

Review on the Utilization of Local ASP in the Niger-Delta for Enhanced Oil Recovery

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Abstract

The Niger-Delta basin have produced for more than 50years using the natural or primary recovery system, and has transitioned into secondary recovery after which the enhanced oil recovery (EOR) is utilized. The primary and secondary recovery systems are barely able to produce 30-35% of the oil initially in place leaving 65-70% residual oil in the reservoir. With the increase in energy demand, difficulty in detection of potential hydrocarbon reservoir and increase in drilling cost, there is need to optimally recover residual oil accumulated in the reservoir. Chemical enhanced oil recovery (CEOR) which uses alkaline, polymer, surfactant and a combination of these is utilized to recover trapped oil through a combination of mechanisms. These chemicals are expensive, imported and bedeviled with several challenges. Studies have shown the potentials of local materials to favourably match and compete with conventional chemicals in EOR. This work is a review study that focuses on local materials deployment for ASP formulation to enhance the recovery of oil. The biggest challenge for local materials is that most of them are edible. Interestingly, the use of agro-wastes from plants with similar features as the edible local materials has been suggested for ASP formulation and these edible local materials shall be cultivated in large quantities to meet global consumption and industrial utilization thereby providing jobs and also creating wealth. Some of these local agro-materials are stable in saline environment and at elevated temperatures in comparison with the conventional chemicals. The utilization of local ASP materials will reduce oil production cost; improve Nigerian economy as their cost will be independent on the global oil price, transform waste to wealth and above all job opportunities creation for Nigerians. From the review, studies show that several local materials and process mechanisms were considered for CEOR. Results from these studies showed the potentials of local materials in replacing conventional materials in EOR with local surfactant such as carica papaya extract and detergent yielding 94.1% and 96.6% displacement efficiency; local alkali - Akanwu and palm bunch ash yielded 99.1% and 97.5% displacement efficiency while local polymer - Okro and Terminalia mantaly (TM) yielded 99.1% and 90% displacement efficiency respectively. The hybridization of the local materials in AP, AS, SP and ASP gave a displacement efficiency above 70%. From the study, the aforementioned local materials have evidently proven to be effective substitute to conventional CEOR materials while materials like require further modification and processing to adequately match the conventional agents.

Keywords: Wettability alteration; Enhance oil recovery; Mobility control; Interfacial tension reduction.

1. Introduction

Fossil fuels' contribution to energy demand globally stood at about 85% with volume estimation of 87 million BPD (barrels/day) and this raised the urgent need for recovery of oil in spite of decline in oil productivity. Oil is produced by three stages viz: tertiary, secondary and primary recovery (PR) techniques [1]. The secondary and primary techniques can only recover 20-40% of hydrocarbon (HC) reserves while tertiary recovery (TR) approach can only recover

60% of oil in place (OIP) [2]. The PR approach uses the natural energy of the reservoir for production, whereas in the case of decline, injection of water or natural gas is carried out for pressure maintenance of the reservoir and consequently through secondary recovery (SR) technique oil recovery is achieved [3]. With SR becoming inefficient arising from factors like capillary forces and mobility ratio (MR), the TR approach is then deployed [4]. The TR approach involves introduction of materials or approaches that excludes water and natural gas for trapped oil displacement [5]. It is grouped into miscible flood process, microbial flood process, thermal flood process and chemical flood process [4]. The miscible flood process is grouped into the multiple contact process and single contact, with the single contact process entailing the use of alcohol or inert gas for miscibility while multiple contact entails injection of methane which relies on phase chemical exchange to attain miscibility. In the microbial flood process, micro-organisms are deployed for the formation of polymers or/and surfactant in the reservoir for EOR [6]. The thermal flood process makes use of hot water, in-situ combustion and cyclic steam injection to raise reservoir temperature for oil production. The chemical, microbial and miscible flood processes are viable in light crude oil bearing reservoirs, while thermal flood process is viable in heavy crude oil bearing reservoir. The density of crude oil plays a significant role in the application of these flooding techniques [4]. Of the mentioned EOR methods, CEOR technique is adjudged to be the most promising due to its higher efficiency, economic and technical feasibilities as well as reasonable capital cost [7]. Understanding of the mechanism of CEOR technique through technological advancement due to higher oil prices enabled the application of this EOR method with great popularity in the 1980s. CEOR techniques increase oil recovery through increment in the effectiveness of injected chemical into the permeable sand thereby displacing the oil. Dependent on EOR process type, injected chemicals with water slug cause alteration of fluid-rock and/or fluid-fluid interaction in the porous formation. This includes reduction of the IFT existing between the displacing and displaced fluid (oil) or increment in injectant viscosity to improve conformance and mobility control. Besides, the chemicals injected alter the rock wettability thereby increasing oil permeability [8]. Traditionally, the CEOR techniques are namely: surfactant flooding, alkaline flooding and polymer flooding [9]. However, these conventional CEOR methods are bedeviled with several limitations. As a result of adsorption phenomena, surfactant and alkali efficiency are lost when they flow in porous media. Polymers, with increase in injectant viscosity as main recovery mechanism and consequently mobility at elevated temperature and reservoir brines conditions suffer loss of viscosity. Subsequently, various modes of CEOR flood processes were designed, studied and applied for oil recovery enhancement, to wit: binary mix of alkaline-polymer (AP) [10], surfactant-polymer (SP), alkali-surfactant (AS), and finally alkaline/surfactant/polymer (ASP) slug [11]. The synergy of these combined chemicals yielded improved efficiency when applied in oil wells [12].

2. Chemical flooding

In the chemical flood process, substances such as alkaline, polymer and surfactant are deployed to displaced oil trapped within the pore spaces of the reservoir. The chemical flood process is the most deployed EOR process after secondary recovery due to its efficiency and cost [13]. The aim of CEOR is to improve the macroscopic and microscopic displacement of mobilized oil from entrapped pores of the reservoir to the production well. These can be achieved by EOR processes through interfacial tension (IFT) reduction, capillary number increase arising from capillary force reduction, rock wettability alteration, pH control and mobility ratio improvement between mobilizing and mobilized fluid leading improved sweep efficiency [4]. These substances to wit: polymers, surfactant and alkalis are introduced into the reservoir for mobilization of trapped oil using the various EOR mechanisms. Several studies have been carried out on the suitability of CEOR for low and medium crudes, and its application in different reservoir rocks [14]. Also, different researchers have revealed the potentials of local substances in recovery of residual oil on the basis of concentration [15], injection rate [11], stability at elevated temperatures [16], stability at elevated saline environment [17] and modification [18-19]. These local substances have been suggested as alternatives for the conventional chemicals used in chemical flood process of EOR, with the likelihood of creating wealth

from waste as well as employment opportunities. These developments will reposition the oil industry for tertiary oil recovery; benefit not only the upstream industry but also the nation at large [4].

3. Chemicals EOR (CEOR) methods

3.1. Alkaline flooding

Alkali flooding as an EOR method, utilizes alkali for oil recovery factor improvement. The technique though different from other EOR approaches on the ground that by saponification reaction, chemicals which aid oil recovery during EOR process are in situ generated [20]. Reaction between caustic alkali and organic acid to generate soap is termed Saponification reaction as depicted by eq. 1 [21].



where: HA - pseudo-acid component; A⁻ - soap component.

In alkaline flood process, the alkali reacts with the acidic component of the crude oil in the reservoir to form surfactant (soap), which lowers interfacial tension (IFT) existing between oil and water and emulsify crude oil thus, causing oil recovery improvement. In addition to IFT reduction, the generated soap (surfactant) also lowers capillary pressure and changes wettability (i.e. water-wet reservoir is achieved with its injection) [22]. Successful alkaline flood process not only lowers IFT but also provides better correlated recovery efficiency with emulsion stability and wettability alteration [23]. The effectiveness of the flood process and the amount of in-situ soap produced relates directly to the acidity of the reservoir oil. Crude oil is said to be acidic when its total acid number (TAN) upon non-aqueous titration goes beyond 0.5g KOH/g [4]. The TAN of crude oil can be used to measure naphthenic acids in the reservoir [24]. Alkaline flooding has been successfully deployed in reservoir whose crude oil has high acid content. In many cases, soap formed through the injection of alkali may be unable to reduce IFT optimally; thus, the alkali is injected with certain quantity of appropriate surfactant so that at reservoir conditions the mixture of soap and surfactant will optimally operate [4].

Alkali undergoing saponification reaction for in-situ soap generation requires such alkali to have pH of 9.5 and above. The maximum percentage of the acid that generates soap is 25%. Previous studies have shown that at low acid concentration, the mixture of alkali and surfactant will increase IFT, however at medium acid concentration, a low IFT is produced [25]. Apart from the aforementioned IFT reduction and emulsification processes, other postulated mechanisms responsible for improved oil recovery through alkali flooding include: disruption of rigid films, wettability alteration and oil-phase swelling [26]. These divergent mechanisms are as a result of the reservoir rock and crude oil's dissimilar chemical character under distinct environments like salinity, temperature, pH, as well as hardness concentration. Various crude oil in diverse reservoirs exhibit very wide disparate behaviours whenever they come into contact with alkali. Depending on rock mineralogy, interaction of the rock with alkali occurs in many ways namely: hydrolysis and surface exchange, incongruent and congruent dissolution reactions as well as formation of insoluble salt by reacting with the fluid's hardness ions and the rock surface exchanges. Several materials have been used as conventional alkaline flooding agents, viz: sodium carbonate (Na₂CO₃), sodium metaborate (NaBO₂), sodium bicarbonate (NaHCO₃), sodium orthosilicate (Na₂O.nSiO₂: n=0.49-0.59), ammonium hydroxide (NH₄OH), sodium hydroxide (NaOH) and ammonium carbonate ((NH₄)₂CO₃). The alkali selection for use depends on the mineral content, clay and formation type, and availability of divalent cations. At elevated temperature, NaOH strongly interact with sandstone surface thereby increasing porosity resulting in weight loss of sandstone and as such are less preferred. It also generates OH⁻ through dissociation. Na₂O.nSiO₂ forms weakly dissociating silicic acids that causes free H⁺ ions removal from solution. Moreover, caustic consumption which results from caustic alkali dissolution in silicate minerals poses highly detrimental factor during its field application [11]. Na₂CO₃ remains the most preferred of all the alkalis because it is cheap and, in porous media possesses better transport properties. Nonetheless, calcium and other divalent cations pres-

ence causes alkalis precipitation like Na_2CO_3 except soft brine is utilized. These inorganic alkalis are generally associated with scale and corrosion problems. NaBO_2 has better tolerance in the presence of divalent ions and has been suggested to replace Na_2CO_3 [27]. Meanwhile, in reservoirs that contain clay minerals NaHCO_3 is most preferred. Finally, because alkali precipitation occurs in carbonate reservoirs as a result of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) presence, sandstone reservoirs remains the most preferred of all formations for alkali flooding. High cost of conventional alkali and high demand, have necessitated the need for several studies on local alternatives. Alkali can be obtained locally from agro-waste materials such as plantain peel ash, saw dust, wood ash, palm bunch ash, banana leaves, cocoa pod, maize cob and sugar beet waste. On dissolution of these local materials in water generates alkaline solutions according to Eqs.3 and 4 [4]:



Rahman *et al.* [28] conducted an experiment on surfactant-alkali extraction from ground nuts soap and maple wood ash respectively. Result showed that 2-4%wt concentration of surfactant extract from ground nut soap and 2-6%wt concentration of alkali extract from maple wood ash significantly lowered IFT between water and oil interface. They also noticed that solution of \maple wood ash with 6% alkalinity almost matched 0.5% and 0.75% synthetic NaOH solution and synthetic Na_2SiO_3 respectively. Obot and Onyekonwu [24] utilized palm bunch ash and akanwu potash for alkaline flooding. Result showed that potash gave the best recovery of 75.9%, while palm bunch ash gave 61.9% recovery and akanwu + palm bunch ash had the least recovery of 61.3%. This is an indication of the effectiveness of both materials as excellent EOR agents. Akpoturi and Ofesi [29] conducted EOR study for light and intermediate crude oil using NaOH, KOH, Na_2CO_3 , and Palm Bunch ash as local alkali. Though the local alkali performed lesser than KOH and NaOH, it yielded displacement efficiency of 21.54% and 50% for intermediate and light crude oil respectively. Uzoho *et al.* [15] carried out alkaline flooding using potash, *Elaeis guineensis* and *Musa sapientum* at concentrations of 1%wt and 2%wt. Potash yielded better displacement efficiency of 93.5 and 99.1% than the two other local materials at both concentration of 1wt% and 2wt% with stable displacement efficiency achieved at 2wt% concentration. Obuebite *et al.* [16] studied phase behavior of potash with soft and hard brine at elevated temperature. Potash showed a high solubility and tolerance for divalent ions under high temperature, with the potential of been used directly in hard water. Potash further showed decline in pH value with increase in salinity, with type II micro-emulsion achieved at optimum salinity. Uzoho and Onyekonwu [19] carried out comparative study of conventional and local EOR agents using akanwu, palm bunch ash and plantain peel ash as local materials while KOH, NaOH and Na_2CO_3 (soda ash) as conventional materials. From the result akanwu had the highest recovery as such best local alkali while KOH had better recovery than the other conventional agents with local alkalis exhibiting better stability at higher concentrations than the conventional alkalis despite having lower pH value. Akanwu performed better at lower pH than KOH and this is attributed to the dynamic viscosity of akanwu which is higher than that of KOH.

3.1.1. Alkali flooding mechanisms

One key alkaline flooding mechanism is that surfactant (termed soap different from synthetic surfactant injected into the reservoir) is in situ generated when acid component of crude oil reacts with alkaline solution [21]. The reaction is as given in equation 1. Thus, addition of surfactant to alkali as in ASP process causes alkali to reduce surfactant adsorption on grain surfaces. This makes surfactant to work very efficiently, with less surfactant injected. Other mechanisms include oil entrainment, emulsification, wettability alteration and bubble entrapment [26].

3.1.2. Alkaline flooding challenges

Alkaline Flooding with all its EOR potentials is plagued by precipitation and scaling problems. The injection of alkaline solution into formation raises the concentration of CO_3^{2-} , OH^- and SiO_3^{2-} ,

and this forms inorganic scales and precipitates upon reaction with divalents calcium and magnesium. The likelihood of precipitates and scales damaging the formation have led the industry to avoid consideration of alkaline flood with emphasis placed on more alkaline free options such as SP flooding [23].

3.2. Surfactant flooding

Surfactant flooding, a proven EOR approach is utilized for the mobilization of residual oil that is trapped in the reservoir [5-6]. The injection of surfactant into reservoir is aimed at oil recovery factor improvement via the alteration of fluid-fluid interaction by reduction of IFT between brine and oil, and rock/fluid properties through wettability alteration of porous medium [4,11]. Naturally, surfactant also called surface-active agent [5,30] is amphiphilic. That is to say surfactants have both hydrophilic group which is the head and non-polar or hydrophobic group which is the tail. The non-polar or hydrophobic group is usually oil-soluble while hydrophilic group is often water-soluble with the formation of the lipophobic hydrophilic group by moieties which are classified on the basis of the inherent organic compound. The moieties are namely: carboxylates, quaternary ammonium salts, alcohols, polyoxyethylenated chains, sulfonates, and sulphates [30]. Schramm *et al.* [31] described the hydrophilic head of the surfactant as the property used in anionic, cationic, non-ionic and zwitter-ionic grouping of surfactant as depicted in Table 1. Anionic surfactants are the best surface-active substances for CEOR and this is due to their resistance to retention. Nonionic surfactant is usually utilized as co-surfactant after a compatibility test is run with surfactant. Aside the 4 major categories of surfactants, Gemini has been considered for EOR, due to its low critical micelle concentration, low IFT, and viability in low permeable reservoir. Surfactant type and its concentration play critical role in influencing the efficiency of a surfactant flood process. When injected in higher concentrations, surfactant assembles into bulks of large molecules referred to as micelle. According to Uzoho *et al.* [4], micelles are circular clusters of hydrocarbons generated when certain amounts of surfactant in aqueous solutions attains critical point. Before surfactant flooding, pre-flush containing substances like Sodium Tripolyphosphate are injected to pre-condition the reservoir [32]. Fresh water can also be injected to alter the hardness and salinity of the formation brine as well as reduce surfactant adsorption to the rock surface. For water-flooding process, it's near impossible for the injectant to mobilize the displaced fluid in the pore spaces, and this is due to capillary forces defined by the capillary number. The capillary number is linked to oil recovery and residual oil saturations, and increases with residual oil saturation reduction. Increasing displacing fluid viscosity, increasing injection fluid velocity and IFT reduction, increases capillary number and this can be achieved by utilizing surfactant [11]. IFT reduction at oil/water interface subdues the capillary forces leaving the trapped oil, and this leads to flow of oil droplet from the pore spaces of the rock. Thus, surfactant flooding causes displacement efficiency improvement at the microscopic level by utilizing the aforementioned mechanisms and wettability alteration or combination of both. This prompted the need to analyze the phase behavior, IFT capability, wettability and adsorption of surfactants [33]. The study of phase behavior of surfactant slugs for IFT reduction have been evaluated for the purposes of analyzing the zones where solubilisation caused by micelle become high, with microemulsion almost independent of parameters such as structure, temperature, pressure and slug concentration. Phase behaviors are studied using ternary diagram, with oil, water and surfactant forming microemulsion [11]. In reality 3 scenarios exist for a defined system, with the scenarios identified as Winsor type I, Winsor type II and Winsor type III. Winsor type I and II are 2-phase fluid system with Winsor I relating to oil while Winsor II relates to water existing with microemulsion. In Winsor type III, water, oil and surfactant mixture exist in microemulsion with equilibrium attained between the oil, water and surfactant. The adsorption of surfactant on the pore throats of the rock is one of the major ways retention occurs, and has been recognized as a major factor for determining success of EOR [34]. The adsorption mechanism in various instances depends on solid properties, solvent and surfactant. Surfactant adsorption is a process by which surfactant molecules transfer from bulk solution to an interface. A large chunk of surfactant is lost due to adsorption which results to high flooding

cost, thus making the surfactant flooding almost not economically viable. To reduce the surfactant retention, co-solvents are used in flood process to inhibit the formation of highly viscous phase which causes the surfactant to be adsorbed in pore spaces of the reservoir [4]. Adsorption of surfactant is dependent on surfactant type, concentration, pH, molecular weight, salinity and reservoir heterogeneity. Several materials have been utilized as conventional surfactant EOR agents: lauryl sulphate, alkyl benzene sulfonate, methyl ester sulfonate, Shell Enordet 0242 and Teepol. These materials despite their EOR potentials are plagued with high cost, thermal stability and adsorption issues, which increases with increasing salinity [5]. In a bid to address these challenges and increase local content participation, several studies have been carried out using locally sourced materials, viz: soap and detergent, agro-extracts, alcohol.

Momodu [35] carried out an EOR study using local bar soap, liquid soap and detergent as surfactants. The result showed that detergent had better oil recovery than bar soap and liquid soap. The performance of detergent was due to presence of Na compounds in the detergent. In a similar work, Chiabuotu [36] used local detergent and palm bunch soap. He work also show that local detergent performed better than palm bunch soap. He attributed the performance of local detergent to a metallic phosphate component of phosphoric acid called sodium triphosphate which aided the surfactant in its performance through the counteraction of calcium salt effect. Aggrey-Tams [37] carried out comparative EOR study on black soap, truck soap and local detergent. The local detergent despite producing relatively no emulsion had better recovery of 78.29% than black soap and truck soap. Uzoho and Onyekonwu [19] carried out performance evaluation of local detergent and sodium dodecyl sulfate as EOR surfactant agents. Result showed the performance of both surfactants peaked at 1%wt concentration with local detergent yielding better displacement efficiency than sodium dodecyl sulfate. Izuwa *et al.* [30] carried out local surfactant suitability evaluation for EOR using palm bunch ash, ripe plantain peel ash, and unripe plantain peel ash for local soaps production while sodium lauryl sulfate and alkyl benzene sulfonate were used as control samples. The investigation was centered on the effect of certain parameter, to wit: temperature, surfactant concentration, salinity effect on IFT reduction. Both ripe and unripe plantain ash soap showed sensitivity to temperature and salinity variation due to their non-ionic surfactant features, with salinity increase yielding IFT reduction until 30000ppm after which IFT value started to increase. The IFT reduction for the control samples were attributed to improved solubility between the aqueous and oleic phases due to ion exchange. Uzoho *et al.* [15] compared the EOR capabilities of local gin (kai-kai), *Cocos nucifera*, *Vernonia amygdalina*, *Carica papaya* leaves extract and nkankan (an Eastern Nigerian native plant). Result showed that *Carica papaya* leaf extract performed better than *Cocos nucifera*, *Vernonia amygdalina*, local gin and nkankan with displacement efficiency of 94.1%. Result also showed EOR superiority of *cocos nucifera* over local gin, which was attributed to the presence of yeast. Abraham [38] carried out performance evaluation of bio-based and industrial surfactants for EOR application using extract from local castor oil and industrial methyl ester sulfonate. At 60 and 25°C temperature, the extract from castor oil had better IFT reduction with better recovery than the industrial methyl ester sulfonate at increased brine concentration. Their study showed the potential of increasing brine concentration to lower IFT at optimum surfactant concentration. Obuebite *et al.* [39] conducted low cost high-performance surfactant-flood evaluation using sodium dodecyl sulfate, alkasurf-x, palm kernel oil (*Elaeis guineensis*) and moringa leaf (*Moringa oleifera*). Their result revealed *Moringa oleifera* and alkasurf-x as compatible solutions. The preliminary flood for critical micelle concentration determination gave rise to 0.2%wt, 0.4%wt and 0.5%wt for sodium dodecyl sulfate, alkasurf-x and moringa oleifera, respectively with corresponding 20%, 22.7% and 18.8% additional recovery when flooded with 3%wt brine solution. A phase behavior study carried out on alkasurf-x and moringa oleifera yielded type II micro-emulsion, with both surfactants also showing compatibility and free of precipitations. Abel [40] experimented on the EOR potentials of palm wine, fermented starch and local gin. Result proved dry gin to be better surfactant with oil recovery of 82.99%, palm wine had 75.19%, fermented starch had 57.40% with early breakthrough observed in palm wine and fermented starch. Thus, local surfactants have shown potentials in EOR. However, problems such as retention and pore blockages lower

formation permeability and increases injection cost and this had led to nano-technological EOR investigations [41].

Table 1. Surfactant types (after [11,44])

Surfactant type	Limitation	Advantage
Anionic e.g. sodium stearate, sodium dodecyl sulphate, benzene sulphonate,	High adsorption when carbonate formation is involved Responsive to high salinity	Lowers IFT in crude oil that is non-reactive Stability of clay Affordable Adsorption is low in sandstone
Cationic e.g. dodecyl trimethyl ammonium bromide	Adsorbed by sand and anionic clay sources, Responsive to high salinity	N/A
Non-ionic e.g. alkyl phenol ethoxylate, ethylene oxide, propylene oxide, polyoxy ethylene alcohol	Ionization in water cannot be achieved	Alters wettability in a reactive crude oil Less sensitivity to salty environment than cationic and anionic Show surfactant behavior when dissolved in aqueous solution
Zwitter ionic	Not yet deployed for oil recovery	N/A

3.2.1. Surfactant flooding mechanisms

Improvements in pore-scale displacement efficiency are made by surfactant flooding through wettability alteration or IFT reduction mechanisms or combination of the two mechanisms.

3.2.1.1. Interfacial tension (IFT) lowering

IFT is the force of attraction which exists at the interface between molecules of liquids (crude oil and water) within the pores of the reservoir rock, and this force needs to be broken for recovery to take place. This mechanism is predominant when surface active substances are applied to the reservoir rock containing oil and water. The introduction of surface-active agent lowers the adhesion forces existing at the interface, and this leads to a drop in the capillary pressure existing between oil and water. High IFT relates directly to a high capillary pressure, resulting in low relative permeability [42]. For a water-flood process, it is realistically impossible for water to mobilize oil in the porous space, and this is due to capillary forces which is defined by the capillary number (N_c) [11] as given in equation 5.

$$N_c = \frac{\mu v}{\sigma \cos \theta} \quad (5)$$

where: μ - mobilizing fluid viscosity; v - mobilizing Darcy velocity; θ - contact angle and σ - IFT between the mobilizing fluid (water) and mobilized fluid (oil).

The rise in capillary number can be achieved by improving viscosity of displacing fluid, improving velocity of injection fluid and IFT reduction [43]. IFT reduction at oil/water interface subdues the capillary forces leaving the trapped oil, causing oil droplet to flow from the pore spaces of the rock to form an oil zone [42]. Consequently, the higher the N_c , the higher the oil recovery. For typical brine flooding, the N_c is between 10^{-7} - 10^{-6} . Thus, increase in N_c from the stated value to a range of 10^{-2} will drastically reduce to the barest minimum the residual oil saturation and this will cause an increment in oil recovery factor. From Eq. (5), the achievement of this will be in three different ways: (a) increase in displacing fluid viscosity (μ); (b) increase in injection fluid velocity (v) and (c) reduction of IFT (σ). Increase in injection fluid velocity can increase injection pressure thereby making it to be higher than the reservoir fracture pressure, thus, fracturing reservoir rock. Meanwhile, the utilization of polymer solutions to increase displacing fluid viscosity increases N_c about 100 times [43]. Practically, it is only IFT reduction method that can be utilized to increase N_c by 1000 times. The achievement of this is only done with the assistance of surfactants. Thus, injection of surfactant solutions together with brine into oil reservoirs results in the reaction of hydrophilic head with water and interaction of hydrophobic tail with the crude oil components. Occurrence of adsorbed film takes place due to the interaction between surfactant's alkyl tail and the crude oil, thereby,

reducing the IFT at the oil/water interface [44]. IFT reduction at the oil/water interface lessens the strength of the capillary forces that withheld the trapped oil, hence, enabling flow of oil droplets with ease from the reservoir rock pore throats forming oil bank downstream [11].

3.2.1.2. Wettability alteration

Wettability is the inclination or propensity of solid surface for certain fluid type with other immiscible fluids presence [45]. In the reservoir system, wettability controls and dictates the location, fluid flow and distribution within the defined reservoir [46]. The importance of this petrophysical property cannot be overemphasized because it controls oil recovery properties such as relative permeability and capillary pressure, and can be categorized into water-wet, oil-wet and mixed wet [47]. Surface imaging test, Zeta potential measurement, contact angle measurement and spontaneous imbibition are various ways of wettability measurements, but contact angle and zeta potential are the most widely used wettability determination methods. Contact angle refers to the point where oil/water interface meet at the rock surface, with angles above 90 degrees defining oil-wet rock while angles below 90 degree defining water-wet rock surface. Zeta potential is explained as an electro kinetic potential existing between bulk phase surrounding the surface and particle surface. Spontaneous imbibition relates to the tendency of the wetting phase to mobilize the non-wetting phase [48] at static conditions, while surface image gives information on the changes in rock surface feature as a result of wettability alteration approach. The alteration of wettability of a surface from oil-wet to water-wet reduces the capillary forces, improves reservoir's oil permeability. Hence, oil recovery is less easily achieved in oil-wet in comparison to water-wet reservoirs. The utilization of surfactant for the alteration of wettability has been studied exclusively for both unconventional and conventional reservoir rocks [45]. For the case of unconventional (tight and shale) reservoirs which are characterized by ultra-low and or low permeability, surfactants addition at appropriate/optimum concentrations into frac-fluids have been reported to cause performance improvement of hydraulic fracture treatment through matrix wettability alteration, and consequently flow of fluid behaviour [4,11]. Accordingly, occurrence of spontaneous imbibition takes place with the penetration of aqueous phase into the matrix, thereby overcoming capillary forces that trap the oil in place, thus, resulting in higher recovery of oil. In a similar vein, surfactants are utilized as active agents for oil recovery from conventional carbonate and sandstone reservoirs. The mechanism by which surfactants alter the wettability of conventional rocks is called cleaning mechanism, in which oil-wet layer desorption by surfactant takes place, thereby changing the rock's state to be more water-wet. Preferentially, treatment of sandstone reservoirs are carried out with anionic surfactants while treatment of carbonate reservoirs are done with cationic surfactants due to their charge likeness that makes them very efficient for various reservoir rock systems [49]. In carbonate reservoirs, crude oil's negatively charged organic components adsorb on the rock pores' positively charged mineral surfaces. With addition of cationic surfactants, the interaction of ion-pair formation take place between the crude oil anionic components and the surfactant monomer (mainly carboxylate) that are adsorbed on rock surfaces from crude oil. Thereafter, from the rock the material adsorbed at the surface of the rock is desorbed. Subsequently, occurrence of water imbibition and oil ejection out of core material takes place. Thus, oleic phase desorption from the rock surface changes or alters rock wettability to water-wet [14]. Hence, expulsion of more oil occurs,. Contrarily, anionic surfactants fail to desorb carboxylate group that are inherent in oleic phase from surface of the pore because their surface charges are /alike. Instead, there is inducement and creation of weak capillary forces by these surfactants through hydrophobic interaction of the oleic phase and the surfactant's hydrophobic tail [50]. Albeit, these interactions also displace the oil, though not as efficient and effective as the interaction of ion-pair and oil-wet condition is changed to neutral wet. Meanwhile, adsorption of nonionic surfactants on rock surfaces is achieved through ion exchange and polarization of n-electrons [51]. Cationic surfactants on the overall are more efficient and effective wettability agents in comparison to other types of surfactants [50-52].

3.2.2. Surfactant flooding challenges

The key challenge confronting surfactant flooding is retention of surfactant. Surfactant retention could be as a result of phase trapping, adsorption or precipitation. Surfactant adsorption process is the dominant mechanism for surfactant retention. The adsorption of surfactant on rock pores causes decrease and loss of surfactant concentration, thus, reducing the amount of molecules of surfactant available for reduction of IFT of water-oil interface, consequently reducing the economic feasibility of the CEOR technique [53]. The process of adsorption takes place when the surfactant energetically favours the interface as compared to the bulk phase. Thus, liquid-solid interface adsorption takes place through molecule transfer of the surfactant to the liquid-solid interface from the solution of the bulk phase [54]. The rock surfaces and chemicals interaction by electrostatic interaction, viz: van der Waals interaction, lateral and chemical interaction, hydrophobic bonding, hydrogen bonding, and various species solvation which results in π -electrons polarization are responsible for adsorption of surfactant on rock pores. Adsorption of surfactant is higher with existence of opposite charges between the rock surfaces and surfactant molecules. In reservoir, surfactant adsorption depends on the surfactant nature (i.e. surfactant chemical structure) and the rock surface nature. Additionally, other factors which dictate the process of surfactant adsorption in the reservoir rocks are viz: reservoir fluids composition, pH, salinity (electrolyte concentration), temperature, and the solution condition. Surfactant concentration notwithstanding, conditions of high-salinity favour high adsorption of surfactant [55]. Contrariwise, temperature increase as a result of onset of elevated kinetic energy decreases surfactant adsorption. Meanwhile, at varying pH the surfactant adsorption amount is dependent on surfactant resultant charge that will react with available charges at the surface. For example, increase in sandstone surface pH causes the surface to be negatively charged, and this would reduce anionic surfactant. Also, anionic surfactant adsorption will increase with reduction of the pH. Prevention of adsorption of chemical at the liquid-solid interface can be achieved by binding the surfactant chemical molecules at liquid-air or the liquid-liquid interface. In this regard, studies suggested that specific reservoir rock be matched to screening and selection of surfactant through surface charge as surfactant adsorption reduction mechanism in reservoirs [52].

3.3. Polymer flooding

Polymer flooding can be incorporated/introduced whenever waterflooding of oil reservoir becomes inadequate as a result of the phenomena of viscous fingering leading to early water breakthrough. Polymer flooding process involves injection of water-soluble polymers of higher molecule weight along with water slug for increase of the injectant viscosity. The increase in the injectant viscosity leads to improvement in the conformance and mobility control of injected slug thereby eradicating the phenomena of viscous fingering. Consequently, there is suppression of early water breakthrough usually encountered during waterflooding process with increment in oil recovery factor achieved. Polymer flood process generally, does not lower the residual oil saturation but enables it to be attained in a quicker and more economic manner, thus lowering water production. The success of polymer flooding lies in its early injection during the production life of the reservoir [11]. Polymer can be in biological or synthetic form, though biologically produced polysaccharides have shown to be better polymers than synthetically produced PAMs [4]. This is due to the vulnerability of PAMs to mechanical shear and saline environment unlike the polysaccharide. The presence of saline substance in water leads to the collapse of the molecular chain of polymer, and these results in a lower solution viscosity [25]. Increased concentration of polymers is utilized to reduce the salinity effect and stabilize high viscosity formation water. The aqueous solution of polymer exhibits non-Newtonian behavior, with its apparent viscosity tied to concentration, shear rate, oxidation, hydrolysis, microbial attack and temperature [11]. Several conventional polymer EOR agents have been used for polymer flooding which include: partially hydrolyzed polyacrylamide (HPAM), carboxymethyl hydroxyethyl cellulose, hydroethyl cellulose, hydrolyzed PAMs, glucan, floppam, hengfloc and xanthan gum, with HPAM as very commonly utilized for EOR application [56] and this is due to

its good solubility in water, high resistance to bacteria attack, mobility control and low cost. Despite the aforementioned attributes of HPAM, its sensitivity to temperature, pH, salinity, hardness and shear forces, has led to xanthan gum as the popular polymer. Xanthan gum is obtained from the fermentation of glucose and its isomer fructose by various bacteria. The biopolymer is comprised of polysaccharide chains which reinforce its resistance in the presence of shear forces, salinity and temperature [4]. Successful implementation of polymer flooding has taken place in numerous oilfields either on commercial or pilot scale for many decades. These include: the Canadian Pelican Lake field and East Bodo Reservoir, Chinese Daqing oil-field, and Oman Marmul field and Suriname Tambaredjo field, to mention but a few [23]. In addition, there has been increasing importance of polymer flooding to the energy market recently, with the reported incremental oil production from Chinese Daqing oil field of about 300,000 bbl/day being most notable of its contributions [57]. These conventional polymer materials despite their EOR potentials are plagued with high cost and polymer molecules retention issues [4]. In a bid to address these challenges and increase local content participation, several studies have been carried out using locally sourced materials.

Several researches have been conducted on the utilization of local polymers for EOR. Abdulraheem *et al.* [18] carried out a comparative study of rate dependent polymer flooding using modified gum arabic, natural gum arabic, xanthan gum and hengfloc polymer samples. The modified gum arabic performed much better than natural gum arabic, hengfloc and xanthan gum as it yielded additional 41% oil recovery compared to the local materials counterpart with recovery of 28.81%,. The modification of the gum arabic improved its EOR capabilities and reduced the viscosity. Further studies to determine the performance of the gum arabic at variable injection rate, yielded the best recovery at 2cc/min injection rate. Fadairo *et al.* [58] carried out a comparative EOR study using gum arabic and bio-polymer synthesized from banana peels. Result showed the viability of bio-polymer from banana waste in recovering 25.58%, 16.71%, and 14.55% of the oil originally in place at three different concentrations. They compared polymer flooding using bio-polymer from banana waste with water-flood and gum arabic polymer flood against time. The bio-polymer from banana waste gave the best oil recovery within the shortest time unlike that of gum arabic and water-flood. Ihebuzor and Onyekonwu [59] utilized local soup thickeners (ogbonno and okra) and starch extracts in his experimental study of polymer flooding with gum Arabic. Okra despite being less viscous than gum arabic and ogbonno, yielded the best oil recovery while ogbonno gave the least recovery. Samuel and Onyekonwu [60] carried out a comparative study on the performance of ogbonno and cassava starch as EOR polymer agents. Result revealed starch as better polymer for EOR than ogbonno,, though ogbonno showed better mobility ratio. Ajabuego and Onyekonwu [61] also conducted a comparative study on displacement efficiency using ogbonno, achi and exudate gum. Result showed exudate gum as the best polymer as it performed better than ogbonno and achi, with 35.48% recovery. Uzoho *et al.* [15] carried out polymer flooding using *irvingia gabonensis*, *abelmoschus esculentus*, *brachystegia eurycoma*, *detarium microcarpum* and *mucuna flagellipes*. Result showed *abelmoschus esculentus* as the best polymer compared to other local materials, though performance decline at concentrations above 1%wt was noticed while *brachystegia eurycoma* and *detarium microcarpum* showed better displacement efficiency with increase in concentration. Uzoho and Onyekonwu [19] compared *abelmoschus esculentus* with PAM in polymer flooding. Result showed *abelmoschus esculentus* as better polymer than PAM as it yielded additional 18.7% oil recovery compared to PAM which yielded additional 12.73% oil recovery. Gbonhinbor *et al.* [62] and Obuebite *et al.* [17] explored the viability of local edible foods such as beans and ewedu respectively. Polymer flood study by Gbonhinbor and Onyekonwu [62] evaluated the performance of aqueous beans (common beans) in improving the recovery of oil. His work revealed the polymeric behavior exhibited by natural protein sources as it performed better than conventional water-flood. Obuebite *et al.* [17] studied the effect of salinity and divalent ions on local biopolymer using okra, ewedu and editan as polymers. For hard brine solution, the local materials showed variable displacement efficiency at different range of concentrations with peak performance attained at 0.5%wt concentration and for soft brine solution, the local materials also showed variable displacement

efficiency at different ranges of concentration with peak performance attained at 1% concentration. Obuebite *et al.* [63] carried out a comparative study of synthetic and natural polymer for EOR using corchorus olitoris (jute leaf), pectin (citrus), PAM and terminalia mantaly (TM) as polymers. They studied polymer behaviour at different brines and the study led to the selection of pectin, PAM and TM as possible polymer for flood process in both soft and hard brine. TM performed better than PAM and pectin at all concentration considered, as it yielded a maximum of 89% and 90% recovery in soft and hard brine respectively at 2%wt concentration. In order to ascertain the stability of local polymers at elevated temperatures, Osuji and Onyekonwu [64] conducted stability evaluation on achi and offor as local polymers at elevated temperatures. Achi and offor despite being limited by microbial attack maintained stability at temperature of 60°C. The modification of local polymers has matched the conventional polymers as indicated by the stability study conducted by Onaiwu *et al.* [65].

3.3.1. Polymer flooding mechanism

Oil recovery by polymer flooding is achieved through the combination of mechanism of disproportionate permeability reduction (DPR), viscoelastic nature of polymers and mobility control.

3.3.1.1. Disproportionate permeability reduction (DPR)

Polymer flooding causes improvement in sweep efficiency through DPR. Because some reservoirs are heterogeneous in nature, there is uneven permeability distribution in these reservoirs (ie. different layers having different permeabilities). This results in excessive water production been channeled through layers of high permeability, and this leads to large volumes of movable gas and oil remaining trapped in zones of low permeability, thus causing low recovery at the primary and secondary production stages [66]. The challenges confronting the production of highly heterogeneous reservoir through secondary and primary recovery approaches can be surmounted by using polymeric materials. The interactions of high permeable streaks having tight spot are the characteristics of these reservoirs. The thief zones function as channels for injected drives at the same time bypassing hydrocarbon in tight spot with resultant reservoir ineffective sweep. However, when cross-linking agents are injected with selective reduction/plugging of high permeable streak, secondary drives are then rechanneled to zones of oil bearing thereby improving or ensuring proper sweep. Design of the process can be in a manner that cross-linking of the agents is carried out before injection or in-situ activation of the cross-linking is conducted with the appropriate catalyst [11]. This mechanism of recovery can be deemed a standalone enhanced recovery process utilizing chemical(s) or otherwise technique to improve secondary recovery schemes. Generally, polymer gels are considered the commonest agents utilized for this method [42]. During polymer floods, the injected polymer solutions into heterogeneous reservoir causes buildup of flow resistance to water in the reservoir sections it penetrates, thereby, reducing water relative permeability (k_{rw}) while ensuring that oil relative permeability (k_{ro}) is reduced very minimally or at all no reduction took place. This mechanism is called DPR. The increased polymer resistance to water subsequently directs the water injected into poorly swept or un-swept layers of the porous rock via discrimination of flow channels and layered formation on pore throats by the retained polymer, leading to an elevated oil recovery [43].

3.3.1.2. Mobility control

The increase in viscous force in pore spaces of the reservoir by thickening the displacing fluid in contrast to the displaced fluid aids enhancement of the displacement process [42]. The ratio of mobility of the displacing or mobilizing fluid to the displaced or mobilized fluid is termed mobility ratio, as depicted in Eq. 5:

$$M = \frac{K_w \mu_o}{K_o \mu_w} \quad (5)$$

where: M - mobility ratio; μ_o - oil viscosity (cP); μ_w - water viscosity (cP); K_o - permeability to oil (mD); and K_w - permeability to water (mD).

Mobility ratio decides how stable an oil displacement process could be. An increase in flow resistance of the mobilizing fluid by materials like polymer, prevent viscous fingering which could lead to poor sweep of the desired reservoir section [11]. If $M > 1$, this is an indication that oil is less mobile than water, thus depicting unfavorable condition with water fingering through oil zone which leads to early breakthrough and reduced oil displacement efficiency. To achieve high macroscopic sweep efficiency, M should be ≤ 1 . The ability to achieve $M \leq 1$ in order to obtain high macroscopic sweep efficiency is termed mobility control. Polymer presence in the displacing phase increases the injectant viscosity and consequently, stable front of the displacing phase results, completely void of channels and viscous fingers within the reservoir thus yielding higher oil recovery [9]. Before any EOR process is carried out, the mobility control behavior of the displacing fluid polymer materials should be evaluated in the laboratory on the basis of their concentration at varying temperatures [11].

3.3.1.3. Polymer viscoelasticity

Polymeric molecules' viscoelasticity is another mechanism responsible for the improvement in the macroscopic efficiency observed when polymer flooding is carried out in reservoirs. Improvement in recovery through this mechanism takes place with change of capillary number alone [67]. Polymers unlike Newtonian fluid, goes through series of contraction and expansion when they flow through the pore spaces of the reservoir. The knowledge of micro-flow mechanism is critical to design of polymer flood scheme and promotion of the effect of polymer displacement [68]. This aids polymeric molecules to produce extra "elastic viscosity" which enhances microscopic and macroscopic displacement efficiency. The effect of polymer viscoelastic properties on macroscopic sweep efficiency was investigated by Veerabhadrapa [69] and Urbissinova *et al.* [70]. The elastic variation of polymer solution with similar shear viscosity was produced using polymers with different molecular weight distribution but same average molecular weight. From their individual experimental result, high elastic solution of polymer showed a fairly higher flow resistance in pore spaces and stable flood front thereby lowering fingering. This resulted in lower residual oil saturation, higher sweep efficiency and improved recovery of oil. The recovery from viscoelastic-polymer solutions would be more than estimated based on either apparent viscosity from flow in porous media or shear viscosity derived from rheometer [11].

3.3.2. Polymer flooding challenges

The major goal of polymer addition to displacement fluids remains to increase the injected brine viscosity. However, noticeable interactions like dispersions forces and electrostatic interactions occur between rock surfaces and transported polymer molecules in the reservoir [4,11,15]. These cause polymer molecules retention and results to injection fluid bank formation, partially or wholly denuded of polymer which is dependent on the extent of retention of polymer molecules transported. Thus, the required target viscosity is higher than the final injectant viscosity in the reservoir thereby reducing the polymer flood effectiveness and efficiency. Polymer retention in pores of the reservoir is influenced by rock permeability, molecular weight, polymer concentration and type, salinity, clay minerals presence, temperature and flow rate. Polymer retention remains a major factor that controls the economic viability of any polymer flood process since they affect viscosity of the polymer solution that is injected into the reservoir, rock permeability, and ultimately oil recovery process. Polymer adsorption, hydrodynamic retention and mechanical entrapment are the 3 major polymer retention mechanisms [11].

3.4. Alkaline-surfactant-polymer (ASP) flooding

The technique of ASP flooding involves alkali, surfactant as well as polymer solutions injection to achieve EOR. ASP solution combines the in-situ surfactant generation behavior of the alkali, IFT reduction of the surfactant and mobility control of the polymer to improve oil recovery [71-72]. The efficiency of an ASP solution can be influenced by the compatibility of the alkali, polymer and surfactant. Because of the integrated synergy of the injected slug's individual component, this technique is generally seen to be the most promising CEOR process [71].

The combination of chemicals improves both pore scale as well as volumetric sweep efficiency. The first slug is composed of surfactant and alkali which mobilizes the residual oil trapped in the reservoir pore space. Thereafter, the injection of polymer slug is carried out for control of mobility ratio and then volumetric sweep efficiency. Finally, the injection of drive water and freshwater slug is carried out for chemical recovery optimization [4,15,73].

Several researches have been carried out on ASP flooding using conventional ASP agents. Solomon *et al.* [74] studied the compatibility of xanthan gum in ASP solution containing sodium hydroxide (NaOH), shell enordet and gum arabic. Gum arabic performed better than NaOH and shell enordet individually. ASP formulation of 0.1wt% NaOH , 0.5wt% shell enordet and 0.4wt% xanthan gum yielded better recovery than other formulations including NaOH , shell enordet, xanthan gum and gum arabic. Ojo *et al.* [25] conducted ASP flooding using sodium dodecyl sulfate ($\text{C}_{12}\text{H}_{24}\text{SO}_4\text{Na}$), partially hydrolyzed polyacrylamide (PHPAM) and NaOH solutions. The ASP formulation achieved good mobility ratio but low oil recovery at elevated viscosities. This was attributed to increased concentration of alkaline which lowers the polymer's viscoelastic effect. This is an indication that ideal concentration for each flooding process is essential in addition to the ASP solution's viscosity. They reported that $\text{C}_{12}\text{H}_{24}\text{SO}_4\text{Na}$ (0.1-3%wt concentration), PHPAM (0.5-1%wt concentration) and NaOH (0.5-1%wt concentration) ASP flood formulation gave the best recovery. Ujuanbi *et al.* [32] suggested alkaline, surfactant and polymer concentrations of 1%-2%, 0.3%-1% and 0.1%-0.3% respectively as suitable for ASP flood based on their study. These concentrations however vary depending on fluid and rock properties of the reservoir rock. ASP Core flood tests carried out by chemflooding yielded 17-18% incremental recovery of oil over waterflooding with ASP solution as 0.6wt% of Na_3PO_4 (alkali) + 0.3wt% of surfactant + 0.1wt% polymer solutions. Successful application of ASP flooding has been carried out with excellent performance in China with the inclusion of Xingjiang conglomerate reservoirs, Daqing sandstone reservoirs, and complex fault blocks of shengli reservoirs. In oil field of Daqing, ASP formulation of 0.75-1.6% wt Na_2CO_3 , 0.5-3.5%wt surfactant and 0.1-0.5%wt polymer were utilized for IFT reduction between Daqing oil and water with attendant oil recovery enhancement achieved [4,11]. These conventional ASP materials despite their huge EOR potentials are plagued with high cost, scaling issues, surfactant precipitation, produced emulsions treatment pitfall and produced water disposal difficulty in conformity with set standard/limit [4]. In a bid to address these challenges and increase local content participation, diverse studies have been carried out using locally sourced materials.

Several researches have also been conducted on the utilization of ASP local materials for EOR applications. These materials are, to wit: plant-based or bio-based chemicals, Agro-waste and by-products from plant and food processing. These local ASP materials can provide higher range of salinity tolerance than sulphonate surfactants and some of the materials can be applied at elevated temperatures than PAMs. They are termed "green chemicals" that assist in the reduction of the overall EOR operations environmental footprint [4,15]. The utilization of these agro-wastes will lower production cost, enable waste conversion to wealth, ensure profit maximization and job opportunities creation. These local materials namely: akawu, palm bunch ash, soya beans, archi, ogbonno, local gin, detergent, palm wine, xanthan gum, okra, exudate gums to mention a few can serve as excellent EOR agents [20]. Ojukwu *et al.* [75] conducted ASP flooding using ogbonno, palm bunch and soya beans as polymer, alkaline and surfactant respectively. Result revealed ASP solution as the best EOR as it recovered more oil than individual chemicals. From the study, increase in viscosity as a result of increased polymer (ogbonno) concentration lowered recovery. Peter and Onyekonwu [76] conducted comparative study of locally sourced and imported materials for ASP flood with 20,000ppm NaOH , 12500ppm archi, 12500-6500ppm polyanoic cellulose polymer, soap from palm bunch ash, plantain peel and 5000ppm Alkyl aryl Sodium sulfonate selected for the ASP design. The local ASP formulation yielded displacement efficiency of 64.07% while the foreign ASP formulation yielded 78.13%. Uzoho *et al.* [15] conducted ASP flooding at optimum concentration of potash, carica papaya leaf extract and abelmoschus esculentus after selections from wide range of local surfactants, polymers and alkali. Result showed displacement efficiency of 90%, though efficiency recorded was less than AP, AS, and SP flooding. The result showed incompatibility

of the local agents. They stated that the conditions for more effective ASP flood are: oil saturation >45, viscosity < 35cp and °API < 19. These conditions are also stated for the individual materials, viz: polymer, surfactant and alkali as depicted in Table 3. They attributed the poor performance of the ASP flooding to the use of crude oil with viscosity of 38cP and °API > 19, which are greater than the margins for better performance of ASP flood. Table 2 depicts the utilization of some ASP local materials for EOR operation. From Table 2, it is evident that the \local materials possess the potentials to replace the conventional materials if improved upon. Thus, from the literature and Table 3 the Niger Delta possesses enough local materials\that can be utilized to formulate ASP for EOR processes.

Table 2. Some local ASP materials for EOR.

Alkaline material(s)	Surfactant material(s)	Polymer material(s)	Max. Rec. (%)	Remark	Reference
	Starch (fermented) Palm wine Local gin		57.40 75.19 82.99	Local gin recorded the highest recovery. Palm wine and fermented starch breakthrough before oil recovery was observed during the flood process.	[40]
	Ethanol Alcohol (palm wine)		69 77	The flood process involving alcohol gave the best recovery compared to mixtures involving alcohol-water.	[77]
Palm bunch ash	Soya beans (Lecithin)	Ogbonno	79.3	An optimum recovery was attained with the ASP flood process unlike when the reagent were flooded individually. The polymer chemical recorded low recovery at high viscosity and optimum recovery at low viscosity.	[75]
Akanwu + Palm bunch ash Palm bunch ash Akanwu (potash)			61.3 61.9 75.9	Flood process involving Akanwu (potash) yielded a better EOR compared to the other approach.	[24]
Palm bunch ash	Soya beans	Okra	76	At high concentration, the palm bunch ash caused a drop in the viscoelastic impact of the local polymer in the solution	[25]
Palm Bunch Ash Potassium Hydroxide Sodium Carbonate Sodium Hydroxide	Soya Bean	Irvingia Gabonensis Brachystegia Eurycoma seed	> 20	Palm Bunch Ash yielded 20% and 50% for light and medium crude. SP yielded optimum recovery at 20:80 ratio for light and medium crude. Using NaOH as Alkali, AP solution with local polymer yielded optimum recovery at 60:40 ratio	[78]
		Ewedu Okro Editan	> 40 > 40 > 20	Okro give the best EOR in soft brine. In hard brine, the polymer's performance is dependent on optimum concentration	[17]
Sodium hydroxide	Soap (palm bunch ash) Soap (Plantain peel ash) Alkyl aryl Sodium sulfonate	Archi Polyionic- cellulose- polymer	> 63.7	Using NaOH as alkali source, ASP formulation with foreign surfactant and polymer yielded an optimum recovery of 88.6% Using NaOH as alkali source, ASP formulation with local polymer and surfactant yielded an optimum recovery of 77% Highest recovery was obtained when AP slug ratio is 50:50 and 60:40	[76]
Elaeis guineensis Potash	Cocos Nucifera Local Gin	Abelmoschus-esculentus Irvingia-Gabonensis	> 80	Potash yielded the best efficiency for alkaline EOR process. Carica Papaya yielded the best efficiency for surfactant EOR.	[15]

Alkaline material(s)	Surfactant material(s)	Polymer material(s)	Max. Rec. (%)	Remark	Reference
Musa sapientum	Carica Papaya Nkankan Vernonia Amygdalina	Mucuna-Flagellipes Brachystegia-Eurycoma, Detarium- Microcarpium		Abelmoschus esculentus yielded the best recovery for polymer EOR. ASP flooding had above 88% displacement efficiency, but showed incompatibility and performed lower than SP, AS and AP flooding when compared with the three.	
	Castor Oil (extract) Methyl Ester Sulfonate		46.42 37.93	Surfactant from castor oil reduced IFT and yielded a better oil recovery than methyl ester sulfonate	[38]
Akanwu Palm bunch ash Plantain peel ash NaOH Potassium-hydroxide Sodium Carbonate	Xero detergent (XD) Sodium Dodecyl sulphate (SDS)	Achi, Ukpo Ogbonno Offor Modified-Ogbonno Okro PAM	> 85	Akanwu and sodium carbonate produced the best EOR for alkaline flooding. XD was able to yield an favorable EOR and could replace SDS Okra performed better than PAM	[19]
		Corchorus- Olu-torius (Jute leaf) Pectin (Citrus) Terminalia-mantaly	>60 >80	TM performed better than other polymer substances for EOR in both soft and hard brine. There is an increase in oil recovery with increased concentration of TM polymer. Jute Leaf failed stability test and was not used in EOR process	[63]
NaOH	Sparkle soap	Offor	39.58	Pore spaces are blocked as their occurred absorption of water and solidification by offor,	[64]

Table 3. Merits and demerits of chemical flood materials [4].

Flooding type	Merit	Demerits	Screening Constraints
Alkaline	Lowers IFT, lowers surfactant adsorption and Alters wettability	Not applicable to carbonate rocks, high caustic consumptions and scale production	Gravity: 13-35 API, Viscosity: < 200cp, Depth: < 9000ft, Temp.: <200°F, Ave. Perm.: >200md
Surfactant	Lowers IFT, Improves aquifer remediation of oil alteration in soil and bedrock aquifer	High cost, Adsorption on the rock surface Micelle formation at elevated concentration.	Gravity: (medium to high), Viscosity: < 300cp, Temp.: <212°F Salinity: 0.5-12% Oil Saturation: moderately high
Polymer	Improves volumetric sweep efficiency, Lowers mobility ratio	Vulnerable in elevated temperature and salinity, wellbore plugging, microbial degradation, Limited to high porosity and permeability reservoir.	Gravity: >18, API viscosity: < 200cp, Depth: < 9000ft, Temp.: < 225°F, Oil saturation >10%, Avg. perm. > 20mD

3.4.1. Challenges of ASP flooding

The technology of ASP flooding though successful in many field applications in various countries of the world, like any other EOR process is plagued with certain challenges. These challenges are namely: Operational Difficulties, scaling issues and surfactant precipitation, produced emulsions treatment pitfall and produced water disposal difficulty in conformity with set standard.

3.4.1.1. Operational difficulties

ASP flooding in actual operation is still plagued with certain difficulties, to wit: low volume injection or injection well plugging, inadequate dissolution or polymer degradation, and equipment corrosion by composite flooding materials [79]. The makeup of ASP flooding agents is

complex and results in the consideration of rock formations, water and oil physicochemical properties during design optimization, and this increases the difficulty involved in ASP flooding formulation design. Presently, the material used for composite oil displacement during ASP flooding process is in high demand, very costly with high temperature resistance, salt tolerance characteristic and alkali resistance displacing agent lacking and these are unsuitable for thermal reservoirs, brine reservoir or carbonate reservoir [11,44].

3.4.1.2. Scaling issues and surfactant precipitation

Precipitation occurs when divalent metal cations that are present in formation brines react with alkali. The material precipitated, deposit scales on the wellbore equipment, thus, fouling it. For this reason, application of ASP in carbonate reservoirs is deemed unsuitable [11].

3.4.1.3. Produced emulsions treatment

The breakthrough in production well of ASP slug injected chemicals enables the synergetic interaction existing between these chemicals to attract them to the water/oil interface, thereby inducing stable emulsion. The emulsions produced, unlike conventional emulsion are stable thermodynamically and difficult to demulsify as they remain highly concentrated at the water-oil interfaces. The stability of the enhanced emulsion is due to steric and electrostatic effects of the injected polymers, surfactants, and soap. Stable emulsion presence in the fluid produced from oil wells poses great difficulty during separation and processing in the separator [73].

3.4.1.4. Disposal treatment for ASP produced water

Stable emulsion presence in water produced from the ASP flooding process remains a key concern during the produced water treatment to meet set disposal requirement. The emulsified water as a matter of fact exhibits high suspended solids and oily content, which is very difficult to dispose because of the injected chemicals adsorption on the oil droplets' surface. The necessity to conform/meet the set standard for produced water disposal aboard makes the entire process strenuous [44,73].

4. Conclusion

Presented in this study is a review of CEOR and the application of local CEOR materials in the Niger-Delta. The CEOR mechanisms of operation, challenges, solutions and the local materials were explored and studied.

The stability and CEOR potentials of local bio-polymers such as gum arabic could be significantly enhanced when the local polymer is blended with local agents such as xanthomas specie. Bio-polymer despite degradation action by bacteria have shown potentials in improving oil recovery but when treated with chemicals such as biocides, pesticides and formaldehyde, insignificant bacterial action was achieved with great improvement in oil recovery.

The performance of ASP, AP, SP and AS binary materials' mixture improved recovery by above 70% when compared to the use of individual chemicals for flood operations. *Carica papaya* extracts and local detergent with displacement efficiency of 94.1% and 96.6% respectively, demonstrated their abilities as alternatives to conventional surfactant such as sodium dodecyl sulfate in CEOR process. The emulsion produced during experimental core flood process using local soap can be mitigated by addition of co-solvents such as alcohol and dry gin in a case where local soap is used as surfactant, though local soap did not perform excellently well as it yielded displacement efficiency of 53.39%.

With displacement efficiency of 99.1% and 90% respectively, okra and TM demonstrated their ability to completely replace conventional polymer such as PAM in CEOR process. Local potash (akanwu) and palm bunch ash can be considered as an alternative for conventional alkali, as they yielded 99.1% and 97.5% displacement efficiencies respectively.

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