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## THE ROLE OF POLYMERS IN ADVANCING PETROCHEMICAL INDUSTRIES DURING CRUDE OIL EXTRACTION PROCESSES

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### ABSTRACT

Polymers, with their viscoelastic nature and complex molecular structure, significantly enhance oil recovery (EOR). This text elucidates the mechanisms underpinning their application in EOR, categorizing them into synthetic and natural (bio) polymers, each with distinct properties. A variety of EOR techniques employing polymers, like foam, alkali-polymer, surfactant-polymer, alkali-surfactant-polymer, and polymeric nanofluid flooding. Most polymers are pseudoplastic under shear, with biopolymers offering the benefits of salt resistance and thermal stability; however, plugging might result in the wellbore area, and they degrade. Despite its complexities, associative polyacrylamide shows promise, though hydrolyzed polyacrylamide remains the industry standard. Notably, alkali-surfactant-polymer flooding proves effective at various scales, and polymeric nanofluids hold potential for future EOR applications.

### KEYWORDS

Polymers, petrochemical industries, crude oil extraction.

### INTRODUCTION

Following primary and secondary extraction, substantial oil often remains trapped in reservoirs (Gbadamosi,2018). EOR targets this residual oil

(Agi,2022). EOR methods are primarily thermal or nonthermal. Thermal EOR, however, is impractical for deep, thin reservoirs or those with underlying aquifers

due to excessive heat loss (Saboorian-Jooybari,2016). Moreover, its environmental impact, marked by substantial greenhouse gas emissions contributing to global warming, limits its use (Guo, K , 2016)Consequently, nonthermal EOR has gained prominence for conventional or heavy oil extraction.. Chemical EOR, a cold ( nonthermal) technique, offers efficient and easily implemented oil recovery enhancement (Ngouangna,2020). Alkalies, surfactants, nanoparticles, and polymers are among the chemicals modifying reservoir Some of the fluid-fluid and rock-fluid properties that can enhance oil recovery. These interactions enhance the displacement at the pore scale and increase overall sweep efficiency. Polymers, in particular, excel in both properties. Their effectiveness is evident in numerous field applications, including Daqing (China), Pelican Lake (Canada), and West Cat Canyon (USA) (Delamaide,2014). Polymers exhibit viscoelasticity, displaying pseudoplastic and shear-thickening behaviors under porous media stress. Their viscosity-enhancing properties create a favorable mobility ratio in the reservoir (Firozjii,2020) reducing viscous fingering and recovering previously untouched oil for improved efficiency. The polymers' macromolecular structure enables oil film recovery from tight reservoir spaces through pulling and stripping (Sheng, 2011).Furthermore, by swelling and reducing water permeability, polymers disproportionately reduce permeability, aiding in oil recovery( Wei,2014).

Polymer-based EOR significantly reduces injected water volumes, especially beneficial in water-scarce onshore and desert regions. Additionally, polymer use lowers water cut in production wells, crucial for offshore operations requiring treated produced water. Given these advantages, A variety of polymers have been investigated for EOR, which can be broadly classified into two categories: natural polymers (biopolymers) and synthetic polymers. (Abidin,2012). Biopolymers, synthesized from naturally obtained plants, are eco-friendly. Composed of sugar monomers linked by O-glycosidic bonds, their characteristics depend on monomer properties, linkages, and chemical modifications ( Xia,2020) Known for super thickening and low cost (Rock ,2020) biopolymers benefit from abundant raw materials and inexpensive large-scale fermentation production. Their flexible macromolecular structure allows for modifications and diverse oil recovery applications. polymers based on Acrylamide are synthetic EOR agents known for their superior rheology and viscoelasticity. Containing carboxylate and amide groups, partially hydrolyzed polyacrylamide (HPAM) is the industry standard (Kamal,2015), PAM and HAPAM are also other types of synthetic alternatives). On the contrary synthetic polymers have susceptibility to salinity, hardness, low pH, high shear rates and high temperature.(Olajire,2014). Polymer EOR applications fall into two main categories: standalone polymer flooding and polymer-

enhanced processes. The latter includes foam, alkali-polymer, surfactant as well as polymeric nanofluid flooding that take advantage of exceptional characteristics exhibited by polymers for the purpose of making sure other components are stable. This text delves into recent polymer EOR advancements, covering polymer flooding mechanisms, biopolymer and synthetic polymer properties, critical parameter

influences, and the evaluation of different polymer EOR methods.

## METHODS

### Methods of using polymers to improve oil extraction.

#### Mobility Ratio

The mobility ratio assesses the relative ease with which the injected fluid (water) moves compared to the oil it displaces. In standard water injection operations, this ratio (M) is calculated as follows:

$$M = \frac{\lambda_w}{\lambda_o} = \frac{k_{rw}/\mu_w}{k_{ro}/\mu_o} = \frac{k_{rw}\mu_o}{k_{ro}\mu_w} \quad (1)$$

Where:

- $\lambda_w$  represents water mobility
- $\lambda_o$  denotes oil mobility
- $k_{rw}$  indicates water relative permeability
- $k_{ro}$  signifies oil relative permeability
- $\mu_w$  is the viscosity of water
- $\mu_o$  is the viscosity of oil

Crucially, the mobility ratio (M) gauges the stability of oil displacement. In waterflooding, water seeks the easiest path, causing uneven displacement (viscous fingering, Figure 1a). This occurs due to a significant the difference in viscosity between water and oil ( $M > 1$ ). Consequently, much oil remains trapped in the reservoir. Ideally, water mobility should be reduced relative to oil. A mobility ratio below 1 (Figure 1b)

creates a stable displacement front, curbing or eliminating viscous fingering. This ensures more injected fluid displaces oil towards the production well. Incorporating water-soluble polymers into the injected water increases its viscosity. This reduction in water mobility helps to limit water flow and improves the efficiency of oil recovery. (Figure 2) (Gbadamosi,2019).

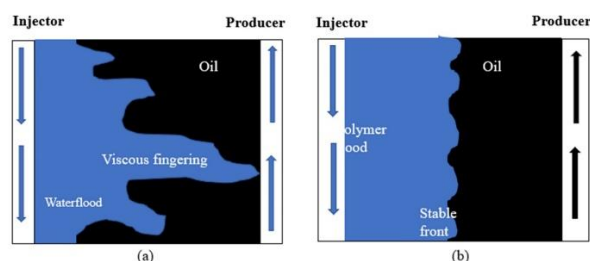


Figure 1. Waterflooding process ( $M > 1.0$ ); (b) polymer flooding process ( $M < 1.0$ ) (Olajire, 2014).

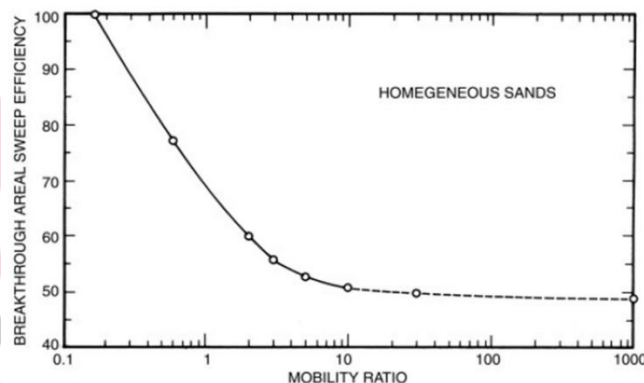


Figure 2. Effect of mobility ratio on sweep efficiency (Xia,2020)

### Disproportionate Permeability Reduction (DPR)

DPR is different technique enhancing oil recovery through polymer flooding. Most oil reservoirs display heterogeneous structures with varying permeability across different layers. (Mishra,2014)

Waterflooding preferentially channels through high-permeability zones, accelerating water breakthrough and trapping oil in lower-permeability regions,

reducing overall recovery. Polymer flooding addresses this issue. In water-wet reservoirs, injected polymer adsorbs onto the rock, forming a swollen film that impedes water flow while allowing oil passage. Additionally, polymer chains interlock, further restricting water flow. This induced resistance diverts water towards previously unswept areas, improving oil recovery. (Al-Sharji,2001)





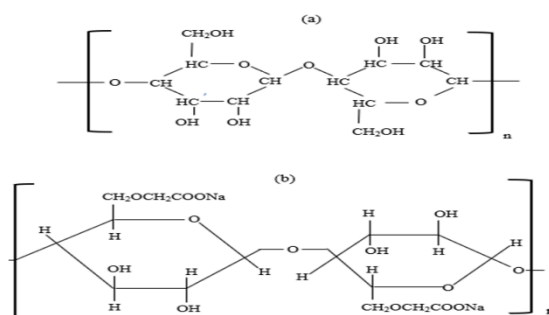
resistance against salinity, shear forces, and divalent ions.

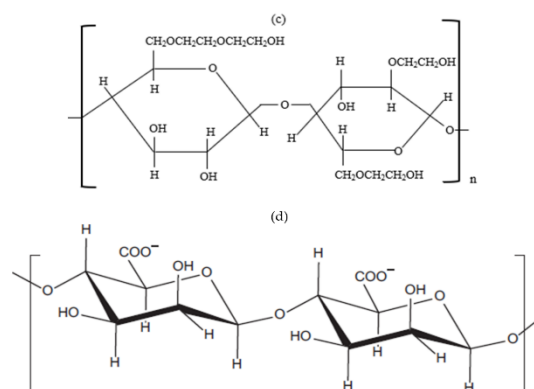
Xanthan gum exhibits superior stability to HPAM in challenging reservoir environments. In solution, it undergoes an order-to-disorder conformational change. Ionic concentration causes the structure to transition from a disordered to an ordered state due to charge screening effects. Zhong et al. (2013) investigated xanthan viscosity under varying ionic strengths and concentrations. At lower concentrations (600 mg/L), inorganic cations decreased the viscosity of the polymer solution., with divalent ions (Ca<sup>2+</sup>) exerting a stronger effect than monovalent ions (Na<sup>+</sup>) (Xu, 2016). Conversely, at higher concentrations, viscosity increased with cation addition. A 5000 mg/L xanthan solution containing 200, 500, or 1000 mg/L of Ca<sup>2+</sup> ions exhibited a 475% increase in viscosity. (Zhong, 2013). Xanthan thermal stability is linked to solution salinity. Ordered structures (high ionic concentration) enhance stability, while disordered structures (low ionic concentration) promote instability (Kamal,2015). Xanthan gum exhibits non-Newtonian behavior, often described by the Ostwald and Herschel-Bulkley

equations. At low shear rates, high viscosity results from hydrogen bonding and polymer entanglement, creating macromolecular clusters. Conversely, increasing shear rates lower viscosity, a shear-thinning property aiding field injection. This pseudoplasticity stems from polymer chain alignment, disentanglement, and aggregate dispersion within the fluid (Ghoumrassi-Barr, 2016).

### Cellulose

Cellulose, the Earth's most abundant biopolymer, originates in plant cell walls and certain eukaryotes. its molecular formula is (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>, where n signifies the degree of polymerization. This biopolymer, linked by β-(1,4) glycosidic bonds (Figure 4), exhibits properties shaped by its structural arrangement. Cellulose's network structure offers resistance to mechanical stress and high temperatures (Combariza, 2021), but also leads to uneven swelling and insolubility. To align with petroleum industry demands, cellulose polymers often undergo surface modification (Zhu, 2021). Hydroxyethylcellulose, carboxymethylcellulose, and nanocellulose exemplify common EOR applications.





**Figure 4.** (a) Cellulose, (b) carboxymethylcellulose, (c) hydroxyethylcellulose, and (d) nanocellulose

Hydroxyethyl cellulose, a non-ionic cellulose derivative, is an environmentally benign polymer. It is produced by chemically modifying insoluble cellulose. Its rigid polymer chain provides resistance to salinity, temperature, and shear. Hydrolysis of acetal linkages at low pH compromises stability, though it remains stable at neutral and high pH. Oxidation and degradation present further challenges. However, hydrophobically modified hydroxyethylcellulose, which is produced by modifying the macromolecular chain, provides enhanced properties for EOR. Intermolecular interactions between hydrophobic segments and the polymer backbone enhance rheology (Bai, nd). Liu et al. (2017) modified hydroxyethyl cellulose with bromo dodecane, observing increased viscosity, elasticity, and tolerance

to high salinity, elevated temperatures, shear forces, and acidic or alkaline conditions.

Carboxymethylcellulose (CMC), a derivative of cellulose, is synthesized by treating insoluble cellulose with chloroacetic acid in an alkaline medium. (Figure 4b). CMC structure varies according to the degree of hydroxyl group substitution on anhydroglucose linkages. The substitution pattern within  $(C_6H_{10}O_5)_n$  impacts CMC properties (Pu, 2018). Hydroxyl group replacement with alkali metals improves water solubility. CMC rheology and viscoelasticity depend on concentration. Above a critical concentration, elastic behavior predominates, while below this threshold, viscous properties prevail (Xia, 2020).

Nanocellulose emerged from advancements in nanotechnology, focusing on materials with at least one dimension measuring between 1 and 100

nanometers. Its nanofibrillar structure, derived from cellulose, makes it an ideal candidate for various applications.

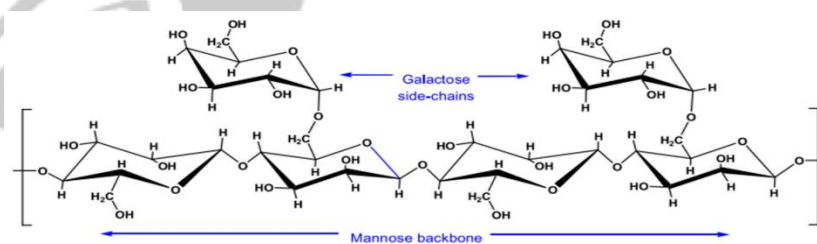
Nanocellulose boasts high functionality due to its template-like structure, reduced density, extra-large surface area, and biodegradability. Li et al. (2015) classified it into three main categories: cellulose nanocrystals, cellulose nanofibrils, and bacterial nanocellulose. The abundance of surface hydroxyl groups enhances its solubility in polar solvents. To increase hydrophobicity and modify its colloidal and interfacial behavior, charged compounds can be adsorbed onto the nanocellulose surface.

### Guar Gum

Guar gum is a hydrophilic biopolymer derived from the endosperms of *Cyamopsis psoraloides* and *Cyamopsis*

tetragonolobus. It is composed of linear chains of (1-4)- $\beta$ -d-mannopyranosyl units with (1-6)- $\alpha$ -d-galactopyranosyl branches (see Figure 5). Although it is soluble in polar solvents, it remains insoluble in organic solvents, showcasing its strong hydration properties.

it exhibits shear-thinning behavior at increased shear rates (Adimule, 2022). Salinity enhances guar gum's viscosity, while divalent cations can induce precipitation at high concentrations. Temperature also influences its viscosity: low temperatures increase viscosity due to reduced solubility, while high temperatures decrease it. Despite its potential, guar gum's incomplete hydration poses a significant risk of plugging in reservoir formations.



**Figure 5.** Molecular structure of guar gum

### Welan Gum

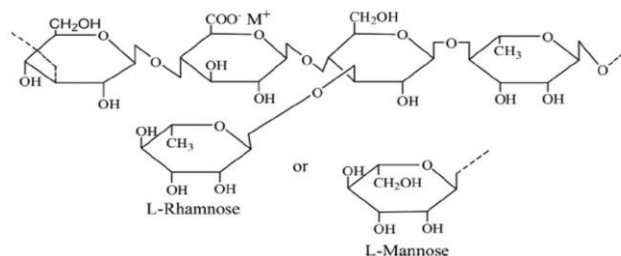
It is a non-gelling, negatively charged polysaccharide synthesized via bacterial fermentation of sugar by *Alcaligenes* species. Its molecular structure is characterized by a repeating pentasaccharide unit (Figure 6), composed of:

- $\beta$ -1,3-linked D-glucopyranose

- $\beta$ -1,4-linked D-glucuronopyranose
  - $\beta$ -1,4-linked D-glucopyranose
  - $\alpha$ -1,4-linked L-rhamnopyranose
  - A single monosaccharide side chain attached to the O-3 position of the 4-linked glucopyranose
- Additionally, acetyl and glyceryl groups are attached to the repeating units. Notably, 33% of the



monosaccharide side chains consist of  $\alpha$ -L-mannopyranose, and the remaining two-thirds are  $\alpha$ -L-rhamnopyranose (Xu, 2015).



**Figure 6.** Molecular structure of welan gum

Welan gum demonstrates greater viscosity compared to xanthan gum with the same molecular weight. in aqueous solutions due to its unique three-fold double-helix chain configuration. However, the polymer's anionic charges make its viscosity and viscoelasticity susceptible to the presence of inorganic cations such as sodium ( $\text{Na}^+$ ) and calcium ( $\text{Ca}^{2+}$ ). These ions shield the polyelectrolyte, causing the polymer chain to contract and coil. While high temperatures lead to some chain degradation, welan gum's glyceryl groups contribute to maintaining the double-helix structure, preserving viscosity at elevated temperatures. Overall, The molecular structure of welan gum offers enhanced resistance to salt and temperature variations when compared to xanthan gum.

Welan gum exhibits pseudoplastic behavior at reduced shear rates. This shear-thinning property arises from the alignment of macromolecular chains along the

direction of flow.. At low shear, chains stretch and intertwine, forming flow-resistant aggregates, leading to high viscosity. Conversely, increasing shear rate disentangles and disperses these aggregates, reducing solution viscosity (Ji,2020).

#### Schizophyllan

it is a non-ionic biopolymer produced by fermenting the *Schizophyllum* fungus using glucose as a carbon source (Gunaji, 2020). Its molecular structure, as depicted in Figure 7, consists of a linear chain of  $\beta$ -(1,3)-linked D-glucose residues with a single  $\beta$ -(1,6)-linked D-glucose unit for every three main chain residues (Pu, 2018).

The outstanding physicochemical characteristics of schizophyllan solutions originate from its rigid triple-helical structure and the intermolecular hydrogen bonding (Grisel, 1996). This distinctive configuration grants the polymer exceptional tolerance to high

salinity and temperature. Furthermore, schizophyllan displays shear-thinning properties when exposed to shear forces.

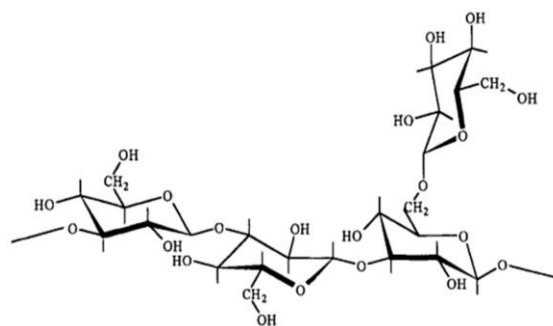


Figure 7. Molecular structure of schizophyllan

### Synthetic Polymers

A variety of synthetic polymers have been explored for enhancing oil recovery in laboratory settings. These polymers are primarily categorized into three main groups:

- Polyacrylamide (PAM): This is the base polymer, known for its long molecular chains and water solubility.
- Hydrolyzed Polyacrylamide (HPAM): Derived from PAM, HPAM has some amide groups replaced with carboxylate groups, improving its water solubility and viscosity.
- Hydrophobically Associating Polyacrylamide (HAPAM): This polymer combines the properties of PAM and HPAM with additional hydrophobic groups, enhancing its ability to interact with oil and improve oil recovery.

### Polyacrylamide (PAM)

it is a widely recognized thickening agent employed in EOR due to its substantial molecular weight (exceeding  $1 \times 10^6$  g/mol). In its original, unmodified structure, PAM is nonionic (Figure 8), which leads to considerable adsorption onto mineral surfaces within the reservoir. This adsorption greatly restricts its direct use in chemical EOR processes.

However, given its inherent properties, PAM serves as a foundational polymer for subsequent modifications. The industry has explored various alterations to PAM to mitigate adsorption and enhance the desired physicochemical characteristics necessary for effective EOR applications.

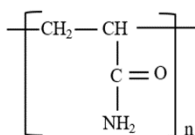


Figure 8. Molecular structure of PAM

### HPAM

Hydrolyzed Polyacrylamide (HPAM) is the preferred polymer for large-scale polymer flooding operations due to its robustness against the intense mechanical stresses prevalent in reservoir environments. Additionally, HPAM demonstrates resistance to bacterial degradation and offers economic viability. This polymer is produced either by the copolymerization of sodium acrylate and acrylamide or through the partial hydrolysis of polyacrylamide and

polyacrylic acid, as illustrated in Figure 9. (Olajire, 2014).

When dissolved in water, the polymer chain stretches due to electrostatic repulsion along its backbone, leading to an increase in the viscosity of the solution. The viscous characteristics of HPAM are affected by various factors, including molecular weight, concentration, degree of hydrolysis, salinity, temperature, and shear rate. (Veerabhadrappe, 2013).

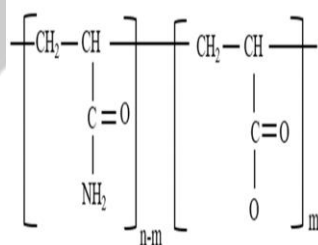


Figure 9. Molecular structure of HPAM

HPAM with lower molecular weight displays reduced viscosity compared to high molecular weight HPAM, which is characterized by high viscosity and elasticity. (Veerabhadrappe, 2013).

Increasing HPAM concentration leads to a higher solution viscosity. The ideal hydrolysis degree (DOH) of acrylamide lies within the range of 25-35%. A lower DOH

produces insoluble polymers, whereas a higher DOH results in sensitivity to brine salinity and hardness, negatively affecting viscosity (Gbadamosi, 2018). Brines reduce HPAM's thickening ability through cation screening, diminishing electrostatic repulsion and hydrodynamic volume (Wever, 2011). HPAM solution viscosity is influenced by temperature, decreasing with

increasing temperature due to reduced intermolecular interactions caused by amplified polymer chain thermal motion (Chul, 2012). HPAM exhibits both shear-thinning and shear-thickening properties under shear stress conditions.

### HAPAM

HAPAM was created to address the limitations of PAM and HPAM by incorporating comonomers into the acrylamide polymer backbone. These comonomers enhance the polymer's molecular weight, thereby improving its rheological properties and stability under high temperature and salinity conditions. A range of salt- and temperature-resistant comonomers has been utilized in the production of HAPAM. Consequently, HAPAM exhibits superior mobility control and enhances oil recovery during oil displacement. The improved oil recovery associated with HAPAM is linked to elastic turbulence generated by intermolecular interactions among hydrophobic comonomers within porous media. HAPAM's performance is defined by its critical aggregation concentration (CAC), which indicates the shift from low rheology due to intramolecular interactions to high rheology resulting from intermolecular interactions (Afolabi, 2013).

Despite HAPAM's superior performance in numerous laboratory tests, its widespread field application remains limited. This constraint might be due to the reliance of synthesized HAPAM functionality on the specific type and characteristics of the comonomer used in its production process.

Crucially, Choosing the appropriate comonomers necessitates careful evaluation, as their effectiveness is influenced by preparation techniques and essential reservoir conditions like salinity and temperature, which complicates the overall process. In conditions of elevated salinity and divalent ion concentrations, HAPAM displays varying rheological behavior that is affected by factors such as polymer concentration, the molecular structure of HAPAM, and the type of hydrophobe used.

Sarsenbekuly et al. (2017) developed a new low-molecular-weight HAPAM and examined its viscosity response to varying water salinity. The polymer's rheology displayed a non-linear pattern. Initially, viscosity decreased with increasing salinity up to 20,000 mg/L NaCl, due to reduced repulsion and chain compression caused by electrolyte-induced hydration of ionic groups. Above this concentration, viscosity rose to 80,000 mg/L NaCl, resulting from increased hydrophobic association, decreased solubility, and promoted intermolecular aggregation, expanding the polymer's hydrodynamic volume. Quan et al. (2016) reported comparable properties for amphoteric HAPAM synthesized from DOAC and sodium-4-styrenesulfonate monomers..

To evaluate the impact of synthesizing procedure on HAPAM properties, Maia et al. (2005) produced HAPAM through acrylamide and dihexylacrylamide micellar copolymerization, characterized using NMR and DLS. The polymer's rheological behavior in

response to varying salinity was investigated under different preparation conditions. At first, the introduction of 0.5 g/L of polymer powder into saline solutions (ranging from 0 to 100 g/L NaCl) resulted in a reduction in viscosity, attributed to cation screening of the charged polymer components, which caused intramolecular associations. Following this, the addition of salt powder to the polymer solution caused the viscosity to rise, reaching a maximum at 60 g/L NaCl before decreasing. Ultimately, when polymer solution was added to different saline solutions, the viscosity increased due to enhanced interactions between the polymer and salt..

Temperature impacts HAPAM rheology based on polymer concentration. Below the CAC, viscosity diminishes with increasing temperature, as observed by Sarsenbekuly et al. (2017) and Yang et al. (2019) with lower HAPAM concentrations or N-vinyl-2-pyrrolidone addition. Conversely, above the CAC, viscosity initially increases due to intermolecular hydrophobic aggregate formation, driven by an endothermic entropic process (Shi, 2013). Nevertheless, at higher temperatures, this structure disintegrates, reducing viscosity as molecular motion intensifies (Zhao, 2015). Quan et al. (2016) reported similar behavior with amphoteric HAPAM, attributing the initial viscosity increase to hydrophobic aggregation.

#### **POLYMER FLOODING**

Polymer-based enhanced oil recovery (EOR) has shown significant success in boosting recovery rates for

medium, heavy, and extra-heavy oil reservoirs, resulting in extensive laboratory, pilot, and field-scale applications. However, most field implementations have focused on sandstone formations because of the complex characteristics of carbonate rocks, which include vugs, fractures, and various heterogeneities. The effectiveness of polymer flooding relies on a complicated interaction of reservoir rock and fluid properties, including lithology, location, depth, porosity, permeability, heterogeneity, oil viscosity, temperature, salinity, hardness, oil saturation, and the properties of the polymer itself (Standnes, 2014).

#### **BINARY COMBINATION OF POLYMERS AND OTHER ADDITIVES FOR EOR**

##### **Polymer Foam Flooding**

Gas injection is an early enhanced oil recovery (EOR) method that involves pumping hydrocarbon or non-hydrocarbon gases to displace residual oil (Rafati, 2018). While gaseous at surface conditions, these substances become supercritical fluids under reservoir pressures and temperatures (Johns, 2013). Gas injection is categorized into two types: miscible flooding and immiscible flooding. Miscible flooding, conducted above the minimum miscibility pressure, utilizes mass transfer, swelling, reduced oil viscosity, and interfacial tension to recover oil. Conversely, immiscible flooding operates below this pressure, maintaining reservoir pressure. Nonetheless, gas flooding experiences issues with inadequate areal and vertical sweep efficiency, gravity override, gas

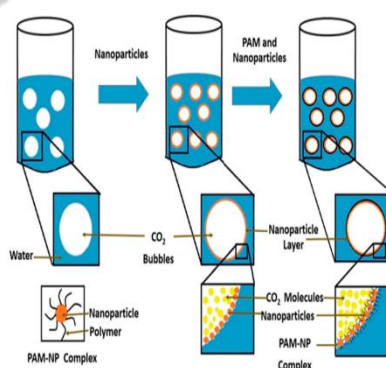


segregation, and channeling through high-permeability areas (Adebayo, 2021). To address these challenges and enhance gas mobility, foamed-gas injection was created and tested in the field.

The foam in missing porous media includes dispersed gas within a consistent liquid phase separated by thin films of liquids which are known as lamellae. (Majeed, 2021). Foam forms when a liquid containing a foaming agent contacts gases like N<sub>2</sub>, CO<sub>2</sub>, or air with sufficient mechanical energy. Foam generation processes include leave behind, snap-off, and bubble division (Adebayo, 2021). In reservoirs, foam reduces gas relative permeability and increases apparent fluid viscosity, controlling gas mobility. This increased viscosity stems from bubble-induced drag on pore walls, while gas trapping decreases gas relative permeability. The foam diverts the subsequent fluid from the high- to the lower-permeability zones in

heterogeneous reservoirs. Despite their potential, foams are inherently unstable due to drainage, coalescence, and coarsening. To improve foam stability for EOR, various surfactants, proteins, polymers, ionic liquids, and nanoparticles have been studied (Said, 2022).

Polymers have been specifically studied for foam stabilization. Their viscoelastic nature enables effective foam stabilization at low concentrations, improving economic feasibility. Polymers increase foam viscosity and stability, reducing liquid drainage (Azdarpour, 2015). Consequently, polymer-stabilized foams demonstrate superior mobility control during oil recovery. Polymers also serve as additives in surfactant- or nanoparticle-stabilized foams, preventing surfactant or nanoparticle desorption from lamellae interfaces, thus inhibiting foam coalescence and extending half-life (Figure 10).



**Figure 10.** Schematics of polymer-stabilized nanoparticle foam

Synthetic and biopolymers have shown exceptional foam stabilization capabilities. Wang et al. (2008)

investigated HPAM's impact on alpha olefin sulfonate (AOS) foam stability, finding optimal foam volume and

stability at 0.1 wt%. HPAM enhanced surface tension and foam viscosity. Hernando et al. (2018) compared associative and PAM-stabilized foams, revealing amphiphilic polymers offered superior foam stability due to stronger surfactant interactions. These foams exhibited slower kinetics, higher pressure drop, and greater stability. Ahmed et al. (2017) contrasted a new associative polymer (Superpusher B 192) with HPAM, demonstrating superior foam strength and doubled apparent viscosity for the associative polymer. This improved rheology enhanced bulk solution properties and tolerance. In contrast, AOS-based foam showed rapid liquid drainage and decay. Associative polymer-stabilized foam achieved 28% incremental oil recovery compared to 14% for polymer-free foam, highlighting the hydrophobic chain's contribution to foam performance (Hernando, 2016).

Bashir et al. (2019) studied CO<sub>2</sub> foam stability and viscosity in systems combining nanoparticles, polymers, and oil under harsh reservoir conditions. Fumed silica and rice husk ash nanoparticles, along with xanthan gum, were tested. Higher polymer molecular weight and smaller nanoparticles led to improved foam stability due to enhanced oil emulsification into tiny droplets that easily pass through foam lamellae without surfactant loss. Wei et al. (2020) explored the combined impact of xanthan gum and alkyl polyglycoside on oil-laden foam stability. Polysaccharides thickened liquid films, stabilizing foams through increased interfacial elasticity, denser

adsorption layers creating pseudoemulsion films, and higher liquid viscosity inhibiting drainage.

Nanocellulose grafted onto the surface acted to drain liquids and thicken foam films. Zhang et al. showed that mixing lignin-cellulose nanofibrils with cationic and anionic surfactants obtained firm foams, impeding drainage of liquids. Furthermore, it has been discovered that the composites formed by welan gum and hydroxylpropyl methylcellulose can significantly stabilize foams via their shear-thinning properties and physical interactions..

Polymer foam efficiency and effectiveness are influenced by factors beyond polymer type, including oil phase viscosity, salinity, and temperature. Higher oil phase viscosity increases foam vulnerability to destruction, while elevated temperature destabilizes foams. Conversely, increased salinity enhances foam stability by reducing liquid drainage and coalescence. Dehdari et al. (2020) compared the impact of light and heavy oil on PVA-stabilized foams with surfactants and nanoparticles, finding heavy oil to be more destabilizing. They also observed that increased aqueous phase salinity enhanced foam stability with PVA. However, polymer-stabilized foams generally exhibit better temperature stability. Fu and Liu (2020) investigated CO<sub>2</sub> foam stability with nanoparticles, surfactants, and hydroxyethylcellulose under varying salinity and temperature. Increased temperature reduced CO<sub>2</sub> foam apparent viscosity and accelerated

film drainage, while the polymer enhanced thermal resistance.

Polymer-enhanced foam provides multiple benefits for EOR, effectively extracting both conventional and heavy oil from diverse reservoir types. Beyond oil production, recent research indicates its superior potential for gas sequestration and storage compared to traditional foams. Optimizing polymer characteristics is essential for successful polymer foam flooding, and incorporating nanoparticles can improve performance. While some studies suggest minimal impact of polymer molecular weight on foaming ability, others report enhanced foam stability with higher molecular weight.

### Alkali-Polymer Flooding

Alkali-polymer flooding synergistically combines alkaline and polymer solutions for enhanced oil recovery. This approach addresses the limitations of standalone alkaline flooding. Alkali injection alters fluid-fluid and rock-fluid properties, including interfacial tension and wettability. Alkali reacts with crude oil naphthenic components, generating in-situ surfactants that reduce interfacial tension and create stable emulsions. However, alkalis' limited mobility, especially in heavy oil reservoirs, necessitates polymer addition for improved oil displacement.

Alkali influence on polymer behavior varies based on alkali concentration, pH, and polymer type, potentially altering solution ionic strength or pH (Sheng, 2017). With synthetic polyacrylamide, alkalis accelerate

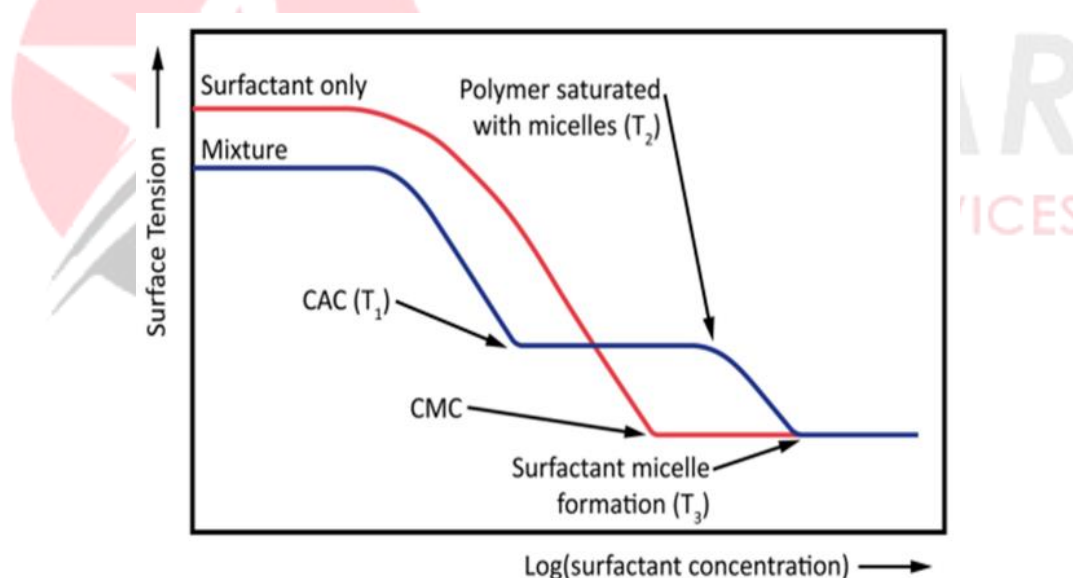
hydrolysis. Low alkali concentrations yield low-viscosity polymers, This is attributed to the tight coil conformation.. Increasing alkali concentration elevates pH, inducing electrostatic repulsion, expanding the hydrodynamic radius, and increasing viscosity. Chul et al. (2012) observed HPAM viscosity increases with NaOH addition in brine and temperature, but high alkali concentrations reduce viscosity due to increased ionic strength. This lower viscosity can enhance polymer injectivity in tight formations. Reintroducing waterflooding decreases ionic strength, expanding the polymer and increasing resistance to flow, diverting water to unswept zones, and improving sweep efficiency. Similar alkali effects on biopolymers (xanthan gum) have been reported (Medica, 2020).

### Surfactant-Polymer Flooding

Surfactants, with their hydrophobic groups, enhance pore-scale displacement efficiency by reducing interfacial tension, altering wettability, and stabilizing emulsions. This approach proves effective for recovering capillary-trapped oil but may fall short in heavy oil reservoirs. Polymers, conversely, increase injectant viscosity, improve mobility ratio, and enhance volumetric sweep efficiency without significantly influencing microscopic processes. Achieving optimal recovery necessitates combining surfactant and polymer flooding to address both microscopic and macroscopic displacement inefficiencies (Liu,2017). Careful chemical selection is crucial for surfactant-polymer (SP) flooding efficiency, as incompatible

surfactant and polymer properties can induce phase separation. Injection slug design varies based on flooding objectives. Competitive adsorption between chemicals reduces pore space availability for subsequent chemicals, potentially impacting recovery. Polymer pre-injection can minimize surfactant adsorption and enhance conformance control. Conversely, polymer as a secondary slug addresses viscous fingering during water and surfactant flooding (Gbadamosi,2019). Despite sequential injection, surfactant-polymer interactions via diffusion and dispersion must be considered in screening criteria development.

Numerous studies have investigated the reciprocal influence of surfactants and polymers. Interfacial tension (IFT) measurements as a function of polymer and surfactant concentrations highlight this interaction. Polymer addition introduces two critical concentration points, replacing the system's CMC, as illustrated in Figure 11. The initial critical aggregation concentration (CAC) precedes the CMC, marking surfactant molecule adsorption and polymer chain interaction. The subsequent polymer saturation concentration exceeds the CMC, characterized by surfactant micelle formation around polymer molecules (Druetta,2018).



**Figure 11**

Depending on surfactant and polymer charges, interactions are attributed to electrostatic or hydrophobic effects. Afolabi (2019) examined sodium dodecyl sulfate (SDS) impact on poly(acrylamide-co-N-

dodecylacrylamide) rheology, observing increased viscosity until SDS reached CMC, followed by a decrease. This behavior resulted from surfactant-polymer hydrophobic interactions. Similarly, Yusuf et

al. (2021) investigated sodium dodecyl benzene sulfonate's influence on carboxymethyl cellulose (CMC) rheology, emulsion, and wettability, noting viscosity increase until CMC, followed by a decrease. Hydrophobic microdomain formation at high surfactant concentrations disrupted surfactant-polymer intermolecular forces, reducing viscosity.

Moreover, Kalam et al. (2020) explored spacer nature and counterions in a new polyoxyethylene cationic surfactant on the rheology of cationic polyacrylamide polymers.. Increasing surfactant concentration reduced shear viscosity and elasticity, while elevated temperature decreased storage and complex viscosity. Introducing a phenyl ring into the Gemini surfactant spacer enhanced viscosity and storage modulus. Chloride counterions outperformed bromide counterions in improving polymer rheology. Ge et al. (2021) investigated the effect of betaine surfactant structure on surfactant-polymer (SP) mixture rheology. Short-chain betaine surfactants negatively impacted polymer solution viscosity due to electrostatic shielding. Conversely, high concentrations of long-chain betaine surfactants positively influenced surfactant-polymer flooding viscosity.

To minimize chemical injection volumes, recent studies have developed polymeric surfactants by merging amphiphilic surfactants with polymer macromolecules into a single compound. These novel chemicals exhibit surface activity, influencing fluid-fluid and rock-fluid

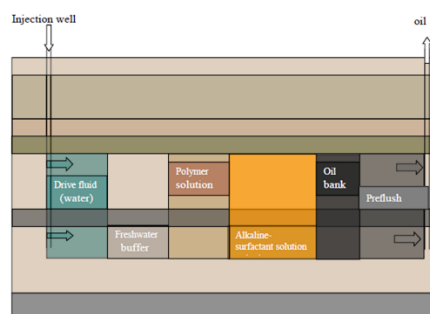
interactions. While not achieving ultralow interfacial tension (IFT) like conventional surfactants, polymeric surfactants reduce IFT to approximately 10-1 mN/m, facilitating stable microemulsion formation. These surfactants also demonstrate favorable rheological properties, reducing injectant mobility and exhibiting advantageous for field applications. In essence, While on the other hand, polymeric surfactants combine interfacial properties typical of classic surfactants with the viscoelastic properties of a polymer. (Raffa,2016).

The solution properties of polymeric surfactants are far better than conventional polymers due to the presence of hydrophobic units in them. Intramolecular hydrogen and van der Waals tensile bonds in the functional group formed enhance the bulk viscosity and viscoelasticity. Kumar et al. studied the anionic polymeric surfactant derived from *Jatropha* and found that the viscosity increased with concentration along with the pseudoplastic behavior at higher shear rates. Babu et al. (2015) synthesized a polymeric surfactant based on castor oil, and non-Newtonian behavior was developed, which exhibited viscosities from 10 to 40 cP, much superior to the viscosities shown by normal or conventional surfactants. Pal et al. (2016) measured the rheological performance of synthesized polymeric methyl ester sulfonate for EOR and found higher storage and loss moduli with increasing concentration of the surfactant.

Polymeric surfactants exhibit superior IFT reduction and wettability alteration compared to conventional







**Figure 12.**

Laboratory studies confirm the efficacy of alkaline-surfactant-polymer (ASP) flooding in improving oil recovery from reservoirs. Sui et al. (2020) reported a 44.5% increase in oil recovery compared to waterflooding when using ASP on active oil under conditions of 62 °C and 1700 psig. Zhabbasbayev et al. (2018) noted an additional oil recovery of 19-37% when applying ASP to viscous oils (407.4 and 300 cP) from Russian fields. Panthi et al. (2017) achieved incremental oil recoveries of 47.8% and 44.9% over waterflooding by utilizing ASP as a secondary and tertiary recovery method for viscous oil, incorporating sodium metaborate, propoxy sulfate surfactant, and HPAM polymer. Fu et al. (2016) reported a 20% increase in oil recovery through the use of a combination of organic alkali and petroleum sulfonate surfactant in ASP flooding. Liu et al. (2008) successfully extracted 98% of residual oil from dolomite and silica sandpicks via ASP flooding. Ghosh et al. (2019) explored ASP in low-permeability tight carbonate reservoirs, achieving recovery rates of 77-87% of the original oil in place through tertiary ASP flooding while modeling

geochemical interactions. Panthi et al. (2016) demonstrated that secondary surfactant flooding reduced oil saturation to 3.1% and raised cumulative oil recovery to 95.6% in a carbonate reservoir.

To investigate the environmental concerns related to the toxicity of conventional surfactants used in ASP flooding, recent research has focused on developing and evaluating natural and biosurfactants as alternatives. Kesarwani et al. (2021), From karanj oil, synthesized a biodegradable surfactant., resulting in a 32% increase in oil recovery during sandpack flooding. Nowrouzi et al. (2020) developed a natural surfactant derived from soapwort, achieving ultralow interfacial tension and altering wettability in sandstone cores. An ASP slug composed of sodium hydroxide, soapwort surfactant, and HPAM led to a 32.1% incremental oil recovery. In another study, Nowrouzi et al. (2020) utilized hollyhock mucilage as a natural polymer and a waste chicken fat-based anionic surfactant for ASP, resulting in a 27.9% incremental oil recovery in sandstone reservoirs.

### **Polymeric Nanofluid Flooding**

Although polymers boost oil recovery, their efficiency is curtailed by adsorption, retention, and chemical, mechanical, or thermal degradation. While temperature and salt-resistant polymers exist, cost and complexity impede their widespread use. Combining inexpensive nanoparticles with polymers produces innovative materials with enhanced characteristics for improved oil recovery (EOR) have emerged. Nanoparticles engage with polymers via hydrogen bonding, electrostatic interactions, van der Waals forces, and steric repulsion. These polymeric nanofluids demonstrate salt tolerance, temperature resistance, and improved rheology. Decreased adsorption and increased stability within porous media enhance their oil recovery efficiency. Additionally, these nanofluids modify fluid-fluid and rock-fluid interactions (Agi, 2020).

Enhanced rheology of PNFs under HTHS conditions arises from hydrogen bonding and nanoparticle-induced shielding of polymer chains (Figure 13). Agi et

al. (2020) showed starch-based PNFs outperform xanthan gum in rheological properties. Rezaei et al. (2016) modified montmorillonite nanoclay, resulting in improved rheology, shear resistance, and oil recovery when combined with HPAM. Maurya and Mandal (2016) observed increased viscosity in polyacrylamide upon SiO<sub>2</sub> nanoparticle addition. Hu et al. (2017) reported enhanced rheological and thermal stability for silica nanoparticle-seeded acrylamide polymer, explaining this by a hydrogen-bonded 3D network that protects the polymer and reduces degradation (Figure 14). Li et al. (2017) highlighted the excellent rheology of nanocellulose-based PNFs, while Agi et al. (2020) reported good rheological behavior of okra mucilage-derived PNFs in brine. Corredor-Rojas et al. (2019) showed enhanced rheological properties, salt tolerance, thermal stability, and shear resistance in modified silica nanoparticle-xanthan gum polymer nanofluids (PNFs).

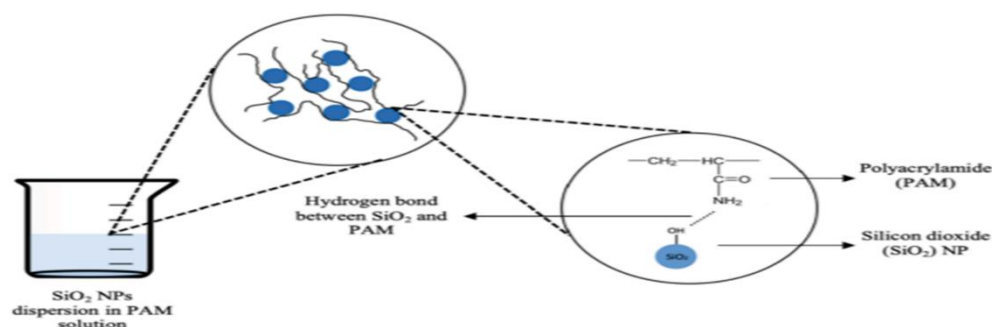


Figure 13.

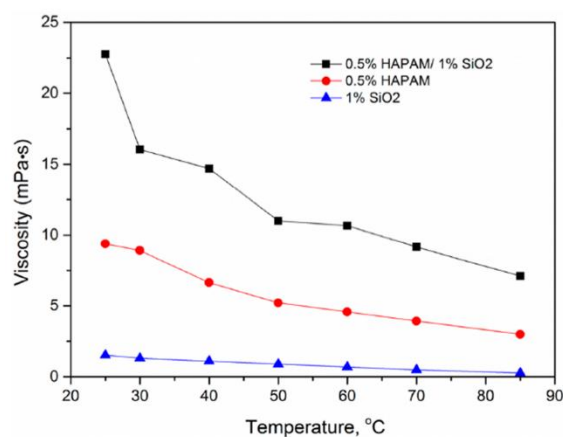


Figure 14.

Beyond enhanced rheology, salinity, and thermal resistance, polymeric nanofluids demonstrate reduced adsorption and improved stability within porous media. Bagaria et al. (2013) observed lower adsorption and greater stability of iron oxide nanoparticle (IONP). steric repulsion-induced stability of IONP-acrylamide polymer nanofluids on silica.. Cheraghian and co-workers, 2014, reported reduced adsorption of silica and clay nanoparticle-based polymeric nanofluids on sandstone cores. Xue et al., 2014, confirmed the stability and transport properties of IONP-poly(AMPS-co-AA) copolymer nanofluid under high temperature high shear conditions. Iqbal et al., 2017, reported iron oxide nanoparticle stability at 120 °C using poly(AMPS-co-AA) copolymer. Zhao et al., 2017 observed starch-graphene nanoparticle PNF stability. Vasconcelos et al. (2022) reported the ethylenediamine-modified graphene oxide nanoparticles to be stable up to 90

days, with a viscosity increase of 146% compared to HPAM.

Additionally, nanoparticles within polymers reduce IFT, altering wettability and stabilizing emulsions. Nanofluids stabilized by polymers have very excellent properties. Corredor and co-workers (2019) reported a 66.7% IFT reduction using polymeric nanofluids. Sharma et al. (2016) observed reduced oil-water IFT with nanoparticle-doped polyacrylamide. Bera et al. (2020) demonstrated nanoparticle-induced guar gum polymer's ability to alter wettability from oil-wet (115°) to water-wet (72°) conditions. Gbadamosi et al. (2019) reported aluminum nanoparticle-HPAM's wettability alteration. Saha et al. (2018) observed xanthan gum and silica nanoparticle-based foam's long-term stability. Pal et al. (2019) demonstrated improved emulsion packing and stability with HPAM and SiO<sub>2</sub> nanoparticle-stabilized emulsions. Kumar et al. (2017) reported carboxymethylcellulose and SiO<sub>2</sub>

nanoparticle-stabilized emulsions' stability over a wide temperature range and reduced IFT.

#### FINANCIAL IMPLICATIONS OF POLYMER USE IN EOR

Polymer injection for chemical EOR provides economic advantages by boosting oil production and curtailing water production. Incremental oil recovery enhances project profitability, while lower water cut minimizes treatment costs and compared waterflooding and polymer flooding costs in Daqing oilfield, finding polymer flooding costs of approximately 9 USD/bbl, equivalent to waterflooding costs. Water cut reduction from 90-95% to 70% with quadrupled oil recovery through polymer injection highlights its economic viability, especially with current high oil prices. China leads in polymer flooding applications with over 3000 wells and 300 million barrels of cumulative oil production (Keykhosravi,2021). The USA and Canada also utilize polymer flooding, particularly in heavy oil reservoirs.

#### CONCLUSIONS

This review assessed the utilization of polymers in enhancing oil recovery through chemical methods. The review encompassed a detailed examination of polymer types and their underlying mechanisms, along with binary polymer-additive combinations for EOR. Recent polymer flooding studies were summarized. While HPAM remains prevalent, other polymers show promise. Careful reservoir rock and fluid property screening is essential for successful polymer applications. Polymer-additive combinations yielded

positive results, with EOR types benefiting from incremental oil recovery. Most studies focused on sandstone reservoirs, necessitating further research on carbonate reservoir applications. Scaling issues persist in ASP flooding. Optimal injection sequence configuration for surfactant-polymer flooding needs improvement. Rock-fluid interactions for surface-active agents are still poorly understood, and polymeric nanofluid phase equilibrium behavior remains unclear.

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