

Application of Acrylates in Enhanced Oil Recovery

A.N. El-hoshoudy^{1,2,*}, S.M. Desouky¹, and S. Gomaa²

¹Production department, Egyptian Petroleum Research Institute, Naser City, Cairo, Egypt.

²Petroleum Engineering Department, Faculty of Engineering, British University in Egypt, Elshorouk City, Cairo, Egypt.

Abstract

Currently, enhanced oil recovery (EOR) acquire increased attention to recover more residual oil trapped after the primary and secondary process in petroleum reservoirs. EOR comprise different technologies involving chemical, thermal, miscible flooding techniques. Chemical flooding by the polymer is a widely implemented method on the academic and industrial scale. In this chapter, the authors discuss polymer flooding using polyacrylates that involve hydrolyzed polyacrylamide (HPAM), hydrophobically associated polyacrylamides (HAPAM), which grafted with different vinyl monomers such as acrylic acid, methyl methacrylates, and 2-acrylamido-2-methylpropane sulfonic acid (AMPS). These polymers increase the viscosity of injected brine solutions, as a result, decrease mobility ratio and enhance sweeping efficiency, so the water act as a piston, which pushes oil in front of it, and consequently increase the recovery factor. The advantages and disadvantages of these polymers as well as comparing different flooding scenarios are reported.

Corresponding author: A.N. El-hoshoudy, Production department, Egyptian Petroleum Research Institute, Naser City, Cairo, Egypt. Email: azizchemist@yahoo.com

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Introduction

Polymer flooding is a common EOR technique, in which solutions of a high molecular weight water-soluble polymer is pumped into the reservoir in order to increase the water phase viscosity to obtain favorable mobility and minimize channeling effects, improving sweeping and displacement efficiencies [1]. With the world's attention on enhancing fossil-fuel production to satisfy national promotion and daily energy consumptions. Enhanced oil recovery (EOR) is of considerable academic and technological interest[2]. Crude oil recovery occurs through three distinct phases, firstly production results from the natural energy of the fluids and the rock decompression[3], where it recovers 5 to 15% of the initial reserve. The second stage is known as secondary recovery involving the injection of fluids such as water or gas to boost and maintain the reservoir pressure, so force the oil into the wellbores of producing wells and recovery factor reach 10-20% [4-6]. The last stage is combined under the name of Enhanced Oil Recovery (EOR), which recover between 10 and 35% of additional oil and comprise thermal, miscible and chemical methods. EOR can be defined as any processes that increase oil recovery by reduction of the residual oil saturation (S_{or}) after primary and secondary production. Virtually, EOR technologies involve the injection of fluids not normally present in the reservoir (e.g. polymers, foams, surfactants) in order to increase oil recovery [7]. Tertiary or enhanced oil recovery aims to recover the remaining original oil in place (OOIP) [7] and increase the ultimate oil recovery of the reservoir through one or more sophisticated techniques including chemical, thermal, and miscible flooding[8] for recovering up to an additional 40 % of the OOIP. Several kinds of literature discuss the application of polymer flooding in enhanced oil recovery. Dabbous,1977 [9] conducted the flooding tests in heterogeneous porous media showed that preinjection of the polymer could result in better flooding efficiency. Platt and James,1981[10] prepared poly (alpha-alkoxy) acrylamides and claimed improved stability in brine solutions. Similar claims were made by Hunter, 2008 [11] and Cao et al, 2015[12]who prepared N-substituted PAM/AA via ethoxylation. Talley, 1993[13] disclosed terpolymers of acrylamide, acrylonitrile and acrylic acid, the latter optionally alkoxylated with ethylene oxide. McCormick et al, 1982&2014 [14, 15])

copolymerize sulfonated monomers such as 2-acrylamido-2-methylpropane sulfonic acid (AMPS) with acrylamide monomers. Martin et al, 1983[16] studied the synthesis of polyacrylamide containing imide rings and concluded that they are less susceptible to alkaline hydrolysis than PAM. Moreover, they studied the viscosity retention in brine for hydrolyzed PAM/AA versus copolymerized PAM/AA and found little difference in the two, claiming that shear resistance of the hydrolyzed PAM/AA was superior to the copolymers. Osterloh and Jante, 1992[17] mention that surfactant adsorption is minimized in the presence of polymer thus the use of a surfactant-polymer flood could be highly favorable and justified. Farouq-Ali and Thomas, 2001[18] also discuss the limitations of the use of polymer floods and mention that being introduced earlier in the life of a water flood is a better option. They also report incremental oil recoveries in the order of 5% on average. Schramm, 2000 [19] discusses the concept of "Low Tension Polymer Flood" (LTPF). He concluded that; the flood in the first instance was conducted by co-injection of the surfactant and polymer and, due to chromatographic effects, the polymer moved ahead of the surfactant. Du and Guan, 2004[20] discuss the field application of polymer floods and conclude that when applied after the reservoir has been extensively flooded by other means, polymer floods have been unsuccessful. Another observation they make is that in reservoirs of low average permeability, injectivity of the floods greatly reduced with the addition of a polymer and resulted in poor performance. El-hoshoudy et al group [21-29] discuss the preparation and application of different hydrophobically modified polyacrylates and their modified nanocomposites as well as biopolymers and their composites in the field of enhanced oil recovery. They also reported about the use of 1-vinyl imidazole surfmer for the synthesis of polyacrylamide-SiO₂ nanocomposite for severe polymer flooding conditions. Other literature reported about the use of quaternary ammonium-based surfmer with polyacrylamide co-polymer for flooding in carbonate rock[30]. Others reported about modification of starch biopolymers through grafting with different vinyl monomers to be applied in enhanced oil recovery applications[31, 32]. Gou et al [33]reported about copolymerization of acrylamide (AM), acrylic acid (AA), 1-acrylamido

ethyl-2-oleic imidazoline (ACEIM) with the sodium salts of 3-(diallyl-amino)-2-hydroxypropyl (NDS) or 2-acrylamido-2-methylpropane sulfonic acid (AMPS) for polymer flooding at harsh reservoir conditions of high salinity and temperature. Hsieh et al [34] describe the synthesis of water-soluble polymers suitable for enhanced oil recovery applications through polymerization of acrylamide, N-vinyl-2-pyrrolidone, sodium 2-acrylamido 2-methylpropanesulfonate and N, N-dimethylacrylamide. Lai et al [35] synthesize a novel hyperbranched polymer using acrylamide (AM), acrylic acid (AA), N-vinyl-2-pyrrolidone (NVP), and dendrite functional monomer as raw materials by redox initiation system in an aqueous medium to be applied in enhanced oil recovery. Liu et al [36] fabricated a novel star-like hydrophobically associative polyacrylamide used in enhanced oil recovery (EOR) processes in harsh reservoir conditions. Pu et al [2] reported about the synthesis of a novel water-soluble core-shell hyperbranched polymers (HBPAMs), consisting of nano silica core, hyperbranched polyamidoamide (PAMAM) as subshell and linear hydrophilic chains as the outermost layer, through in-situ free radical polymerization strategy. Raffa et al [1] fabricate amphiphilic copolymers based on Poly(ethylene glycol) methyl ether acrylate (PEGA) by Atom Transfer Radical Polymerization (ATRP). AP(PEGA) homopolymer, a block copolymer with styrene PS-**b**P(PEGA), and an analogous terpolymer including also sodium methacrylate (MANa) in the poly(PEGA) (PPEGA) block, PS-**b**P(PEGA-**co**-MANa) have been prepared and characterized to be applied in polymer flooding. Sun et al [37] synthesize a novel amphiphilic polymer based on radical copolymerization of acrylamide, dodecyl polyoxyethylene acrylate (DPEA), and N-(1,1,3,3-tetramethyl butyl) acrylamide (TBA), using potassium persulfate-sodium bisulfite as initiator-activator for enhanced oil recovery (EOR). Tian and Xu [38] prepare a copolymer act as a profile control agent via copolymerization of vinyl triethoxy silane (VTEOS) as a temperature tolerant monomer and Isobutane-Ethylhexyl acrylate (2-EHA) as a salt-resistant monomer with acrylamide monomer (AM) during a free radical copolymerization process. Tong et al [39] fabricate mono-dispersed poly (acrylamide-co-sodium acrylate) hydrogel microparticles with a controlled water absorbance capacity in a droplet

microfluidic device which can be used for enhanced oil recovery application. Xu et al [40] proposed a new polymer synthesized from acrylamide (AM), 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and 10-hydroxydecylmethacrylate. This polymer thickening the formation brine in harsh reservoir conditions and emulsify the crude oil, in such a way that the accumulative oil recovery of polymer floods using this polymer is expected to be far greater than that of a conventional polymer such as HPAM. Zhang et al [41] reported about the radical polymerization of acrylamide, acryloyl morpholine, and 2-acrylamide-2-methyl propane-sulfonate in water initiated with ammonium persulfate or 2,2-azo bis(2-methylpropionamide) dihydrochloride to produce copolymer for enhanced oil recovery (EOR) applications. The categories of different EOR methods comprise;

Thermal Flooding

Injection of steam has historically been the most widely applied EOR method. Heat from steam or hot water dramatically reduces heavy oils viscosity, thus improving its flow. The process involves: cyclic steam injection ("huff and puff", where steam is first injected, followed by oil production from the same well); Continuous steam injection (where steam injected into wells drives oil to separate production wells); hot water injection, and steam assisted gravity drainage (SAGD) using horizontal wells, among others.

Miscible Flooding

Miscible EOR employs supercritical CO₂ to displace oil from a depleted oil reservoir. CO₂ improve oil recovery by dissolving in, swelling, and reducing the viscosity of the oil. In deep high-pressure reservoirs, compressed nitrogen has been used instead of CO₂. Hydrocarbon gases (natural gas and flue gas) have also been used for miscible oil displacement in some large reservoirs. These displacements may simply amount to "pressure maintenance" in the reservoir [42]. CO₂ miscible flooding in crude oil reservoirs is a successful technique to reduce its amount in the atmosphere, in addition to increasing the mobility of the oil and, consequently, increase the reservoir productivity. It is preferred other than hydrocarbon gases since it does not only increase oil recovery but also causes a reduction of greenhouse gas emissions. Moreover, it is a cheap

technology as an ultimate long-term geologic storage solution for CO₂ owing to its economic productivity from incremental oil production offsetting the cost of carbon sequestration, and exhibit high displacement efficiency and the potential for environmental contamination decrease through its disposal in the petroleum reservoir[43].

Chemical Flooding

Chemical flooding involves the injection of an agent not normally present in the reservoir to enhance the oil displacement. The chemical flooding processes involve the injection of three kinds of chemicals; alkaline, surfactant, and polymer (soluble and cross-linked polymers), in addition to other chemicals such as foaming agents, acids and solvents[19] and/or combination of alkaline-surfactant-polymer flooding (ASP), and surely the most important substance in these methods is polymer flooding[44]. In the polymer flooding method, water-soluble polymers aimed to shut-off the high-permeability areas of the reservoir and increase injected water viscosity to increase the swept areas in the reservoir [45] leading to a more efficient displacement of moderately viscous oils. Addition of a surfactant to the polymer formulation may, under very specific circumstances, reduce oil-water interfacial tension and hence remobilizing the trapped oil [46], changing the wettability of the surface, forming emulsions, so enhance the oil production. For some oils, alkaline may convert some naphthenic acids within the oil to surfactants due to the formation of in-situ surfactant. The alkaline may also play a beneficial role in reducing surfactant retention in the rock. For all chemical flooding processes, the inclusion of a viscosifier (usually a water-soluble polymer) is required to provide an efficient sweep of the expensive chemicals through the reservoir.

Other EOR Flooding Processes

Over the years, a number of other innovative EOR processes have been conceived. These methods exhibit varying degrees of promise but require additional development before practical applications. These methods including the following categories;

Injection of Carbonated Water

In which, carbon dioxide (CO₂) is dissolved into the water phase before injecting into the reservoir. The

dissolved CO₂ will transfer from the water phase to the oil phase due to the chemical potential difference of the CO₂ in two phases (as a driving force). This interphase mass transfer reduces the oil viscosity, lowers the oil-water interfacial tension (IFT), and causes oil swelling, which will be responsible for the reconnection of isolated residual oil ganglia, mobilizing the trapped oil[47].

Microorganisms

application of microorganisms in enhanced oil recovery known as microbially enhanced oil recovery (MEOR). MEOR involves that microbial metabolites are produced in the reservoir rock formation, which makes them more effective. Furthermore, microorganisms metabolize different hydrocarbons at different rates, so boost oil recovery[48].

Foams and Other Formulations

Foam is employed to improve the displacement efficiency by which the displacing fluid sweeps the reservoir and increase the recovered oil amount[49].

Generally, a flow sheet of EOR processes, worldwide EOR project categories, and different flooding techniques are shown in Figures 1-3 respectively.

Properties of Acrylates Polymers

Most polymers used in enhanced oil recovery applications is anionic acrylamide-based polymers which characterized by high molecular weight 4-30 million Dalton and high polydispersity index (PDI) and derived from [3]; 1) Copolymerization of acrylamide and sodium acrylate (or/ and sodium Acrylamido-Tertio-Butyl Sulfonate (ATBS)), where copolymerization of acrylamide and sodium acrylate leads to polymer with a more uniform distribution of the anionic charges; 2) Co-hydrolysis or post-hydrolysis of a polyacrylamide; 3) Copolymerization or ter-polymerization of acrylamide with other ionic or non-ionic functional monomers. Polyacrylate polymers exhibit Non-Newtonian behavior (display pseudo plastic criteria) in which viscosity decrease with a shearing increase [30-32]. Since viscosity related to shear rate by the following equation

$$\mu = K\gamma^{-n} \quad \text{..... (Eq1)}$$

Where γ is the shear rate (s^{-1}), μ is the viscosity, cp; K & n are constants. The minus sign indicates the inverse relationship as indicated in figure 4. Polyacrylamide co-polymers containing a sulfonated

Enhanced oil recovery methods										
Non-Thermal Methods					Thermal Methods				Others	Combination EOR
Gas EOR		Chemical (Water-Based EOR)		Bio	Hot Water	Steam		In situ Combustion	Electrical Beam Heating	WAG & SWAG
Miscible Gas	Immiscible Gas									
Enriched Gas Drive (Hc's Gases)	Acidic Gases (CO ₂ Immiscible & Sour Gases)	Liquid Solvent	Emulsion	Microbial EOR		Cyclic and Steam Injection	huff and puff VAPEX+ Steam	THAI		Miscible CO ₂ +SAGD
Vaporizing Gas Drive	N ₂ immiscible	Micellar	Surfactant	Enzyme EOR		Continuous (Drive) Steam In jection	SAGP	Combustion with additives	ASP+CO ₂	
Acidic Gases (CO ₂ Miscible & Sour Gases)	Inert Gas	AS/SP/ASP	(Gel Treat-ment & Polymer Flooding)			SAGD		CAGD	Foams	Foam + Miscible CO ₂
N ₂ Flooding		Flue Gases					VAPEX			

Figure 1. Flow sheet of enhanced oil recovery methods [50].

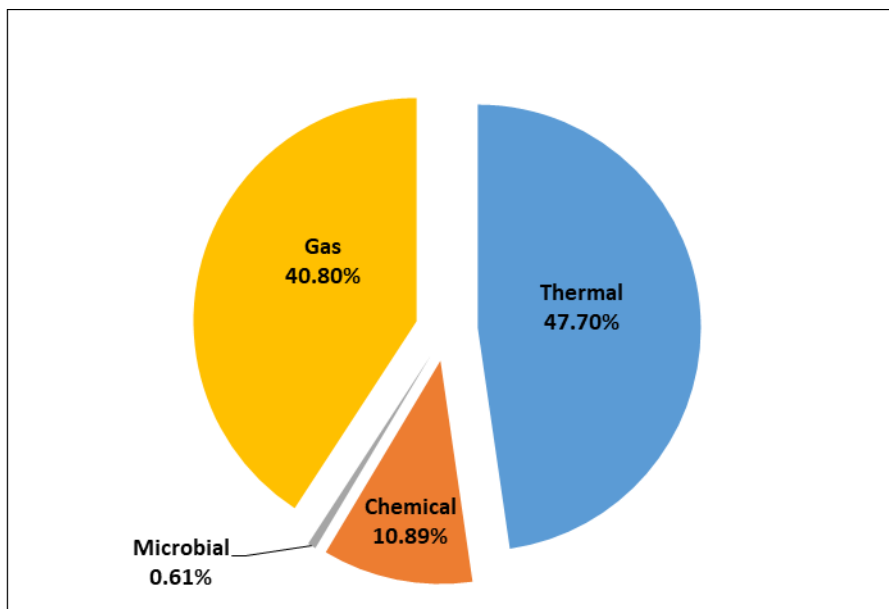


Figure 2. Worldwide EOR project categories, 1959-2010 [51].

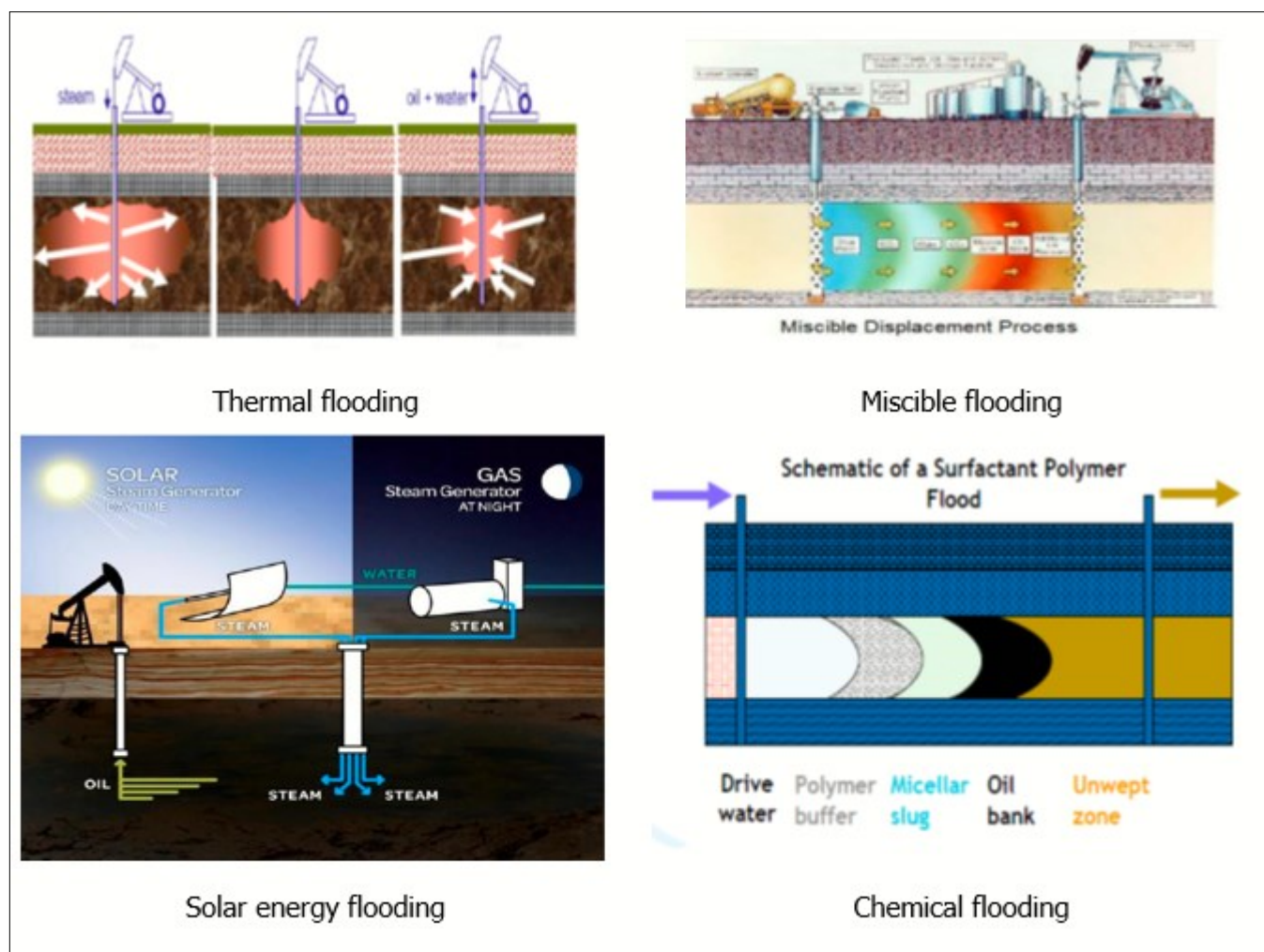


Figure 3. Different EOR flooding techniques

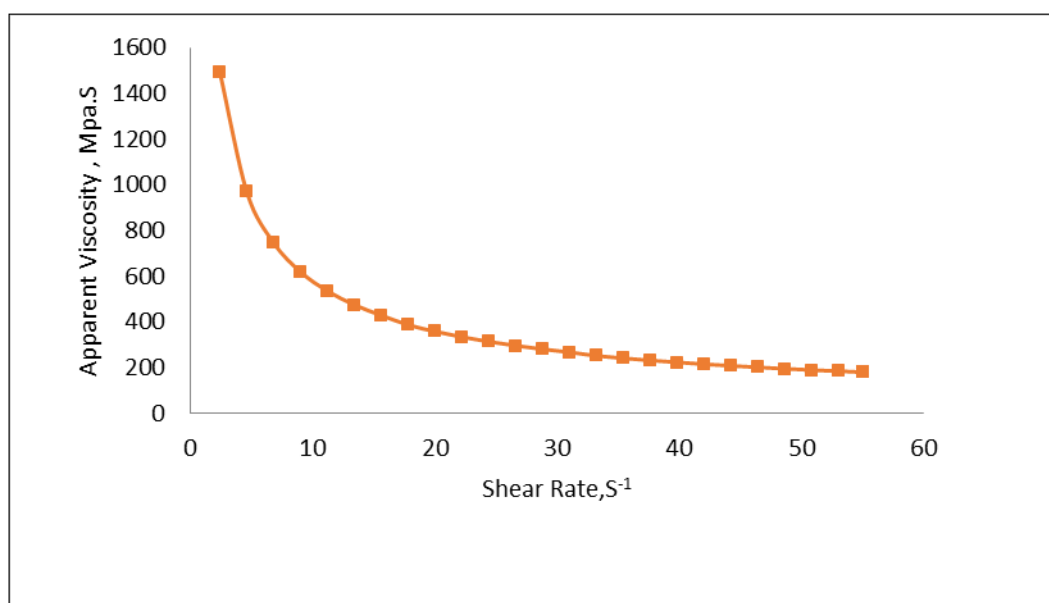


Figure 4. Effect of shear rate on viscosity

monomer are the best candidates for salt tolerance. Under reservoirs conditions, polymers are susceptible to chemical degradation due to the formation of free radicals which attack the polymer chain and result in a reduction of hydrodynamic volume. This chemical degradation occurs owing to; 1) decreasing the intramolecular/intermolecular bindings (hydrogen and van der Waal's) bonding by electrolytes addition which results in compressing the thicknesses of the electric double layer and hydration layer of the ionic groups, so shield ionic repulsion and causes macromolecular chain contraction with small hydrodynamic volumes, resulting in apparent viscosity reduction; 2) by salinity increase, the solution charge is neutralized, so polymer chain condenses, and viscosity reduction occurs [29, 52]. Moreover, increasing of temperature increase polymer hydrolysis degree and generating a higher charge density of anionic functionalities along the polymer backbone. This behavior resort to dissociation of polymer chains specially polyacrylamides in carboxyl groups, which in turn react with divalent cations in the petroleum reservoir. Recently, another range of commercial polymers called associative polymers has been developed to obtain very high resistance factors in the reservoir. These polymers contain both hydrophobic and hydrophilic moieties. The hydrophobic parts can associate in water and provide very high viscosities and resistance factors but with a good propagation in cores [53]. More attention has been paid to multifunctional polymers, especially imidazole- and imidazoline-containing polymers which show a wide range of potential applications[33] in addition to other vinylated monomers. In recent decades, many studies demonstrated that acrylamide (AM) copolymerized with an applicable functional monomer, such as **N**, **N**-dimethylacrylamide, methacrylamide, **N**-vinyl-2-pyrrolidone (NVP), 2-acrylamido- 2-methyl-1-propane sulfonic acid (AMPS), sodium allyl sulfonate, acrylic acid (AA), and ethylene sulfonic acid, could obtain more satisfying polymer possessing better temperature-resistance and salt-resistance for EOR[35]. The rheological and viscosity values of polyacrylates are provided in table 1.

Addition of water-soluble polymer could thicken the formation brine through molecular chain extension, and greatly improve overall oil recovery. This attractive

EOR technique referred to as polymer flooding [40]. Several publications reported about the synthesis of different hydrophobically associated polyacrylamides (HAPAM) and their modified copolymers, as well as the introduction of special functional groups for improvement of water-solubility, temperature resistance, anti-shear property, and salt tolerance of partially hydrolyzed polyacrylamide (HPAM). Sulfonate groups attached to the PAM chain can improve effectively the performance on confronting harsh environments like high temperature or high salinity[33].

Polymer Flooding Process

Polymer flooding can be carried alone or in combination with other fluids such as alkaline materials for solubilizing the oil and comprise sodium carbonate, caustic soda, borate, and metaborate compounds, silicates, metasilicates, amines, basic polymeric species, or by combination with surfactant molecules[3]. Polymer flooding can increase recovery up to 5-30% OOIP [54]. Polymer flooding process involves the injection of polymer "slug" followed by continued long-term water flooding to drive the polymer slug and the oil bank in front of it toward the production wells as shown in Figure 5. When water is injected into a reservoir, it seeks the path of least resistance (usually the layers of highest permeability) to the lower pressure region of the offset producing wells. If the oil in place has a higher viscosity than the injected water, the water will finger through this oil and result in a low sweep efficiency, or bypassed oil. Flooding tests generated according to the following steps; 1) The sand was firstly cleaned and evacuated then saturated by brine for 14 days followed by oil saturation, then brine flooded until oil cut ceased (i.e. oil cut <1%) and the residual oil amount calculated; 2) the polymer solution with different slug concentrations was flooded at simulated reservoir temperature to determine recovery factor.

Principle and Mechanism of Polymer Displacement

One of the routine screening parameters used for a preliminary analysis of a reservoir is the mobility ratio that represents effects of relative permeability and viscosity of water and oil on mobility based on Darcy's Law [44].

$$M = \frac{\lambda_w}{\lambda_o} = \frac{K_w / \mu_w}{K_o / \mu_o} = \frac{K_w \mu_o}{K_o \mu_w} \dots\dots (1)$$

Table 1. Rheological and viscosity of polyacrylates at different shear rates[42].

Shear rate, S^{-1}	<i>Apparent Viscosity, cp</i>	<i>Shear Stress, Pa</i>
2.42	276.97	8.93
4.62	225.20	13.87
6.82	198.81	18.08
9.02	181.80	21.88
11.22	169.54	25.38
13.42	160.09	28.67
15.62	152.50	31.80
17.82	146.21	34.78
20.02	140.86	37.65
22.22	136.24	40.42
24.42	132.18	43.11
26.62	128.59	45.71
28.82	125.36	48.25
31.02	122.44	50.73
33.22	119.79	53.16
35.42	117.35	55.53
37.62	115.11	57.86
39.82	113.04	60.14
42.02	111.11	62.38
44.22	109.31	64.59
46.42	107.62	66.76
48.62	106.04	68.90
50.82	104.55	71.01
53.02	103.14	73.09
55.00	101.94	74.93
55.00	101.94	74.93
55.00	101.94	74.93
55.00	101.94	74.93
55.00	101.94	74.93

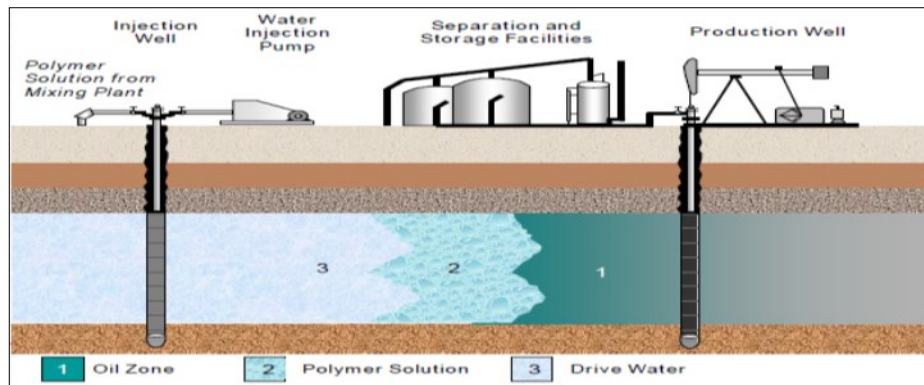


Figure 5. Polymer flooding mechanism [42, 55]

Where

M	Mobility ratio
λ_w	Water phase mobility
λ_o	Oil phase mobility
K_w	Relative permeability of water phase, MD
K_o	Relative permeability of oil phase, MD
μ_w	Water phase viscosity, cp
μ_o	Oil phase viscosity, cp

Mobility ratio (M) is defined as mobility of the displacing phase divided by the mobility of the displaced phase. Water-soluble polymer reduce water mobility through different mechanisms: (1) increase the water phase viscosity; 2) reduce the relative permeability of water to the porous rock by adsorption/retention of the polymer in the rock pore throats[56] and thereby creating a more efficient and uniform front to displace unswept oil from the reservoir; 3) Another parameter is the viscoelasticity associated with the use of high Molecular weight (M_w) or associative polymers which will recover additional entrapped oil compared to a conventional Newtonian fluid injection[3, 57]. With a reduced mobility ratio, the sweeping efficiency is increased and, as a consequence, oil recovery is enhanced[58]. If the mobility ratio ($M \leq 1$), the sweeping and displacement efficiencies of the oil by the water phase will be efficient and pistons like fashion [59]. By contrast, if the mobility ratio ($M > 1$), is considered "unfavorable" and unstable because the more mobile displacing fluid will flow more readily than the displaced fluid, and lead to serious viscous fingerings or channel through the oil causing "breakthrough" leaving behind regions of unswept oil. As a result, some

of the residual oil is bypassed resulting in poor recovery [60]. There is also a secondary effect, in which the polymer restores part of the reservoir pressure after its passage (residual resistance factor) [58]. This occurs because the polymer builds up a resistance to flow in the portions of the reservoir it penetrates, due to the selective reduction of relative permeability that results from its adsorption[58]. This increased resistance to flow diverts subsequently injected water into poorly swept areas. Polymer adsorption reduces the relative permeability to the wetting phase more than the relative permeability to the non-wetting phase in water-wet reservoirs [58, 61]. The reduction of the relative permeability to water is due to the improved competitive effects of both pore-size restriction and wettability brought about by polymer adsorption[58]. The most widely used polymers in enhanced oil recovery involve partially hydrolyzed polyacrylamides (HPAM) and hydrophobically associated polyacrylamides (HAPAM).

Partially Hydrolyzed polyacrylamide (HPAM)

HPAM consists of a large proportion of intermediate hydrophilic amide groups and hydrophilic

carboxyl groups. Both amide groups and carboxyl groups are linearly introduced onto the backbone of polymeric chains, providing HPAM with favorable solubility and desirable viscosity in fresh water and low salinity formation water [36]. HPAM is a synthetic linear chain copolymer of acrylamide and acrylate monomers [62]. They are flexible chain appears as a random coil and since it is a polyelectrolyte, it will interact with ions in solution. The main polyacrylamides used are anionic in nature[3]. Many key aspects need to be considered for the design of a polymer flood such as reservoir characteristics (lithology, stratigraphy, fractures), distribution of remaining oil, well pattern and spacing, polymer degradation, rheology of the polymer solution, compatibility with other chemicals, cost effectiveness [3]. HPAM show good viscosifying properties, available in various molecular weights up to 30 million Dalton of relatively low price and can be used for temperatures up to 99 °C depending on brine hardness, so used currently in EOR applications. It is produced generally as free-flowing powders or as self-inverting emulsions. Some experiences reported that acrylamide-based polymers have some disadvantages, such as easy hydrolysis, easy adsorption in the stratum, poor shear stability and poor thermal stability[38], and can be summarized as follow;

High sensitivity to thermal, mechanical and chemical degradation at high temperatures) typically above 200°F and exhibit decreasing viscosity by temperature increase[63].

Highly susceptible to the presence of oil, surfactant and other reservoir chemicals.

Precipitation can occur if Ca^{2+} or Mg^{2+} is present in the water also, their carboxyl groups are screened by positive ions, leading to reduced viscosity and a limited application in wells with high temperature and salinity[64] due to ionic groups shielding, which reduces repulsion and causes chain contraction.

Undergoes molecular weight degradation upon heating in oxygen presence [65].

Respond to physical or chemical stimuli, such as temperature, solvent, mechanical stress, radiation (UV, visible light), and ionic strength [66].

In polymer flooding, the ratio R_h/R_g [pore throat radius (R_h) to gyration radius (R_g)] of a polymer chain

should be greater than five [67] so, HPAM cause pore throat plugging after a given time [68] because of its large molecular size [69].

A comparison of different flooding scenarios indicating the cumulative oil recovery, resistance factor and residual resistance factor are summarized in table 2.

Hydrophobically Associated Polyacrylamide (HAPAM)

Most widely used water-soluble polymers including polyacrylamide and partially hydrolyzed polyacrylamide, are not suitable for high temperature, high salinity, and high flow rate injection owing to hydrolysis, decomposition, degradation, shear damage [35, 62], so these polymers modified by addition of hydrophobic moieties on the backbone structure[36] to develop a novel temperature and salinity resistant mobility control agents (polymers) which known as hydrophobically associated polyacrylamides (HAPAM)[77]. These polymers class have attracted much attention on both academic and industrial laboratories for polymer flooding in enhanced oil recovery [78, 79] because of their unique structures and properties, including their thickening properties, shear thinning, and anti-polyelectrolyte behavior which has been widely investigated in oil chemistry additives such as mobility control agents and rheology modifiers[80]. In addition to enhanced thermal stability, relative permeability modifiers, sweeping efficiency, salt-tolerance behavior and high viscosifying properties for IOR or EOR applications[81]. These polymers synthesized by modification of partially hydrolyzed polyacrylamide (HPAM) through grafting or incorporating hydrophobic chain cross-linking segments onto their hydrophilic main chain [33] or by copolymerization of hydrophilic and hydrophobic monomers [82]. They considered as promised EOR candidates for polymer flooding in high salinity reservoirs, owing to their unique characteristics[83] which can be summarized as follow;

In aqueous solutions, above a critical association concentration (C^*), their hydrophobic groups develop intermolecular hydrophobic associations in nanodomains, leading to building up of a 3D-transient network structure in high ionic strength medium [84] so, providing excellent viscosity building capacity [79, 85, 86], remarkable rheological properties and better stability with respect to salts than the

Table 2. Comparison of the different flooding reports

Reported works	Cumulative oil recovery	Resistance factor	Residual resistance factor	Applied polymer type
Qiao and Zhu[70]	72.8%	×		Modified cationic starch
Ghosh et al[71]	×	×	0.96 – 1.22	Polyacrylamide composite
Lai et al[72]	×	11.8	2.4	hyperbranched polyacrylamide polymer
Salehi et al[73]	×	×	1.98	Sulfonated polyacrylamide hydrogels
Singh and Mahto [74]	×	14.21	1.11	Polyacrylamide graft starch/ clay nanocomposite hydrogel
Chuan et al[75]	×	9.38	3.39	surfmers-co-poly acrylates crosslinked hydrogels
El-hoshoudy et al[76]	85.35%	18.3	9.0	Modified cationic starch

unmodified HPAM precursors [87].

Reduce interfacial tension at the solid/liquid interface, since hydrophobic moieties associates forming aggregates or micelles.

Shows an unusual adsorption isotherm[88] so, can be considered as a wettability modifier.

Does not undergo mechanical degradation under high shear stress such as those encountered in pumps and near the wellbore area, since the physical links between chains are disrupted before any irreversible degradation occurs, also they reform and retain their viscosity upon shear decreasing [89].

Highly resistance to physicochemical conditions (temperature, pH, and ion content) prevailing around the wells, so considered a prospective EOR candidate as thickeners or rheology modifiers in high temperature, high-pressure reservoirs [90-92], reservoir stimulation[93] and tertiary oil recovery [94].

Hydrophobically associating polyacrylamide are prepared conveniently by a micellar polymerization method, a lot of small molecule surfactants need to be added in order to enable hydrophobic monomer to be solubilized into micelles, and the addition of small

molecule surfactants brings many negative influences [95]. When hydrophilic surfmers are adopted to prepare HAPAM, homogeneous phase copolymerization of hydrophilic surfmers and acrylamide in aqueous solution can be carried out because of their solubility in water, and those drawbacks caused by the addition of small molecule surfactants can be avoided completely. Furthermore, when the concentration of surfmers is above their critical micellar concentration (CMC), their copolymerization with acrylamide follows the macroblock copolymerization mechanism, namely, surfmer molecules will incorporate into the macromolecular main chains as macroblock form. The macroblock macromolecular structure leads to more effectively hydrophobic associating of the hydrophobic side chains, stronger thickening property of HAPAM [81] and improved salinity resistance of HAPAM. Surfmers can copolymerize with the main monomer and they become covalently bound to particles surface forming integral polymeric materials. As a result, desorption of surfactant from the polymer particles or migration in the polymer films is impeded. Such improvements of latex and/or polymer stability properties[96] have been reported for mechanical stability, electrolyte stability of the latex[97], a decrease

of surfactant migration[98] and control of surface charge density[99].

Conclusion

Enhanced oil recovery is a widely implemented technology nowadays due to a sustained energy crisis associated with overgrowing human civilization. These aspects impose on chemists and scientists to discover and develop novel materials and techniques to maximize trapped oil in the reservoirs. One of these developed technologies is polymer flooding through copolymerization of different acrylate monomers which can withstand salinity, temperature, PH and bacterial degradation, in addition to increasing water phase viscosity. In this work, properties of acrylate polymers, as well as rheological and solution properties, were investigated at simulated reservoir conditions of high salinity and temperature. Moreover, the mechanism and techniques of polymer flooding were considered. On the other hand, a comparison between hydrolyzed and hydrophobically associated polymers was evaluated with respect to EOR applications. Several authors do their best effort in this field and already synthesize different polymers, but the increased energy demand impose more and more research on these applications.

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