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Druetta, P.; Picchioni, F.

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Full Length Article

Branched polymers and nanoparticles flooding as separate processes for enhanced oil recovery

P. Druetta, F. Picchioni*

Department of Chemical Engineering, ENTEG, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands

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ABSTRACT

Since it was first theorized more than half-century ago, nanotechnology has proven to be the perfect boost for existing technologies and the oil industry has made use of this avant-garde discipline to upsurge the productivity of mature oilfields. With respect to polymer flooding, recent research has stressed the importance of the (macro) molecules' architecture on the physical properties. This paper presents the numerical simulation of these two agents in standard, not combined, oil recovery processes. The polymer solution viscosity is calculated considering the polymer's architecture, its degradation and the salinity. The nanoparticles affect the carrier-phase viscosity and the rock formation wettability, which modifies the oil mobility. Results evidenced the improved capabilities of branched (i.e. star/comb) polymers with respect to traditional linear ones. The modified architecture improves not only the rheological but also the viscoelastic properties, which ultimately increases the microscopic sweeping efficiency. Nanoparticles increase slightly the carrier phase viscosity, but their main recovery mechanism is their adsorption onto the rock and subsequent wettability modification, reducing the residual oil saturation. Furthermore, it is also important to properly characterize both the particles' average size and also their aggregation rate, since these affect the recovery efficiency. Simulations show the importance of a good characterization of oil recovery agents and their effect on the phases' physical properties as well as the potential of nanoparticles to act as a boost of traditional enhanced recovery processes.

1. Introduction

The exploitation of an oilfield can be divided in three stages, depending on the physical mechanisms employed by the oil extraction [1–3]. Originally, natural driven techniques and later water injection were the only ways to produce oil [4,5]. Nonetheless, after these processes around 50% of the original oil in place (OOIP) remained still trapped in the reservoir [6,7]. Therefore, during the last 50 years the oil industry and researchers have focused on increase the recovery factor by means of what is known as Tertiary or Enhanced Oil Recovery (EOR). The use of standards technologies in EOR allowed increasing the performance of oilfields after waterflooding. Although the sweeping factor was increased, a significant percentage of the OOIP remains still trapped even after the profitable limit of standard EOR processes. The attention was then focused on boosting their efficiency. During the last 15 years researchers have looked for ways to increase the efficiency of these methods, and the response came through from the nanotechnology, thanks to the exceptional properties of the materials at these length scales [8]. With respect to polymer flooding, the

development of novel, hyperbranched (macro)molecules has yielded improved sweeping efficiencies when compared to traditional, linear-based ones.

1.1. Nanotechnology in EOR

Since Richard Feynman's already famous talk "There's Plenty of Room at the Bottom" [9], the development and applications of nanotechnology in the industry have not stopped growing. These find today applications in various branches of the oil and gas industry, namely: drilling, completion, exploration and downstream operations. The first general study of migration, adsorption of nanoparticles in porous media was presented by Ju [10,11]. A mathematical and experimental study was performed of a sweeping process in a 1D medium, considering the adsorption and changes in both the porosity and absolute permeability generated by silicon nanoparticles. The model was validated with experimental results and served as the basis for many of the simulators developed thereafter. Following the study of the application of nanoparticles in porous media for EOR processes, El-Amin [12–14]

* Corresponding author.

E-mail address: f.picchioni@rug.nl (F. Picchioni).URL: <http://www.rug.nl/research/product-technology/> (F. Picchioni).<https://doi.org/10.1016/j.fuel.2019.115996>

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developed a multiphase, multicomponent simulator for oil recovery processes using only nanoparticles. This model used an implicit and iterative resolution to solve the differential equations and was based on the simulator developed by Ju [15,11], expanding it to contemplate a number of physical phenomena occurring in the rock formation. A similar work was developed Zhang [16,17], who carried out numerical simulations and validations with laboratory experiments in single-phase (water-saturated) 1D models. The combined use and synergy of chemical EOR agents and nanoparticles has attracted also the attention of several researchers, as a way to improve EOR techniques. With this respect, Kumar [18] and Maurya [19] reported the improved capabilities of surfactant acting with nanoparticles and their synergy in coreflooding tests. This combination exhibit an enhanced drop-size stability as well as an increase in the viscoelastic properties of the solution. Furthermore, Maurya [20] also studied the EOR performance of polymer-grafted-nanoparticles, showing that the combination of these agents could improve the oil recovery by means of enhanced rheological and interfacial properties along with a modification of the rock's wettability.

1.2. Aim of this work

The paper presents a five-component (water, petroleum, polymer, nanoparticles and salt) simulator for nanotechnology in chemical EOR, along with the study of a new viscosity model considering the polymer's architecture. The nanoparticles model considers all the effects on porous medium and fluids, namely: aggregation, retention, rheology, and changes in permeability and porosity. On the other hand, the polymer module extends the model previously developed, including a novel relationship between architecture and phase properties. The salt component is also considered, expressed as a function of the total dissolved solids (TDS) content in the water phase. Numerically speaking, the model uses a second order discretization scheme with flux limiter functions [21–24]. This model can be also applied to underground flow in several disciplines, not only in EOR but also in CO₂ storage, like mentioned in the literature [25].

2. Description of the model

2.1. Physical model

The process of a nanoparticles-polymer flooding is modeled using a 2D geometrical configuration, based on a geometric pattern usually found in the oil industry. The five-spot scheme is a good model which relatively satisfies this requirement. It consists of a square domain, with constant or variable properties, where an injection well is placed at the center, and four producing wells are located at the corners. During this analysis, a simplification of the model was performed in what is known as quarter five-spot (Fig. 1). The physical model is composed by a domain (Ω), representing an oilfield of known geometric characteristics, with determined physical properties, absolute permeabilities (K) and porosity (ϕ). The flow is considered isothermal, incompressible and 2-dimensional (since it is assumed that the vertical permeability is negligible when compared to horizontal ones). The domain is then discretized in a system of $n_x \times n_y$ blocks to perform the numerical simulation. Darcy's law is valid and gravitational forces are negligible compared to the viscous ones [27,7,6].

2.2. Mathematical model

The compositional model represented by the Darcy and mass transport equations (Eqs. (1)–(4)) is used due to its versatility to accurately represent the transport of a number of components in porous media. The general characteristics of this system were already explained in a previous paper of the same model during its validation and application to a standard polymer flooding [26,28–30].

Fig. 1. Schematic representation of the quarter 5-spot used for the EOR simulations [26].

$$\vec{u}^j = -\frac{k_r^j}{\mu^j} \cdot \vec{\nabla} p^j; \quad j = o, a \quad (1)$$

$$\frac{\partial(\phi z_i)}{\partial t} + \nabla \cdot \sum_j V_i^j \cdot \vec{u}^j - \nabla \cdot \sum_j D_i^j \cdot \nabla \cdot V_i^j = -\frac{\partial(\phi A d_i)}{\partial t} + q_i; \quad i = p, np, w, s, pol \quad (2)$$

$$D_i^j = dm_i^j \cdot \phi \cdot S^j \cdot \delta_{ij} + \|\vec{u}^j\| \cdot \frac{dl^j}{\|\vec{u}^j\|^2} \cdot \left(\frac{(u_x^j)^2}{u_y^j \cdot u_x^j} \frac{u_x^j \cdot u_y^j}{(u_y^j)^2} \right) + dt^j \cdot \begin{pmatrix} 1 - \frac{(u_x^j)^2}{\|\vec{u}^j\|^2} & -\frac{u_x^j \cdot u_y^j}{\|\vec{u}^j\|^2} \\ -\frac{u_y^j \cdot u_x^j}{\|\vec{u}^j\|^2} & 1 - \frac{(u_y^j)^2}{\|\vec{u}^j\|^2} \end{pmatrix} \quad (3)$$

$$\phi c_r \frac{\partial p^a}{\partial t} + \vec{\nabla} \cdot (\lambda \cdot \nabla p^a) = \frac{\partial}{\partial t} \left(\phi \cdot \sum_i A d_i \right) - \vec{\nabla} \cdot (\lambda^o \cdot \nabla p^c) + q_t \quad (4)$$

3. Physical properties

The physical properties modified by polymer and nanoparticles are described in this section. Thus, the following phenomena are also considered using models described in the literature: residual saturations, disproportionate permeability reduction (DPR), inaccessible pore volume (IAPV) and capillary pressure [26,31].

3.1. Chemical component partition

The most relevant part of a compositional numerical simulation is to understand how the components distribute among the phases, which is known as the system's phase behavior. It is assumed that oil and water remain in the oleous and aqueous phases, respectively and that the polymer and salt remain only in the aqueous phase ($V_s^o = V_{pol}^o = 0$). Regarding the nanoparticles, a similar concept to the partition coefficient used for surfactants was adopted in order to represent how these distribute between the phases. Depending on their wettability, HLPN (hydrophobic and lipophilic polysilicon nanoparticles), NWPN (neutral wet polysilicon nanoparticles) or LHPN (lipophobic and hydrophilic polysilicon nanoparticles), they will tend to be present in the oleous or aqueous phase, respectively.

$$\text{Solubilization Coefficient} = I_{np}^a = \frac{V_p^a}{V_{np}^a} \quad (5a)$$

$$\text{Swelling Coefficient} = L_{wnp}^o = \frac{V_w^o}{V_{np}^o} \quad (5b)$$

$$\text{Partition Coefficient} = k_{np} = \frac{V_{np}^o}{V_{np}^a} \quad (5c)$$

Since it was assumed that petroleum and water remain in their respective phases, both swelling and solubilization coefficients are equal to zero ($L_{wnp}^a = L_{wnp}^o = 0$). The value of k_{np} is determined by the type of nanoparticles employed: HLPN (for $k_{np} \gg 1$), LHPN (for $k_{np} \approx 0$) and NWPN (for $k_{np} \approx 1$). In this case the nanoparticles partition coefficient is independent on the salt content.

3.2. Interfacial tension

The interfacial tension depends on the presence and concentration of the nanoparticles as well as the polymer components. In this simulation a simplified interfacial tension (IFT) correlation was adopted. Nevertheless, the oil-water (no chemical) IFT is dependent on the salinity. In this simulator a correlation is employed to modify this value considering the TDS, as presented in Eq. (6) [32].

$$\sigma_{salt}^{ow} = \sigma_H^{ow} + 0.0334 \cdot \text{Temp} \cdot \ln(1 + 4.43 \cdot V_s^a) \quad (6)$$

In order to model the influence of the nanoparticles, a piece-wise, linear correlation is employed [33–36,32,37,20]. The IFT varies linearly with the concentration of the nanoparticles from a maximum value (σ_{salt}^{ow}) to its minimum constant value at higher concentrations (σ_{np}^{ow}). This effect on the IFT occurs only when the nanoparticles migrate to the interface and reduce the interfacial energy between aqueous and oleous phases, which is a similar concept to the one employed to characterize the polymer's influence. In this simulator, this is considered negligible since it is assumed that the polymer is fully soluble in the aqueous phase.

With respect to the influence of nanoparticles on the interfacial properties, the layer of particles generates a lower IFT between the two phases, in a similar way like surfactants work, but using a different principle [38]. This behavior can be explained using the free energy term,

$$F_\psi = \oint \Psi dA \quad (7)$$

where Ψ is a function of the surface tension. The reduction of the interfacial free energy requires either the IFT reduction, which is done by adding surfactants, or the reduction of the contact area, which is the effect of adsorbed particles. This formulation shows that neutral wetting nanoparticles can reduce the overall interfacial free energy not by reducing the IFT itself, but by removing parts of the energetically unfavorable fluid-fluid interface area.

3.3. Aggregation of nanoparticles

The aggregation of nanoparticles is the formation of clusters by particles, or when small clusters aggregate to form a bigger ones due to the balance of forces in the system explained, for example, by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [39–43]. The gradual increase in the size of these clusters can cause the sedimentation of the nanoparticles in the porous medium, separating them from the nanofluid, which it is an undesired effect. On the other hand, clusters can also be broken and generate smaller ones if the diameter or number of nanoparticles in the same reaches a critical limit [44–49]. This phenomenon is considered in the simulation, adopting an exponential law to take into account the change in the average diameter of the nanoparticles as a function of time. In addition, based on the work of Jiang [44], it is considered a maximum possible size of the cluster of nanoparticles, above which it undergoes a splitting process in identical clusters of smaller size, with the properties being calculated for this new average diameter.

Fig. 2. Viscosity ratio $g_{viscosity}$ as a function of the numbers of arms and the molecular weight relationship.

$$\frac{dDia_{np}}{dt} = K_{agg} \cdot Dia_{np} \quad (8)$$

3.4. Phase viscosities

A step-wise procedure was adopted in the new simulator to calculate the viscosity of the aqueous phase. The first step consists in calculating the phase viscosity considering only the TDS. During this paper a modification to the classical approach was used (e.g., UTCHEM [31]), considering the dependence on the salt in the pure water/brine viscosity [50–52]. Finally, the influence of the polymer and nanoparticles is taken into on the phase viscosity, considering as well in this case the polymer molecules' architecture on the rheological properties. The first step is to determine the viscosity ratio between a linear polymer used as reference, and a branched one with the same total molecular weight [21,23,24,53–55]. Eq. (9) is used in the simulator to calculate this ratio (Fig. 2),

$$g_{viscosity} = \frac{1}{(1 + \rho \cdot f)^3} [1 + 2f \cdot \rho + (2f + f^2)\rho^2 + (3f^2 - 2f)\rho^3] \quad (9)$$

where f is the number of arms of the polymer and ρ is the relationship between the molecular weights of the arms and backbone [56]. The number of arms depends on the polymer used for the EOR process and in this study the polymers developed by Wever [8] were used as example, who synthesized branched polymers up to a maximum of 17 arms. Next, the viscosity of the aqueous phase at zero shear-rate is calculated using the following formulation,

$$\mu_{0sr} = \mu_w \{1 + [k_1(g_v, f) \cdot [\eta] \cdot V_{pol}^a + k_2(g_v, f) \cdot [\eta]^2 \cdot V_{pol}^a + k_3(g_v, f) \cdot [\eta]^3 \cdot V_{pol}^a] C_{SEP}^{Sp}\} \quad (10)$$

Finally, the influence of nanoparticles is taken into account, using one of the several correlations present in the literature to calculate the nanofluid's relative viscosity. Since aggregation and retention phenomena are involved, a formulation was used considering both the concentration and nanoparticles' size in the phase [31,57–59].

$$\mu_{np} = \mu_{cf} \cdot [1 + (2.5 + \eta_1 e^{-Dia_{np}/d_w}) \cdot V_{np}^a + (6.2 + \eta_2 e^{-Dia_{np}/d_w}) \cdot V_{np}^a] \quad (11)$$

where V_{np}^a is the concentration of particles in the phase, Dia_{np} is the average size of the nanoparticles or clusters, d_w is the diameter of the carrier fluid molecules and $\eta_{1,2}$ are correlation constants. It is noteworthy that the present simulator does not incorporate the effects that can be found with associating polymers and nanoparticles [60–62]. It is deemed that further research on the topic should be carried out so as to be able to elaborate mathematical models considering this interaction

to calculate the viscosity of semi-dilute polymer solutions with nanoparticles. The rheological behavior of the aqueous phase is then calculated using the Unified Viscosity Model (UVM), whilst for the oleous phase it is assumed to Newtonian behavior, although the presence of nanoparticles in the oleous phase may vary its viscosity [63,64].

3.5. Retention and adsorption

The rock formation properties can be altered due to the presence of nanoparticles. Four different mechanisms have been proposed to explain this phenomenon: (1) nanoparticle adsorption onto the rock surface, (2) mechanical entrapment (when the nanoparticles are larger than the pore throat), (3) sedimentation or gravity settling, and (4) log-jamming (when nanoparticles smaller than the pore throat accumulate and lead eventually to the throat/channel blockage) [38]. The adsorption process occurs when particles or polymer molecules form onto the surface of the formation rock. This irreversible phenomenon will cause a loss of the chemicals in the phases in the porous media, making the whole process economically unfeasible in case of high rates of adsorption. This is due to the fact that extra EOR agents would be necessary and the interfacial properties will be decreased [31]. The net rate loss of nanoparticles in the porous medium is quantified in Eq. (4) [25,10]

$$Ad_{np} = (F_{SP} \cdot v_1 + v_2 + v_3) \quad (12)$$

where v_1 represents the volume of the nanoparticles in contact with the phase j available on the pore surfaces per unit bulk of the porous medium, v_2 is the volume of the nanoparticles entrapped in the pores of the phase j per unit bulk of porous medium due to plugging and bridging, and v_3 is the release rate of nanoparticles from pore walls by colloidal forces, considering both the salinity of the system and the possible charge of the nanoparticles. The last term represents an extension of the models previously reported and it is based on the work developed by Sbai [25].

The first term can be expressed by a critical velocity for surface deposition. Below this value only the phenomenon of retention of the particles in the porous formation occurs, and above it a combination of effects of retention and entrainment takes place. The model for expressing v_1 is according to a step-wise function (or Heaviside) based on the critical velocity.

$$v_1^{<n>} \Rightarrow \begin{cases} \alpha_1 \cdot u^j \cdot V_{np}^a & \text{if } u^j \leq u_{crit}^a \\ \alpha_1 \cdot u^j \cdot V_{np}^a - \alpha_2 \cdot v_1^{<n-1>} \cdot (u^j - u_{crit}^j) & \text{if } u^j \geq u_{crit}^a \\ v_1^{<0>} = 0 & \forall \Omega \end{cases} \quad (13)$$

where α_1 is the coefficient for surface retention of the nanoparticles in the phase j in the rock formation, α_2 is the coefficient for entrainment of the nanoparticles in the phase j and v_{crit} is the critical velocity for the phase j . The data necessary to calculate the critical velocity as a function of the nanoparticle size were obtained from Ju [10,11,15] (Fig. 3). This study considers spherical-shaped particles and clusters but it is deemed that, in future models, the critical velocity should be also expressed as a function of the shape as well.

$$u_{crit}^j [\text{m/day}] = 0.00992736 \cdot Dia_{NP} [\text{nm}] + 0.0009936 \quad (14)$$

For the term v_2 is used a formulation similar to the term of retention in v_1 , and is expressed according to the following function,

$$v_2^{<n>} \Rightarrow \begin{cases} \alpha_3 \cdot u^j \cdot V_{np}^a \\ v_2^{<0>} = 0 & \forall \Omega \end{cases} \quad (15)$$

where α_3 is the pore blocking constant in the phase j . Finally, the term v_3 is calculated according to Sbai [25] and it is a function of the salinity (TDS) in the medium.

$$v_3^{<n>} \Rightarrow \begin{cases} -\alpha_4 \cdot v_1^{<n>} \cdot (C_{sc} - V_s^a) \\ v_3^{<0>} = 0 & \forall \Omega \end{cases} \quad (16)$$

where α_4 is the constant rate of colloiddally induced mobilization of in-situ nanoparticles. Eq. (16) means that colloidal release of particles from phase j is limited by the critical salinity C_{sc} . This depends as well on the type of nanoparticles and the mineralogy of the rock formation.

3.6. Change in absolute porosity and porosity

The sedimentation, adsorption and retention of the nanoparticles (by blocking and bridging) in the pore throats affect the flowability in these sections and are one of main mechanisms of formation damage. The first parameter to be analyzed is the decrease of the porosity due to the deposition of the nanoparticles. The model developed by Ju [10,12,14,13] was chosen to calculate the instantaneous porosity in the medium.

$$\phi_{i,j}^{<n>} = \phi_{i,j}^{<n-1>} - \sum_{i=1}^3 (v_i^{<n>} - v_i^{<n-1>}) \quad (17)$$

Also the absolute permeability is affected by these processes. The model considers the variation of permeability due to parameter v_2 calculated with Eq. (15) by the following expression,

$$K_{i,j}^{<n>} = K_{i,j}^{<0>} \left[(1 - f_K) k_f + f_K \frac{\phi_{i,j}^{<n>}}{\phi_{i,j}^{<0>}} \right]^{n_K} \quad (18)$$

where $K_{i,j}^{<0>}$ is the initial absolute permeability, k_f is a constant for fluid seepage allowed by the plugged pores or residual permeability of blocked pores, and n is an experimental coefficient ranging from 2.5 to 3.5. Finally, the f_K is the fraction of the original cross-sectional area or unplugged pores open to flow.

$$f_K = 1 - \sum_j \gamma_{fi} \cdot v_2^j \quad (19)$$

Where γ_{fi} is the coefficient of flow efficiency for the nanoparticles. Finally, it is presented how the different types of nanoparticles can alter the wettability and relative permeability. In order to calculate the area covered by the nanoparticles a criterion is adopted, which assumes spherical particles touching each other. With this, the specific area of the particles can be calculated as,

$$a_{np} = \frac{\text{Area}}{\text{Volume}} = \frac{6}{Dia_{np}} \quad (20)$$

Therefore, using the total volume of nanoparticles adsorbed or entrapped in the porous media and considering the specific area previously calculated, it is obtained the total surface of the rock formation covered with particles in contact with the fluids. This area is given by the following expression,

$$a_{t,i,j} = \frac{6 \cdot \beta_{np}}{Dia_{np}} (v_1 + v_2 + v_3)_{i,j}^{<n>} \quad (21)$$

where β_{np} is the surface area coefficient. For the total specific area of a porous medium the Kozeny-Carman equation is used, which relates the porosity and the absolute permeability of a rock formation [65,66]. Carman modified this expression by noting that the streamlines in a porous medium were not straight and parallel to each other. So, he added a term to Kozeny's equation, which is known as hydraulic tortuosity [67–70].

$$S_v = \frac{Ko \cdot \phi^3}{T^2 \cdot \sqrt{K_x^2 + K_y^2}} \quad (22)$$

where S_v is the total specific area of the porous medium, Ko is the Kozeny constant and T is the tortuosity. Initially considered independent of the porosity, it was later demonstrated that the tortuosity

Fig. 3. Critical velocity (left) and retention parameters (right) as a function of the particle size.

depended on the latter, with a limit of 1 when porosity tended to unity, increasing monotonically as the latter decreases. The following relationship was adopted in the simulator, based on the work developed by Matyka [71].

$$T = 1 - 0.77 \cdot \ln \phi \quad (23)$$

With the result of Eqs. (21) and (22) the fraction of the porous medium surface covered by the nanoparticles is then calculated, hence the degree of modification in the rock's wettability (Fig. 4). With respect to the cause of this wettability modification, it has been theorized that it may have two potential underlying mechanisms [38]. The first reason could be the pressure gradient created due to the solid-like ordering fluid "wedge" in the vicinity of the rock-nanofluid-oleous contact line (known as disjoining pressure), or the nanoparticle adsorption onto the solid surface, resulting in a friction reduction. The presence of salt will lower the repulsive forces between nanoparticles, thus the pressure driving the wedge will be decreased. Therefore, an increase in the TDS has a negative effect on oil removal when using nanofluids. The reference case is the relative permeabilities without the presence of the nanoparticles ($a_{t,i,j} = 0$). On the other hand, if $a_{t,i,j}/S_v \geq 1$, it means that the entire surface per unit of volume in the porous medium is completely covered by the nanoparticles, adsorbed or entrapped in the rock formation and pore throats, and the maximum wettability change is achieved. In this case, the new relative permeabilities will be $k_r^{a^*}$ and $k_r^{o^*}$. Finally, when only part of the surface is covered ($0 < a_{t,i,j}/S_v < 1$), a linear interpolation between the values above mentioned is adopted according to the following expression [10,13,14,11,72].

Fig. 4. Relative permeability modification based on the adsorption of nanoparticles.

$$k_{r,NP}^{a,o} = \min \left(1, k_r^{a,o} \cdot \left[1 + \frac{a_{t,i,j}}{S_v} (\theta_{a,o} - 1) \right] \right) \quad (24)$$

where $\theta_{a,o}$ represent the maximum possible modification of the rock wettability due to the adsorption of the nanoparticles ($\theta_{a,o} = k_r^{a,o^*}/k_r^{a,o}$).

4. Results and discussion

4.1. Introduction

The objective of this paper is to determine the advantages of using nanoparticles and their principal displacement mechanisms, along with the influence of the polymer's architecture on the sweeping efficiency, considering both as separate, individual processes. These studies consist in the analysis and comparison of nanoparticle flooding with polymer and secondary waterflooding, including an brief discussion of the different parameters presented so far in this paper. For the purpose of the simulations, it is assumed during this paper that nanoparticles remain in the aqueous phase (lipophobic-hydrophilic particles).

The combined use of polymers and nanoparticles has been already studied by the authors, showing its potential as a new EOR technique [73]. The presence of both (hyper)branched molecules and nanoparticles improved the displacing phase rheological and viscoelastic properties, improving both the macro- and microscopic sweeping efficiencies. Moreover, the nanoparticles adsorb onto the rock formation, modifying the wettability, which improves a later displacing process with polymers. This has also another advantage when the nanoparticles are injected first: its adsorption reduces the available area for the polymer molecules to be adsorbed, decreasing the chemical losses and therefore, improving the process performance from both a technical and economical point of view.

4.1.1. Data

The main geometrical parameters of the simulation, along with the initial boundary conditions and physical properties are listed in Tables 1 and 2. These are aimed at representing a standard, low-viscosity oilfield after a traditional, primary recovery stage.

4.2. Influence of the Polymer's architecture

The architecture of polymers plays an important role in rheological properties. This approach has already been reported as an alternative to develop new polymers with higher TDS resistance and viscosifying properties. The simulator considers comb- or star-shaped molecules. The simulations were carried out using two reference cases for the porous medium, which is oil-wet. These are the standard case of secondary recovery/waterflooding (2-phases, 2-components), and a

Table 1
Geometrical and simulation parameters used in the model.

Geometrical Data of the Reservoir					
Length (axis X)	500 m	Length (axis Y)	500 m	Reservoir thickness	5 m
n_x elements	40	n_y elements	40		
Rock Properties					
Formation porosity	0.25	k_{xx}	200 mD	k_{yy}	200 mD
Initial Conditions					
S_o	0.70	S_o^r (EOR)	0.35	$S_d^r = S_o^r$	0.15
Simulation Data					
Total time	3000 days	NP's inj. time	100 days	z_{npIN}	0.2
		Pol. inj. time	100 days	z_{polIN}	0.025
Phases Physical Properties					
μ^{aH}	1 cP	μ^{oH}	10 cP	Oil density	850 kg/m ³
Water density	1020 kg/m ³	IFT	50 mN/m		

Table 2
Wells operational conditions.

Physical Data					
Number of wells	2	Well radius	0.25 m	Skin factor	0
Operating Conditions					
Total flowrate	1400 STB/day	Bottomhole pressure	55,160 kPa		

polymer flooding (2-phases, 3-components) with a linear macromolecule. Aimed at studying the polymers' architecture, different scenarios were simulated, varying the number of arms as well as the molecular weight ratio between backbone and arms, but keeping the degradation rates constant.

Since the polymer injection concentration is the same for all cases, those with a larger number of arms or molecular weights present the best results. It is observed that they had a greater sensitivity to the number of arms than to the initial structure of the polymer. It is noteworthy that, for the same number of arms, polymers with a comb structure performed slightly better than star-shaped ones. This is due to the relationship expressed in Eq. (9), especially between the $M_{w,arm}/M_{w,bb}$ molecular weights, relating the viscosity of linear with comb- and star-shaped polymers for the same total molecular weight (Fig. 5). The results are presented in Table 3 and Figs. 6 and 7, along

Fig. 5. Viscosity ratio for the number of arms tested.

with the comparison with the two above mentioned reference cases.

Though the maximum pressure drop was sensibly higher, the values at the end of the recovery process are similar for the chemical EOR cases, whereas for the waterflooding they tend to be smaller due to the DPR phenomenon (Fig. 6 – bottom). With respect to the influence of the polymer architecture in the water phase viscosity, it is important to mention that this approach (i.e., branched polymers) was initially conceived as an alternative to traditional, linear charged polymers (such as HPAM). The latter used the presence of these charges in the polymer structure as a way to increase the viscosifying properties by means of the polymer uncoiling due to the ionic interaction between the charges. However, these polymers are sensitive to the presence of cations dissolved in the aqueous phase (TDS). This phenomenon, known as charge screening, hinders the interaction between the negative charges in the polymer molecules, reducing the solution viscosity, which is considered in Eq. (10) by the term C_{SEP}^{Sp} . On the contrary, neutral hyperbranched polymers do not depend on ionic interactions in order to increase the water viscosity and therefore their rheology behavior is not dependent on the TDS. The main mechanism in branched polymers to increase the viscosity (as well as the elastic properties) is the entanglement between the molecules' arms. Finally, Fig. 8 depicts the pressure profile during the flooding with a branched polymer.

4.3. Nanoparticle flooding

Nanoparticles have emerged over the past 15 years as a mean to increase the sweeping efficiency of EOR methods, from chemical to thermal [64,74,60]. The objective of this paper is to study the use of nanoparticles to recover low/medium viscosity oils, without taking into account the upgrading chemical reactions like those occurring for instance in steam flooding. The effects of nanoparticles on the porous medium and on the present fluids are well-known, namely: decrease in interfacial tension, increase in carrying phase viscosity, wettability alteration and the disjoining pressure phenomenon [75–77].

The effect of nanoparticles is studied from two different perspectives. The first part is oriented to study the effect of aggregation rate and initial size on oil recovery and rheological properties. In a second part it was included the phenomenon of particles' adsorption onto the rock formation and how this alters the wettability. In addition, it was mentioned that the nanoparticles in solution are subject to a system of forces causing them to aggregate into clusters, increasing their size. This aggregation rate also affects the sweeping efficiency of the nanofluid. The results of these analyzes are presented in Table 4 and Fig. 9.

Although the recovery factor has been increased with respect to waterflooding, the values obtained are lower than those of polymer flooding because the viscosifying properties of the nanoparticles are not as effective as the polymer's (Fig. 10). Moreover, since there is no modification in the wettability of the rock, and because the latter is this oil-wet, the relationship between the phases' viscosities plays an important role.

The best results in this process were obtained with the smallest particles and the lowest aggregation rates. The variation for the four cases chosen for study is presented in Fig. 9. In some of these simulations the particles (or aggregates) have reached the maximum allowed diameter, after which they have been split into particles/clusters of equal size, modifying the viscosity of the aqueous phase (Fig. 11) [39,78,44]. In addition to the rheological and interfacial phenomena, nanoparticles are known for their effect on the rock wettability [34,79,11,80]. In strongly oil-wet media the viscosity difference between the phases can pose a serious problem for oil recovery. The adsorption of nanoparticles changes the properties of the rock, transforming it into water-wet or mixed wettability media. In strongly water-wet media the viscosity difference affects to a lesser extent the mobility ratio, and hence the sweeping efficiency. However, previous nanoparticles models did not consider the influence between the chemical species during the adsorption process. For this new analysis four

Table 3
Results of the recovery process for different polymer architectures and reference cases.

Case	Oil recovered		Case	Oil recovered	
	m^3	%OOIP		m^3	%OOIP
Reference Waterflooding	44,310	23.6	8 - $M_{w,bb} = 500$ kDa	58,900	31.4
Reference Linear Polymer	56,880	30.6	12 - $M_{w,arm} = 300$ kDa	65,800	35.1
4 - $M_{w,arm} = 300$ kDa	57,870	30.9	12 - $M_{w,bb} = 500$ kDa	63,450	33.8
4 - $M_{w,bb} = 500$ kDa	56,830	30.3	16 - $M_{w,arm} = 300$ kDa	67,460	36.0
8 - $M_{w,arm} = 300$ kDa	61,740	32.9	16 - $M_{w,bb} = 500$ kDa	69,100	36.9

Fig. 6. Oil recovery and fractional flow for different schemes (top left), and flowrates (top right) and pressure drop (bottom) as a function of time for the polymer flooding with 16 arms and $M_{w,bb} = 500$ kDa.

Fig. 7. Final oil saturation profile for the reference waterflooding (left) and the polymer flooding with 16 arms and $M_{w,arm} = 300$ kDa (right).

Fig. 8. Pressure profiles (in MPa) after 250 days (left) and 3000 days (right) for the polymer flooding with 16 arms and $M_{w,arm} = 300$ kDa.

Table 4

Results of the recovery process for different nanoparticles flooding schemes.

Case $Dia < 0 > / Dia_{max} / K_{agg}$	Oil recovered		Case $Dia < 0 > / Dia_{max} / K_{agg}$	Oil recovered	
	m^3	%OOIP		m^3	%OOIP
Reference Waterflooding	44,310	23.6	5/250 nm/5 $\times 10^{-4}$ day $^{-1}$	47,280	25.2
5/250 nm/10 $^{-4}$ day $^{-1}$	47,330	25.2	40/250 nm/5 $\times 10^{-4}$ day $^{-1}$	45,330	24.2
5/250 nm/5 $\times 10^{-3}$ day $^{-1}$	46,600	24.9	100/250 nm/5 $\times 10^{-3}$ day $^{-1}$	44,930	24.0

Fig. 9. Oil recovery, fractional flow (top left), flowrates (for the 5/250 nm/10 $^{-4}$ day $^{-1}$ case – top right), and pressure drop (bottom) as a function of time for the reference case and several nanoparticles schemes.

Fig. 10. Aqueous phase viscosity after 500 days in the 5/250 nm/ 10^{-4} day^{-1} (left), and 40/250 nm/ $5 \times 10^{-4} \text{ day}^{-1}$ (right) cases.

Fig. 11. Particles aggregation diameters as a function of time.

different scenarios were selected, included in Table 5, considering the adsorption process. The results are presented in Table 5 (compared to Table 4 – in red numbers) and Figs. 12 and 13.

The wettability alteration has a major influence on the recovery factor, comparing the results from Table 4 with those presented in Table 5. Nevertheless, the wettability alteration modified the flowability conditions in the porous medium, lowering the mobility ratio for the same aqueous/oleous viscosities. This is evidenced more when the particles and/or the aggregation rate are bigger (Fig. 12). However, even though the wettability alteration was indeed higher with bigger particles, there are several factors due to which the sweeping efficiency was not the highest. Firstly, the viscosity of the water phase was lower with bigger clusters/particles. Secondly, the porosity and absolute permeability reduction were also substantially higher with bigger particles, which hindered the flow of oil to the production well (Fig. 13).

From this point a major conclusion is drawn regarding the

Fig. 12. Oil saturation profile after 3000 days for the 5 nm/250 nm/ 10^{-1} day^{-1} case considering the adsorption of nanoparticles.

nanoparticles flooding: even though they alter the rheological properties of the solution, this is not their main advantage in a recovery process. This is confirmed by the results, in which the maximum viscosities are lower than those in the non-adsorption case, but nevertheless the oil recovered is substantially higher (Figs. 12 and 13). Nanoparticles in oil-wet media should be mainly used as a mean to alter the formation properties. The wettability alteration also alters the mobility ratio by counteracting the viscosity difference with the relative permeabilities (Fig. 14). It is evident then that the degree of alteration depends on the flowability of the water phase in the porous media. The highest adsorption values are obtained in the wells' regions, where concentrations tend to be higher, which can also be appreciated in the absolute permeability reduction after the flooding (Fig. 15).

Table 5

Oil recovery for previous nanoparticles flooding considering adsorption and wettability alteration.

Case	Oil recovered		Case	Oil recovered	
	m^3	%OOIP		m^3	%OOIP
$Dia < 0 > / Dia_{max} / K_{agg}$			$Dia < 0 > / Dia_{max} / K_{agg}$		
5/250/ 10^{-4} day^{-1}	54,490	29.1 (+3.8)	40/250/ $5 \times 10^{-4} \text{ day}^{-1}$	49,750	26.5 (+2.4)
5/250/ $5 \times 10^{-3} \text{ day}^{-1}$	52,420	28.0 (+3.1)	100/250/ $5 \times 10^{-3} \text{ day}^{-1}$	51,730	27.6 (+3.6)

Fig. 13. Aqueous phase viscosity (left – in mPa·s) after 500 days, and nanoparticles adsorbed in the porous media (right) after 3000 days, for the 5/250 nm/ 10^{-4} day^{-1} case, considering the adsorption of nanoparticles.

Fig. 14. Factors altering the relative permeability of the oleous phase for the 5/250 nm/ 10^{-4} day^{-1} (left) and 100/250 nm/ $5 \times 10^{-3} \text{ day}^{-1}$ (right) cases, considering the adsorption of nanoparticles.

Fig. 15. Absolute permeability reduction in the 5/250 nm/ 10^{-4} day^{-1} (left) and the 100/250 nm/ $5 \times 10^{-3} \text{ day}^{-1}$ (right) cases, after 3000 days of simulation considering the nanoparticles adsorption.

5. Conclusions

This paper presents and applies the research done so far on nanotechnology and polymer chemistry into a simulator for EOR processes. The simulations were aimed at understanding how the polymers' architecture affect the recovery factor and at describing the potential of using nanoparticles in EOR processes.

The study consisted in using both agents in separate flooding processes, discussing the physical mechanisms involved. The polymer's architecture proved to be an important factor, as reported by several authors. Comb polymers yielded slightly better recovery factors than star-shaped ones, and substantially higher than the reference linear polymer. The viscosifying properties are determined by the number of arms and the relationship between arms and backbone's molecular

weights. The degradation model chosen allowed obtaining different variations in the molecular weights of arms and backbone, which can vary the structure depending on the time from comb- to star-shaped polymers. Nevertheless, it is considered that more advanced architecture and degradation models should be developed in order to increase the accuracy of the simulator. On the other hand, nanoparticles increased the oil recovered by reducing the interfacial tension between the phases and by modifying the rock wettability, allowing the oil to flow more easily, even without increasing significantly the water phase viscosity.

All in all, the simulations allowed establishing the main mechanisms used in nanoparticles flooding as well as determining the importance of the polymer's architecture. The nanoparticles can be used as a way to improve the oil recovery after waterflooding, but it is considered that their main functionality is to boost traditional EOR processes, acting combined with a different EOR agent. On the other hand, the importance of the architecture will allow synthesizing new polymers for EOR using the desired properties obtained with simulators such as the one presented in this paper.

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