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Polymer viscosifier systems with potential application for enhanced oil recovery: a review

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Abstract. Due to the growing demand for oil and the large number of mature oil fields, Enhanced Oil Recovery (EOR) techniques are increasingly used to increase the oil recovery factor. Among the chemical methods, the use of polymers stands out to increase the viscosity of the injection fluid and harmonize the advance of this fluid in the reservoir to provide greater sweep efficiency. Synthetic polymers based on acrylamide are widely used for EOR, with Partially Hydrolyzed Polyacrylamide (PHPA) being used the most. However, this polymer has low stability under harsh reservoir conditions (High Temperature and Salinity – HTHS). In order to improve the sweep efficiency of polymeric fluids under these conditions, Hydrophobically Modified Associative Polymers (HMAPs) and Thermo-Viscosifying Polymers (TVPs) are being developed. HMAPs contain small amounts of hydrophobic groups in their water-soluble polymeric chains, and above the Critical Association Concentration (CAC), form hydrophobic microdomains that increase the viscosity of the polymer solution. TVPs contain blocks or thermosensitive grafts that self-assemble and form microdomains, substantially increasing the solution's viscosity. The performance of these systems is strongly influenced by the chemical group inserted in their structures, polymer concentration, salinity and temperature, among other factors. Furthermore, the application of nanoparticles is being investigated to improve the performance of injection polymers applied in EOR. In general, these systems have excellent thermal stability and salinity tolerance along with high viscosity, and therefore increase the oil recovery factor. Thus, these systems can be considered promising agents for enhanced oil recovery applications under harsh conditions, such as high salinity and temperature. Moreover, stands out the use of genetic programming and artificial intelligence to estimate important parameters for reservoir engineering, process improvement, and optimize polymer flooding in enhanced oil recovery.

1 Introduction

Oil is the most important energy source in the world and its production is crucial for the global economy. With industrial development and population growth, oil demand tends to increase by about 1.5% a year on average. Furthermore, it is estimated that petroleum will be the largest contributor to world energy needs for at least the next two decades (El-Hoshoudy *et al.*, 2017a; Firozjaii and Saghafi, 2019; International Energy Agency, 2019; Kamal *et al.*, 2015a).

Crude oil can be obtained from three different processes, namely primary, secondary and enhanced oil recovery. Primary recovery involves extracting crude oil using the natural energy from the reservoir, whereby it is possible to recover about 5.0% to 15.0% of the initial reserve. Secondary recovery involves injection of immiscible fluids such as water, gas (or both) to displace the oil without changing the reservoir's natural conditions, enabling an additional recovery factor of 10.0% to 30.0%. Enhanced Oil Recovery (EOR) methods allow maximizing oil production with additional production of approximately 10.0% to 35.0% over secondary recovery, using unconventional techniques involving injection of chemicals, thermosensitive fluids, microbiological agents and miscible gases, among others (Firozjaii and Moradi, 2018; Mogollón *et al.*, 2019; Rellegadla *et al.*, 2017; Thomas *et al.*, 2012).

Due to the increased demand for oil, the lower discovery of new reservoirs and the large number of mature oil fields, *i.e.*, those that have already gone through their production plateau where output is now declining, EOR methods are being increasingly applied since they allow changing the displacement mechanism in the reservoir rock to boost the

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oil recovery factor (Abidin *et al.*, 2012; Bai *et al.*, 2015; El-Hoshoudy *et al.*, 2017a). Among the EOR techniques, chemical Enhanced Oil Recovery (cEOR) stands out, which consists of the application of polymers, surfactants, alkalis or mixture of these components. In this category, polymer flooding is generally considered to be the most promising technique, representing about 77.0% of cEOR (Rellegadla *et al.*, 2017; Sheng *et al.*, 2015; Thomas, 2016).

Polymer application can increase the viscosity of the injection fluid, decreasing the water–oil mobility ratio and water breakthrough, improving the sweep efficiency and thereby increasing the oil recovery factor (Jung *et al.*, 2013; Rellegadla *et al.*, 2017; Sedaghat *et al.*, 2013).

Several polymers can be applied in cEOR, of which acrylamide-based polymers stand out due to their wide availability and relatively low cost. Of them, Partially Hydrolyzed Polyacrylamide (PHPA) is used most for this purpose (Abidin *et al.*, 2012; Data *et al.*, 2018; Firozjaii and Saghafi, 2019). PHPA has high viscosifying power due to its high molecular weight and the electrostatic repulsion of the carboxylate groups present in its structure, which provide a higher hydrodynamic volume in solution, increasing the viscosity of the polymeric solution (Kamal *et al.*, 2015a; Leblanc *et al.*, 2015; Li *et al.*, 2017).

However, PHPA poses stability problems under harsh reservoir conditions (high salinity and temperature), especially in the presence of divalent cations, where the polymer solution's viscosity decreases considerably, reducing the polymer flooding efficiency. Thus, the alternatives to overcome these limitations of PHPA are the use of Hydrophobically Modified Associative Polymers (HMAPs), Thermo-Viscosifying Polymers (TVPs) and nanoparticles (Abdullahi *et al.*, 2019; Chen *et al.*, 2013; Data *et al.*, 2018; Gbadamosi *et al.*, 2019a; Liu *et al.*, 2017a; Sarsenbekuly *et al.*, 2017a; Wang *et al.*, 2011).

Hydrophobically modified associative polymers consist of water-soluble macromolecules modified with small fractions of hydrophobic chains. These have a Critical Association Concentration (CAC), so that amounts close to the CAC cause the formation of hydrophobic microdomains that increase the viscosity of the polymer solution (Data *et al.*, 2018; El-Hoshoudy *et al.*, 2017a; Kamal *et al.*, 2015a). TVPs have blocks or grafts with Low Critical Solution Temperature (LCST), incorporated in the main water-soluble chains of the polymer, having the common behavior of macromolecules at room temperature. But above the association temperature (T_{ass}), thermosensitive sequences self-assemble and form microdomains, greatly increasing the polymer solution's viscosity (Cao *et al.*, 2015; Chen *et al.*, 2013; Li *et al.*, 2017; Wang *et al.*, 2010).

The main aim of this review is to summarize the contemporary research involving the various polymer flooding techniques for enhanced oil recovery and present the benefits of applying HMAPs, TVPs and nanoparticles to improve the oil recovery factor under harsh reservoir conditions (high salinity and temperature). In addition, to present the use of artificial intelligence to estimate important parameters for reservoir engineering and to improve the polymer flooding process.

2 Polymer flooding

Polymer flooding is a chemical enhanced oil recovery method in which water-soluble polymers with high molecular weight are added to the injection fluid to increase its viscosity and thus to reduce its mobility ratio, providing greater sweep efficiency and an increase in oil recovery. Polymer injection is considered one of the most promising EOR techniques due to its good efficiency and technical and economic viability (Choi *et al.*, 2016; Data *et al.*, 2018; Gbadamosi *et al.*, 2019b; Pope, 2011; Rellegadla *et al.*, 2017; Stavland *et al.*, 2010).

This method was proposed for EOR in the mid-1960s and since then many studies and applications have been implemented in several oil fields, both in pilot and commercial scale. Currently, this method's importance is growing in the global energy market (Delamaide *et al.*, 2014; Khamis *et al.*, 2018; Mahran *et al.*, 2018; Manrique *et al.*, 2017). According to Gbadamosi *et al.* (2019b), polymer flooding has been successfully applied in many fields, such as *Daqing in China, Tambaredjo in Suriname, Eastern Bodo and Pelican Lake reservoirs in Canada*, and *Marmul in Oman*, among others. Of these examples, the application of polymer flooding in the Danqing field stands out based on the results, where output increased by up to 300 000 barrels per day (Cheraghian and Hendraningrat, 2016).

According to *SNF* (2020), polymer flooding presents a satisfactory Utility Factor (UF), which consists of the relationship between the amount of polymer (in kg) needed to recover an additional barrel of oil, characterizing the method's economic feasibility. Studies of pilot plant projects have indicated that the average UF for polymer injection is one ton of polymer to increase the oil production by 80 barrels. Thus, polymer flooding can increase oil production by about 20%, at a cost of \$3 to \$6 per extra barrel of oil.

One of the most important parameters for this cEOR process is the water–oil mobility ratio, which represents the effects of relative permeability and oil and water viscosity on the mobility of these fluids, following Darcy's Law (Eq. (1)), where M is the mobility ratio between water–oil; λ_{w} is the mobility of the aqueous phase; λ_{o} denotes the mobility of the oil phase; μ_{w} is the viscosity of water; μ_{o} is the viscosity of the oil; k_{w} represents the relative permeability of the aqueous phase; and k_{o} is the relative permeability of the oil phase (El-Hoshoudy *et al.*, 2019; Stavland *et al.*, 2010):

$$M = \frac{\lambda_w}{\lambda_o} = \frac{k_w/\mu_w}{k_o/\mu_o} = \frac{k_w \cdot \mu_o}{k_o \cdot \mu_w}. \tag{1}$$

The application of polymers promotes an increase in injection water viscosity (μ_{w}) and a decrease in the relative permeability of the aqueous phase (k_{w}) in the reservoir. Hence, the mobility ratio decreases ($M \leq 1$) and causes a uniform front flow, acting as a piston to push the oil into the producing well, thus increasing the sweep efficiency and the oil recovery factor (Fig. 1b) (Abidin *et al.*, 2012; Ferreira and Moreno, 2020; Kamal *et al.*, 2015a; Thomas, 2016). On the other hand, water flooding increases the

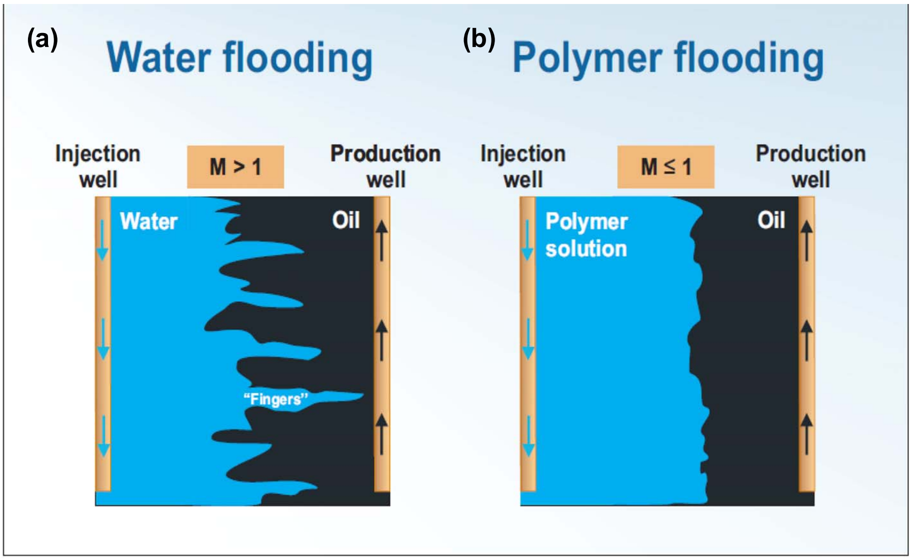

Fig. 1. Comparison between water flooding and polymer flooding, where: (a) water flooding forms "fingers" and decreases sweep efficiency, and (b) polymer flooding standardizes the front flow and increases the sweep efficiency.

mobility ratio ($M > 1$) due to the lower viscosity of the injected fluid, forming "fingers" in the reservoir, failing to displace a large amount of recoverable oil and reducing the sweep efficiency (El-Hoshoudy *et al.*, 2019; Kamal *et al.*, 2015a; Rellegadla *et al.*, 2017; Fig. 1a).

Another important factor for the mobility ratio is the Buckley–Leverett model, which describes the frontal advance of immiscible displacement, such as the displacement of oil by the action of water, in a linear one-dimensional or almost one-dimensional reservoir, introducing a discontinuity of saturation. In this way, the displacement of the front-advance in fractional flow can be described according to equation (2), where S_D corresponds to the saturation of the displacement fluid; θ is the displacement time; u represents the distance along the flow path; q_t characterizes the total rate of fluid flow through the section; A is the section area; Φ is the porosity; and f_d corresponds to the fractional flow of the displacement fluid (Buckley and Leverett, 1942; Dashtbesh *et al.*, 2021; Guérillot *et al.*, 2020):

$$\left(\frac{\partial u}{\partial \theta}\right)\begin{matrix}0\\ S_D\end{matrix} = \frac{q_t}{A\Phi}\left(\frac{\partial f_D}{\partial S_D}\right)\begin{matrix}0\\ \theta\end{matrix}. \quad (2)$$

Other important parameters for polymer flooding are the resistance factor (R_F*) and the residual resistance factor (R_{RF}), which are obtained from oil recovery simulation tests in rock plugs (core flooding) and can indicate the efficiency of the oil displacement process. R_F* corresponds to the ratio between the brine mobility rate and polymer solution mobility (Eq. (3)). R_{RF} refers to the ratio between brine permeability before the polymer injection process and after the polymeric solution has flowed through the rock plug (Eq. (4)) (Ferreira and Moreno, 2020; Leiting *et al.*, 2010; Maia *et al.*, 2009; Wang *et al.*, 2018a):

$$R_{F^*} = \frac{\lambda_{\text{brine}}}{\lambda_{\text{polymer solution}}}, \quad (3)$$

$$R_{RF} = \frac{k_{w\,(\text{before polymer flooding})}}{k_{w\,(\text{after polymer flooding})}}. \quad (4)$$

The polymer flooding technique can be applied in several sandstone and carbonate fields in order to increase oil recovery (Ferreira and Moreno, 2020). According to Wei and Romero-Zerón (2014), injection of polymers is not recommended for reservoirs containing oil with viscosity higher than 200 mPa s, because under these conditions it would be necessary to add a very high concentration of polymer, which is not economically feasible. Furthermore, the high viscosity of the solution could pose fluid injectivity problems in the reservoir. Thus, the polymer concentration generally ranges from 1000 to 3000 ppm (Kamal *et al.*, 2015a; Wei and Romero-Zerón, 2014).

According to Wu *et al.* (2012), the candidate polymer for polymer flooding application needs to have certain characteristics, such as good solubility in brine; adequate viscosifying power even at low concentrations; low adsorption on the rock surfaces; and mechanical, chemical and thermal stability under reservoir conditions. Furthermore, the efficiency of using polymer solutions depends on several factors, such as concentration and polymer structure, salinity, temperature, pH, reservoir rock type and oil viscosity, among others (Jung *et al.*, 2013).

The polymers evaluated for polymer flooding are classified into two major groups: synthetic polymers and biopolymers (Firozjaii and Saghafi, 2019; Gbadamosi *et al.*, 2019b; Rellegadla *et al.*, 2017; Sheng *et al.*, 2015).

In the class of synthetics, the highlights are Acrylamide-based polymers (AM), with Partially Hydrolyzed Polyacrylamide (PHPA) being used most for cEOR due to its low cost, excellent viscosity properties and good physicochemical characteristics (Abidin *et al.*, 2012; Mahran *et al.*, 2018; Stavland *et al.*, 2010). Many research groups have conducted studies of the application of PHPA for polymer flooding (Choi *et al.*, 2014, 2016; Clark et al., 2015;

Gao, 2011, 2013; Hashmet *et al.*, 2014a, b; Khamis *et al.*, 2018; Levitt *et al.*, 2013; Manichand *et al.*, 2013; Oliveira *et al.*, 2019; Rostami *et al.*, 2018b; Zhang *et al.*, 2011a).

The high viscosifying power of PHPA is directly related to its molecular weight and degree of hydrolysis, which typically ranges from 10% to 35%. As the degree of hydrolysis increases, more carboxylate groups become available, increasing the number of negative charges with mutual electrostatic repulsion, generating higher hydrodynamic volume in solution, with consequent increase in viscosity (Ma *et al.*, 2015; Mahran *et al.*, 2018; Nwidee *et al.*, 2016).

However, a very high degree of hydrolysis can cause greater sensitivity to the salinity of the medium, since in brines containing divalent cations, mainly Mg^{2+} and Ca^{2+}, precipitation occurs due to the complexation between the divalent cations and PHPA carboxylate groups, decreasing the solubility in water. Another problem is the poor performance of PHPA in high-temperature reservoirs. This favors thermal hydrolysis of the polymer chains' amide groups, generating more carboxylate groups and increasing the susceptibility to precipitation in high-salinity conditions (El-Hoshoudy *et al.*, 2019; Oliveira *et al.*, 2019; Wever *et al.*, 2011).

Besides acrylamide-based synthetic polymers, biopolymers are another class of macromolecules used for cEOR, especially Xanthan Gum (XG) (Jang *et al.*, 2015; Kamal *et al.*, 2015a; Rangel *et al.*, 2012; Wei and Romero-Zerón, 2014).

Xanthan gum is a water-soluble polysaccharide with high molecular weight produced from the fermentation of *Xanthomonas campestris* bacteria. Due to its rigid chain, XG has low sensitivity to salinity and hardness, higher thermal stability in high-temperature reservoirs and greater shear strength than polyacrylamides (Ghoumrassi-Barr and Aliouche, 2016; Nwidee *et al.*, 2016).

Thus, several studies have been published on the application of this biopolymer in cEOR (Ghoumrassi-Barr and Aliouche, 2016; Jang *et al.*, 2015; Moura and Moreno, 2019; Wei *et al.*, 2014; Xu *et al.*, 2013). However, xanthan gum has high sensitivity to degradation by microorganisms, higher production cost than PHPA, and high risk of blocking the rock pores due to the high content of cellular debris, restricting its use in large-scale field applications (Firozjaii and Saghafi, 2019; Rostami *et al.*, 2018b; Wei *et al.*, 2014).

To minimize these limitations of the major synthetic polymers and biopolymers used for EOR, hydrophobically modified associative polymers and thermo-viscosifying polymers have been developed (Data *et al.*, 2018; El-Hoshoudy *et al.*, 2017a; Kamal *et al.*, 2015b; Li *et al.*, 2017; Liu *et al.*, 2017a; Sarsenbekuly *et al.*, 2017a; Wang *et al.*, 2011). The main studies performed and the evolution of research focused on the application of these polymers are presented in Sections 3 and 4, respectively.

3 Hydrophobically Modified Associative Polymers (HMAPs)

Hydrophobically Modified Associative Polymers (HMAPs) have been developed to improve the performance of injection polymers in reservoirs with high salinity and temperature. HMAPs compose a class of water-soluble macromolecules formed by inserting small amounts of hydrophobic groups into a water-soluble polymeric chain. They are produced by copolymerization reactions of a hydrophobic monomer with a hydrophilic one or by grafting these groups on the water-soluble polymeric chain. To ensure solubility in aqueous media, the concentration of these hydrophobic fractions must be less than 5% w/v (El-Hoshoudy *et al.*, 2017a; Kamal *et al.*, 2015a; Liu *et al.*, 2017a; Mahran *et al.*, 2018; Zou *et al.*, 2013).

The viscosity properties of HMAPs are directly related to the hydrophobic association effect of the groups inserted in the main chain, and the rheological behavior in solution is determined by the CAC of these polymers. Thus, below the CAC (diluted regime) intramolecular interactions of hydrophobic groups in solution are favored, slightly increasing the system's viscosity. At concentrations above the CAC (semi-diluted regime), intermolecular associations dominate intramolecular ones, forming a network structure, resulting in a significant increase in the viscosity of the polymeric solution (Afolabi *et al.*, 2019; Azad *et al.*, 2018; Bai *et al.*, 2018; Zhang *et al.*, 2015). Figure 2 depicts the mechanism of HMAPs' action, with increased viscosity as a function of polymer concentration.

The first hydrophobically modified associative polymers were produced by Dubin and Strauss (1967) by copolymerization of alkyl vinyl ether with maleic acid. However, the application of these systems in EOR was patented by Landoll (1985), based on modified Hydroxyethylcellulose (HEC) with long alkyl chains containing from 8 to 25 carbon atoms.

In 2007, HMAPs were tested on a pilot scale in the *Bohai Bay field in China* under severe salinity conditions. The results were a 25 000 m^3 increase in oil production and a 41% decrease in water production, indicating promise as EOR additives (Zhou *et al.*, 2007). Since then, several researchers have conducted studies of the production and application of HMAPs for polymer flooding (Data *et al.*, 2018; Gou *et al.*, 2015; Han *et al.* 2018; Leiting *et al.*, 2010; Liu *et al.*, 2017a; Wang *et al.*, 2012; Xie *et al.*, 2019; Zhong *et al.*, 2009).

Zhong *et al.* (2009) synthesized a hydrophobically modified acrylamide-based terpolymer with sodium 2-acrylamide-2-methylpropane sulfonate (NaAMPS) and 2-Vinyl Naphthalene (VN), and evaluated the stability of the polymer solution during 90 days at 80 °C with brine containing sodium chloride (NaCl). They found that the HMAP tested presented good stability, maintaining 88.3% of initial viscosity. This behavior can be explained by incorporation of VN chains in the terpolymer, since the presence of aromatic groups increased the chain stiffness and avoided hydrolysis of the amide groups at high temperatures, minimizing polymer degradation.

Maia *et al.* (2009) performed a comparative study between polyacrylamide and acrylamide copolymer with N-N-dihexylacrylamide, evaluating the effect of salinity on their rheological behavior and the potential applicability of these systems in EOR from core flooding experiments in a porous medium. They found that the addition of NaCl

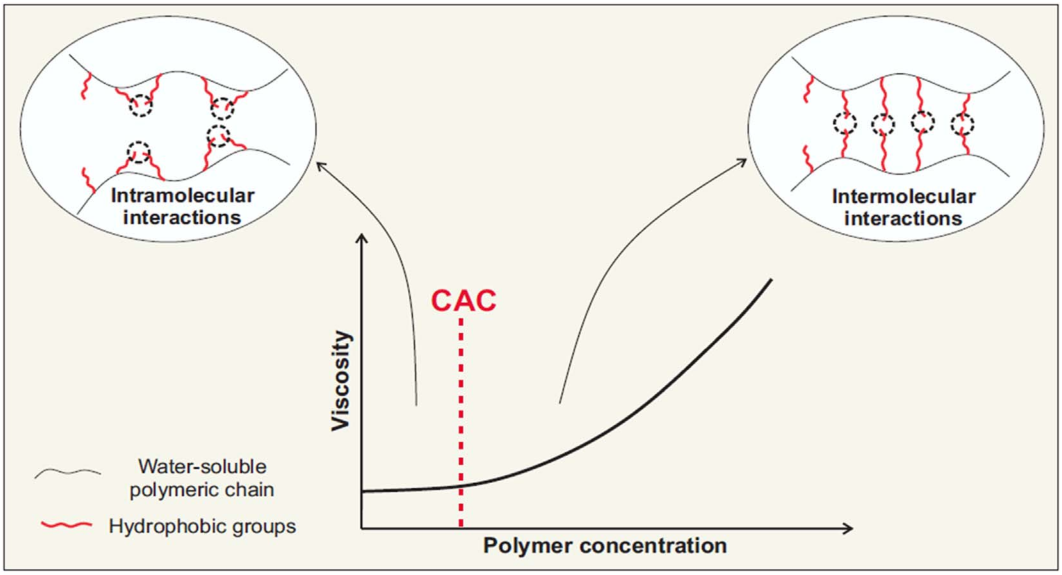

Fig. 2. Mechanism of HMAPs' action on polymer solution viscosity as a function of concentration.

promoted an increase in viscosity of the HMAP, and the F_R^* of the solution of the copolymer was greater than that of commercial PHPA, indicating this copolymer as a promising agent to improve sweep efficiency. The comparison of HMAP and PHPA regarding resistance factor was also studied by Leiting *et al.* (2010), who obtained similar results.

Zhang *et al.* (2011b) developed terpolymers formed by different concentrations of AM, 2-Trimethylammonium Ethyl Methacrylate Chloride (TMAEMC) and 5,5,5-Triphenyl-1-Pentene (TP) and found that the rising viscosity of the solutions was highly dependent on the quantity of hydrophobic aromatic groups (TP) in the chains and the polymer concentration. The best viscosification performance was observed above the CAC (0.25 g dL^{-1}), by favoring intermolecular interactions. Furthermore, they found that the AM-TMAEMC-TP terpolymer had good salinity and temperature resistance.

Lai *et al.* (2012) conducted a comparative study between PHPA and a terpolymer composed of AM, Acrylic Acid (AA) and N, N-Divinylnonadeca-1,10-Dien-2-Amine (DNDA) and found that the terpolymer had higher salinity and temperature tolerance and excellent shear strength. Besides this, porous medium tests were performed simulating water flooding and polymer flooding with PHPA and HMAP at concentration of 2000 ppm in NaCl brine at 65 °C. Recovery factors of 59.1%, 60.2% and 63.8% were observed, respectively. The overall results showed the benefits of polymer flooding to increase oil recovery and the efficiency of the HMAP analyzed as a viscosifying agent for application in EOR.

Leiting *et al.* (2012) also performed a comparative study between PHPA 3830 (22×10^6 g/mol) and hydrophobically modified polyacrylamide (12×10^6 g/mol), commercially known as HAWP 0312, evaluating the viscosities of polymer solutions at 1250 ppm in injection brine and the performance through porous medium tests. They observed that the viscosities of PHPA and HAWP polymer solutions at the shear rate of 7.34 s^{-1} (an estimated rate at which the fluid passes through the porous medium) were 15.7 and 298 mPa s, respectively. Due to the higher viscosity of the HAWP solution, its F_R^* in the porous medium was approximately 3.5 times greater than that of PHPA, leading to a 14.8% increase in the oil recovery factor. Wang *et al.* (2012) and Zhang *et al.* (2012) also conducted comparative studies between commercial PHPA and hydrophobically modified polymers and observed better properties and performance of HMAP under reservoir conditions.

Zou *et al.* (2013) developed a hydrophobically modified polyacrylamide with cyclodextrin (HCMPAM) and evaluated the stability of this polymer under extreme salinity and temperature conditions compared to a PHPA solution with similar molecular weight. They observed that HCMPAM had higher stability and apparent viscosity in brine with 60 000 ppm of Total Dissolved Salts (TDS), with viscosity retention of 45.7% at 10 s^{-1} when raising the temperature from 50 °C to 120 °C, while PHPA presented retention of 8.9%, indicating its lesser stability under severe temperature conditions.

Moreover, Zou *et al.* (2013) reported that the use of hydrophobically modified polymer increased the oil recovery factor by 5.7%, so they considered it a good alternative for application in reservoirs with high temperature and high mineralization. Deng *et al.* (2014) also found good salinity resistance of HMAPs and indicated their possible application in reservoirs with high salinity. The same year, Wei and Romero-Zerón (2014) studied the properties of commercial HMAP under reservoir conditions.

According to Zhang *et al.* (2015), a commercial Hydrophobically Associative Polyacrylamide (HAPAM) with 25.4% hydrolysis degree can be considered a promising agent for polymer flooding, since it presented higher viscosity and superior recovery factor in comparison with a PHPA solution in synthetic brine with 20 000 ppm TDS at high temperatures.

Gou *et al.* (2015) used 3-(2-(2-heptadec-8-enyl-4,5-dihydroimidazol-1-yl) ethylcarbamoyl) acrylic acid (NIMA), 3-(diallylamino)-2-hydroxypropyl sulfonate (NDS), AM and AA to produce acrylamide-based copolymers, respectively called AM-AA-NIMA and AM-AA-NDS-NIMA. They found that the presence of the NDS group provided better properties to the copolymer based on porous simulation tests to compare its efficiency with that of a PHPA solution. The application of the AM-AA-NDS-NIMA polymer solution at 2000 ppm increased the oil recovery factor by 15.46% under simulated reservoir conditions.

Jiang *et al.* (2015) developed a DTHAP copolymer consisting of AM, AA, AMPS and N-Phenethyl-N-Tetradecyl Methacrylamide (PETMAM) and evaluated the influence of temperature, salinity and aging, along with its performance under reservoir conditions. DTHAP showed higher resistance to temperature and salinity and better stability compared to PHPA. The oil recovery factor increased by 9.8% after injecting 2000 ppm solutions into synthetic brine with 40 000 ppm TDS. Thus, the insertion of aromatic groups in acrylamide-based copolymers can be considered promising to improve the performance of polymers in reservoirs with high salinity and temperature.

HMAP injection was evaluated by Patokina (2015) in a project implemented from 2013 to 2015 in the *Perm field in Russia*, with the injection of a polymeric solution at 1000 ppm under constant monitoring. Process efficiency results were not reported, but they estimated additional oil production of 34.2 million barrels, an increase of 18.93% in the oil recovery factor.

Zhang *et al.* (2015) compared the application of PHPA and a Hydrophobically Associative Polyacrylamide (HAPAM) in homogeneous and heterogeneous models, evaluating the possible limitations of the application of associative polymers. They found that the HAPAM $R_F{}^*$ and R_{RF} tended to be higher than those of PHPA, but the effective viscosity of PHPA was higher than that of HAPAM at 2000 ppm (below the CAC of the hydrophobically modified polymer). At this same concentration, PHPA had better displacement efficiency in homogeneous models, while in heterogeneous models (with a permeability ratio of 2.8) HAPAM performed better. Thus, the application of HAPAM in polymer flooding has some limitations, so further studies should be carried out to improve some properties of this HAPAM.

El-Hoshoudy *et al.* (2017b) evaluated the influence of concentration, salinity tolerance, and temperature resistance of a HAPAM compared to a PHPA solution. They noted that the optimal concentration of HAPAM was 2000 ppm, the polymer exhibited temperature resistance and salinity tolerance, and generally had better properties than PHPA. Furthermore, they were able to recover 20.8% of the oil by injecting a 2000 ppm solution in brine with 40 000 ppm of TDS at temperature of 90 °C, making the formulation a good candidate for application in reservoirs with extreme salinity and temperature conditions. A study of salinity tolerance and temperature resistance of a new HMAP was also conducted by Sarsenbekuly *et al.* (2017a), with satisfactory results.

Liu *et al.* (2017a) produced a hydrophobically modified Hydroxyethylcellulose (HEC) with Bromodecane (BD-HMHEC) and evaluated the influence of concentration, salinity, temperature and recovery efficiency compared to water flooding and HEC solution flooding. They observed that the BD-HMHEC solution's CAC value was around 4000 ppm and this solution was more efficient than the HEC solution at high temperatures (60 °C to 90 °C) and presented greater salinity tolerance. In addition, the use of BD-HMHEC increased oil recovery by 7–14% compared to HEC injection in simulation tests in porous media.

Wang *et al.* (2018a) also conducted studies of the application of BD-HMHEC, compared with HEC injection, and evaluated the influence of concentration, porous medium permeability, and injection rate on $R_F{}^*$ and R_{RF} from simulations of polymer injection in a porous sandstone medium. Initially, they found that $R_F{}^*$ and R_{RF} were close in the polymeric solutions at 2000 ppm, but when reaching the concentration of 4000 ppm, BD-HMHEC reached the CAC, which significantly increased the viscosity of the polymeric solution due to the formation of intermolecular interactions, producing higher $R_F{}^*$ and R_{RF} values. Moreover, they observed that in rock plugs with high and medium permeability and at different injection rates, hydrophobically modified polymer solutions performed better and were considered promising for application in EOR.

The application of BD-HMHEC was also studied by Bai *et al.* (2018). However, they evaluated the influences of temperature, shear rate and concentration on the viscosity of the polymeric solutions in synthetic brine with 15 296 ppm TDS. They reported the formation of hydrophobic aggregates after the CAC, indicating higher viscosifying power of BD-HMHEC, with greater $R_F{}^*$ and R_{RF} values and oil recovery factors compared to HEC application.

Li *et al.* (2018) compared the rheological properties of PHPA, HMAP and Cyclodextrin-modified HMAP (HMAP-CD) solutions, to determine the process efficiency by studying the behavior in sandstone-based porous media. They found that the HMAP solution had higher viscosity and elastic modulus (G') values than the HMAP solution, but the cyclodextrin-modified structure had better properties than the hydrophobically modified polymer. From the porous medium tests, they noted that the PHPA, HMAP and HMAP-CD solutions presented final oil recovery factors equal to 50.0%, 68.8% and 74.5%, respectively. Thus, the incorporation of cyclic groups in the hydrophobically modified structure of polyacrylamides can be considered a promising alternative to improve the efficiency of polymers for EOR. Investigation of modified polyacrylamide with cyclodextrin groups was also performed by Xie *et al.* (2019).

Azad *et al.* (2018) conducted a comparative analysis of commercial PHPA and HMAP with molecular weights in the range of 16–20 × 10^6 g/mol and 25% hydrolysis degree (Flopaam 3630S and Superpusher C319, respectively). They mainly evaluated the effect of hydrophobic associations by comparing the rheological properties of the polymeric solutions at concentrations of 1000 and 2000 ppm. They observed a small difference between the viscosities of the solutions at 1000 ppm, since the associative polymer showed only intramolecular interactions. A considerable difference was observed between the viscosities of the polymeric solutions at 2000 ppm due to the formation of intermolecular interactions upon reaching the CAC, presenting higher R_F^* than the PHPA solution.

Comparative studies between commercial HMAP and PHPA were also carried out by Han *et al.* (2018), evaluating pore retention and the viscosity of these polymers. They found that the hydrophobically modified structure was the most promising for polymer flooding. Zhong *et al.* (2018) also compared HMAP and a commercial polymer, evaluating the displacement mechanism of polymer solutions. They concluded that the hydrophobically modified polymer had better properties for application in EOR. Similar studies were also performed by Zhang *et al.* (2019), who noted that the injection of HMAP in porous media increased the oil recovery factor by 18.7% compared to PHPA injection.

Abirov *et al.* (2019) performed porous media tests with commercial PHPA and HMAP solutions simulating conditions of the *Turgay Southern Basin reservoir in Kazakhstan*, where severe salinity and temperature conditions prevail (92 000 ppm TDS and 82 °C). They reported that the associative polymer was more stable and efficient in the simulated reservoir conditions and recommended its pilot scale application.

Quan *et al.* (2019) developed a hydrophobically modified xanthan gum (XG-C16) by grafting hexadecyl groups in the hydroxyl groups of the main XG chain through esterification reactions and compared its properties with those of pure XG. They observed that the solution XG-C16 showed greater temperature resistance and salinity tolerance than the XG solution. They also found that the CAC of XG-C16 was 1600 ppm, and starting at this concentration, there was a significant increase in the viscosity of the solution, indicating the association of the hydrophobic groups of the modified polymer.

Peng *et al.* (2019) studied the effect of adding silica nanoparticles in hydrophobically modified polyacrylamide with N, N-dimethyl octadecyl ammonium groups (NP-HMAP) and found that the presence of silica improved the viscosity and viscoelasticity of the polymeric solution at high temperatures. Thus, the addition of nanofillers was cited as a way to further improve the properties of hydrophobically modified polymers.

In general, hydrophobically modified polymers have better thermal stability, salinity tolerance and oil recovery efficiency than unmodified polymers. Thus, they can be considered promising viscosifying agents for EOR in reservoirs with harsh conditions (high salinity and temperature) (El-Hoshoudy *et al.*, 2017a; Liu *et al.*, 2017a; Zhang *et al.*, 2019). Table 1 shows the summary of the main scientific developments in this area and the evolution of the studies.

4 Thermo-associative or Thermo-Viscosifying Polymers (TVPs)

Thermo-Viscosifying Polymers have also emerged as alternatives to improve the efficiency of polymer flooding in reservoirs with high salinity and temperature. TVPs are obtained by chemical modification through the insertion of hydrophobic thermosensitive blocks or grafts having Low Critical Solution Temperature (LCST) in the main chain of a water-soluble polymer. The main thermosensitive groups incorporated in these chains are copolymers of Poly (Ethylene Oxide)-Poly(Propylene Oxide) (PEO-PPO), poly (N-isopropylacrylamide) (PNIPAM) and Macromonomers based on Acrylamide Diacetone (MPAD), among others (Chen *et al.*, 2013; Li *et al.*, 2017; Roy *et al.*, 2013; Sarsenbekuly *et al.*, 2017b; Su and Feng, 2018; Zhu *et al.*, 2013).

These structures behave like water-soluble macromolecules at room temperature, but above the critical association temperature (T_{ass}) or LCST, the thermosensitive sequences are reversibly self-aggregated by the formation of physical interactions, forming hydrophobic microdomains that increase the viscosity of the polymeric solution (Kamal and Sultan, 2017; Kamal *et al.*, 2015a; Li *et al.*, 2017; Wang *et al.*, 2010). The schematic representation of the association mechanism of these TVP systems is shown in Figure 3.

Hourdet *et al.* (1994) developed the first TVP for oil industry application, from the incorporation of PEO thermosensitive sequences modified with poly(acrylic acid) amine groups. According to the authors, an increase in viscosity was observed at temperatures higher than the LCST and the thermo-viscosification effect was more pronounced in TVP with higher PEO content in its structures, indicating the ability of PEO sequences to form microdomains and increase the viscosity of polymeric solutions.

After this initial study of TVP application in the oil industry, several authors carried out further research in this area (Chen *et al.*, 2013; Leblanc *et al.*, 2015; Li *et al.*, 2017; Reichenbach-Klinke *et al.*, 2018; Sarsenbekuly *et al.*, 2017b; Wang *et al.*, 2010, 2011; Zhu *et al.*, 2013).

Wang *et al.* (2010) developed a thermo-viscosifying system from free radical copolymerization of Acrylamide (AM) with the macromonomer MPAD, producing the water-soluble copolymer P(AM-co-MPAD). They prepared TVP and PAM solutions in deionized water and brine containing different concentrations of KCl. They then evaluated the influence of temperature on each one. They found that the viscosity of the PAM solution decreased with increasing temperature while the P(AM-co-MPAD) showed the opposite behavior when the TVP reached the T_{ass}. Furthermore, they noted that the T_{ass} can be adjusted with the variation of the salinity of the system, because the increase in the salt content caused a decrease in the T_{ass}, increasing the viscosity of the polymeric solution at lower temperatures.

Wang *et al.* (2011) performed a comparative study between P(AM-co-MPAD) with a molecular weight of 6.5 × 10^6 g/mol and PHPA with 1.2 × 10^7 g/mol, dissolved

Table 1. Summary of the main developments regarding hydrophobically modified associative polymers.

Year	Activity	Authors
1967	Developed the first HMAP from the copolymerization of alkyl vinyl ether with maleic acid	Dubin and Strauss
1985	Patented these systems, highlighting the study of modified hydroxyethylcellulose	Landoll
2007	Tested HMAPs on a pilot-scale in the Bohai Bay field in China	Zhou *et al.*
2009	Synthesized a hydrophobically modified acrylamide-based terpolymer with sodium 2-acrylamide-2-methyl propane sulfonate and 2-vinylnaphtalene	Zhong *et al.*
2009	Performed a comparative study between polyacrylamide and acrylamide copolymer with N, N-dihexylacrylamide	Maia *et al.*
2010	Compared HMAP and PHPA regarding resistance factor	Leiting *et al.*
2011b	Developed terpolymers formed by acrylamide, 2-trimethylammonium ethyl methacrylate chloride and 5,5,5-triphenyl-1-pentene	Zhang *et al.*
2012	Conducted a comparative study between PHPA and a terpolymer of acrylamide, acrylic acid, and N, N-divinylnonadeca-1,10-dien-2-amine	Lai *et al.*
2012	Performed a comparative study between PHPA and commercial hydrophobically modified polymers	Leiting *et al.*; Wang *et al.*; Zhang *et al.*
2013	Developed hydrophobically modified polyacrylamides with cyclodextrin and evaluated their stability under extreme salinity and temperature conditions	Zou *et al.*
2014	Verified the good salinity resistance of HMAPs and recommended their application in reservoirs with high salinity	Deng *et al.*
2014	Studied the properties of commercial HMAP under reservoir conditions	Wei and Romero-Zéron
2015	Considered the commercial HMAP with 25.4% hydrolysis degree a promising agent for polymer flooding	Zhang *et al.*
2015	Used 3-(2-(2-heptadec-8-enyl-4,5-dihydroimidazol-1-yl) ethylcarbamoyl) acrylic acid, 3-(diallylamino)-2-hydroxypropyl sulfonate (NDS), acrylamide and acrylic acid to produce HMAP	Gou *et al.*
2015	Developed a copolymer of AM, AA, AMPS and N-phenethyl-N-tetradecyl methacrylamide and evaluated the influence of temperature, salinity and aging on its performance	Jiang *et al.*
2015	Evaluated the injection of HMAP in the Perm field in Russia	Patokina *et al.*
2015	Developed comparative studies between PHPA and HAPAM, evaluating the possible limitations of the application of a hydrophobically associative polymer	Zhang *et al.*
2017b	Evaluated the influence of concentration, salinity tolerance, and temperature resistance of HAPAM and PHPA	El-Hoshoudy *et al.*
2017a	Studied the salinity tolerance and temperature resistance for a new HMAP	Sarsenbekuly *et al.*
2017a	Produced a hydrophobically modified hydroxyethylcellulose with bromodecane and evaluated the influence of several factors	Liu *et al.*
2018a	Conducted comparative studies between BD-HMHEC and HEC	Wang *et al.*

(Continued on next page)

Table 1. (Continued)

Year	Activity	Authors
2018	Studied the application of BD-HMHEC	Bai *et al.*
2018	Compared the rheological properties of PHPA, HMAP, and cyclodextrin-modified HMAP solutions	Li *et al.*
2018	Performed comparative studies of commercial HMAP and PHPA	Azad *et al.*; Han *et al.*; Zhong *et al.*
2019	Observed that the injection of HMAP in porous media increased the oil recovery factor by 18.7% compared to PHPA injection	Zhang *et al.*
2019	Conducted studies of modified polyacrylamide with cyclodextrin	Xie *et al.*
2019	Performed porous media testing with commercial PHPA and HMAP, simulating conditions of the Turgay Southern Basin reservoir in Kazakhstan	Abirov *et al.*
2019	Developed a hydrophobically modified xanthan gum and compared its properties with unmodified xanthan gum	Quan *et al.*
2019	Studied the effect of adding silica nanoparticles in hydrophobically modified polyacrylamide with N, N-dimethyl octadecyl ammonium groups	Peng *et al.*

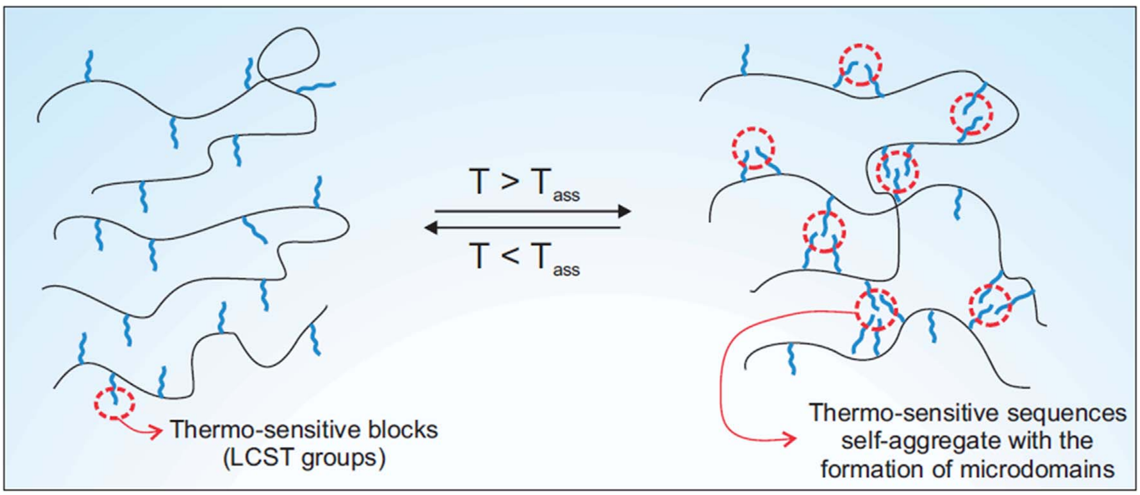

Fig. 3. Association mechanism of thermo-viscosifying polymers.

in synthetic brine with 32 868 ppm TDS, simulating the conditions of the *Shengli field in China*. The effect of polymer concentration was evaluated based on the viscosifying capacity of TVP along with the influence of temperature on the performance of the tested polymers under high salinity conditions.

The PHPA caused a reduction in apparent viscosity and elastic modulus (G') with increasing temperature, indicating the low stability of this polymer under severe conditions of salinity and temperature. On the other hand, P(AM-co-MPAD) exhibited an increase in viscosity and G' reached T_{ass}, indicating the self-aggregation of thermosensitive sequences and the formation of microdomains. Besides this, the increase in the concentration of the thermosensitive polymer caused a decrease in T_{ass} due to the greater number of LCST side chains. According to the results, the studied TVP is a good alternative to decrease the mobility ratio ($M < 1$) of the fluid injected in reservoirs with high salinity and temperature, and consequently to increase the sweep efficiency (Wang *et al.*, 2011).

Chen *et al.* (2013) compared solutions containing 2000 ppm of PHPA and P(AM-co-MPAD) in synthetic brine (32 868 ppm TDS) with molecular weights of 1.2×10^7 g/mol and 5.2×10^6 g/mol, respectively. They evaluated the rheological properties of the fluids, the influence of temperature on the behavior of polymeric molecules by cryogenic transmission electron microscopy (Cryo-TEM), and the oil recovery efficiency from tests in a porous medium, simulating conditions of high salinity and temperature of the *Shengli Reservoir in China*.

They observed loss of viscosity and reduction of G' in the PHPA solution, while the TVP solution showed an increase in G' and higher viscosity by a factor greater than 7, with a temperature ranging between 25 °C and 80 °C. The solutions were tested in a porous medium and oil recovery factors of 2.1% were observed in the PHPA solution and 13.5% in the TVP solution, indicating the latter system as promising for EOR. Furthermore, the formation of self-aggregates with increasing temperature was observed by Cryo-TEM analyses, causing an increase in the viscosity of the TVP solution (Chen *et al.*, 2013).

Kamal *et al.* (2015b) carried out a comparative study of P(AM-AA-MPAD) (a terpolymer with thermo-viscosifying property), PHPA, and a sulfonated tert-butyl acrylamide and acrylamide copolymer P(AM-co-ATBS), with molecular weights of 7.08×10^6 g/mol, 10×10^6 g/mol and 8×10^6 g/mol, respectively. They verified the influence of salinity on the properties of TVP, using deionized water, synthetic seawater with 57 643 ppm TDS and formation brine with 213 734 ppm TDS. They observed that the thermo-viscosification property was improved with the increase in salinity, since the higher salt concentrations caused a decrease in T_{ass}, leading to higher viscosity of the solution in formation brine in the evaluated temperature range (20 °C to 90 °C).

In addition, the authors evaluated the rheological behavior of the three polymers (5000 ppm) studied in synthetic seawater. Initially, there was lower viscosity of TVP compared to the other two commercial polymers, due to its lower molecular weight. With the increase in temperature, the viscosities of the solutions of PHPA and P(AM-co-ATBS) declined, but increased in the solution of TVP due to the formation of microdomains after T_{ass}. This behavior is very suitable for polymer injection in EOR, since the low viscosity of the initial solution guarantees the good injectability of the polymer in the reservoir and the high viscosity in severe conditions of salinity and temperature increases the oil recovery (Kamal *et al.*, 2015b).

Leblanc *et al.* (2015) also compared an AM-ATBS copolymer, commercially known as Flopaam AN132SH, with the commercial thermosensitive polymer DP/TLB132. Like Kamal *et al.* (2015b), better viscosifying properties of TVP were verified in relation to the commercial copolymer evaluated.

Considering that the injection of polymers is a long-term process, possibly lasting months or years, polymer degradation must be minimized to avoid decreased viscosity of the solution. Therefore, it is very important to evaluate a polymer's stability under reservoir conditions. In this context, Li *et al.* (2017) studied the thermal stability of a TVP produced with the macromonomer MPAD (1.01×10^7 g/mol) and compared it with the commercial polymer PAM (1.20×10^7 g/mol). The solutions with 2000 ppm of polymer in synthetic brine with 101 000 ppm TDS were evaluated at temperatures of 45 °C and 85 °C.

Viscosity losses of 4% and 52.5% were observed in the solutions of PHPA after 30 days of aging at 45 °C and 85 °C, respectively. For TVP solutions, losses of 18.7% and 74.3% were observed at 45 °C and 85 °C, respectively. Thus, the TVP solution showed more pronounced degradation in reservoir conditions, and thus had a higher percentage of viscosity loss. Furthermore, tests were carried out in a porous medium simulating temperature conditions in the *Daqing* (45 °C) *and Shengli* (85 °C) *fields in China*. The TVP system showed good injectability and a higher $R_F{}^*$, contributing to oil recovery factors of 16.4% and 15.5% at 45 °C and 85 °C, respectively, while PAM had oil recovery factors of 12.0% and 9.2%. Therefore, this TVP system was considered a promising option for application as a viscosifying agent in EOR fluids (Li *et al.*, 2017).

Akbari *et al.* (2017a, b) evaluated the performance of four acrylamide-based copolymers containing 2-acrylamide-2-methylpropane sulfonate groups (AMPS), one of them with a thermosensitive side group. The aim of this study was to evaluate the effects of salinity, injection water hardness, shear rate and temperature on the viscosity of polymeric solutions. The authors found that the thermosensitive polymer had better properties and was a promising viscosifying agent for application in EOR.

Sarsenbekuly *et al.* (2017b) observed that the viscosifying behavior of commercial TVPs was strongly dependent on polymer concentration, salinity and temperature. When comparing a PHPA (16×10^6 g/mol) and TVP (6×10^6 g/mol) in synthetic brine with 9583.74 ppm TDS at temperature of 30 °C, they observed higher viscosity and elastic modulus of TVP in comparison with PHPA, despite the latter's lower molecular weight. In addition, they noted that the temperature was paramount in determining the properties of this polymer, since its viscosity increased six-fold by raising the temperature from 30 °C to 90 °C. Similar results were observed by Reichenbach-Klinke *et al.* (2018).

Wang *et al.* (2018b) performed a comparative study between the copolymer of AM, NaAA and AA (PAMA) and three TVPs formed by PAMA and Pluronic (PEO_n – PPO_m – PEO_n triblock copolymer): TVP-P1 (PAMA and PEO_{100} –PPO_{65} – PEO_{100}); TVP-P2 (PAMA and PEO_{132} – PPO_{50} – PEO_{132}); and TVP-P3 (PAMA and PEO_{76} – PPO_{29} – PEO_{76}). Initially, the rheological behavior of the TVP solutions was evaluated and a higher viscosity of the TVP-P1 solution was found in the temperature analysis range (25 °C to 95 °C), due to the presence of more PPO groups, responsible for forming physical connections above the $T_{ass.}$ The behavior of TVPs was highly dependent on their chemical structures and the content of thermosensitive group in the polymer chain.

TVP-P1 was evaluated regarding thermal stability and by tests in a porous medium to check the injectivity and the oil recovery potential in comparison with the PAMA

Table 2. Summary of the main activities involving TVPs.

Year	Activity	Authors
1994	Developed the first polymer with thermo-viscosifying property for the oil industry	Hourdet *et al.*
2010	Produced a thermo-viscosifying system from AM and MPAD copolymerization	Wang *et al.*
2011	Conducted a comparative study between P(AM-co-MPAD) and PHPA, evaluating the effects of several factors	Wang *et al.*
2013	Developed poly [acrylamide-poly (oxyethylene octylphenol ether acryl ester)] and evaluated its thermo-associative capacity	Zhu *et al.*
2015b	Carried out a comparative study between the terpolymer with thermo-viscosifying property P(AM-AA-MPAD), PHPA and P(AM-co-ATBS)	Kamal *et al.*
2015	Evaluated the performance of AM-ATBS copolymer and commercial TVP	Leblanc *et al.*
2017	Studied the thermal stability of TVP produced with the macromonomer MPAD	Li *et al.*
2017a and 2017b	Evaluated the performance of four acrylamide-based copolymers containing 2-acrylamide-2-methylpropane sulfonate groups and one them with thermosensitive side groups	Akbari *et al.*
2017b	Observed that the viscosifying behavior of commercial TVPs is extremely dependent on polymer concentration, salinity and temperature	Sarsenbekuly *et al.*
2018	Performed studies with commercial TVPs	Reichenbach-Klinke *et al.*
2018b	Performed a comparative study between the copolymer of AM, NaAA, and AA (PAMA) and the TVPs formed by PAMA and Pluronic (PEO_n-PPO_m-PEO_n)	Wang *et al.*

solution. There was a 10.3% loss in the viscosity of the TVP solution and 26.2% for PAMA, indicating greater resistance of this TVP to thermal degradation. Furthermore, the thermo-viscosifying system showed good injectability and tests simulating conditions in the Daqing reservoir indicated an increase of 2.1% in the oil recovery factor with the application of the thermosensitive system (Wang *et al.*, 2018b).

In general, TVP systems have good properties and can be considered promising options for use in harsh reservoir conditions (high salinity and temperature) (Divers *et al.*, 2018; Kamal *et al.*, 2015b; Li *et al.*, 2017; Roy *et al.*, 2013; Su and Feng, 2018; Wang *et al.*, 2011). The summary of the main activities investigated regarding TVPs and the evolution of studies is shown in Table 2.

5 Polymer systems with nanoparticles

The application of nanoparticles in polymer flooding is being investigated as an alternative to improve the rheological properties, salinity and temperature tolerance and shear resistance of injection polymers, and hence to increase the oil recovery factor. Nanoparticles are materials with particle sizes in the range of 1–100 nm, and their performance is directly related to their small size, which allows a larger contact surface, resulting in nanofluids with satisfactory properties for application in enhanced oil recovery (Cheraghian and Hendraningrat, 2016; Gbadamosi *et al.*, 2019a; Rellegadla *et al.*, 2018).

Several research groups have studied the formation of hybrid systems of nanofillers with polymers for EOR application, such as the use of nanoparticles of silica (SiO_2), titanium oxide (TiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3) and nickel oxide (NiO), as well as nanoclays and carbon nanotubes, among others (Abdullahi *et al.*, 2019; Cheraghian, 2016; Corredor *et al.*, 2019; Giraldo *et al.*, 2017; Haruna *et al.*, 2019; Nguyen *et al.*, 2015; Rellegadla *et al.*, 2018; Zeyghami *et al.*, 2014; Zhu *et al.*, 2014a).

Zhu *et al.* (2014a) carried out a comparative study between a Hydrophobically Associating Polyacrylamide (HAPAM) and a hybrid system of HAPAM/silica nanoparticles and evaluated the rheological behavior of aqueous solutions. They found that the addition of nanosilica

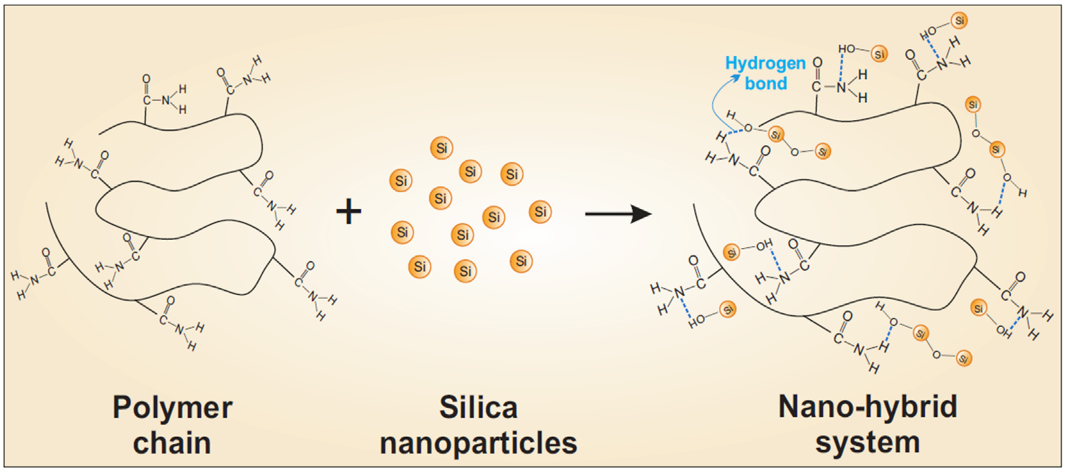

Fig. 4. Representative scheme of the formation of a nano-hybrid system.

promoted an increase in the apparent viscosity and storage modulus of the HAPAM solutions, and the viscosity increased considerably by raising the concentration of silica nanoparticles from 0.5 wt% to 2.5 wt%. Hybrid systems also showed greater thermal stability and salt tolerance, the latter effect due to the interaction between the nanosilica and the polymer through hydrogen bonding between the silanol groups of the nanosilica and amide groups of HAPAM, reinforcing the polymeric structure (Fig. 4).

In the same year, Zhu *et al.* (2014a) studied the effect of silica nanoparticles on the properties of solutions of Hydrophobically Associating Partially Hydrolyzed Polyacrylamide (HAPHPA) and evaluated the efficiency of the nano-hybrid system in increasing the oil recovery factor under high salinity and temperature conditions. Solutions of 5000 ppm HAPHPA were prepared in brine with 32 868 ppm TDS ($[Ca^{2+}] + [Mg^{2+}] = 873$ ppm). The addition of 1.0 wt% silica nanoparticles increased the viscosity from 26.3 mPa s to 136.9 mPa s, under shear rate of 10 s^{-1} at 85 °C. Furthermore, core flooding tests showed that HAPHPA injection caused an oil recovery factor of 5.44%, while for HAPHPA-nanosilica hybrid the factor was 10.57%. Thus, this system can be considered promising for EOR application.

Cheraghian (2016) evaluated the effect of incorporating titanium dioxide nanoparticles on the viscosity of PHPA solutions and compared the oil recovery potential of PHPA solutions and the PHPA/TiO_2 hybrid nanosystems. For this, solutions of 3150 ppm of PHPA in synthetic brine were used and TiO_2 nanoparticles were added at concentrations of 1.9, 2.1, 2.3, and 2.5 wt%. The systems were evaluated for viscosity and in core flooding tests. The author observed that the addition of TiO_2 promoted an increase in the viscosity of PHPA solutions (shear rate of 10 s^{-1}), and the system with 2.3 wt% of TiO_2 showed the best results. Furthermore, the application of this nano-hybrid system increased oil recovery by 4% compared to the application of the PHPA solution. Thus, the use of these nanoparticles was considered a promising method to improve the performance of this polymer for EOR.

Rezaei *et al.* (2016) carried out a comparative study of the rheological properties of PHPA solutions and systems formed by the addition of Surface Modified Clay Nanoparticles (SMCN) with tetraethylammonium chloride (PHPA-SMCN). The viscosities of the solutions were evaluated at temperatures of 30, 60 and 90 °C and the salinity tolerance of the polymer systems was verified by varying the salinity of the brine from 2000 to 100 000 ppm TDS (76.2% NaCl, 1.5% $MgCl_2$, 3.7% $CaCl_2$, and 18.6% Na_2SO_4). They observed that the addition of SMCN promoted an increase in the viscosity of the solutions, improving the resistance to salinity and temperature and increasing stability. In addition, tests in porous media were performed and indicated that the application of SMCN can be promising for polymer flooding, because it increased the oil recovery factor by 33% compared to the PHPA application.

Giraldo *et al.* (2017) evaluated the effect of applying SiO_2 nanoparticles on decreasing thermal degradation and improving the rheological behavior of PHPA. Stability tests were carried out under an oxidative atmosphere and without the presence of oxygen (70 °C for 14 days), which indicated greater thermal stability of hybrid systems formed with silica nanoparticles, with a viscosity reduction of up to 46% in relation to the PHPA solutions. In addition, the application of these nanoparticles increased the viscosity of the polymeric solutions, and thus would allow the application of a lower dosage of PHPA in the polymer flooding process, reducing operating costs.

Zheng *et al.* (2017) studied the incorporation of silica nanoparticles (DNS) and SiO_2 with surface modified by the silane coupling agents hexadecyltrimethoxysilane (DNS-HD) and hexamethyldisilazane (DNS-HM) in aqueous PHPA solutions and evaluated the application of nanosystems for EOR under simulated conditions of the *Shengli field in China*. Rheological analyses of the solutions in Shengli brine, at temperatures of 30–80 °C, indicated that the addition of DNS increased the viscosity of the PHPA solutions, and this effect was stronger at higher SiO_2 concentrations. The best result was obtained with 2.0 wt% DNS. However, nanosilica surface-modification further improved the apparent viscosity and thermal stability of the hybrid systems. This occurred because the modifications provided a slightly hydrophobic character to the nanoparticles, which tended to associate and form microdomains in the aqueous solution tested. Therefore, the systems formed by this nanofiller had hydrogen bonds characteristic of silanol groups with PHPA, which together with the associative effect of the hydrophobic groups improved the properties of the PHPA solutions.

In addition, displacement tests in core flooding systems at 80 °C were performed, which indicated oil recovery factors of 7.08% for PHPA, 7.70% for PHPA-DNS, 9.25% for PHPA-DNS-HD and 10.54% for PHPA-DNS-HM. Therefore, the modifications were favorable to improve the oil recovery factor and the DNS-HM nanoparticles were considered promising to improve the polymer flooding process (Zheng *et al.*, 2017).

Liu *et al.* (2017b) investigated the association of nanofiller with Hydrophobically Modified Polyacrylamide (HAPAM) by inserting silica nanoparticles in the polymeric matrix (SHAPAM). Polymer solutions containing 2000 ppm of PHPA, HAPAM, and SHAPAM were compared for application in reservoirs with severe salinity and temperature conditions. HAPAM showed better properties than PHPA, but the insertion of nanoparticles (SHAPAM) caused the formation of more rigid structures, with viscosity values 3.6 times higher than the HAPAM solution, along with high tolerance to salinity and temperature, indicating the insertion of nanoparticles as a promising method. In addition, the oil recovery factors with the injection of PHPA, HAPAM and SHAPAM solutions were 9.2%, 12.5% and 20%, respectively.

Hu *et al.* (2017) also evaluated the incorporation of SiO_2 nanoparticles in PHPA solutions, under high temperature and salinity conditions, and found an improvement in the rheological properties of PHPA solutions by transforming them into PHPA-SiO_2 hybrid nanosystems.

Rellegadla *et al.* (2018) studied the effect of incorporating nickel Nanoparticles (NPs) in Xanthan Gum (XG) solutions and evaluated the efficiency of the nanopolymer system for the recovery of residual oil from sand packed bioreactors with oil collected from the *Ankleshwar oil fields in India*, in comparison with the injection of a solution of XG and suspension of nickel nanoparticles. They found that the insertion of nickel nanoparticles increased the intrinsic viscosity of the XG solution, and the recovery tests with the XG solution, NPs and XG-NPS system indicated oil recoveries of 4.48%, 4.58%, and 5.98%, respectively. Hence, they considered the use of nanopolymer systems to be a good alternative to improve the polymer flooding process.

Corredor *et al.* (2019) also analyzed the incorporation of nanoparticles in xanthan gum solutions. They observed that the addition of surface-modified SiO_2 and unmodified SiO_2 favored the increase in the viscosity of XG solutions, while TiO_2, Al_2O_3, $Fe(OH)_3$ nanoparticles did not promote increased viscosity.

Haruna *et al.* (2019) evaluated the effect of the incorporation of Multi-Walled Carbon Nanotubes (MWCNTs) on the rheological properties and efficiency of oil recovery using solutions of copolymers and acrylamide terpolymers, aiming at application in reservoirs with high salinity and temperature. They noted that the incorporation of MWCNTs improved the viscoelasticity and viscosity of the polymeric dispersions. In addition, MWCNTs increased the oil recovery efficiency at 85 °C in *American Petroleum Institute* (*API*) brine and in alkaline pH brine. The results demonstrated this is an alternative to improve the performance of polymers applied in EOR.

Abdullahi *et al.* (2019) evaluated the incorporation of Al_2O_3, SiO_2, and TiO_2 nanoparticles in PHPA solutions in different brines at varying temperatures. They found that the addition of 0.1 wt% of nanoparticles increased the salt tolerance of PHPA solutions, since the nanoparticles have a shielding effect against the cations present in synthetic brines containing divalent cations. Thus, the hybrid nanosystems had better rheological performance than the pure PHPA solution, and the PHPA/Al_2O_3 system had the highest viscosity, followed by PHPA/SiO_2 and PHPA/TiO_2, with the lowest viscosity among the hybrid nanosystems. In addition, oil recovery tests were carried out in packed sand saturated with intermediate oil, where PHPA/Al_2O_3, PHPA/SiO_2, and PHPA/TiO_2 systems produced additional recoveries of 15%, 10%, and 6%, respectively, in relation to the solution of PHPA. Thus, the use of nanoparticles can be considered promising to improve the polymer flooding process.

Yadav *et al.* (2020) studied the influence of salinity, temperature, shear rate, nanofiller concentration and polymer concentration on the rheological behavior of PHPA/SiO_2 hybrid nanosystems. They observed that the increase in polymeric concentration and content of silica nanoparticles favorably acted by increasing the viscosity of the systems. The salinity and shear rate had a negative effect on rheological behavior, reducing the viscosities of the systems. The evaluation of the influence of temperature (80.15 to 110.68 °C) showed that the viscosity decreased with rising temperature until 107 °C, after which the viscosity increased due to the interaction of long chains with the nanoparticles used in high concentration, increasing the cohesive force in the solution and the viscosity. Thus, the addition of a high concentration of silica nanoparticles can be a good option for reservoirs with high temperatures.

Haruna *et al.* (2020) studied the effects of the incorporation of nanoparticles on the rheological properties, thermal stability and degradation of PAM solutions under HTHS conditions. For this, silica nanoparticles and SiO_2 nanoparticles modified with (3-aminopropyl) triethoxysilane ($MSiO_2$) were used, forming the hybrid nanosystems SiO_2/PAM and $MSiO_2$/PAM, respectively. They found that the addition of nanoparticles increased the viscosity, thermal stability and salinity tolerance of the polymer systems. The PAM, SiO_2/PAM, and $MSiO_2$/PAM solutions showed viscosity reductions of 75%, 45%, and 10%, respectively, after aging for 90 days. This indicates that the modification of the surface of the nanoparticles can further improve the properties of hybrid nanopolymer systems. Furthermore, enhanced oil recovery tests were carried out simulating HTHS conditions at 85 °C and with solutions in API brine and formation brine of the *Ghawar field in Saudi Arabia*. The addition of nanoparticles

Table 3. Summary of the main activities carried out involving polymer systems with nanoparticles.

Year	Activity	Authors
2014a	Compared the rheological behavior between a Hydrophobically Associating Polyacrylamide (HAPAM) and a hybrid system of HAPAM/silica nanoparticles in aqueous solutions	Zhu *et al.*
2014b	Evaluated the effect of silica nanoparticles on the properties of solutions of Hydrophobically Associating Partially Hydrolyzed Polyacrylamide (HAPHPA)	Zhu *et al.*
2016	Investigated the effect of incorporating titanium dioxide nanoparticles on the viscosity of PHPA solutions and compared the oil recovery potential of PHPA solutions and the PHPA/TiO_2 hybrid nanosystems	Cheraghian
2016	Performed a comparative study of the rheological properties of PHPA solutions and systems formed by the addition of surface-modified clay nanoparticles	Rezaei *et al.*
2017	Evaluated the effect of applying SiO_2 nanoparticles on decreasing thermal degradation and rheological behavior of PHPA	Giraldo *et al.*
2017	Studied the incorporation of silica nanoparticles (DNS) and SiO_2 surface-modified by the silane coupling agents hexadecyltrimethoxysilane (DNS-HD) and hexamethyldisilazane (DNS-HM) in aqueous PHPA solutions	Zheng *et al.*
2017b	Conducted studies of the association of silica nanoparticles with hydrophobically modified polyacrylamide	Liu *et al.*
2017	Evaluated the incorporation of SiO_2 nanoparticles in PHPA solutions, under high temperature and salinity conditions	Hu *et al.*
2018	Studied the effect of incorporating nickel Nanoparticles (NPs) in Xanthan Gum (XG) solutions	Rellegadla *et al.*
2019	Conducted studies of the incorporation of nanoparticles (SiO_2, TiO_2, Al_2O_3, Fe$(OH)_3$) in Xanthan Gum (XG) solutions	Corredor *et al.*
2019	Evaluated the effect of the incorporation of Multi-Walled Carbon Nanotubes (MWCNTs) on the rheological properties and efficiency of oil recovery using solutions of copolymers and acrylamide terpolymers	Haruna *et al.*
2019	Evaluated the incorporation of Al_2O_3, SiO_2, and TiO_2 nanoparticles in PHPA solutions in different brines and temperatures	Abdullahi *et al.*
2020	Developed a study of the influence of salinity, temperature, shear rate, nanofiller concentration, and polymer concentration on the rheological behavior of PHPA/SiO_2 hybrid nanosystems	Yadav *et al.*
2020	Studied the effects of incorporating silica nanoparticles and SiO_2 nanoparticles modified with (3-aminopropyl) triethoxysilane ($MSiO_2$) on the rheological properties, thermal stability and degradation of PAM solutions	Haruna *et al.*

increased the oil recovery factor in both brines and the best system was $MSiO_2$/PAM. So, the addition of these modified nanoparticles can improve oil recovery under harsh conditions.

In general, the application of nanoparticles for the production of hybrid nanopolymer systems improves the performance of the injection polymers applied in EOR, increasing the viscosity of the systems and improving oil recovery (Abdullahi *et al.*, 2019; Cheraghian, 2016; Liu *et al.*, 2017b; Rezaei *et al.*, 2016; Zheng *et al.*, 2017; Zhu *et al.*, 2014b). The summary of the main activities carried out involving application of nanoparticles and the evolution of studies is shown in Table 3.

The summary of the main mechanisms of action and advantages of the viscosifying polymer systems to improve the polymer flooding process can be observed in Table 4.

Table 4. Summary of the main mechanisms of action and advantages of viscosifying polymer systems to improve the polymer flooding process.

System	Mechanism	Advantages*
Hydrophobically Modified Associative Polymers (HMAP)	Hydrophobic association effect of the groups inserted in the main chain	– Better thermal stability and tolerance to salinity; – Substantial increase in viscosity above the CAC; – Increased oil recovery factor.
Thermo-Viscosifying Polymers (TVP)	Thermosensitive sequences are reversibly self-aggregating by the formation of physical interactions, forming hydrophobic microdomains	– Improved the polymer performance under HTHS conditions; – Increased viscosity with higher temperatures, above LCST; – Increased oil recovery factor.
Polymer systems with nanoparticles	Physical or chemical interactions between nanoparticles and functional groups in the polymer chain	– Improved thermal stability and salinity tolerance; – Improved rheological properties; – Allowed application of lower polymer concentration; – Increased oil recovery factor.

* Advantages in relation to the application of PHPA solutions for polymer flooding.

6 Artificial intelligence application

Over the last decades, the use of genetic programming and artificial intelligence has gained great importance in the reservoir engineering, as it allows the creation of computer models to obtain satisfactory results with high precision in several oil fields. These devices were created to generate models and accurate correlations from a database with different field conditions, aiming to determine the best working conditions to obtain promising results, based on the genetic algorithm that consists of a metaheuristic technique of search belonging to evolutionary computing algorithms group applied to optimize solutions and detect problems (Amirian *et al.*, 2018; Kamari *et al.*, 2017; Rostami *et al.*, 2016, 2017c).

Considering that performing some tests on a laboratory scale takes time, extensive planning, and relatively high costs, the mathematical strategy of genetic programming emerges as an alternative to estimate results from a wide range of experimental conditions acquired from databases, allowing optimization of results. Thus, several authors have studied the application of genetic programming in many areas of science and engineering, obtaining promising results over the last decade (Kamari *et al.*, 2017; Karkevandi-Talkhooncheh *et al.*, 2018; Rostami *et al.*, 2017c, 2018a).

Artificial Neural Networks (ANNs) correspond to information processing methods capable of creating models from complex data input and output relationships, identifying important data patterns, and being widely applied to process control, analysis techniques, data processing, experimental value estimation, failure detection, pattern recognition, among others (Amirian *et al.*, 2018; Corredor-Rojas *et al.*, 2018; Rostami *et al.*, 2016, 2018a).

Artificial neural networks can also be used to develop models that allow estimating the carbon dioxide (CO_2) adsorption equilibrium in activated carbon. Normally, this equilibrium is determined by Sips and Langmuir isotherms, however, the development of algorithms based on artificial neural networks can be an alternative for the acquisition of more efficient results and without the restriction of work at constant temperatures (Rostami *et al.*, 2018a). Thus, Rostami *et al.* (2018a) developed a multi-layer feed-forward neural network algorithm to estimate CO_2 adsorption from a wide range of thermodynamic conditions found in the literature. It was verified that the developed model showed greater precision, performance and presents itself as a more promising method when compared to traditional isotherms.

To estimate the efficiency of the thermal enhanced oil recovery process, Rostami *et al.* (2016) developed an innovative Least Square Support Vector Machine (LS-SVM) algorithm to create a model capable of predicting the effective thermal conductivity in dry sandstones. This method consists of an artificial intelligence technique that is more advantageous than traditional techniques based on artificial neural networks because they present high reproducibility, accuracy, and greater reliability of the results. Thus, 280 experimental data of effective thermal conductivity in dry sandstones present in the literature were collected, containing information on temperature, pressure, porosity, and solid density. Then, the LS-SVM model was developed to predict the effective thermal conductivity. It was found that the method is more accurate than traditional artificial intelligence models, allowing for satisfactory and reproducible results to improve the thermal enhanced oil recovery and the traditional numerical simulation in dry sandstones.

In addition to artificial intelligence methods known as ANN and SVM (computational models that establish complex relationships and do not have an obvious correlation between input and output conditions), genetic-based calculations such as Genetic Programming (GP), Gene Expression Programming (GEP), and Genetic Algorithm (GA) can be used to obtain greater accuracy of correlations, more practical and simpler models for users, and can be integrated with conventional software and simulators to determine accurate correlations for each step of a study process (Rostami *et al.*, 2017a, b).

Rostami *et al.* (2017c) used the GP method to estimate the interfacial tension between hydrocarbon/water in reservoirs, starting from the association of mathematical tools and a wide range of experimental conditions obtained from literature data. Thus, the use of artificial intelligence allowed to obtain a fast and efficient correlation system to estimate interfacial tension values, making it possible to obtain satisfactory results for the oil industries. GP was also used as a mathematical strategy by Rostami *et al.* (2017a) to estimate the thermal conductivity of supercritical CO_2. Thus, it was observed that the developed algorithm presents a good correlation and can be promising to estimate the thermal conductivity in industrial processes that use supercritical CO_2.

The GEP method was used to estimate the solubility of CO_2 in processes of CO_2 flooding in oil reservoirs, aiming to improve this method of enhanced oil recovery. For this, the GEP soft computing technique was developed to establish correlations of the solubility of CO_2 in dead and live oil systems. Furthermore, they evaluated the predictive ability of ANN for the solubility of CO_2 (using comprehensive data from literature databases) and compared it with the GEP model. Thus, it was found that the ANN technique presented slightly better results only in simulations with live crude oil, but in general, the GEP method is a reliable and highly accurate model to estimate the solubility of CO_2 in live and dead oils, being a promising algorithm for this application (Rostami *et al.*, 2017b).

Kamari *et al.* (2017) developed a comparative study on the estimates of interfacial tension between CO_2-brine from the GEP, LS-SVM, and Decision Tree (DT) modeling methods with the ANN data found in the open literature. Thus, it was found that the DT and ANN methods were the most accurate models to determine the interfacial tension between CO_2-brine. The DT consists of a regression decision tree modeling, where the dataset is subdivided into smaller groups (a tree with nodes that represent the subsets), after building the tree with the data, cross-validation and the estimate is obtained through the model. In addition, it was found that the GEP technique had the lowest reliability and precision for determining the interfacial tension between CO_2-brine, however, it is the model that can provide faster estimates for the process.

In addition to the promising applications of artificial intelligence and genetic programming in estimating important parameters for reservoir engineering and process improvement, these methods can also be applied to estimate and optimize polymer flooding processes in enhanced oil recovery, through estimating values of viscosity of polymeric solutions and the prediction of the performance of these injection fluids in reservoirs. In this context, several authors have developed researches focused on this area (Rezaian *et al.*, 2010; Kang *et al.*, 2016; Amirian *et al.*, 2018; Corredor-Rojas *et al.*, 2018; Rostami *et al.*, 2018b).

Rezaian *et al.* (2010) applied the artificial neural network model to estimate the minimum amount of Polyvinyl Acetate (PVA) needed to increase water viscosity and simultaneously promote a decrease in oil viscosity, and thus improve the polymer flooding process. To test the effectiveness of the created network, experimental tests were carried out and these showed agreement between the estimated percentages and those obtained in the experiment. Thus, it was found that the ideal amount of PVA for this application was 15.0% and to recover 100 bbl of oil it would be necessary to use about 7.5 bbl of polymer. Thus, it appears that the use of artificial intelligence can be a promising alternative to improve EOR processes.

Kang *et al.* (2016) used artificial neural network models to estimate the viscosity of polymer solutions of three commercial acrylamide-based polymers, known as Flopaam 3330S, Flopaam 3630S and AN125, with hydrolysis degrees between 25% and 30% and molecular weights of 8.0×10^6 g/mol, 20.0×10^6 g/mol and 8.0×10^6 g/mol, respectively. For this, parameters that influence the viscosity of these solutions were taken into consideration, such as polymer concentration, degree of hydrolysis, molecular weight, temperature, shear rate, and brine cation concentration. The only method used to estimate the unmeasured viscosity of a polymer solution in EOR was the Carreau model with Lee correlation, however, under conditions of low salinity and high molecular weight of the injection polymers, the correlation is not accurate. Thus, three ANN models were created (one for each evaluated polymer) and it was found that the model estimated viscosity values similar to those experimentally measured, being more accurate than the Carreau–Lee method. Thus, the application of artificial intelligence to estimate the viscosity of polymeric solutions can be considered a fast, reliable, and promising method to improve the EOR process.

Rostami *et al.* (2018b) also used artificial intelligence to estimate the viscosity of PHPA solutions from neural network models. It can be seen that the models can be promising to estimate viscosity values of polymeric solutions because they have high precision and reliability. Furthermore, it was found that temperature was the most influential parameter in the models, with a negative effect on the viscosity of the PHPA solution.

Corredor-Rojas *et al.* (2018) developed a Multilayer Perceptron (MLP) neural network model to predict the viscosities of PHPA-based nanopolymer systems and xanthan gum nanosystems. MLP is an artificial intelligence computer system applied to find complex correlations between inputs and outputs of a system, comprising a network model that includes several layers, the inputs being assigned to the first layer, the output to the last layer, and the relationships between input-output layers are called hidden layers. In this system, each layer has a determined number of neurons, with the number of neurons in the first layer corresponding to the number of input variables, hidden layers have neurons defined by trial-error and only one neuron for the last layer, corresponding to the output of the model. To obtain an efficient neural network, different numbers of neurons were considered and the system was tested with Bayesian Regularization (BR),

Table 5. Summary of the main activities involving artificial intelligence.

Year	Activity	Authors
2018a	Developed a multi-layer feed-forward neural network algorithm to estimate the CO_2 adsorption equilibrium in activated carbon	Rostami *et al.*
2016	Studied an innovative Least Square Support Vector Machine (LS-SVM) algorithm to create a model capable of predicting the effective thermal conductivity in dry sandstones	Rostami *et al.*
2017a	Used the Genetic Programming (GP) method to estimate the interfacial tension between hydrocarbon/water in reservoirs	Rostami *et al.*
2017c	Performed a GP as a mathematical strategy to estimate the thermal conductivity of supercritical CO_2	Rostami *et al.*
2017b	Studied a GEP method to estimate the solubility of CO_2 in processes of CO_2 flooding in oil reservoirs	Rostami *et al.*
2017	Developed a comparative study on the estimates of interfacial tension between CO_2-brine from the GEP, LS-SVM, and DT modeling methods with the ANN	Kamari *et al.*
2010	Applied the artificial neural network model to estimate the minimum amount of PVA needed to improve the polymer flooding process.	Rezaian *et al.*
2016	Studied artificial neural network models to estimate the viscosity of polymer solutions of three commercial acrylamide-based polymers	Kang *et al.*
2018b	Used artificial intelligence to estimate the viscosity of PHPA solutions from neural network models.	Rostami *et al.*
2018	Developed a MLP neural network model to predict the viscosities of PHPA-based nanopolymer systems and xanthan gum nanosystems	Corredor-Rojas *et al.*

Levenberg-Marquardt (LM), Resilient Backpropagation (RB), and Scaled Conjugate Gradient (SCG) algorithms, which consist of different methods to train MLP networks from real data. Thus, it was found that the BR-MLP model was the most promising among the others to estimate the viscosity of nanopolymeric systems, presenting an R^2 of 0.999 and an error of 2.46%. The BR-MLP neural network model can be considered highly accurate to estimate viscosity under different conditions of shear, temperature, polymer type, concentration of nanoparticles and polymer, among others.

The summary of the main activities carried out involving the application of artificial intelligence and genetic programming is shown in Table 5.

7 Conclusion

Among the chemical enhanced oil recovery methods, the injection of polymers as viscosifying agents stands out due to its efficiency and technical and economic feasibility. Several synthetic polymers and biopolymers can be used for this EOR technique, in particular application of partially hydrolyzed polyacrylamide, because of its good viscosifying property, abundant availability and low cost. However, PHPA has stability problems in reservoirs with severe salinity and temperature conditions. Thus, the use of Hydrophobically Modified Associative Polymers (HMAPs), Thermo-Viscosifying Polymers (TVPs) and nano-hybrid systems have been widely studied.

This extensive bibliographic survey indicates that several factors influence the performance of HMAPs and TVPs, such as polymer concentration, type of chemical group inserted in the water-soluble polymer chain, salinity, temperature and shear rate, among others. In general, both HMAPs and TVPs can provide significant improvements in salt tolerance as well as temperature and shear resistance, increasing the oil recovery factor based on tests in porous media, among others. Furthermore, the application of nanoparticles for the production of hybrid nanopolymer systems can improve the performance of the injection polymers applied in EOR, increasing the viscosity of the systems and improving oil recovery.

In general, hydrophobically modified associative polymers and thermo-viscosifying polymers are promising alternatives for application as viscosifying agents for enhanced oil recovery, especially in harsh reservoir conditions (high salinity and temperature). In addition, the application of nanoparticles also is promising to improve the polymer flooding process.

This review depicts the evolution of studies of the injection of these polymer systems for EOR, indicating the importance of conducting further research in this area to find innovative solutions to improve oil recovery efficiency. Furthermore, it can be seen the promising applications of artificial intelligence and genetic programming in estimating important parameters for reservoir engineering and these methods can also be applied to estimate and optimize polymer flooding processes in enhanced oil recovery, through estimating values of viscosity of polymeric solutions and the prediction of the performance of these injection fluids in reservoirs.

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