pressure occurred in the 55 °C displacements.
For LCO₂ displacements, as the temperature increased from 20 to 29 °C, the maximum-differential pressure decreased by around 7.6% (from 5.26 to 4.858 bar), the quasi-differential pressure declined by around 58% (from 0.365 to 0.154 bar), and the corresponding time dropped by around 37.5% (from 3.2 to 2 min). The slight reduction in the maximum-differential pressure of the liquid CO₂ displacements as temperature increased is likely to be associated with the smaller increase in the experimental temperature (20–29 °C), the dense-nature of liquid CO₂, and the lower miscibility of liquid CO₂ with oil [2] in comparison to that of gaseous and supercritical CO₂ displacements.

For ScCO₂ displacements, increasing the temperature from 33 to 55 °C caused the maximum-differential pressure to decrease by 28.7% (from 1.564 to 1.115 bar), the quasi-differential pressure to decline by around 54% (from 0.059 to 0.027 bar), the corresponding time to decline by around 56% (from 1.6 to 0.7 min), and the differential pressure oscillations to appear for the first time. The appearance of the differential pressure oscillations as temperature increased can be related to the reduction in the applied viscous forces and the increase in the capillary forces due to the increasing interfacial tension [65,78] and the decreasing contact angle [71]. Importantly, the point at which the capillary forces were insufficient to overcome the viscous forces occurred at 55 °C, leading to the blockage of CO₂ production during these oscillations.

According to Equation (1), the reduction in the maximum and quasi-differential pressures as temperature increases is the net result of the increase in capillary forces and the reduction in viscous forces. As temperature increases, capillary forces increase because of the increasing CO₂–oil interfacial tension [65,78] and the decreasing contact angle [71] due to the decreasing CO₂ solubility [72,73], while the viscous forces decrease because of the decreasing viscosities of oil and CO₂. However, the change in CO₂ viscosity is likely to have little impact on the reduction in the viscous forces in comparison to that caused by oil viscosity reduction as temperature increased. Increasing temperature caused a large reduction in the viscosity of the oil used in these displacements. The oil sample was provided by the BP Exploration Operating Company Limited, but, due to confidentiality, the specified properties of the oil sample cannot be disclosed. Increasing temperature causes only a slight change in CO₂ viscosity; the highest reduction occurred with supercritical CO₂ displacement. For illustration, increasing the temperature from 33 to 55 °C causes the CO₂ viscosity to (1) increase from 16.187 to 17.07 × 10⁻⁶ (Pa-s) for the 40 bar GCO₂ displacement, (2) decrease from 20.743 to 18.9 × 10⁻⁶ (Pa-s) for the 70 bar GCO₂ displacement, and (3) decrease from 53.837 to 22.26 × 10⁻⁶ (Pa-s) for the 90 bar ScCO₂ displacement. On the other hand, increasing temperature from 20 to 29 °C for the liquid CO₂ displacements causes the CO₂ viscosity to decrease from 81.56 to 63.902 × 10⁻⁶ (Pa-s) [81].
3.1.3. The Effect of Injection Rate on the Differential Pressure Profile of CO$_2$–Oil Displacements

Figures 13–16 show the effect of increasing injection rate on the differential pressure profile of gaseous, liquid and supercritical CO$_2$–oil drainage displacements. The results reveal that the increase in the CO$_2$ injection rate led to a substantial increase in the differential pressure for the displacements conducted at both subcritical and supercritical conditions. The magnitude of the increase in the differential pressure depends on the CO$_2$ phase as well as the fluid pressure range for the gaseous CO$_2$ displacements; the highest increase in the maximum-differential pressure occurred in the ScCO$_2$ displacements, and the lowest in the high-fluid-pressure GCO$_2$ displacements conducted at 70 bar.

For low-fluid-pressure GCO$_2$ displacements (40 bar), increasing the injection rate from 0.4 to 1 mL/min caused the maximum-differential pressure to increase by around 34% (from 1.196 to 1.604 bar), the differential pressure at the end of the displacements to increase by around 166% (from 0.408 to 1.084 bar), and the corresponding time to reduce by around 57% (from 12.3 to 5.3 min). However, for higher-fluid-pressure GCO$_2$ displacements performed at 70 bar, increasing the injection rate from 0.4 to 1 mL/min caused the maximum-differential pressure to increase only by around 4.6% (from 3.438 to 3.597 bar), the quasi-differential pressure to decrease by about 31% (from 0.699 to 0.481 min), and the corresponding time to decrease by 72.4% (from 2.9 to 0.8 min). For LCO$_2$ displacements, as the injection rate increased from 0.4 to 1 mL/min, the maximum-differential pressure increased by about 94% (from 3.533 to 6.847 bar), the quasi-differential pressure declined by around 14.34% (from 0.272 to 0.233 bar), and the corresponding time decreased by around 57% (from 12.3 to 5.3 min). For ScCO$_2$ displacements, increasing the injection rate from 0.4 to 1 mL/min caused the maximum-differential pressure to increase by about 105% (from 1.564 to 3.211 bar), the quasi-differential pressure to increase by 54.24% (from 0.059 to 0.091), and the corresponding time to decline by 50% (from 1.6 to 0.8 min).

According to Equation (1), the increase in the differential pressure can be related to the increase in the applied viscous forces due to the increase in the CO$_2$ injection rate. The observed considerable increase in the differential pressure profile with injection rate increased demonstrates the high impact of viscous forces despite the large viscosity contrast between the displacing fluid (CO$_2$) and the displaced one (oil). The observed reduction in the quasi-differential for high-fluid-pressure GCO$_2$ displacements and LCO$_2$ displacements is likely to be related to the increase in the endpoint relative permeability with the increasing injection rate due to increasing viscous forces [66,82,83].

![Figure 13](image)

**Figure 13.** Effect of injection rate on the differential pressure profile of low-pressure GCO$_2$–oil displacements conducted at 40 bar and 33 °C.
Figure 14. Effect of injection rate on the differential pressure profile of high-pressure GCO$_2$–oil displacements conducted at 70 bar and 33 °C.

Figure 15. Effect of injection rate on the differential pressure profile of LCO$_2$–oil displacements conducted at 70 bar and 20 °C.

Figure 16. Effect of injection rate on the differential pressure profile of ScCO$_2$–oil displacements conducted at 90 bar and 33 °C.
3.2. The Production Behaviour of CO₂–Oil Displacements as a Function of CO₂ Phase

This section deals with the impact of fluid pressure and experimental temperature on the cumulative produced volumes and transient outflow rates of CO₂ and oil of gaseous, liquid, and supercritical CO₂ displacements. To avoid repeatability, the impact of injection rate was not presented as it was similar to that presented in the fluid pressure and temperature sections below.

3.2.1. The Effect of Fluid Pressure on Production Behaviour of CO₂–Oil Displacement

Figures 17–19 show the impact of increasing fluid pressure on the cumulative produced volumes. In general, increasing fluid pressure caused an increase in the cumulative produced volumes of low-fluid-pressure GCO₂ displacements but a reduction in the cumulative produced volumes of high-fluid-pressure GCO₂ displacements, LCO₂ displacements, and ScCO₂ displacements. For GCO₂ displacements, increasing fluid pressure reduced the time required to achieve most of the oil production.

![Figure 17. Effect of fluid pressure on the cumulative produced volumes of oil and CO₂ for low-fluid-pressure GCO₂–oil displacements conducted at 33 °C and 0.4 mL/min.](image)

The data from Figure 17 show that the increase in fluid pressure results in an increase in the cumulative produced volumes of the low-pressure GCO₂–oil displacements. As the fluid pressure increased from 40 to 60 bar, the ratio of the cumulative produced volumes to the cumulative injected volumes at the end of the displacements increased from 0.65 to 0.95. The increase is likely to be related to the increase in displacement efficiency and the impact of gas expansion.

The data from Figures 18–20 show that increasing fluid pressure resulted in a decrease in the cumulative produced volumes of high-fluid-pressure GCO₂ displacements, LCO₂ displacements, and ScCO₂ displacements; the highest reduction occurred in the ScCO₂ displacements, while the lowest occurred in LCO₂ displacements. The cumulative produced volumes of the high-fluid-pressure GCO₂ displacements at the end of experiment were higher than the total cumulative injected volumes. On the other hand, the cumulative produced volumes of the LCO₂ and ScCO₂ displacements were less than the total cumulative injected volumes. The observed reduction in the cumulative produced volumes as fluid pressure increased can be related to the increase in gas compressibility and CO₂ solubility [72,73]. As the fluid pressure increased from 65 to 70 bar for the high-pressure GCO₂ displacements, the ratio of the total produced volumes to the total injected volumes at the end of displacements decreased from 1.05 to 1.02%. As the fluid pressure increased from 70 to 80 bar and then to 90 bar for the LCO₂ displacements, the ratio of the total produced volumes to the total injected volumes at the end of displacements decreased from 92.6 to 91.6% and then to around 90.6%. This means that every 10 bar increase in fluid pressure led to about a 1% reduction in production volumes. However, as the fluid pressure increased from 75 to 80 bar sand then to 90 bar for the ScCO₂ displacements, the ratio of the total produced volumes to total injected volumes at the end
of displacements decreased from 99.5 to 97.5% and then to around 91.5%. It is worth noting that the increase in the cumulative produced volumes occurred only during the first period, and later the injection and production profiles became equal. The equality between the injection and production profiles suggests that the produced CO$_2$ shrinks to its normal volume after leaving the water bath, causing no increase in the produced volumes. Thus, the increase in the cumulative produced volumes can be related to oil production, which mainly occurred during the early stages of the experiments. The equality between the injection and production profiles can be used as an indicator to show when most of the oil production occurred.

The data from Figures 17 and 18 show that increasing fluid pressure results in a decrease in the time required to achieve most of the oil production, from around 20–25 min for the low-fluid-pressure GCO$_2$ experiments (40 and 60 bar) to around 5 min for the high-fluid-pressure GCO$_2$ experiments (65 and 70 bar). After most of the oil production has occurred, the cumulative produced volumes and the cumulative injected CO$_2$ volumes show a constant linear trend with time. For the low-pressure GCO$_2$ experiments conducted at 40 bar, the production profile is characterized by a slight increase during the first 25.5 min followed by a constant linear trend. On the other hand, the production profile of the 60 bar GCO$_2$ displacements is characterized by a continuous increase over time. The main reason behind the highest reductions in the corresponding times and the increase in cumulative produced volumes over time, with the increase in fluid pressure, is the increase in displacement efficiency and CO$_2$ density. Increasing CO$_2$ density means less time was required to reach the differential pressure required for the injected CO$_2$ to enter the core sample at the first time.

**Figure 18.** Effect of fluid pressure on the cumulative produced volumes of oil and CO$_2$ for high-fluid-pressure GCO$_2$–oil displacements conducted at 33 °C and 0.4 mL/min.

**Figure 19.** Effect of fluid pressure on the cumulative produced volumes of oil and CO$_2$ for LCO$_2$–oil displacements conducted at 20 °C and 0.4 mL/min.
were less than the cumulative injected volumes. Nevertheless, the increase in temperature caused a very slight increase in the cumulative produced volumes. At the end of the displacements, the ratio of the cumulative produced volumes to the cumulative injected volumes at the end of the displacements to increase from 0.51 to 0.55; nonetheless, the displacement conducted at 33 °C showed the highest ratio (0.65), the reason is not clear. As the temperature increased for the high-fluid-pressure GCO₂ displacements (70 bar), the ratio of the cumulative produced volumes to the cumulative injected volumes at the end of the displacements were 1.02, 1.04, and 1.07 for the displacements conducted at 33, 45, and 55 °C, respectively. The observed increase in the cumulative produced volumes as temperature increased can be related to increases in displacement efficiency and decreases in gas compressibility and solubility.

The data from Figure 23 show that the cumulative produced volumes during LCO₂ displacements were less than the cumulative injected volumes. Nevertheless, the increase in temperature caused a very slight increase in the cumulative produced volumes. At the end of the displacements, the ratio of the cumulative produced volumes to the cumulative injected volumes were 0.914, and 0.918 for the displacements performed at 20 and 29 °C, respectively. This slight increase might reflect the lower sensitivity of liquid CO₂ to pressure and temperature changes in comparison with gaseous and supercritical CO₂ displacements.

**Figure 20.** Effect of fluid pressure on the cumulative produced volumes of oil and CO₂ for ScCO₂–oil displacements conducted at 33 °C and 0.4 mL/min.

3.2.2. The Effect of Experimental Temperature on the Differential Pressure Profile of CO₂–Oil Displacements

Figures 21–24 show the impact of increasing temperature on the cumulative produced volumes. The results reveal that increasing temperature caused an increase in the cumulative produced volumes.

The data from Figure 21 show that the cumulative produced volumes of low-fluid-pressure GCO₂ displacements (40 bar) were less than the cumulative injected volumes. On the other hand, the cumulative produced volumes of high-fluid-pressure GCO₂ displacements (70 bar) were higher than the cumulative injected volume, as shown in Figure 22. The increase in temperature caused an increase in the cumulative produced volumes. Increasing the temperature from 45 to 55 °C for the low-fluid-pressure GCO₂ displacements (40 bar) caused the ratio of the cumulative produced volumes to the cumulative injected volumes at the end of the displacements to increase from 0.51 to 0.55; nonetheless, the displacement conducted at 33 °C showed the highest ratio (0.65), the reason is not clear. As the temperature increased for the high-fluid-pressure GCO₂ displacements (70 bar), the ratio of the cumulative produced volumes to the cumulative injected volumes at the end of the displacements were 1.02, 1.04, and 1.07 for the displacements conducted at 33, 45, and 55 °C, respectively. The observed increase in the cumulative produced volumes as temperature increased can be related to increases in displacement efficiency and decreases in gas compressibility and solubility.

The data from Figure 23 show that the cumulative produced volumes during LCO₂ displacements were less than the cumulative injected volumes. Nevertheless, the increase in temperature caused a very slight increase in the cumulative produced volumes. At the end of the displacements, the ratio of the cumulative produced volumes to the cumulative injected volumes were 0.914, and 0.918 for the displacements performed at 20 and 29 °C, respectively. This slight increase might reflect the lower sensitivity of liquid CO₂ to pressure and temperature changes in comparison with gaseous and supercritical CO₂ displacements.
Figure 21. Effect of experimental temperature on the cumulative produced volumes of oil and CO\(_2\) for low-pressure GCO\(_2\)–oil displacements conducted at 40 bar and 0.4 mL/min.

Figure 22. Effect of experimental temperature on the cumulative produced volumes of oil and CO\(_2\) for high-pressure GCO\(_2\)–oil displacements conducted at 70 bar and 0.4 mL/min.

The data from Figure 24 show that, for ScCO\(_2\) displacements, increasing the temperature from 33 to 55 °C caused a substantial increase in the cumulative produced volumes. At the end of the displacements, the ratio of the cumulative produced volumes to the cumulative injected volumes were 0.915 and 1.06 for the displacements performed at 33 and 55 °C, respectively. As temperature increased, the behaviour of supercritical CO\(_2\) became very similar to that of high-pressure gaseous CO\(_2\) displacements, as shown in Figure 22, as the cumulative produced volumes for both displacements were much higher than the cumulative injected volumes.
produced oil was measured, and the residual oil saturation was calculated. The average differential viscosity and potentially its influence on relative permeability. In this study, when the flooding experiment was finished, the volume of the displacing (e.g., oil or brine) can travel from the injection point through the formation [35]. The change in CO2 state is likely to change the mobility of the fluids due to its impact on viscosity and potentially its influence on relative permeability. In this study, when the flooding experiment was finished, the volume of the displacing (e.g., oil or brine) can travel from the injection point through the formation [35]. The change in CO2 state is likely to change the mobility of the fluids due to its impact on viscosity and potentially its influence on relative permeability. In this study, when the flooding experiment was finished, the volume of the displacing (e.g., oil or brine) can travel from the injection point through the formation [35].

3.3. The Effect of Fluid Pressure, Temperature, and Injection Rate on Endpoint Effective (Relative) Permeability and Residual Oil Saturation as a Function of CO2 Phase

Effective permeability of CO2 is of practical interest for CO2 sequestration in subsurface formations [84]. Relative permeability of gas–oil is particularly important in reservoirs that are characterized by gas drive, gas cap expansion, or gas injection [82]. Relative permeability data is a key factor for the determination of the efficiency, integrity, injectivity, and plume migration of CO2 sequestration process [35,85] as well as for the designing and making decisions for reservoir improvement [86], fluid flow in porous media [87], breakthrough time [7], and mobility of the displacing and displaced fluids [7,35]. The mobility of the fluids governs the injection rate and pressure increase during CO2 injection, as well as the distance that the displacing fluid (CO2) and displaced (e.g., oil or brine) can travel from the injection point through the formation [35]. The change in CO2 state is likely to change the mobility of the fluids due to its impact on viscosity and potentially its influence on relative permeability. In this study, when the flooding experiment was finished, the volume of the produced oil was measured, and the residual oil saturation was calculated. The average differential pressure and the average CO2 outflow rate of the last period were used to calculate the endpoint
effective \(K_{rCO_2}\) and relative permeabilities \(K_{rCO_2}\) of CO\(_2\) using Darcy’s law \[66,83\]. Then, the core sample was weighed to confirm the calculated residual oil saturation \(S_{or}\). The CO\(_2\) viscosity at the fluid pressure and the experimental temperature was calculated using the Peace software website \[81\].

The data from Table 1 shows that the \(S_{or}\) was in ranges of 0.65–0.7, 0.56–0.6, 0.49–0.59, and 0.44–0.56 for the low-fluid-pressure GCO\(_2\)–oil displacements, high-fluid-pressure GCO\(_2\)–oil displacements, ScCO\(_2\)–oil displacements, and LCO\(_2\)–oil displacements, respectively. The lowest recovery occurred in the low-fluid-pressure GCO\(_2\)–oil displacements, whilst the highest oil recovery occurred in the LCO\(_2\)–oil displacements. The data demonstrate the impact of CO\(_2\) phase and the operational conditions on oil recovery. The amount of oil recovery depends on many factors, including relative permeability, wetting conditions, viscous fingering, gravity tonguing, channelling, amount of crossflow/mass transfer \[86\], mobility ratio, and capillary number \[88\]. The change in CO\(_2\) phase and the operational conditions are likely to have an influence on most of the listed factors, leading to their impact on the displacement efficiency. The highest recovery with liquid CO\(_2\) phase can be associated with its highest capillary number (due to its highest viscous forces and lowest capillary forces), lowest mobility ratio, and potentially its most stable front displacement in comparison to that of gaseous and supercritical CO\(_2\) phases. The highest viscous forces and the lowest mobility ratio of the liquid CO\(_2\) phase in comparison to that of gaseous and supercritical CO\(_2\) phases can be associated with its highest viscosity, while the lowest capillary forces of the liquid CO\(_2\) phase can be related to its lowest IFT, providing a constant contact angle for the three phases of CO\(_2\). For illustration, for LCO\(_2\) displacements conducted at 90 bar and 29 \(^\circ\)C, GCO\(_2\) displacements performed at 70 bar and 33 \(^\circ\)C, and ScCO\(_2\) displacements conducted at 90 bar and 33 \(^\circ\)C, the viscosity of the LCO\(_2\), GCO\(_2\), and ScCO\(_2\) phases is 63.902, 70.743, and 53.837 × \(10^{-6}\) (Pa·s), respectively \[81\]. The CO\(_2\)–oil IFT decreases as pressure increases due to increases in CO\(_2\) solubility and increases as temperature increases due to decreases in CO\(_2\) solubility \[41\]. Therefore, the CO\(_2\)–oil IFT of LCO\(_2\) displacement is less than that of GCO\(_2\) displacements, due to its higher pressure and lower temperature, as well as less than that of ScCO\(_2\) displacements due to its lower temperature.

On the other hand, Table 1 reveals that the \(K_{rCO_2}\) was in ranges of 0.015–0.1, 0.034–0.412, 0.144–0.657, and 0.079–0.281 for the low-fluid-pressure GCO\(_2\)–oil displacements, high-fluid-pressure GCO\(_2\)–oil displacements, ScCO\(_2\)–oil displacements, and LCO\(_2\)–oil displacements, respectively. This data also demonstrates the impact of CO\(_2\) phase and the operational conditions on the endpoint CO\(_2\) relative permeabilities. In general, the lowest \(K_{rCO_2}\) was observed in the low-fluid-pressure GCO\(_2\)–oil displacements, whilst the highest was obtained in the ScCO\(_2\) displacements. The data show also a wide range of endpoint CO\(_2\) relative permeabilities from low to high values. The change in relative permeability with CO\(_2\) phase and operational conditions can be related to their potential strong influence on the capillary number, viscous forces, capillary forces, flow regimes \[82,89\], and capillary end effect; thus, in turn, the CO\(_2\) phase and operational conditions will have a strong impact on relative permeability data \[76,87,90\]. Bennion and Bachu \[90\], Liu \[76\], and Parvazdavani \[87\] observed an impact for the operational conditions on relative permeability.

On the other hand, the observed lowest endpoint relative permeabilities of the low-pressure GCO\(_2\)–oil displacements are likely to be related to the impact of high capillary forces and low viscous forces, due to their higher interfacial tension and lower viscosity, in comparison to the other displacements. Nevertheless, the highest \(K_{rCO_2}\) of ScCO\(_2\)–oil displacements is likely to be associated with the highest ability of the supercritical CO\(_2\) phase to alter the wettability towards less water-wetting status in comparison to gaseous and liquid CO\(_2\) phases \[30,76\] (for more information, see Section 3.1). Generally, the observed low endpoint CO\(_2\) relative permeability and the wide range of the endpoint CO\(_2\) relative permeabilities agree well with the findings of Moortgat et al. \[7\], Parvazdavani et al. \[87\], and Müller \[35\]. The results of Moortgat et al.’s simulation study suggest that the \(K_{rCO_2}\) of the CO\(_2\)-rich phase may be lower than that of the oil phase \[7\]. However, the results of Parvazdavani et al.’s experimental and modelling study reveal a wide range of GCO\(_2\) endpoint relative permeabilities depending on the pressure range and the core sample origin; for illustration, they found that increasing
the pressure from 500 psi (34.5 bar) to 800 psi (55 bar) caused the \( K_{rCO_2} \) to range from 0.34 to 0.68 for the sandstone sample and from 0.25 to 0.56 for the dolomite sample [87]. The comparison of Müller for relative permeabilities of SCO\(_2\)-brine systems showed a wide range of relative permeability data that vary between 0.07 and 1 [35].

The data from Table 1 show that increasing fluid pressure caused the \( K_{rCO_2} \) of liquid \( CO_2 \) to decrease by about 0.017 and that of gaseous and supercritical \( CO_2 \) to increase by 0.034 and 0.261, respectively. On the other hand, increasing the fluid pressure resulted in a decrease in the residual oil saturation of the subcritical \( CO_2 \) phases by 0.12 and 0.11, respectively; however, this led to an increase in the residual oil saturation of the supercritical \( CO_2 \) phase by 0.04. It is worth mentioning that, for the GCO\(_2\) experiments, the displacement conducted at 65 bar experienced the highest \( K_{rCO_2} \), which might be related to its highest gas expansion impact and low capillary forces in comparison to low-fluid-pressure GCO\(_2\) displacements; the highest expansion impact is due to its highest density reduction as \( CO_2 \) entered the water bath (see Section 3.1.1). However, in the ScCO\(_2\) experiments, the displacement conducted at 80 bar experienced the lowest endpoint \( CO_2 \) relative permeability and the lowest residual oil saturation; the reason for this is not entirely clear. The increase in the viscous forces can explain the observed increase in the relative permeability for gaseous and supercritical \( CO_2 \) displacement, but not the reduction for liquid \( CO_2 \) displacement. The reason for the reduction might be related to the increasing dissolution of liquid \( CO_2 \) in oil as pressure increased, which could result in a reduction in the amount of the free movable liquid \( CO_2 \), thus reducing its relative permeability. The increase in gaseous permeability as fluid pressure increased agrees with the finding of Parvazdavani et al. [87], who observed that increasing fluid pressure for GCO\(_2\)-oil displacements led to a high increase in the relative permeability of GCO\(_2\) [87]. On the other hand, the reduction and increase in the residual oil saturation with subcritical \( CO_2 \) phases and supercritical \( CO_2 \) phase, respectively, can be associated with the observed increase and decrease in the differential pressure, as shown in Figures 3–6. The increase and reduction in the differential pressure were related to viscous and capillary forces (for more information, see Section 3.1.1). Therefore, the reduction in the residual oil saturation as fluid pressure increased in the case of the subcritical \( CO_2 \) phases can be associated with the increase in the viscous forces and the reduction in mobility ratio. However, the increase in residual oil saturation as fluid pressure increased in the case of the supercritical \( CO_2 \) might be related to the reduction in capillary forces; this indicates that capillary forces complemented viscous forces; thereby, its reduction led to a reduction in oil production [67]. The results indicate that viscous forces were dominant in subcritical \( CO_2 \) displacements, while capillary forces were dominant in supercritical \( CO_2 \) displacements.

Increasing the experimental temperature caused the \( K_{rCO_2} \) of the three \( CO_2 \) phases to increase by 0.084, 0.085, 0.378, and 0.024 for the LCO\(_2\), the low-fluid-pressure GCO\(_2\), and the high-fluid-pressure GCO\(_2\) and ScCO\(_2\) displacements, respectively. On the other hand, increasing the experimental temperature caused the residual oil saturation to increase by 0.12 for LCO\(_2\) displacements. Nevertheless, it led to a decrease in the residual oil saturation by 0.05, 0.02, and 0.06 for the low-fluid-pressure GCO\(_2\) and high-fluid-pressure GCO\(_2\) and ScCO\(_2\) displacements, respectively. It should be noted that, for the 70 bar GCO\(_2\) displacements, increasing temperature from 45 to 55 °C reduced the endpoint \( CO_2 \) relative permeability from 0.412 to 0.342; this reduction could be associated with the appearance of differential pressure oscillations, as shown in Figure 10. The increase in relative permeability as temperature increased could be associated with the increase in the \( CO_2 \) injection rate [82,89] due to expansion effect (see Section 3.1.2). Skauge [82] and Rostami [89] observed that the increase in the displacement velocity leads to a higher gas relative permeability and can slightly affect the oil relative permeability [82,89]. The reduction in the residual saturation of the LCO\(_2\) displacements can be associated with the reduction in differential pressures due to increasing temperature, as shown in Figures 9–12. That is, the increase in the residual oil saturation as temperature increased can be associated with the reduction in the viscous forces in the case of liquid \( CO_2 \) phase. However,
the reduction in the residual oil saturation, i.e., increasing displacement efficiency, as temperature increased in the case of gaseous and supercritical CO$_2$ phases might be related to the reduction in oil viscosity as well as the increase in CO$_2$ injection rate inside the core sample because of the gas expansion impact. Increasing displacement efficiency can be seen through the increase in the cumulative produced volumes of gaseous and supercritical CO$_2$ phases as temperature increased (see Figures 22 and 24).

Increasing the injection rate caused the $K_{\text{CO}_2}$ of the three CO$_2$ phases to increase by 0.185, 0.09, and 0.252 for the LCO$_2$ and high-fluid-pressure GCO$_2$ and ScCO$_2$ displacements, respectively. In addition, increasing the injection rate led to the reduction of the residual oil saturation of the three CO$_2$ phases by 0.07, 0.02, 0.03, 0.1 for the LCO$_2$, low-pressure GCO$_2$, and high-fluid-pressure GCO$_2$ and ScCO$_2$ displacements, respectively. It should be noted that, as injection rate increased from 0.4 to 1 mL/min for the low-pressure GCO$_2$ (40 bar), the $K_{\text{CO}_2}$ experienced no change. The increase in the differential pressure due to increasing viscous forces could be the reason behind the increase in $K_{\text{CO}_2}$ [66,83] and the reduction in the residual oil saturation with increasing injection rate [82].

### Table 1. Effect of fluid pressure, temperature and injection rate on the endpoint CO$_2$ effective (relative) permeability and oil recovery as a function of CO$_2$ phase.

| Parameter          | Experiment                  | $K_{\text{CO}_2}$ (mD) | $K_{\text{CO}_2}$ Oil Recovery | $S_{or}$ |
|--------------------|-----------------------------|-------------------------|-------------------------------|----------|
| **Fluid Pressure Effect** |                             |                         |                               |          |
| LCO$_2$–oil       | 70 bar; 0.4 mL/min; 20 °C    | 2.782                   | 0.096                         | 0.44     | 0.56     |
| LCO$_2$–oil       | 90 bar; 0.4 mL/min; 20 °C    | 2.287                   | 0.079                         | 0.56     | 0.44     |
| GCO$_2$–oil       | 40 bar; 0.4 mL/min; 33 °C    | 0.446                   | 0.015                         | 0.30     | 0.70     |
| GCO$_2$–oil       | 60 bar; 0.4 mL/min; 33 °C    | 0.822                   | 0.028                         | 0.35     | 0.65     |
| GCO$_2$–oil       | 65 bar; 0.4 mL/min; 33 °C    | 1.417                   | 0.049                         | 0.40     | 0.60     |
| GCO$_2$–oil       | 70 bar; 0.4 mL/min; 33 °C    | 0.991                   | 0.034                         | 0.41     | 0.59     |
| ScCO$_2$–oil      | 75 bar; 0.4 mL/min; 33 °C    | 4.996                   | 0.173                         | 0.45     | 0.55     |
| ScCO$_2$–oil      | 90 bar; 0.4 mL/min; 33 °C    | 4.167                   | 0.144                         | 0.51     | 0.49     |
| **Temperature Effect** |                             |                         |                               |          |
| LCO$_2$–oil       | 90 bar; 0.4 mL/min; 20 °C    | 2.287                   | 0.079                         | 0.56     | 0.44     |
| LCO$_2$–oil       | 90 bar; 0.4 mL/min; 29 °C    | 4.710                   | 0.163                         | 0.44     | 0.56     |
| GCO$_2$–oil       | 40 bar; 0.4 mL/min; 33 °C    | 0.446                   | 0.015                         | 0.30     | 0.70     |
| GCO$_2$–oil       | 40 bar; 0.4 mL/min; 45 °C    | 1.572                   | 0.054                         | 0.33     | 0.67     |
| GCO$_2$–oil       | 40 bar; 0.4 mL/min; 55 °C    | 2.895                   | 0.1                             | 0.35     | 0.65     |
| GCO$_2$–oil       | 70 bar; 0.4 mL/min; 33 °C    | 0.991                   | 0.034                         | 0.41     | 0.59     |
| GCO$_2$–oil       | 70 bar; 0.4 mL/min; 45 °C    | 11.906                  | 0.412                         | 0.40     | 0.60     |
| GCO$_2$–oil       | 70 bar; 0.4 mL/min; 55 °C    | 9.870                   | 0.342                         | 0.43     | 0.57     |
| ScCO$_2$–oil      | 90 bar; 0.4 mL/min; 33 °C    | 11.717                  | 0.405                         | 0.41     | 0.59     |
| ScCO$_2$–oil      | 90 bar; 0.4 mL/min; 55 °C    | 12.413                  | 0.430                         | 0.47     | 0.53     |
| **Injection Rate Effect** |                             |                         |                               |          |
| LCO$_2$–oil       | 70 bar; 0.4 mL/min; 20 °C    | 2.782                   | 0.096                         | 0.44     | 0.56     |
| LCO$_2$–oil       | 70 bar; 1 mL/min; 20 °C      | 8.120                   | 0.218                         | 0.51     | 0.49     |
| GCO$_2$–oil       | 40 bar; 0.4 mL/min; 33 °C    | 0.446                   | 0.015                         | 0.30     | 0.70     |
| GCO$_2$–oil       | 40 bar; 1 mL/min; 33 °C      | 0.420                   | 0.015                         | 0.32     | 0.68     |
| GCO$_2$–oil       | 70 bar; 0.4 mL/min; 33 °C    | 0.991                   | 0.034                         | 0.41     | 0.59     |
| GCO$_2$–oil       | 70 bar; 1 mL/min; 33 °C      | 3.599                   | 0.125                         | 0.44     | 0.56     |
| ScCO$_2$–oil      | 90 bar; 0.4 mL/min; 33 °C    | 11.717                  | 0.405                         | 0.41     | 0.59     |
| ScCO$_2$–oil      | 90 bar; 1 mL/min; 33 °C      | 18.992                  | 0.657                         | 0.51     | 0.49     |

### 4. Conclusions

In this paper, the effect of fluid pressure, temperature, and injection rate on CO$_2$ behaviour during the flooding of an oil-saturated Berea sandstone core sample has been investigated as a function of CO$_2$ phase. The results indicate that fluid pressure, experimental temperature, and injection rate significantly influence the differential pressure profile, cumulative produced volumes, endpoint CO$_2$ relative permeability, and oil recovery. The trend and the size of the changes depend on the CO$_2$ phase as well the pressure range for GCO$_2$ displacements. The data indicate that, as fluid pressure increases,
the capillary forces have a stronger impact on the differential pressure profile of supercritical CO\textsubscript{2}–oil displacements than that on subcritical CO\textsubscript{2}–oil displacements. As temperature and injection rates increased, the viscous forces become more dominant than capillary forces.

In summary, for all fluid pressures, temperature, and injection rates, the differential pressure profile is characterized by a strong increase, followed by a high reduction until it reached the value of quasi-differential pressure; the rate of the increase and reduction in the differential pressure depends on the CO\textsubscript{2} phase and the pressure range for the GCO\textsubscript{2} displacements. In general, liquid CO\textsubscript{2} phase gave the highest differential pressure magnitude, while gaseous CO\textsubscript{2} phase gave the lowest. Increasing fluid pressure caused an increase in the differential pressure profile of subcritical CO\textsubscript{2} displacements but a reduction in that of supercritical CO\textsubscript{2} displacements; the magnitude of the change in the differential pressure depends on the CO\textsubscript{2} phase and the pressure range of GCO\textsubscript{2} displacements. The highest percentage increase occurred in low-fluid-pressure GCO\textsubscript{2} displacements, whilst the lowest occurred in LCO\textsubscript{2} displacements. In addition, increasing fluid pressure for low-pressure GCO\textsubscript{2} displacements increased the frequency of the differential pressure oscillations and reduced the entry pressure and its associated time. Increasing temperature caused a reduction in the differential pressure profile for the three CO\textsubscript{2} phases along with the appearance of the pressure oscillations in the case of gaseous and supercritical CO\textsubscript{2} displacements. The magnitude of this reduction in the differential pressure depends on the CO\textsubscript{2} phase and the pressure range for the GCO\textsubscript{2} displacements; the highest reduction occurred in high-fluid-pressure GCO\textsubscript{2} displacements, while the lowest occurred in LCO\textsubscript{2} displacements. The increase in injection rate caused a substantial increase in the differential pressure of the three CO\textsubscript{2} phases with the highest percentage increase occurred in the ScCO\textsubscript{2} displacements and the lowest in the high-fluid-pressure GCO\textsubscript{2} displacements conducted at 70 bar.

The increase in fluid pressure caused an increase in the cumulative produced volumes of low-fluid-pressure GCO\textsubscript{2} displacements, but a reduction in those of high-fluid-pressure GCO\textsubscript{2}, LCO\textsubscript{2}, and SCO\textsubscript{2} displacements; the largest reduction occurred in the ScCO\textsubscript{2} displacements, while the lowest occurred in the LCO\textsubscript{2} displacements; increasing fluid pressure reduced the time required to achieve the majority of the oil production. However, increasing temperature caused an increase in the cumulative produced volumes; the lowest increase occurred in LCO\textsubscript{2}–oil displacements.

The residual oil saturation was in the range of around 0.44–0.7; liquid CO\textsubscript{2} gave the lowest, and low-fluid-pressure gaseous CO\textsubscript{2} gave the highest. The endpoint CO\textsubscript{2} relative permeability was in the range of about 0.015–0.657; supercritical CO\textsubscript{2} gave the highest, and low-pressure gaseous CO\textsubscript{2} gave the lowest. Increasing fluid pressure caused the endpoint relative permeability of liquid CO\textsubscript{2} to decrease, but that of gaseous and supercritical CO\textsubscript{2} to increase. However, increasing fluid pressure caused the residual oil saturation to decrease for the subcritical CO\textsubscript{2} displacements but to decrease for the supercritical CO\textsubscript{2} displacements. Increasing the experimental temperature caused the endpoint relative permeability of the three CO\textsubscript{2} phases to increase. However, increasing the experimental temperature caused the residual oil saturation to increase for liquid CO\textsubscript{2} displacements but to decrease for gaseous and supercritical CO\textsubscript{2} displacements. Increasing the injection rate caused the endpoint relative permeability of the three CO\textsubscript{2} phases to increase and the residual oil saturation to decrease.

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