

Review Article

Potentials of Enzyme Enhanced Oil Recovery: A Review

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Abstract: In this paper, the progresses of understanding of the enzymes application in hydrocarbon production from extensive experimental and field studies are reviewed. Enzyme enhanced oil recovery is an emerging method of improving oil production in an environmentally friendly way, but the mechanisms underlying this process are not clearly understood. Also, detailed studies on enzyme enhanced oil recovery applications are not readily available. From the comprehensive review carried out in this study, we observed that most of the works done on enzyme enhanced oil recovery processes were not properly detailed and the different experimental procedures adopted makes coherent understanding of the process difficult. Evident however in all the studies from the laboratory experiments and field applications, is the capacity of enzyme to improve oil production from both sandstone and carbonate rocks. Also, we have identified and highlighted the physicochemical properties of the enzymes commonly used for enhanced oil recovery and their effects on oil recovery process in order to improve the understanding of their applicability in relevant hydrocarbon reservoir. Furthermore, the challenges and future research directions for enzyme enhanced oil recovery applications have been pinpointed in this study. Having unfold the enhanced oil recovery potential of enzyme, a clarion call is thereby made for deeper studies on this emerging method of improving oil production. This study is relevant to the design and application of enzyme enhanced oil recovery process in both carbonate and sandstone reservoirs.

Keywords: Enzyme, Enhanced Oil Recovery (EOR), Carbonate, Sandstone, Core Flooding, Field Application

1. Introduction

Enzyme enhanced oil recovery is an emerging enhanced oil recovery (EOR) method. A number of studies have reported positive effect of enzyme applications in both laboratory-scale and field-scale (e.g. [1-5]). However, the mechanisms underlying this process are not clearly understood and detailed studies on enzyme enhanced oil recovery applications are not readily available. From the analysis of previous studies on enzymes used for EOR processes, different authors used different names such as enzyme, bio-enzyme, biological enzyme, protein-enzyme, greenzyme etc. but in this work, a generic name 'enzyme' has been adopted for the ease of readability and understanding of the paper. Enzymes are environmental friendly just like any other biological agents, but they have additional advantage of re-applicability due to their catalytic nature [6]. Enzyme production for EOR

application has evolved over the years and different types of commercial products are now available. In this paper, a comprehensive review on recent applications of enzymes in oil recovery processes are presented in order to improve understanding of the process. Also, the challenges and future research directions for enzyme enhanced oil recovery applications have been pinpointed.

2. Background Studies on Enzyme

Enzymes are biological catalysts that expedite reactions that will otherwise proceed slowly without them [7, 8]. The ability of enzymes to catalyse reactions independent of biological membranes in vivo has made it possible for them to be used in preparation of wide range of products that can be produced by in vitro and fermentation methods [9]. All known enzymes are proteins but all proteins are not enzymes [7]. By

nature, all natural proteins have surface activity potential due to the presence of both hydrophilic and hydrophobic groups in their molecules. However, because of different factors that influence physicochemical process at the interface, natural proteins are slow and inefficient as surface active agents [10]. Hence, proteins can be modified into enzymes with largely amphiphilic compounds and enhanced surface activity. Enzymes are interfacially active molecules consisting of one or more polypeptide, peptide or amino acids chain as hydrophilic part while the hydrophobic part is made up of long hydrocarbon chain such as fatty acid or carboxylic group [10, 11].

Most earlier studies on proteins and enzymes were carried out in the aqueous solutions but later studies unfolded the high potential of enzyme in organic solvents as detailed by Klibanov [12]. He unveiled the great potential of using enzymes in anhydrous organic solvents and demonstrated how their activities are enhanced in different media. According to him, the enzymatic activity can be enhanced in organic solvents by adopting the following rules: hydrophobic media should be used for best results, enzymes need to be lyophilised from aqueous solutions at optimal pH of its enzymatic activity and diffusion of enzyme in the organic solvent should be ensured through rigorous agitation. Hence, there has been an increase in the use of enzyme to produce surface active agent compounds due to the fact that a wide range of enzymes function effectively under near anhydrous conditions. This property has therefore made possible production of high concentration of reactants in non-aqueous solvents and also enables reversible reaction of hydrolytic enzymes in systems [9].

2.1. Enzyme Structure and Substrate Binding

Enzymes are macromolecules with large number of protein molecules that can be folded and bent into a specific three-dimensional structure, but they usually have small areas known as active site to which substrate actually binds. Generally, enzyme demonstrates specificity for substrate based on the shape and charged properties of their active site thereby, avoiding contamination from any byproducts. The process by which enzyme interacts with substrate can be explained with the lock and key hypothesis that was first hypothesised by Emil Fisher in 1894 [8]. The binding of the substrate to the active site of enzyme is usually stabilised by the rest of protein molecules in the enzyme. It is worth noting that though most enzymes consist of solely protein, there are some enzymes that contain non-protein component commonly referred to as cofactor. The cofactor may be another organic molecule known as co-enzyme or an inorganic molecule usually metal ion like iron, copper, zinc etc. When the cofactor is tightly and permanently bonded to the protein, it is commonly known as prosthetic group of the enzyme [8]. Enzyme activity can be affected by different variables such as system temperature, chemical composition of the environment such as pH, presence of electrolytes as well as concentration of the substrate. Enzymes as globular protein respond to change in their environment through their conformational changes

and they exhibit thermodynamically stability in aqueous solutions due to their high hydrophilic nature [10, 13]. Generally, proteins are broadly grouped into hard protein with very little structural changes upon adsorption on surfaces and soft protein with tendency to undergo reorientation conformational changes during surface adsorption [14].

2.2. Enzymes Applications

Depending on the catalytic function of enzymes, they are used for different applications such as: food industries, detergent production, animal nutrition, cosmetics, textile, leather and paper industries as well as hydrocarbon production [15-17]. Aside the direct usage of enzyme in specific application, they can also be synthesized into different surface active agents such as monoglycerides, sugar fatty acid esters, amino acid-based surfactants, phospholipids, peptide surfactants and anomerically pure alkyl glycosides [18-23]. Comprehensive review studies on enzyme applications in different fields with the exception of hydrocarbon production have been presented by Jegannathan and Nielsen [16] and Li et al. [15] and they can be accessed for detailed information. The focus of this study is therefore limited to enzyme applications in enhanced oil recovery processes, because this aspect of enzyme application has not received much attention.

3. Physicochemical Properties of Enzymes

The effective performance of enzymes in EOR processes is dependent on their interaction with rock and fluids relevant to their applications. The most important physicochemical properties of enzymes as related to EOR includes: solubility and precipitation, adsorption, wettability, interfacial tension, emulsification and stability. The summaries of studies on the physicochemical properties are presented in this section.

3.1. Solubility and Precipitation

Solubility of surface active compounds like enzymes in water is determined by the presence of ionic or highly polar group while their solubility in organic solutions is based on the nature of their hydrophobic group [24]. The non-ionic compounds interact with aqueous solutions through hydrogen bonding due to presence of high oxygen atoms in their molecules. However, at high temperature, this hydrogen bonds break gradually and cause their molecules to precipitate out of the solution. Generally, solubility of these compounds is influenced by electrolyte concentration, counter-ions of multi-valent salts, the size and branching of their hydrophobic moiety. Enzymes solubility in fluids relevant to hydrocarbon reservoirs is fundamental to their successful EOR applications because their insolubility can lead to pore blockage, which may invariably result in reduction in oil production as opposed the desired increase in oil production. Xia [10] noted that solubility of most proteins increase with an increase in temperature at constant pH and ionic strength, but proteins are said to be denatured when their solubility decreases and they

precipitate when completely denatured.

Also, precipitation involving bulk-phase separation of surface active compound molecules in aqueous solution is one of the mechanisms by which they reduce the overall free energy of the system [24]. Their respective concentration in the system, salinity and temperature are some of the factors that influence their precipitation in the reservoir rock pores [25]. The presence of divalent ions such as Ca^{2+} and Mg^{2+} in brine usually generate reactions from most surface active compounds thereby, resulting in their precipitation in multi-component brines. Hence, most experimental studies are normally carried out in monovalent salt solutions, which is not a good representative of the reservoir brines that are multi-component in nature. In a recent study carried out by Udoh and Vinogradov [26], they observed no precipitation of enzyme in all the brines investigated which includes 3 molarity single salt solutions of CaCl_2 and MgCl_2 .

Udoh et al. [3] also investigated enzyme solubility in different salt solutions at varied temperatures (25, 50 and 70°C) and they observed enzyme solubility in all brines investigated at these temperatures. Most studies that reported on enzymes EOR however did not investigate their solubility. For instance, in the enzyme EOR study carried out by Jabbar et al. [27], they observed hard scale in the tubing used for enzyme slug injection, of which they did not know the source. This suggests the possibility of enzyme interactions with the tubing material and/or the transporting medium but since no prior test on the enzyme's behaviour in the brine was carried out, it was difficult to conclude on the source of the observed scale. It is therefore needful that an investigation of solubility of enzymes in relevant fluids be conducted before their EOR applications because this will give an idea of their solubility behaviour in the reservoirs.

3.2. Adsorption

Enzymes have interfacial capacity that enables them to interact with immiscible phases and their application in reservoir system characterised by rock and fluids interactions could alter this natural process. Adsorption of enzyme on the rock surfaces is the major mechanism by it alters wettability of the rock but if its adsorption is too much; it can lead to economic loss [25, 28]. The adsorption process can be physical interaction (physisorption) in which adsorption reduces generally with increase in temperature or chemical interaction (chemisorption) with adsorption increasing with increase in temperature [29]. Adsorption of enzyme on rock surfaces can result from different mechanisms such as: ion exchange, ion pairing through hydrogen bonding, formation of aggregates on the solid surface, dispersive forces via Van der Waal and hydrophobic bonding [30, 31].

Enzyme adsorption is a complex process that is dependent on different characteristics of both the rock and fluid systems such as pH, ionic strength, divalent ions of the aqueous solution, type of rock samples as well as temperature of the system [30, 32, 33]. In addition, enzyme adsorption is concentration dependent; at low concentration, globular protein adsorbs on surfaces with side-on-type configuration

in a perpendicular manner to the surface. However, at high concentration, adsorbed molecules are oriented on the surface in end-to-type configuration with molecules closely packed together or they may undergo surface crystallisation that also results in closely packed arrangement and thereby increasing their adsorption [31]. Some previous studies have investigated enzyme adsorption capacity on different surfaces such as: silica, hematite, carbonate rock of varied grain sizes, negatively and positively charged surfaces etc. [32, 34-37]. It is worth noting that there are limited studies on enzyme adsorption in relation to hydrocarbon production system and the available ones are based on static adsorption tests to the best of our knowledge. Furthermore, all these studies were limited to aqueous enzyme solutions interaction with solid surfaces in the absence of oil. This may however not be a true replicate of what is obtainable in a dynamic rock and fluid system that exist in the hydrocarbon reservoirs. Hence, there is need for more studies on enzyme adsorption in fluids and on rock surfaces relevant hydrocarbon production system.

3.3. Wettability

Wettability describes the preference a solid surface has for a given fluid in the presence another. The reservoir rocks are heterogeneous in nature with diverse mineral composition and each of these minerals may show different preferences for the saturating oil and water in the rock pores thereby making wettability characterisation difficult [38, 39]. The reservoir rock wettability relates oil-rock and water-rock interfacial tensions to oil-water interfacial tension and this strongly impact the relative distribution and flow of oil and brine in the reservoir's pores during production [40-42]. Wettability alteration results from adsorption of polar components of any surface active compounds and/or desorption of organic component from the rock surface [43, 44]. The degree of the alteration is determined by interactions between the oil components, mineral surface of the rock and brine chemistry [45-47]. Wettability alteration is a fundamental factor that influences the behaviours of water flooding, EOR processes, relative permeability, electrical properties, capillary pressure and residual oil saturation [41, 46].

Recent studies [46, 48, 49] have shown that small change in water chemistry generates strong effect on oil displacement in crude-oil-rock-brine system. Wang et al. [50] investigated wettability alteration potential of enzyme based on contact angle changes, imbibition process and work of adhesion. Their results showed that enzyme can alter sandstone wettability from weakly oil-wet to strongly water-wet in short time while it alters limestone wettability slowly. They also reported the potential of enzyme to increase the driving force of water imbibition in water-wet reservoir while decreasing resistance force in oil-wet reservoir drainage process; the enzyme also reduced oil work of adhesion thereby enhancing its desorption from the rock surface.

He and Zhang [51] also carried out quick analysis on enzyme capacity to flush oil in oil-sand-enzyme solution mixtures and they observed oil extraction from the sand surfaces and a clear separation of oil and water mixture.

Khusainova et al. [52] on the other hand investigated wettability alteration potential of enzymes with contact angle and adhesion measurements on calcite surfaces. They observed oil droplet adhesion in most of the enzymes aqueous solutions but absolute non-adhesion was observed with one of them. Also, from their contact angle measurements, a range of $38 \pm 7^\circ$ angles was observed while reduction of approximately 15° in contact angle was observed with application of the same enzyme. This was related to the enzyme capacity to alter the surface wettability. Nasiri et al. [2] also reported that application of enzyme in sandstone rock alters the rock wettability toward more water-wetness.

On the contrary, wettability alteration from weakly oil-wet/neutral-wet to more water-wet condition was hypothesised as one of the possible factors that militated against positive effect of enzyme EOR applications in three of the four wells in carbonate reservoir studied by Jabbar et al. [27]. They however did not carry out any wettability investigations on the reservoir used in their study. Udoh and Vinogradov [53] on the other hand carried out experimental study on wettability alteration potential of an enzyme in a spontaneous imbibition test. Their results showed that the enzyme used has the capacity to modify the carbonate rock surface from strongly oil-wet to less oil-wetness. Also from their zeta potential measurements, they showed how injection of enzyme in low salinity brine into a carbonate rock with initial positively charged rock-brine interface was changed to negatively charged. Thereby, modifying the rock-brine and oil-brine interactions, which was a demonstration of rock surface wettability alteration potential of enzyme. Wang [54] also investigated the wettability alteration potential of enzyme solution on quartz chip. The results of their tests showed that the surface of the quartz chip was modified toward water-wetness as evident by increase and decrease of the hydrophilicity and lipophilicity of the chip surface respectively.

3.4. Interfacial Tension

Studies have shown that some macromolecular compounds possess some properties that could be compatible with two distinct immiscible phases and hence, reduce the natural forces existing at the interface [24, 44]. An understanding of the forces acting at interfaces such as surface tension at liquid-air interface, interfacial tension between liquid-liquid and adsorption/adhesion between liquid-solid play a fundamental role in many processes such as emulsification, solubilisation, enhanced oil recovery etc. There is however no specified method for direct measurement of the number of active interfacial site in a system, they are usually inferred by measurement of interfacial properties such as surface tension and interfacial tension (IFT) [55]. The effect of any surface active compounds on interfacial interaction that takes place at water-air and water-oil interfaces is a function of many factors such as nature of the compound, ion-strength of the aqueous solutions and oil composition [44]. In fluid-fluid interactions, enzyme adsorption at the liquid interface involves its interaction with the two phases thereby resulting to unfolding

of the protein molecules with the hydrophilic part contacting water phase while the hydrophobic parts contact the oil phase [56]. Transport of protein molecules from the bulk of solution to the interface is usually controlled by diffusion. At low concentration, the rate of diffusion is slower than adsorption rate but at higher concentration, the rate of adsorption is dependent on protein-surface interaction.

Interfacial tension reduction is one of mechanisms attributed to effective enzyme EOR process [17]. Wang et al. [50] investigated the IFT reduction potential of enzyme on crude oil-brine system. Their results showed that the enzyme reduces oil-brine IFT as its concentration increases and its optimum concentration was found to be 5-8% at which the lowest IFT of 0.01-0.11 mN/m was observed and beyond which the IFT increases with the increase in enzyme concentration. Wang [54] also reported reduction in IFT with the use of enzyme and the lowest IFT of 0.48 mN/m being obtained with 0.2% concentration. The study also showed that increase in the brine salinity of the enzyme solution resulted in reduction in IFT. Feng et al. [17] also related the observed increased recovery in their study to enzyme emulsification that is related to IFT, even though they did not carry out any direct IFT test in their study. Nasiri et al. [2] on the other hand, investigated the effect enzyme on oil-brine IFT and they observed IFT reduction. They also investigated the effect of varied concentration of enzyme on oil-brine IFT using two crude oils and Sea water, from which they observed IFT reduction with increase in enzyme concentration. IFT reduction from 25 to 7 mN/m with 0.5 wt.% enzyme and 11 to 5 mN/m with 1 wt.% enzyme was observed with two crude oils.

Further study by He and Zhang [51] on enzyme concentration variation effect on IFT of Chaoyanggou oilfield fluids identified 0.5-2% concentrations as effective concentrations at which lowest IFT of 0.201-0.252 mN/m were attained. Also from the recent study carried out by Rahayyem et al. [4], IFT reduction was observed with increase in enzyme concentration. The use of 0.1-3 wt% concentrations resulted in IFT reduction from about 6.5 mN/m to close to 0 mN/m and optimum concentration was identified as 1.5 wt.%. They also investigated the effect of increasing NaCl concentrations on IFT modification using fixed concentration of enzyme (1.5 wt.%) and they observed no clear trend with increase in brine salinity. Udoh and Vinogradov [53] also reported IFT reduction capacity of an enzyme in different brines and they also observed IFT reduction with increase in enzyme concentrations. The IFT reduction also increases with increase in brine salinity, which was similar to the result of the study by Wang [54].

3.5. Emulsification

Emulsion system is defined by three regions: disperse phase, continuous phase and interfacial layer consisting of emulsifier and/or stabiliser such as amphiphatic molecules like enzymes [57]. The amphiphilic nature of any surface active compounds enables them to partition preferentially at interface of oil-water at varied degrees resulting to emulsification of oil in

water or water in oil as the case may be [58]. Water-in-oil and oil-in-water emulsions are commonly encountered in oil production and emulsification has been identified as one of the mechanisms by which enzyme mobilises residual oil saturation during EOR processes [2, 59, 60]. Stable emulsion is of utmost importance for efficient application. A stable emulsion can be described as a process whereby normal occurrence of separation is slow down over a period of time and stability of emulsion is dependent on the properties of the surface active compound or emulsifier in the system [61].

In oil-water medium, enzyme stabilised emulsion or micro-emulsion by first contacting oil-water interface through their hydrophilic part and then unfold to expose the hydrophobic part to the oil phase [10]. The adsorption of enzyme to the oil surface is spontaneous and after adsorption, the molecules undergo structural rearrangement. The initial adsorption of enzyme can be due to diffusion while subsequent adsorption could result from hydrophobic interactions between the hydrophobic sides of enzyme and the oil phase [10]. Al-Wahaibi et al. [62] investigated emulsion activity of two aqueous lipopeptide with different liquid hydrocarbons, that includes heavy and light crude oil. From which they observed varied responses but emulsion index obtained for crude oil was between 50-55% with one of them not being able to emulsify heavy crude oil.

Herrero et al. [57] on the other hand used infrared spectroscopic analysis to study the structural features and interactions of oil-in-water emulsions stabilised with protein. They noted that when protein works as emulsifier in oil-in-water emulsion, it adsorbs at the interface between the dispersed oil droplets and continuous water phase and then undergo unfolding and restructuring to form a stabilising layer at the droplet surface. In most of the studies carried out on protein/enzyme emulsion activity, the effect of salinity that may impede this process in real applications is often neglected. Though in the recent work by Udoh et al. [3], investigation of the emulsification activity of enzyme in brines of different salinity was carried out. Their results showed that the enzyme has emulsion index above 50% in all the brines and the emulsification activity the enzyme was monotonic with time. This was said to be an indication of the enzyme capacity to aggregate and mobilise dispersed oil phase in continuous water phase during displacement process. The ability of enzyme to generate and stabilise emulsion is really needful in oil production especially at residual oil saturation, when dispersed oil droplets are trapped in continuous water phase in the reservoir pores.

3.6. Stability

Enzyme stability is the process that describes its capacity to maintain its required activities in a given situation and over a required period of time. For enzyme to be relevant and useful for EOR processes, there is need for it to be stable within a wide range of pH, high temperatures and high salinity conditions that are prevalent in the hydrocarbon reservoirs. Studies on effects of the system salinity, temperature and pH on enzyme stability were reviewed and presented in this

section.

3.6.1. Salinity Effect

Ionic strength of aqueous solutions affects solubility of any surface active compounds by altering their potential and thereby causing either salting-in or salting-out effects. Salting-in describes the process whereby solubility of these surface active compounds is increased within certain salinity range while the salting-out describes their precipitation at relatively high salinity [10, 44]. Also, the presence of salts in enzyme aqueous solutions can lead to attraction between water molecules and dissociated salt ions which will invariably reduce the number of water molecules available for their hydrophilic group interactions. This disrupted hydrated structure can result in increased hydrophobic interaction between their hydrophobic groups, thereby promoting attraction between their aggregated molecules and hence, reduction in the surface tension [63]. This hydrophobic interaction is the fundamental mechanism by which protein, nonionic and zwitterionic surface active compounds respond to electrolyte [10].

In the previous study by Feng et al. [17], the adaptability of 8% modified enzyme in brines of different salt compositions and salinities was investigated. Their results showed that enzyme performance was improved in NaCl solutions of 0.5-10% concentration range but 0.5-1% concentrations were identified as the optimal concentrations. For CaCl₂ solution, the performance lays between 0.05-1.0 g/L and the optimal concentration range of 0.05-0.4 g/L were observed, but in MgCl₂ solution, the performance range and optimum concentrations were defined as 0.05-0.4 g/L and below 0.2 g/L respectively. Also, the recent study by Udoh and Vinogradov [26] used surface tension measurements to monitor the surface activity of an enzyme in brines of different compositions and concentrations. Their results showed that the surface activity of the enzyme was maintained in all brines and temperatures investigated. The enzyme however showed some instabilities in NaCl solutions but its stability was enhanced in 3 molarity brine. This was taken to be an indication of the suitability of this enzyme application in EOR processes characterised by high salinity formation brine.

This was further buttressed by the studies carried out by Ott et al. [6] and He and Zhang [51] in which enzyme EOR applications were implemented with the formation brine of their respective reservoir. This further showed the capacity of enzymes to withstand high salinity and their efficiency in such salinity medium. Also in the enzyme EOR study carried out by Jabbar et al [27] on four carbonate wells with salinity range of 222,000 - 247,300 ppm, they observed no difference in the behavior of the wells before and after its applications, which suggest its stability in that reservoir system.

3.6.2. Temperature Effect

The effect of temperature on aqueous and interfacial behaviour of enzymes is dependent on the thermodynamics process that is specific to each system. An increase in system temperature can lead to an increase in the mobility of the surface molecules and total entropy of the surface hence,

reduction in the system free energy. Solubilisation also increases with an increase in temperature due to increased dehydration. Intermolecular interactions between protein molecules is based on hydrophobic interaction and this usually lead to protein insolubility, while protein-water interaction is based on the polar and charged amino acid which invariably increase protein solubility in water [10].

Previous studies have reported different effects of temperature on enzyme adsorption such as increased adsorption [64, 65], decreased adsorption [66-68], both effects [69] and no effect [70]. However, common to all enzymes is a peculiar denaturation temperature above which their molecules get denatured [10, 56]. Proteins are said to be denatured when they lose their characteristic properties such as solubility, surface activity and enzyme activity and their solubility decreases when completely denatured. At constant pH and ionic strength, solubilisation of most proteins increases with increase in temperature [10]. Proteins however usually have temperature ranges at which they undergo maximum activity above which they are denatured. Increase in temperature has been identified as the fundamental factor that causes protein denaturation due to destabilisation of intermolecular and intramolecular bonding in protein structure [10]. Norde and Kylema [64] however observed that temperature effect on protein adsorption depend on pH. They noticed that the effect of temperature on protein adsorption is minimal around the isoelectric point of protein but further from the isoelectric point, an increase in temperature resulted to steeper initial part of adsorption isotherm and a lower plateau value.

The effect of temperature on emulsification process of 8% modified enzyme over a temperature range of 30-110°C was investigated by Feng et al. [17]. From which they identified temperature range of 30-60°C as the preferential temperatures for its better performance while 100°C temperature was associated with carbohydrate coking. Furthermore, from the study on effect of temperature on adsorption of an enzyme carried out by Udoh [37], reduction in enzyme adsorption was observed with increase in temperature. Also, from the study on effect of temperature on EOR process of enzyme in carbonate rock conducted by Udoh and Vinogradov [5], they observed that increase in temperature generally enhanced the recovery process with or without enzyme addition due to reduction in oil viscosity. However, from their flooding effluent analyses, they observed that increase in temperature modified the dynamic crude-oil-rock-brine interactions in enzyme-low salinity brine flooding process. While no significant effect of change in temperature was observed with high salinity flooding.

3.6.3. Solution pH Effect

Similar to the temperature effect, enzyme usually have pH range in which their activity is maximized and beyond which their activity decreases, the optimal pH range for most enzymes varies from 6 to 8 [7]. Change in pH can lead to alteration of the ionization of the active site on enzyme and the substrate thereby modifying the rate of binding of substrate to

the active site [8]. At reservoir condition, the pH of the formation water is said to be about 5 due to the presence of acidic gases and under this condition, the rock surfaces of most sandstones are negatively charged while that of carbonates are positively charged [71, 72]. Increase in pH of aqueous solution in a porous reservoir rock will make the surfaces of sandstone and carbonate rocks to become more negatively and positively charged respectively, while decrease in pH will generate the reverse effects on both rocks. Hence, interactions of enzyme with the reservoir rock and fluids may modify its performance.

However, most of the studies that investigated the effect of system pH on enzyme performance observed little or no effect. For example, Udoh and Vinogradov [26] investigated the aqueous behaviour of an enzyme in brines of different pH based on their composition and they observed stable behaviour of enzyme in all brines. Jabbar et al. [27] also monitored the pH of the system during their enzyme EOR applications in four carbonate reservoir wells and they observed slight reduction in pH of two wells (wells 1 and 2), while no pH change was observed with the other two wells (wells 3 and 4). Furthermore, Udoh and Vinogradov [5] also monitored the pH of all the effluents from their carbonate core flooding and they observed distinct pH trend at low temperature. However, at high temperature, all the effluents pH had similar range that plateaued at around 7.8. This signifies that enzyme injection in carbonate rock can influence the pH of the system but this can be modified by the buffering effect of the rock at elevated temperature. Further studies are however required for better understanding of the process.

4. Oil production and Enhanced Oil Recovery

Conventionally, EOR processes are usually implemented after secondary recovery but recent studies have showed that they are applicable at any production stage and different EOR methods exist [35]. Recently, there have been increased studies on EOR potential of enzymes due to their biodegradability, renewable sources, eco-friendly nature and adaptability to high temperature and salinity. The review of some of the previous studies on enzymes EOR applications are presented in this section and the summaries of these studies are presented in Table 1.

4.1. Laboratory Experiments on Enzyme EOR

Feng et al. [17] reported on the enzyme applications in both laboratory experiments and reservoir field tests. From the results of their core flooding experiments on core samples aged for seven days using 3%, 6% and 10% modified enzyme concentrations, improved recoveries of 12.4-16.3%, 13.9-20% and 15.7-21.1% respectively were observed. They also investigated the EOR potential of modified enzyme in a micro-model displacement process. From which improved oil mobility with the used of modified enzyme was observed and the effective enzyme application was associated with

conversion of oil-wet sections into water-wet and emulsification process. Wang et al. [50] also carried out three core flooding experiments with three enzyme concentrations (1%, 2% and 5%) on three different handmade cemented rock samples. They recorded 90-95% oil recoveries from the floodings and no significant recovery difference was observed with the use of the three enzyme concentrations, although the highest recovery was achieved with 5% concentration.

The EOR potential of enzyme was also investigated by Nasiri et al. [2] in core flooding and spontaneous imbibition experiments with Berea sandstone and Sea water. Two flooding tests were carried out with 1% enzyme-brine injection in tertiary mode on two separate core samples. An oil recovery of 42% OOIP with 10 pore volume (PV) water injection and increased recovery of 11% with 34 PV injection was made from the first core, while recovery of 47% OOIP with 10 PV water injection and increased recovery of 3.5% with 40 PV injection was recorded from the second core. This variance was related to difference in their wetting conditions based on the observed core behavioral difference. For the first core, they noted that most of the oil was produced before water breakthrough at 0.37 PV while for the second, more oil production was observed after breakthrough at 0.33 PV although most of the oil was produced before breakthrough. Also from the spontaneous imbibition investigations carried out, they observed delay in imbibition of enzyme-brine system in comparison with the untreated brine but the former however showed higher total oil production of 2% OOIP over the untreated brine.

Furthermore, the potential of enzyme EOR has been investigated in low permeability tight formation usually characterised by oil recovery that is less than 10% [73]. In the study of Salahshoor et al. [74], enzyme EOR investigation was conducted on two Berea sandstone and eight Woodford shale outcrops in spontaneous imbibition tests. Oil recovery from enzyme solution imbibition was compared with deionized water imbibition and their results showed that enzyme solution with 10 wt.% concentration recovered 50% and 10-20% oil relative to deionized water in sandstone and shale respectively. They however found 5 wt.% enzyme concentration more effective in shale than 10 wt.% and they also observed no significant difference in the enzyme EOR performance in clay-rich and carbonate-rich rocks used in their study. Also, the potential of enzyme EOR applications in secondary, tertiary and post-tertiary flooding of carbonate core plugs was investigated by Udoh et al. [3]. The results of their study showed that using 1 wt.% enzyme in low salinity injection brine resulted in additional recoveries of 6.28% and 1.86% in tertiary and post-tertiary modes respectively. The highest recovery of 82.76% was however achieved in secondary flooding with enzyme-low salinity brine injection.

Rahayyem et al. [4] also investigated the enzyme EOR process at micro-scale level with the use of polydimethylsiloxane microfluidic devices. The optimal concentration of 1.5 wt.% was adopted based on interfacial tension measurements and a total recovery of 92% OIIP was observed, but when 0.5 wt.% concentration injection was used, 86% recovery was made. The EOR capacity of enzyme was

also investigated by Udoh and Vinogradov [5] in carbonate core flooding experiments carried out at 23 and 70°C. The results of their study showed that that enzyme injection in low salinity brine can improve oil recovery at both temperatures. At low temperature, incremental recoveries of 14.83% and 5.68% were made over continuous high salinity and low salinity water flooding respectively while at high temperature, incremental recoveries of 10.10% and 2.14% respectively were made. The observed improved recovery was attributed to combined effects of IFT reduction and electric double layer expansion. Wang [54] also carried out seven oil displacement experiments with different concentrations (2-8%) of enzyme and incremental recoveries of 3.8-6.8% over water injection were reported.

Furthermore, from the results of the spontaneous imbibition and core flooding tests on enzyme EOR capacity conducted by Udoh and Vinogradov [53], enzyme applications improved oil production in both conditions. They however observed slight discoloration in produced oil during enzyme application and the reason for this observation was not known thereby requiring further investigations. In their core flooding, incremental recoveries of 14.83% and 5.68% over formation brine and controlled salinity brine flooding respectively were obtained with enzyme application in the secondary flooding. The observed improved recovery was attributed to combined effects of wettability alteration, rock dissolution and IFT reduction. From the review of all these studies, it is observed that most of the studies were not detailed and the different experimental procedures adopted makes coherent understanding of the process difficult. Evident however in most these studies is the capacity of enzyme to improve oil production from both sandstone and carbonate rocks.

4.2. Field Scale Implementation of Enzyme EOR

Gray [1] reported on enzyme EOR application in Prue Ranch (Anacacho) Oilfield in Frio County, Texas. 7 v% of enzyme prepared in 2% potassium chloride solution was used for well treatment and improved oil production with a peak of 8.81 bbl./day average monthly production was observed. This was said to be double of the average production of 4.34 bbl./day that was made before treatment. Feng et al. [17] also reported on the enzyme EOR tests conducted on Dagang oilfield, China. In their Dongying group, a daily oil production of 23.4 bbl. with formation pressure decline and plugging of part of the production zone was observed before the enzyme treatment. However, after the treatment, they observed decrease in produced water from 85% to 54% and increased oil recovery of 41.6 bbl. per day. This incremental recovery was associated with unplugging of low permeability layers that opened oil flow paths and reduces water flow. A positive effect of enzyme treatment was also observed with similar treatment carried out on their Baise oilfield. Increment in produced oil from 4.4 bbl./day to 12.4 bbl./day was observed in one of their wells but they however identified wells with water-cut range of 50-90% as most compatibly wells for enzyme application. Jain and Sharma [75] also reported on the outcome of the case study of Mann oil field, Southeast Asia in

which enzyme EOR was implemented. An incremental recovery of 530 barrels of oil was achieved within thirteen months of implementation in their first well, while an incremental recovery of 1636 barrels of oil was attained within nine months of treatment in the second well.

Furthermore, Ott et al. [6] reported the success story of the enzyme applications in two test wells carried out on a mature oil reservoir in Mann Field located in Salin sub-basin of the central basin of Myanmar, Southeast Asia. The wells were treated with 2% enzyme concentration diluted in formation brine and within the first thirteen months of implementation, 530 bbl. incremental oil recovery was attained in the first well while, 1636 barrels of incremental oil was observed in the second well within nine months of implementation. He and Zhang [51] also investigated the potential of enzyme on de-pressurisation modification of ultra-low permeability Daqing Chaoyanggou Oilfield with low water flooding oil recovery. They observed that water absorption capacity of the water wells was strengthened and de-pressurisation stimulation was enhanced with introduction of enzyme in the system. The use of enzyme was also associated with cumulative increased oil recovery of 2208t but increase in ion concentration and salinity of the associated produced water was observed. This was interpreted as an indication of new production section development and oil layer displacement.

The first application of enzyme EOR in carbonate reservoir was reported by Jabbar et al. [27]. This field application was carried out on one of the carbonate reservoirs in the Middle Eastern without any prior laboratory test on rock and fluid compatibility of the process. The results of their pilot tests showed that the application of enzyme EOR poses no risk to flow assurance and the environment. However, an increase in oil production with no significant decrease in the water cut was only observed in one well out of the four wells investigated. They related the increased oil recovery to well stimulation and/or better well stability (less slugging). Following the enzyme application in the first well, improved stability (no slugging) was observed. They believed that the removal of salt and debris from the gas lift orifice valve during the injection enhanced the average producing time of the well, which invariably resulted in higher productivity of the well. In the second well, no incremental oil production was observed and this was hypothesised to the possibility of gas lift orifice blockage and wettability alteration from weakly oil-wet/neutral-wet to more water-wet. Also, no incremental oil was observed from their third and fourth wells. Enzyme efficiency for enzyme EOR from this study was found to be equivalent to 75 bbl incremental oil production per injected barrel of enzyme. Wang [54] also reported on field test that was performed at the GAO I thin reservoir with some tertiary infilling adjustment wells. Before the enzyme treatment, the average liquid production and daily oil production were 12.0t and 2.1t respectively. The well was treated with injection of 0.5 PV enzyme at 0.8% concentration that was preceded by injection of 0.03 PV of water for about three months. After the treatment, the average daily oil production of the well was increased from 2.1t to a peak value of 3.6t and this was

associated with 0.8% decrease in water-cut. They also observed that the average injection pressure of the individual injection well decreased from 12.8 MPa to 12.1 MPa, while their respective injection volume increased by 16 m³.

4.3. Mechanisms of Efficient Enzyme Enhanced Oil Recovery

Different mechanisms have been proposed for the improvement of oil recovery during enzyme EOR applications. The mechanisms identified from the available research works are presented in this section and summaries of the studies on enzyme EOR are presented in Table 1. From the study of Nasiri et al. [2] on enzyme application in Berea sandstone, wettability alteration towards increasing water-wetness and IFT reduction were inferred as the mechanisms underlying effective enzyme application. Jain and Sharma [75] however attributed the successful implementation of enzyme EOR in Mann oilfield to degradation of alkanes with long chain length (C10-C40) and reduction of paraffin content of the oil. Also, from the study of enzyme application in carbonate reservoirs carried out by Jabbar et al [27] in which increased oil recovery was observed in only one of the four wells tested, the increased recovery was attributed to well stimulation effect. They also hypothesised wettability alteration from weakly oil-wet/neutral-wet to more water-wet condition as a possible factor that mitigated against increased oil recovery in other wells. They however did not carry out any wettability investigation on the rock and fluids used in their study. Furthermore, this assertion is contrary to other studies that attributed effective enzyme EOR to wettability alteration toward water-wetness.

Rahayyem et al. [4] however proposed IFT reduction and wettability alteration towards strongly water-wetness as mechanisms for effective enzyme application. This was based on their experimental study on enzyme EOR process at micro-scale level with the use of polydimethylsiloxane microfluidic devices. The proposed mechanism is similar to the suggested mechanisms by Nasiri et al. [2] but it is however contrary to Jabbar et al. [27] hypothesis. Also, from the experimental study carried out by Udoh and Vinogradov [53] on enzyme EOR application in which positive effect of enzyme was observed, the associated mechanisms proposed for the process were wettability alteration toward less oil-wetness that resulted from modification of rock-brine interfacial charge, rock dissolution and IFT reduction. More so, combined effects of IFT reduction and electric double layer expansion were proposed as the underlying mechanisms for effective enzyme EOR by Udoh and Vinogradov [5]. This was based on their study on the EOR potential of an enzyme in fluids and temperature relevant to reservoir. The interfacial reduction is said to promote mixing, while enzyme adsorption and electric double layer expansion enhanced wettability alteration toward less oil-wetness and desorption of oil from the rock surfaces and hence, improved recovery. Also from the study of enzyme EOR conducted by Salahshoor et al. [75] on shale formation, wettability alteration and change in IFT were attributed to the effective enzyme application observed.

5. Challenges and Future Research

Even though a lot of studies have demonstrated the EOR capacity of enzymes, more studies under different conditions relevant to hydrocarbon reservoirs are still required for better understanding of the process. The following are the identified challenges and recommendations for further research studies:

- 1) Although evident in most of the studies on enzymes EOR is their capacity to improve oil production from both sandstone and carbonate rocks. However, most of these studies were not detailed and different experimental procedures were adopted which makes coherent understanding of the process difficult.
- 2) Even though there have been increased studies on enzyme EOR but most of these studies were not carried out with brines relevant to hydrocarbon reservoirs. Which means that the results may not be a true representation of what is obtainable in real reservoir condition. Hence, more studies on enzyme EOR in fluids relevant to hydrocarbon reservoirs are required.
- 3) Enzymes solubility in fluids relevant to hydrocarbon reservoirs is fundamental to their successful EOR applications because their insolubility can lead to pore blockage, which may invariably result in reduction in oil production as opposed the desired increase in oil production. Most of the studies did not investigate enzymes solubility before their EOR applications in the enclosed porous media, which makes it difficult for them to know the effects of the interactions in the system.
- 4) The presence of divalent ions such as Ca^{2+} and Mg^{2+} in brine usually generate reactions from most surface active compounds thereby, resulting in their precipitation in multi-component brines. Most experimental studies have been carried out with monovalent salt solutions, which is not a good representative of the reservoir brines that are multi-component in nature.

- 5) There are limited studies on enzyme adsorption in relation to hydrocarbon production system and the available ones are based on static adsorption tests, which may not be a true replicate of what is obtainable in a dynamic rock and fluid system. There is therefore need for more studies on enzyme adsorption in fluids and on rock surfaces relevant hydrocarbon production system.
- 6) Different mechanisms have been proposed for enzymes EOR. These mechanisms are however debatable and the influencing parameters require further understanding. The interactive behaviour of enzymes in relevant conditions need further studies.
- 7) In order to improve the fundamental understanding of enzyme EOR processes, theoretical and numerical investigations have to be explored.

6. Conclusion

In this review, enzymes application in oil production systems have been discussed. Attention was paid on the physicochemical properties of enzymes, their EOR potentials as well as the possible mechanisms underlying their effective applications in hydrocarbon rocks. Enzyme enhanced oil recovery is an emerging EOR method with possible great potential but it is still in its infancy stage and it will require a lot of studies for its potential to be fully harnessed. Although a number of studies have been carried on enzyme EOR and there is a general concession on its positive effect but most of these studies are not comprehensive enough to give a good understanding of the process. This is evident from the summarised papers above, different mechanisms were proposed by these authors and these were based on different types of experiments and implementation methods. Hence, further studies are required to unravel the potential of enzyme enhance oil recovery process.

Table 1. Summary of previous work on enzyme EOR applications.

S/N	Reservoir type	(%)	K (mD)	Salinity	Application process
1	Limestone	8-19	1-35	247,300 ppm	3-stages injection
	Dolomitic	8-15	0.15	-	3-stages injection
		13-24	0.51	222,000 ppm	3-stages injection
		10-19	135	-	3-stages injection
2	Mann oil field, Myanmar (sandstone)	18	10-250	-	-
3	Berea Sandstone core plugs	21.6-22.27	576-632	36,317 ppm	Core flooding
4	Polydimethylsiloxane (PDMS) microfluidic	-	-	-	microfluidic
5	Manmade cemented plug	14.2-38.6	123.2-1030	2817 mg/l	Core flooding
6	Mann Field, Myanmar (well 1)	24-27	10-250	-	4-day well shut-in
	Mann Field, Myanmar (well 2)	24-27	10-250	-	4-day well shut-in
7	Daqing Chaoyanggou Oilfield	15	$4.2 \times 10^{-3} \mu\text{m}^2$	-	4 types of enzyme used
8	Prue Ranch (Anacacho) Oilfield, Hitzfelder	zero	zero	-	7% enzyme in 2% KCL solution
9	Dagang field	32.3	916	6534 mg/L	huff and puff test with 4days shut in
	Baise oilfield	15-20	30-300	-	huff and puff test
10	Carbonate core plug	26-33	127-132	8.3 mM & 3M	core flooding
11	Carbonate core plug	26-33	127-132	8.3 mM & 3M	core flooding
12	Carbonate core plug	25-33	127-130	8.3 mM & 3M	core flooding
13	GAO I sandstone	-	0.111 m ²	-	2-stages injection
14	Berea sandstone	17.90-18.33	-	-	spontaneous imbibition

S/N	Reservoir type	(%)	K (mD)	Salinity	Application process
	Woodford shale	9.56-13	-	-	spontaneous imbibition

Table 1. Continues.

S/N	Enzyme conc	Injection rate	Additional recovery	Mechanism	Reference
1	-	12 bbl/min	1550 bbl of incremental oil recovery	well stimulation effect	[27]
	-	13 bbl/min	No incremental oil	-	[27]
	-	45 bbl/min	No incremental oil	-	[27]
	-	46 bbl/min	No incremental oil	-	[27]
2	2%	-	4 bopd increased recovery	Degradation of alkanes with long chain length and reduction of paraffin content.	[77]
3	1% and 10%	0.1-0.5 cc/min	3.5-11% OOIP core flooding	wettability alteration	[2]
4	2%	-	6-12% OOIP	IFT reduction	[4]
5	1%, 2%, 5%	-	-	IFT reduction and wettability alteration	[50]
6	2%	-	530 bbl incremental oil in 13 months	-	[6]
	2%	-	1636 bbl incremental oil 9 months	-	[6]
7	0.5-5%	-	cumulative increased oil recovery of 2208t	-	[51]
8	7%	4.2 bbl/min	-	-	[1]
9	8%	-	2409 bbl incremental oil in 60 days	-	[17]
	8%	-	496.4 bbl additional	-	[17]
10	1%	1 ml/min & 3 ml/mn	14.83% & 5.68% incremental recovery	wettability alteration, rock dissolution and IFT reduction	[53]
11	1%	1 ml/min & 3 ml/mn	10.10% & 2.14% incremental recovery @ 70C	wettability alteration, rock dissolution and IFT reduction	[5]
12	1%	1 ml/min & 3 ml/mn	1.86% & 6.28% incremental recovery	IFT reduction and emulsification	[3]
13	1%	-	increase from 2.2t to 3.6t	-	[54]
14	5 & 10 wt. %	-	50%	-	[74]
	6 & 10 wt. %	-	10-20%	-	[74]

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