



Plenty of Room at the Bottom: Nanotechnology as Solution to an Old Issue in Enhanced Oil Recovery

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Abstract: During the past half-century, the prefix "nano" attached to several words, such as "technology", "motors", "device", and so on has denoted cutting-edge research fields and topics at the forefront of classical scientific disciplines. Possible application fields have been frequently evoked, even if real-life examples are still difficult to find. The present review analyzes how nanotechnology is utilized in enhanced oil recovery (EOR) processes so as to increase the efficiency of mature oilfields. Nanotechnology in EOR is classified into three categories: nanoparticles/nanofluids, nanoemulsions, and nanocatalysts. The advantages at the nanoscale are also described and discussed, including an overview of manufacturing methods as well as the concerns about their possible environmental impacts. Clearly, nanotechnology has the potential to boost EOR techniques, although there are still many questions and drawbacks to be tackled.

Keywords: EOR; petroleum; nanotechnology; nanocatalysts; nanofluids; nanoemulsions

1. Introduction

It is undeniable that oil has radically changed how we live and how our economy works in a way that no kind of fuel in the past has ever done. The changes generated in both our society and economy over the past 200 years are more than evident. However, oil is not a renewable energy source and many authors have speculated about the future of the oil industry [1]. It is obvious that the global economy is not ready to replace traditional fossil fuel-based energy sources. This implies two possible outcomes: either we start exploiting unconventional oil sources, increasing the price of refined products; or we make better use of conventional oil reservoirs. Enhanced oil recovery (EOR) aims at developing the latter, thus factually bridging the transition towards the use of renewable energy sources. Throughout the operation of an oilfield, three different stages can be distinguished. The first stage (i.e., primary recovery) is based on the production of oil by natural drive mechanisms. Then, the secondary recovery stage takes place. A fluid (i.e., water or an immiscible gas) is injected in order to displace the oil to producing wells. These two recovery stages can then account for 50/55% of the initial oil in place (IOIP). Then, the tertiary stage or EOR begins.

The main objective of all EOR processes is to diminish the oil saturation below the residual oil saturation (S_{or}). This is defined as the saturation during a waterflooding at which the oil production becomes discontinuous and the capillary forces immobilize the remaining oil [2]. EOR aims at modifying the physical and/or chemical properties in the fluids and/or the reservoir, and can be classified into three main branches (Figure 1). Even though nanotechnology is not an EOR technique per se, the unique features found at the nanoscale allow the performance of current methods to be improved. The use of nanotechnology in chemical EOR has recently been reported in the form of polymer nano-composites (PNPs or polymer-coated nanoparticles) [3–5] and silica nanoparticles [6–9].

The aim of this work is to describe the use of nanotechnology for EOR purposes by focusing on the physical characteristics of the nanoscale. The reader interested in other EOR techniques which have already been applied is kindly referred to more specific literature for this application [10].



Figure 1. Scheme with the most relevant oil recovery techniques, from primary and secondary recoveries (or conventional mechanisms) to tertiary or enhanced oil recovery (EOR), and possible applications of nanotechnology in EOR. Figure adapted from Ref. [11].

Nanotechnology-assisted EOR processes rely on one (or several) of the following factors: mobility control using viscosity-increasing solutions, altering the rock wettability, reducing the interfacial tension (IFT), and lowering the oil viscosity by means of nanocatalysts. The efficiency depends on how the process behaves at both the macro- and microscale. The microscopic efficiency considers the displacement of the fluids at a poral scale and measures how effective the displacing agent is in mobilizing oil in place (i.e., where the rock and oil make contact). At this level of magnitude, the geometry of the pores, viscous forces, capillary pressure, rock wettability, and rheological behavior (including viscoelasticity) play a major role. The macroscopic efficiency is the relationship between the connected reservoir volume being swept by the injected fluid(s) and the volume of oil originally in the reservoir. The parameters affecting this factor are: the rock heterogeneity and its anisotropy, the absolute permeability, the mobility ratio (M), and the gravitational segregation. The mobility ratio is a relationship between two fluids present in a porous medium that allows determination of how easily one will flow with respect to the other through the reservoir. The sweeping efficiency increases as M decreases, so it is considered as an indicator of the stability and efficiency of the displacement process. As the mobility increases ($M \gg 1$), the flow becomes unstable due to the difference in the flowing capabilities [12]. Thus, a large viscosity difference between both fluids causes the fingering of water through the more viscous oil.

The relationship between nanotechnology and the petroleum industry is not new, but it has been developing for the past 30 years (in the case of nanocatalysts). In downstream processes such as petroleum refining, zeolites are employed to extract up to 40% more gasoline in catalytic cracking units than their predecessors [13]. In upstream operations, the first application of nanotechnology was the development of nano-enhanced materials [14,15]. By means of nanotechnology, lighter equipment capable of withstanding harsh conditions was produced. Nanotechnology could also be used to

develop new metering techniques with nano-sensors for high-temperature, high-pressure deep wells and hostile environments; for reservoir characterization; fluid flow monitoring; new imaging and computational methods allowing better discovery, sizing, and reservoir characterization; as well as new cementing materials [15–22].

Recovery mechanisms in EOR operation can also be enhanced using nanotechnology [14,23–27]. Moreover, the scale of the nanomaterials makes the suitable injection into porous media relatively easy, even in low-permeability fields where, statistically, the pore throat width ranges between 100 and 10,000 nanometers. Concerning EOR operations, one of the most relevant topics at present is how the nanoparticles behave in the harsh conditions present in oilfields (i.e., high pressure, high temperature, and high salinity), and how these conditions affect the particles' recovery efficiency [28–31]. Generally speaking, there are three main nanotechnologically-enhanced processes in EOR: (a) the addition of nanoparticles in the displacing agent enhancing its rheological properties, which are known as nanofluids; (b) the use of nanoparticles as stabilizing agents in the formation of nanoemulsions; and finally, (c) active nanoparticles working as nanocatalysts injected in order to perform in-situ upgrading operations in the porous medium before extraction.

Nanofluids, mainly consisting of nano-sized colloidal dispersions, have successfully been developed in laboratories, and the upcoming challenge is to develop techniques for cost-efficient industrial-scale production techniques [32]. They can be designed to be compatible with reservoir fluids/rocks and be environmentally friendly [16]. Some newly developed nanofluids have shown extremely improved properties in applications such as drag reduction, binders for sand consolidation, gels, wettability alteration, and anticorrosive coatings [33,34]. In heavy oil reservoirs where EOR thermal production processes are usually utilized, the application of nanotechnology yielded several breakthroughs. Nanocatalysts for in-situ upgrading of heavy oil, what some authors have defined as an "underground refinery" [35–37], constitute a novel approach to dealing with these systems.

Aim of This Review

To date, several reviews have been written about the role and potential of nanotechnology in the petroleum industry, in both down- and upstream processes. These have mostly been focused on the use of nanotechnology for drilling and completion [22,38–40], reservoir imaging and characterization [38–40], numerical modeling of nanoparticles in porous media [22], downstream refining [39], and sensing and production operations (e.g., well stimulation) [22,38–40]. However, to the best of our knowledge, a comprehensive review of all the possible applications of nanotechnology in EOR processes is still lacking, including an extensive analysis of the physical mechanisms involved and a description of laboratory- and field-scale applications [22,39–41]. The purpose of this review is then to present the developments in this field, describing the theory and exposing the conclusions, advances, and points requiring further research.

2. Nanofluids

Nanofluids can be defined as dilute liquid colloidal suspensions of nanoparticles (with volumetric concentrations ranging from 0.0001% to 10%) when at least one of their principal dimensions is smaller than 100 nm [42]. Since Choi [43] coined the term, numerous publications and research have dealt with the applications of nanofluids in different fields [44,45]. Broadly speaking, nanoparticles have a core/shell structure, with different geometric configurations and material combinations that allow them to fulfill a broad spectrum of requirements (Figure 2).

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Figure 2. Schemes of the different core/shell nanoparticles: (**a**) spherical core/shell, (**b**) hexagonal core/shell, (**c**) multiple small core materials coated by a single shell material, (**d**) nanomatryushka material, and (**e**) movable core within a hollow shell material. Figure reproduced from Ref. [46].

Decreasing the particle size leads to a change in the interatomic spacing. This can be related to compressive strains induced by the internal pressure due to the nanoparticles' small radius of curvature [32]. Nanoparticles and nano-dimensional layers can adopt different crystal structures than those shown by normal bulk material. There are several techniques or processes capable of creating these nanostructures with different degrees of quality, speed, and cost. These approaches can be classified into two categories: bottom-up and top-down [35,47,48]. Top-down methods are those in which nanoparticles are prepared from bulk materials, generating isolated or atom clusters using distribution techniques involving physical methods such as laser beam processing, milling or grinding, or photolithography. As advantages, top-down methods offer reliability and device complexity, but they generally imply relatively high energy consumption and produce more waste. On the other hand, bottom-up methods involve molecular components as starting materials linked to each other by means of chemical reactions as well nucleation and growth processes so as to promote the formation of nanoparticles [49–51]. These latter techniques can be split into three different categories: chemical synthesis, self-assembly, and positional assembly. So far, according to the literature [52], positional assembly (even though it presents drawbacks as a manufacturing tool) is the only technique allowing single atoms or molecules to be placed deliberately one-by-one in the lattice.

The potential benefits of nanotechnologies have been welcomed as far as health and environmental aspects are concerned (e.g., in water sanitation). Nevertheless, some concerns have been expressed since the features being exploited might also have a negative impact on human health and the environment. The former could generate possible long-term side effects associated with medical applications and the biodegradability of nanomaterials [53]. One of these examples was reported with nanoparticles as possible adsorbents/catalysts for heavy oil recovery and upgrading [35,36]. These were injected in a porous medium where a percentage remained deposited. They will persist in-situ for many years, but so far no study has been carried out on the long-term environmental effect of these nanocatalysts. A sustainable nanocatalyst should present—besides a higher activity, durability, and selectivity—recyclability in a cost-effective process [35].

2.1. Nanofluids and Enhanced Oil Recovery

Nanofluids in EOR is a relatively new field of research [15,22,54]. Silicon nanoparticles are currently the most common type of nanoparticles used due to economic reasons and their effectiveness in rock surface modification. Polysilicon nanoparticles (PSNPs) are an odorless ultrafine powder composed mainly of SiO₂ [55]. Nanoparticles are generally characterized by a high-energy state of

their surfaces. As such, they are applicable in EOR since they easily adsorb onto the surface of the rock formation, altering its wettability. PSNPs can be classified according to the effect they have on the wettability of the rock as: hydrophobic and lipophilic nanoparticles (HLPNs), lipophobic and hydrophilic nanoparticles (LHPNs), and neutral wet nanoparticles (NWPNs). When a colloid of PSNPs and solvent is injected in a porous media, four different phenomena will take place: adsorption, desorption, blocking, and transport. Since PSNPs can be considered as Brownian particles, different forces are responsible for the interactions between PSNPs and porous walls: the attractive potential energy of London-van der Waals, gravity, inertia, electrostatic forces between the particles, repulsion energy of electric double layers, Born repulsion, buoyancy, acid-base interaction, and hydrodynamics [56]. Since the mass and volume of nanoparticles are practically negligible, gravity and buoyancy forces are much smaller than the others. Nevertheless, due to the action of attractive forces, nanoparticles can undergo agglomeration and form larger particles/clusters of particles with significant mass, which may result in the deposition and destabilization of the suspension. If particles and porous media have opposite charges, then, depending on particles' relative position, there might be a significant gravity-opposing force. Considering only the bulk suspension, the most relevant forces affecting the particles' stability are the attractive van der Waals and repulsive electrostatic forces, described by the classical DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory. When the resultant of these forces is negative, the attraction is larger than repulsion between PSNPs and porous wall, causing PSNPs to be adsorbed.

2.2. Effect of Nanoparticles on Reservoir and Fluid Properties

Formation damage is an economic problem that is undesirable from the operational point of view, and can be caused by different unfavorable mechanisms, including (among others) chemical, physical, biological, and thermal interactions between formation and fluids. Nanoparticles can also be a source of formation damage, which is one of the most relevant topics regarding nanoparticle transport that should be analyzed before beginning EOR operations.

2.2.1. Aggregation and Retention in Porous Media

Porous media are generally composed of a complex and random structure of channels and throats. Four different mechanisms lead to formation damage [57,58]: (1) nanoparticle adsorption onto the rock surface, (2) mechanical entrapment (i.e., nanoparticles larger than the pore throat), (3) sedimentation or gravity settling, and (4) log-jamming (i.e., nanoparticles smaller than the pore throat accumulating and eventually leading to the blockage of the channel) (Figure 3).

The retention of nanoparticles will alter some reservoir properties. For instance, nanoparticles modify the absolute permeability. This can be expressed as a function of the initial absolute permeability and a flow efficiency factor of the cross-sectional area open to flow [32]. Besides, the retention process also modifies the phases' relative permeabilities, a product of the wettability alteration. The latter comes to a limit when all the surface of the rock are covered by the nanoparticles reaching the maximum wettability alteration in the porous media. From that moment on, further retention of nanoparticles will affect the porosity and absolute permeability [59]. Related to this phenomenon is the aggregation or creation of larger clusters with similar nanoparticles (i.e., homoaggregation) or other colloidal/suspended particles (i.e., heteroaggregation). This increment in the size, and therefore in its critical velocity, can lead to sedimentation in the channels or throats. Moreover, these clusters can subsequently capture free nanoparticles, leading to a secondary aggregation process, increasing their size until a critical "diameter" is reached and the cluster collapses and is divided into several smaller pieces. Both the adsorption of nanoparticles and the heteroaggregation processes depend on a number of factors, namely: type of rock formation, pH, and the ionic strength or the salinity. Nevertheless, not all collisions of nanoparticles will form clusters, since this could be hampered by, for instance, steric or electrostatic hindering [60].



Figure 3. Mechanisms of nanoparticles' entrapment in porous media. Figure adapted from Ref. [58].

2.2.2. Effect on Rheology and Viscoelasticity

Experiments have evidenced that the addition of nanoparticles into water increases the shear viscosity. Water molecules layered at the nanoparticles' surface decrease the fraction of adjacent mobile fluid molecules, increasing the shear viscosity and elastic properties [61,62]. This effect becomes more noticeable in polymer/nanoparticle solutions in which the storage and loss moduli are strongly affected by the nanoparticle concentration. This enhances the viscoelastic properties of the sweeping agent and therefore increases the oil recovery factor [63,64]. The former can be increased by either increasing the nanoparticle concentration, or by modifying the size of the particles [65]. Einstein was the first to study the influence of particles on the viscosity of a fluid at very low volume fractions (c < 0.02), predicting a linear increase with the particle volume concentration. Since Einstein's formula, new correlations have been published taking into account, among others, particle size and shape, higher volume concentration, temperature, pH, and size distribution [66,67]. It is important to note that there are contradictory results in the literature, showing different trends with respect to the viscosity dependency on the particle size: both an increase and a decrease were observed with smaller particle sizes as well as an independence of the rheological properties on the particle size [66,68]. However, in accordance with Meyer [66], it is considered that the increase in viscosity in nanofluids comes from two major sources: fluid-particle and particle-particle interactions. These are dependent on the overall surface area of the nanoparticles. At the same concentration, smaller particles show a larger surface area, and thus the viscosity should be higher. Nanoparticle aggregation is then one of the major causes of detriment in the rheological properties of nanofluids.

The rheological properties of different nanofluids have been reported: organic/inorganic hybrid aqueous solutions composed by mixing silica nanoparticles and hydrophobically associating polyacrylamide (HAPAM) [8], hydrolyzed polyacrylamide (HPAM) [6,7,55], sulfonated polyacrylamide (SPAM) [6], acrylamide-styrene-AMPS (2-acrylamido-2-methylpropane sulfonic acid) copolymers (PA-S) [69], and aqueous solutions [56]. The use of nanoclays as nanoparticles for EOR purposes was also considered along with polymers and surfactant/polymer systems: using with HPAM [70] or HPAM-SDS (sodium dodecyl sulfate) [71]. Moreover, advanced alternating EOR processes were described in the literature using silica nanoparticles in water-alternating-gas techniques [72,73]. Hybrid nanofluids (polymer/nanoparticles) exhibited improved viscosity properties and their tolerance to heat and saline environment (total dissolved solids or TDS > 120,000 ppm) was also enhanced, as was their long-term thermal stability (Figure 4a,b). In the flooding experiments, the nanofluid solutions exhibited better results than those obtained for water or polymer

solutions (Figure 4c). Research on biopolymers was also performed using xanthan gum, which is used in the upstream industry as a rheological enhancer, mixed with nanoparticles [8,74]. These studies represent clear examples of the development of hybrid nanofluid technologies with different kinds of polymers, which have a potential use in the upstream oil and gas industry. Nevertheless, these hybrids might also be useful in different areas of science.



Figure 4. Rheological properties and EOR performance of the nano-copolymer and hydrolyzed polyacrylamide (HPAM). Effect of shear rate on viscosity for polymer solutions (0.2 wt%) prepared with distilled water (**a**); viscosity versus temperature for HPAM and AM/AA/NSFM solutions (0.5 wt%) ($\dot{\gamma} = 7.34 \text{ s}^{-1}$) (**b**); and core flooding experimental results of AM/AA/NSFM and HPAM (0.2 wt%) at 65 °C (**c**). Figure reproduced from Ref. [63]. AM/AA/NSFM: acrylamide/acrylic acid/nano-SiO₂ functional monomer.

The interactions between nanoparticles and polymers as a function of their concentrations play a major role in their viscosifying properties. For example, a reinforced three-dimensional network structure was formed in the HAPAM/silica system [8]. The formation of this network is attributed to the chemical bonds created between carbonyl groups in the polymer backbone and silanol functionalities in the nanoparticles, considered to act as a sort of physical crosslinker among the macromolecules. Below a certain critical aggregation concentration (CAC), the intramolecular hydrophobic association is dominant in HAPAM solutions, forming small aggregates. In this condition, the polymer chains have a small chance of interacting with silica nanoparticles. As the polymer concentration increases to the CAC, inter-molecular hydrophobic associations become more predominant in the solution, thus creating a network of polymer chains. At even higher concentrations (>CAC), the strong associations caused by the number of hydrophobic groups have a negative effect on the interaction between polymer and silica nanoparticles (Figure 5).



Figure 5. Interaction between hydrophobically associating polyacrylamide (HAPAM) polymer and silica nanoparticles as a function of the polymer concentration. Figure adapted from Ref. [8]. CAC: critical aggregation concentration.

2.2.3. Effect on Interfacial Tension

Silica hydrophilic nanoparticles have also proven to have an effect on the IFT. Nanoparticles migrate to the interface, thus reducing the oil/brine contact. This works similarly to surfactants, but using a different principle [54,75]. The mechanisms behind the adsorption of neutral particles are explained using the lattice-Boltzmann method, and then they were compared with those of surfactants [76]. Surfactants adsorb at the liquid/liquid interface due to their well-known amphiphilic properties, whilst neutral wetting nanoparticles adsorb due to the fact that maintaining a particle–fluid interface requires less energy. This behavior can be explained considering the free energy of the system. The reduction of the latter requires either the reduction of interfacial tension (achieved using surfactants), or the reduction of the area of contact, which is indeed the effect of adsorbed nanoparticles. In emulsions nanoparticles can also break up oil droplets (Figure 6), making it easier to migrate through the porous media [76].



Figure 6. Oil droplet breakup in the presence of nanoparticles: the droplet without particles in a steady state condition (**a**); and snapshots of the droplet covered with particles at different times until the breakup (**b** to **g**). Figure adapted from Ref. [76].

Different kinds of nanoparticles were investigated concerning their influence on the interfacial properties: polysilicon nanoparticles (PSNPs) [9,77,78], amphiphobic nanoparticles based on functionalized carbon nanotubes (CNTs) [79], oxides of different metals (e.g., Al, Zn, Mg, Fe, Zr, Ni, Ti) [6,9], and magnetic nanoparticles [80]. One of the reported advantages of the novel compound $CoFe_2O_4$ -chitosan nanoparticles is their biodegradability, which makes them more environmentally friendly than traditional products (Figure 7).



Figure 7. The effects of CoFe₂O₄-chitosan nanoparticles on interfacial tension (IFT). Figure reproduced from Ref. [80].

2.2.4. Effect on the Rock Wettability and Surface Wetting

In order to change the wettability, nanoparticles need to be adsorbed onto the rock surface [32]. It has been suggested that the improvement in contact line motion may have two potential underlying mechanisms, affected by the nanoparticles' presence [54,81,82]. These could be either the pressure gradient created due to the solid-like ordering fluid "wedge" in the vicinity of the three-phase contact line (Figure 8, left), or the nanoparticle adsorption onto the solid surface, resulting in a reduction of the friction (Figure 8, right).



Figure 8. Schemes of the nanoparticle ordering in the wedge of a spreading meniscus (**left**), and the lubrication effect provoked by nanoparticle adsorption onto the solid (**right**). Figure adapted from Ref. [81].

Pioneering work on this topic was presented by Wasan [83,84]. The wetting and spreading behavior of liquids over solid surfaces changes if these contain nanoparticles, surfactant micelles, globular proteins, or macromolecules. The process of spreading thin nanofluid films is driven by the structural disjoining pressure gradient. The disjoining pressure can be defined as the pressure originating when two surface layers reciprocally overlap [32,82]. The film tension is high near the vertex, caused by the particles ordering in the wedge confinement. As the tension in the film increases towards the top of the wedge, it causes the nanofluid to spread at the wedge tip. This results in an enhanced dynamic spreading behavior (Figure 9).



Figure 9. Nanoparticles in a wedge film. Scheme of the experimental set-up (**top**) and the nanoparticle distribution in a wedge film (**bottom**). Latex particles had diameter 1 µm. Figure adapted (top) and reproduced (bottom) from Ref. [83].

The result of this is that nanoparticles exert a large pressure throughout the wedge film relative to the bulk solution, eventually separating both phases [32]. An analytical expression based on the Ornstein–Zernike equation is as follows [84]:

$$\Pi_{st}(h) = \begin{cases} \Pi_1 \cos\left(\omega h + \phi_2\right) e^{-\kappa h} + \Pi_2 e^{-\delta(h-d)} & \text{for } h \ge d, \\ -P & \text{for } 0 \le h < d, \end{cases}$$
(1)

where *d* is the nanoparticle diameter and the other parameters ($\Pi_1, \phi_2, \omega, \kappa$) are fitted as cubic polynomials, functions of the nanoparticle's volume fraction. The term *P* is the nanofluid bulk osmotic pressure. The film–meniscus microscopic contact angle, θ_e , is related to the disjoining pressure by means of the Frumkin–Derjaguin equation [83,84]:

$$\Pi_0(h_e)h_e + \int_{h_e}^{\infty} \Pi(h)dh = \sigma_{o/nf}(\cos\theta_e - 1) = S,$$
(2)

where $\sigma_{o/nf}$ is the IFT between oil and nanofluid, *S* is the spreading coefficient, h_e is the equilibrium thickness of a thin film, Π_0 is represented by the sum of the droplet capillary and hydrostatic pressures, and Π is the disjoining pressure represented by the terms, $\Pi = \Pi_{vw}$ (van der Waals) $+\Pi_d$ (electrostatic or steric) $+\Pi_{st}$ (long-range structural forces). In different experiments using reflected-light digital video microscopy techniques, the spreading dynamics (and its underlying mechanism) in liquids containing different latex and silicon nanoparticles was studied (Figures 9 and 10) [83,85–87]. When an oil drop is surrounded by the nanofluid, the nanoparticles will concentrate and reorder around the drop, creating a wedge-like region between the surface and the oil drop (Figure 11).



Photomicrograph of oil drop on a solid surface

Figure 10. Scheme and photomicrograph depicting inner and outer contact lines and the nanofluid film region. Figure reproduced from Ref. [86].





This might have significant applications in EOR. The positioning of the nanoparticles inside the wedge is a consequence of the increase in the entropy of the overall dispersion caused by allowing a higher degree of freedom for the nanoparticles in the bulk liquid [82,83]. The electrostatic repulsion between the particles rises as the size of the nanoparticles decreases, therefore increasing the structural

disjoining pressure. The force is then maximum at the tip of the wedge (Figure 12). The spreading increases with a decrease of the film thickness (i.e., the number of particle layers in the film) [83] (Figures 11 and 13). Concerning the presence of salt, increasing its concentration will lower the repulsive forces between nanoparticles, and thus the pressure driving the wedge film will be reduced. Due to this, an increase in the TDS has a negative effect on oil removal when using nanofluids.



Figure 12. Pressure on the walls of a 0.5° contact angle wedge at the vertex as a function of the dimensionless radial distance. Particle volume fraction $V_m = 0.36$ and particle diameter d = 10 nm. Figure reproduced from Ref. [84].



Figure 13. Scheme of the disjoining pressure acting on an oil droplet. Figure reproduced from Refs. [84,85].

A key factor in oil recovery is how oil droplets detach from solid surfaces. In order to study how nanofluids can improve this mechanism, a series of simulations via molecular dynamics techniques were performed with these droplets immersed in charged nanoparticle suspenions [88]. According to the results, suspensions of charged hydrophobic nanoparticles can be used as high-performance agents in detaching oil droplets from solid surfaces in EOR applications. The process of detachment can be divided into three stages [88,89]: the contact line shrinks because of the decrease in the IFT, induced by the surfactant adsorption at the oil–water interface; the diffusion of water detaches the oil

from the solid substrate/wall in the vicinity of the contact line; and finally, the droplet detaches when the contact radius becomes sufficiently small.

Besides these analyses, the way in which different nanoparticles alter the rock wettability, modifying the contact angle and the relative permeability, has also been throughly discussed. Al-Anssari [90] investigated the use of nanofluids to alter oil-wet carbonate rocks. Scanning electron microscope (SEM) (Figure 14) and atomic force microscope (AFM) images verified the adsorption process of the particles onto the calcite surface, forming larger clusters. This process was also evidenced by the significant change of the rugosity of the rock samples: the original calcite surface was flat, but the nanofluid changed its rugosity significantly, yielding an irregular coating layer spread along the surface. These results are consistent with AFM measurements on the treated calcite substrate, where higher surface roughnesses were found after the nanofluid treatment. Several kinds of nanoparticles have been reported in the literature as agents to modify the wettability of rock formations, but the most common material tested is PSNP [7,77,78,90–92]. Besides polysilicon nanoparticles, the following materials were also tested: carbon-based fluorescent nanoparticles [77], oxides of different metals (e.g., Al, Zn, Mg, Fe, Zr, Ni, Ti) [92] (Figure 15), and polymer-coated nanoparticles (PNPs) [4].

Nanoparticles have also proved to have a potential use as scale inhibitors. Scale formation can cause the production channels to become blocked, leading to a significant reduction in productivity/recovery efficiency. Scale inhibitors are applied in order to prevent or lower the amount of scale formation. Silica nanoparticles can also be used as a scale inhibitor. An optimum amount of silica nanoparticles can reduce the scale deposition, which is still a challenging research topic in the oil industry, as is the design of environmentally friendly scale inhibitors [91].



Figure 14. SEM images of an oil-wet calcite surface before (**top**) and after (**bottom**) the nanofluid treatment with 4 wt% SiO₂ in 5 wt% NaCl brine, showing the irreversibly adsorbed silica nanoparticles. Figure reproduced from Ref. [90].



Figure 15. Microscopic images of oil droplets (flipped image) at 26 °C in the presence of brine (1), Al₂O₃ nanofluid (2), TiO₂ nanofluid (3), and SiO₂ nanofluid (4). Figure reproduced from Ref. [92].

3. Nanoemulsions

An emulsion consists of at least two immiscible liquids, where one of these liquids is dispersed as small droplets in the other [93,94]. Standard emulsions usually have droplets with mean radii between 100 nm and 100 µm. Nanoemulsions are generally defined as emulsions containing droplets with mean radii between 10 to 100 nm [95–97] or, according to different sources and authors, covering the size range 50 to 500 nm [98]. Nanoemulsions exhibit the typical properties of all emulsions, but with some specific characteristics that distinguish them from standard macroemulsions [95]. The droplet size is smaller than the wavelength of light ($r \ll \lambda$), causing them to be transparent or slightly turbid. Furthermore, the droplet size leads to a better stability to gravitational separation and aggregation than conventional emulsions [95,96]. Gravity forces have a negligible effect, whilst Brownian motion is likely to put the droplets into motion and provide them with a driving force for destabilization processes. Besides, the Laplace pressure excess inside the droplets is quite large due to their size, and the droplets are difficult to deform (i.e., shear, elongation, or break), provided that the IFT is very low.

Unlike microemulsions (size range < 50 nm), which are also transparent or translucent and present thermodynamic stability, nanoemulsions are only kinetically stable. Nanoemulsions are generally stabilized by the use of surfactants, but solid particles suspended in one phase can also stabilize emulsions. Emulsions stabilized by means of solid particles have been studied for a long time, and were named after Pickering, who discovered that the droplets' coalescence is suppressed when solid particles are adsorbed at the oil–water interface (Figures 16 and 17) [99]. The solid particles adsorb at the interface of the two liquids, thereby creating a physical barrier that hinders coalescence [100,101]. The Pickering emulsions' stability is significantly affected by several parameters, among them the composition of the organic and aqueous phases, the contact angle, particle size and concentration, and particle/particle interactions at the interface [100].



Figure 16. SEM image of 10 μ m-diameter colloidosome composed of 0.9 μ m-diameter polystyrene spheres. The colloidosome was formed with an oil droplet containing 50 vol% vegetable oil and 50 vol% toluene, and a water phase containing 50 vol% glycerol (**A**). The close-ups show the 0.15- μ m holes that define the permeability (**B**,**C**). Figure reproduced from Ref. [102].



Figure 17. Scheme of a water-in-oil emulsion stabilized with surfactant and nanoparticles. Figure reproduced from Refs. [35,103].

So far, emulsions have been considered in EOR processes as an independent technique, but the combination of these with different fluids might also yield interesting results. One of these combinations is with CO₂. Because of the low density, and more importantly very low viscosity of the supercritical and liquid CO₂, the macroscopic sweep efficiency of CO₂-related EOR processes is poor. Surfactant-stabilized CO₂ foams is one way to solve the mobility problem, but a different one arises: the long-term stability. The surfactant-stabilized foams require continuous regeneration. Moreover, a fraction of the surfactant is adsorbed on the rock, increasing material-related costs. So, the use of nanotechnology was a novel way to tackle this issue by using nanoparticles in stabilizing CO₂ foams (Figure 18). Some results [104,105] showed that nanoparticle foams are notably more stable than surfactant ones due to the nanoparticles' high adsorption energy at the gas–liquid interface. Moreover, the attraction between nanoparticles and the gas–liquid interface is believed to help in minimizing the nanoparticle loss to the rock formation, and silica nanoparticles are expected to withstand the harsh reservoir conditions better than standard surfactants [22,104].

Nanoemulsions containing oilfield chemicals can be used in many applications, such as well treatments (e.g., scale inhibition, fracture acidizing, etc.), flow assurance, deposit removal and clean-up, and also for EOR operations [95,106]. The nanoparticles reported in the literature as stabilizers are: SWCNTs (single-wall carbon nanotubes)/silica nanoparticles [107], MWCNTs (multi-walled carbon nanotubes)/silica nanoparticles [108] (Figure 19), hydrophilic SiO₂ or partially hydrophobic clay [104,109], spherical nanoparticles of cross-linked polystyrene [110], and zinc oxide (ZnO) or aluminum oxide (Al₂O₃) [111]. Besides these stabilizers, the possibility of using surfactant along with the SWCNTs/silica nanohybrid was studied [107]. This system showed an improved dispersion stability at the expense of reducing the interfacial activity of the nanoparticles, causing them to stay in the aqueous phase (Figure 20). These could also be used to support a catalytic conversion of oil products in porous media (see **Nanocatalysts**).



Figure 18. Foam stability results in (**a**) SDS surfactant; (**b**) nanoparticle-stabilized CO₂ foam; (**c**) foam coalescence as a function of the bubble diameter; and (**d**) foam quality represented as a function of the bubble density (bubbles/mm²) (scale bars = 400 μ m). Figure reproduced from Ref. [104].



Figure 19. (a) SEM image of a nanohybrid structure with a resolution of 500 nm; and (b) Transmission electron microscope (TEM) image of the nanohybrid structure. The carbon nanotube structure as well as the silica particles are clearly distinguished Figure reproduced from Ref. [108].





Figure 20. Scheme of nanohybrid particles carrying catalytic species in the oil and water phases (**top left** and **right**, respectively). (**bottom**) TEM image of Si nanoparticles and SWCNTs (single-wall carbon nanotubes) after ultrasonication in water for 3 hours. Figures (top left and right) adapted from Ref. [107]; Figure (bottom) reproduced from Ref. [99].

A major problem remaining to be tackled lies in the stability of nanofoams as the temperature increases [109]. However, nanofoams showed better stability and tolerance than SDS foams due to the presence of nanoparticles. The bubbles in the nanohybrid maintained their spherical or ellipsoidal shape because of the enhanced surface dilational viscoelasticity (Figure 21) [112].

This property was tested in oil recovery processes from dead pore ends. The SiO_2/SDS foam recovered more oil due to the improved viscoelasticity properties as well as a reduction in the IFT (Figure 22). The nanoparticles on the bubble surface improved the stability resistance, mainly against Ostwald ripening and film rupture [109]. When the bubbles entered the dead-end pore, the microforces acting on the oil droplet also contributed to improve the sweeping efficiency (Figure 23).



Figure 21. Behavior of foams at different temperatures and as a function of time: (1) SDS at 60 °C, (2) SiO₂/SDS at 60 °C, (3) SDS at 80 °C, and (4) SiO₂/SDS at 80 °C. Figure reproduced from Ref. [109].



Figure 22. Residual oil displacement in a dead-end being swept by different fluids: (**a**) brine, (**b**) SDS foam, and (**c**) SiO_2/SDS foam flooding. Figure reproduced from Ref. [109].



Figure 23. Difference between the displacement of an oil droplet on a pore wall using SDS foam (**left**) and SiO₂/SDS foam (**right**). Figure reproduced from Ref. [109].

In the flooding experiments, the nanoemulsions also exhibited better results than those obtained for standard waterflooding or EOR processes (Figure 24) [77,111]. A different line of research involved the application of CO_2 foams stabilized with silica nanoparticles [113]. These nanoemulsions in EOR flooding processes showed that nanoparticle CO_2 foams increased the oil recovery as compared to the standard CO_2 gas flooding (Figure 25) techniques, achieving a better sweeping efficiency [104].



Figure 24. Oil recovery during EOR flooding: (**top left**) 0.5 wt % SDS, (**top right**) 0.1 wt % SiO₂ + 0.5 wt % SDS, (**bottom left**) 1.5 wt % SiO₂ + 0.5 wt % SDS, and (**bottom right**) 2.0 wt % SiO₂ + 0.5 wt % SDS. Figure reproduced from Ref. [109].



Figure 25. Comparison of the oil recovery after a waterflooding with CO_2 vs. nanoparticle– CO_2 foams. Images of initial oil in place (IOIP), secondary recovery, and CO_2 flood (**top left**); nanoparticle-stabilized CO_2 foam flooding (**top right**); cumulative oil recovery (**bottom left**); and an enlarged plot of the recovery after the waterflooding (**bottom right**). Figure reproduced from Ref. [104].

3.1. Nanoemulsion Stability

Nanoemulsions will eventually evolve according to several physicochemical mechanisms liable to affect any kind of emulsion (Figure 26), but with some particularities [22,93,94]. Generally speaking, the small droplet size of nanoemulsions confers a better physicochemical stability than conventional emulsions. Ostwald ripening or molecular diffusion is the main mechanism for nanoemulsion destabilization. Compared to conventional emulsions, nanoemulsions present better stability to gravitational separation (i.e., sedimentation or creaming) and droplet aggregation (i.e., flocculation and coalescence), but they are more susceptible to Ostwald ripening and chemical degradation [93]. In addition, since nanoemulsions are transparent or slightly turbid, ultraviolet (UV) and visible light can penetrate into them easily, which may trigger light-sensitive chemical degradation reactions [114].



Figure 26. Schematic diagram showing the most common instability mechanisms that take place in emulsions. Figure reproduced from Ref. [115].

Ostwald Ripening

Ostwald ripening is an important physical process which takes place because larger particles are thermodynamically more stable than smaller particles. Then, the mean size of the droplets in an emulsion increases over time as the system tries to lower its overall energy [93,116]. The mechanism involved in this process is the Kelvin effect, whereby small droplets have higher local oil solubility than larger ones due to the difference in the Laplace pressures [96]. The difference in the chemical potential of dispersed phase droplets as a function of the droplet size was given by Lord Kelvin [95]:

$$c(r) = c(\infty)e^{\frac{2\gamma V_m}{rRT}},$$
(3)

where $c(\infty)$ represents the bulk phase solubility, c(r) is the solubility surrounding a particle of radius r, and V_m is the molar volume of the dispersed phase. Furthermore, the quantity $\left(\frac{2\gamma V_m}{rRT}\right)$ is referred to as the characteristic length. Theoretically speaking, the process should lead to the formation of one single drop. This does not take place in practice since the rate of this phenomenon decreases as the droplet size increases [95]. Ostwald ripening can be quantitatively studied using plots of the cube of the radius as a function of time t (Lifshitz–Slyozov–Wagner theory) (Figure 27) [117]:

$$\omega = \frac{dr^3}{dt} = \frac{8}{9} \left[\frac{c(\infty)\gamma V_m D}{\rho RT} \right],\tag{4}$$

where *D* is the diffusion coefficient of the disperse phase in the continuous phase and ρ is the disperse phase density. In order to prevent Ostwald ripening, several methods were proposed [116]. Firstly, the addition of a second disperse phase component that is insoluble or nearly insoluble in the continuous phase (e.g., Tadros [95] suggested A–B–A block copolymers). If the secondary component has zero solubility in the continuous phase, the size distribution does not deviate from the initial condition ($\omega = 0$). Secondly, modifying the interfacial film at the oil/water (O/W) interface. According to the previous equations, a reduction in γ will lead to a decrease of this phenomenon. Polymeric

surfactants adsorbed at the O/W interface which do not desorb during ripening could lower the rate, and thus the ripening (Gibbs–Marangoni Effect) [118].



Figure 27. Ostwald ripening plots for alkane oil nanoemulsions stabilized using a SDS–polyethylene glycol (PEG) surfactant system. Figure reproduced from Ref. [96].

3.2. Preparation of Nanoemulsions

Stable nanoemulsions can be prepared either by high-or low-energy techniques [93,95,119]. High-energy processes use mechanical devices which are capable of generating disruptive forces, mixing and disrupting the oil and water phases, leading to the formation of small oil droplets [93,96]. These methods utilize mechanical energy devices which create nanoemulsions by means of transferring kinetic energy to the system, generating disruptive forces which eventually break up the phases. The most common equipment used are ultrasonicators, high-pressure homogenizers [97], and microfluidizers (Figure 28). High-pressure homogenization and microfluidization are used for the synthesis of nanoemulsions at a laboratory and industrial scale, whilst ultrasonication is used only at laboratory scale. One disadvantage is that these techniques usually require sophisticated instruments and high energy input. An advantage is that they allow a greater control of particle size and composition, and thus of the stability, rheology, and turbidity of the emulsion. Examples of these techniques include high-pressure microfluidic homogenization, ultrasonic emulsification, flow focusing, and satellite droplets [96,120–124].



Figure 28. (top) High-energy processes such as high-pressure homogenization and the ultrasonication break macroemulsion droplets into smaller droplets. (bottom) Basic scheme of a microfluidizer. Figures reproduced from Refs. [125] (top) and [126] (bottom). O/W: oil-in-water.

Since the energy demand is by far the major disadvantage of the previous methods, a possible solution is to develop techniques based on different physical phenomena, which are less energy-demanding. These low-energy approaches depend on the spontaneous formation of tiny oil droplets when the solution or environmental conditions are altered [95]. They are mainly dependent on the variation of interfacial phenomena/phase transitions as well as the surfactant physicochemical properties and oil to produce nanoemulsions [127]. Low-energy processes were developed taking into account the phase behavior and properties of the involved components, leading to the formation of nanodroplets [128]. These can be achieved either by changing the spontaneous curvature of non-ionic surfactants with changes in the temperature (keeping the composition constant), which is known as the phase inversion temperature, which is known as the emulsion inversion point (EIP) method [106]. An advantage of this method is that it uses the available energy of the whole system to form the nanoemulsion. On the other hand, the disadvantages are, among others, the complexity, the precise approach required, and the use of synthetic surfactants [130]. The most widely used low-energy methods include spontaneous emulsification, PIT, the solvent displacement method, the

phase inversion composition method (i.e., self-nanoemulsification method), membrane emulsification, and liquid–liquid nucleation [127,131].



Figure 29. Diagram describing the formation of nanoemulsions using the phase inversion temperature (PIT) method. Figure reproduced from Ref. [115]. W/O: water-in-oil.

4. Nanocatalysts

In heterogeneous catalysis processes, a desirable property is to present the maximum surface possible between the catalyst and the reactants in order to improve the reaction. This is the main reason why nanotechnology stepped into this field. A nanocatalyst is then defined as a substance with catalytic properties which have at least one nanoscale dimension, thus enhancing its catalytic capabilities [35,132]. Nanocatalysts can be classified into four different classes: nanoparticulate, nanoporous, nanocrystalline, and supramolecular catalysts [133]. A different classification sorts them as: mineral, water-soluble, oil-soluble, and dispersed [134]. Nanoparticles and nanoemulsions present improved capabilities to displace oil, but they face a problem when they are injected into heavy oil reservoirs. The high mobility ratios lead to the formation of channels or fingering. One solution may be injecting nanocatalysts to trigger in-situ chemical reactions to upgrade the oil by lowering the asphaltene and resin contents-a concept sometimes referred to as "underground refinery" (Figure 30) [22,35–37,135]. In order to assess the effectiveness of the upgrading process, some parameters should be evaluated. Two of the most significant parameters are the H/C atomic ratio and the number of carbon atoms per molecule (Figure 31). Any upgrading process whereby the number of carbon atoms in a molecule decreases (i.e., cracking) and the H/C increases (i.e., hydrogenation of unsaturated bonds) can be assessed as an indication of heavy oil upgrading.



Figure 30. Schematic representation of in-situ heavy oil recovery and upgrading, coupling ultradispersed nanocatalyst and the steam-assisted gravity drainage (SAGD) process. Light oil is then produced at the surface and the heavy molecules, solids, and minerals remain underground. Figure reproduced from Refs. [35,103].



Figure 31. Hydrogen-to-carbon ratio for several petroleum cuts. Figure adapted from Ref. [136].

The implementation of standard thermal EOR processes in heavy oil or bitumen reservoirs requires extensive heating [137]. Steam application is costly due to, among other, the infrastructure required, the possible environmental impacts, and its operational costs [138]. This is the point where nanotechnology started to be used to improve the steam flooding, mobilizing heavy oils in the reservoir. The main advantages of using nanocatalysts to enhance traditional EOR processes are [35]: (a) improved catalytic performance [135,139,140], (b) the probability of contacts among reactants is increased due to the nanocatalyst dispersion, (c) the propagation of nanocatalysts and in-situ reactions cause bitumen dissolution and viscosity reduction of the recovered oil, and (d) successful in-situ refining processes reduce the downstream operating costs as well as the environmental impact associated with the production of bitumen (e.g., solid waste by-products, greenhouse gas (GHG) emissions, SO_x/NO_x production, and fresh water consumption). However, there are still some topics

which need to be addressed. The economic aspect is one of them: further research is needed to improve the catalysis process. However, an even more serious topic is the catalysts' efficiency in the rock matrix. The activity of the catalysts depends, among other things, on the temperature field homogeneity in the porous medium. When the superheated water is injected into the formation, the oil surface temperature will be high, yet the temperature will gradually decrease as the distance from the injection point increases, causing the catalyst to lose its activity. The development of nanocatalysts capable of dealing with this gradient is also deemed necessary.

The first reported application of using metals in an upgrading process in oil by aquathermolysis was made by Clark [141]. In this study, aqueous metal salts were used along with a steam stimulation process, showing that produced oil had improved physical characteristics. The studies carried out on the topic were focused mainly on the particles used as nanocatalysts, and a minor part dealt with the technologies used to increase the temperature in order to trigger the upgrading processes. The materials reported in the literature are: VO^{2+} [142], Ni [36,37,142–146], Fe [142,143,147], W [36,37,144,148], Mo [36,37,144], Cu [143,147], Zr [148], Co [147], Cr [147], Pd [147], C [149], SiO₂ [150], SiO₂/nanoFe [151], K₃PMo₁₂O₄₀ [152], and nanoclays (montmorillonite (MMT), modified with a quaternary ammonium salt) [153].

As in every mass transport phenomenon, two important aspects must also be considered: the stabilization and transportation of the nanocatalysts [143]. It is crucial that the nanoparticles move at the oil-water interface for the upgrading to take place. Furthermore, it is desirable to keep the nanoparticles in the reservoir after the catalysis process, causing negligible damage to the permeability of the porous media. These improved properties caused an increase in the recovery efficiency in laboratory flooding experiments [36,37]. The influence of the nanoparticles was appreciated in experiments under different injection conditions: the recovery of vacuum gas oil (VGO-a product of vacuum distillation columns) without nanocatalysts; the recovery of diluted VGO, again in absence of nanoparticles; and the recovery in the presence of trimetallic nanocatalysts in emulsion with VGO. The results evidenced the nanocatalysts' effectiveness for thermal EOR purposes compared with the first two cases (Figure 32). This influence was also demonstrated using nanoclays on asphaltene deposition in a vapor extraction process (VAPEX) [153]. The results showed a high content of precipitated asphaltenes in the nanoclay matrix, implying that asphaltenes were adsorbed by the nanoclays (Figure 33). However, there is an inherent problem in the whole process, and this is how to transport the nanoclays down to the porous media. There are some restrictions in the carrier fluid, since water is not suitable due to the clay swelling.



Figure 32. Recovery performance of hot vacuum gas oil (VGO) in the presence of trimetallic ultra-dispersed nanocatalysts at 320 and 340 °C. Figure reproduced from Ref. [36].



Figure 33. Asphaltene adsorption by Na⁺ montmorillonite (MMT) nanoclays. Figure adapted from Ref. [153].

A different method to be used as carriers for the catalytic metals involves the use of amphiphilic nanoparticles into the water injection, which can also act as emulsion stabilizers (Figure 34) [147]. These particles take part in in-situ upgrading reactions (i.e., oxidation and hydrogenation), and are also able to modify the rock formation's wettability.

Туре	Description	Schematic
Carbon/Oxide Nanoparticle Nanohybrids	(1) SWCNT/silica	Nor
	(2) MWCNT/alumina	-252-
	(3) Functionalized MWCNT/alumina	·ME
	(4) Onion carbon/silica	
Janus particles	(5) Partially-hydrophobized silica	
(1) -50 µm	(2) 	(3)
(4)	(5)	
0	50 µm 50 µm	appro /

Figure 34. (top) Schematic description of different nanohybrids being used as emulsion stabilizers and support of metal clusters; and (**bottom**) optical microscopy images of water/decalin emulsions stabilized by these nanohybrids. Figure reproduced from Ref. [147].

Regarding the heating techniques employed, several authors have proposed microwaves or electrical devices in order to set up the temperature for the cracking process [137,145,149]. The effect

of different micron-sized powders on heavy oil viscosity without steam treatment using alternative heating methods (i.e., electrical or microwave techniques) was discussed. A greater viscosity reduction ratio, shorter reaction times, lower required temperature, and longer viscosity regression time [152] could be achieved (Figure 35). Overall, though this process proved to be efficient in laboratory-scale experiments, there is still research to do in terms of how to make it applicable to real field production, stimulating an entire portion of an oilfield with electromagnetic waves.



Figure 35. Comparison of oil recoveries with and without nickel particles considering different total energy inputs. Figure reproduced from Ref. [145].

4.1. Chemistry and Kinetics of the Process

In EOR steam injection applications, the heat is employed for visbreaking (i.e., thermal cracking) the heavy oil/bitumen—this means that not only physical but also chemical processes take place [154–156]. These chemical reactions between the rock, steam, and oil cause what is called aquathermolysis. The hydrolysis of aliphatic sulfur linkages and the cracking of the large complex molecules present in the crude oil are the main characteristics of these reactions [138]. The result of these reactions is a decrease in the content of heavy products, such as bitumens/asphaltenes/resins, lowering the viscosity, the molecular weight, and the sulfur content and increasing H/C ratio, as well as saturated and aromatic hydrocarbons [142,154]. The presence of nanocatalysts in the porous media is considered to enhance the oil recovery by at least two principal mechanisms [35,36]: the in-situ upgrading of heavy oils, and the wettability alteration of a rock formation by coating with nanoparticles (see Nanofluids). The presence of nanocatalysts in heavy oil/bitumen formations generates a change in the way the components react, creating new paths for reactions to take place. A number of researchers proposed different kinetics models for the hydrocracking of heavy oils and bitumen [157–159], as well as the influence of nanocatalysts in the reaction kinetics [135,160,161]. Nevertheless, the structure of molecules such as resins and asphaltenes makes the kinetics complex, and the grouped lumping concept and the definition of "pseudo-components" represents a good approach for this study (Figure 36).



Figure 36. Detailed lumped kinetic reaction schemes for hydrocracking, proposed by Krishna (left) and Sanchez (right). Figures adapted from refs. [157,158].

Several experiments showed that aquathermolysis reactions took place via the production of reactive species from organosulfur compounds which later polymerized or reacted with water, yielding smaller fragments [155,156]. These components participated in subsequent reactions generating others, such as hydrogen sulfide, hydrogen and carbon oxides. Based on the results obtained, an overall reaction scheme was proposed [154,162–164]:

$$\underbrace{\frac{Steam, 200/300\ ^{\circ}C}{Minerals}} CH_4 + H_2S + CO + CO_2 + H_2 + Hydrocarbons_{C \ge 2}.$$
(5)

Furthermore, the kinetics above the aquathermolysis region were also studied [159]. The evolution of chemical reactions in the upgrading of several heavy oil cuts over the temperature range from 360 to 420 °C was discussed, rendering the following reaction sequence for thermal cracking:

$$Asphaltenes \longrightarrow Coke + HO + LO + H_2 + CH_4 + CO + CO_2 + C_2H_6 + ... + Hydrocarbons_{C \ge 3} + H_2S HO \longrightarrow Coke + LO + CH_4 + C_2H_6 + C_{3+} LO \longrightarrow Coke + CH_4 + C_2H_6 + C_{3+},$$
(6)

where *HO* and *LO* represent heavy and light oil, respectively. This reaction model yielded poor matches for the generation of carbon oxides, though provided a reasonable match for H_2S production. Then, the process starts with the cleavage of *C–S* bonds present in bitumen/asphaltenes, releasing hydrogen sulfide (H_2S). The reduction in the oil viscosity requires the decomposition of big and complex molecules such as asphaltene (Figure 37) or resins (visbreaking process). Aquathermolysis starts in the mentioned bonds since their dissociation energy is the lowest in the molecules.



Figure 37. Example of an asphaltene molecule. The blue atoms represent nitrogen, red atoms oxygen, white atoms hydrogen, yellow atoms sulfur, and grey atoms carbon. Figure adapted from Ref. [165].

This hydrolysis is achieved via the water gas shift reaction (WGSR). Additionally, it was proposed that gaseous H_2S and CO may react, producing carbonyl sulfide (COS) and hydrogen, then acting as hydrogen donor according to the following reactions [166]:

$$\begin{array}{l} H_2S + CO \longrightarrow COS + H_2, \\ COS + H_2O \longrightarrow CO_2 + H_2S. \end{array}$$

$$(7)$$

The carbon monoxide produced reacts with the water phase through the WSGR, generating hydrogen. The hydrogen then reacts with the unsaturated molecules of oil, producing lighter and saturated molecules via hydrogenolysis or hydrogenation reactions, which can be catalyzed with Ni nanoparticles. The use of different hydrogen donors on aquathermolysis processes also improves the quality of the heavy oil [134]. The most common hydrogen donor used is tetralin ($C_{10}H_{12}$). The reaction of tetralin can be described as a two-step process in which the tetralin firstly transfers hydrogen to the oil and is converted into DHN (decahydronaphthalene). Then, the latter transfers additional hydrogen to form naphthalene, which further upgrades the crude oil (Figure 38). During an upgrading process with catalysts, the heavy molecules are decomposed in the presence of hydrogen in order to saturate the free radicals (Figure 39) [167].



Figure 38. Two-step model for the transfer of hydrogen from tetralin to heavy oil. Figure adapted from Ref. [168]. DHN: decahydronaphthalene.



Figure 39. Proposed mechanism of hydrocracking. Figure adapted from Ref. [167].

4.2. Factors Affecting Nanocatalysts in EOR Applications

4.2.1. Type, Size, and Concentration of Nanoparticles

The viscosity–concentration combination can significantly alter the rheology of the produced oil, and therefore the efficiency of the EOR process [138,143,169]. This behavior can be attributed to chemical or physical processes generated by the particles. The exothermic chemical reactions are an example of the positive processes. As an example of negative processes, the coordination of the metal species with asphaltene causes an increase of viscosity above a certain concentration (Figure 40).

Decreasing the particle size increases the surface-to-volume ratio. This improves both the chemical and physical properties of nanoparticles. Furthermore, another significant property is the increased dispersion efficiency. However, at high concentrations, the viscosities of micro- and nano-mixtures become very close (Figure 41) [143]. These results may be connected to the high contact area of nanoparticles, which renders a higher likelihood of particles' aggregation.



Figure 40. The effect of different metal species on the viscosity of a heavy oil at a fixed temperature (25 °C) as a function of the nanocatalyst concentration for: \blacklozenge iron; \blacksquare copper; and \blacktriangle iron oxide (III). Figure reproduced from Ref. [170].



Figure 41. Comparison of the effect on the absolute viscosity of the iron particle size (at 25 °C) as a function of the catalyst concentration: ♦ micron-sized iron; ■ nano-sized iron. Figure reproduced from Ref. [170].

This dependence is supported by experiments considering the grinding time of the nanoparticles [144]. As the latter increased (i.e., particle size decreased), the ratio of the viscosity reduction increased (Figure 42). The metal particles may increase the oil viscosity after the aquathermolysis process due to coordination reactions of nanoparticles with heavy oil molecules. This is an important reason why nanoparticle concentrations should be carefully selected beforehand.



Figure 42. Viscosity reduction ratio of nano-NiWMoC catalyst synthesized at different milling times (**left**) and viscosity reduction ratio vs. particle size (**right**). Figures reproduced from Refs. [144] (left) and [149] (right).

Two important purposes of transition metal species are catalyzing the hydrogenation reactions and improving thermal conductivity [138,142]. However, in the case of oil sands, the effect of temperature and permeability on the nanoparticle mobility should also be taken into account (Figure 43) [37]. The reason is that higher temperatures favor particle collision due to the heavy oil viscosity reduction, yielding higher aggregation rates. Further analyses are then necessary to determine the effective size of the nanocatalyst to secure penetration in the porous media, taking into account that changes in temperature are likely to result in settling, separation, and possible agglomeration of the nanocatalyst.



Figure 43. Environmental scanning electron microscope (ESEM) microphotographs of Ni-Mo-W nanoparticles deposited on low-permeability oil sands at the (**a**) top and (**b**) bottom of the reactor column at a temperature of 320 °C. Figure reproduced from Ref. [37].

4.2.2. Heat Transfer

The thermal properties of the heavy oil/bitumen are an important limitation for the development of energy-efficient thermally enhanced recovery techniques. Better thermal properties obtained with nanoparticles can result in a faster heat distribution during thermal EOR processes. The thermal conductivity enhancement by means of metallic particles with high thermal conductivities has been studied by several authors [43]. Recent work on liquids' thermal conductivity enhancement using nanoparticles has led to further examination of the nanofluids' thermal conductivity enhancement using nanoparticles to results showed different results, from anomalous thermal conductivity enhancement using nanoparticles to results showing thermal properties according to the values predicted. It is advised to carry out further research to determine the origin of these anomalous results. Experimental

data and measurement methods are still lacking consistency, and additional experiments are deemed necessary [173].

4.2.3. Crude Oil Composition

The results of viscosity reduction on different oils with nanocatalysts presented by different authors showed a significant difference in reduction values [137,143]. This was theorized to be related with a chemical effect more than a strictly physical one. A possible reason for the viscosity reduction is the breakage of the C-S bonds in asphaltene/resin molecules. However, when the content of sulfur becomes negligible, other chemical bonds with higher dissociation energy may be broken so as to reduce the viscosity. Core mineralogy also plays a significant role in the generation of CO_2 , and the amount of H_2S produced depends on the oil composition, mineralogy, and time [159].

4.2.4. Porous Media

The physical properties of the rock formation also affect the performance of the catalyst process. The permeability has a significant impact on the retention (Figure 44). The chemical composition of the porous media also plays a role in the performance of the process. The oil reservoir generally consists of several metallic carbonates. The presence of certain compounds, such as calcite (CaCO₃) or siderite (FeCO₃), increases the production of carbon dioxide at the steam injection temperature [134]. Clay mineral surfaces have a negative charge, so when the catalyst is injected, the metal cations (e.g., VO²⁺ and Ni²⁺) will be adsorbed onto the surface via electrostatic forces. These reactions can generate products similar to amorphous silica alumina catalysts which are commonly utilized in catalytic cracking processes [134,142].

4.3. Inhibition of Formation Damage

One of the problems that should be addressed is the deposition of unstable polar heavy hydrocarbons such as asphaltenes. The presence of asphaltenes in heavy oil can lead to the adsorption and deposition onto the rock matrices, affecting formation properties such as porosity, permeability, and wettability [174,175]. Nanomaterials have been proposed as a way to inhibit the asphaltene deposition, minimizing the possibility of damage in the rock formation and wells as well as upgrading heavy oils and reducing their viscosity [135,174]. The function of nanoparticles is to adsorb the asphaltenes and then adsorb onto the porous media, delaying the precipitation of asphaltenes [7,174].



Figure 44. Effect of the absolute permeability and injection flowrate on the recovery of Ni nanoparticles and the outlet concentration. Figure reproduced from Ref. [170].

5. Conclusions

Throughout this review, it was presented and discussed how nanotechnology can be employed in EOR applications in order to increase the efficiency of existing recovery techniques. Many authors agree that nanotechnology allows EOR issues to be addressed from a novel point of view. The special features found at the nanoscale enhance the properties and/or performance of common processes/materials in many branches of science. EOR techniques are not exempt, so new ways to improve the traditional methods using nanotechnology are highly advisable.

For the purposes of this analysis, it has been considered that the employment of nanotechnology in EOR can be divided into three subgroups, namely: the use of nanoparticles in the synthesis of nanofluids, the creation of nanoemulsions with surfactants or nanoparticles, and finally the use of active metals that can act as nanocatalysts for the in-situ upgrading of heavy oil cuts. Besides this classification, other different topics have been introduced, such as nanoparticle manufacturing methods and concerns about the impact that nanotechnology may have on the environment. Clearly, nanotechnology is a recent branch of science, and although much progress has been made lately, there are still many questions to be answered. This can be appreciated in the fact that most of the literature found on direct applications at the nanoscale is recent, and numerous investigations are still being carried out. For instance, there are several environmental concerns regarding the application of nanoparticles, not only in EOR but in all branches of science. How these particles affect our health and their long-term effect on the environment are still being investigated. Production methods are also currently being researched in order to produce smaller sizes as well as less variability in the size.

Among the possible uses in EOR, the employment of nanoparticles to create "smart fluids" or nanofluids is by far the most developed. Thanks to the pioneering work carried out by Wasan and Nikolov, the disjoining mechanism of the oil drop was also analyzed. The same procedure has also been adopted to analyze the nanoemulsions, which in laboratory tests have demonstrated improved stability characteristics. The main problem reported in the nanoemulsions—which should still be subjected to further investigation—is their stability under the harsh conditions usually found in reservoirs (high pressure, high temperature, and the presence of dissolved salts). Finally, the use of active metal nanoparticles acting as nanocatalysts was introduced and studied, predominantly for the recovery and upgrading of heavy oil cuts. These present numerous complications for extraction, such as reduced flowability due to their high content of resins and asphaltenes. Nanocatalyst employment has shown great potential, acting as an "underground refinery" which improves and pretreats the oil, increasing its mobility and reducing the viscosity. However, as was presented in this review, some research must still be done in this area to tackle some issues, such as improving the dispersion of nanocatalysts in the rock formation.

As is presented in the literature, it is deemed that EOR is not an exclusive field belonging to a single discipline. The use of nanotechnology in EOR as a tool to enhance traditional techniques has demonstrated a promising future, although there are still many unanswered questions. Nanotechnology cannot be addressed as an independent recovery process in EOR, but instead as a way to enhance the standard recovery techniques. This cannot be described as a new branch of applied sciences but, such as every process in EOR, a combination of different disciplines working together for the greater good. It is the intersection of the already well-known disciplines in EOR together with nanotechnology, which lends its unique features, allowing the development of a whole new branch of research in the oil industry. This review shows clearly how using new technologies to deal with old problems can be an interesting approach to increasing or enhancing the productivity or performance of current processes. This does not apply exclusively to the oil industry, but is an example of a novel course of action applicable to all branches of science. It is to our best understanding that future research not only at the laboratory scale, but also in real field tests, will allow nanotechnology to give a boost to facilities which were considered to be at the limit of their operational life. Author Contributions: Methodology, Formal Analysis, Investigation, Resources, Writing—Original Draft Preparation, P.D.; Writing—Review & Editing, P.R.; Writing—Review & Editing, Supervision, Project Administration, F.P.

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Abbreviations

The following abbreviations are used in this manuscript:

EOR	Enhanced Oil Recovery
IOIP	Initial Oil in Place
PNP	Polymer-Coated Nanoparticle
IFT	Interfacial Tension
PSNP	Polysilicon Nanoparticle
HLPN	Hydrophobic and Lipophilic Nanoparticle
LHPN	Lipophobic and Hydrophilic Nanoparticle
NWPN	Neutral Wet Nanoparticle
DLVO	Derjaguin, Landau, Verwey, and Overbeek theory
HAPAM	Hydrophobically Associating Polyacrylamide
HPAM	Hydrolyzed Polyacrylamide
SPAM	Sulfonated Polyacrylamide
AMPS	2-Acrylamido-2-methylpropane Sulfonic Acid
SDS	Sodium Dodecyl Sulfate
TDS	Total Dissolved Solids
AM	Acrylamide
AA	Acrylic Acid
NSFM	Nano-SiO ₂ Functional Monomer
CAC	Critical Aggregation Concentration
CNT	Carbon Nanotube
SEM	Scanning Electron Microscope
AFM	Atomic Force Microscope
PIT	Phase Inversion Temperature
EIP	Emulsion Inversion Point
VGO	Vacuum Gas Oil
VAPEX	Vapor Extraction Process
DHN	Decahydronaphthalene

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