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EOR Processes, Opportunities and Technological Advancements

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Abstract

Enhanced oil recovery (EOR) processes are well known for their efficiency in incrementing oil production; however, the selection of the most suitable method to adopt for specific field applications is challenging. Hence, this chapter presents an overview of different EOR techniques currently applied in oil fields, the opportunities associated with these techniques, key technological advancements to guide the decision-making process for optimum applicability and productivity and a brief review of field applications.

Keywords: enhanced oil recovery (EOR), mobility ratio, interfacial tension (IFT), capillary number, viscosity

1. Introduction

1.1. Oil recovery processes

Oil reservoirs run through series of production stages classified as primary (natural drive mechanism), secondary and tertiary recovery techniques. These stages designate production from a reservoir in a sequential pattern [1] with different recovery efficiencies over time (**Figure 1**). Oil recovery is predominantly influenced by capillary number (N_c) at the microscopic scale and mobility ratio (M) at the macroscopic scale [2]. Capillary number denotes the ratio of viscous forces to interfacial tension (IFT) forces (Eq. (1)):

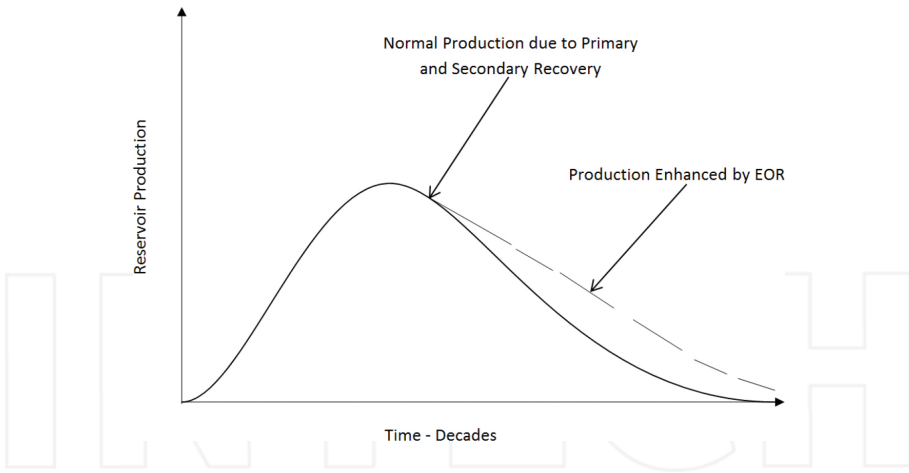


Figure 1. Reservoir production stages as a function of time [7].

$$N_c = V\mu / \sigma \quad (1)$$

where N_c represents capillary number; V is Darcy's velocity; μ is viscosity of displacing fluid; and σ is the interfacial tension (IFT) between the displaced and the displacing fluid [2–4]. It has been experimentally shown that an increase in capillary number (from a typical value around 10^{-7}) decreases residual oil saturation. This can be accomplished by an increase in the velocity of the injected fluid (i.e. Darcy's velocity, V) and/or viscosity of the displacing fluid (μ) and/or a reduction in IFT (σ) [5]. However, substantial increase in capillary number is required, thus, surfactant or alkaline flooding [6] is recommended as the most feasible option for micro-scale displacement. Mobility ratio (M) is the ratio of the mobility of the displacing fluid to the mobility of the displaced fluid Eq. (2):

$$M = \lambda_{ing} / \lambda_{ed} \quad (2)$$

and

$$\lambda = k / \mu \quad (3)$$

where M is mobility ratio; λ_{ing} is displacing fluid mobility; λ_{ed} is displaced fluid mobility; k is effective permeability (m^2); and μ is fluid viscosity (Pa s) [2]. The stability of displacement, which is of key importance for macroscopic displacement efficiency, is ultimately determined by the mobility ratio (M) [2]. If M is less than or equal to 1 ($M \leq 1$), it is considered favourable, and displacement efficiency increases (**Figure 2**); however, if $M > 1$, the mobility ratio is seen as unfavourable [2] and residual oil will be inefficiently displaced.

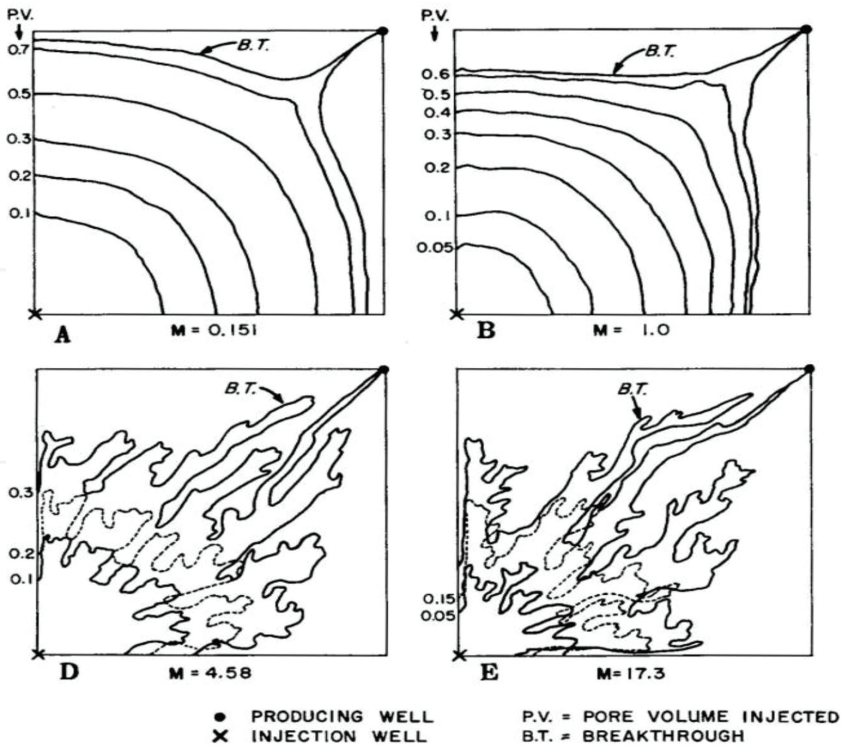


Figure 2. Displacement fronts during waterflooding for different mobility ratios and pore volumes injected until breakthrough [8].

Oil recovery efficiency is greatly dependent on the microscopic and macroscopic displacement efficiency. Generally, microscopic displacement efficiency measures the extent to which the displacing fluid mobilises the residual oil once in contact with the oil [1, 3, 9], and it is greatly controlled by factors such as rock wettability, relative permeability, IFT and capillary pressure [2]; note that a decrease in oil viscosity, IFT or capillary pressure of the displacing fluid can increase the microscopic efficiency [10].

Macroscopic displacement efficiency, otherwise known as volumetric sweep efficiency, measures the extent to which the displacing fluid is in contact with the oil-bearing parts of the reservoir (metre to hectometre scale, Eq. (4)) [1, 2, 9, 11], and it is influenced by the rock matrix heterogeneities and anisotropy, displacing and displaced fluid mobility ratio and injection and production well(s) positioning [1, 3]. The product of microscopic (E_d) and macroscopic (E_v) displacement efficiency yields the overall displacement efficiency (E) of any oil recovery displacement process [1].

$$E = E_d E_v \quad (4)$$

and

$$E_v = E_i E_a \quad (5)$$

where E_i is the vertical sweep efficiency [3] and E_a is the areal sweep efficiency.

Natural drive mechanisms recover oil during the initial or primary production stage of a reservoir by means of the natural energy present in the reservoir without the need of supplying any additional energy [12–15]. These natural mechanisms use the pressure difference between the reservoir and the producing well bottom [15–17]. The total recoverable oil using this method is considered inefficient, as recovery is usually less than 25% of the original oil-in-place (OOIP) [2].

Secondary recovery techniques are applied when the natural reservoir drive is depleted ineffectively and inadequately for augmenting production. This technique involves injection of either natural gas or water [3, 12] to stimulate oil wells and maintain reservoir pressure in the injection wells [2, 12]. The injected fluids act as an artificial drive to supplement the reservoir energy [9, 18]. Such fluids boost the flow of hydrocarbon towards the wellhead [19]. If the injected fluid is water, the process is usually termed waterflooding; if the injected fluid is gas, the process usually involves pressure maintenance operations [17, 20]. Gas-cap expansion into oil columns (wells) displaces oil immiscibly due to volumetric sweep-out [1]. Diverse methods are used for fluid injection into oil reservoirs to support the natural forces [17]. Recovery efficiencies in the secondary stage vary from 10 to 40% of the original oil-in-place [16, 17, 20]. Other gas processes, whose mechanisms entail oil swelling and viscosity reduction, or favourable phase behaviour [1], are enhanced oil recovery (EOR) processes. Tertiary recovery techniques otherwise called enhanced oil recovery (EOR) processes demonstrate enormous potential in recovering stranded oil trapped at the pore scale after primary and secondary recovery techniques by capillary pressure-driven snap-off [21], which leaves behind in the reservoir about one-third of OOIP [22]. The stranded oil is often located in regions considered inaccessible [23–25]. EOR methods can extract more than half of the total OOIP and significantly more than the primary and secondary recovery methods [26]. Notably, the impact of EOR on oil production is colossal as an increase in recovery factor by only 1% can yield 70 billion barrels of conventional oil reserves globally without the exploitation of unconventional resources [2]. In comparison to primary and secondary recovery methods, EOR undeniably is a better alternative as its contributions to global oil production entails a more economically feasible process.

2. Enhanced oil recovery (EOR)

Improved oil recovery (IOR) is often erroneously used in place of enhanced oil recovery (EOR). IOR and EOR are two different concepts: IOR is a wider concept that embroils ultimate recovery of oil by any means [2]. The EOR is mainly driven by the ability to recover more oil at an economically feasible production rate [27]. The EOR can be described as a subset of IOR

[28]. EOR uses several processes and technologies (**Figure 3**) to increase or uphold recovery from existing fields [29]. These processes often involve the injection of fluid(s) and most recently microbes into a reservoir. These fluids, in turn, supplement the reservoir natural energy for effective oil displacement into the producing well thus yielding an interaction between injected fluid and the reservoir rock/oil system that creates a favourable condition for oil recovery [1]. The key drive for EOR spins around its capability of turning residual cumulative oil into reserves with oil (million barrels) produced from existing fields [30–32], which is achieved by overcoming the physical forces confining hydrocarbons underground (**Table 1**) [1, 33].

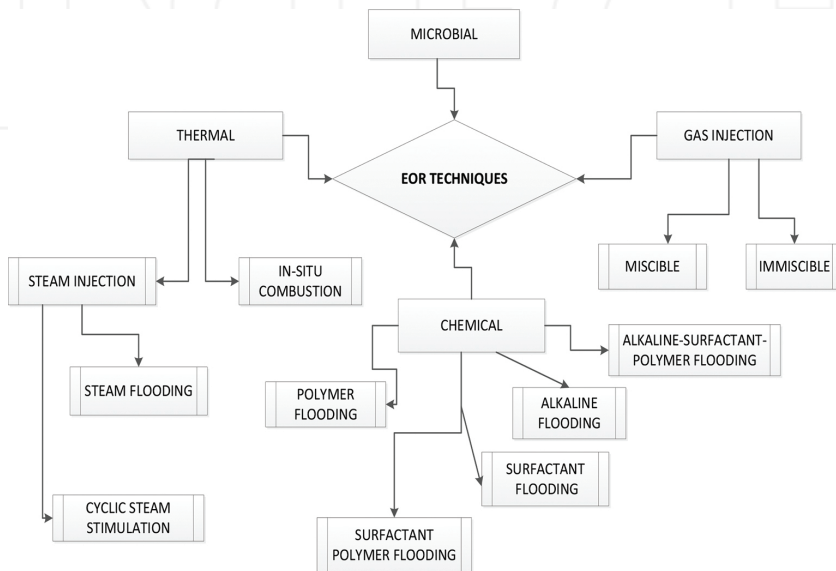


Figure 3. Classification of EOR techniques.

2.1. Thermal EOR (TEOR)

Oil recovery using thermal techniques involve the introduction of heat energy into oil reservoirs. Reservoir temperatures are substantially increased to achieve a significant decrease in oil viscosity [34], which yields a corresponding oil mobility effect. During the process, usually, a shift in rock wettability occurs, which enhances the chances for better oil recovery [29]. Current reports predict that only approximately 30% of the global oil reserves are light oil while the remaining 70% are heavy crude oils [34]. Increasing recovery of these heavier crudes can unlock approximately 300 billion bbl (Bbbl) of oil [35]; thus, TEOR is mainly applicable to heavy and viscous oil formations [34]. The TEOR is considered an effective technique for unlocking such heavy oil reservoirs. Several billion barrels of oil have been recovered using TEOR; for instance, more than 4 Bbbls of oil were produced in the USA through steam flooding

(SF) from 1980 to 2002 [36]. Despite its effectiveness in heavy oil formations, TEOR can also be deployed in light oil reservoirs [29]. TEOR is perhaps the best used EOR method for up surging production particularly steam flooding [37], although the environmental footprint is enormous when compared to conventional oil production [29].

EOR method	Mechanisms	Field applications	Technological development	Merits	Demerits	References
Thermal EOR (TEOR)						
<i>In Situ</i> combustion (ISC)	Air is injected into the reservoir as a dry process or with water (wet process) and oil ignition is performed alongside	India, Romania, Canada, U.S.	HPAI	<ul style="list-style-type: none"> Suitable in both deeper and shallow reservoirs Production is increased through a combination of mechanisms 	<ul style="list-style-type: none"> Eco-unfriendly (emissions from surface steam generation) Mobility control issues Expensive cost of operation 	[1, 28, 29, 37, 41, 42, 54, 61, 63 – 66]
Steam injection						
<ul style="list-style-type: none"> Cyclic steam stimulation Steam flooding 	Steam is injected into a well over a period Steam is injected into dedicated injection wells to displace oil towards a production well	Brazil, Venezuela, U.S., Indonesia, the former Soviet Union, Trinidad, Oman, China, Tobago, Canada,	THAI, Fast-SAGD, NCG-SAGD, OTSG, ST-EOR, GOGD, TAGOGD and TGD			
<ul style="list-style-type: none"> Steam assisted gravity drainage (SAGD) 	Oil is heated by circulating steam at a temperature that improves oil flow	Canada, Venezuela				
Chemical EOR (CEOR)						
Polymer flooding	Polymers are injected into the reservoir followed by water	Brazil, China, Oman, Canada, Suriname, Mexico, Argentina, Austria, U.S, India	PAM, HPAM, xanthan gum, HPAMAMPS, SAPc	<ul style="list-style-type: none"> Inexpensive processes Possibilities for incremental oil 	<ul style="list-style-type: none"> High tendency for chemical incompatibility Issues with creating contact with the formation oil 	[1, 25, 63], [68, 67, 86] [88, 109, 117–120]
Surfactant-polymer (SP) flooding	Separate surfactant slug and polymer slug are injected into the reservoir					
Surfactant flooding	Aqueous surfactants	Indonesia, Bahrain, U.S.				

EOR method	Mechanisms	Field applications	Technological development	Merits	Demerits	References
	solutions are injected into the reservoir					
Alkaline flooding	Aqueous solution of alkaline chemicals are injected into the reservoir	Hungary, India, U.S., Russia				
Alkaline-surfactant-polymer (ASP) flooding	Injections of blends of Alkali, Surfactants and Polymers in water into formation	China, U.S., India, Venezuela				
Gas EOR (GEOR)						
Miscible flooding	Injection of gas (CO ₂ , lean hydrocarbons) is performed to achieve miscibility with oil at pressures equal or higher than the minimum miscibility pressure (MMP)	CO ₂ –U.S., Canada, N ₂ – U.S., Mexico Hydrocarbon gases – U.S., Venezuela, Libya, Canada	WAG, SWAG, PWAG, GAGD	<ul style="list-style-type: none"> • Production yields outweighs implementation expense • Significant amount of oil is recoverable especially with CO₂ flooding 	<ul style="list-style-type: none"> • Presence of unfavourable mobility ratio • Limited gas sources and separation issues 	[1, 25, 63, 68, 121, 132, 138, 140–142]
Immiscible flooding	Gas(N ₂ , CO ₂ etc.) is injected below the MMP					
Microbial EOR (MEOR)						
Microbial	Microorganisms are injected into oil reservoirs for recovery purposes	Malaysia, India, Russia, Australia, Trinidad-Tobago, China, Former East Germany; Norway, Saudi Arabia; Poland; Canada, Oman, U.S., Romania, Hungary, Former Czechoslovakia	AMEC, Selective plugging, Indigenous microbiota stimulation, GEMEOR, EOR	<ul style="list-style-type: none"> • Low operational costs • Eco-friendly 	<ul style="list-style-type: none"> • Slow and low oil recovery capability • Requires multiple and often complex procedures 	[14, 15, 19, 153, 162–165, 168, 169]

Table 1. Comprehensive breakdown of EOR processes.

2.1.1. Evolution of thermal EOR techniques

The early history of thermal recovery dates back to 1865 [34]; however, the first industrially significant TEOR project was conducted in 1931 close to Woodson, TX [38]. This was a steam injection test [34]. An advanced steam injection (cyclic steam injection) was later discovered upon release of accrued reservoir fluid pressure through a retrograde flow of injected steam; that coincidentally resulted in considerable oil production instead of the expected steam [34]. Subsequent large-scale TEOR projects were conducted in Tia Juana [39] and Mene Grande fields, both located in Venezuela. Upon discovery of the Venezuelan field (Mene Grande), steam flooding was selected as the optimal TEOR method, and a continuous steam injection over several weeks was deployed, with the wells shut in for short time intervals to support heat transfer within the reservoir [29].

2.1.2. Thermal EOR classification

The two key types of thermal EOR techniques are *in situ* combustion (ISC) and steam injection. Steam injection includes three basic categories [28]: namely, cyclic steam stimulation (CSS; huff-and-puff), steam flooding and steam-assisted gravity drainage (SAGD).

2.1.3. Mechanisms of TEOR techniques

2.1.3.1. *In situ* combustion

In *in situ* combustion, air is injected into viscous oil reservoirs to generate heat by burning a portion of the existing oil [28, 29, 40, 41]. The ISC can be a forward or reverse process, which is mainly dependent on the combustion front. The combustion fronts move in the direction of the injected air (forward combustion) or away from the air (reverse combustion). In practice, forward combustion process is generally adopted. Oil recovery is achieved using this process through the energy generated by the combustion reaction between the injected air and the oil:

- The oil is ignited and air is constantly injected to propagate the combustion front away from the well [10, 42].
- Reservoir fluids are displaced at the elevated temperatures (600–700°C) zone.
- The fluids advance towards the production wells [42] and the lighter ends are transported downstream which mixes with the crude oil.
- The heavy ends are burned resulting in the production of large amount of flue gases [10, 42].

Process benefits. ISC efficiently displaces oil in the regions contacted by the hot fluids in the advancing front, oil recovery rates are mostly high and this process is more cost effective than steam flooding as it uses air. There is a negligible effect of reservoir permeability on the ISC processes, which is effective for oil recovery in various formations as follows [10]:

- Deep reservoirs: depths up to 11,000 ft.
- Shallow reservoirs: <1500 ft.

- Light oils: >30° API.
- Heavy oils: 10–20° API.

Process limitations. Compressed air must be used and the operational variables are complex and difficult to control (i.e. controlling the advancing combustion front) [1]. The ISC process requires very high temperatures, in the order of 700°C and above. The high temperature of this process often damage production tubing and equipment (i.e. failure of pumps, valves, etc.) [43]. Furthermore, an adequate knowledge (i.e. rigorous laboratory evaluation) of the ISC dynamics is required for understanding the stability of the combustion front [44].

2.1.3.2. Steam injection

Steam injection entails the injection of steam into shallow, thick and permeable reservoirs containing high viscosity crude [32]. Steam injection processes include steam flooding, cyclic steam stimulation (CSS) and steam-assisted gravity drainage.

In steam flooding, steam is injected into dedicated injection wells, so that the reservoir fluids are driven towards a separate set of producers [45]. Oil recovery is achieved through:

- Constant injection of steam into the formation.
- The injected steam heats the chamber around the injection well.
- The chamber expands in the direction of the production well leading to oil viscosity reduction [46] and substantial oil displacement.

Process benefits. The introduction of steam into the reservoir efficiently displaces oil [47] by heating the oil to a temperature at which its viscosity is sufficiently decreased [48]. Steam flooding is the most applied EOR technique worldwide because it is very effective in rendering high oil recovery ratios. Higher sweep efficiency is achieved with steam flooding than with the application of cyclic steam stimulation or CCS.

Process limitations. Steam flooding is an expensive venture. Significant heat loss (i.e. heating of injection tubing, heating of overburden and under burden rock, etc.) occurs during the extensive steam injection periods [43]. Avoidance of sand plugging at the bottom hole [49], prevention of steam channelling [50] and improvement of steam sweep efficiency [51] are still key challenges of steam flooding operations, especially in super heavy oil formation. Early steam breakthrough at the producing wells decreases the rate of recoverable oil [49].

Cyclic steam stimulation is applied in three stages as follows [45, 52]:

- *Steam injection.* In this stage, adequate quantities of steam are injected during a pre-established period of time.
- *Soaking stage.* After the injection of the required volume of steam, the well is shut-in for several days or weeks to maximise heat transfer and heating of the oil that results in oil viscosity reduction [52, 53].
- *Production stage.* The well is open to production. Initially, a high oil flow rate is attained; however, it progressively decreases. Oil production might be supported by artificial lifting.

As the reservoir temperature declines, the oil flow rate drops significantly; at this point in time, another cycle of CSS is applied to re-attain the high oil production rates [52, 53]. CCS applied for several cycles, until commercial oil flow rates are obtained.

Process benefits. CSS is effective in reducing the viscosity of the oil due to the cyclic application of steam in the same well with potential for substantial oil recovery, especially in heavy oil reservoirs having thick pay zones (>15 m) [54]. However, the CSS oil recovery factor is low in comparison to steam flooding.

Process limitations. The CSS process is complex. Excessive heat loss occurs and the radius of the heated zone is insignificant [55]. Application of CSS in thin heavy oil (<6 m) reservoirs is uneconomical [54].

In steam-assisted gravity drainage (SAGD), steam is constantly injected using two horizontal wells—the upper steam injector well and the lower producer well (collects the heated oil and water). The injector and producer wells counterbalance the effect of high viscosity of the oil through prolonged steam (heat)—oil contact and provide the drive force for the movement of the oil towards the producer well [56]. SAGD is influenced by the gravity drainage of the heated oil and condensed water [57]. The process efficiency is predominantly controlled by fluid mobility. In SAGD, oil recovery is achieved when:

- The upper horizontal well injects steam into a chamber at a temperature that significantly reduces the viscosity of the heavy oil and/or bitumen, which improves oil flow.
- At the edge of the chamber, heat is released through condensation [57] and reduction in oil viscosity occurs.
- Then the heated oil drains by gravity through the steam chamber towards the production well (lower horizontal well) [58].
- The injection of steam and production of oil occurs concurrently and constantly [59]

and the oil production rate is controlled by the expansion of the steam chamber [56].

Process benefits. SAGD is very efficient in recovering bitumen and heavy oil. Oil production increases with the increase in oil pay thickness (>15 m) [60], thus production can be considered economical.

Process limitations. Possible loss of injected steam due to poor process control which can lead to low oil recovery rate. SAGD oil production is considered uneconomical in pay zones with thickness <15 m [61], due to the high steam-to-oil ratio (SOR) required.

This process is susceptible to low mobility control and rapid gravity segregation. The mobility control is considered a limitation as the steam viscosity is much lower than the viscosity of the oil and water. Similarly, the density of steam is much lower than the density of oil and water [1]. Thus, an upward migration of steam to the top of the reservoir often occurs and the steam overrides a larger part of the heavy oil zone. This issue can be partially controlled by heat conduction away from the steam contact [1]. Other limitations of the SAGD process are the significant production of CO₂ emissions during steam generation at surface facilities, heat losses and equipment problems due to the high temperature of the process [1].

2.1.4. TEOR field applications

TEOR, specifically steam injection, and *in situ* combustion have shown great potential worldwide. Steam injection projects have been reported in California, Indonesia, Oman, Alberta (Canada), Venezuela and the former Soviet Union [37]. Field trials of steam injection have been conducted in Brazil, China, Trinidad and Tobago [29]. CSS has been applied in California, Alberta and Venezuela. ISC projects have been reported in Romania, the USA, Canada and India [29]. SAGD is mainly carried out in Alberta, Canada for the recovery of bitumen. SAGD has also been tried in Venezuela, although it has not been very successful [29, 37].

2.1.5. Technological advancement in TEOR techniques

New areas of research have been considered to tackle fiscal and environmental issues related to TEOR processes (i.e. huge capital expenditures and significant generation of CO₂ emissions). These recent advances comprise the development or improvement of several TEOR process such as the Toe-to-Heel Air Injection (THAI) process [62], Fast-SAGD [60], Enclosed Trough Solar Once-Through Steam Generator (OTSG) EOR System [64], Solar Thermal Enhanced Oil Recovery (ST-EOR) [29], Gas-Oil Gravity Drainage (GOGD), Thermally Assisted Gas-Oil Gravity Drainage (TAGOGD), Tertiary Gravity Drainage (TGD) [65] and High-Pressure Air Injection (HPAI) [29, 63].

2.2. Chemical EOR techniques (CEOR)

In chemical EOR (CEOR) techniques, oil is recovered through the injection of chemicals [62, 66, 67]. CEOR is predominantly suitable for heavily depleted and flooded formations (i.e. mature reservoirs) [68]. Typical chemicals are polymers, surfactants, alkalis and formulated mixtures thereof [62, 33, 69]. The efficiency of such formulations is normally screened in laboratory studies [69–71] and each chemical has different effects on oil production [72]. For example, the application of surfactants or alkali or its mixtures can substantially reduce the interfacial tension between brine and oil [69, 73–75]; significantly improving the microscopic sweep efficiency at the pore scale [76, 77]. Mobility ratios can be considerably improved by adding polymers to the injected water [62, 78]. The addition of polymer to the injection brine increases the viscosity of the aqueous phase, which leads to an improved macroscopic displacement, as water under-riding is lessened [79]. The addition of surfactants improves the microscopic displacement efficiency through: (a) the reduction of the oil-water interfacial tension [72, 80, 81] and (b) the production of oil-water emulsions [62], which mobilises residual oil. The addition of alkalis induces the *in situ* formation of natural surfactants by reacting with the acidic components contained in the crude oil (generally heavy oils). These natural surfactants function in the reservoir in the same fashion as synthetic surfactants [62, 82].

2.2.1. Evolution of chemical EOR

In the last few years, CEOR has been undergoing a rebirth. Since the 1960s, polymer flooding has been globally the most widely used of the three types of CEOR techniques [83]. CEOR has

experienced significant chemical developments since its first applications in the 1960s and 1970s [83]. For example, micellar flooding in the 1970s and 1980s was very effective in light and medium oil reservoirs, where CEOR processes applied micellar floodings at surfactant concentrations ranging from 2 to 12% [83]. However, the concentrations of surfactant used have notably decreased to values ranging from 0.1 to 0.5% [84]; while at the same time, micellar floodings at these low surfactant concentrations have demonstrated significantly increased efficiency. In the face of the current oil price instability, interest in surfactant for CEOR processes, have maintained a constant growth trend [84]. However, at present, the high cost of surfactants makes very difficult the economic justification for field applications of surfactant flooding.

2.2.2. Chemical EOR classification

The most common CEOR techniques are polymer, surfactant, alkaline, surfactant-polymer (SP) and alkaline-surfactant-polymer (ASP) flooding.

2.2.3. CEOR techniques and oil recovery mechanisms

2.2.3.1. Polymer flooding

For several decades, hydrogel polymers have been used for mobility control. Likewise, polymers in combination with surfactants and alkalis have been applied over the years to improve both the microscopic and macroscopic sweep efficiency [85]. In recent times, several new polymers for EOR (**Table 2**) have been developed such as synthetic polymers (i.e. polyacrylamide or PAM) (**Figure 4**), hydrolysed polyacrylamide (HPAM), biopolymers (i.e. xanthan gum) and superabsorbent polymer composite (SAPC) [4, 66, 85].

Polymers	Molecular weight	Polymer description	EOR application	References
Hydrogel		<ul style="list-style-type: none"> Non-newtonian or pseudo plastic fluids The fluid viscosity is a function of shear rate 	<ul style="list-style-type: none"> Used mainly for mobility control Used in combination with surfactants and alkali for improvement of sweep efficiency 	[85]
Polyacrylamide (PAM)	$>1 \times 10^6$ g/mol	<ul style="list-style-type: none"> First synthetic polymer used for thickening aqueous solutions The thickening potentials exist in its large molecular weight >High adsorption capacity on mineral surfaces 	<ul style="list-style-type: none"> Increases the brine viscosity Improves EOR performance 	[4, 66, 85]

Polymers	Molecular weight	Polymer description	EOR application	References
Hydrolysed polyacrylamide (HPAM):	>20 million Da	<ul style="list-style-type: none"> • copolymers of PAM and polyacrylic acid (PAA) or acrylamide and acrylic acid • PAM is partially hydrolysed to form HPAM. This is achieved by reacting PAM with a base (sodium) to reduce the strong adsorbing behaviour of PAM • The degree of hydrolysis is usually in the range of 15–35% 	<ul style="list-style-type: none"> • The most commonly used polymer for EOR • Oil recovery using HPAM is high owing to its viscoelasticity • Depending on the stability of the brine, HPAM can be used at a temperature up to 99 °C 	[4, 66, 85]
Xanthan gum	$2 \times 50 \times 10^6$ g/mol	<ul style="list-style-type: none"> • A biopolymer produced by microbial (<i>Xanthomonas campestris</i>) action (through glucose or fructose fermentation) • Possess substantial hydrolytic degradation above 70 °C • Acts like a partially stiff rod with a fair resistivity to mechanical degradation • Xanthan gum for EOR is often in broth or concentrated form which makes it easy to dilute at suitable concentrations 	<ul style="list-style-type: none"> • Effective for use in high salinity brine • Fairly compatibility with surfactants when used for EOR 	[4, 85, 89]
Superabsorbent polymer composite (SAPC)		<ul style="list-style-type: none"> • Crosslinked hydrophilic polymers which have the potential to retain water in swollen form 	<ul style="list-style-type: none"> • Effective for used as plugging agents in EOR processes 	[85, 90]

Table 2. Effective polymers for EOR processes.

Among these polymers, HPAM (**Figure 4**) remains the most effective and commonly used polymer for enhanced oil recovery. According to Sheng [4], the effectiveness of HPAM relies in the following chemical features: (1) the lack of oxygen single bonds (-O-) in the polymer backbone (carbon chain) provides thermal stability; (2) the presence of non-ionic hydrophilic group (i.e. -CONH₂) promotes chemical stability and (3) the carboxyl group (-COO-) resulting from the hydrolysis of the amide groups reduces the adsorption tendency of HPAMs onto rock surfaces and increases its viscosity.

Other characteristics that makes HPAM very attractive for EOR includes: (1) fairly easy application with great potential for incremental oil at standard reservoir conditions (i.e. low temperatures and low salinity and hardness concentration); (2) availability of the polymer in

various molecular range (>20 million Da); (3) the cost of the polymer is relatively low; and (4) its viscosifying and psychochemical characteristics [85].

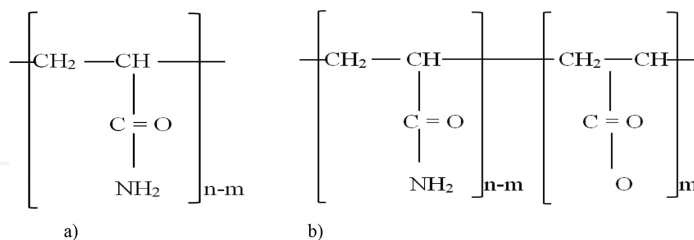


Figure 4. Structure of: (a) polyacrylamide (PAM), and (b) partially hydrolysed polyacrylamide (HPAM) (refer to Table 2).

Xanthan gum is a biopolymer also commonly used for EOR applications. The main limitation of this biopolymer is its vulnerability to microbial degradation. Salt compliant microbes (aerobic and anaerobic) have the potential to degrade the xanthan gum chains, which results in viscosity loss [86–88]. Therefore, biocides are injected alongside with xanthan gum to avert microbial degradation [85]. However, xanthan performs remarkably well in brines having high salinity concentrations [85]. Generally, high salinity brines (i.e. 10,000 ppm TDS) polyacrylamide co-polymers shows lower viscosities than biopolymers [4]. Nonetheless, HPAMs have better potential for reducing the water relative permeability than xanthan during flow through formation rocks.

In polymer flooding, polymers (dissolved in water) are injected into the reservoir, followed by a long-term waterflooding, which is performed to drive the slug and the oil bank in the direction of the production wells. The addition of polymer to the injected brine increases the viscosity of the aqueous phase and reduces the effective permeability to water due to polymer retention (adsorption and mechanical trapping) in the formation rock.

The main objective of polymer flooding is to lower the mobility ratio of the waterflooding process. It is well established that the lower the mobility ratio, the more stable the displacing fluid front, and the more efficient the macroscopic displacement process. Therefore, mobility ratio (M) should be controlled to values less than one ($M < 1$) to prevent the onset of viscous fingering of the water phase through the oil phase, which will result in unswept regions, where oil is left behind the displacement front [1, 77].

The overall mechanisms of oil recovery by polymer flooding are as follows:

- Increasing of the water viscosity.
- Decreasing of the effective permeability to water due to polymer retention.
- Decreasing of the water-oil mobility ratio that improves the macroscopic sweep efficiency.

Process benefits. Polymers are effective brine viscosifying agents [85] and successfully reduced the effective permeability to brine (i.e. polymer retention). Overall, polymer flooding is a cost-effective EOR process.

Process limitations. Some of the limitations of polymer flooding are their susceptibility of polymers to thermal (i.e. high temperature reservoirs), chemical (i.e. high salinity and hardness concentration in the injected and formation brine), mechanical and bacterial degradation. Some polymer systems are incompatible with the reservoir fluids and conditions (i.e. temperature). The application of polymer flooding in low permeability rocks may cause problems of injectivity and formation plugging [85].

2.2.3.2. Surfactant flooding

Surfactants are amphiphilic in nature (hydrophobic and hydrophilic) and are soluble in water and organic solvents. Surfactants effectively reduce the interfacial tension (IFT) between oil and water (i.e. brine). Four basic categories of surfactants (**Table 3**) exist: anionic, cationic, non-ionic and zwitterionic [91, 92].

Surfactants	Surface charge	Mechanism
Anionic	Negative	<ul style="list-style-type: none"> • Most globally used surfactant for EOR • Displays low adsorption on reservoir rock surfaces (e.g. Sandstone) • Effective wettability alteration agent • Effective IFT reduction agent
Cationic	Positive	<ul style="list-style-type: none"> • Low cost in comparison to Cationic • Effective for wettability alteration in carbonate rocks than in sandstone. • Considered relatively unsuitable for application in sandstone (negatively charged) reservoirs due to its strong adsorption behaviour onto the rock surface
Nonionic	No ionic charge	<ul style="list-style-type: none"> • Mainly function as a copolymer. • Effective for improving phase behaviour of a system • Tolerant to high salinity and hardness
Zwitterionic	Positive and negative	<ul style="list-style-type: none"> • Fairly effective IFT reduction agent • Effective for IFT reduction • The effect of electrolytes, pH and temperature changes on zwitterionic is negligible • Exhibits better temperature resistance and salt tolerance than other surfactant types

Table 3. Effective EOR surfactants [4, 194].

In surfactant flooding applications, a dilute aqueous surfactant solution [93] is injected into the reservoir. Mechanistically, the injected surfactant migrates to the oil-water interface reduces the interfacial tension (IFT) between oil and water and essentially increases the miscibility of these phases [3]. To put this into perspective, in a typical waterflooding process, IFT is approximately 30 mN/m; the addition of small concentrations of surfactant (in the range of 0.1–5.0 wt%) to the injected water [1–3, 33, 94, 95] can significantly reduce IFT to values of 0.01 mN/m or lower [33]. The critical micelle concentration (CMC), phase behaviour and oil

solubilisation ratio [97] are key parameters for the characterisation of the efficiency of the surfactant formulation. For effective oil displacement:

- Dilute aqueous surfactant solutions are injected in slugs.
- The injected slugs must attain ultra-low IFT.
- This leads to the mobilisation of the residual oil and creation of oil banks, which allows the continuous phase flow of oil and water [96].

Process benefits. Effective reduction of the interfacial tension between brine and water that significantly enhances the microscopic sweep efficiency.

Process limitations. The achievement of ultra-low IFT for effective residual oil mobilisation is a complex process. Large amounts of surfactants are required to achieve substantial oil recovery. The viscosity of the surfactant formulation is often lower than that the viscosity of the oil, thus, to augment the viscosity of the surfactant slug, the addition of polymers to the surfactant formulation is required. The high cost of surfactants makes its deployment in the field highly dependent on oil price [97].

2.2.3.3. Alkaline flooding

Alkaline flooding involves the injection of an aqueous solution of alkaline chemical such as sodium hydroxide, sodium carbonate or sodium orthosilicate in a slug form [2, 98, 99] (Table 4); the most commonly used alkaline chemical is sodium hydroxide [3].

Alkaline	Characteristics
Sodium hydroxide NaOH	<ul style="list-style-type: none">• Most commonly used alkaline for EOR• Used for IFT reduction• Corrosion and scale formation issues
Sodium orthosilicate Na ₄ O ₄ Si	<ul style="list-style-type: none">• Reduces water hardness through formation of silicates which are less soluble than the hydroxides• Better IFT reduction potentials than sodium hydroxide in hard water• Precipitation or scale formation issues
Sodium carbonate Na ₂ CO ₃	<ul style="list-style-type: none">• Weaker alkali in comparison to sodium hydroxide and sodium orthosilicate• Corrosion and scale formation issues

Table 4. Effective alkaline chemicals for EOR [4].

During alkaline flooding, the alkaline solution and organic acids present in the crude oil react to form natural surfactants *in situ*, which cause the reduction of IFT between the brine and oil. Natural surfactants induce the formation of oil and water emulsions and wettability alteration of the reservoir rock [3, 93, 100]. All these physicochemical interactions occur at the oil-water rock interfaces, which invariably improves oil recovery.

Process benefits. Alkaline flooding shows potential for heavy oil recovery in thin formations [101]. This process promotes effective IFT reduction and crude oil emulsification. Overall, alkaline flooding is characterised for low operational costs.

Process limitations. Scale formation is a serious issue during alkaline flooding. Furthermore, the low viscosity of the alkaline solution is associated with the occurrence of unfavourable fingering and poor volumetric sweep efficiency [102].

2.2.3.4. *Surfactant-polymer (SP) flooding*

In surfactant-polymer flooding, separate surfactant and polymer slugs are injected into the reservoir. The alternate injections of surfactant and polymer slugs have the potential to sweep larger reservoir volumes and to increase oil displacement efficiency.

The mobility control is established during SP flooding by injecting the chemical slugs according to the following injection scheme: surfactant slug, polymer slug [103], polymer buffer (to protect the integrity of the polymer slug) and chase water [104].

Accurate formulation of the surfactant-polymer (SP) mixture can promote capillary number increase (due to the presence of surfactants through IFT reduction) and reduction in mobility ratio. However, an incompatible SP formulation can cause surfactant and polymer phase separation even when oil is not present [103]. Two essential factors for consideration during SP flooding are: (a) IFT reduction and (b) viscosity increase [13, 104, 105]. In addition, the effective permeability to water is reduced due to polymer retention in the formation rock [106]. Therefore, an overall improvement of mobility ratio and sweep efficiency [106, 107] is achieved rendering incremental oil recovery [108].

Process benefits. Accurate SP formulation can achieve ultra-low oil-brine IFT, which promotes effective displacement of residual oil saturation.

Process limitations. The main limitation of the SP flooding process is chemical incompatibility among the additives and brine (injection and formation brine).

2.2.3.5. *Alkaline-surfactant-polymer (ASP) flooding*

ASP flooding uses alkali-surfactant-polymer cocktails for further improvement of oil recovery efficiency [107, 109]. The key reasons for the combination of the three chemicals are IFT reduction and mobility ratio improvement [2]. Alkali decreases surfactant adsorption onto rock surface through an increase of the negative charge density at the rock surface yielding a more water-wet surface [95, 110]. Surfactant decreases the IFT [111] between oil and brine, which promotes oil mobilisation and oil bank formation, whereas polymer offers mobility control [106]. The amount of chemical consumed per unit volume of oil produced during ASP flooding is usually low when the three chemical slugs (alkaline, surfactant and polymer) are injected in sequence or as a single slug [2, 100].

Process benefits. ASP is a cost-effective process. The synergistic effects of the ASP mixture make this process attractive for EOR applications.

Process limitations. Some of the limitations of the ASP process are related to issues with chemical separation, emulsions instability and scale formation that could make the process complex.

2.2.4. *Technological advancement in CEOR techniques*

Research has led to recent advances in CEOR aiming to improve the economic feasibility of the field application of CEOR processes. Particularly, the development and improvement of effective polymers for EOR is noticeable. Some of these polymers include polyacrylamides (PAM) [66, 85], hydrolysed polyacrylamide (HPAM—the most commonly used polymer) [66, 85], biopolymers (i.e. xanthan gum) [4, 85] and superabsorbent polymer composite (SAPC) [86]. Other recent modified polymers are hydrolysed polyacrylamide-acrylamido methyl propane sulfonic acid (HPAM-AMPS) co-polymers, and sulphonated polyacrylamides, which are produced as powders and self-inverting emulsions that are suitable for high temperature applications ranging from 104 to 120°C [85].

2.2.5 *CEOR field applications*

CEOR projects implemented in the United States in the 1980s did not show technical and/or economic success. However, in the last decade CEOR successes, specifically polymer flooding, which is the most applied CEOR method worldwide [112], has been reported in China [28, 113], along with ASP flooding successfully implemented at pilot and commercial scale in the Daqing, Xinjiang and Shengli oil fields in China [114].

Polymer flooding has also been reported in Canada (East Bodo field), Oman (Marmul field), Suriname (Tambaredjo field) and Mexico (Vacuum field) [115]. Other countries that have reported successful applications of ASP flooding are India (Viraj field), Venezuela (Lagomar LVA field) and in the United States (Cambridge Minnelusa field, the West Kiehl and Tanner fields in Wyoming, and Lawrence field in Illinois) [115, 116]. Surfactant flooding has been reported in Indonesia (Baturaja formation in the Semoga field), Bahrain (Mauddud field), Texas (Yates field and the Cretaceous Upper Edwards reservoir) and Wyoming (Cottonwood Creek field). Surfactant-polymer flooding has been reported in China (Gudong field) [115]. Alkali flooding has been reported in Hungary (H field), India (North Gujarat field), Russia (W field) and the United States (Whittier field in California) [115].

2.3. **Gas injection EOR (GEOR) technique**

In EOR gas injection (**Figure 5**), oil is displaced towards the production wells by injecting gas. Two predominant factors determine the success of this process: (a) the displacement efficiency and (b) the sweep efficiency. The displacement efficiency is the percentage of oil displaced by the injected fluid, whereas sweep efficiency accounts for the reservoir volume contacted (swept by) the injected fluids [12]. Gases commonly used for GEOR are carbon dioxide, hydrocarbon gases and nitrogen [62]. Among these gases, CO₂ is the most frequently applied and it accounts for over 50% of the GEOR production [67, 117]. For instance, in 2009, Ferguson et al. [118] reported that 101 GEOR projects in the US produced approximately 250,000 barrels of oil per day. In the United States, CO₂-EOR has been considered the best GEOR method to produce incremental EOR [119]. Nevertheless, GEOR processes are often associated with viscous and density fingering [1, 120].

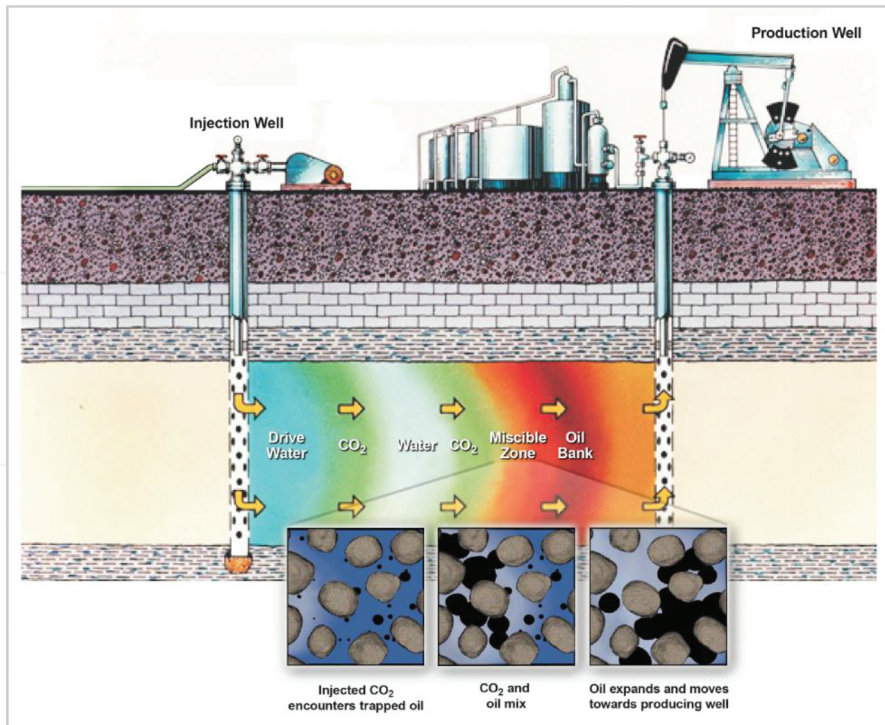


Figure 5. CO₂ gas injection EOR [121].

2.3.1. Evolution of gas injection EOR

Gas injection was first developed in the United States, where it is still largely applied. Gas injection is one of the oldest fluid injection processes implemented for pressure maintenance. The first gas injection project was a pressure maintenance job initiated in 1864, after drilling the Drake well in Titusville, Pennsylvania. The project was aimed at boosting fast oil production [12]. In 1930, the earliest gas drive project was successfully performed in West Texas [122]. In the 1970s, another gas injection trial was performed at the Surry County, Texas [119]. In the past two decades, gas injection has gained significant interest and recent projects are focused in combining hydrocarbon recovery with CO₂ geo-storage [123]. Geological storage of CO₂ (CO₂-EOR) is one of the most promising technologies for promoting ultimate oil recovery, while it simultaneously alleviates the problem of greenhouse gas accumulation in the atmosphere [124, 125]. CO₂-EOR has been extensively deployed since the mid-1980s in the Permian Basin of West Texas with high profit margins achieved over the past three decades [126].

2.3.2. Types of gas injection

The two main gas injection processes involve miscible and immiscible gas flooding.

2.3.3. Mechanisms of gas injection for EOR

2.3.3.1. Miscible flooding

In miscible gas flooding, gas completely mixes with the crude oil through single or multiple contacts between the gas phase and the crude oil phase. The gas injected reaches miscibility with the crude oil at or above the minimum miscibility pressure (MMP) [127]. MMP is the minimum pressure at which crude oil becomes miscible with the injected gas at the reservoir temperature [121]. MMP is a determining factor during miscible gas (e.g. CO₂) flooding, as displacement efficiency is highly dependent on it [128]. CO₂ achieves miscibility with crude oil through multiple contacts between the oil phase and the CO₂ phase. In this mechanism of multiple contact miscibility, light hydrocarbons (lighter-low carbon, low density) from the crude oil are transferred (vaporised) into the CO₂ phase. Progressively, the gas phase becomes richer in the vaporised light hydrocarbons, which continuously change the composition of the gas phase that eventually becomes heavier and denser. This heavier gas phase condenses into the crude oil zone ahead of the displacement front (i.e. miscible zone) causing the reduction in crude oil viscosity and density [121]. As miscibility occurs between the residual oil and the injected CO₂, the IFT between the gas and the oil phase becomes zero, thus this mixture is displaced as a single phase from the pores of the rock towards the producing well [121]. Very low residual oil saturation is achieved as the interfacial tension (IFT) in the miscible zone reduces to zero, thus there is no interface between oil and gas anymore [62, 129].

Process benefits. Miscible gas injection increases the overall displacement efficiency, minimises residual oil saturation, promotes ultra-low (near zero) IFT and increases oil production significantly. Based on operational costs, miscible gas flooding is usually more cost effective [115] in comparison to TEOR flooding methods.

Process limitations. Miscible gas injection requires higher (expensive) operational costs (i.e. high gas compression costs). The changes in the crude oil density during the miscibility process can alter the flow path of the oil during the period when the lighter hydrocarbons vaporise into the CO₂ gas phase or when the rich gas phase (CO₂ plus light hydrocarbons) dissolves (condenses) into the oil phase [130]. Failure in miscibility may occur if pressure is not at or above the MMP leading to an unsuccessful miscible displacement process.

2.3.3.2. Immiscible flooding

Immiscible gas flooding entails the injection of gas below the MMP. Below the MMP, there is no miscibility between CO₂ and oil [174]. Technically, immiscible flooding produces about half of the recovery of miscible gas flooding [131]. During immiscible flooding, incremental oil recovery is mainly achieved through oil swelling, which improves the macroscopic displacement efficiency [127]. At microscopic level, three-phase (oil-gas-water) flow is observed with a complex interplay of the different phases [63, 132, 133]. Although these microscopic processes are still poorly understood, there is clearly significant potential to further improve oil recovery at the pore level. Notably, constant immiscible gas flooding with gases such as CO₂ is more favourable to light oil than heavy oil reservoirs [134]. To improve recovery in heavy oil formations using CO₂, co-injection or the injection of water alternate gas, known as the WAG

process, is performed to somehow control viscous fingering, gas channelling and early gas breakthrough. Upon injection of water and gas into the reservoir, a portion of the injected gas (CO_2) usually dissolves in the oil that leads to oil viscosity reduction [134]. A recent advancement in immiscible flooding is polymer water alternate gas (PWAG) for overcoming viscous fingering and improvement of sweep efficiency [134].

Process benefits. Immiscible gas injection improves oil displacement efficiency. The oil recovery potential from the application of this process is higher from light oil formations [134].

Process limitations. Viscosity ratios of the injected gas (i.e. CO_2) to oil (light or heavy oil) are unfavourable [134] triggering the occurrence of gravity override and viscous fingering through permeable zones [134], early gas breakthrough and poor sweep efficiency [135]. This process renders poor oil recovery potentials in heavy crude oil formations in comparison to thermal EOR.

2.3.4. Technological advancement in GEOR techniques

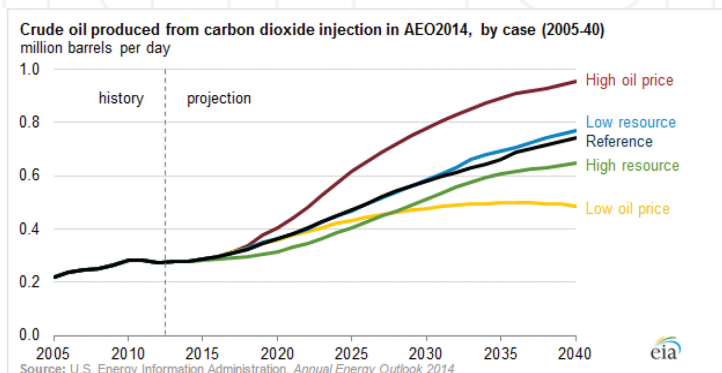
Advances in gas injection EOR include water alternate gas (WAG) injection; the simultaneous water alternate gas injection (SWAG) [136], polymer water alternate gas (PWAG) injection [134], the development of CO_2 gas membrane separation technology and field applications of immiscible gas-assisted gravity drainage (GAGD) [137, 138].

2.3.5. GEOR field applications

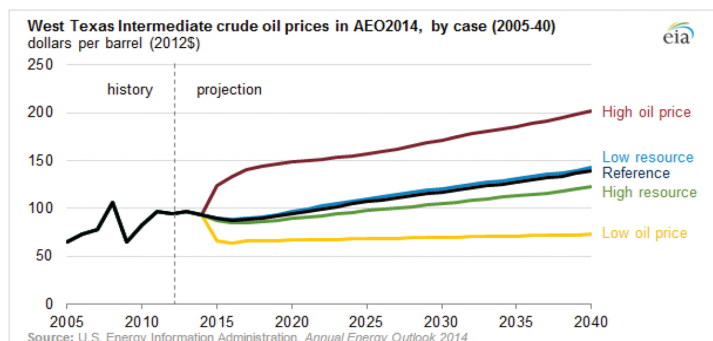
As previously mentioned, CO_2 , N_2 and hydrocarbon gases are used in GEOR. Technically, the injection of carbon dioxide (CO_2) and hydrocarbon gases achieve higher oil recovery efficiencies. However, natural gas is expensive and there is growing concern about its impact as greenhouse gas; thus, CO_2 is considered the most appropriate gas for injection, although oil recovery using CO_2 is also a costly venture. Certain costs are often associated with its deployment such as: (a) cost of the CO_2 itself which can add about \$20–30 per barrel of oil produced [139]; (b) cost of surface facilities for separation of the CO_2 from the production streams and compressing it back into the oil reservoir; and (c) financial costs for the time delay associated with the re-pressurising of old reservoirs [139]. According to the US Energy Information Administration, Annual Energy Outlook (AEO) 2014 report (**Figure 6**), the application of CO_2 for EOR purposes appears to be dependent on oil prices. Hence, an economic feasibility study is recommended to ascertain whether or not a specific CO_2 -EOR project is viable. For instance, an analysis between crude oil produced from CO_2 injection and the cost of injection using a case study was conducted for current, and forecasted (**Figure 6a** and **b**) projects to examine how oil prices would affect the feasibility of field implementation of CO_2 -EOR. **Figure 6(a)** shows oil production in million barrels per day using CO_2 -EOR and **Figure 6(b)** shows the West Texas Intermediate (WTI) crude oil prices (past and future projections) for different cases: a reference case that accounts for 10% of total US crude oil production, low and high oil prices and high and low oil and gas resources. **Figure 6(a)** clearly shows the effect of crude oil price and hydrocarbon resources on crude oil production. At low oil prices, the WTI crude oil is expected to reach \$73 per barrel by 2040 (**Figure 6b**) with CO_2 -EOR production expected to

reach 480,000 barrels per day by 2040, which is less than 35% of the reference case. Therefore, this scenery will not favour the field application of CO₂-EOR [139]. While in the high oil price case (\$202 per barrel that is 45% higher than in the reference case), expectations are that oil production will be 960,000 barrels per day by 2040 (30% higher than in the reference case of 740,000 barrels per day), which favours the profitable application of CO₂-EOR in old oil fields [139]. At the reference case, 10% of total US crude oil production is achieved using CO₂-EOR against the low oil price case (8%) and high oil price case (12%) [139]. **Figure 6(b)** also indicates that the low oil and gas resource case projects are more profitable than the high oil and gas resource case projects [139].

Despite the high production costs associated with CO₂-EOR processes, CO₂ injection into oil reservoirs at high pressure reduces the oil viscosity and causes oil to swell, which in turn yields an increase in cumulative volume of produced oil and in the percentage of recoverable oil [139]. In the United States, large oil production has been achieved through miscible CO₂



a)



b)

Figure 6. CO₂-EOR projected dependence on oil price. (a) CO₂-EOR as a function of time, oil price and hydrocarbon resources. (b) West Texas Intermediate (WTI) crude oil price as a function of time, number of fields that can profitable produced oil using CO₂-EOR technology and hydrocarbon resources [139].

flooding, specifically from West Texas, Wyoming and Mississippi oil fields, where natural sources of CO₂ are readily available at affordable price [131]. In North America, the majority of miscible CO₂ flooding projects are currently taking place in carbonates reservoirs in the Permian Basin of West Texas and in Saskatchewan, Canada (Weyburn-Midale oil field) [28]. CO₂-EOR successes in the United States are due to the readily available CO₂ sources located adjacent to oil fields, whereas in Canada, the CO₂ sources are located in North Dakota [28]. Prospective candidate oil fields for CO₂-EOR have been determined in Louisiana, Texas, the Gulf Coast, Mississippi, Alabama and in onshore areas of Florida [131]. Nevertheless, these fields are located away from existing natural CO₂ sources [131]. The incremental CO₂-EOR oil production from different regions in the United States (see **Table 5**) was 282,000 bpd in 2012; while in 2014 a constant oil production rate of 280,000 bpd was attained in 2014. A production rate growth to 615,000 bpd is expected by 2020 [140].

Year	Region / CO ₂ -EOR oil production in thousands barrels per day (MBPD)				
	Rockies	Gulf coast	Mid-continent	Permian basin	Total production
2012	36	43	17	186	282
2015	55	73	37	241	405
2020	103	153	58	301	615

Table 5. USA regional CO₂-EOR oil production projection [140].

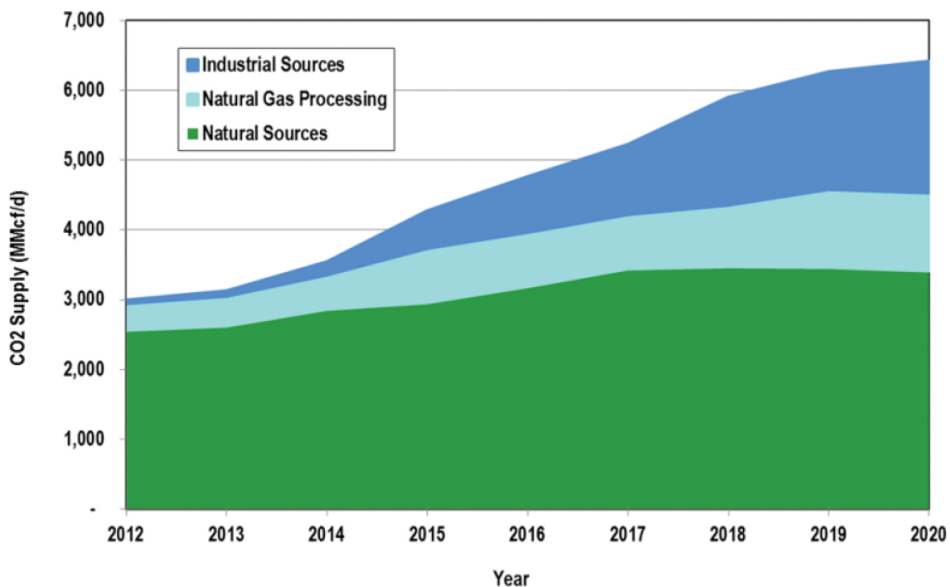


Figure 7. U.S. EOR supply and storage of CO₂ for EOR [140].

In the United States, the utilisation of CO₂ from natural gas processing and other industrial CO₂ sources for EOR amounted to 0.4 MMcf/d in 2012 [139]. It is predicted that by 2020, the volume of CO₂ will reach approximately 6.4 MMcf/d (**Figure 7**) and the key CO₂ sources will be obtained from industrial plants along the Gulf Coast and natural CO₂ sources. **Figure 8** displays the projected sources of CO₂ for EOR operations by 2020.

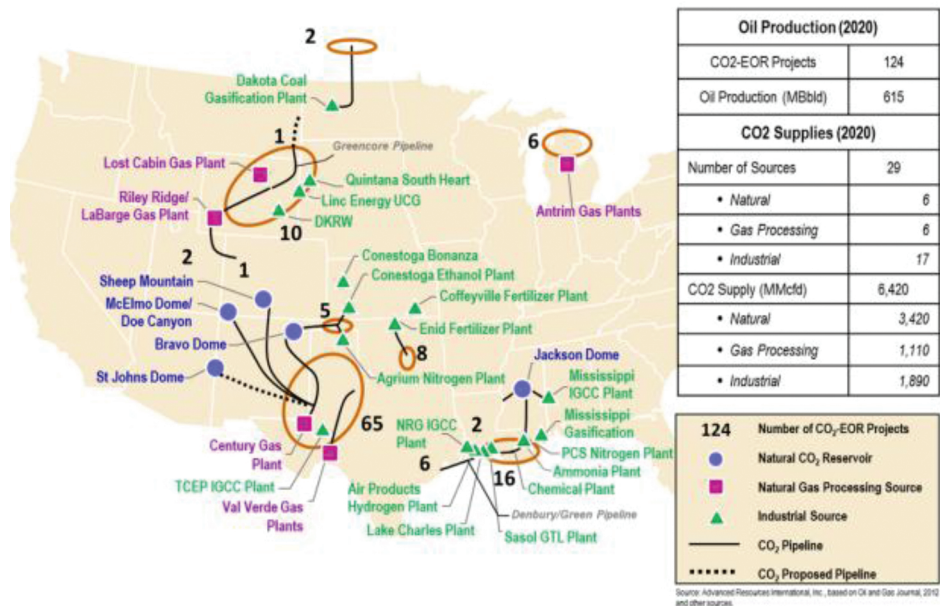


Figure 8. Projected CO₂-EOR operations and CO₂ sources by 2020 [140].

However, in the absence of a local CO₂ market, hydrocarbon gases, which are also excellent solvents for light oil reservoirs, can be used for oil production augmentation. For instance, hydrocarbon gases have been applied in Libya, Alaska, Canada and Venezuela [28]. Other gases aside CO₂ and hydrocarbon gases have been moderately applied. In the 1950s, N₂ gas was used for well completion and well workover processes [141]; N₂ has also been extensively used in oil field operations such as reservoir pressure maintenance, gas lift and gas cycling [111]. Most recently, N₂ has been used as a substitute for CO₂ due to its inert and noncorrosive nature. N₂ is most suitable for deep light to medium oil reservoirs [2, 111, 113] with a proven high recovery rate of about 45–90% of the original oil-in-place (OOIP) [111]. N₂ is considered economically viable for oil recovery by miscible gas displacement in high-pressure reservoirs where the high cost and poor accessibility to CO₂ and natural gas are an issue (**Figure 9**) [111, 142].

Miscible displacement conditions can be achieved using N₂ at high pressure, alongside with the reduction in oil viscosity [143]. N₂ gas injection has been reported for the Hawkins Field (Texas), Cantarell Field (Mexico) and Elk Hills (California) [144].

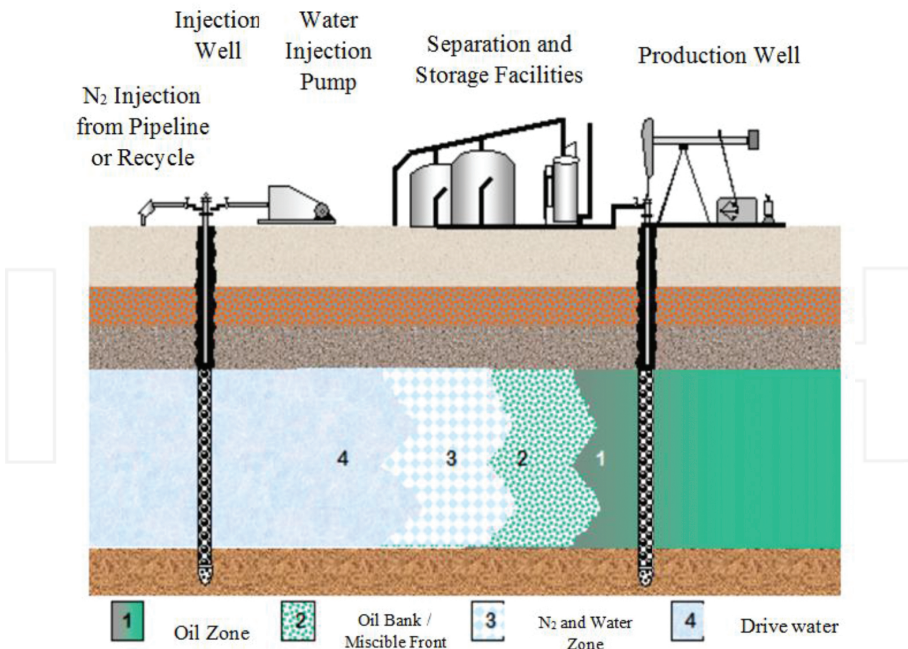


Figure 9. Nitrogen gas displacement EOR [111].

2.4. Microbial EOR

2.4.1. Microbial EOR techniques (MEOR)

In MEOR, indigenous or exogenous bacteria can be activated or injected into the reservoir to generate metabolic chemicals that interact with the crude oil and increase oil production [19]. For these applications, bacteria should be small, spherical and less than 20% of the size of the pore throats in the formation [145]. Small cell size (between 0.5 and 5.0 μm) penetrates easily through the reservoir porous medium [146]. Typically, mixed microbial populations are used in combination with metabolic products such as solvents, acids or gases to increase recovery and prolong the life span of the oil wells [14, 15, 19]. These metabolic products are produced by different bacteria (microbes) and exhibit different functionalities in MEOR processes. Solvents such as acetone, butanol and propan-2-diol (produced by *Clostridium*, *Zymomonas* and *Klebsiella*) reduce oil viscosity and thus improve oil mobility [147, 148]. *Clostridium*, *Enterobacter* and *Methanobacterium* produce methane and hydrogen, which reduce IFT, oil viscosity [149] and increase oil mobilisation. Among several microbes used for MEOR processes, *Clostridium* microbes are the most applicable owing to their resistant endospores that enable survival at unfavourable conditions [150]. *Bacillus* strains are also effective MEOR agents [19, 20].

2.4.2. Evolution of microbial EOR (MEOR)

The MEOR process was first proposed by Beckmann in 1926, though it was brought to recognition in the 1940s through the work by ZoBell [151]. The first MEOR implementation happened in 1954 in the Lisbon fields in Union County, Louisiana, USA [14, 55]. The acceptance of MEOR as an oil recovery technique found worldwide resistance for decades. One of the reasons was that microbiology was less than 100 years old at the time this EOR technique was proposed. Therefore, the effectiveness of the MEOR process was viewed as a mere curiosity [19]. Prior to the 1940s university laboratories conducted MEOR research [145]. These research efforts continued and eventually led to MEOR growth from extended laboratory work in the 1980s to field level in the 1990s [19].

2.4.3. Mechanism of MEOR

MEOR involves the application of bacteria in oil reservoir for recovery purposes. The bacteria are mostly naturally occurring bacteria in reservoir rocks, hydrocarbon utilising or non-pathogenic [16]. These bacteria produce desired EOR chemicals *in situ* through metabolic reactions [19], that results from multiple biochemical process steps to generate the EOR chemicals [14, 15]. Nutrients (e.g. fermentable carbohydrates) are injected to provide favourable conditions for microbial metabolism [15], which results in the production of biosurfactants, biopolymers and gases (Table 6) [19].

MEOR agents (Microbes)	Functionality
Biosurfactants (i.e. Bacillus, Arthrobacter)	<ul style="list-style-type: none">• IFT reduction between oil and water• Promotes oil emulsification owing to reduced IFT• Improvement of residual oil displacement• Effective for wettability alteration
Biopolymers (i.e. Bacillus, Xanthomonas)	<ul style="list-style-type: none">• Water viscosity can be greatly improved which promotes mobility control• Effective for selective plugging
Bacterial consortia (Biogases: Clostridium, Enterobacter; BioSolvents: Clostridium, Zymomonas; Bioacids: Clostridium, Enterobacter)	<ul style="list-style-type: none">• Used for modifying viscosity of the formation water and injectivity profile• Produces gases such as N₂, CH₄, CO₂, and H₂ that are effective in promoting oil viscosity reduction, IFT reduction, and oil swelling• Produces solvents such as alcohols and ketones which dissolves in oil and promotes IFT reduction and oil emulsification• Produces acids that promotes dissolution of clays increasing porosity and permeability
Biomass (i.e. Bacillus, Xanthomonas)	<ul style="list-style-type: none">• Effective for selective plugging within the porous media• Effective for altering rock wettability• Effective for the partial degradation of crude oil• Displaces oil through bacterial growth between the oil and the surface of rock and water

Table 6. Effective agents for MEOR adapted from [14, 19].

Biosurfactants. Biosurfactants are biodegradable and more effective in emulsifying aqueous hydrocarbon mixtures than synthetic surfactants [152]. Biosurfactants can be produced in bioreactors *ex situ* and injected as an aqueous surfactant formulation into the reservoir. As surfactant migrates towards the oil-aqueous interface, IFT is reduced and capillary number increases displacing and recovering residual oil [19, 152].

The production of *in situ* biosurfactants takes place by injecting the biosurfactant-producing microbes into the formation ensuring proper propagation of the microbes into the oil reservoir [153]. Selected nutrients are also injected to stimulate the growth of the biosurfactant-producing indigenous microbes in the reservoir [152].

Biopolymers. Biopolymers are mainly used for selective plugging of high permeability thief zones. In this MEOR application, bacteria in aqueous solutions are injected into the formation that preferentially flows through the high-permeability pathways, where the growth of biomass plugs the pore throats, leading to permeability reduction [19]. Plugging of high permeability thief zones diverts waterflood towards the lower permeability oil saturated areas.

Bacterial consortia. Bacterial consortia are used for the selective production of biogases (i.e. methane, carbon dioxide and hydrogen), biosolvents (i.e. acetone, ethanol, 1-butanol, butanone, etc.) and bioacids (i.e. acetic, propionic, butyric, etc.). In a pressure-depleted formation, biogases assist in pressure build-up and at high pressures, biogases can dissolve within the oil phase reducing its viscosity [19]. Bioacids are capable of dissolving carbonate rocks leading to porosity and permeability increase in the oil formation [19, 147]

Process benefits. MEOR is environmentally friendly as the MEOR bioproducts are biodegradable [14], low oil production costs, MEOR is not dependent on oil price like the conventional CEOR processes and MEOR consumes less energy than the TEOR processes [19, 154]. MEOR is economically attractive for application in marginally producing oil fields because the injected bacteria and nutrients are low priced [14].

Process limitations. The MEOR process is complex because it depends on the reservoir chemistry for bacteria functionality and isolation. MEOR renders low incremental oil recovery [19].

2.4.4. MEOR field applications

MEOR field projects have been conducted worldwide in past decades. In Australia, MEOR was applied in the Alton field producing approximately 40% of incremental oil after 1 year of treatment application [155]. In the Asian region, MEOR has also been deployed in China, India and Malaysia [156, 157]. Notable MEOR successes with incremental oil productions ranging up to 204% at field trials have been reported in Argentina, US, Romania, India and Russia [158]. Other MEOR application successes at laboratory and field scale have been reported in Bulgaria, Canada, Former East Germany, Saudi Arabia, the Netherlands, Oman, Romania, Norway and Hungary [159].

2.4.5. *Technological advancements in MEOR*

MEOR has developed from laboratory studies between the 1940s and 1980s to successful field applications in the last two decades [19]. Several advances have been made in its application such as the injection of adapted mixed enrichment cultures (AMEC) into reservoirs [160, 161], the stimulation of indigenous microbiota through the use of salts and oxygen alongside water injection [162], and the selective plugging of high-permeability channels through the use of ultra-micro-bacteria formed by selective starvation [163]. Recently, the two notable advances in MEOR are genetically engineered micro-organisms EOR (GEMEOR), and the enzyme EOR (EEOR). Both advances involve the growing of microbes that can withstand extreme reservoir conditions using genetic engineering tools and techniques [19].

3. EOR techniques

3.1. Production performance

In thermal EOR, oil production is increased in heavy oil formations through several mechanisms such as oil viscosity reduction, oil swelling and steam flashing and stripping [1]. Among the TEOR techniques, steam flooding has the highest potential for additional oil recovery than CSS, SAGD and ISC. Steam flooding requires intensive heating and trillions of barrels of heavy oil are recovered as a result of this intense heating [29]. In chemical EOR, polymer flooding exhibits better oil production potentials in comparison to SP and ASP. Whereas ASP demonstrate better recovery efficiency than SP as it prolongs the production life of the formation [107]. In gas injection EOR, the most effective and promising method is CO₂ injection. Although CO₂ is capable of displacing oil by miscible and immiscible flooding, miscible flooding has proven to be more efficient. Although, immiscible flooding shows lower recovery factors, it may still be economical due to the lower cost of the immiscible gases, e.g. N₂ [164]. Microbial EOR is economically attractive; however, a longer time interval is a requirement to attain incremental oil production. More so, oil production rates are often low when compared to the oil production rates of TEOR, CEOR and GEOR processes [19].

3.2. Cost of EOR Implementation

TEOR projects are expensive ventures. A vast capital is required for project operations, specifically, steam generation and injection [26], which are often large scale and require high financial costs for multiple injection wells. Likewise, steam generators for such projects are usually high priced, yet essential components. CEOR is cost-effective in comparison to TEOR, since the chemicals for its operations are readily accessible and relatively cheap [3, 165], although surfactant injection remains an expensive undertaking [98]. Gas injection is again a relatively expensive practice when compared to CEOR and MEOR, but more cost-effective than the TEOR processes. However, the incremental oil production usually outweighs the production costs, especially for immiscible gas injection [2]. MEOR is a much cheaper alternative owing to the low energy requirements unlike TEOR. The application of MEOR is

independent of oil price [19, 59], and thus it is considered economical. However, MEOR operations involve complex mechanisms [14, 15] that require proper technical understanding for its application. Therefore, cost should not be the only factor considered for adopting MEOR in the field.

3.3. Environmental friendliness

Thermal EOR, in comparison to microbial, chemical and gas EOR, is eco-unfriendly due to the generation of large volumes of greenhouse gas emissions. Specifically, the production of steam from the combustion of fossil fuels significantly increases emissions of carbon dioxide and nitrous oxide [26]. ISC also contributes to gas emissions such as CO₂, H₂S, CO and volatile hydrocarbons, which are generated during this process [41, 166]. Steam injection has fewer hydrocarbons, which are generated during this process [41, 166]. Steam injection has less environmental sustainability than ISC, since no current control measures over gas emissions during the steam generation process are in place [29]. MEOR is an eco-friendly method in comparison to thermal, chemical and gas methods [19] as MEOR does not release polluting and/or toxic gases such as H₂S and CO; thus, MEOR offers a better environmental sustainability.

4. Global EOR status and some case studies

EOR gas injection projects were stagnant in the mid-1908s [167], while thermal and chemical EOR processes experienced a decline in the 1980s [167]. However, since 2000, GEOR projects have been on the rise due to the growth in the implementation of CO₂-EOR projects [167]. Minor increases in thermal projects have been observed in recent times due to the increase in

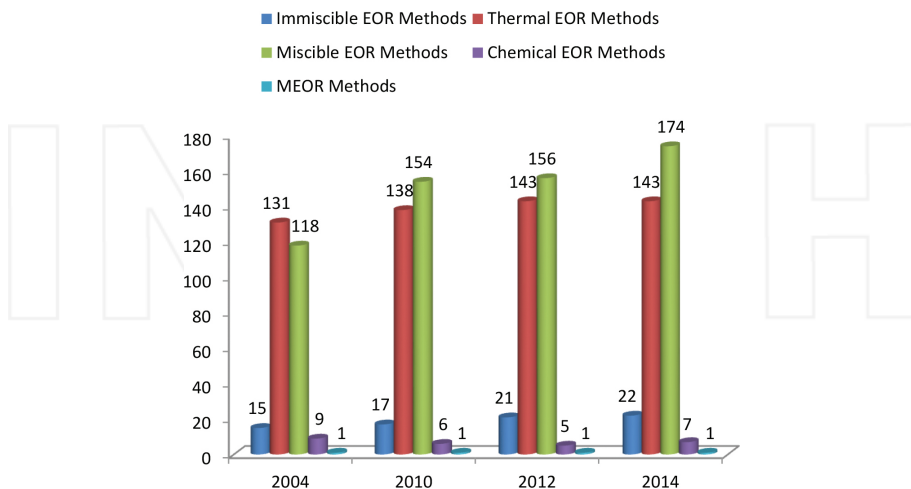


Figure 10. Global EOR project status [93].

the application of high-pressure air injection (HPAI) projects [167]. Between 2004 and 2014, gas EOR (i.e. miscible flooding) and thermal EOR techniques have been the most extensively applied EOR processes worldwide (**Figure 10**) [94].

The global oil demand has been steadily on the rise (**Figure 11**), with the exception of the temporary drop in oil demand between 1979 and 1983. Simultaneously, there has been a continuous decline in conventional oil resources. According to the U.S. Energy Information Administration, the worldwide oil consumption in 2014 increased by 1.2 million b/d, which on average corresponded to 92.4 million b/d [168]. At the end of year 2015, oil production reached approximately 97 million b/d [169], increase that was equivalent to a rise in oil consumption of 1.4 million b/d [170]. Expectations are that global oil consumption will grow by 1.4 million b/d in 2016 and 1.5 million b/d in 2017 (**Figure 11**). It is also important to mention that since 2014 to present, there is more oil supply than oil demand, which is clearly reflected by the drop in oil price. However, the current excess in oil supply comes from the exploitation of unconventional oil resources (i.e. tight reservoirs).

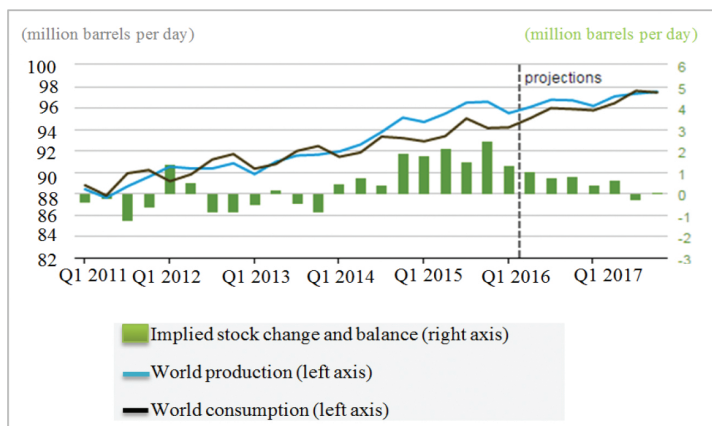


Figure 11. Global oil production and consumption [170].

The dramatic increase in oil demand over time has constantly prompted the quest for novel methods to enhance oil production. In 1998, global EOR projects achieved the production of 2.3 million b/d from steam flooding in the Duri field (Indonesia), which was the largest steam flooding project at the time [3]. EOR production of 480,000 b/d was further reported in Canada and China with an EOR production of 280,000 and 200,000 b/d, respectively [3].

In recent times, the EOR global market has experienced an unceasing progression in its growth pattern. In 2012, the global EOR market was 2095 million barrels [171]. By 2013, it further increased to 2681.6 million barrels. Globally, EOR contributes around 3.5% of daily oil production [172, 173], which corresponds to approximately 3 million barrels of oil per day [28]. A compound annual growth rate of 29.9% has been projected through 2014–2020; thus, a much

higher growth above 16,000 million barrels is expected by 2020 that will amount to about US \$ 283 billion [173].

4.1. Impact of EOR in the Kern River oil field (California)

The Kern River heavy oil field near Bakersfield, California, was discovered in 1899 [174]. In 1961, heavy oil production was approximately 19,000 b/d, which was considered low and prompted the introduction of steam flooding in 1964 and 1966 [174]. Steam flooding increased heavy oil production to 53,000 b/d in 1966 and production peaked at 141,000 b/d in 1985, followed by a lower production rate of 80,000 b/d [175]. After more than 100 years of production, the field is still producing and 60% of the oil output has been achieved by steam flooding EOR [176]. Kern River (a sandstone formation) has demonstrated the efficacy of thermal EOR for heavy oil reservoirs. In this field, a 60% recovery factor of the original oil-in-place (OOIP) has been achieved, which is significantly higher than the average global recovery factor of 32–35%. In the Kern River oil field, primary recovery and hot water injection produced around 5–10% to 15–25%, respectively, of the OOIP [176].

4.2. Impact of EOR on Russian oil fields

Russia, which is the second largest oil producer in the world, had an estimated ultimate oil production of 4.6 million b/d in 1988 [175, 177]. Russian's oil recovery factors have been on the decline in the last 30 years because of the depletion of giant fields [178]. The breakdown of the Soviet Union in 1991 also contributed to a production decrease of approximately 2.2 billion b/d [175]. In the 1960s, the oil recovery factor was 50%, but by 1993, the recovery factor dropped to 40% [178, 179]. Further decline (560 kb/d) in Russian's oil production is expected between 2014 and 2020. Projections indicate that the total production of liquid hydrocarbons in Russia will fall from 10.9 Mb/d in 2014 to 10.4 Mb/d by 2020. However, an increase in production of natural gas liquids (NGL) and condensate is expected by 2020 owing to the projected higher

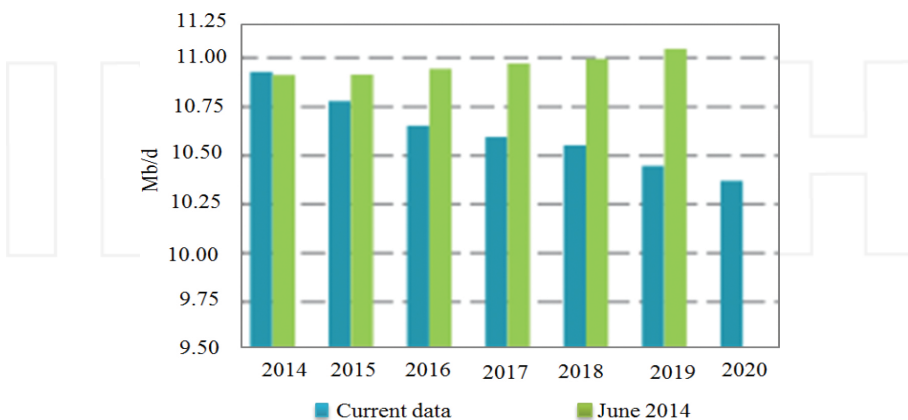


Figure 12. IEA: The Oil Market Report (OMR) on current Russian oil production [180].

gas production rate with and average NGL output of 975 kb/d [180]. **Figure 12** shows the current Russian oil production and production projections up to 2020.

Several EOR techniques (TEOR, GEOR and MEOR) have been deployed in Russian oil fields, even though MEOR applications are restricted [181]. GEOR, specifically, miscible gas flooding, is considered the EOR process with the greatest potential [182]. Although, several EOR processes have been implemented in Russian oil fields, estimations of the actual number of implemented EOR projects are difficult to obtain. Based on oil companies' data, Russian oil production from 1996 to 2000 increased by 2.5–2.8 times [178]. Current Russian EOR oil production is approximately 17–18 MM tons with chemical EOR processes accounting for 81–82% of the incremental oil production and 0.35–0.4 MM tons of oil production from gas flooding and WAG applications [178]. Projections indicate that gas EOR technologies, WAG and combined technologies will be adopted in Russia in the near future [178].

4.3. Impact of EOR on the Cantarell oil field (Mexico)

Cantarell is the biggest oil field in Mexico [183]. Oil production commenced in 1979. Between 1980 and 1996, the production capacity of the Cantarell oil field was 1 MMbd. In 2000, nitrogen flooding was initiated and by 2005, the field responded to nitrogen flooding with an outstanding production increase [174]. The initial results were great, however, subsequently production dropped by approximately 400,000 bpd [183]. This oil production behaviour might indicate that nitrogen injection could be viewed as a method that accelerates oil recovery without upsurging ultimate recovery [174, 183].

4.4. Impact of EOR on the Oman oil field

Oman is the largest oil and natural gas producer in the Middle East outside the OPEC. Oil production peaked in year 2000 at 970,000 b/d and then declined to 710,000 b/d in 2007 [184]. The decline was prevented through the application of several EOR techniques, which increased production again to 919,000 b/d in 2012. Henceforth, Oman's incremental oil and natural gas

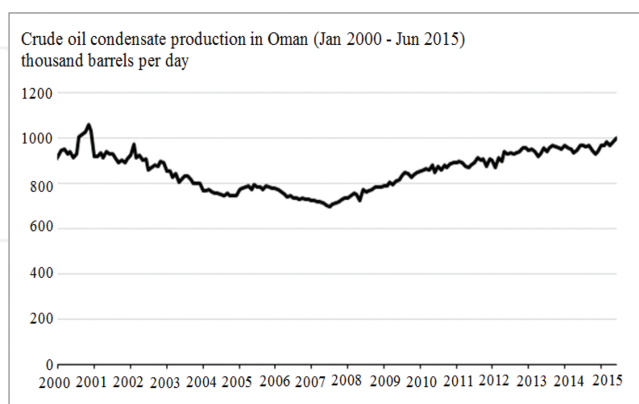


Figure 13. EOR impact on Oman Oil Production [186].

production is highly dependent on advanced extraction technologies [185]. EOR techniques such as polymer, miscible gas flooding and steam injection have been the main drivers of the country's rebounding oil production since 2007 [184]. In the Marmul oil field, polymer flooding produced about 75,000 b/d in 2012. Polymer flooding has been more effective than steam injection [184]. Miscible gas injection, which was deployed in the Harweel oil field cluster, improved the oil production rate to 23,000 b/d in 2012. Steam injection has also been deployed in the Mukhaizna, Marmul, Amal-East, Amal-West and Qarn Alam oil fields, among others [184]. Currently, oil production in Oman has remained on the increase since 2007 with a notable production increase of over a million b/d in 2015 (**Figure 13**) [186]. Projections indicate that the application of thermal EOR in the Amal-East and Amal-West oil fields will increase oil production by 23,000 b/d in 2018 [184]. In Oman's oil fields application of conventional and advanced EOR techniques will promote further production growth [185, 186]. Currently, expectations are that 16% of Oman's oil production will come from EOR projects this year (2016), which is more than five times the EOR production in 2012 [185].

4.5. Impact of EOR on the U.S. Permian Basin

The United States Permian Basin has shown successful deployment of EOR processes since the early 1970s [187], which started with two large CO₂-EOR projects [188]. In 1985, CO₂ was injected into the Denver Unit of the giant Wasson (San Andres) oil field to remediate the sharp decline of oil production that dropped from approximately 90,000 to 40,000 b/d. Upon deployment of the CO₂ flooding project, oil production increased to about 50,000 b/d [189]. In 2009, 105 miscible and 61 immiscible CO₂-EOR applications were implemented in the U.S. within the Permian Basin producing over 182,000 b/d [188]. In the United States, the number of CO₂-EOR projects has continuously increased over the years. In 2010, production rates of approximately 200,000 b/d in the Permian Basin were achieved using CO₂-EOR in oil fields ranging from the fieldwide CO₂ flood in the giant Wasson (San Andres) oil field to the small 160-acre pilot CO₂ flood at Dollarhide Clearfork reservoir [32, 190, 191]. **Table 7** presents details of several CO₂-EOR projects implemented in the Permian Basin [32].

Oil Fields	Seminole	Means	Wasson	Slaughter**	Kelly Snider	Total
Primary operator	Hess	ExxonMobil	Occidental	Occidental	Kinder Morgan	
Total field production (b/d) year 2010	16,500	10,000	51,100	18,800	29,600	126,000
Incremental CO₂-EOR production (b/d) year 2010**	16,500	8,700	44,600	11,200	26,500	107,500

Note: *Joint recovery from six Wasson units and **Joint recovery from nine Slaughter units.

Table 7. CO₂-EOR oil recovery from the Permian Basin [32].

In 2012 and 2015, incremental oil production from CO₂-EOR operations in the Permian Basin was estimated at 186,000 and 241,000 b/d, respectively, with further projections of 301,000 b/d by 2020 [141].

5. Conclusions

Crude oil recovery takes place in three production stages primary, secondary and tertiary oil recovery processes. On average, oil recovery from the primary and secondary production stages is approximately one-third of the original oil-in-place (OOIP), while the remaining two-thirds of the oil, can be partially recovered through the application of tertiary processes also known as enhanced oil recovery (EOR) processes, which are key drivers for incremental oil recovery. EOR processes include thermal (TEOR), chemical (CEOR), gas flooding miscible and immiscible (GEOR) and microbial or MEOR processes.

- Thermal EOR techniques are applied for the recovery of heavy oils. In particular, steam-flooding is the dominant thermal EOR technique worldwide. Increase in oil productivity is achieved through viscosity reduction, oil swelling, steamstripping and thermal cracking [1].
- Chemical EOR techniques are suitable for application in mature oil fields. Globally, oil recovery using CEOR techniques have remained insignificant since the 1990s with the exception of China [79, 193]. Among the CEOR techniques, polymer/surfactant flooding through IFT reduction between the displacing liquid (i.e. water) and oil has the best potential for ultimate oil recovery [1]. However, polymer flooding is less complex and the most widely deployed technique for mobility control [83, 112].
- Miscible and immiscible gas injection or GEOR are suitable for application in light, condensate and volatile oil reservoirs [114]. CO₂ is considered the most widely used gas for GEOR injection especially in the US Permian Basin, where most of the CO₂ field projects have been deployed. In the US, continuous growth of CO₂ flooding projects is expected. N₂ and hydrocarbon gas injection projects have been deployed in Canada and the US, although incremental oil recovery from these processes has been negligible.
- MEOR is a promising and eco-friendly recovery process with potential for future incremental oil recovery [19]. The main downsides of MEOR are longer time intervals are required to attain incremental oil production and MEOR renders the lowest oil recovery in a given period in comparison to other EOR techniques.

Huge potentials for incremental oil recovery exist through the application of EOR processes; however, the volume of recoverable oil is greatly dependent on the implemented EOR technique. Among the key EOR techniques deployed in oil fields, miscible gas injection EOR and thermal EOR processes are currently the most commonly used techniques in the field. Continuous evolution of EOR processes in the near future should take a synergistic approach from different EOR technologies.

Nomenclature

AMEC	adapted mixed enrichment cultures
CEOR	chemical enhanced oil recovery
CSS	cyclic steam stimulation
EEOR	enzyme EOR
EOR	enhanced oil recovery
Fast-SAGD	fast-steam assisted gravity drainage
GAGD	gas assisted gravity drainage
GEMEOR	genetically-engineered microorganisms enhanced oil recovery
GEOR	gas enhanced oil recovery
GOGD	gas-oil gravity drainage
HPAI	high-pressure air injection
HPAM	hydrolysed polyacrylamide
HPAM-AMPS	hydrolysed polyacrylamide-acrylamide methyl propane sulfonic acid
ISC	<i>in situ</i> combustion
MEOR	microbial enhanced oil recovery
NCG- SAGD	non-condensable gas-steam assisted gravity drainage
NGL	natural gas liquids
OTSG	enclosed trough solar once-through steam generator
PAM	polyacrylamide
PWAG	polymer water alternate gas injection
SAGD	steam assisted gravity drainage
SAPc	superabsorbent polymer composite
ST-EOR	solar thermal enhanced oil recovery
SWAG	simultaneous water alternate gas injection
TAGOGD	thermally assisted gas-oil gravity drainage
TEOR	thermal enhanced oil recovery
TGD	tertiary gravity drainage
THAI	toe to heel air injection
WAG	water alternate gas injection

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