Application of Nanoparticles in Enhanced Oil Recovery: A Critical Review of Recent Progress

Xiaofei Sun *, Yanyu Zhang, Guangpeng Chen and Zhiyong Gai

College of Petroleum Engineering, China University of Petroleum (East China), Qingdao 266580, China; yyzhang@upc.edu.cn (Y.Z.); chengpupc@163.com (G.C.); gezhiyong1@126.com (Z.G.)

* Correspondence: xfsun@upc.edu.cn; Tel.: +86-130-2167-8278

Abstract: The injected fluids in secondary processes supplement the natural energy present in the reservoir to displace oil. The recovery efficiency mainly depends on the mechanism of pressure maintenance. However, the injected fluids in tertiary or enhanced oil recovery (EOR) processes interact with the reservoir rock/oil system. Thus, EOR techniques are receiving substantial attention worldwide as the available oil resources are declining. However, some challenges, such as low sweep efficiency, high costs and potential formation damage, still hinder the further application of these EOR technologies. Current studies on nanoparticles are seen as potential solutions to most of the challenges associated with these traditional EOR techniques. This paper provides an overview of the latest studies about the use of nanoparticles to enhance oil recovery and paves the way for researchers who are interested in the integration of these progresses. The first part of this paper addresses studies about the major EOR mechanisms of nanoparticles used in the forms of nanofluids, nanoemulsions and nanocatalysts, including disjoining pressure, viscosity increase of injection fluids, preventing asphaltene precipitation, wettability alteration and interfacial tension reduction. This part is followed by a review of the most important research regarding various novel nano-assisted EOR methods where nanoparticles are used to target various existing thermal, chemical and gas methods. Finally, this review identifies the challenges and opportunities for future study regarding application of nanoparticles in EOR processes.

Keywords: nanoparticles; enhanced oil recovery (EOR); review study; water flooding; gas injection; thermal methods; chemical flooding

1. Introduction

Oil recovery operations are subdivided into three stages: primary, secondary, and tertiary [1]. Primary production results from the displacement energy naturally existing in a reservoir, such as solution-gas drive, gas-cap drive and natural water drive, etc. [2]. Secondary recovery processes are waterflooding and gas injection. Tertiary processes use miscible gases, chemicals and or thermal energy to displace additional oil after the secondary recovery process [3]. There are some mechanistic distinctions between secondary and tertiary processes. The injected fluids in secondary processes supplement the natural energy present in the reservoir to displace oil. The recovery efficiency mainly depends on the mechanism of pressure maintenance. However, the injected fluids in tertiary processes interact with the reservoir rock/oil system. These interactions might result in lower interfacial tensions (IFT), oil swelling, oil viscosity reduction, wettability modification, or favorable phase behavior. In some situations, the so-called tertiary process might be applied as a secondary operation. Therefore, the term 'tertiary recovery' fell into disfavor in literature and the designation of "EOR" became more accepted [3].

As the production rates of existing fields are declining and the frequency of new exploration has become greatly lower in the last decades, the significance of EOR techniques is highly understood by oil companies and authorities. It is well known that there are three major categories of available EOR technologies (Figure 1) [4–9].

(1)　Thermal methods mainly introduce heat into heavy oil reservoirs by various methods, such as cyclic steam simulation (CSS), steam flooding and steam-assisted gravity drainage (SAGD), to better the flow ability of the heavy oil or bitumen in reservoirs by changing its physical properties (viscosity and density).

(2)　Gas methods utilize hydrocarbon gases (CH_4, C_3H_8 or natural gas) or non-hydrocarbon gases (N_2, or CO_2) that dissolve in oil. In this way, the injected gas can improve oil recovery by decreasing oil viscosity and expanding oil volume.

(3)　Chemical methods mainly involve the use of long-chained molecules called polymers to increase the effectiveness of waterflood, or the use of detergent-like surfactants to help lower IFT that often prevents oil droplets from moving through a reservoir.

Figure 1. The categories of available EOR technologies.

In brief, all these EOR methods tend to recover more oil from reservoirs by various mechanisms such as IFT reduction, wettablility alteration, mobility control, change of physical properties and gravity drainage.

However, it also can be seen from Figure 1 that all these traditional EOR processes face some important challenges. For example, for gas methods, the injected gas often quickly penetrates through reservoirs from injection wells to producing wells, resulting in a large amount of residual oil remaining uncovered in reservoirs because of the high mobility ratio of injected gas and oil [10,11]. Moreover, chemical processes are often limited by the high cost of chemicals, possible formation damages, and losses of chemicals [12,13]. Therefore, less expensive, more efficient, and environmentally friendly EOR methods are greatly needed. Nanoparticles (NPs) offer novel pathways to address the unsolved challenges. NPs are defined as particles with size ranges from 1 nm to 100 nm [14], and show some useful characteristics as EOR agents when compared to the available injection fluids used in the traditional EOR processes such as gas, water and chemicals:

Ultra-small size: One of the most important challenges to chemical processes is pore plugging and injected chemicals trapped in porous media which result in reducing formation permeability and increasing the injection cost [15]. Commonly used NPs, such as SiO_2, TiO_2 and Al_2O_3, are in the order of 1 nm–100 nm (Figure 2), which is smaller compared to pore and throat sizes [16]. Thus, they can easily flow through porous media without severe permeability reduction and becoming trapped which

increases the EOR effectivity of the injection fluids. In addition, due to ultra-small size of NPs, they have the ability to penetrate some pores where traditional injection fluids are unable to. Thus, NPs can contact more swept zones, and increase the macroscopic sweep efficiency.
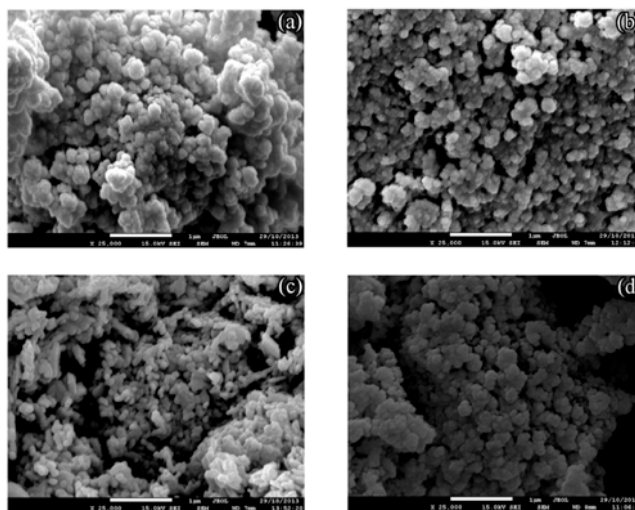

Figure 2. FESEM images of some commonly used NPs: (**a**) TiO_2; (**b**) Al_2O_3; (**c**) NiO; (**d**) SiO_2 [16].

Very high surface to volume ratio: Due to their small particle size, NPs have a very high surface to volume ratio (Figure 3). The large surface area increases the proportion of atoms on the NP surface [17]. Figure 3 explains the concept of the increasing surface area with decreasing size of the particles. At each step in Figure 3, the same mass and volume of the sample, but a higher surface area results with each smaller size.
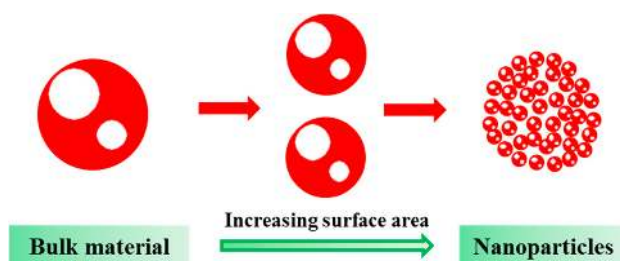

Figure 3. A schematic diagram of NPs with high surface to volume ratio.

Low costs and environmental friendliness: One concern of using chemicals on the field scale is the injection cost. Because the price of NPs is usually cheaper than chemicals, NPs can be widely applied for EOR at oilfields. Moreover, most of the NPs used are environmentally friendly materials compared to chemical substances. For example, most of the silica NPs are silicon dioxide, which is the main component of sandstone. In short, NPs are very cost effective and environmentally friendly.

Due to the aforementioned characteristics of NPs, they provide many potential solutions to the existing challenges faced by traditional EOR methods. Therefore, this paper provides an overview of the latest studies about NPs to enhance the oil recovery and paves the way for researchers who are interested in the integration of these progresses. The first part of this paper addresses studies about the major EOR mechanisms of NPs used in the forms of nanofluids, nanoemulsions and nanocatalysts. This part is followed by a review of the most important research regarding various novel nano-assisted EOR methods where NPs are used to target various existing thermal, chemical and gas methods. Finally, this review identifies the challenges and opportunities for future study regarding application of nanoparticles in EOR processes.

2. EOR Mechanisms

Understanding the EOR mechanisms of NPs is important for nano-assisted EOR processes when NPs are used as novel EOR agents. Recent studies about the interactions of nanofluid, oil and rock have revealed some EOR mechanisms. However, the EOR mechanisms of NPs are still not totally understood. Nowadays, the applications of NPs in EOR processes can be summarized into three major approaches: nanofluids, nanocatalysts and nanoemulsions. The following sections discuss their respective EOR mechanisms in combination with their corresponding EOR processes.

2.1. Nanofluids

A nanofluid is simply defined as a base fluid with NPs that have an average size of less than 100 nm in colloidal suspension [18]. The base fluid can be any liquid such as oil, water or gas. Generally, nanofluids formed by adding various NPs in water or brine are used to improve water flooding recovery. The EOR mechanisms of nanofluids have already been investigated in literatures, which mainly includes disjoining pressure, pore channels plugging, viscosity increase of injection fluids, IFT reduction, wettability alteration and preventing asphaltene precipitation. The schematic of the EOR mechanisms of nanofluids is shown in Figure 4.
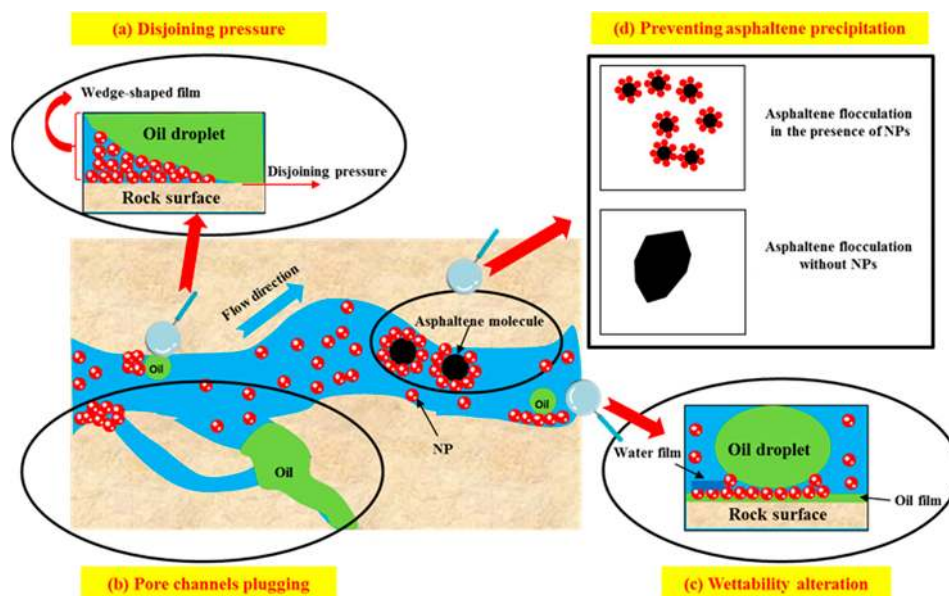
Figure 4. The schematic of the EOR mechanisms of nanofluids.

2.1.1. Disjoining Pressure

The NPs in the nanofluids can form a self-assembled wedge-shaped film on contact with oil phase as shown in Figure 4a. The wedge film acts to separate the oil droplets from the rock surface, thereby recovering more oil than previously possible with conventional injection fluids. The wedge-shaped film is formed due to the existence of a pressure, called structural disjoining pressure [19,20].

The generation of the structural disjoining pressure is osmotic. Driven by an injection pressure of nanofluids, the injected nanofluids exert a pressure forcing the NPs in the confined region forward, and they tend to arrange themselves in well-ordered layers. This arrangement increases the entropy of the nanofluids due to the greater freedom of the NPs in the nanofluids. The result of this arrangement exerts additional disjoining pressure at that interface more than that in the bulk liquid. This conclusion was proved by the simulated shape of the meniscus profile in the wedge region in both the presence and the absence of NPs (Figure 5).

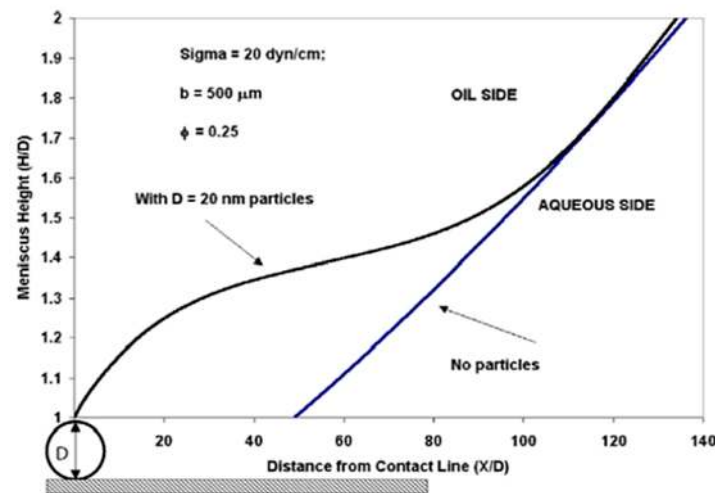**Figure 5.** The simulated shape of the meniscus profile in the wedge region [21].

It can be seen from Figure 5 that the contact line of the oil, rock and nanofluid is more forward than that of the bulk liquid [21]. The Brownian motion and electrostatic repulsion between NPs are the energies that generate this disjoining pressure. NP size, amount of the NPs, temperature, salinity of the base fluid, and the characteristics of the rock surface affect the magnitude of the disjoining pressure. For example, the force caused by a single NP is extremely weak. However, when large amounts of NPs are present, the force can be upwards of 50,000 psi at the vertex [20].

2.1.2. Pore Channels Plugging

Pore channel plugging can be caused by two mechanisms: mechanical entrapment and log-jamming (Figure 6) [22]. Mechanical entrapment occurs because the diameter of injected components is larger than pore channels that they flow through (Figure 6a). Generally, pore channels are in microscale, thousand times bigger than NPs. Therefore, NPs are able to penetrate pore channels without mechanical entrapment. However, it is noted that some metal NPs may block pore channels due to their large size [23,24]. Thus, before these NPs are injected into reservoirs, the evaluation process should be conducted to insure the feasibility of enhancing oil recovery.
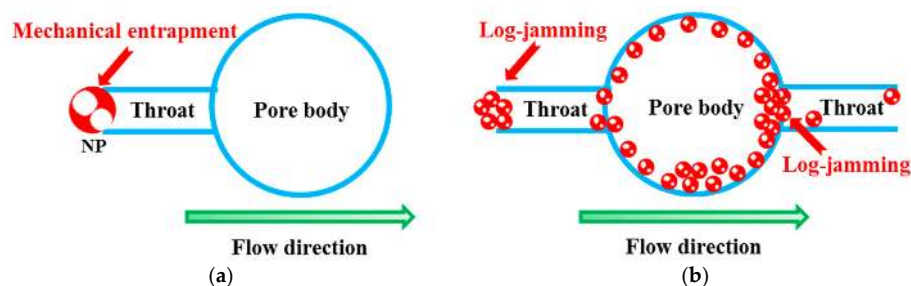
Figure 6. The schematic of two mechanisms causing pore channels plugging: (**a**) mechanical entrapment; (**b**) log-jamming.

Log-jamming is plugging of pore channels that are larger than each NP. When a nanofluid flows from pores to throats, the narrowing of flow area and the differential pressure will lead to a velocity increase of the nanofluid. The small H_2O molecules will flow faster than the NPs causing accumulation of NPs at the entrance of the pore throats (Figure 6b). In some cases, plugging of pore throats due to log-jamming is beneficial to improve the performance of nanofluid flooding. It can be seen from Figure 4b that, in the very small pore throat, Log-jamming results in NPs accumulation and blockage

of the pore throat. The pressure builds up in the adjacent pore throat, forcing out the oil trapped in the pore throat. Once the oil is freed, the surrounding pressure drops and the plugging gradually disappears and the NPs start to flow with the water. This can be considered as temporary log-jamming. This phenomenon is mainly governed by the concentration and size of NPs, flow rate and the diameters of pore throats.

2.1.3. Decreasing the Mobility Ratio of Injected Fluids

One of the important parameters for EOR processes is mobility ratio. The mobility ratio can be obtained by the following expression [25]:

$$M = \frac{\lambda_i}{\lambda_o} = \frac{k_{ri}/\mu_i}{k_{ro}/\mu_o} = \frac{k_{ri}\mu_o}{k_{ro}\mu_i} \tag{1}$$

where λ_i and λ_o are injected fluids and oil mobilities, respectively. k_{ri} and k_{ro} are the relative permeabilities of the injected fluids and oil, respectively; μ_i and μ_o are the effective viscosities of the injected fluids and oil, respectively. According to the equation, a higher mobility ratio exists during the displacing processes because the viscosity of a traditional injected fluid, such as water, CO_2 or chemical, is often lower than that of oil. The high mobility ratio easily causes viscous fingering of injected fluids within oil, poor conformance, and poor sweep efficiency. The mobility ratio can be decreased by viscosity reduction of oil phase or viscosity enhancement of injected fluids. Nanofluids can solve the above mentioned problem because adding NPs in traditional fluids can increase the effective viscosity of injected fluids. Shah and Rusheet [26] found that the viscosity of CO_2 nanofluids (1% CuO NPs in gas phase CO_2) was 140 times greater than that of CO_2. Furthermore, Molnes et al. [27] found that the shear viscosity of aqueous medium was increased when cellulose nanocrystals were dispersed in de-ionized water.

The viscosity of a nanofluid is influenced by several factors, such as shear rate, temperature and NP concentration. For example, the viscosity of the SiO_2 nanofluid increases with decreasing shear rate. The increasing rate of its viscosity at lower temperature is higher than that at higher temperature (Figure 7) [28].
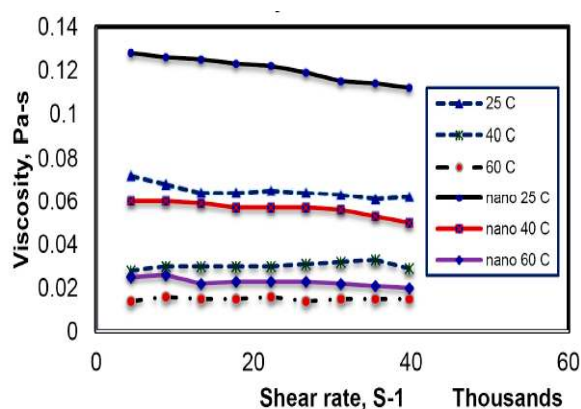
Figure 7. Influence parameters of viscosities of SiO_2 nanofluids [28].

For nanocellulose nanofluids, the shear dependence of viscosity is generally subjected to two distinct stages. When shear rates are low, viscosities decrease linearly with shear rates in the first stage, suggesting a pronounced shear-thinning behavior. As shear rates increase, a transition occurs at the second stage; i.e., shear viscosities increase with shear rates. It is believed that nanocellulose is rearranged to form the ordered networks again and leads the viscous property to recover [29]. Furthermore, the viscosity of nanofluids increases with increasing NP concentration and brine salinities. The type of NPs also affects the viscosity of nanofluids. At the same concentration, the viscosity of the

SiO_2 nanofluid is higher than that obtained by the Al_2O_3 nanofluid [30]. Iron oxide also can increase the viscosity of the injected fluids causing the increase in the sweep efficiency [31].

2.1.4. IFT Reduction

IFT is one of the main parameters used to determine fluids' distribution and movement in porous media. Therefore, it is necessary to obtain the IFT between oil and injected fluids for evaluation of an EOR technique. Some types of NPs also have been considered as potential agents to reduce IFT, which is one of the main EOR mechanisms for nanofluid flooding.

The IFT between crude oil and nanofluids is usually measured using the pendant drop method [5]. During the experimental process, an oil droplet is generated from the end of a capillary needle in a nanofluid at experimental pressure and temperature. The IFT value is calculated by analyzing the complete shape of the oil droplet by an accurate video system and analysis software.

Hendraningrat et al. [32,33] measured the IFT between synthetic oil and nanofluids by the pendant drop method. The results showed that adding NPs into brine reduced the IFT from 14.7 mN/m to 9.3 mN/m. In addition, increasing nanofluid concentration from 0.01 wt % to 0.05 wt % decreased the IFT from 9.3 mN/m to 5.2 mN/m. Therefore, IFT is sensitive to nanofluid concentration, and decreases as nanofluid concentration increases. Li and Parvazdavani [34,35] also carried out similar experiments to study the effect of SiO_2 NPs on IFT, and they believed that SiO_2 NPs have more impact on IFT reduction than wettability alteration.

Recently, some experiments were conducted to compare the IFT values between crude oil and various metal nanofluids. For instance, Adel et al. [30] compared the effects of SiO_2 and Al_2O_3 nanofluids on IFT at ambient pressure and temperature. They found that the IFT clearly decreased when either of them was added into brine. The SiO_2 nanofluid had a lower IFT value than the Al_2O_3 nanofluid. Therefore, SiO_2 nanofluid had the potential to produce more oil from reservoirs. Alomair et al. [16] furthered to compare the ability of three NPs (Al_2O_3, SiO_2 and NiO) to reduce IFT between the crude oil and nanofluids. They found that the SiO_2 NPs resulted in the lowest IFT value and NiO had the lowest reduction on IFT. The main reason for the IFT reduction is high adsorption of NPs that modifies oil and water surface.

2.1.5. Wettability Alteration

The definition of rock wettability is the tendency of a fluid to adhere to the rock surface competing with another immiscible fluid [36]. It is a key factor to govern oil recovery by affecting capillary pressure, fluids saturation, and relative permeability. Recent years, nanofluids have been considered as potential agents to alter wettability (Figure 4c).

Currently, there are three main experimental methods that are commonly used by researchers for wettability measurement: the contact angle method, the Amott test and the core displacement test [37–41]. Among them, the contact angle method is the most universal used approach to determine wettability. The wettability can be easily obtained by the rules shown in Figure 8.
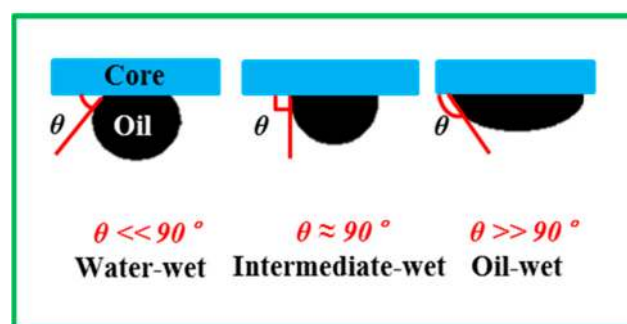

Figure 8. A schematic diagram of rock wettability conditions of a rock-brine/nanofluid-oil system [41].

The Amott test mainly uses the wettability index (I_w) to determine wettability that combines spontaneous and forced displacement at room condition. The definition of I_w is as follows:

$$I_w = \frac{V_{o1}}{V_{o1} + V_{o2}} - \frac{V_{w1}}{V_{w1} + V_{w2}} \tag{2}$$

where V_o and V_w describe oil volume from imbibition process and water volume from drainage process, respectively. Subscript '1' means spontaneous displacement process and '2' means forced displacement process. I_w ranges from -1, as completely water-wet, to 1, as completely oil wet and 0 is considered as neutral wettability.

The core displacement test also can be used to determine wettability alterations by comparing the changes in residual water saturation (S_{wr}), oil relative permeability (k_{ro}) and the point where the water and oil relative permeabilities are equal (crossover point) before and after nanofluid treatment. Based on Craig's rules, if the S_{wr} increases, the k_{ro} and the crossover point move to the right after nanofluid treatment, the wettability is changed from an oil-wet to a water-wet condition (Figure 9) [37].

Based on the aforementioned experimental methods, many studies were performed to investigate the effects of various nanofluids on the wettability alteration. The experimental results reported in literatures are listed in Table 1.

In the literature, some authors have conducted systematic studies about the effects of various nanofluids on the wettability alteration of different types of rocks (sandstone, carbonate and shale). Li et al. [42] performed Amott tests to measure I_w and reported that SiO_2 NPs changed oil wet sandstone cores to neutral wet. Then, Roustaei and Bagherzadeh [43] experimentally investigated the impact of SiO_2 NPs on the wettability of a carbonate reservoir rock. Also, the results showed that SiO_2 NPs could be treated as wettability modifiers for carbonate cores. For fractured limestones, Al-Anssari et al. [28] found that the SiO_2 nanofluids induced wettability alteration on oil-wet and mixed-wet calcite substrates, consistent with the results of Roustaei and Bagherzadeh. In addition, Mahdi et al. [44] found that nano-biomaterials have the ability to alter the wettability of shale from oil-wet to water-wet due to simultaneous utilization of nano and biomaterials.
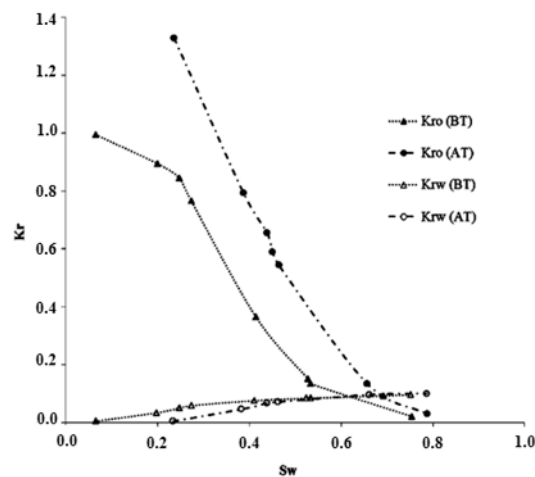
Figure 9. Relative permeability curves. The symbols are experimental data. The notation AT and BT indicates that measurements were carried out after or before nanofluid treatment [37].

In order to understand how oil viscosity affects the wettability alteration of rock surfaces, Maghzi et al. [45] conducted an experiment to study the change of contact angles when the glass surfaces coated by a SiO_2 nanofluid and heavy oil with different viscosity and found that the SiO_2 NPs also caused wettability alteration from oil-wet to water-wet regardless the viscosity of measured oil.

Recently, the feasibility of metal NPs to alter wettability has been investigated in addition to SiO_2 NPs. Hendraningrat, et al. [46] investigated the role of Al_2O_3 NPs on wettability alteration by

the aforementioned three methods. They found that dispersing Al_2O_3 nanofluids could alter the wettability of the sandstone cores from a strongly oil-wet to a strongly water-wet condition. Then, Hendraningrat et al. [47] investigated nano-Al_2O_3 and TiO_2 and compared them with SiO_2. The results showed that TiO_2 changed the quartz plate to be more strongly water-wet. Karimi et al. [48] found that ZrO_2-based nanofluids (ZrO_2 NPs and mixtures of nonionic surfactants) had the same influence on the wettability alteration of a carbonate reservoir rock.

Actually, the wettability alteration caused by nanofluids can be affected by many factors, such as NP concentration and size and water salinity. Li et al. [34] conducted contact angle measurement of crude oil against silica nanofluids with various concentrations on synthetic silica, and concluded that water wetness increased with increasing the NP concentration. Then, Hendraningrat et al. [49] found that NP size influenced obviously wettability by using the Amott-test method. Contact angle of aqueous phase decreased as NP size decreased. This is because the electrostatic repulsion force between the NPs is bigger when amount of NPs is large and size is small. In addition, Hendraningrat, et al. [46] found that the alterations in wettability depend on the degree of water salinity, ionic composition, initial porous medium wettability, solid system and duration of NP interaction in the fluid-rock system. Al-Anssari et al. [28] studied the reversibility of NP adsorption and observed that NP adsorption was mainly irreversible, although a partially reversible behavior existed after washing the surface with acetone and/or distilled water.

Recently, some authors try to analyze the reasons why the NPs can result in wettability alteration of rock surfaces by some novel characterization techniques. For example, Karimi et al. [48] proved that NPs adsorbed on the calcite forming of nano textured surfaces by scanning electron microscopy (SEM) images and energy dispersive X ray (EDX) (Figure 10). Al-Anssari et al. [28] tested the surface modification with SEM–EDS and atomic force microscopy (AFM) measurements. It was observed that the distribution of the NPs on the surface were homogeneous after nano-modification (Figure 11) [50,51].
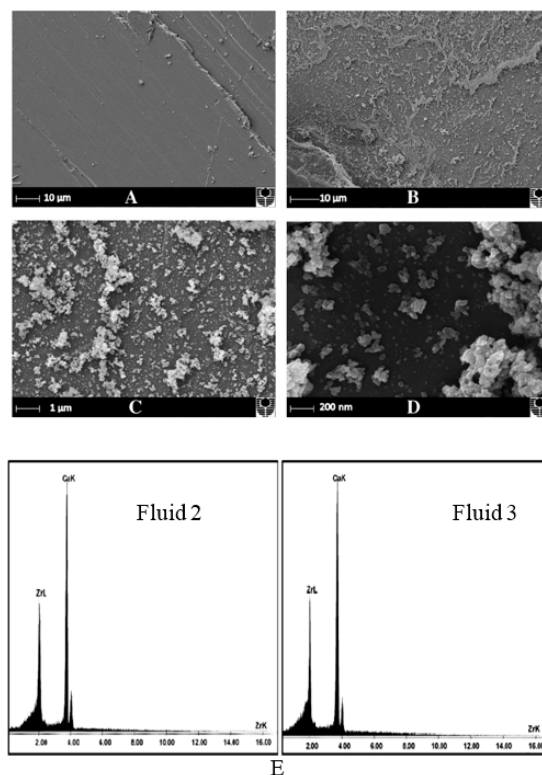

Figure 10. SEM images of the measured calcite surface: (**A**) before; (**B**) after nano-modification; (**C**) high resolution; and (**D**) maximum resolution; (**E**) EDX analysis of carbonate rocks aged in fluids [28].

Table 1. Summary on experimental studies about wettability alteration by nanofluids.

| References	NPs/Base Fluids	Oil Type	Oil Properties		Rock Type	Measurement Methods	Influence Factors
			Density (kg/m^3)	Viscosity (cp)			
Al-Anssari et al. [28]	SiO$_2$/brine	N-decane	N/A	N/A	Calcite	Contact angle method	NP concentration, salinity, time, and reversibility of NP adsorption
Li et al. [34]	SiO$_2$/brine	Light oil	826	5.1	Glass	Contact angle method	NP concentration
Giraldo et al. [37]	Al$_2$O$_3$/anionic surfactant solution	Heavy oil	895	64	Sandstone	Contact angle method, Amott test and core displacement test	NP concentration
Li et al. [42]	SiO$_2$/brine	Light oil	847	15.3	Sandstone	Amott test	NP type and concentration
Roustaei et al. [43]	SiO$_2$/brine	Light oil	857	11	Carbonate	Contact angle method	NP concentration
Mahdi et al. [44]	SiO$_2$-biomaterial/water	Heavy oil	925	200	Shale	Contact angle method	NP concentration
Maghzi et al. [45]	SiO$_2$/brine	Heavy oil	933	870	Glass	Contact angle method	NP concentration
Hendraningrat et al. [47]	(SiO$_2$, Al$_2$O$_3$, TiO$_2$) + Povidone/brine	Light oil	826	5.1	Quartz	Contact angle method	NP type
Karimi et al. [48]	ZrO$_2$ + Surfactants/distilled water	Heavy oil	861	425	Carbonate	Contact angle method, Amott test	Aging time, type of nonionic surfactants and
Hendraningrat et al. [49]	SiO$_2$/brine	Light oil	826	5.1	Sandstone	Contact angle method, Amott test	NP size
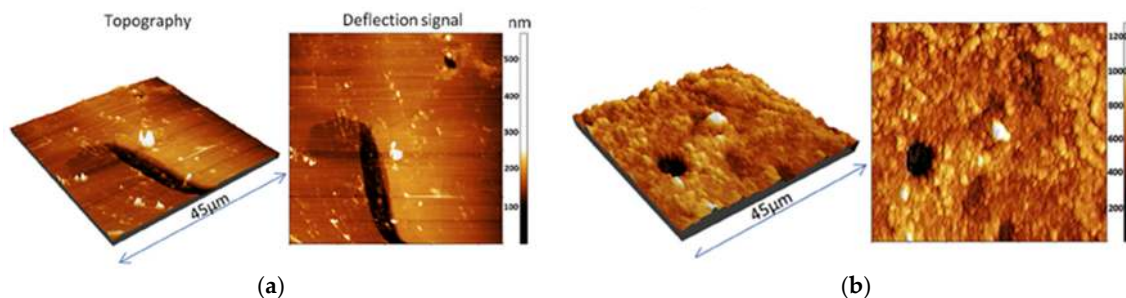
Figure 11. Atomic force microscopy (AFM) images of the measured calcite surface: (**a**) before; (**b**) after nano-modification [28].

2.1.6. Preventing Asphaltene Precipitation

Some EOR techniques, such as CO_2 miscible flooding, may cause significant asphaltene precipitation due to special reservoir conditions, which leads to wettability alteration, formation permeability reduction, and transportation pipelines blockage, etc. [52–54]. Therefore, a solution to prevent asphaltene precipitation is vital for these EOR techniques to improve oil recovery.

Some researchers proved that NPs can solve the asphaltene problems effectively and not cause environmental hazards (Figure 4d). For example, Abu Tarboush and Husein [53] found that NPs had the ability to stabilize asphaltene precipitation. From the knowledge gained, Alomair et al. [16] tested the mixed SiO_2-Al_2O_3 nanofluids on asphaltene precipitation and observed that as the nanofluid concentration increased, asphaltene precipitation was delayed further. Recently, Kazemzadeh et al. [55] conducted a set of experiments to determine how SiO_2, NiO, and Fe_3O_4 NPs prevented asphaltene precipitation by a micromodel. They found that the presence of the NPs leaded to the adsorption of the NPs onto the asphaltene molecules surface, which significantly reduced the asphaltene flocculation in the porous media.

Some studies have investigated the effects of various factors, such as asphaltene and water content, temperature and contact time on the asphaltene adsorption onto NP surfaces [56,57]. The results showed that the extent of asphaltene adsorption onto the NPs increased with increasing the contact time. Actually, large amounts of asphaltene were adsorbed onto the NP surface in a short period of time. The asphaltene adsorption was increased with the increase of asphaltene content and the decrease of temperature and the amount of existing water.

2.2. Nanoemulsions

A nanoemulsion is a kind of emulsion that is stabilized by NPs, which demonstrates a great ability to overcome the challenges encountered with conventional emulsions stabilized by surfactants or colloidal solids [58]. Actually, nanoemulsion droplets fall in the same droplet length-scale (<100 nm) as a microemulsion, but they are a kinetically controlled systems that can retain their morphology with the change in oil volume fraction. Therefore, nanoemulsions can withstand harsh conditions (high temperatures, pressures, shear and salinity) to remain stable in reservoirs and have a wider application range compared with microemulsions [59]. In addition, the high viscosity of nanoemulsion can effectively control mobility ratio during flooding, which is very important for improving heavy oil recovery, rather than polymers that are relatively large and have high retention on reservoir rocks [60,61]. Finally, nanoemulsions are small enough to penetrate through pore throats without much retention. Therefore, they are suited to large-scale applications in field scales [62]. All these advantages of nanoemulsion contribute to improve oil recovery and attract great interest for researchers and oil companies.

The most commonly used NPs for emulsions are silica NPs. The wettability of these NPs can be adjusted by the amount of silanol groups on their surface [19]. The NPs can be made hydrophilic with high percentage (over 90%) of silanol groups on the surface, and consequently they form stable

oil-in-water (o/w) emulsions. On the other hand, when the silica particles are only coated about 10% on their surface by silanol groups, they are hydrophobic and yield water-in-oil (w/o) emulsions. Furthermore, when the nanoparticles are only partially coated with silanol groups (e.g., 70%), they become particles with "intermediate hydrophobicity;" the stable emulsion type they generate depends on the oil polarity, i.e., formation of o/w emulsions are favored with nonpolar oils whereas w/o emulsions are preferred with polar oils [20].

The phenomena of emulsification have been observed in some micromodel experiments during nanofluid flooding processes, which is shown in Figure 12. The main reasons for the effect of NPs on emulsion are discussed by some studies. Images obtained by an optical microscope showed that the uniform size of the NPs generate a compact, well-structured monolayer at the aqueous/non-aqueous phase interface to make the emulsion extremely stable even under high temperatures (Figure 13) [16].
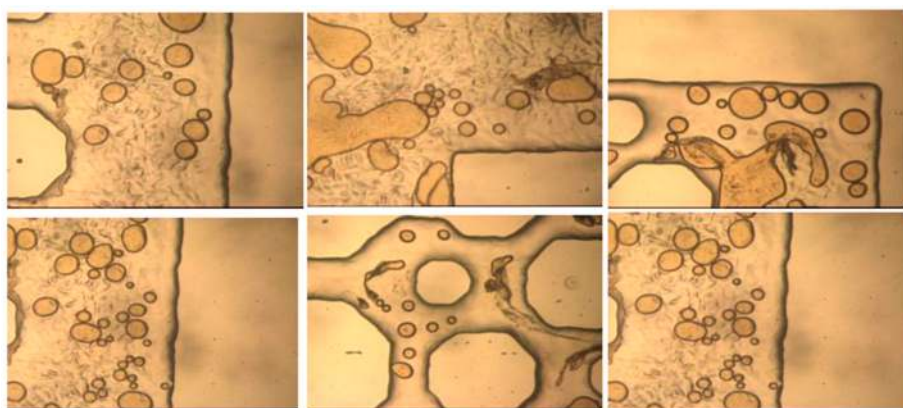
Figure 12. Emulsions observed in the micromodel experiments during nanofluid flooding processes [34].

(**a**) (**b**)
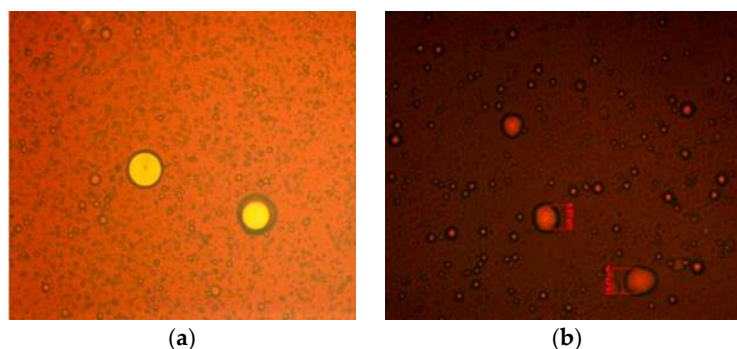
Figure 13. Particle size analysis of crude oil under an optical microscope at X200 magnification: (**a**) mixed with 30,000 ppm saline water; (**b**) mixed with the Al_2O_3 nanofluid [16].

In addition to generate w/o or o/w emulsions by using NPs, the silica NPs can be used to stabilize supercritical CO_2-in-water emulsion, and water-in-supercritical CO_2 emulsion [63,64]. These nanoemulsions can be used for improving oil recovery, especially for CO_2 flooding or CO_2 sequestration because they can maintain stable under harsh reservoir conditions (high temperatures, pressures, shear and salinity).

2.3. Nanocatalysts

Nanocatalysts can be defined as nano-sized metal particles used as catalysts that occur during steam injection into heavy oil reservoirs [65]. Compared with traditional catalysts, nanocatalysts have several advantages, shown in Figure 14 [65–67]. They can be used to conduct upgrading in heavy oil

reservoirs converting bitumen to lighter products by some chemical reactions. These reactions are called aquathermolysis. The presence of nanocatalysts, such as nickel and iron, catalyzes the breaking of carbon-sulfur bonds within asphaltenes, increasing saturates and aromatics in the heavy oil, which can be described as follows [68]:

$$R\text{-}S\text{-}R \text{ (organic sulphur compound)} + H_2O \rightarrow CO + H_2S + \text{lighter organic compound} \qquad (3)$$

Figure 14. The advantages with the usage of nanocatalysts compared with traditional catalysts.

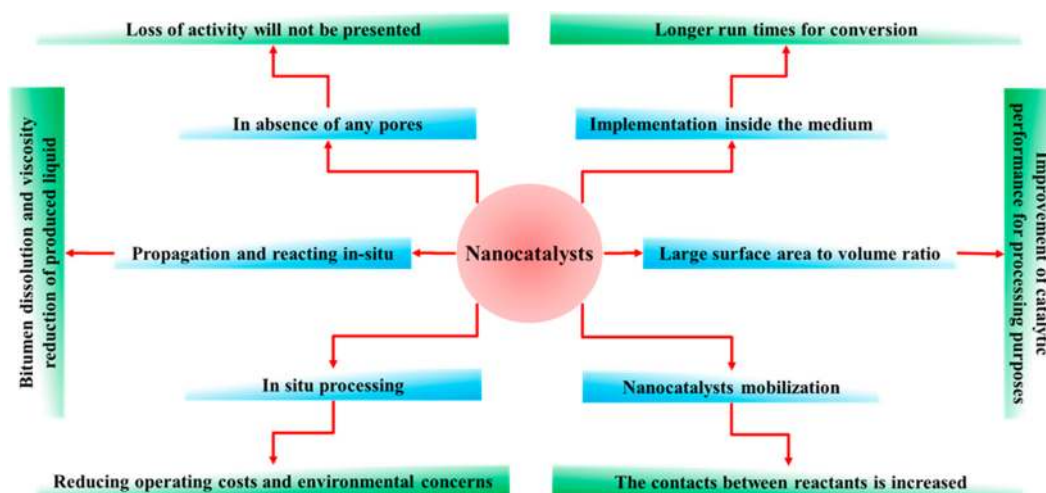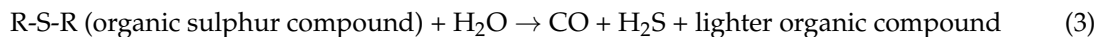The produced CO reacts with water during the water gas shift reaction and produces hydrogen. These reactions occur in the temperature range of the thermal EOR processes (200 to 300 °C). The produced hydrogen molecules attack the unstable and unsaturated molecule of oil and produce lighter and saturated molecules by means of hydrogenolysis [69].

Furthermore, one of the significant mechanisms of aquathermolysis is to decrease heavy oil viscosity. Shokrlu et al. [70] found that nickel NPs with concentration of 500 ppm resulted in viscosity reduction from 2700 mPa·s to 1900 mPa·s. This effect of NPs on viscosity was also observed by Clark et al. [71,72] when they used metal ionic solutions as catalysts in an aquathermolysis process. The main reason for this phenomenon is that the larger specific surface area of nanocatalysts causes more reactivity compared to micron-sized catalysts. That is to say, larger surface area of the nanocatalysts results in an increase in the contact area of oil with the nanocatalysts and better interaction between them.

3. Application of Nanofluid Flooding as a Tertiary Recovery Technique

It is well-known that water flooding is the most practical used secondary oil recovery approach [73]. However, for this method, the oil can be bypassed at the macroscopic level, and be trapped at the microscopic level in reservoirs due to capillary forces. Therefore, significant researches have aimed at finding new EOR agents to be added to the injection water that could reduce trapping and increase the macroscopic sweep efficiency. With the advancement in nanosciences, one of the ides is using NPs to assist water flooding performance and achieving high oil recovery. Many studies have showed promising results and increased oil recovery by nanofluid flooding in laboratory experiments. Some of the details of experiments for nanofluid flooding are summarized on Table 2.

Table 2. Summary on the experiments for nanofluid flooding.

References	NPs/Base Fluids	Oil Type	Oil Properties		Core Properties		Parameters	Incremental Oil Recovery (%)
			Density (kg/m^3)	Viscosity (cp)	Type	Size (mm) L/D		
Alomair et al. [16]	Al_2O_3, SiO_2, NiO, TiO_2/brine	Heavy oil	950	206.88	Sandstone core	6.73/3.80	NP type	−16.94–23.72
Adel et al. [30]	SiO_2, Al_2O_3/brine	Medium crude oil	851	75	Sandstone	7.20/2.50	NP type and concentration	SiO_2 (8.74–13.88) Al_2O_3 (−8.12–−4.65)
Tarek and El-Banbi [31]	Fe_2O_3 + Al_2O_3 + SiO_2/brine	Mineral oil	919	5.12	Sandstone	58.46–76.30 25.20–25.28	Injection mode and salinity	0.9–9.49
Hendraningrat et al. [32]	SiO_2/brine	Light oil	826	5.1	Sandstone	4.08–4.83/3.78–3.80	Permeability, NP concentration, PV	5.93–14.29
Hendraningrat et al. [33]	SiO_2/brine	Paraffinic oil	803	1.956	Sandstone	4.80/3.79	Injection timing	Secondary (8) Tertiary (<2)
Li et al. [34]	SiO_2/brine	Light oil	826	5.1	micromodel	N/A	NP concentration, two phase flow behavior, emulsions and adsorptions	N/A
Li et al. [34]	SiO_2/brine	Light oil	826	5.1	Sandstone	48.02–48.34 37.90–37.93	NP concentration	4.26–5.32
Li et al. [42]	SiO_2/brine	Light oil	847	15.3	Sandstone	4.50/3.83	NP type and concentration	5–15
Roustaei et al. [43]	SiO_2/brine	Light oil	857	11	Carbonate	8–8.50/3.84	Ageing time	9–12, 16–17 (24 h)
Mahdi et al. [44]	SiO_2-biomaterial/water	Heavy oil	925	200	Micromodel (Shale)	N/A	NP concentration, shale orientation, length, distance, injection pressure,	28–40
Maghzi et al. [45]	SiO_2/brine	Heavy oil	933	870	Micromodel	N/A	NP concentration	8.7–26
Hendraningrat et al. [47]	SiO_2, Al_2O_3,TiO_2/brine	Light oil	826	5.1	Sandstone core	38.00/40.10	NP type	7–11
Hendraningrat et al. [49]	SiO_2/brine	Light oil	826	5.1	Sandstone	3.97–12.99/3.80	NP size, permeability, injection rate, rock wettability, temperature	0–8.41
Hendraningrat et al. [49]	SiO_2/brine	Light oil	826	5.1	Sandstone	4.01–4.10 3.78–3.82	permeability and NP concentration	0–9.9
Kazemzadeh et al. [55]	SiO_2,NiO, Fe_3O_4/solution	Asphaltene + toluene	N/A	N/A	Micromodel	N/A	NP type and concentration	SiO_2 (22.6) NiO (14.6) Fe_3O_4 (8.1)
Adel et al. [74]	SiO_2/brine	Light oil	851	75	Sandstone	7.20/2.50	NP size and concentration	5–10
EI-Diasty [75]	SiO_2/Brine	Mineral oil	891	N/A	Sandstone	76.97/25.23	NP size and concentration	9–19
Ogolo et al. [76]	SiO_2 et al./Ethanol et al.	Medium crude oil	911	53.28	Sandpack	N/A	Base fluid and NP type	13.3–24.1
Ehtesabi et al. [77]	TiO_2/brine	Medium crude oil	920	41.21	Sandstone core	6.30/3.70	NP concentration	10–14
Haroun et al. [78]	CuO, NiO, Fe_2O_3/brine	Medium crude oil	887	47.9	Carbonate	3.81/3.81	NP type	Fe_2O_3 (8.19) NiO (7.59) CuO (14.07)
Tarek [79]	Fe_2O_3 + Al_2O_3 + SiO_2/brine	Mineral oil	919	5.12	Sandstone	71.98–78.2 25.24–25.57	Mixture concentration	8.99–20.42

3.1. Preparation of Nanofluids

Preparation of nanofluids is the first step in nanofluid flooding. The delicate preparation of a nanofluid is important because nanofluids need special requirements such as an even suspension, stable suspension, low agglomeration of particles, and no chemical change of the fluid [80]. Coagulation/agglomeration is a main problem during preparation of nanofluids [81]. Unstability of nanofluids will lose their potential benefits when they are injected into reservoirs. Stability of nanofluids depends on the preparation methods, NP characteristics, type of basefluids, surfactants, pH, ultrasonication, etc.

There are several methods used for enhancing the stability of nanofluids [82].

(1)   Changing the pH value: Isoelectric point (IEP) is the value of pH at which a particular molecule carries no net electric charge, or hydration forces are negligible. When the pH of nanofluids is equal or close to the IEP, nanofluids become unstable. Zeta potential is zero at the isoelectric point, repulsive forces between NPs suspended in basefluid are zero and there is a tendency of coagulation [83]. Hydration forces between NPs must be high in order to enhance the stability of nanofluids [84]. A stable nanofluid must have pH around 7 because very high or low pH values may damage the heat transfer surface due to corrosion especially at high temperature [84].

(2)   Using surfactants: Surfactants can act as a bridge between NPs and basefluids which creates continuity between NPs and basefluids [85]. Hydrophilic NPs such as oxides NPs will be easily dispersible into the polar basefluids like water. However, when there is a need to disperse hydrophobic NPs into polar base fluids and hydrophilic into non-polar basefluids, then addition of surfactants is required to stabilize the nanofluids. It should be mentioned that the addition of surfactant which affect the thermophysical properties of nanofluids.

(3)   Using ultrasonic vibration: Ultrasonication is an accepted physical technique to disperse agglomerated NPs into the basefluid [86–88]. To disperse the aggregates of NPs, ultrasonication bath- or probe-based ultrasonic devices are most commonly used. The probe-based ultrasonic devices operates at very high frequency. So, there may be the probability of contamination of nanofluids due to the detachment of very minute metal particles from the surface of metal probe. This may affect the stability of nanofluids adversely.

The use of these techniques depends on the required application of the nanofluid. Selection of suitable surfactants depends mainly upon the properties of the solutions and particles. Stability of NP dispersion in base fluid is indicated by zeta potential value, high zeta potential value indicates good stability.

3.2. SiO$_2$ Nanofluid Flooding

The most commonly used NPs in the literatures are SiO$_2$ NPs. Hendraningrat et al. [32] studied the possibility of using SiO$_2$ nanofluid for EOR in sandstones (9–400 mD) and concluded that the SiO$_2$ NPs are suitable for EOR in water-wet sandstone. They also pointed out that NP concentration is an important factor for low permeability water-wet sandstones because higher NP concentrations had a tendency to block porous media. In addition to sandstones, SiO$_2$ nanofluids also have huge potential in EOR of oil-wet carbonate reservoirs [43]. Furthermore, Li et al. [42] conducted core flooding experiments to study the effect of hydrophilic silica nano-structure particles and hydrophilic silica colloidal NPs on oil recovery. They observed the same results that injecting both types of nanofluids could increase oil recovery even though with very low concentration.

3.3. Influence Parameters of SiO$_2$ Nanofluid Flooding

In order to maximize oil recovery of nanofluid flooding, it is crucial to have a clear depiction of some influencing parameters that may affect the displacement process. From Table 2, it is found that many factors, such as temperature, base fluids, NP type, NP size and injection time, have great

effects on performance of SiO_2 nanofluid flooding. Hendraningrat et al. [33] studied the injection time for nanofluid flooding and found that the performance of nanofluid flooding as secondary mode was much better than as tertiary mode. As secondary mode, nanofluid flooding had almost 8% higher ultimate oil recovery. Then, Hendraningrat et al. [49] investigated the effects of NP size, rock permeablitiy, initial rock wettablitiy and temperature on oil recovery. They confirmed that smaller NP size and higher temperature resulted in higher incremental oil recovery. Increasing permeability didn't show proportional relationship to increment oil recovery. Hence, nanofluid flooding has potential in a wide range of reservoir rock permeabilities. Moreover, they expected that with increasing the injection rate, the small water molecules would accelerate faster than the NPs. So the NPs would agglomerate and block the pore throat and hence reducing the oil recovery. Also, Adel et al. [74] conducted several flooding experiments to study the effect of NP size on oil recovery and found that the higher final recovery factors were obtained when the NPs with smaller size were used in experiments. EI-Diasty [75] evaluated the effect of NP size (5 to 60 nm) on SiO_2 nanofluid flooding by Egyptian sandstones. They reached the same conclusions as Hendraningrat et al. [49] and Adel et al. [74]. Furthermore, Roustaei and Bagherzadeh [43] reported that aging of nanofluid in cores contributed to increased oil recovery. The experimental results showed that oil recovery factors increased by 16% and 17%, respectively, when the nanofluid was aged for 24 h in two core samples. Tarek and EI-Diasty [31] reported that nanofluid slugs could be used as an alternative for continuous injection as it could be more economically attractive.

3.4. Metal Oxides Nanofluid Flooding

With the advancement in nanosciences, some researchers have investigated the use of some metal oxides NPs and proven their ability as EOR agents and their advantages over SiO_2 NPs. For example, Ogolo et al. [76] investigated the performance of eight NPs (oxides of aluminum, zinc, magnesium, iron, zirconium, nickel, tin and silicon) and four base fluids (distilled water, brine, ethanol and diesel oil) for enhanced oil recovery. The results obtained from the experiments showed that Al_2O_3 NPs dispersed in brine and distilled water had the tendency to improve oil recoveries through reduction of oil viscosity. Magnesium and zinc oxide in distilled water and in brine resulted in permeability problems due to their large diameter. Adel et al. [30] performed experiments to compare the potentials of SiO_2 and Al_2O_3 nanofluids used to improve the oil recovery. They found experimentally that SiO_2 NPs with different concentrations could be used to improve the recovery factor. However, the oil recoveries of Al_2O_3 NP were not better than that of water flooding. In addition, Hendraningrat et al. [47] investigated Al_2O_3 and TiO_2 and compared them with SiO_2. The results showed that the highest total oil recovery was achieved by using TiO_2. Then, Ehtesabi et al. [77] found that TiO_2 NPs in low concentration could enhance heavy oil recovery in flooding experiments on a laboratory scale. Meanwhile, Haroun et al. [78] proposed a new EOR method, called electrokinetics (EK)-assisted nanofluid flooding. In this process, EK (direct current voltage of about 2 V/cm) was applied to increase oil recovery of nanofluid flooding. They compared the performances of several NPs (FeO, CuO and NiO) with EK after waterflooding stage in the carbonate cores from Abu Dhabi and found that CuO produced better results than FeO and NiO due to exhibiting both higher density and electrical conductivity.

3.5. Other Nanofluid Flooding

Except for the abovementioned NPs, other commonly used nanomaterials are mentioned in the literature, such as cellulose nanocrystals (CNC) and micro-gel nano-spheres. Molnes et al. [27] investigated the injectivity of CNC in a high-permeable sandstone core, and found that CNC has potential as additives in injection water for EOR. Then, Heggset et al. [89] found that CNC has temperature stability that was stable after heating to 140 °C for three days. Wei et al. [29] also believed that nanocrystals are supposed to be a promising flooding agent in the near future. They proved that sweep volume improvement, emulsification and entrainment were the main mechanisms for nanocrystal nanofluid flooding by visual EOR experiments in a micromodel.

Moreover, Kanj et al. [90] performed an experimental study on nanofluids ($BaSO_4$, $BaFe_{12}O_{19}$) core flood experiments in the ARAB-D formation of the giant Ghawar field in Saudi Arabia. Meanwhile, Wang et al. [91], prepared a polyacrylamide micro-gel nano-spheres and used them to enhance the recovery of Zhuangxi heavy oil (its viscosity is 238 mPa·s at 55 °C,) in a sand-pack model. They confirmed experimentally the promising future of nanospheres in EOR. For carbonate reservoirs. Kanj et al. [92] presented the first laboratory plus field trial of NPs application on the giant Ghawar oil field at Saudi Arabia. The formation was Arab-D carbonate rock. Their challenges involve a high temperature reservoir greater than 100 °C and high connate water salinity about 120,000 ppm. The NP used is called A-Dots. They are carbon based fluorescent NPs. Carbon NPs represent a unique class of nanomaterials that are generally synthesized through a hydrothermal treatment process. The recovery factor achieved experimentally using A-Dots NPs was exceeding 96% lab scale.

3.6. Mixture Nanofluid Flooding

A single nanofluid does not have all the favorable advantages required for a particular EOR process. However, in some practical applications, a trade-off between several characteristics of various NPs is required and that is where the use of mixtures of nanofluids comes in. Some authors have found that using nanofluid mixtures is favorable for increasing the recovery since it combines the advantages of different NPs. Alomair et al. [16] performed nanofluid mixture flooding tests on heavy oil using Berea sandstone cores. The experimental results showed that a mixed nanofluid of SiO_2 and Al_2O_3 at 0.05 wt % had the highest incremental oil recovery among all the nanofluids due to its capability to hinder asphaltene precipitation and reduce the emulsion viscosity and IFT values. Then, Tarek and EI-Diasty [31] proved that the use of mixtures of nanofluids (40% Fe_2O_3 + 35 Al_2O_3 + 25% SiO_2) successfully recovered additional oil from oil reservoirs. The mixtures of nanofluids could cause additional recovery beyond what a single nanofluid could. Then, Tarek [79] conducted several experiments with different concentrations of NP mixtures on a high permeability core starting directly with tertiary recovery. They found that the optimum nanofluid mixture concentration depended on both the fluid and rock properties. The main reason suggested for the oil recovery improvement is that mixtures of nanofluids have a high packing efficiency at the interface that might positively affect the oil recovery.

According to the literature, nanofluid mixture flooding can be used as a better technique for EOR than single nanofluid flooding. However, this method also has its disadvantages. Firstly, the systematic and rigorous preparation and evaluation of nanofluid mixtures is time consuming. Moreover, the implementation process of nanofluid mixture flooding is more complex. Finally, the cost of nanofluid mixture flooding is higher than that of single nanofluid flooding.

3.7. Glass Micromodel Experiments

Except for the aforementioned core flooding tests, the glass micromodel experiment is a major means used in the study of the microscopic recovery of oils during nanofluid flooding [34,44,45,55]. By this kind of glass micromodel, the microscopic behavior of oil and nanofluid two-phase flow and fluid distribution in porous media can be continuously monitored during the experiments. This is a significant advantage to detect the movement of nanofluid interfaces, and investigate the microscopic EOR mechanism of nanofluid flooding.

Maghzi et al. [45] performed five-spot glass micromodel experiments with heavy oil and discovered that the sweep efficiency was enhanced during silica nanofluid flooding and increased with the increase of the NP concentration. Then, Li et al. [34] studied three different concentrations of nanofluids as tertiary recovery agents after water flooding. They reported that nanofluids could release oil droplets trapped by capillary pressure and the nanofluids with high NP concentration could stabilize o/w emulsions. Mahdi et al. [44] conducted a series of tests on a micromodel containing shale strikes to study the effects of nano-biomaterials as EOR candidates on heavy oil recovery. They found that the highest efficiency was 78%, which was obtained when one pore volume of biopolymer

and SiO$_2$ NPs were injected. Presence of shales in the pore media decreased the oil recovery and breakthrough time compared with the homogeneous porous media. Recently, Kazemzadeh et al. [55] investigated the effects of SiO$_2$, NiO, and Fe$_3$O$_4$ NPs on oil recovery by a glass micromodel. They found that SiO$_2$ is the most effective NP for improving oil recovery. NiO and Fe$_3$O$_4$ NPs followed.

4. Nano-Assisted Thermal EOR Methods

The continuing decline of conventional oil resources has motivated the oil industry to develop various thermal methods for producing the abundant heavy oil resources worldwide, especially in Venezuela, Canada, and the United States [93]. These thermal methods, such as CSS, steam flooding, SAGD and in-situ combustion, mainly take advantage of heat to reduce heavy oil viscosity [94,95]. However, these production and subsequent upgrading processes often result in high greenhouse-gas emissions and serious water pollution. In-situ upgrading of heavy oil in reservoirs by nanocatalysts in combination with various thermal EOR methods is a promising new idea. It is an environmental-friendly approach for unlocking heavy oil resources by leaving waste hydrocarbons, solids, and minerals under the ground, along with produced oil with immediate viscosity and density.

4.1. Feasibility Study

Nanocatalysts have shown promising applications in various thermal EOR methods to improve oil recovery such as SAGD, electromagnetic heating process, CSS etc. For instance, Nassar et al. [96] was the first to propose in-situ upgrading of heavy oil by adding nanocatalysts in combination with SAGD (Figure 15). Then, in order to investigate the effect of reaction severity and nanocatalysts on solid and gaseous products, Hashemi et al. [97] studied for the first time in situ upgrading of Athabasca bitumen using Ni–W–Mo nanocatalysts in a continuous flow mode. The results showed that nanocatalysts bettered the quality of Athabasca bitumen by improving the bitumen properties such as decreasing the density, viscosity and microcarbon residue. In addition, Nassar et al. [98] investigated the effects of NP type on heavy oil recovery. They found that NiO had higher oxidation ability, adsorption capacity, and catalytic potency than Co$_3$O$_4$ and Fe$_3$O$_4$ [99].
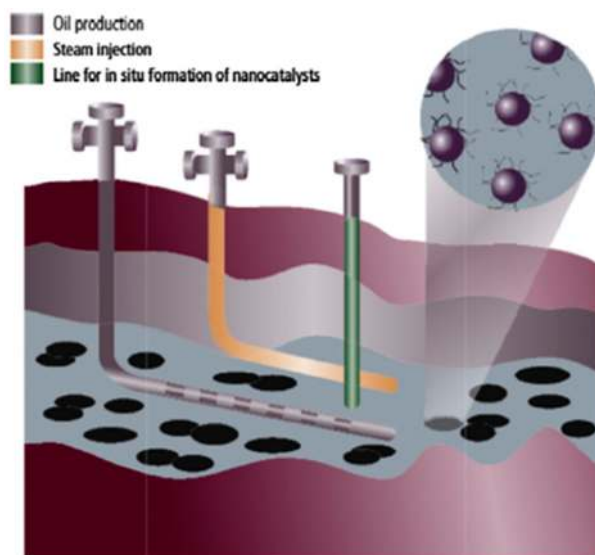
Figure 15. The schematic diagram of the nano-assisted steam-assisted gravity drainage (SAGD) process.

Greff et al. [100] investigated the effects of nanocatalysts on electromagnetic heating processes for heavy oil recovery. They found that nano-nickel catalysts improved the performance of electromagnetic heating processes. This is because of the increased cracking and vaporization which was demonstrated by Greff and Babadagli [101] to take place in the presence of nanocatalyst and microwaves. In addition,

nano-nickel catalysts increased the efficiency of microwave heating for heavy oil production, which recovered more oil with a faster rate and a lower total energy input.

Moreover, Greff et al. [101] reported that nickel NPs improved the recovery of CSS by 10%. Then, Shokrlu and Babadagli [102] also studied the effects of nickel NPs on the recovery of CSS. The results showed that the nickel NPs increased the recovery factor by approximately 22% when the NPs were injected together with a cationic surfactant and xanthan-gum polymer. Sveistrup et al. [103] also believed that the combination of surfactant and xanthan gum can be used as viscosifying agents in EOR processes. Farooqui et al. [104] confirmed the beneficial aquatthermolysis effect brought by the use of nickel NP shown in the previous research (Shokrlu and Babadagli [102]). Except for the laboratory experiments, The CSS field pilot tests using nanocatalysts were conducted in Liaohe oilfields in China [42,91]. This is considered the first real application of nanocatalysts in oilfields.

Hashemi et al. [23] reported that the presence of trimetallic nanocatalysts in the hot fluid enhanced the bitumen recovery. This is because the contact between nanocatalysts with the hot gases results in the production of lighter components by catalytic hydrocracking of bitumen and the subsequent viscosity reduction of bitumen.

4.2. Transport of Nanocatalysts inside Porous Media

In order to place nanocatalysts in contact with more oil in reservoirs during nano-assisted thermal EOR processes, one of the essential requirements is the propagation of nanocatalysts in oil over long distances in reservoirs. Therefore, one of the obvious concerns is the feasibility of transporting the nanocatalysts in reservoirs to contact enough oil without formation damage.

Habibi et al. [105] pointed out that the study of interactions between fines and pore surfaces and investigating the governing forces are important issues to describe the mechanism of transport of nanocatalysts inside porous media. Ahmadi et al. [15] found that the magnitude of the electric double layer repulsion in comparison with the London-van der Waals attraction between fines and media grain particles was considerably diminished when MgO nanoparticle was used to coat the porous media resulting in fine fixation. Godinez and Darnault [106] believed that deposition process is a key retention mechanism of nano-TiO$_2$ in saturated porous media. As the solution pH approached the point of zero charge of nano-TiO$_2$, the mobility and transport of nano-TiO$_2$ were limited due to the reduction of electrostatic interaction forces leading to the increase in the deposition rate coefficients. Vecchia et al. [107] injected microscale zerovalent iron (ZVI) at a concentration of 20 g/L, amended with xanthan gum (3 g/L) in 0.46 m long columns. The tests proved that xanthan gum is an excellent stabilizing agent and delivery vehicle of ZVI particles.

The feasibility of propagating nanocatalysts through reservoirs was investigated by Zamani et al. [108,109]. They confirmed that the propagation of nanocatalysts in an oil sands packed bed column at typical pressure and temperature of SAGD recovery process is feasible, as neither major permeability reduction nor pore plugging were observed. Then, Zamani et al. [24] examined the effects of permeability, connate brine salinity, temperature and NP concentration on the propagation of NPs in porous media. The results showed that the temperature, connate-water salinity, permeability and NP concentration have no effects on transport of nanocatalysts inside porous media.

However, it is noteworthy that the results reported by Zamani et al. were obtained at low temperatures and without taking the cracking reaction into account which indicated that nanocatalysts could transport through the porous beds. Hashemi et al. [110] studied the transport of nanocatalysts (Ni–Mo–W) in oil sands at high temperature and pressure, and found that aggregation of nanocatalysts occurred at high temperatures and different sand permeability. The authors showed that the deposition tendency for nanocatalysts was strongly affected by the type of metal, temperature, and sand permeability. Increasing the temperature favored the aggregation, which was attributed to the increase in frequency of particle collision because of heavy oil viscosity reduction and subsequently, higher aggregation rate. Further, a high-permeability-oil-sands-packed bed has a lower amount of deposited nanocatalysts compared to the low-permeability medium. Again, deposition of nanocatalysts mainly

occurred at the entrance of the injection zone and rapidly decreased across the reaction zone. Ju and Fan [111] also found that NP adsorption at pore walls, and pore throat blocking, occur at a higher frequency closer to the inlet by experiments. However, the same for the low temperature experiments, deposition of nanocatalysts inside the porous media has a meager influence on medium permeability. Again, pressure drop analysis showed no major permeability damage across the reaction zone [110].

One of the most important aspects of nanocatalyst transport inside porous media is the control over the particle size during the injection and reaction times. In addition to pressure drop via permeability reduction, particle size would impact on dispersion ability, adsorption affinity and catalytic activity of nanoparticles inside the medium [110]. Nassar et al. [98,99] performed a series of experimental studies on this important aspect with successful results. It should be noted that most of these studies are at the initial steps for fulfilling the idea of in-situ upgrading with the promising results to future enhancement in the area of heavy oil technologies.

Except for the abovementioned experiments, mathematical simulation methods also can provide valuable information on the transport behavior of nanocatalysts in porous media. Modeling of mass transfer and deposition behavior of fine particles in cylindrical channels were studied by several researchers [112–114]. Molina [115] developed a mathematical model which took into account the geometry of channels, fluid properties, NP size and concentration. Despite the very large effort, by changing the physical properties of media and geometry, it is required to conduct new experiments to estimate the coefficient existed in the mathematical model equations. Moreover, Ju et al. [116] presented mathematical models regarding changes in reservoir properties (porosity and absolute permeability) due to adsorption of NPs. However, the mathematical modeling of such processes is still very complex and still requires novel description and solution methods. Significance of nanocatalysts for improving heavy oil recovery needs further research.

In conclusion, propagation of nanocatalysts inside the porous media is feasible and nanocatalysts could be controllably delivered through oil sands porous media into a targeted heavy oil reservoir, where they could work as catalysts for heavy oil upgrading. However, some portion of injected particles could be retained inside the porous media. Nonetheless, the deposited particles inside the medium can potentially increase the activity of the medium and could be predicted by mathematical modeling [115].

5. Nano-Assisted Chemical EOR Methods

By expansion of nanotechnology, the simultaneous application of NPs and chemical substance, such as polymer, surfactant and emulsion, has been studied for improving the oil recovery of traditional chemical processes. In this section, the latest research results about various nano-assisted chemical EOR methods are discussed in detail.

5.1. Nano-Assisted Polymer Flooding

Recently, the use of polymer flooding as a chemical method has increased in oil reservoirs worldwide [117]. However, the occurrence of high shear rates in reservoirs during polymer flooding easily results in degradation of polymers, decreasing their viscosity [118]. Therefore, how to control the degradation of polymers under harsh conditions is one of the key problems to develop widely this technique. Recently, many researchers have found that NPs could be utilized as rheology control agents in polymer flooding.

Maghzi et al. [119] evaluated experimentally the effects of silica NPs on the rheological behavior of polyacrylamide solutions in water. The analysis showed that NPs improved pseudo-plasticity behavior of polymer solutions in low shear rates. This increase can be a reason for EOR during core flooding experiments by nano-assisted polymer flooding in comparison with traditional polymer flooding.

Zeyghami et al. [120] found that addition of silica NPs increased the viscosity of sulfonated polyacrylamide solutions, and its effect on hydrolyzed polyacrylamide increased with the increase of

NP concentrations. In addition, increasing electrolyte concentration decreased the effect of nano silica on viscosity and caused a severe coagulation problem.

Recently, Cheraghian and Khalilinezhad [121] developed a novel nanofluid based on polyacrylamide clay and proved that it is a suitable agent in polymer flooding for improving heavy oil recovery. The coreflood experiments showed a 5% increase in oil recovery for the nanoclay polymer solution in comparison with the polymer solution after 1 PV fluid injection.

In order to observe the microscopic behavior of polymer solutions with NPs in porous media, Maghzi et al. [119,122] studied the performance of silica NPs in polyacrylamide solution in a five-spot glass micromodel saturated with heavy oil. They observed that the silica NPs caused an increase in oil recovery of polymer flooding by a factor of 10%, and strong water-wetting of the medium after flooding. Then, Maghzi et al. [123] researched further the effect of silica NPs on the polyacrylamide performance in the presence of salts during polymer flooding of heavy oil by the same experimental setups. The results showed that the oil recovery decreased by increasing the salt concentration during the polyacrylamide flooding. However, the effect of the salt concentration on oil recovery of polyacrylamide flooding with silica NPs was lower. Moreover, the viscosity of silica nano-suspension in polyacrylamide was higher than that of polyacrylamide solution at the same salinity.

5.2. Nano-Assisted Surfactant Flooding

Surfactant flooding is known as a common chemical method for enhancing oil recovery. Many papers have been published about the effects of NPs as additives in surfactant flooding. The use of NPs can change surfactant properties and therefore increase the influence of surfactant solution on oil recovery processes.

Firstly, NPs can effectively reduce IFT between water and oil due to its presence at the interfacial layers [124]. When the NP concentration is low, NPs decreased IFT due to their absorption on the liquid surface. However, when NP concentration is high, NPs nearly completely remove the surfactant from the bulk aqueous phase and there is no free surfactant available in the bulk [125]. In addition, a study showed that adding non-ferrous metal NPs in an anionic surfactant permitted a 70%–79% reduction of IFT [126].

Secondly, the use of Al_2O_3 NPs with an anionic surfactant can change rock wettability from oil-wet to water-wet and also increase ultimate oil recovery [37]. Recently, Mohajeri et al. [127] also found that C12TAB (a cationic surfactant)/ZrO_2 NPs could alter the wettability to a water-wet condition.

Finally, some researchers found that the presence of NPs could result in rheological changes and therefore increasing viscosity, which affected the oil recovery of surfactant flooding [124,125]. Furthermore, Suleimanov et al. [126] found that NPs added to the surface-active agent solution caused flow character modification from Newtonian to non-Newtonian and a consequent viscosity increase by 2 times. This is a great achievement because this nano-surfactant solution can effectively control the mobility ratio in surfactant flooding processes.

Collectively, addition of NPs in surfactant solutions can release residual oils remaining in reservoirs and improve oil recovery because of IFT reduction, spontaneous emulsion formation, wettability alteration, and flow characters modification.

In addition, it is noted that adsorption of surfactant onto the NPs can also possess the ability to prevent the aggregation of NPs dispersed in nanofluids. The surfactants cover the surface of NPs with a long loop and tail which extends out into the nanofluids. Sterically stabilized nanofluids remain well dispersed or stable for a longer period [128]. Therefore, adsorption of surfactant onto NPs is also a potential mechanism for nano-assisted surfactant flooding.

5.3. Nano-Assisted Emulsion Flooding

Recently, nanoemulsions have attracted interest and enthusiasm for being used in chemical EOR processes [129]. Qiu et al. [130] evaluated the potential application of NP-stabilized solvent base emusion injection to enhance heavy oil recovery in the Alaska North Slope area. The experimental

results showed that addition of NPs to micro-emulsions increased the viscosity of the micro-emulsion, resulting in a favorable mobility ratio. NPs also help form in situ oil emulsification which could mobilize the bypassed heavy oil and form a favorable miscible flooding recovery.

6. Nano-Assisted Gas EOR Methods

Gas injection techniques have been used commercially worldwide for more than 40 years [131]. However, improvement in sweep efficiency is one of the most pressing technical challenges to enable wider application of these techniques. The existence of NPs provides a novel approach to improve the performance of these techniques.

6.1. Nano-Assisted Gas Flooding

Surfactants can be used to generate foam and reduce gas mobility, which improve the sweep efficiency and successfully increase oil recovery of gas flooding in some field tests. However, the harsh environmental conditions in reservoirs, such as high temperature, salinity and rock surface adsorption, are the main handicaps to widely use surfactants in gas injection processes. NPs are of interest in gas EOR as an alternative to surfactants as gas-in-water foam stabilizers due to their special characteristics such as excellent chemical stability even under harsh reservoir conditions, low retention on mineral surface, and the ability to produce highly stable foams.

Silica NPs are commercially available and widely studied for this purpose. For example, Espinosa et al. [132] reported that using silica NPs could form CO_2-in-water foams without the aid of surfactants. Andrew et al. [133] observed that 50% SiOH NPs could strongly adsorb at the CO_2-water interface and generated highly stable CO_2 foams. They also observed that stable CO_2 foam could be generated with the help of silica NPs at 5000 ppm [134]. The core flooding tests showed that the generated CO_2 foam could markedly reduce CO_2 mobility. With the increase of nano-silica concentration and flow rate, the foam mobility decreased and the foam resistance factor increased [134]. In addition, Aminzadeh et al. [135] also found NPs could be used to improve sweep efficiency during liquid CO_2 injection in a brine filled sandstone core for CO_2 sequestration because of generated CO_2/water foam. NP-stabilized foam led to higher CO_2 trapping after the initial CO_2 injection. Le et al. [136] studied mixtures of SiO_2 NPs and surfactants for EOR in high temperature reservoirs. They performed experiments mixing various types of surfactant solutions with SiO_2 NPs. Some of the mixtures showed great potentials for EOR application due to their resistance to adsorption onto rock surface, and thermostability at 91 °C.

Nguyen et al. [137] evaluated NP-stabilized CO_2 foam stability and effectiveness in EOR of different types of oils (light, medium and heavy oils) at micromodel scales. All three oils showed substantial additional oil recovery and a potentially valuable reservoir homogenization effect because NP-stabilized CO_2 foam flooding resulted in significantly smaller oil-in-water emulsions (Figure 16). These results highlighted the pore-scale dynamics, effectiveness, and potential for NP- stabilized CO_2 foam flooding in enhanced oil recovery.
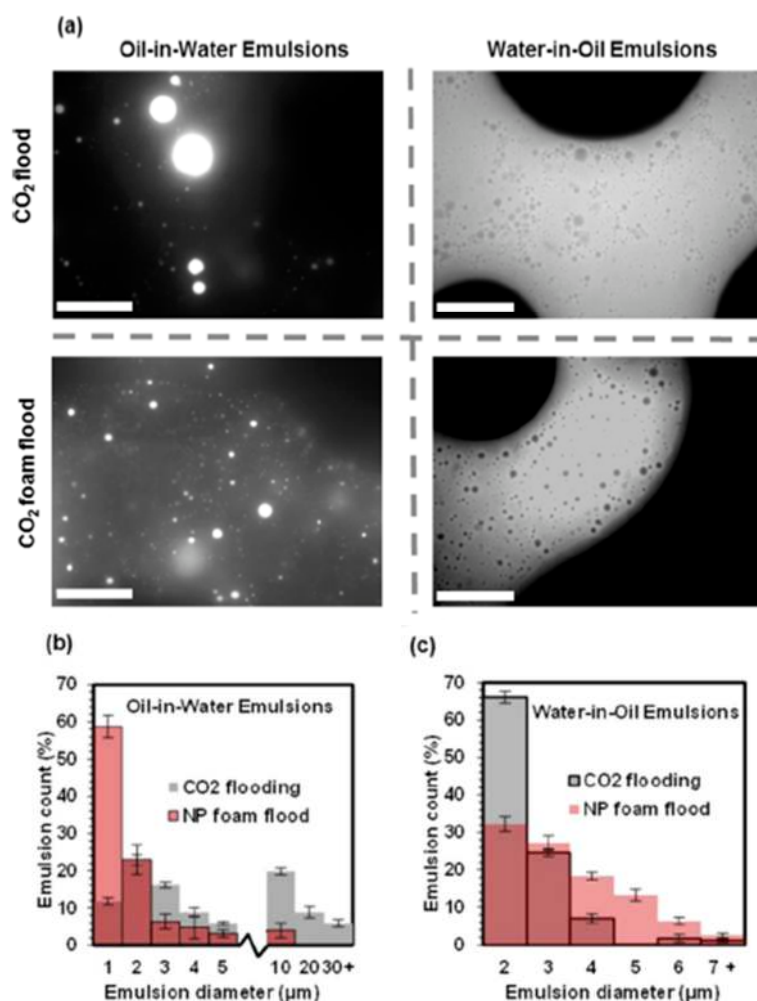
Figure 16. Micrometer-scale quantification of emulsion sizes: (**a**) images of o/w and w/o emulsions produced by a CO_2 flood and a NP-stabilized CO_2 foam flood; (**b**) size distribution of oil-in-water emulsions; (**c**) size distribution of water-in-oil emulsions [137].

Mo et al. [138] observed that SiO_2 stabilized CO_2 foam improved oil recovery after waterflooding in sandstone. The effects of pressure, temperature, and rock samples on the performance of CO_2 foam on residual oil recovery were also investigated. The results indicated that the residual oil recovery by CO_2/nano silica flooding increased as the pressure was increased and temperature decreased. The NP-stabilized CO_2 foam was also observed to improve oil recovery from limestone and dolomite after water flooding.

Yu et al. [139] studied the effects of particle structure (amorphous and crystalline silica nanoparticles) and wettability on supercritical CO_2 foam generation and the supercritical CO_2 foam behaviors such as foam morphology, foam resistance factor and mobility. The results showed that CO_2 foams stabilized by crystalline silica and amorphous silica exhibited similar flow behaviors. The CO_2 bubble size decreased significantly with the increase in hydrophobicity of silica nanoparticles. The silica NP with the highest hydrophobicity showed the greatest reduction of foam mobility under the conditions of wide-ranged phase ratios and total flow rates. In addition to SiO_2 NPs, Espinosa et al. [132] described the development of a CO_2-foam stabilized by PEG-coated NPs.

Worthen et al. [140] presented a turnkey approach for using surface treated NPs in reservoirs and outlined the key details of NP design for CO_2 EOR, which includes foam stability tests, transportability through cores, foam generation when coinjecting NPs and CO_2 in cores, quantification of CO_2 viscosity enhancement, and field-scale simulations.

Except for CO_2 gas, Singh and Mohanty [141] firstly found that aqueous foams could be created by the surface-modified NPs solutions and N_2. The experiments in Berea sandstone cores showed that the generated immiscible foams could recover a significant amount of oil over water flood. These recoveries were comparable to or higher than those obtained when a surfactant was used as the foaming agent.

Another application of NPs is to increase both the density and viscosity of an injected gas. In this way, the mobility is effectively controlled in gas flooding, which improves gas sweep efficiency and oil recovery. For example, Shah and Rusheet [26] conducted CO_2 nanofluid (CuO NPs saturated with CO_2) core flood experiments on EOR of heavy oil. The results showed that NPs CO_2 nanofluid recovered 71.30% of the heavy oil due to swelling and displacing of heavy oil, 13.30% higher than a conventional CO_2 core flood. The mechanism is that both density and viscosity of CO_2 increase by adding NPs. The viscosity of CO_2 nanouids proved to be 140 times greater than conventional CO_2. Then, Jafari et al. [142] investigated application of CO_2 saturated with silica NPs in continuous injection for heavy oil recovery. The results were consistent with the results from Shah and Rusheet [26].

6.2. Nano-Assisted Water Alternating Gas Flooding

It is known that water alternating gas flooding (WAG) is mainly applied to improve sweep efficiency through mobility control. Its EOR mechanism is alternately flooding oil reservoirs with water and gas, and the gas can occupy parts of the pore space that would otherwise be occupied by water flooding [143]. Presence of NPs in WAG process is a novel EOR method, called NWAG, which is mainly used in intermediate and oil-wet reservoirs. This method can economically and efficiently improve oil recovery by simultaneously improving macroscopic and microscopic sweep efficiencies. It is noted that NPs can be used in both the gas and water phases to enhance oil recovery during NWAG processes.

Khezrnejad et al. [144] studied the NWAG process in a two dimensional glass micromodel. The micromodel studies indicated that adding a small amount of SiO_2 and Al_2O_3 NPs to the brine can enhance residual oil recovery by 15%–20%. Concentration and type of NPs have a significant effect on oil recovery. SiO_2 NPs are more efficient than Al_2O_3 NPs in terms of oil recovery.

Moradi et al. [145] studied experimentally NWAG injections performed on carbonate core samples saturated with crude oil. The results showed more than 20% incremental in recovery factor by the NWAG process in comparison with the traditional WAG process. Therefore, the NWAG process is feasible to overcome the problems of the WAG process and further improve oil recovery in field scales.

Jafari et al. [142] investigated application of CO_2 saturated with silica NPs in WAG process for heavy oil recovery. They observed that the water breakthrough happened later and the oil recovery factor increased in nano-saturated CO_2 than pure CO_2 injection due to the formation of nano-stabilised o/w emulsions.

In addition to the numerous abovementioned experimental studies, robust mathematical modeling of NWAG process can also provide valuable information on practical applications. Zhang et al. [146] simulated NWAG process by Eclipse and CMG. In this process, a tracer was applied in the simulations to determine the locations of NPs underground and its concentration. The simulation results showed that NPs mainly located around injection wells and high permeable zones. The NWAG process had a great potential in improving WAG performance, and it performed better with existence of natural fractures. Recently, Matroushi, et al. [147] investigated the feasibility of using NWAG approach in the field scale by simulation. The simulation showed that application of NWAG improved the oil recovery for 13% compared to the traditional WAG process. The injection time of the NWAG process is 6 months (5 months nanofluid and 1 month CO_2) and NWAG ratio is 2:1.

7. Challenges and Opportunities for Future Research

Although NPs are proved to be potential candidates as the agent in many EOR processes, most of them are limited to laboratory research and not suitable for field scale applications. Several challenges still remain before these nano-assisted EOR methods can be used in practical field applications:

(1) Preparation of nanofluids faces several technical challenges. NPs always tend to aggregate at the results of the strong Vander Waals interactions under the harsh reservoir conditions. Therefore, the main technical challenge is to generate a homogeneous suspension of NPs [77].

(2) Currently, most of the research is still focused on nanofluid flooding process. The mechanisms of other nano-assisted EOR methods mentioned in this paper and the interaction among NPs, rock properties and initial reservoir fluid during these processes are not clearly understood.

(3) Although some experiments were conducted to study metal NPs and proved their ability as EOR agents. However, the studies that try to investigate their advantages over SiO_2 NPs still have some divergences among themselves. Moreover, the research on mixture nanofluids is still in its infant stage. The lack of enough experimental research on nanofluid mixtures hinders their wide application in EOR processes.

(4) Reaching a fundamental understanding of various nano-assisted EOR methods requires performing accurate calculation and comprehensive modeling, which remains a challenge. However, it is still lack of suitable theoretical investigation and mathematical models to accurately describe these processes because the nano-assisted EOR methods involve complex procedures and unclear mechanisms.

The immediate need is to pay more attention to the following research areas:

(1) Conduct further experimental research to meet the abovementioned challenges, which involves improving nanofluid stability, control of the dispersion state of nanofluids, understanding the EOR mechanisms of the nano-assisted EOR methods, and exploring novel applications of nanofluid mixtures.

(2) Conduct studies on the theoretical investigation and mathematical models for the various nano-assisted EOR processes to understand the fundamental EOR mechanisms. This also will help the engineers to select suitable nano-techniques and reduce risks for application on field scales.

(3) Explore nano-assisted EOR applications in pilot projects and oilfields. The design and operational experiences acquired from traditional EOR methods should be exploited in development efforts to enable nano-assisted EOR to be applied in practical pilot and oilfield applications in the near future. Furthermore, in order to take these nano-assisted EOR methods to the next level, there is a need to develop cost-effective and environmentally-acceptable NPs.

8. Conclusions

This paper presented a critical review of the most recent research progress in the application of NPs for enhanced oil recovery. The reviewed literature shows that the traditional EOR methods face many challenges, some of which are well solved by NPs, as they have some unique properties, such as ultra-small size, very high surface to volume ratio, low costs and environmental friendliness. Therefore, NPs have been considered as potential agents to enhance oil recovery.

NPs have great potential for EOR in the forms of nanofluids, nanoemulsions and nanocatalysts. Their EOR mechanisms depend on their respective application processes. Nanofluids can be used as a tertiary recovery technique to increase oil recovery of water or gas flooding. Nanocatalysts are always used together with thermal EOR methods to perform in-situ upgrading inside reservoirs by aquathermolysis. Nanoemulsions have a relatively wider application scope including water, gas and chemical flooding.

SiO_2 is the most widely used NP in nanofluid flooding, and has huge potential in enhanced oil recovery for carbonate and sandstone reservoirs. Recently, studies have explored the potential of

other metal oxides NPs such as Al_2O_3, TiO_2 and CuO. Because a single nanofluid does not possess all the favorable characteristics required for a particular EOR purpose, some authors have studied the favorability of using mixtures of nanofluids for increasing the recovery since they combine the advantages of different NPs.

Many parameters, such as types and sizes of NPs, temperature, injection time, etc., have significant effects on the performance of nanofluid flooding. The oil recovery of nanofluid flooding increases with decreasing NP size and injection rate and increasing temperature. Increasing permeability doesn't show proportional relationship to increment oil recovery. The performance of nanofluids flooding as secondary mode is much better than as tertiary mode. Aging of nanofluid contributes to increase oil recovery.

NPs have great potential as catalysts to enhance oil recovery of traditional thermal EOR methods such as SAGD, CSS and electromagnetic heating process. However, one of the concerns with these methods is the feasibility of transporting nanocatalysts through porous media without causing damage to the formation. Aggregation of nanocatalysts often occurs at high temperatures, and is strongly affected by pressure drop, temperature, permeability, NP type and size. Development of mathematical simulation methods can provide valuable information on transport behavior of nanocatalysts in porous media.

The simultaneous application of NPs and chemicals, such as polymer, surfactant and emulsion, has been studied for improving oil recovery of traditional chemical processes. For nano-assisted polymer flooding, adding silica NPs can improve pseudo-plasticity behavior of polymer solutions and stabilize polymer solutions. NPs along with surfactants can result in improving oil recovery and releasing residual oils due to IFT reduction, spontaneous emulsion formation, wettability alteration, and modification of flow characters. Moreover, nano-assisted emulsion flooding is also a promising technique for enhanced oil recovery at laboratory scale.

NPs can be used to better the performance of various gas injection methods by various forms. NP-stabilized gas (CO_2 or N_2) foam flooding has great potential for EOR application. Another application of NPs is to control the mobility in gas flooding by increasing both the density and viscosity of injected gases. The NWAG process is a novel potentially feasible process for enhanced oil recovery. NPs can be used in both the gas and water phases during NWAG processes. In addition to experimental studies, robust mathematical modeling can be used to simulate NWAG process in field scale.

Author Contributions: Xiaofei Sun, Guangpeng Chen and Zhiyong Gai contributed to obtain the literatures Xiaofei Sun contributed to draft the manuscript. Yanyu Zhang reviewed the final paper and made important suggestions and recommendations for paper revision.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Al-Mjeni, R.; Arora, S.; Cherukupalli, P.; Van Wunnik, J.; Edwards, J.; Felber, B.J.; Jackson, C. Has the time come for EOR? *Oilfield Rev.* **2011**, *22*, 16–37.
2. Ahmed, T. *Oil Recovery Mechanisms and the Material Balance Equation Reservoir Engineering Handbook*, 4th ed.; Gulf Professional Publishing: Houston, TX, USA, 2010; pp. 733–809.
3. Green, D.W.; Willhite, G.P. *Enhanced Oil Recovery*; Society of Petroleum Engineers (SPE): Richardson, TX, USA, 1998; Volume 6.
4. Kong, X.; Ohadi, M. Applications of micro and nano technologies in the oil and gas industry—Overview of the recent progress. In Proceedings of the Abu Dhabi International Petroleum Exhibition & Conference, Abu Dhabi, UAE, 1–4 November 2010.

5.　Ayatollahi, S.; Zerafat, M.M. Nanotechnology-assisted EOR techniques: New solutions to old challenges. In Proceedings of the SPE International Oilfield Nanotechnology Conference and Exhibition, Noordwijk, The Netherlands, 12–14 June 2012.

6.　Alvarado, V.; Manrique, E. Enhanced oil recovery: An update review. *Energies* **2010**, *3*, 1529–1575. [CrossRef]

7.　Viebahn, P.; Vallentin, D.; Hoeller, S. Integrated assessment of Carbon Capture and Storage (CCS) in South Africa's power sector. *Energies* **2015**, *8*, 14380–14406. [CrossRef]

8.　Silva, I.G.; de Melo, M.A.; Luvizotto, J.M.; Lucas, E.F. Polymer flooding: A sustainable enhanced oil recovery in the current scenario. In Proceedings of the Latin American & Caribbean Petroleum Engineering Conference, Buenos Aires, Argentina, 15–18 April 2007.

9.　Souza, J.C.; Cursino, D.F.; Pádua, K.G. Twenty years of steam injection in heavy-oil fields. In Proceedings of the SPE Latin American and Caribbean Petroleum Engineering Conference, Rio de Janeiro, Brazil, 20–23 June 2005.

10.　Ahmadi, Y.; Eshraghi, S.E.; Bahrami, P.; Hasanbeygi, M.; Kazemzadeh, Y.; Vahedian, A. Comprehensive Water–Alternating-Gas (WAG) injection study to evaluate the most effective method based on heavy oil recovery and asphaltene precipitation tests. *J. Petrol. Sci. Eng.* **2015**, *133*, 123–129. [CrossRef]

11.　Sun, X.; Dong, M.; Zhang, Y.; Maini, B.B. Enhanced heavy oil recovery in thin reservoirs using foamy oil-assisted methane huff-n-puff method. *Fuel* **2015**, *159*, 962–973. [CrossRef]

12.　Chang, H.L.; Zhang, Z.Q.; Wang, Q.M.; Xu, Q.M.; Guo, Z.D.; Sun, H.Q.; Cao, X.L.; Qiao, Q. Advances in polymer flooding and alkaline/surfactant/polymer processes as developed and applied in the People's Republic of China. *J. Petrol. Technol.* **2006**, *58*, 84–89. [CrossRef]

13.　Vargo, J.; Turner, J.; Vergnani, B.; Pitts, M.J.; Wyatt, K.; Surkalo, H.; Patterson, D. Alkaline-surfactant-polymer flooding of the cambridge minnelusa field. *SPE Reserv. Eval. Eng.* **2000**, *3*, 552–558. [CrossRef]

14.　Krishnamoorti, R. Extracting the benefits of nanotechnology for the oil industry. *J. Petrol. Technol.* **2006**, *58*, 24–26. [CrossRef]

15.　Ahmadi, M.; Habibi, A.; Pourafshari, P.; Ayatollahi, P. Zeta Potential Investigation and Mathematical Modeling of Nanoparticles Deposited on the Rock Surface to Reduce Fine Migration. In Proceedings of the SPE Middle East Oil and Gas Show and Conference, Manama, Bahrain, 25–28 September 2011.

16.　Alomair, O.A.; Matar, K.M.; Alsaeed, Y.H. Nanofluids application for heavy oil recovery. In Proceedings of the SPE Asia Pacific Oil & Gas Conference and Exhibition, Adelaide, Australia, 14–16 October 2014.

17.　Zhang, L.D.; Liu, Y.Z. Preparation and application technology for ultrafine powder. *J. North China Inst. Technol.* **2001**, *22*, 32–43.

18.　El-Diasty, A.I.; Ragab, A.M.S. Applications of nanotechnology in the oil & gas industry: Latest trends worldwide & future challenges in Egypt. In *North Africa Technical Conference and Exhibition*; Society of Petroleum Engineers: Cairo, Egypt, 2013.

19.　Mcelfresh, P.M.; Olguin, C.; Ector, D. The application of nanoparticle dispersions to remove paraffin and polymer filter cake damage. In Proceedings of the SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, LA, USA, 15–17 February 2012.

20.　Aveyard, R.; Binks, B.P.; Clint, J.H. Emulsions stabilized solely by colloidal particles. *Adv. Colloid Interface Sci.* **2003**, *100*, 503–546. [CrossRef]

21.　Chengara, A.; Nikolov, A.D.; Wasan, D.T.; Trokhymchuk, A.; Henderson, D. Spreading of nanofluids driven by the structural disjoining pressure gradient. *Adv. Colloid Interface Sci.* **2004**, *280*, 192–201. [CrossRef] [PubMed]

22.　Skauge, T.; Spildo, K.; Skauge, A. Nano-Sized particles for EOR. In Proceedings of the SPE Improved Oil Recovery Symposium, Tulsa, OK, USA, 24–28 April 2010.

23.　Hashemi, R.; Nassar, N.N.; Almao, P.P. Enhanced heavy oil recovery by in situ prepared ultradispersed multimetallic nanoparticles: A study of hot fluid flooding for Athabasca bitumen recovery. *Energy Fuels* **2013**, *27*, 2194–2201. [CrossRef]

24.　Zamani, A.; Maini, B.; Almao, P.P. Flow of nanodispersed catalyst particles through porous media: Effect of permeability and temperature. *Can. J. Chem. Eng.* **2012**, *90*, 304–314. [CrossRef]

25.　Lyons, W.C.; Plisga, G.J. *Standard Handbook of Petroleum and Natural Gas Engineering*; Gulf Professional Publishing: Houston, TX, USA, 2011.

26.　Shah, R.D. Application of nanoparticle saturated injectant gases for eor of heavy oils. In Proceedings of the SPE Annual Technical Conference and Exhibition, New Orleans, LA, USA, 4–7 October 2009.

27. Molnes, S.N.; Torrijos, I.P.; Strand, S.; Paso, K.G.; Syverud, K. Sandstone injectivity and salt stability of cellulose nanocrystals (CNC) dispersions—Premises for use of CNC in enhanced oil recovery. *Ind. Crops Prod.* **2016**, *93*, 152–160. [CrossRef]

28. Al-Anssari, S.; Barifcani, A.; Wang, S.; Maxim, L.; Iglauer, S. Wettability alteration of oil-wet carbonate by silica nanofluid. *J. Colloid Interface Sci.* **2016**, *461*, 435–442. [CrossRef] [PubMed]

29. Wei, B.; Li, Q.; Jin, F.; Li, H.; Wang, C. The potential of a novel nanofluid in enhancing oil recovery. *Energy Fuels* **2016**, *30*, 2882–2891. [CrossRef]

30. Ragab, A.M.; Hannora, A.E. A Comparative investigation of nano particle effects for improved oil recovery–experimental work. In Proceedings of the SPE Kuwait Oil and Gas Show and Conference, Mishref, Kuwait, 11–14 October 2015.

31. Tarek, M.; El-Banbi, A.H. Comprehensive investigation of effects of nano-fluid mixtures to enhance oil recovery. In Proceedings of the SPE North Africa Technical Conference and Exhibition, Cairo, Egypt, 14–16 September 2015.

32. Hendraningrat, L.; Li, S.; Torsaeter, O. A coreflood investigation of nanofluid enhanced oil recovery. *J. Petrol. Sci. Eng.* **2013**, *111*, 128–138. [CrossRef]

33. Torsater, O.; Engeset, B.; Hendraningrat, L.; Suwanro, S. Improved oil recovery by nanofluids flooding: An experimental study. In Proceedings of the SPE Kuwait International Petroleum Conference and Exhibition, Kuwait City, Kuwait, 10–12 December 2012.

34. Li, S.; Hendraningrat, L.; Torsaeter, O. Improved oil recovery by hydrophilic silica nanoparticles suspension: 2 phase flow experimental studies. In Proceedings of the IPTC 2013: International Petroleum Technology Conference; European Association of Geoscientists & Engineers, Beijing, China, 26–28 March 2013.

35. Parvazdavani, M.; Masihi, M.; Ghazanfari, M.H. Monitoring the influence of dispersed nano-particles on oil–water relative permeability hysteresis. *J. Petrol. Sci. Eng.* **2014**, *124*, 222–231. [CrossRef]

36. Van, S.L.; Chon, B.H. Chemical flooding in heavy-oil reservoirs: From technical investigation to optimization using response surface methodology. *Energies* **2016**, *9*, 711. [CrossRef]

37. Giraldo, J.; Benjumea, P.; Lopera, S.; Cortes, F.B.; Ruiz, M.A. Wettability alteration of sandstone cores by alumina-based nanofluids. *Energy Fuels* **2013**, *27*, 3659–3665. [CrossRef]

38. Anderson, W.G. Wettability literature survey part 5: The effects of wettability on relative permeability. *J. Petrol. Technol.* **1987**, *39*, 1453–1468. [CrossRef]

39. Amott, E. Observations relating to the wettability of porous rock. Transactions. *Aime* **1959**, *216*, 156–162.

40. Anderson, W.G. Wettability literature survey-Part 1: Rock/oil/brine interactions and the effects of core handling on wettability. *J. Petrol. Technol.* **1986**, *38*, 1125–1144. [CrossRef]

41. Teklu, T.W.; Alameri, W.; Kazemi, H.; Graves, R.M. Contact angle measurements on conventional and unconventional reservoir cores. In Proceedings of the Unconventional Resources Technology Conference, San Antonio, TX, USA, 20–22 July 2015.

42. Li, S.; Genys, M.; Wang, K.; Trosaeter, O. Experimental study of wettability alteration during nanofluid enhanced oil recovery process and its effect on oil recovery. In Proceedings of the SPE Reservoir Characterisation and Simulation Conference and Exhibition, Abu Dhabi, UAE, 14–16 September 2015.

43. Roustaei, A.; Bagherzadeh, H. Experimental investigation of SiO_2 nanoparticles on enhanced oil recovery of carbonate reservoirs. *J. Petrol. Explor. Prod. Technol.* **2015**, *5*, 27–33. [CrossRef]

44. Mohebbifar, M.; Ghazanfari, M.H.; Vossoughi, M. Experimental investigation of nano-biomaterial applications for heavy oil recovery in shaly porous models: A pore-level study. *J. Energy Resour. Technol.* **2015**, *137*, 1–7. [CrossRef]

45. Maghzi, A.; Mohammadi, S.; Ghazanfari, M.H.; Kharrat, R.; Masihi, M. Monitoring wettability alteration by silica nanoparticles during water flooding to heavy oils in five-spot systems: A pore-level investigation. *Exp. Therm. Fluid Sci.* **2012**, *40*, 168–176. [CrossRef]

46. Hendraningrat, L.; Torsæter, O. Understanding fluid-fluid and fluid-rock interactions in the presence of hydrophilic nanoparticles at various conditions. In Proceedings of the SPE Asia Pacific Oil & Gas Conference and Exhibition, Adelaide, Australia, 14–16 October 2014.

47. Hendraningrat, L.; Torsaeter, O. Unlocking the potential of metal oxides nanoparticles to enhance the oil recovery. In Proceedings of the Offshore Technology Conference-Asia, Kuala Lumpur, Malaysia, 25–28 March 2014.

48. Karimi, A.; Fakhroueian, Z.; Bahramian, A.; Khiabani, N.P.; Darabad, J.B.; Aniz, R.; Arya, S. Wettability alteration in carbonates using zirconium oxide nanofluids: EOR implications. *Energy Fuels* **2012**, *26*, 1028–1036. [CrossRef]

49. Hendraningrat, L.; Li, S.; Torsater, O. Effect of some parameters influencing enhanced oil recovery process using silica nanoparticles: An experimental investigation. In Proceedings of the SPE Reservoir Characterization and Simulation Conference and Exhibition, Abu Dhabi, UAE, 16–18 September 2013.

50. Nikolov, A.; Kondiparty, K.; Wasan, D. Nanoparticle self-structuring in a nanofluid film spreading on a solid surface. *Langmuir* **2010**, *26*, 7665–7670. [CrossRef] [PubMed]

51. Winkler, K.; Paszewski, M.; Kalwarczyk, T.; Kalwarczyk, E.; Wojciechowski, T.; Gorecka, E.; Pociecha, D.; Holyst, R.; Fialkowski, M. Ionic strength-controlled deposition of charged nanoparticles on a solid substrate. *J. Phys. Chem. C* **2011**, *115*, 19096–19103. [CrossRef]

52. Abdallah, W.A.; Taylor, S.D. Surface characterization of adsorbed asphaltene on a stainless steel surface. *Nucl. Inst. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* **2007**, *258*, 213–217. [CrossRef]

53. Tarboush, B.J.A.; Husein, M.M. Adsorption of asphaltenes from heavy oil onto in situ prepared NiO nanoparticles. *J. Colloid Interface Sci.* **2012**, *378*, 64–69. [CrossRef] [PubMed]

54. Amin, J.S.; Nikooee, E.; Ayatollahi, S.; Alamdari, A. Investigating wettability alteration due to asphaltene precipitation: Imprints in surface multifractal characteristics. *Appl. Surf. Sci.* **2010**, *256*, 6466–6472. [CrossRef]

55. Kazemzadeh, Y.; Eshraghi, S.E.; Kazemi, K.; Sourani, S.; Mehrabi, M.; Ahmadi, Y. Behavior of asphaltene adsorption onto the metal oxide nanoparticle surface and its effect on heavy oil recovery. *Ind. Eng. Chem. Res.* **2015**, *54*, 233–239. [CrossRef]

56. Nassar, N.N.; Hassan, A.; Pereira-Almao, P. Thermogravimetric studies on catalytic effect of metal oxide nanoparticles on asphaltene pyrolysis under inert conditions. *J. Therm. Anal. Calorim.* **2011**, *110*, 1327–1332. [CrossRef]

57. Haindade, Z.M.W.; Bihani, A.D.; Javeri, S.M.; Jere, C.B. Enhancing flow assurance using Co-Ni nanoparticles for dewaxing of production tubing. In Proceedings of the SPE International Oilfield Nanotechnology Conference and Exhibition, Noordwijk, The Netherlands, 12–14 June 2012.

58. Mandal, A.; Bera, A.; Ojha, K.; Kumar, T. Characterization of surfactant stabilized nanoemulsion and its use in enhanced oil recovery. In Proceedings of the SPE International Oilfield Nanotechnology Conference and Exhibition, Noordwijk, The Netherlands, 12–14 June 2012.

59. Binks, B.P.; Lumsdon, S.O. Influence of particle wettability on the type and stability of surfactant-free emulsions. *Langmuir* **2000**, *16*, 8622–8631. [CrossRef]

60. Binks, B.P.; Philip, J.; Rodrigues, J.A. Inversion of silica-stabilized emulsions induced by particle concentration. *Langmuir* **2005**, *21*, 3296–3302. [CrossRef] [PubMed]

61. Binks, B.P.; Rodrigues, J.A. Inversion of emulsions stabilized solely by ionizable nanoparticles. *Angew. Chem.* **2005**, *117*, 445–448. [CrossRef]

62. Zhang, T.; Davidson, D.; Bryant, S.L.; Huh, C. Nanoparticle-stabilized emulsions for applications in enhanced oil recovery. In Proceedings of the SPE Improved Oil Recovery Symposium, Tulsa, OK, USA, 24–28 April 2010.

63. Dickson, J.L.; Binks, B.P.; Johnston, K.P. Stabilization of carbon dioxide-in-water emulsions with silica nanoparticles. *Langmuir* **2004**, *20*, 7976–7983. [CrossRef] [PubMed]

64. Adkins, S.S.; Gohil, D.; Dickson, J.L.; Webber, S.E.; Johnston, K.P. Water-in-carbon dioxide emulsions stabilized with hydrophobic silica particles. *Phys. Chem. Chem. Phys.* **2007**, *9*, 6333–6343. [CrossRef] [PubMed]

65. Hashemi, R.; Nassar, N.N.; Almao, P.P. Nanoparticle technology for heavy oil in-situ upgrading and recovery enhancement: Opportunities and challenges. *Appl. Energy* **2014**, *133*, 374–387. [CrossRef]

66. Yoosuk, B.; Kim, J.H.; Song, C.; Ngamcharussrivichai, C.; Prasassarakich, P. Highly active MoS_2, $CoMoS_2$ and $NiMoS_2$ unsupported catalysts prepared by hydrothermal synthesis for hydrodesulfurization of 4, 6-dimethyldibenzothiophene. *Catal. Today* **2008**, *130*, 14–23. [CrossRef]

67. Almao, P.P. In situ upgrading of bitumen and heavy oils via nanocatalysis. *Can. J. Chem. Eng.* **2012**, *90*, 320–329. [CrossRef]

68. Hyne, J.B. *Aquathermolysis: A Synopsis of Work on the Chemical Reaction Between Water (Steam) and Heavy Oil Sands during Simulated Steam Stimulation*; Alberta Oil Sands Technology & Research Authority: Edmonton, AB, Canada, 1986.

69. Callaghan, C.A. Kinetics and Catalysis of the Water-Gas-Shift Reaction: A Microkinetic and Graph Theoretic Approach. Ph.D. Thesis, Naval Undersea Warfare Center, Worcester, MA, USA, 2006.

70. Shokrlu, Y.H.; Babadagli, T. Transportation and interaction of nano and micro size metal particles injected to improve thermal recovery of heavy-oil. In Proceedings of the SPE Annual Technical Conference and Exhibition, Denver, CO, USA, 30 October–2 November 2011.

71. Clark, P.D.; Clarke, R.A.; Hyne, J.B.; Lesage, K.L. Studies on the effect of metal species on oil sands undergoing steam treatments. *Aostra J. Res.* **1990**, *6*, 53–64.

72. Clark, P.D.; Hyne, J.B. Studies on the chemical reactions of heavy oils under steam stimulation condition. *Aostra J. Res.* **1990**, *29*, 29–39.

73. Willhite, G.P. *Waterflooding*, 3rd ed.; Society of Petroleum Engineers: Richardson, TX, USA, 1986.

74. Ragab, A.M.S.; Hannora, A.E. An experimental investigation of silica nano particles for enhanced oil recovery applications. In Proceedings of the SPE North Africa Technical Conference and Exhibition, Cairo, Egypt, 14–16 September 2015.

75. El-Diasty, A.I. The potential of nanoparticles to improve oil recovery in bahariya formation, Egypt: An experimental study. In Proceedings of the SPE Asia Pacific Enhanced Oil Recovery Conference, Kuala Lumpur, Malaysia, 11–13 August 2015.

76. Ogolo, N.A.; Olafuyi, O.A.; Onyekonwu, M.O. Enhanced oil recovery using nanoparticles. In Proceedings of the SPE Saudi Arabia Section Technical Symposium and Exhibition, Al-Khobar, Saudi Arabia, 8–11 April 2012.

77. Ehtesabi, H.; Ahadian, M.M.; Taghikhani, V. Enhanced heavy oil recovery using TiO_2 nanoparticles: Investigation of deposition during transport in core plug. *Energy Fuels* **2014**, *29*, 1–8. [CrossRef]

78. Haroun, M.R.; Alhassan, S.; Ansari, A.A.; Kindy, N.A.M.; Sayed, N.A.; Kareem, B.A.A.; Sarma, H.K. Smart nano-EOR process for abu dhabi carbonate reservoirs. In Proceedings of the Abu Dhabi International Petroleum Conference and Exhibition, Abu Dhabi, UAE, 11–14 November 2012.

79. Tarek, M. Investigating nano-fluid mixture effects to enhance oil recovery. In Proceedings of the SPE Annual Technical Conference and Exhibition, Houston, TX, USA, 28–30 September 2015.

80. Li, S.; Eastman, J.A. Measuring thermal conductivity of fluids containing oxide nanoparticles. *J. Heat Transf.* **1999**, *121*, 280–289.

81. Wang, X.Q.; Mujumdar, A.S. A review on nanofluids-part I: Theoretical and numerical investigations. *Braz. J. Chem. Eng.* **2008**, *25*, 613–630. [CrossRef]

82. Devendiran, D.K.; Amirtham, V.A. A review on preparation, characterization, properties and applications of nanofluids. *Renew. Sustain. Energy Rev.* **2016**, *60*, 21–40. [CrossRef]

83. Russel, W.B.; Saville, D.A.; Schowalter, W.R. Colloidal dispersions. *J. Chem. Technol. Biotechnol.* **1992**, *54*, 201–202.

84. Wen, D.; Ding, Y. Experimental investigation into the pool boiling heat transfer of aqueous based γ-alumina nanofluids. *J. Nanopart. Res.* **2005**, *7*, 265–274. [CrossRef]

85. Yu, H.; Hermann, S.; Schulz, S.E.; Gessner, T.; Li, W.J. Optimizing sonication parameters for dispersion of single-walled carbon nanotubes. *Chem. Phys.* **2012**, *408*, 11–16. [CrossRef]

86. Ruan, B.; Jacobi, A.M. Ultrasonication effects on thermal and rheological properties of carbon nanotube suspensions. *Nanoscale Res. Lett.* **2012**, *7*, 127. [CrossRef] [PubMed]

87. Kavitha, T.; Rajendran, A.; Durairajan, A. Synthesis, characterization of TiO_2 nano powder and water based nanofluids using two step method. *Eur. J. Appl. Eng. Sci. Res.* **2012**, *1*, 235–240.

88. Nadler, M.; Mahrholz, T.; Riedel, U.; Schilde, C.; Kwade, A. Preparation of colloidal carbon nanotube dispersions and their characterisation using a disc centrifuge. *Carbon* **2008**, *46*, 1384–1392. [CrossRef]

89. Heggset, E.B.; Chinga-Carrasco, G.; Syverud, K. Temperature stability of nanocellulose dispersions. *Carbohydr. Polym.* **2017**, *157*, 114–121. [CrossRef] [PubMed]

90. Kanj, M.Y.; Funk, J.J.; Al-Yousif, Z. Nanofluid coreflood experiments in the ARAB-D. In Proceedings of the SPE Saudi Arabia Section Technical Symposium, Al-Khobar, Saudi Arabia, 9–11 May 2009.

91. Wang, L.; Zhang, G.; Ge, J.J.; Li, G.; Zhang, J.Q.; Ding, B. Preparation of microgel nanospheres and their application in EOR. In Proceedings of the International Oil and Gas Conference and Exhibition in China, Beijing, China, 8–10 June 2010.

92. Kanj, M.Y.; Rashid, M.; Giannelis, E. Industry first field trial of reservoir nanoagents. In Proceedings of the SPE Middle East Oil and Gas Show and Conference, Manama, Bahrain, 25–28 September 2011.

93. Feng, L.; Du, B.; Tian, J.; Long, W.; Tang, B. Combustion performance and emission characteristics of a diesel engine using a water-emulsified heavy fuel oil and Light diesel blend. *Energies* **2015**, *8*, 13628–13640. [CrossRef]

94. Shijun, H.; Hao, X.; Shaolei, W.; Chenghui, H.; Yang, Y. Physical simulation of the interlayer effect on SAGD production in mackay river oil sands. *Fuel* **2016**, *183*, 373–385. [CrossRef]

95. Ashrafi, O.; Navarri, P.; Hughes, R.; Lu, D. Heat recovery optimization in a steam-assisted gravity drainage (SAGD) plant. *Energy* **2016**, *111*, 981–990. [CrossRef]

96. Nassar, N.N.; Husein, M.M.; Almao, P.P. In-situ prepared nanoparticles in support of oilsands industry meeting future environmental challenges. *Explor. Prod. Oil Gas Rev.* **2011**, *9*, 46–48.

97. Hashemi, R.; Nassar, N.N.; Almao, P.P. In situ upgrading of Athabasca bitumen using multimetallic ultradispersed nanocatalysts in an oil sands packed-bed column: Part 1. Produced liquid quality enhancement. *Energy Fuels* **2013**, *28*, 1338–1350. [CrossRef]

98. Nassar, N.N.; Hassan, A.; Almao, P.P. Application of nanotechnology for heavy oil upgrading: Catalytic steam gasification/cracking of asphaltenes. *Energy Fuels* **2011**, *25*, 1566–1570. [CrossRef]

99. Nassar, N.N.; Hassan, A.; Almao, P.P. Comparative oxidation of adsorbed asphaltenes onto transition metal oxide nanoparticles. *Colloids Surf. A* **2011**, *384*, 145–149. [CrossRef]

100. Greff, J.; Babadagli, T. Use of nano-metal particles as catalyst under electromagnetic heating for viscosity reduction of heavy oil. In Proceedings of the International Petroleum Technology Conference, Bangkok, Thailand, 15–17 November 2011.

101. Greff, J.; Babadagli, T. Catalytic effects of nano-size metal ions in breaking asphaltene molecules during thermal recovery of heavy-oil. In Proceedings of the SPE Annual Technical Conference and Exhibition, Denver, CO, USA, 30 October–2 November 2011.

102. Shokrlu, Y.H.; Babadagli, T. Kinetics of the in-situ upgrading of heavy oil by nickel nanoparticle catalysts and its effect on cyclic-steam-stimulation recovery factor. *SPE Res. Eval. Eng.* **2014**, *17*, 355–364.

103. Sveistrup, M.; van Mastrigt, F.; Norrman, J.; Picchioni, F.; Paso, K. Viability of biopolymers for enhanced oil recovery. *J. Dispers. Sci. Technol.* **2016**, *37*, 1160–1169. [CrossRef]

104. Farooqui, J.; Babadagli, T.; Li, H.A. Improvement of the recovery factor using nano-metal particles at the late stages of cyclic steam stimulation. In Proceedings of the SPE Canada Heavy Oil Technical Conference, Calgary, AB, Canada, 9–11 June 2015.

105. Habibi, A.; Ahmadi, M.; Bastami, A.; Pourafshary, P.; Ayatollahi, S. Mathematical modeling of fines fixation in the sandstone cores soaked by MgO nanofluid. In Proceedings of the International Petroleum Technology Conference, Bangkok, Thailand, 15–17 November 2011.

106. Godinez, I.G.; Darnault, C.J.G. Aggregation and transport of nano-TiO_2 in saturated porous media: Effects of pH, surfactants and flow velocity. *Water Res.* **2011**, *45*, 839–851. [CrossRef] [PubMed]

107. Vecchia, E.D.; Luna, M.; Sethi, R. Transport in porous media of highly concentrated iron micro-and nanoparticles in the presence of xanthan gum. *Environ. Sci. Technol.* **2009**, *43*, 8942–8947. [CrossRef] [PubMed]

108. Zamani, A.; Maini, B.B.; Almao, P.P. Propagation of nanocatalyst particles through athabasca sands. *J. Can. Petrol. Technol.* **2013**, *52*, 279–288. [CrossRef]

109. Zamani, A.; Maini, B.; Almao, P.P. Experimental study on transport of ultra-dispersed catalyst particles in porous media. *Energy Fuels* **2010**, *24*, 4980–4988. [CrossRef]

110. Hashemi, R.; Nassar, N.N.; Almao, P.P. Transport behavior of multimetallic ultradispersed nanoparticles in an oil-sands-packed bed column at a high temperature and pressure. *Energy Fuels* **2012**, *26*, 1645–1655. [CrossRef]

111. Ju, B.; Fan, T. Experimental study and mathematical model of nanoparticle transport in porous media. *Powder Technol.* **2009**, *192*, 195–202. [CrossRef]

112. Adamczyk, Z.; Van De Ven, T.G. Deposition of particles under external forces in laminar flow through parallel-plate and cylindrical channels. *J. Colloid Interface Sci.* **1981**, *80*, 340–356. [CrossRef]

113. Brady, J.F. The long-time self-diffusivity in concentrated colloidal dispersions. *J. Fluid Mech.* **1994**, *272*, 109–134. [CrossRef]

114. Sarimeseli, A.; Kelbaliyev, G. Modeling of the break-up of deformable particles in developed turbulent flow. *Chem. Eng. Sci.* **2004**, *59*, 1233–1240. [CrossRef]

115. Molina, H.J.L. Transport of Catalytic Particles Immersed in Fluid Media through Cylindrical Geometries under Heavy Oil Upgrading Conditions. Ph.D. Thesis, University of Calgary, Calgary, AB, Canada, 2009.

116. Ju, B.; Dai, S.; Luan, Z.; Zhu, T.; Su, X.; Qiu, X. A study of wettability and permeability change caused by adsorption of nanometer structured polysilicon on the surface of porous media. In Proceedings of the SPE Asia Pacific Oil and Gas Conference and Exhibition, Melbourne, Australia, 8–10 October 2002.

117. Abidin, A.Z.; Puspasari, T.; Nugroho, W.A. Polymers for enhanced oil recovery technology. *Proc. Chem.* **2012**, *4*, 11–16. [CrossRef]

118. Cheraghian, G.; Nezhad, S.S.K.; Kamari, M.; Hemmati, M.; Masihi, M.; Bazgir, S. Effect of nanoclay on improved rheology properties of polyacrylamide solutions used in enhanced oil recovery. *J. Petrol. Explor. Prod. Technol.* **2015**, *5*, 189–196. [CrossRef]

119. Maghzi, A.; Mohebbi, A.; Kharrat, R.; Ghazanfari, M.H. An experimental investigation of silica nanoparticles effect on the rheological behavior of polyacrylamide solution to enhance heavy oil recovery. *Petrol. Sci. Technol.* **2013**, *31*, 500–508. [CrossRef]

120. Zeyghami, M.; Kharrat, R.; Ghazanfari, M.H. Investigation of the applicability of nano silica particles as a thickening additive for polymer solutions applied in EOR processes. *Energy Source Part A* **2014**, *36*, 1315–1324. [CrossRef]

121. Cheraghian, G.; Khalilinezhad, S.S. Effect of nanoclay on heavy oil recovery during polymer flooding. *Petrol. Sci. Technol.* **2015**, *33*, 999–1007. [CrossRef]

122. Maghzi, A.; Mohebbi, A.; Kharrat, R.; Ghazanfari, M.H. Pore-scale monitoring of wettability alteration by silica nanoparticles during polymer flooding to heavy oil in a five-spot glass micromodel. *Transp. Porous Med.* **2011**, *87*, 653–664. [CrossRef]

123. Maghzi, A.; Kharrat, R.; Mohebbi, A.; Ghazanfari, M.H. The impact of silica nanoparticles on the performance of polymer solution in presence of salts in polymer flooding for heavy oil recovery. *Fuel* **2014**, *123*, 123–132. [CrossRef]

124. Munshi, A.M.; Singh, V.N.; Kumar, M.; Singha, J.P. Effect of nanoparticle size on sessile droplet contact angle. *J. Appl. Phycol.* **2008**, *103*, 084315. [CrossRef]

125. Ravera, F.; Santini, E.; Loglio, G.; Ferrari, M.; Liggieri, L. Effect of nanoparticles on the interfacial properties of liquid/liquid and liquid/air surface layers. *J. Phys. Chem. B* **2006**, *110*, 19543–19551. [CrossRef] [PubMed]

126. Suleimanov, B.A.; Ismailov, F.S.; Veliyev, E.F. Nanofluid for enhanced oil recovery. *J. Petrol. Sci. Eng.* **2011**, *78*, 431–437. [CrossRef]

127. Mohajeri, M.; Hemmati, M.; Shekarabi, A.S. An experimental study on using a nanosurfactant in an EOR process of heavy oil in a fractured micromodel. *J. Petrol. Sci. Eng.* **2015**, *126*, 162–173. [CrossRef]

128. Zhu, H.; Zhang, C.; Tang, Y.; Wang, J.; Ren, B.; Yin, Y. Preparation and thermal conductivity of suspensions of graphite nanoparticles. *Carbon* **2007**, *45*, 226–228. [CrossRef]

129. Mokhatab, S.; Fresky, M.A.; Islam, M.R. Applications of nanotechnology in oil and gas E&P. *J. Petrol. Technol.* **2006**, *58*, 48–51.

130. Qiu, F. The potential applications in heavy oil EOR with the nanoparticle and surfactant stabilized solvent-based emulsion. In Proceedings of the Canadian Unconventional Resources and International Petroleum Conference, Calgary, AB, Canada, 19–21 October 2010.

131. Chukwudeme, E.A.; Hamouda, A.A. Enhanced oil recovery (EOR) by miscible CO_2 and water flooding of asphaltenic and non-asphaltenic oils. *Energies* **2009**, *2*, 714–737. [CrossRef]

132. Espinoza, D.A.; Caldelas, F.M.; Johnston, K.P.; Bryant, S.L.; Huh, C. Nanoparticle-stabilized supercritical CO_2 foams for potential mobility control applications. In Proceedings of the SPE Improved Oil Recovery Symposium, Tulsa, OK, USA, 24–28 April 2010.

133. Worthen, A.; Bagaria, H.; Chen, Y.; Bryant, S.L.; Huh, C.; Johnston, K.P. Nanoparticle stabilized carbon dioxide in water foams for enhanced oil recovery. In Proceedings of the SPE Improved Oil Recovery Symposium, Tulsa, OK, USA, 14–18 April 2012.

134. Mo, D.; Yu, J.; Liu, N.; Lee, R.L. Study of the effect of different factors on nanoparticle-stablized CO_2 foam for mobility control. In Proceedings of the SPE Annual Technical Conference and Exhibition, San Antonio, TX, USA, 8–10 October 2012.

135. Aminzadeh, B.; Chung, D.H.; Zhang, X.; Bryant, S.L.; Huh, C.; DiCarlo, D.A. Influence of surface-treated nanoparticles on displacement patterns during CO_2 injection. In Proceedings of the SPE Annual Technical Conference and Exhibition, New Orleans, LA, USA, 30 September–2 October 2013.

136. Le, N.Y.T.; Pham, D.K.; Le, K.H.; Nguyen, P.T. Design and screening of synergistic blends of SiO_2 nanoparticles and surfactants for enhanced oil recovery in high-temperature reservoirs. *Adv. Nat. Sci. Nanosci.* **2011**, *2*. [CrossRef]

137. Nguyen, P.; Fadaei, H.; Sinton, D. Pore-scale assessment of nanoparticle-stabilized CO_2 foam for enhanced oil recovery. *Energy Fuels* **2014**, *28*, 6221–6227. [CrossRef]

138. Mo, D.; Jia, B.; Yu, J.; Liu, N.; Lee, R. Study nanoparticle-stabilized CO_2 foam for oil recovery at different pressure, temperature, and rock samples. In Proceedings of the SPE Improved Oil Recovery Symposium, Tulsa, OK, USA, 12–16 April 2014.

139. Yu, J.; Wang, S.; Liu, N.; Lee, R. Study of particle structure and hydrophobicity effects on the flow behavior of nanoparticle-stabilized CO_2 foam in porous media. In Proceedings of the SPE Improved Oil Recovery Symposium, Tulsa, OK, USA, 12–16 April 2014.

140. Worthen, A.; Taghavy, A.; Aroonsri, A.; Kim, I.; Johnston, K.; Huh, C.; Bryant, S.; DiCarlo, D. Multi-scale evaluation of nanoparticle-stabilized CO_2-in-Water foams: From the benchtop to the field. In Proceedings of the SPE Annual Technical Conference and Exhibition, Houston, TX, USA, 28–30 September 2015.

141. Singh, R.; Mohanty, K.K. Foams stabilized by in-situ surface-activated nanoparticles in bulk and porous media. *SPE J.* **2016**, *21*, 121–130. [CrossRef]

142. Jafari, S.; Khezrnejad, A.; Shahrokhi, O.; Ghazanfari, M.H.; Vossoughi, M. Experimental investigation of heavy oil recovery by continuous/WAG injection of CO_2 saturated with silica nanoparticles. *Int. J. Oil Gas Coal Technol.* **2015**, *9*, 169–179. [CrossRef]

143. Agbalaka, C.C.; Dandekar, A.Y.; Patil, S.L.; Khataniar, S.; Hemsath, J. The effect of wettability on oil recovery: A review. In Proceedings of the SPE Asia Pacific Oil and Gas Conference and Exhibition, Perth, Australia, 20–22 October 2008.

144. Khezrnejad, A.; James, L.A.; Johansen, T.E. Water enhancement using nanoparticles in water alternating gas (WAG) micromodel experiments. In Proceedings of the SPE Annual Technical Conference and Exhibition, Amsterdam, The Netherlands, 27–29 October 2014.

145. Moradi, B.; Pourafshary, P.; Farahani, F.J.; Mohammadi, M.; Emadi, M.A. Application of SiO_2 nano particles to improve the performance of water alternating gas EOR process. In Proceedings of the SPE Oil & Gas India Conference and Exhibition, Mumbai, India, 24–26 November 2015.

146. Zhang, K.; Li, Y.; Hong, A.; Wu, K.; Jing, G.; Torsaeter, O.; Chen, S.; Chen, Z. Nanofluid alternating gas for tight oil exploitation. In Proceedings of the SPE/IATMI Asia Pacific Oil & Gas Conference and Exhibition, Nusa Dua, Bali, Indonesia, 20–22 October 2015.

147. Matroushi, M.A.; Pourafshary, P.; Wahaibi, Y.A. Possibility of nanofluid/gas alternating injection as an EOR method in an oil field. In Proceedings of the Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi, UAE, 9–12 November 2015.