



Combinational CO₂ and Polymer Injections for EOR and CO₂ Storage in Depleted Reservoirs: A Mini Review on Laboratory, Simulation and Field Studies

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Abstract

Water-alternating-gas is commonly used in most of the existing enhanced oil recovery (EOR) projects in the world to regulate gas mobility and reduce fingering problems. Unfortunately, the expected recovery factor from most of the fields could not be attained with such EOR method. Development strategies of mature oil fields during the energy transition period may therefore involve the combination of polymer and CO₂ injections to achieve incremental oil recovery and at the same time provide long-term geological storage solution for carbon. This paper therefore presents overview of the processes of polymer and CO₂ floodings, and then highlights the overall benefits to be derived from the combination of CO₂ and polymer flooding techniques in depleted hydrocarbon reservoirs, especially oil reservoirs. Reviews on studies related to the combinational CO₂ and polymer injections are then carried out. Highlights of areas of the combinational CO₂ and polymer injections needing more attention are also mentioned.

Keywords: Improved Oil Recovery; Carbon Sequestration; Polymer-Alternating CO₂ Gas (PAG) Flooding; Mature Oil Fields Development; Chemical Enhanced Oil Recovery

Abbreviations: PAG: Polymer-Alternating CO₂ Gas; OOIP: Original Oil In Place; EOR: Enhanced Oil Recovery; LPG: Liquefied Petroleum Gas; MMP: Minimum Miscibility Pressure; WAG: Water-Alternating-Gas; TDS: Total Dissolved Solids; ROCM: Remaining Oil Compliant Mapping.

Introduction

The recovery rate of mature oil fields at the end of both the primary and secondary recovery phases are generally in the range of 20% to 40% of the original oil in place (OOIP). Although in some cases, recoveries could be lower or higher

[1]. Thomas A, et al. [2] reported a recovery rate of about 15% to 35% on average of the oil in place. Mature fields, also known as brownfields, are present all over the global oil regions. From the study of Godec M, et al. [3], the largest 54 oil basins of the world show an estimated 4.622 trillion barrels of original oil in place (OOIP) in already discovered oil fields (Figure 1), about 0.687 trillion barrels (as of 2000) have been produced and a reported 0.845 trillion barrels of proved reserves, giving an overall recovery efficiency of 33%. Hence, about 3.090 trillion barrels of oil is remaining for enhanced oil recovery (EOR).

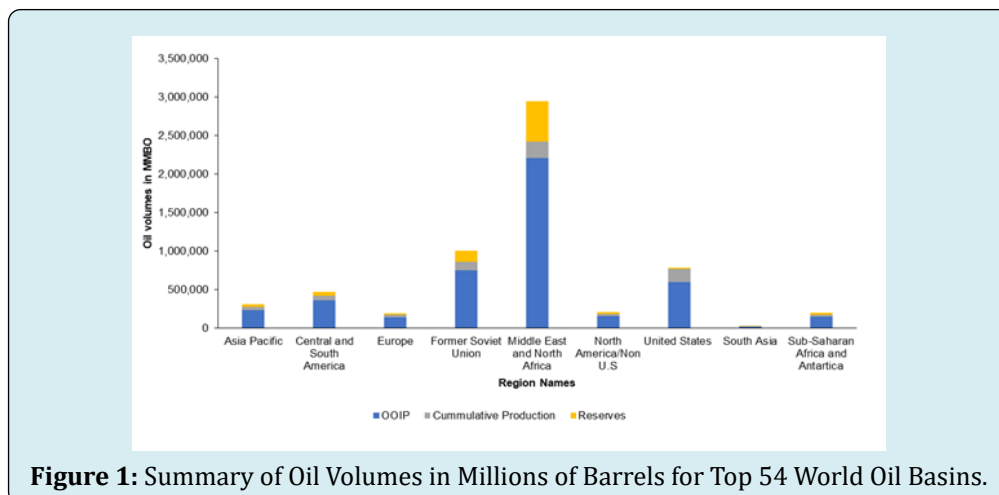


Figure 1: Summary of Oil Volumes in Millions of Barrels for Top 54 World Oil Basins.

Some of the most important brownfields [4-6], are; Daqing field in China, Minas field in Indonesia, Samotlor and Romashikino fields in Russia, Forties filed in UK, Sattfjord in Norway, Prudhoe Bay in Alaska, USA, Cantarell in Mexico, Roncador in Brazil, Bolivar Coastal in Venezuela, Cupiagua-Cuisiana in Colombia, Ghawar field in Saudi Arabia and Agbami field in Nigeria. Most of them have been under production for at least three decades and have already reached their peaks of production in the last decade [6]. Many methods of enhanced oil recovery techniques, most especially CO_2 injection, have been applied successfully in some of the mature fields around the world. A large volume of oil is still left behind in a reservoir, as recovery is typically 5 - 15% of the OOIP, with the current "best practices" of CO_2 -EOR technology. Remson D [7] attributed it to the following reasons: insufficient injection of CO_2 , poor sweep efficiency, poor displacement efficiency, lack of CO_2 contact with remaining oil resources, and inadequate management control. So, summary of options that can boost the recoveries from current "best practices" technologies will include: increasing CO_2 injection volumes, optimizing flood design and well placement, improving the mobility ratio by increasing the viscosity of water by use of polymers, and extending miscibility by reducing the miscibility pressure using liquefied petroleum gas (LPG).

Unfortunately, there is little or no strategic combination of CO_2 and polymer injections in these fields available in open literature. This work therefore looks briefly at the processes of polymer and CO_2 floodings, and then reviews studies related to the combinational CO_2 and polymer injections, available in open literatures. Areas needing more attention are also highlighted.

Overview on the Basics of CO_2 -EOR

Various gases, including natural gas, flue gas, nitrogen and CO_2 in supercritical state, have been used for EOR, with

varying success rates and economic benefits [8]. When temperature and pressure exceed the critical value (31.16°C ; 1,070.6 psia), the CO_2 viscosity, (0.05-0.08 cP), and interface tension are similar to those of gas, but the density is similar to that of liquid, which is helpful for effective oil flooding. Owing to its special properties, CO_2 improves oil recovery by lowering interfacial tension, swelling the oil, reducing oil viscosity, and by mobilizing the lighter components of the oil.

Injection of CO_2 into hydrocarbon reservoirs can provide large underground storage for CO_2 while enhancing hydrocarbon recovery thereby reducing the total expenses [9]. However, not all oil reservoirs are suitable for CO_2 -EOR for technical and economic reasons, Shaw J, et al. [10] suggested that a "YES/NO" screening method could be used for the selection of potential pools for CO_2 flooding that meet certain technical criteria for achieving miscibility. The important technical criteria are:

- The reservoir pressure at the start of a CO_2 flood should be at least 200 psi above the minimum miscibility pressure (MMP) to achieve miscibility between CO_2 and reservoir oil, as reported by Rivas O, et al. [11]. Estimates of CO_2 -crude oil minimum miscibility pressure (MMP) can be found in the report of the National Petroleum Council [12].
- Oil gravity is generally recommended to be greater than 27°API but less than 48°API , because very light oil is not conducive to the development of multi-contact miscibility for miscible flooding.
- The fraction of remaining oil before CO_2 flooding should be greater than 0.25 to ensure an economic outcome for CO_2 -EOR.

Some of the preliminary issues that need to be addressed, as highlighted by Shaw and Bachu [10], for EOR technology include: 1) screening for EOR suitability; 2) technical ranking of suitable reservoirs; and, 3) oil recovery and CO_2 -

sequestration capacity predictions. Other economic criteria can be considered after this preliminary technical evaluation.

CO₂-EOR Processes

Depending on the reservoir pressure, temperature, and oil properties, the injected CO₂ may become miscible or remain immiscible with the reservoir oil. The reservoir pressure is compared with the minimum miscibility pressure (MMP) to know if there is miscibility between CO₂ and reservoir oil. When reservoir pressure is greater than the MMP (the pressure at which more than 80 percent of oil-in-place (OIP) is recovered at CO₂ breakthrough, according to Holm LW, et al. [13]), miscibility is attained leading to multiple-contact or dynamic miscibility with time as displacement occurs. This will cause oil swelling and viscosity reduction thereby improving sweep efficiency and facilitating additional oil recovery [14]. However, When the reservoir pressure is below the MMP or the reservoir oil composition is not favorable, the CO₂ and oil will be immiscible.

Note that; three types of hydrocarbon miscible mechanisms exist: (1) first contact, CO₂ are not miscible on first contact, but they do develop miscibility on multiple

contacts, known as dynamic miscibility, resulting in much improved oil recovery; (2) vaporizing gas drive, also known as high-pressure gas drive, this process achieves dynamic miscibility by in situ vaporization of the intermediate-molecular-weight hydrocarbons from the reservoir oil into the injected gas or CO₂; and (3) the condensing gas drive, sometimes called enriched gas drive [8], this process achieves dynamic miscibility by in situ transfer of intermediate-molecular-weight hydrocarbons (or CO₂ in case of CO₂-EOR) into the reservoir oil.

Overview on the Basics of Polymer EOR

Recently, there are increasing interests in enhanced oil recovery (CEOR) with chemical application, especially polymer flooding, either alone or in combination with other chemical compounds to improve their compatibility and effectiveness in the reservoir [15]. Some of these other chemical compounds are; surfactant and alkaline-surfactant. Concentration and molecular weight of polymer affect its viscosity. Table 1 gives some examples of commercial polymer products that can be used in oilfields.

Product Form	Polymer Type	Monomer	Commercial Product Examples	Comments
Powder	Copolymer	Acrylamide - Sodium acrylate	Flopaam 3630S	Reservoir temperature less than 80°C, medium hardness
	Homopolymer post hydrolysed	Acrylamide	Flopaam 6030S	Reservoir temperature less than 75°C, low hardness
	Copolymer	Acrylamide - ATBS	Flopaam AN125SH	Reservoir temperature less than 95°C, all salinities
	Terpolymers	Acrylamide - Sodium Acrylate - ATBS	Flopaam 5205SH	Reservoir temperature less than 90°C, all salinities
			Flopaam 5115SH	
	Associative polymers	Acrylamide - Sodium Acrylate - Hydrophobic monomer	Superpusher C319	High resistance factor in reservoir
Medium hardness				
Terpolymers	Acrylamide - ATBS-NVP	Flopaam SAV225	Reservoir temperature less than 120°C, all salinities	
Liquid O/W Emulsion	Copolymers	Acrylamide - Sodium acrylate	Flopaam EM533	Reservoir temperature less than 80°C, medium hardness

Table 1: Commercial polymer products for various field conditions [2].

Field practice has shown that polymer flooding can increase recovery of 5-30% of OOIP, with decreased water production and increased oil production; in the range of 0.7 to 1.75 lb of polymer per bbl of incremental oil production [16]. Many examples of technically successful polymer field projects are reported in some literatures. Some field cases,

reported by Sheng J [17], are; the Xiaermen field and the Daqing field in China, the East Bodo reservoir in Canada, the Marmul field in Oman, and the Vacuum field in New Mexico. From field applications experiences reported in Gao P, et al. [18], polymer flood is recommended for oil viscosity less than 100 cP under reservoir temperature in vertical wells,

and sandstone reservoir with oil saturation higher than 30%, reservoir permeability greater than 20 mD, net thickness more than 3 m (10 ft), and reservoir temperature less than 90 °C or 200 °F. However, with horizontal wells, polymer flooding can be recommended for oil viscosity higher than 100 cP.

The selection of reservoirs which have poor waterflooding sweep efficiency due to high oil viscosity and/or large-scale heterogeneity is one of the screening rules for polymer flooding. In other words, reservoirs with poor volumetric efficiency [19], but respect the polymer tolerance limits (temperature, salinity). Recent limits of some important parameters for polymer flooding implementation are: reservoir temperature, less than 130 °C; reservoir permeability, greater than 40 mD; salinity, less than 250,000 total dissolved solids (TDS); oil viscosity, greater than 2 mPa.s but less than 10,000 mPa.s [20,21].

Polymer EOR Processes

Viscosification of the displacing fluid resulting from the addition of polymer, which is favorable for hydrocarbon recovery, is the primary recovery mechanism. The addition of polymer to the displacing fluid increases its viscosity, resulting in a decreased mobility ratio, as defined in Equation 1:

$$M = \frac{\lambda_o}{\lambda_w} = \frac{\mu_o/k_o}{\mu_w/k_w} \quad (1)$$

where; λ , μ , and k are the mobility, viscosity and effective permeability, respectively. The subscripts w and o represent water and oil, respectively.

The relative permeability of water in the reservoir reduced, then increases oil recovery due to increase of fractional flow. If the mobility ratio is one or slightly less, the displacement of the oil by the water will be efficient and the water will not finger through the oil leaving behind regions of unswept oil. Another recovery mechanism according to Wang D, et al. [22] is viscoelasticity, which is associated with the use of high Molecular weight (Mw) or associative polymers, but there is argument whether it applies to real reservoir conditions or not.

Reviews on Studies Related to the Combinational CO₂ and Polymer EOR Techniques

Most of the commercial miscible gas injection projects around the world use water-alternating-gas (WAG) process to regulate gas mobility and reduce fingering problems.

However, majority of the fields with reservoirs of high permeability zones or with natural fractures have not reach their expected recovery factor [23]. So, researchers are proposing advanced and alternative ways to improve recovery: one of such is the application of the combinational CO₂ and Polymer injections, which has been in different forms - for instance, the polymer-assisted CO₂ flooding and the polymer-alternating CO₂ gas (PAG) flooding.

Polymer-Assisted CO₂ Flooding

There are direct CO₂ thickeners - polymers for EOR applications [24-26]. These polymers are soluble in the injected CO₂ with resulting viscosity similar to (or slightly larger than) that of the displaced oil and also thermodynamically stable. Varying the concentration of the added thickeners regulates the CO₂ viscosity [27]. Oligomers, which have low molecular weight, are possible thickeners of CO₂ for EOR processes [28-30] and can be used to address solubility reduction as a result of increment in molecular weight of polymers [31].

There are several studies performed [32-36] showing the benefits of polymer-assisted CO₂ injection in core flooding experiments. The benefits reported generally include: improvement in the density and viscosity of CO₂ and super-critical CO₂ (scCO₂), acceleration and increment of oil recovery, and delay in CO₂ breakthrough. However, Zuberi HA, et al. [36] reported a noticeable increase in the pressure drop with the use of polyfluoroacrylate (PFA), emanating from permeability reduction due to the adsorption of PFA on the rock surface.

Other researchers who have conducted studies on synthesised polymers for CO₂ viscosity enhancement and CO₂-mobility control include: Huang Z, et al. [37], Li Q, et al. [38], Kilic S, et al. [39].

Polymer-Alternating CO₂ Gas (PAG) Flooding

Reviews of studies related to the combinational CO₂ and polymer injections, especially the polymer-alternating gas (PAG) process, show more core flooding experiments and reservoir simulations have been carried out. Abbas AH, et al. [40] carried out a comparative numerical study considering several EOR, such as water flooding, CO₂ flooding, water alternating gas, polymer flooding and polymer alternating gas, in homogenous high permeability reservoir. The designed flooding pattern used was a single producer-single injection scheme. Based on the simulation results, PAG flooding had the highest recovery factor of 56% with incremental recovery of 16%. Also, controlled water cut was achieved with the polymer alternating gas flooding scheme.

In 2018, Yang Y, et al. [41] examined the effectiveness of polymer-alternating-gas (PAG) process to recover viscous oil from highly heterogeneous reservoirs in Liaohe Oilfield in China experiencing low oil recovery. A heterogeneous reservoir model was built using a field case geological model from Liaohe Oilfield in China. Their simulation studies involve five different flooding development methods. Nine injectors and six producers, in a somewhat direct line (but diagonally placed) well pattern, were used. Peng-Robinson equation of state (EOS) was used for fluid modeling, rock adsorption and polymer viscosity (which are two important parameters for polymer flooding) were considered. The results were compared, with respect to recovery factor, oil rate, GOR, saturation profile, etc. Simulation results showed that PAG method increase oil recovery over 10% compared with other EOR methods and PAG was economically successful based on some assumptions. Li W, et al. [42] analyzed the feasibility of PAG through simulation. Models considering both miscible and polymer flooding processes were built to study the performance of PAG. A reservoir model from a typical section of the North Burbank Unit (NBU) was used to compare the performance between PAG, WAG, and polymer flooding. One vertical injector and one producer were diagonally located in the model. Sensitivity analyses of polymer adsorption and concentration were also studied. The feasibility of PAG in reservoirs with different permeabilities, different Dykstra-Parsons permeability variation coefficients (VDPs), and different fluids were also studied. Their study demonstrated that PAG can significantly improve recovery for immiscible/miscible flooding in homogeneous or heterogeneous reservoirs. Song Z, et al. [26] carried out core experiments using magnetic resonance imaging (MRI) technique to study the fundamental characteristics (such as the piston-like displacement front, the phenomena of channeling and fingering, homogenization of the oil saturation distribution with CO₂ injection, and the distribution of oil in porous media) of the combination of polymer and CO₂ flooding processes. Their results showed that mobility ratio was improved with increasing concentration and viscosity of polymer solution. Supercritical CO₂ displacement enhanced oil recovery and reduced consumption of polymer solution compared with alone polymer flooding. In summary, their studies indicated that the combination of polymer and CO₂ flooding was viable and highly efficient.

Zhang Y, et al. [25] carried out experiment of coupled CO₂ and polymer injection for heavy oil reservoirs. The oil recovery performance investigated in a laboratory scale linear coreflood tests, among three EOR modes - water-alternating-gas (CO₂ WAG), polymer-alone flood and, showed better efficiency and higher recovery for the coupled CO₂ and polymer injection.

The Bati Raman heavy oil (10 - 15°API) field in Turkey,

with primary recovery of 1.5% and CO₂-EOR of about 5%, is one of the published examples of oil fields that has experienced polymer injection to improve the sweep efficiency of CO₂. Increased production was observed in 16 production wells after 3 months of injection. The total cost of the polymer treatment was USD 445,000. The payout time was 1 year [43]. Other published reservoir simulation studies [44-46] involving coupled CO₂ and polymer injection in both synthetic and real reservoir models with conventional well patterns generally indicate increase in oil recovery.

Areas needing more Attention: Well Pattern and Injection Sequence

Virtually all of the researches on combinational CO₂ and polymer floodings available in open literature are either polymer-assisted CO₂ flooding or polymer-alternating CO₂ gas (PAG) flooding. For this reason, conventional flood patterns have been widely used. The concurrent (or simultaneous) polymer and CO₂ flooding has yet to be investigated. If such flood sequence is considered, then flood patterns different, but similar to, from the traditional well pattern configuration has to be applied.

Proposed Flood Patterns for Concurrent CO₂-EOR and Polymer Injections

In flooding projects, it is important to select the proper pattern that will provide the injection fluid with the maximum possible contact with the reservoir oil. Flood pattern design development of flooding projects for optimal recovery efficiency relies on the reservoir geology and its properties, hydrocarbon properties, waterflooding sequence, and well-pattern configuration. Injection pattern (or configuration) improves sweep efficiency. Analyses of reservoir performances are mostly through reservoir simulation approach or by the remaining oil compliant mapping (ROCM) process [47].

Verma MK [48] reported that a normal five-spot - one production well at the center and four injection wells at the corners, or an inverted five-spot (four production wells, one injection well) is one of the commonly used patterns for CO₂-EOR or polymer flooding. In some cases, seven- or nine-spot patterns. The well pattern could even be a line drive, where the injection wells are opposite the production wells, if the permeability distribution and other geologic features favor it.

For a strategic combinational CO₂-EOR and polymer flooding - with the right polymer and proper concentration, the following suggested well patterns with the following nomenclatures; 1-1-1, 4-2-1, and 8-4-1, could improve sweep efficiency and also result in optimal recovery efficiency.

The 1-1-1 Well Pattern: This is similar to the direct line drive. However, in this case the lines of the same type of injections are in the same file, likewise that of the production. The 1-1-1 well pattern typically means; one polymer injector-one CO₂ injector- one producer. Existing direct line (or staggered line) well pattern in an oil field can easily be converted into the 1-1-1 well pattern scenario. Figure 2 presents a sketch of the 1-1-1 well pattern showing possible transition zone between the injectors and the producer.

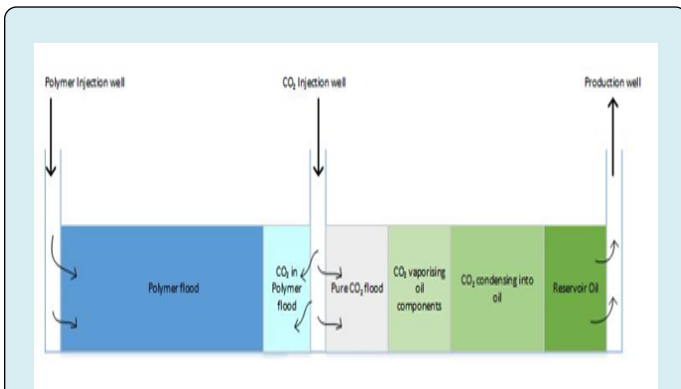


Figure 2: Schematic of the 1-1-1 well pattern showing possible transition zone between the injectors and the producer.

The 4-2-1 Well Pattern: The 4-2-1 well pattern typically means a combination of; four polymer injectors, two CO₂ injectors and one producer, as shown in Figure 3. The regular five-spot can be transformed into the 4-2-1 well pattern with an infill drilling of two CO₂ injection wells in the spacing between the production well and the polymer injection well.

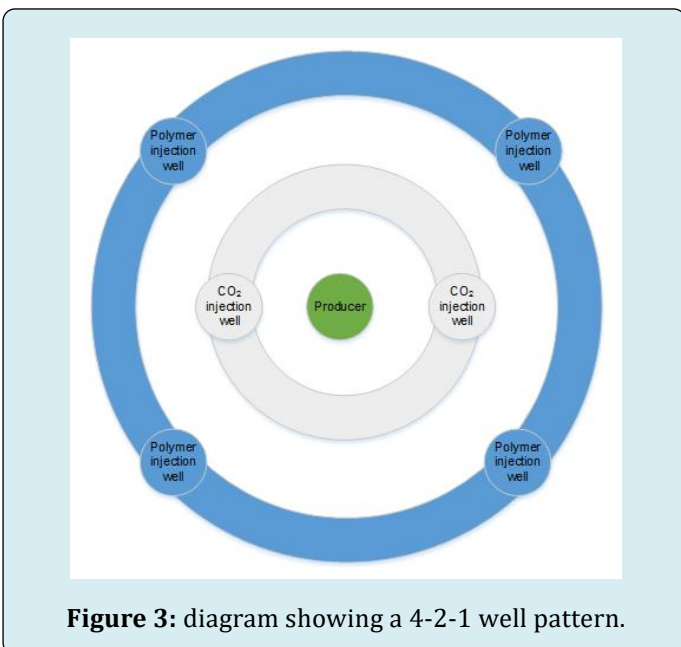


Figure 3: diagram showing a 4-2-1 well pattern.

The 8-4-1 Well Pattern: The 8-4-1 well pattern typically means a combination of; eight polymer injectors, four CO₂ injectors and one producer, as shown in Figure 4. The regular nine-spot existing in an oil field can be changed into the 8-4-1 well pattern with an infill drilling of four CO₂ injection wells in the spacing between the production well and the polymer injection well.

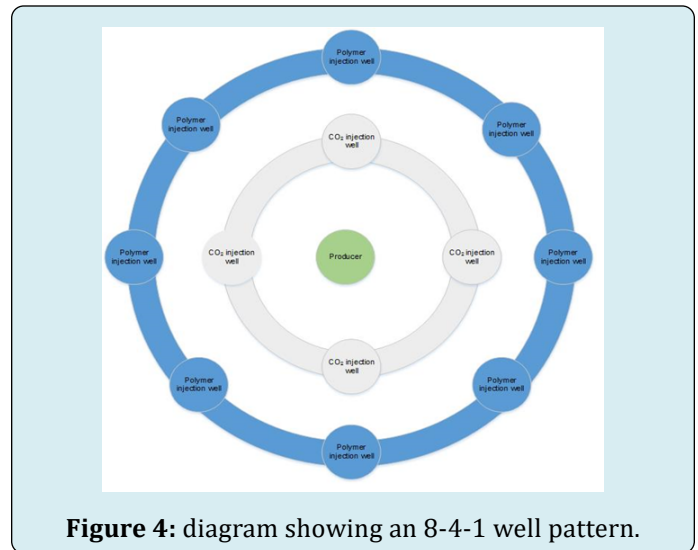


Figure 4: diagram showing an 8-4-1 well pattern.

Note: The recovery method that may be suitable for the combinational CO₂-EOR and polymer flooding could be; firstly, to commence with polymer injection until at least 30% reservoir pore volumes have been affected, and then the continuous injections of both polymer and CO₂. Another recovery method that could be efficient in a combinational CO₂-EOR and Polymer flooding is the gradual tapering (reduction) of polymer injection at the commencement of CO₂ injection and the continuous increase of the injected CO₂ (Figure 5).

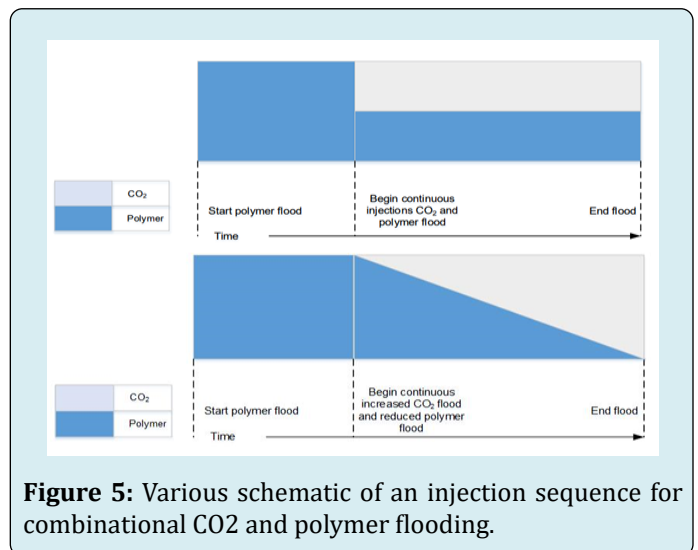


Figure 5: Various schematic of an injection sequence for combinational CO₂ and polymer flooding.

Conclusion and Future Work

Many mature oil fields around the world have either CO₂ or polymer injections as their enhanced oil recovery methods. Combinational CO₂ and polymer injections can be the most viable development strategy for a good number of mature oil fields during the energy transition period because of improvement in the sweep efficiency and mobility, and at the same time providing long-term geological storage solution for carbon. Concurrent CO₂ and Polymer injections has not been studied. For a strategic combinational CO₂ and polymer flooding, new flood pattern configurations that may be suitable for the injections of both CO₂ and polymer and as well as injection sequences that could improve sweep efficiency and also result in optimal recovery efficiency of the flooding process have been suggested. Immediate future work will concern numerical simulation of the combinational CO₂ and polymer injections for oil in a synthetic reservoir model. Its performances on oil recovery will be compared with other EOR methods.

Declarations

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Conflict of Interest

The authors wish to declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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