A Critical Overview of ASP and Future Perspectives of NASP in EOR of Hydrocarbon Reservoirs: Potential Application, Prospects, Challenges and Governing Mechanisms

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Abstract: Oil production from depleted reservoirs in EOR (Enhanced Oil Recovery) techniques has significantly increased due to its huge demands in industrial energy sectors. Chemical EOR is one of the best approaches to extract the trapped oil. However, there are gaps to be addressed and studied well for quality and cost consideration in EOR techniques. Therefore, this paper addresses for the first time a systematic overview from alkaline surfactant polymer ((ASP)) and future perspectives of nano-alkaline surfactant polymer ((NASP)), its synergy effects on oil recovery improvement, and the main screening criteria for these chemicals. The previous findings have demonstrated that the optimum salinity, choosing the best concentration, using effective nano-surfactant, polymer and alkaline type, is guaranteed an ultra-low IFT (Interfacial Tension). Core flood results proved that the maximum oil is recovered by conjugating nanoparticles with conventional chemical EOR methods (surfactant, alkaline and polymer). This work adds a new insight and suggests new recommendation into the EOR application since, for the first time, it explores the role and effect of nanotechnology in a hybrid with ASP. The study illustrates detailed experimental design of using NASP and presents an optimum micro-model setup for future design of NASP flow distribution in the porous media. The presence of nano along with other chemicals increases the capillary number as well as the stability of chemicals in the solution and strengthens the effective mechanisms on the EOR.

Keywords: nano-alkaline-surfactant-polymer; ASP; EOR; interfacial tension; contact angle; core-flooding

1. Introduction

The United States energy information administration has forecasted that worldwide energy use will surge 28% by 2040. Hydrocarbons are regarded as the vital source of energy in the world [1]. Hydrocarbons are recovered in three stages: primary, secondary, and tertiary. Primary oil recovery or natural drive means production of oil due to a change in the production well pressure [2]. Secondary oil recovery starts when the pressure inside the well drops decreases significantly. In the secondary oil recovery reservoir, pressure increased due to fluid (water or gas) injection [3]. Tertiary recovery is used after the secondary stage to displace the trapped oil. Around 33% STOOIP (Stock Tank Oil Original in Place) recovered after primary and secondary methods [4]. After the secondary stage, high oil saturation remains in the reservoir formation [5]. Many oil companies focused on developing new technology at the beginning of 1980; in the US, oil production was expedited after using chemical flooding [6].

Chemical injection as the main EOR process mobilizes the remaining residual oil saturation by improving oil microscopic/macroscopic displacement efficiency [7,8]. Oil microscopic displacement efficiency is improved by surfactant and alkaline injection. Alkaline enhances the trapped oil mobility by adjusting the pH of in situ water [2]. On the other
The main limitation of CEOR method is the excessive adsorption at the rock surface. When these chemicals are introduced into the formation for oil recovery optimization, an extreme amount of surfactant and polymer is lost on the rock surface. This challenge makes the process very costly and have low efficiency in wettability alteration and IFT reduction.

Recently, nanoparticles were used as an effective chemical EOR method to reduce surfactant and polymer adsorption, to increase oil recovery by modifying wettability, and to reduce oil viscosity and water oil IFT. Recent works have suggested that using ASP in hybrid effectively improves residual oil production in the reservoir pore throats [9]. Recent advances, methods and technologies of these chemicals have not been summed up in detail. Therefore, a critical review on the role and effect of different types and concentrations of surfactant, polymer, alkaline and hybrid on oil recovery is needed.

The main objective of our work is focused on the application of nano-alkaline surfactant polymer in EOR by considering the governing mechanisms of recovery and reservoir conditions. Moreover, the effect and role of hybrid nano-ASP flooding in carbonate and sandstone reservoirs are studied effectively by addressing different EOR mechanisms such as interfacial tension, wettability alteration and mobility control. Accordingly, the following questions would be addressed: (i) Could the new idea and recommendation by utilizing NASP design be successful in providing the multi-functional EOR agents? (ii) What are the advantages and disadvantages of using natural based surfactants in NASP over chemical surfactants, and which kind of surfactant is environmentally-friendly; (iii) What are the main challenges and limitations of ASP? (iv) What are the effects of different parameters on interaction between rock/fluid and fluid/fluid such as concentration and type of EOR agents, operational conditions such as salinity and temperature, and pressure of reservoir and injection conditions on the CEOR efficiencies? (v) How NASP can boost the oil recovery in real field projects? (vii) What are the main governing mechanisms of NASP in microscopic and macroscopic scales? Lastly, the authors will investigate the best scenario or method for guaranteeing the maximum oil recovery through NASP injection.

2. The Mechanisms and Role of NASP in CEOR

The EOR project is hugely controlled by mobility of fluids in the pore spaces. Favorable mobility (M) is achieved through reducing the mobility ratio to less than 1.0. Unstable displacement front occurs if M > 1.0. In this case, the large contrast in oil and water viscosity (displacing phase) fingers into oil (displaced phase) leads to premature breakthroughs at production wells, decreasing oil production. To overcome the viscous fingering issue, a polymer is used to enhance the viscosity of the displacing phase to decrease the mobility of the displaced phase (Equation (1)):

\[ M = \left( \frac{K_{rw}}{K_{ro}} \right) \times \left( \frac{\mu_o}{\mu_w} \right) \]

where \( K_{rw} \) = water relative permeability, \( K_{ro} \) = oil relative permeability, \( \mu_w \) = water viscosity, \( \mu_o \) = oil viscosity. For microscopic sweeping, efficiency using AS (Alkaline Surfactant) has been utilized, in situ soap formation by alkaline flooding is not high enough to reduce IFT (Interfacial Tension) significantly [10]. The concept of using surfactant applies to washing surfaces of the oil reservoir rocks when these oils were trapped due to capillary pressure. ASP synergism is one of the successful CEORs in developing oil recovery in complex reservoir conditions. Moreover, it is cost effective in reservoirs that rely on gravity and imbibition in recovering the oil. Around 32 ASP field projects are surveyed in the literature [11]. Twenty-one field projects were reported in China followed by USA, India, Canada and Venezuela with 7, 2, 1 and 1 projects, respectively. Only one project was performed in an offshore reservoir, which was in Lagomar, Venezuela. Five-spot patterns were used in most of the ASP field projects [11]. Heavy alkylbenzene sulfonate was used in most of the projects. In these projects, pump working life and lifting system were damaged.
due to scale and corrosion. Due to scaling issues, weak alkali is widely used instead of strong alkali. The utilized surfactants were ORS-41HF, ORS-62, biosurfactant local Chinese surfactant product (OP10, KPS-1 and CY1), anionic surfactant (BES), (local petroleum sulfonate (YPS-3A), isobutanol, n-butanol, and isopropyl alcohol (cosurfactant). The main polymer used in an ASP slug was HPAM, 1275A, 3530S, and Pusher 700 [11]. Biopolymer (xanthan) was used only in one project [11].

Table 1 depicts a summary of previous ASP works while highlighting the role and mechanisms of each chemical alone and in hybrid for enhancing oil mobilization. To enhance the mobility and investigate the role of the injected NASP, the volumetric sweeping efficiency micromodel as a future new insight in EOR would have been a new recommendation for oil companies. A micromodel experiment (Figure 1) is a future planned model to investigate the mechanism of the fluid flow on porous media via flow visualization, fluid interactions, pore space geometry and heterogeneity effects. To carry out the test, the oil–wet glass micromodel would be saturated with oil, followed by the injection of the prepared hybrid nano-ASP solution. The micromodel is placed horizontally to avoid the gravity effect. During the tests, high resolution pictures will reveal the fluid distribution in the micromodel taken at various time intervals.

![Micromodel diagram](image_url)

**Figure 1.** Future micromodel set up using NASP.

From the previous lab and experimental works, it is quite clear that, for mobilizing and improving the trapped oil effectively and efficiently, most of the EOR mechanisms such as mobility, IFT, and wettability should be controlled and activated. For this objective, the ASP synergism effect should be addressed extensively and optimum concentration of each chemical should be selected for boosting the oil recovery.
Table 1. Summary of previous experimental and field ASP works alone and in synergy.

| CEOR Type | Ref. | Chemical Name       | Conc. | Porosity % | Permeability (md) | Lithology    |
|-----------|------|---------------------|-------|------------|-------------------|--------------|
| Alkaline  | [12] | Na₂CO₃              | 1.0   | NA         | 405–608           | Sandstone    |
|           |      | NaOH                | 1.0   | NA         | 405–608           | Sandstone    |
|           |      | Na₄SiO₄             | 0.5   |            |                   |              |
|           | [13] | Na₂CO₃              | 0.85  | 25         | 70                | Sandstone    |
|           | [2]  | NaOH                | 0.5   | NA         | 1580              | Sandstone    |
|           | [14] | NaOH                | 0.5   | 33.39      | 6000              | Sandstone    |
|           | [15] | NaOH                | 0.2   | NA         | NA                | Carbonate    |
|           | [2]  | Na₂CO₃              | NA    | 35.5       | 3200              | Sandstone    |
|           | [16] | NaOH                | 0.5   | 38.7       | NA                | Sandstone    |
|           | [17] | NaOH                | 0.2   | NA         | NA                | Sandstone    |
|           | [18] | NaOH                | NA    | 15         | 119               | Sandstone    |
|           | [19] | NaOH                | 4.85  | 20.6       | 25                | Sandstone    |
|           | [20] | NaOH                | 0.15  | 16         | NA                | Sandstone    |
|           | [21] | NaOH                | 0.2   | 30         | 495–320           | Sandstone    |
|           | [22] | NaOH                | 0.5   | NA         | 2110              | Sandstone    |
|           | [23] | NaOH                | 1.0   | NA         | NA                | sandstone    |
|           | [24] | NaOH                | 2.0   | 19.7       | 93.64             | Sandstone    |
|           |      | Na₂CO₃              | 2.0   | 19.6       | 176.25            | Sandstone    |
|           | [25] | Na₂Cl₂              | 1.20  | 35         | 3850              | Sandstone    |
| Surfactant| [26] | Cationic C₁₂TAB     | NA    | 45–50      | 2–5               | Carbonate    |
|           | [27] | SDS                 | 1000  | 52.2       | 250               | Carbonate    |
|           | [25] | OPIO and CY1        | NA    | 35         | 3850              | Sandstone    |
|           | [28] | Anionic surfactant  | NA    | 29.06      | 19.72             | Carbonate    |
|           | [29] | Nonionic surfactants| NA    | NA         | 20.89             | Carbonate    |
|           | [30] | Anionic surfactant  | NA    | 3–5        | NA                | Carbonate    |
|           | [31] | nonionic ethoxy alcohol| 3000–4000 | 3–5       | NA                | Carbonate    |
|           | [32] | Anionic (GAC) surfactants | NA | NA | NA | Carbonate |
|           | [33] | Nonionic (POA)      | 750   | 15.4       | 56                | Carbonate    |
|           | [34] | Nonionic ethoxy alcohol| 50–3500 | NA        | NA                | Carbonate    |
|           | [16] | SDS                 | 1000  | 38.6       | 212               | Sandstone    |
|           | [35] | SDBS                | 250   | 37         | 284               | Sandstone    |
|           | [36] | SLPS                | 1000  | 38         | NA                | Sandstone    |
|           | [37] | SDS                 | 3000  | NA         | NA                | Glass bed    |
|           | [38] | XD                  | 1000  | NA         | NA                | Sandstone    |
|           | [39] | SDBS                | 2000  | 25         | NA                | Sandstone    |
|           | [13] | SDS                 | NA    | 23–29      | 50–94             | Sandstone    |
| CEOR Type | Ref. | Chemical Name | Conc. | Porosity % | Permeability (md) | Lithology |
|-----------|------|---------------|-------|------------|------------------|-----------|
| Polymer   | [12] | PAM           | 3200  | NA         | 405 to 608       | Sandstone |
|           | [36] | Xanthan gum   | 1540  | NA         | 405 to 608       | Sandstone |
|           | [40] | (Gum Arabic/Poly acrid) | 1000 | 37.5       | 3780             | Sandstone |
|           | [41] | HPAM          | 1100  | 21.6       | 420              | Sandstone |
|           | [42] | TVP           | 2000  | NA         | NA               | Sandstone |
|           | [43] | HPAM          | 1800  | NA         | NA               | Sandstone |
|           | [44] | PAM           | 500   | >39        | 100–60           | Sandstone |
|           | [16] | PHPAM         | 1500  | 37.3       | 218              | Sandstone |
|           | [45] | HPAM          | 1200  | 15.2       | 23.34            | Sandstone |
| Alkaline Surfactant | [46] | Xylene + NaOH | 5000 + 10,000 | NA | NA | Carbonate |
|           | [47] | IOS + Na₂CO₃  | (200–10,000) + 5000 | 37 | 2400 | Micromodel |
|           | [48] | Na₂CO₃ + alkyl ether sulfates | 1500 + 50 | NA | NA | NA |
|           | [38] | Na₂CO₃ + XD   | 10,000 + 1000 | NA | NA | Sandstone |
|           | [49] | Na₂CO₃ + SDS  | 10,000 + 10,000 | NA | NA | Sandstone |
|           | [49] | (IOS) + NaOH + Na₄SiO₄ | NA | NA | Sandstone |
|           | [50] | NaOH + SLPS   | 3000 + 300 | 44.7 | 2131 | Sandstone |
|           | [50] | NaOH + SLPS   | 8000 + 1000 | 43.50 | 1994 | Sandstone |
|           | [50] | NaOH + SLPS   | 10,000 + 1000 | 44.21 | 2016 | Sandstone |
|           | [13] | SDS + Na₂CO₃  | 1000 + 8500 | 25 | 70 | Sandstone |
|           | [51] | Na₂CO₃ + sodium alkane sulfonate | (1000–15,000) + 1000 | 41–45 | 790–19,220 | Sandstone |
|           | [52] | Na₂CO₃ + anionic PAM | NA | 15.5 | 21 | Sandstone |
|           | [53] | Na₂CO₃ + Pusher 1000E | 8000 + 600 | 29 | 1400 | Sandstone |
|           | [54] | NaOH + Alcoflood 1275A | 10,000 + 1000 | 20 | 200 | Sandstone |
|           | [55] | NaOH + HPAM   | 10,000 + 1000 | 38.92 | 2350 | Sandstone |
|           | [55] | Ethylenediamine + HPAM | 10,000 + 1000 | 39.41 | 2230 | Sandstone |
|           | [55] | Na₂CO₃ + HPAM  | 10,000 + 1000 | 40.33 | 2420 | Sandstone |
|           | [56] | Na₂CO₃ + anionic PAM | NA | 15.5 | 21 | Carbonate |
|           | [57] | (NaOH + Na₂CO₃) + HPAM | (4000 + 2000) + 250 | 34.43 | 4800 | Sandstone |
|           | [57] | HPAM + (NaOH + Na₂CO₃) | 1000 + (1000 + 2000) | 35.25 | 6400 | Sandstone |
|           | [52] | Na₂CO₃ + Alcoflood 1175 | 10,000 + 800 | 29 | 1400 | Sandstone |
|           | [58] | Na₂CO₃ + PAM  | 10,000 + 1500 | 31 | 840.9 | Sandstone |
|           | [25] | Na₂CO₃ + OP-10 | 1200 + 10,000 | 35 | 3850 | Sandstone |
|           | [59] | Na₂CO₃ + HPAM | 20,000 + 1000 | 27.6 | 2063 | Carbonate |
| CEOR Type                  | Ref. | Chemical Name                                      | Conc.          | Porosity % | Permeability (md) | Lithology            |
|---------------------------|------|---------------------------------------------------|----------------|-------------|-------------------|----------------------|
| Surfactant polymer        | [60] | alkyl ether sulfates + Witco petroleum sulfonate | 1000 + 1000    | 12          | 5.9               | Carbonate            |
|                           | [61] | Amphoteric + PAM                                  | 2500 + 1400    | 29.1        | 3442              | Sandstone            |
|                           | [62] | PAM + SDS                                          | 1000 + 2200    | 21          | 66                | Sandstone            |
|                           | [16] | SDS + PHPAM                                        | 1000 + 2000    | 36.8        | 1224              | Sandstone            |
|                           | [63] | bio-surfactant and biopolymer                      | 1001 + 5000    | 17          | 400               | Sandstone            |
|                           | [61] | PS + PAM                                           | 2000 + 2000    | 21          | 115               | Sandstone            |
|                           | [39] | SDBS + HPAM                                        | 2000 + 2000    | 25          | NA                | Sandstone            |
|                           | [64] | PAM + SDS                                          | 2800 + 1000    | NA          | NA                | Glass micromodel     |
|                           | [61] | (Amphoteric +anionic) + PAM                        | 1200 + 1500    | 15          | 110               | Sandstone            |
|                           | [36] | HPAM + SDS                                         | 1000 + 1000    | 38          | 1410              | Sandstone            |
|                           | [45] | anionic surfactant + HPAM                          | 1200 + 1200    | 15.2        | 23.34             | Sandstone            |
|                           | [43] | SLPS + HPAM                                        | 4000 + 1800    | NA          | 1500              | Sandstone            |
|                           | [65] | KPS + HPAM                                         | 3000 + 115     | 14.7        | 5.08              | Sandstone            |
|                           | [43] | SLPS + (HPAM)                                      | 4000 + 1800    | NA          | 1500              | Sandstone            |
|                           | [60] | NaOH + SDS + PHPAM                                 | 5000 + 1000 + 2500 | NA | NA               | Sandstone            |
|                           | [60] | NaOH + SDS + PHPAM                                 | 5000 + 2000 + 2500 | NA | NA               | Sandstone            |
|                           | [60] | NaOH + SDS + PHPAM                                 | 5000 + 3000 + 2500 | NA | NA               | Sandstone            |
|                           | [66] | Amphoteric Petrostep B-100 + Pusher 700E + Na₂CO₃  | 4000 + 1200 + 20,000 | 8–43 | 1–600             | Carbonate            |
|                           | [67] | Na₂CO₃ + SDS+ PAM                                  | 10,000 + 1000 + 800 | NA | NA               | Sandstone            |
|                           | [16] | NaOH + SDS + PHPAM                                 | 5000 + 1000 + 1500 | 38.7 | NA               | Sandstone            |
|                           | [16] | NaOH + SDS + PHPAM                                 | 7000 + 1000 + 1500 | 38.7 | NA               | Sandstone            |
|                           | [16] | NaOH + SDS + PHPAM                                 | 10,000 + 1000 + 1500 | 38.7 | NA               | Sandstone            |
|                           | [16] | NaOH + SDS + PHPAM                                 | 5000 + 1000 + 1500 | 38.7 | NA               | Sandstone            |
|                           | [68] | Na₂CO₃ + Petrostep B-100 + Alcoflood1175A          | 12500 + 1000 + 1475 | 18 | 845               | Carbonate            |
|                           | [69] | Diethylene glycol butyl ether + alcoflood-2545 + NaBO₂ | 3000 + 10,000 + 10,000 | 17.7 | 239               | Sandstone            |
|                           | [70] | HAPAM + NaOH + heavy alkylbenzene sulfonate        | 1000 + 1200 + 3000 | NA | 252               | Sandstone            |
|                           | [71] | Na₂CO₃ + (anionic BES and lignosulfonate PS) + PAM  | 12,000 + 3000 + 1700 | NA | NA               | Sandstone            |
Table 1. Cont.

| CEOR Type | Ref. | Work Type | Chemical Name | Conc. | Porosity % | Permeability (md) | Lithology | Remark |
|-----------|------|-----------|---------------|-------|------------|------------------|-----------|--------|
| Alkaline  | [12] | Experimental | Na₂CO₃ | 17.2 | 9.42 | 8.91 | | Na₂CO₃ is more effective for oil increment |
|          | [13] | Experimental | 4.4 | | | | | Due to soap formation, Interfacial tension between oleic and aqueous phase reduced |
|          | [2]  | Experimental | 12.4 | | | | | Low salinity leads to O/W emulsions if the salinity is above 0.7 W/O emulsions happen |
|          | [14] | Experimental | 13.33 | | | | | IFT reduction due to soap formation improves oil recovery |
|          | [15] | Experimental | NA | | | | | Alkaline flooding is more applicable for medium crude oil as compared to light crude oil due to a higher ratio of soap formation in medium crude oil |
|          | [2]  | Experimental | 14 | | | | | Alkaline is also applicable and can accelerate oil recovery in horizontal wells |
|          | [16] | Experimental | 13.88 | | | | | Strong base (NaOH) alkaline injection enhanced oil recovery |
|          | [17] | Experimental | NA | | | | | Higher oil recovery due to in situ. Emulsion formation |
|          | [18] | Experimental | 2 | | | | | additional oil guaranteed by changing the wettability |
|          | [19] | Field | 6–8 | | | | | the amount of IFT reduction determines the success of alkali job |
|          | [20] | Field | 2 | | | | | Changing in rock surface wettability directly affects oil recovery |
|          | [21] | Field | 5 to 7 | | | | | Formation of the emulsion by alkaline improves volumetric sweep efficiency |
|          | [22] | Experimental | 12.9 | | | | | The oil displacement experiment proved that oil recovery is enhanced by using alkaline injection |
|          | [23] | Experimental | <1 | | | | | Orthosilicate was very successful at stopping water channeling and increasing oil recovery |
|          | [24] | Experimental | 2.52 | 3.67 | | | | NaOH is more effective than Na₂CO₃ |
|          | [25] | Field | 9.13 | | | | | Ultra-low IFT after alkaline flooding |
|          | [26] | Experimental | 20 | | | | | changing rock surface wettability due to the sulfate that is present in the injection fluid |
|          | [27] | Experimental | 9 | | | | | Oil recovery affected by the type and concentration of the surfactant used in the formation |
|          | [28] | Field | 11.64 | | | | | Higher amount of IFT reduction leads to more oil recovery |
|          | [29] | Field | 30 | | | | | Optimum surfactant concentration is related with brine salinity |
|          | [30] | Experimental | NA | | | | | About 58,000 bbl of oil is produced after using Nonionic surfactants over only three months |
|          | [31] | Experimental | NA | | | | | The performance of anionic surfactants was more effective than nonionic surfactants |
|          | [32] | Experimental | 15.0 | | | | | to optimize surfactant performance injection rate, conc. and volume are the important parameters |
|          | [33] | Experimental | NA | | | | | IFT significantly diminished |
|          | [34] | Experimental | 10.4 | | | | | Nonionic surfactant outperformed cationic surfactant |
|          | [35] | Experimental | NA | | | | | surfactants decreased IFT and changed the contact angle |
| CEOR Type | Ref. | Chemical Name | Conc. | Porosity % | Permeability (md) | Lithology |
|-----------|------|---------------|------|------------|------------------|-----------|
| Surfactant | [16] | Experimental | 17.96 | IFT decreased marginally | | |
| | [35] | Experimental | 2.1 | Due to surfactant degradation, the oil recovery was low | | |
| | [36] | Experimental | 4 | Increase in capillary number yields more oil recovery | | |
| | [37] | Experimental | NA | IFT reduced from 19.59 to 2.82 mN/m | | |
| | [38] | Experimental | 11.5 | At lower concentration, a novel XD yielded a good oil recovery that can be compared with SDS | | |
| | [39] | Experimental | 4.6 | Compared to SP flooding, oil recovery by using surfactant flooding was reduced | | |
| | [13] | Experimental | 7.1 | Adsorption phenomena indicated that SDS was a suitable choice for sandstone formation | | |
| | [12] | Experimental | 11 10.5 | Polymer type selection is critical | | |
| | [36] | Experimental | 10.7 | Increasing the viscosity of water by HPAM improves vertical sweep efficiency | | |
| | [40] | Experimental | 5.2 | Core flood test indicates that this type of polymer is less effective than other polymer types due to less oil improvement | | |
| | [41] | Field | 9.8 | Higher molecular weight improves thermal stability | | |
| | [42] | Experimental | 13.5 | Temperature affects polymer performance | | |
| | [43] | Experimental | 6.3 13.4 | PPG is more effective in higher and lower permeability zones compared to conventional polymer (HPAM) | | |
| | [44] | Field | 7 | Earlier injection of polymer is more profitable | | |
| | [16] | Experimental | 16.12 | High viscosity of polymer leads to an increase in macroscopic displacement | | |
| | [45] | Experimental | 8.80 | From the results, it can be indicated that polymer is used mostly to reach to the unrecoverable oil zones | | |
| | [46] | Field | 10–15 | Alkaline-surfactant flooding offers a potential scheme to recover part of the high residual oil that was not recovered by waterfront | | |
| | [47] | Experimental | NA | Emulsification of heavy oil by AS was effective | | |
| | [48] | Experimental | NA | For mobilizing heavy oil, AS flooding is a very suitable choice | | |
| | [38] | Experimental | 14.58 10.42 | In situ soap by alkali and surfactant reduces IFT significantly | | |
| | [49] | Field | NA | Alkaline is not able to mobilize oil alone, when surfactant added IFT reaches minimum value and oil easily mobilized | | |
| | [50] | Experimental | 12.10 15.80 18.63 | Surfactant and soap (in situ) surfactant formation efficiently reduces IFT | | |
| | [13] | Experimental | 18 | As shown in adsorption phenomena, alkali plays a major role in reducing surfactant adsorption | | |
| | [51] | Experimental | 10.5 | Surfactant reduces the alkaline consumption | | |
| CEOR Type | Ref.   | Chemical Name | Conc. | Porosity % | Permeability (md) | Lithology |
|-----------|--------|---------------|-------|------------|-------------------|-----------|
| Alkaline polymer | [52] Field | NA | AP synergy effect was efficient for improving EOR mechanisms |
|           | [53] Field | 21.1 | AP was sufficient to improve oil recovery |
|           | [54] Field | 17 | Binary system of A and K performance is more significant than using each of the chemicals alone |
|           | [55] Experimental | 21.02 | In AP flooding, alkaline selection plays a critical role in oil recovery improvement |
|           | [56] Field | 26.4 | Soap formation by Na₂CO₃ and viscosity improvement by anionic polymer yielded higher recovery |
|           | [57] Experimental | 18.58 | Conc. of polymer influences oil recovery |
|           | [57] Experimental | 16.56 | Conc. of Alkaline influences oil recovery |
|           | [52] Field | 21.1 | 67% OOIP was recovered by AP |
|           | [58] Experimental | 22.8 | Polymer solution should be injected at a good speed |
|           | [25] Field | 18.12 | alkali cannot to the oil region without polymer |
|           | [59] Experimental | 1.98 | Mobility control improved |
|           | [60] Experimental | 12.0 | Using two surfactants was more effective |
|           | [61] Field | 16.3 | Using surfactant with polymer yield extra oil recovery |
|           | [62] Experimental | 17.25 | Temperature and initial oil saturation affects oil recovery |
|           | [16] Experimental | 20.99 | Better mobility control is obtained by using polymer with surfactant |
|           | [63] Experimental | 15.94 | The binary system demonstrated high interfacial activity with IFT min below 0.01 mN/m |
|           | [61] Field | 13.8 | Synergism of polymer and surfactant further improves oil recovery |
|           | [39] Experimental | 20 | Oil recovery after using dual chemicals (S and P) was higher than the total oil that is produced by using S and P alone |
|           | [64] Experimental | 41 | CMC of SDS is 0.21 means that higher concentrations of CMC have a marginally effect on oil recovery |
|           | [61] Field | 14.5 | Polymer and surfactant synergism developed by choosing the optimum conc. of each |
|           | [36] Experimental | 13.7 | Without polymer injection surfactant cannot go through unsweep zones |
|           | [45] Experimental | 11.29 | Anionic surfactant for sandstone reservoir is very effective |
|           | [43] Experimental | 13.6 | Polymer and surfactant synergistic yields higher oil displacement |
|           | [65] Experimental | 23.96 | Polymer controls mobility control and surfactant reduces IFT |
|           | [43] Experimental | 22.4 | SLPS improves displacement efficiency and (HPAM + PPG) improves sweep efficiency |
Table 1. Cont.

| CEOR Type | Ref.   | Chemical Name | Conc.  | Porosity % | Permeability (md) | Lithology |
|-----------|--------|---------------|-------|------------|-------------------|-----------|
| Alkaline surfactant Polymer (ASP) | [60] Experimental | Alkaline surfactant Polymer (ASP) | 23.69 | Increase in surfactant conc. leads to oil recovery enhancement |
| [66] Experimental | An alkaline surfactant polymer formulation was substantially better in recovering oil than surfactant or polymer surfactant |
| [67] Experimental | A, S and P synergism yielded higher oil recovery. Alkaline reduces surfactant adsorption. Surfactant reduces alkaline consumption and polymer increases the viscosity of water. These three functions play a great role in recovery enhancement |
| [16] Experimental | Effect of different alkaline concentration in ASP slug yields different oil recovery, indicating that optimum concentration of alkaline should be guaranteed |
| [16] Experimental | Optimum concentration of polymer is required during ASP injection for higher oil recovery |
| [68] Field | 28.1 | ASP synergy effect makes the process efficient |
| [69] Field | 10–28 | Pore scale displacement efficiency improved due to synergy of three chemicals |
| [70] Field | >25 | NaOH and heavy alkylbenzene sulfonate reduces IFT dramatically and polymer pushes the heavy oil |
| [71] Experimental | 15.5 | Present the co-surfactant in the ASP slug is critical in releasing the trapped oil in the porous part of the reservoir rock |

Different kind of ASP flooding in different reservoir characteristics, close up percentage of oil improvement. From this table, it is obvious that ASP is one of the promising EOR applications due to its dual efficiency effect, alkaline and surfactant microscopic efficiency, and polymer progresses volumetric sweep. Reservoir fluid and rock property play a vital role for ASP selection, and, for achieving highest oil recovery, suitable ASP type and concentration should be used. For sandstone formation, the convenient surfactant type was used in ASP is SDS. CTAB is mostly used for carbonate due to its surface charge. Lith = Lithology; P = Porosity; Pb. = Permeability; Sst = Sandstone; Carbo. = Carbonate; Qz = Quartz; SDS = sodium dodecyl sulfate; GAC = Guerbet alkoxy carboxylate; POA = polyoxyethylene alcohol; PAM = Polyacrylamide; HPAM = hydrolyzed polyacrylamide; C12TAB = Dodecyltrimethylammonium (bromide); SDBS = Sodium Dodecylbenzene Sulfonate Surfactant; KPS = Potassium persulfate; XD = xylitoldehydrogenase; TVP = thermo-viscosifying polymer; IOS = internal olefin sulfonate; PS = Pulmonary surfactant; SLPS = surfactant like peptides.

3. Natural Surfactants

Natural surfactants mostly derived from the seeds; like chemical surfactants, natural surfactants may be ionic, polymeric, nonionic or amphoteric (Table 2). The critical micelle concentration (CMC) value of synthesized natural surfactant ranges between 9–10 mM, yielding an IFT between 0.075 to 0.125 mNm⁻¹. Natural surfactant can also reduce the contact angle efficiently besides IFT reduction. Several extraction methods are explained for synthesizing natural surfactant, but the main methods were spray dryer, soxhlet extraction, methanolic extraction, and maceration process. Different natural surfactant types versus minimum interfacial tension value are depicted in Figure 2. However, Ref. [72] explored the fact that honeycomb micro-porous structures are effective in separating water from oil, hence it may be very significant in diminishing water-oil IFT.

The previous work results (Table 2) declared that, in addition to the commercial surfactants (Table 1), natural surfactants are effective with decreasing IFT, wettability alteration and adsorption on the solid surface. Nowadays, researchers are focusing on applying this type of surfactant because of some advantages and reasonable features such as cost effectiveness, less toxicity, more stability and effectiveness at high pressure and
temperature and more biodegradabilities as compared to commercial surfactants (Table 1). These kinds of surfactants can increase oil recovery by about 5–40% of OIIP.

Table 2. Summary of natural surfactant types and their properties.

| Ref. | Name                              | CMC     | Type           | IFT From-to mN/m | Contact Angle From-To | Oil Recovery Improvement % | Properties                                          |
|------|-----------------------------------|---------|----------------|------------------|------------------------|---------------------------|------------------------------------------------------|
| [73] | Reetha Extract                    | 2.3     | Natural non-ionic | 18.6 to 7.02     | NA                     | 6.8                       | Applicability of new surfactant and increase oil recovery from 18.5 to 25.3 |
| [74] | Mulberry leaves extract            | 2.6     | Natural cationic | 44 to 17.9       | 62.5° to 42.5          | 7                         | Suitable for carbonate rock                           |
| [75] | Matricaria chamomilla extract      | 0.05    | Natural Nonionic | 30.63 to 12.53   | NA                     | NA                        | Good IFT reduction ability                           |
| [76] | Cordia Myxa plant                 | 0.06    | Natural         | 33 to 16.24      | NA                     | 27                        | Good adsorption                                      |
| [77] | Mahua oil                         | NA      | NA              | 10⁻²             | NA                     | 20                        | Applicable for sandstone reservoir                   |
| [78] | Seidlitzia rosmarinus extract      | 0.08    | Cationic        | 32 to 9          | NA                     | NA                        | The reduced IFT is not as low for EOR application    |
| [79] | Jatropha oil-based                | NA      | Nonionic        | 0.917            | NA                     | 25                        | Good surface activity                               |
| [80] | Henna extract                     | 0.02    | Cationic        | 43.9 to 3.05     | 66 to 37               | 7                         | Good wetting ability                                |
| [81] | Olive leaf extract                | 1.95    | Natural cationic | 36.5 to 14       | NA                     | NA                        | Good adsorption                                      |
| [81] | Spistan leaf Extract              | 2.1     | Natural cationic | 36.5 to 20.15    | NA                     | NA                        | Good associative and interfacial properties          |
| [81] | Prosopi leaf Extract              | 2.3     | Natural cationic | 36.5 to 15.1     | NA                     | NA                        | Good adsorption                                      |

Figure 2. Summary of experimental data for different kinds of natural surfactant.

4. Potential of NASP Synergism

To increase the potential of EOR, the optimum chemical solution is achieved at large injection volumes through injecting alkaline, polymer and surfactant (Figure 3). Oil improvement through ASP flooding has been reported previously. The principle of this method is the reaction between alkali and organic to create petroleum soaps. These petroleum soaps will interact with surfactants to reduce the IFT to minimum value (10⁻⁴ mN/m). In addition, the polymer is used to reduce the viscosity ratio of oil/water interface. Reduction
of IFT and oil viscosity significantly improve vertical and displacement efficiency. ASP flooding is used for heavy oil reservoirs [25]. Recently, nanoparticle is mixed with the chemicals above to reduce the cost of these chemicals, modify the wettability, minimize oil-water IFT and boost oil recovery efficiency. Table 3 examines the types of process efficiencies for each of the methods used in the article, and predicts the amount of efficiency by NASP:

$$E_{ro} = E_{do} E_{a} E_{v} \frac{S_{o} V_{p}}{B_{o}}$$

where $E_{do}$ is the microscopic displacement efficiency increased by using the optimum surfactant and alkaline type and concentration, $V_{p}$ is the permeability variation and $S_{o}$ is the oil saturation. $E_{a}$ and $E_{v}$ are displacement efficiencies of areal and vertical, developed by using the appropriate polymer.

![N A S P flooding](image)

**Figure 3.** ASP chemical flooding sequence for enhancing oil recovery. ASP EOR injection is shown in sequence at the beginning, the preflush is injected then followed by oil bank; after that, nano-alkaline-surfactant is injected to decrease the IFT followed by a polymer to control the mobility via increasing the viscosity; finally, water drive is used to push the solutions.

**Table 3.** NASP oil recovery efficiency prediction and efficiency of ASP alone and in synergy.

| CEOR Type       | Oil Recovery % | Basic Principle                        |
|-----------------|----------------|----------------------------------------|
| Nano            | 5–23           | Improvement in sweep and displacement   |
| Alkaline        | 2–5            | Improvement in displacement             |
| Polymer         | 2–10           | Improvement in sweep                    |
| Surfactant      | 5–15           | Improvement in displacement             |
| SP              | 5–20           | Improvement in sweep and displacement   |
| AP              | 5–18           | Improvement in sweep and displacement   |
| ASP             | 5–25           | Improvement in sweep and displacement   |
| Nano-polymer    | 4–20           | Improvement in sweep and displacement   |
| Nano-surfactant | 5–20           | Improvement in sweep and displacement   |
| NSP             | 8–22           | Improvement in sweep and displacement   |
| NASP            | >25 (predicted by our study) | Improvement in sweep and displacement |
5. NASP Prediction Technical Characteristics

The NASP synergism limits the polymer adsorption and high alkali consumption [82]. Figure 4 illustrates the main reasons for NASP interaction. The predicted technical properties of NASP EOR compared to single element flooding are summarized as follows:

- The amount of surfactant is significantly lowered in NASP system;
- Strong or a weak base alkali is used in the ASP synergy system;
- NASP significantly increases oil recovery since it has physical and chemical (dual) effects;
- It is forecasted that, when the four-element composites (N, A, S, and P) are used together, the IFT rapidly decreases to 0.001 or lower.

6. Screening the Reservoir Rock Properties

Screening criteria can determine the suitable EOR process for the target reservoir rocks and control the cost issue. Sheng [60] summarized the significant parameters of ASP process, EOR, permeability, clay contents, reservoir temperature, pressure, divalent contents, formation water salinity and oil viscosity.

Due to high anionic surfactant adsorption on carbonate, nearly all the chemical (CEOR) processes were conducted on sandstone reservoir rocks. The presence of anhydrate mineral in carbonate formations caused severe alkaline consumption [83]. On the other hand, clays in sandstone reservoirs caused surfactant adsorption. Thus, clay percentage should be lowered for effective and successful ASP flooding. The permeability is another criterion and very critical to polymer injection in the ASP project since a polymer is not able to flow through tight or low permeable reservoirs.

For alkali, the crude oil composition is a very critical point, while, for polymers, it is not significant [83]. The viscosity of oil should be >35 cP for AS projects. The oil viscosity in Chinese fields projects is from 10–70 cP. According to some authors, it is preferred to apply polymer EOR in reservoirs with viscosity of 2000 cP [84].

ASP projects are more convenient in low salinity reservoirs 10,000 ppm of total salinity [85]. The preferable reservoir temperature is 93 °C for ASP, while the average reservoir...
temperature for AS field projects was 27 °C, even up to 80 °C, was documented [85]. Recently, scholars have been thinking about using optimum chemicals, in particular polymers, to withstand high salinity and temperature [85].

7. ASP/EOR Process Challenges

Even though a chemical ASP process is the most effective chemical process for decreasing water cut and oil enhancement, tight oil produced in water emulsion creates huge problems [86]. In addition, several problems and limitations are associated with offshore ASP/EOR applications [87]. Large chemical volumes that are transported to remote sites, and less space availability, lead to difficulty in operation [86]. Extra treatment is needed for the produced fluid containing alkaline, polymer and surfactant. This tight emulsion formation leads to difficulty and limitation in the separation process [86]. Literature revealed that this chemical process works more efficiently in low salinity water reservoirs [87]. Nevertheless, the source of water injection is from the seawater; therefore, alternative chemicals may be needed. Divalent cations in the system are the main source of scaling.

7.1. Operational Difficulties

Like any CEOR injection, ASP are associated with many operational problems such as corrosion, scaling, pump failures, polymer degradation, and low injectivity [82]. In addition, this process is complex in design and needs water and oil analyzing. Moreover, due to a large volume of chemicals, the cost of this process should be analyzed effectively. Finally, this EOR flooding type is not favorable for hot reservoirs or those with saline water [82].

7.1.1. Scaling Issues during ASP Flooding

Calcium and magnesium reaction with the injected alkali leads to a scaling issue. This effect is regarded as one of the ASP limitations since this reaction leads to extreme surfactant precipitation and alkali consumption [88,89]. Several publications reported scaling issues during ASP injection into the reservoir [90–93]. Scales may originate from the alkalis and carbonate mineral’s reaction. According to the literature, silicate scale formation is a very sophisticated mechanism because the problems associated with silicate are poorly understood. In Chinese oil fields, scaling issues have been observed and reported [93].

7.1.2. Surfactant Precipitation

Divalent cationic existences in hard brines cause surfactant precipitation as illustrated in Equation (3):

\[
2R^- + M^{2+} \rightarrow MR_2
\]

where MR$_2$ is the surfactant divalent cation, and R the anionic surfactant. Different factors like temperature, alcohol and salt concentration are responsible for anionic surfactants’ precipitation [94]. In most of the cases, the presence of oil reduces surfactant precipitation efficiently since oil competes for surfactant. Ethoxylate (EO) helps surfactant to resist divalent cations. At lower hardness, monovalent cation is formed from the reaction of multivalent cation with the anionic surfactant [94].

8. Prospects and Future Developments of ASP/CEOR

Based on this review paper, the following conclusions and recommendations can be proposed for this study:

- ASP limitations could be due to alkaline since alkaline reduces polymer viscosity. Thus, a big question is: can SP work more effectively than ASP?
- Due to the carbonate rock complexity, most of the nano-EOR flooding has to be performed on sandstone rocks. Further studies should be implemented for understanding the effect of oil recovery on carbonate rocks;
More sophisticated and advanced tools should be used to accurately examine the role of NASP in changing the wettability and IFT;

Due to the lack of economic data in the research papers, more economic study should be implemented to evaluate the economic performance of NASP in accelerating oil recovery;

HS and HT could limit NASP to work effectively in maximizing oil recovery. This is why a more effective nano, surfactant and polymer should be developed to limit this issue.

More research is needed to evaluate the performance of NASP in sandstone and carbonate reservoirs.

9. NASP Performance Anticipation in Changing the Wettability and IFT

After reviewing and evaluating ASP lab and field projects, it is forecasted that NASP could modify wettability and IFT effectively more than any other previous chemical methods due to the synergism effect of ASN (Alkaline Surfactant Nano), and it may stabilize the polymer solution excellently due to the NP synergism effect. Based on the above points, ultimate oil recovery could be guaranteed by implementing NASP. IFT and contact angle are the main parameters of any EOR type since it is related to the capillary number modification. Due to accuracy and ease of use, pendant drop is considered as one of the main methods to calculate IFT and contact angle. IFT study will be implemented by introducing a drop into a bulk phase under the desired P and T. For contact angle measurement, the drop is completed on a plane solid sample. Pictures captured by a digital camera connected to a computer show the shape of the drop and allow for solving the Laplace equation contact angle and IFT calculation. Figure 5 illustrates IFT and contact angle measurement by using pendant drop.

Figure 5. IFT and contact angle measurement by using pendant drop (oil drop).
10. Core Flooding

For recovery measurement, a dynamic test will be prepared by core-flooding. Different core plugs are used with injecting best chemical, nanofluid and hybrid nanochemical solutions under the reservoir condition. For this purpose, a core sample should undergo several procedures to be prepared and aged. After aging, the brine solution is injected, followed by the injection of a hybrid Nano-ASP solution to study oil recovery from the carbonate rock. Then, the values of oil production are recorded vs. time. Finally, oil recovery is plotted vs. pore volume. This review paper forecasted that oil recovery by NASP could be more than 25% due to the improved mechanisms that have been discussed in the other sections. Figure 6 illustrates NASP core–flood procedure.

Figure 6. Core–flood procedure.

11. Future Design, Materials and Features of NASP Process
11.1. Nano-EOR

Nanoparticles are wide classes of material substances, with sizes between 1–100 nm. Nowadays, the oil and gas industry has attracted much consideration on applications of nanoparticles (NPs). NPs have become widely used due to having unique optical, magnetic and electric features. Mixing nanoparticles with other substance phases is called nanocomposites (NCs). NPs within different dispersion media can be easily transported through the porous media and reach the oil bank due to their smaller sizes, less than micron-sized rock pores. Consequently, NCs can be used to decrease ASP adsorption with the rock surface, altering the wettability of the rock, reducing the interfacial tension (IFT)
and improving oil displacement and recovery (Figure 7). The surface area-to-volume ratio of nanoparticles is too large, where a small concentration of them is needed to induce EOR injection fluids. Combining nanoparticles with the natural polymers develop polymeric nanofluids, thus the resulted NPs would have a better stability, mobility of injection fluids and sweep efficiency.

Figure 7. IFT reduction and wettability alteration by nanoparticles.

Figure 7 highlights that the nanoparticles can alter the wettability and reduce oil water IFT. The mechanism of wettability alteration by nanoparticles is to build a wedge film on the oil droplet and the rock surface. The nano size particles re-arrange themselves between the rock and oil droplet, leading to oil separation and thus altering the wettability from hydrophobicity to hydrophilicity, and decreasing the excessive surfactant adsorption. Moreover, disjoining pressure is regarded as one of the nanoparticle mechanisms in EOR since it responsible for changing the oil wet surface to water wet. This mechanism is highly affected by nanoparticle type and concentration. Different nanoparticle types play different roles in the EOR mechanism process (Table 4).

Table 4. Role of different nanoparticles in EOR mechanisms.

| Nanoparticle | Nano-Composites | EOR Mechanisms                                      |
|--------------|-----------------|-----------------------------------------------------|
| SnO₂, ZrO₂, Carbon nanoparticles | CTAB + Al₂O₃ | Wettability alteration by disjoining pressure       |
| SiO₂         | NiO + SiO₂      | Change wettability of oil by disjoining pressure    |
| ZrO₂         | SDS + ZrO₂      | Decreasing the contact to water wet by disjoining pressure |
| Al₂O₃        | SiO₂ + PAM      | Wettability alteration by disjoining pressure       |
| Fe, SiO₂, GO, TiO₂ | ZrO₂, NiO     | Reduce interfacial tension                         |
| Al₂O₃, CuO, Fe₂O₃ | SDS + Al₂O₃  | Reduce the viscosity of crude                       |
| MgO          | CuO/TiO₂ + PAM  | Optimized permeability                             |
11.2. Summary of Nano (NASP) EOR Flooding

Nanoparticles are very effective in changing the wettability and contact angle. Recently, nanoparticles were mixed with surfactant, polymer and SP to further improve oil recovery. The shape, size, dispersion media, nature and concentration of nanoparticle will govern the most suitable and effective nanoparticles for achieving the best EOR mechanisms (Table 4). The main advantages of using nanoparticles are their large surface areas with spherical nanoparticles being more effective than any other nanoparticle shapes.

The main parameters that control the nanoparticle shape is the temperature, pH and time. In addition, nanoparticles play an astonishing role in improving the oil recovery since smaller nanoparticle size leads to lower IFT and contact angle (Figure 7). Furthermore, lab works hypothesized that optimum concentration should be guaranteed for any EOR application; otherwise, nanoparticles will agglomerate, leading to lower recovery efficiency. Regarding the dispersion media, our review paper finds out that different oil recovery is accomplished through dispersing nanoparticles into different dispersion media. However, Rajabi et al. used the wettability modifier: nanoparticles, surfactant and alkaline, but the highest percent of oil recovery was obtained by nano-surfactant rather than by adding alkaline [95]. The latter did not cause any positive impact on EOR. Furthermore, the oil improvement, using different kinds of nanoparticles, nano-polymers, nano-surfactants and nano-surfactant-polymers, efficiently decreases contact angles and IFT (Table 5), despite the fact that heterogeneity of sedimentary rocks could influence the quantity of oil improvement. The sedimentary rocks, especially carbonate rocks, characterized intensive lithological changes along micrometer-sized scales in both subsurface [96] and near-surface conditions [97]. This heterogeneity in enhanced oil recovery is the main cause behind the failure of oil recovery in the field scale. Therefore, the new model or design (NASP) for future experimental work should be achieved with detailed work on reservoir characteristics, including mineralogy and, of course, by detailed observations (both optical microscope and SEM).

Table 5. Summary of nano, nano-surfactant, nano-polymer and nano-SP flooding. It is concluded that a combination of nanoparticle and nanocomposites with conventional CEOR methods improves the synergism effect. As shown in the summary table, nanoparticles are used to support alkaline and surfactant in IFT reduction and wettability modifications (microscopic improvement). In addition, it is used to lower surfactant costs through controlling surfactant adsorption on the rock surface. In the case of polymers, nanoparticles improve the mobility of the polymeric solution, resulting in better oil sweep efficiency and reducing breakthrough time (macroscopic improvement). Lith = Lithology; Sst = Sandstone; Carbo. = Carbonate; Qz = Quartz.

| Ref. | Nano Type | Lith. | Contact Angle | IFT | Oil Improvement | Remark |
|------|-----------|-------|---------------|-----|-----------------|--------|
|      |           |       | Before | After | Before | After | %     |        |
| [98] | SiO₂      | Qz    | 131    | 38.82 | 19.2   | 17.5  | 2     | Different nanoparticles’ type and size have different performances |
|      | TiO₂      |       | 131    | 21.64 | 19.2   | NA    | 11    |        |
|      | Al₂O₃     |       | 131    | 28.6  | 19.2   | 12.8  | 8     |        |
| [99] | SiO₂      | Sst   | 51     | 30.5  | 21     | 20.3  | 10.1  | Due to NP adsorption, the wettability altered from oil to water wet |
| [100] | SiO₂     | Sst   | NA     | NA    | NA     | NA    | 4.29  | Wedge film creation by nanoparticles |
| [101] | SiO₂     | Sst   | 122    | 16    | 13.62  | 10.69 | 23.5  | Increase in capillary number due to SiO₂ |
| [102] | graphene  | Sst   | NA     | NA    | NA     | NA    | 6.7–15.2 | Size of nanoparticle plays a great role in EOR |
|      | nanosheets|       |        |       |        |       |       |        |
| [103] | SiO₂/TiO₂ | Sst   | 154    | 23    | NA     | NA    | NA    | Spherical shape of nanoparticle improves uniformity |
|      | Al₂O₃/TiO₂|       | 154    | 24    | NA     | NA    | NA    |        |
Table 5. Cont.

| Ref.   | Nano Type | Lith. | Contact Angle | IFT | Oil Improvement | Remark                                      |
|--------|-----------|-------|---------------|-----|-----------------|---------------------------------------------|
|        |           |       | Before | After | Before | After | %               |                                             |
| [104]  | HLP Sst   | 135.5| 95     |       | 26.3   | 1.75  | 32.2           | NPS yields higher oil recovery without creating any damage to the formation |
| [104]  | NWP       | 135.5| 82     |       | 26.3   | 2.55  | 28.57          |                                             |
| [105]  | NiO/SiO₂ NCs Carb. | 174 | 32 | 28 | 1.84 | NA | NiO/SiO₂ Nanocomposite responsible for altering the wettability in carbonate rock reservoir |
| [106]  | LHPN Sst | 35   | <10    |       | NA.    | NA.   | 1.92           | Capillary number improvement leads to oil enhancement |
|        | NWPN Sst  | 35   | 0      |       | NA.    | NA.   | 29.23          |                                             |
|        | HLPN Sst  | 35   | NA.    |       | NA.    |   | 29.01          |                                             |
| [107]  | SiO₂ Sst  | 12   | 40     | 17.5 | 7      | 28    | Temperature affects oil recovery |
| [108]  | TiO₂ Sst  | 55.3 | 61.9   | 17.5 | 12.5   | 6.6   | Temperature affects oil recovery |
|        | SiO₂ Car. | 54.8 | 57.7   | 16.7 | 11.1   | 2.9   | Temperature affects oil recovery |
| [109]  | γ-Al₂O₃ Car. | 119.8 | 40 | NA. | NA. | 11.25 | γ-Al₂O₃ plays the main role in altering the wettability from oil to water wet |
| [110]  | Al₂O₃ Sst | 53.68| 28.6   | NA.  | NA.    | NA.   | As a result of nanoparticle deposition, rock surface altered to water wet |
|        | TiO₂ Sst  | 53.68| 21.6   | NA.  | NA.    | NA.   |                                             |
|        | SiO₂ Sst  | 53.68| 38.8   | NA.  | NA.    | NA.   |                                             |
| [111]  | Al₂O₃ Sst | NA.  | NA.    | NA.  | NA.    | 12.5  | For guaranteeing optimum oil recovery design, engineers should select the effective nanoparticle type and size |
|        | MgO       |      |        |      |        | 1.7   |                                             |
|        | Ni₂O₃     |      |        |      |        | 2     |                                             |
|        | ZnO       |      |        |      |        | 3.3   |                                             |
|        | Fe₂O₃     |      |        |      |        | 9.2   |                                             |
| [112]  | SiO₂ Micrm. | 134.4| 54.52  | 37.5 | 22.1   | 10    | Amine-functionalized silica nanoparticles are more effective than typical nanoparticles |
|        |           | 134.4| 23.71  | 37.5 | 13     | 28    |                                             |
| [113]  | SiO₂ Car. | 140.2| 68.5   | NA.  | NA.    | 7.7   | Disjoining pressure of SiO₂ was the main mechanism to remove the oil from the surface |
| [114]  | SiO₂ Sst  | 135.5| 66     | 26.5 | 1.95   | 25.43 | SiO₂ is more effective for light oil reservoir |
|        |           | 130  | 101    | 28.3 | 7.3    | 14.55 |                                             |
| [115]  | SiO₂ Sst  | NA.  | NA.    | NA.  | NA.    | 5–35  | Arrangement of silicon nanoparticle improves IFT |
| [116]  | LHPN Sst  | 87   | 28     | 28   | 7      | 21    | Wettability is altered when polysilicon is adsorbed on the sandstone pore wall |
| [117]  | TiO₂/SiO₂ NCs Carb. | 138 | 48 | 39 | 13.2 | 26 | Trapped oil is mobilized by the nanocomposite |
| [118]  | LHP Sst   | 14.7 | 9.3    | NA.  | NA.    | 2     | Nanofluid was more effective for secondary recovery |
| [119]  | TiO₂ Sst  | 23   | 18     | 14   | 14     | 14    | Low concentration of TiO₂ improved the oil recovery |
| [117]  | Fe₂O₃/SiO₂ NC Sst | 138 | 52 | 39 | 17.5 | 31 | Nanocomposite was able to alter wettability of the rock surface dramatically |
Table 5. Cont.

| Ref. | Nano Type | Lith. | Contact Angle | IFT | Oil Improvement | Remark |
|------|-----------|-------|---------------|-----|----------------|--------|
|      |           |       | Before | After | Before | After | %     |        |
| [120]| SiO₂      | Sst   | 74     | 1.2   | 16     | 1.4   | 33    | SiO₂ can desorb the oil from the rock |
| [121]| TiO₂      | Sst   | 125    | 90    | NA.    | NA.   | 31    | Higher disjoining pressure as a result of using higher concentration |
| [122]| SiO₂      | Micrm.| 100    | 0     | NA.    | NA.   | 8.7 (0.1 wt%) | Contact angle and IFT are dependent on the weight % of nanoparticle |
| [123]| TiO₂      | Sst   | 18     | 8     | 47.5   | 44.5  | 9.5–13.3 | Decrease in capillary force |
| [124]| ZrO₂      | Carb. | 152    | 44    | NA.    | NA.   | NA.   | Additional IFT reduction after using nanoparticle |
| [125]| Al₂O₃     | Sst   | 131    | 92    | 38.5   | 2.25  | 20.2  | Dispersant agent (propanol) was used for the first time and was effective in IFT reduction |
|      | Fe₂O₃     | Sst   | 132.5  | 101   | 38.5   | 2.75  | 17.3  | |
|      | SiO₂      |       | 134    | 82    | 38.5   | 1.45  | 22.5  | |
| [126]| SiO₂      | Carb. | NA.    | NA.   | NA.    | NA.   | 8.7   | By using nanoparticles, rheological properties of the displacing phase improved |
| [127]| SDS + Al₂O₃ | Carb. | 92     | 75    | 9.88   | 2.75  | NA    | Anionic surfactant is less effective than cationic surfactant for carbonate reservoir |
|      | SDS + ZrO₂ |       | 92     | 84    | 9.88   | 2.78  | NA    | |
| [128]| NaCl + CAPB + SiO₂ | Carb. | 156.2° | 75.1° | 39.63  | 1.10  | 12.2  | Decrease of IFT from 39.63 to 1.10 mN/m leads to oil improvement |
| [129]| SDS + SiO₂ | Micrm.| 73     | 11    | NA.    | NA.   | 13    | Extra heavy oil recovery as compared to SDS alone |
| [130]| 3.22 ZrO₂ + 0.50 g of CTAB | Carb. | 180    | 32    | NA.    | NA.   | 10    | Positive outcome is observed by surfactant and nanoparticle synergism |
|      | rhamnolipid BS-spherical + silica | Carb. | 112    | 8     | NA.    | 1.85  | 26.1  | Spherical shape nanoparticle is more effective than other shape nanoparticle due to uniformity |
|      | rhamnolipid BS-sponge + silica | Carb. | 120    | 17    | NA.    | 1.94  | 25.1  | |
| [132]| ZrO₂ + SDS | Carb. | 152    | 44    | NA.    | NA.   | 8     | From the tests, it was obvious that ZrO₂ is very effective in changing the wettability from oil wet limestone to water wet |
| [133]| SiO₂ + AL-FOTERRA | Carb. | 167    | 146   | 23.2   | 7.2   | 10    | Using nano was effective in additional oil recovery in ambient and HPHT conditions |
| [134]| Anionic surfactant + Al₂O₃ | Carb. | 142    | 0     | NA.    | NA.   | NA    | At relatively low concentrations, Al₂O₃ can improve anionic surfactant to alter the oil wet to water wet more effectively |
| [129]| Al₂O₃/SiO₂ + SDS, CTAB | Carb. | 73     | 11    | NA.    | NA.   | 15    | Small size and high surface area of nanoparticles were very effective |
Table 5. Cont.

| Ref.   | Nano Type                  | Lith. | Contact Angle Before | Contact Angle After | IFT Before | IFT After | Oil Improvement % | Remark                                                                 |
|--------|----------------------------|-------|----------------------|---------------------|------------|-----------|-------------------|------------------------------------------------------------------------|
| [127]  | CTAB + Al$_2$O$_3$          | Carb. | 70                   | 52                  | 8.46       | 1.65      | NA                | Smaller particle size of Al$_2$O$_3$ leads to higher surface energy, resulting in bigger repulsion force |
|        | CTAB + ZrO$_2$              | Carb. | 70                   | 60                  | 8.46       | 1.85      |                   |                                                                        |
| [136]  | non-ferrous metal + anionic surfactant | Sst | 23                   | 19                  | 31.4       | 9.2       | 12-17             | Nanoparticles decrease surfactant adsorption                           |
| [27]   | ZrO$_2$ + SDS ZrO$_2$ + CTAB | Carb. | 101                  | 30                  | 16         | 3.1       | 25                | Cationic surfactant was more effective at altering the wettability     |
| [64]   | Cationic anionic + silica   | NA    | 59                   | 46                  | 45         | 43        | 45                | Nanoparticle size 5-75 was effective at reducing the IFT               |
| [139]  | SiO$_2$ + 2-Poly(MPC)       | Sst   | NA                   | NA                  | 47         | 35        | 5.2               | Using copolymer with nano silica yielded higher oil recovery           |
| [140]  | Silica + DMAEMA             | Sst   | 85                   | 62.2                | 27         | 14        | 9.9               | Nanoparticles reduce polymer adsorption                                |
| [141]  | Nano clay + HPAM            | Sst   | NA                   | NA                  | NA         | NA        | 5                 | Improvement in viscosity after using Nano clay/HPAM                    |
| [142]  | SiO$_2$ + PAM               | Sst   | NA                   | NA                  | 27         | 10.2      | 24.7              | Due to disjoining pressure, oil wet is changed to water wet           |
| [143]  | SiO$_2$ + Xanthan gum       | Sst   | 86                   | 20                  | 17.8       | 6.4       | 7.81              | More oil is produced from unswept areas leading to improving residual oil recovery |
| [144]  | SiO$_2$ + PVP               | Sst   | 54                   | 22                  | 19.2       | 7.9       | 0-6.1             | Oil recovery increases with increasing the concentration of nanoparticles due to improved adsorption ratio |
| [98]   | Al$_2$O$_3$ + PVP           | Sst   | 54                   | 21                  | NA         | NA        | 7-24              | IFT and contact angle improved synergistically, in a nanocomposite form as compared to individual nanoparticle |
| Ref. | Nano Type | Lith. | Contact Angle Before | Contact Angle After | IFT Before | IFT After | Oil Improvement % | Remark |
|------|-----------|-------|----------------------|---------------------|------------|------------|-----------------|--------|
| [62] | SiO₂ + PAM + SDS | Sst | NA. | NA. | NA. | 0.13 | 17.49 | Pressure drop increased to 0.38 MPa |
| [62] | Clay + PAM + SDS | Sst | NA. | NA. | NA. | 0.238 | 18.28 | Higher viscosity as compared to conventional SP |
| [64] | Nanoclay + 2800 PAM + 0.2 SDS | Micrm. | NA. | NA. | NA. | NA. | 6.8 | The injection of nano to SP leads to a more uniform flow pattern in a micromodel, which yields a more stable front |
| [64] | Nanoclay + 3000 PAM + 0.2 SDS | Micrm. | NA. | NA. | NA. | NA. | 8 | |

LHPN = lipophobic and hydrophilic polysilicon nanoparticle; HLPN = hydrophobic and lipophilic polysilicon nanoparticle; NWPN = neutral wet polysilicon nanoparticle; TX-100 = Triton X-100; PVP = Povidone; Polyvinylpyrrolidone; DMAEMA = Dimethylamino-ethyl methacrylate; CTAB = Cetyl trimethylammonium bromide; CAPB = Cocamidopropyl betaine; MPC = methacryloyloxyethyl phosphorylcholine.

This work systematically investigates the potential of NASP suspension for enhanced oil recovery (EOR) in carbonate and sandstone reservoirs. Using NASP (Nano/Alkaline/Surfactant/Polymer) could be proved successfully in future work due to its ability to improve displacement and sweep efficiency.

In the case of NASP, various mechanisms will be activated, and the interaction of them will be important, which we will describe separately to better understand the issue:

I. The capability of the nano-polymer suspensions for improving the oil recovery by the following mechanisms:
   1. Wettability alteration was explored using contact angle measurement; increasing temperature and adding salt to polymeric solutions caused a reduction in shear viscosity, and the addition of NPs to the solutions could relatively recover the viscosity;
   2. The presence of polymers in the nanofluids improved dispersion stability of NPs;
   3. The nano-polymer suspensions could improve the ability of the NPs for wettability alteration and faster equilibrium states obtained than the polymer-free nanofluids.

II. The performance of the nano-surfactant solutions for improving the oil recovery by the following mechanisms:
   1. The adsorption process of these substances is one of the important methods to increase the oil recovery factor from oil reservoirs by wettability alteration;
   2. The results of the IFT experiments of these materials showed that surfactant nanofluid solutions could significantly reduce the IFT value between the oil and water system.

III. Alkaline can activate the following mechanisms:
   1. Interfacial tension reduction;
   2. Wettability alteration;
   3. Control of adsorption of ions;
   4. Improving the emulsion stability;
   5. Inhibitor of clay swelling.

Suitable experimental design is critical for using nanoparticles with chemical EOR. This paper for the first time will investigate a detailed schematic diagram for using nanoparticles in hybrid with ASP for future perspectives.
12. Conclusions

1. To sum up, CEOR was applied to greatly increase the ultimate oil recovery by wettabiliy, IFT and mobility modification. This paper will add a new insight integrating nano-alkaline, polymer and surfactant flooding for the first time by addressing the main mechanism of each one. The main conclusions of this paper are as follows:

2. ASP limitations could be due to alkaline since alkaline reduces polymer viscosity;

3. Due to nano, surfactant, polymer, and alkaline synergy effects, most of the EOR mechanisms are greatly improved, leading to higher oil recovery as compared to using each component alone;

4. The objective behind using NASP in hybrid is to modify wettability, IFT and mobility ratios, which are regarded as the main EOR mechanisms;

5. NASP type and concentration play a major role in changing wettability and reducing IFT to a minimum level;

6. For checking the mobility of chemical EOR, the micromodel is used to find the fluid flow distribution;

7. Nanoparticle type and size play a major role in changing wettability and reducing IFT to the minimum level;

8. Future recommendations by utilizing NASP will probably be a new finding to understand the details about the EOR system in both micro- and macroscale settings;

9. This review paper highlights the fact that natural surfactants are less costly, biodegradable, available, less toxic, more stable, and environmentally friendly, and it can reduce the IFT to an ultra-low value.

10. NASP could effectively boost the oil recovery by more than 25% due to the synergism effect.
Author Contributions: Writing and preparation the original draft, N.S. and R.S.; review and editing, N.S. and A.P.; Methodology and software, N.S., R.S. and A.P. All authors have read and agreed to the published version of the manuscript.

Funding: The study benefited from research funds of the Université Libre de Bruxelles (ULB)-Belgium.

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

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