A Brief Review and Evaluation of Non-Thermal Chemical Flooding for Enhanced Oil Recovery

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ABSTRACT Non-thermal chemical flooding is unique to conventional enhanced oil recovery of using water flooding. This paper investigated non-thermal chemical flooding based on some basic characteristics and theoretical understandings derived from non-thermal chemical EOR methods. Fundamental interfacial tension properties, capillary effects, adsorption behaviors, and the types of non-thermal chemicals such as alkaline, surfactant, and polymers involved in the current enhanced oil recovery techniques.

KEYWORDS: Non-thermal chemical flooding; alkaline-surfactant-polymer; critical capillary number; active oil under reservoir condition; surfactant adsorption loss
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Review Article

INTRODUCTION

This paper presents non-thermal chemical EOR exclusively including critical number(s) of the second critical capillary number effects versus saturation curve that describing the real-time characteristics in low permeability reservoirs. Effects of low and high salinity flooding involved water ion composition, high-pressure alkaline-surfactant flooding behaviors for wettability alteration in reservoir rocks, dilute surfactants wettability alteration in sandstone and carbonate rocks and ASP flooding of active oil in reservoir environment have been involved. Consideration has been taken for the description of the review of the different types of Enhanced oil recovery (EOR) methods from primary, secondary to tertiary enhanced oil recoveries have also been touched. The more advanced stage works today are the tertiary EOR methods that involve more and more complicated oil recovery from thermal to non-thermal chemical injection methods comprise of different types of chemicals' application. In modern times more environmentally friendly greener chemicals are required and being developed to cope with. Reservoir rocks, porosity, permeability, the adsorption ability of oiled rocks, and related criticalities involve a critical number, viscosity, and in terms of the second capillary critical curve have been considered thoroughly. Various reservoir types including sandstone and carbonates and different types of non-thermal chemical flooding of alkali-surfactant (AS), surfactant-polymer (SP), and alkali-surfactant-polymer (ASP) have been described.

METHODS OF OIL RECOVERY

Thermal Enhanced Oil Recovery

After primary and secondary oil recovery by oil gushing by reservoir pressure and later stage by water flooding the residual oil will reach a stage called mature reservoirs. At this stage, the oil extraction by normal method became ineffective due to the heavier oil density and viscosity, and inertia. Petroleum Engineers devised several ways to continue the oil extraction. In this context, two major types of thermal enhancement have been carried out in matured oil reservoirs onshore and offshore alike. Hot water injection or flooding and combustion have been taken to reduce the viscosity of the heavier and heavy oil remaining in these matured oil reservoirs which still contain roughly 50-60% residual oils.

Non-thermal Chemical Oil Recovery

In a later stage of thermal oil recovery since the 1960s better extraction methods have been launched to increase residual oil production further. Chemical oil recovery has become a popular method to this date. Non-thermal chemical oil recovery involves alkaline, surfactant, and polymer flooding in matured oil reservoirs. For high salinity, alkaline-surfactant flooding high-pressure drop happens and creates high viscosity emulsion effects that improved enhanced oil production at this tertiary stage. When the alkaline-surfactant flooding process reaches to certain alkaline-surfactant mixing concentration the effect of microemulsion happens, Interfacial tension will reach the lowest level. This ensures smooth flow of the inject alkaline-surfactant fluids into reservoir rocks to disperse residual oil that is the target to be recovered. The capillary effect of the interfacial tension control part thus forms an important role in the control of interfacial tension in the whole non-thermal chemical flooding process.

Second Critical Capillary Curve

Protocorm Researchers Li *et al*. (2019) considered and reported a second critical capillary effect that affects the completion of non-thermal chemical flooding process in reservoirs enhanced oil recovery (EOR). Discussion of dynamic contact angle and multiphase flow in low permeability reservoirs have been carried out. Large dynamic contact angle resulted from high capillary number indicating that it may not be favorable and noted that the value of capillary number could influence low permeability reservoir's non-thermal chemical flooding. If reservoir rock becomes water-wet or oil-wet both were not good for oil driving and due to this insufficiency, the pores of reservoir rocks may pre-maturely saturate again. Therefore, a second capillary effect in terms of the second critical capillary effect has been proposed. The second critical capillary number may achieve the lowest residual oil saturation and enhance the highest oil recovery (Figure 1).

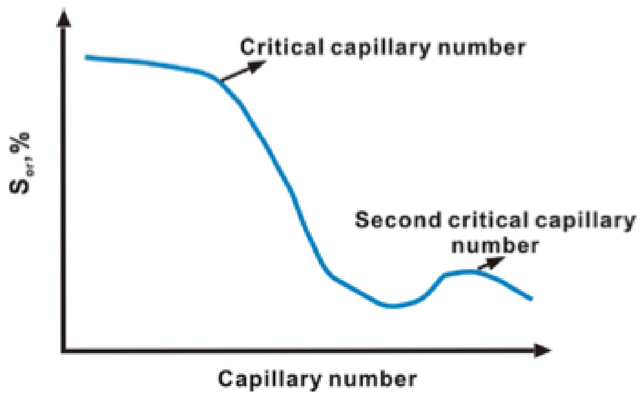

Figure 1. Second critical capillary effect de-saturation curve (Li *et al*., 2019).

Samanta *et al*. (2012) discussed interfacial tension, and Liu *et al*. (2010) has also studied phase behavior, adsorption isotherm in the alkali-surfactant-polymer flooding experiment. The effects of temperature on surface adsorption are essential elements in oil purging from the oil reservoir, researchers have indicated that increased temperature has led to a decrease in adsorption of surfactant due to an increase in kinetic effects.

Karambeigi *et al*. (2016) discussed the phase behavior of microemulsion flooding using brine, surfactant-biodiesel-co-solvent. The response surface methodology was applied to achieve optimum microemulsion formulation. Both spontaneous imbibition onto carbonate cores with synthetic seawater and optimum microemulsion versus oil recovered rate/curve were successfully performed and plotted (Figure 2). Another oil recovery plot of the core-flooding experiment at reservoir temperature conditions was also produced (Figure 3).

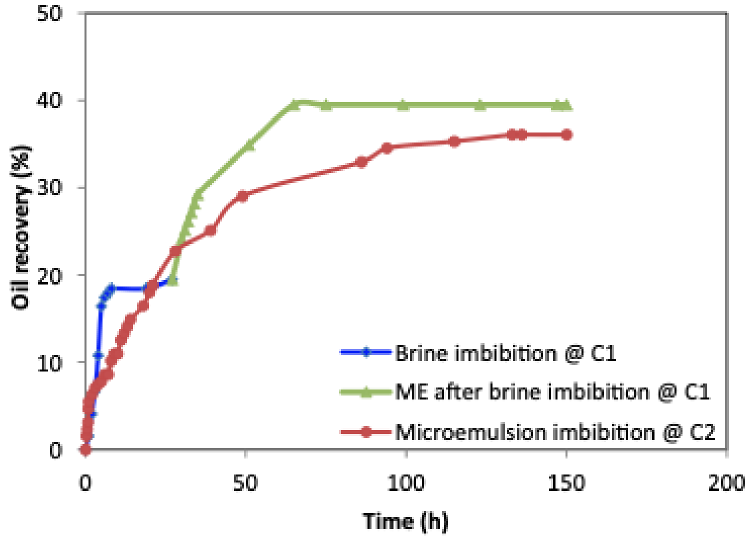

Figure 2. Spontaneous imbibitions of carbonate test core with synthetic marine water versus optimum microemulsion (Karambeigi *et al.*, 2016).

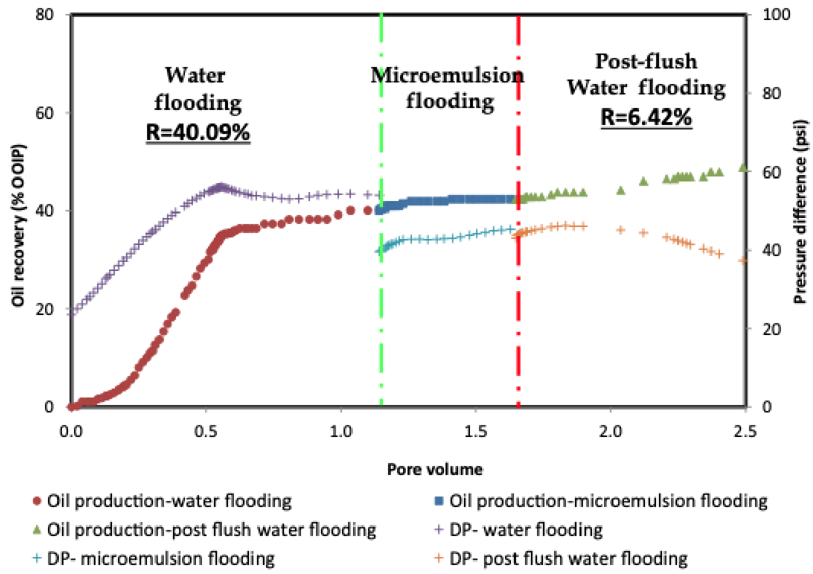

Figure 3. Recovery plot of core-flooding with pressure versus pore volume (Karambeigi *et al.*, 2016).

Anjirwala *et al*. (2017) compared NaCl and $CaCl_2$ potential in EOR. The reduction of salinity of seawater salinity is an important issue. Low salinity waterflooding has a contributing role in alteration in the sandstone environment. Samanta *et al*. (2012), Sun *et al*. (2020) and Guo (2017) have discussed the mechanism of ASP flooding. These researchers considered that there has been more effective ASP flooding for oil with high acid content. Sun *et al*. (2020) have presented their studies results on two large-scale ASP flooding injections with good production performance recently.

Shen *et al*. (2009) noted that ASP flooding displaced residual oil in high-permeability formation rocks more easily. The remaining residual oil in the more difficult permeability layers by increasing both sweeping volume and dispersing pressure. The current study displayed a good comparison of ASP results with consideration of various data and information obtained with good formulations.

Alkaline, surfactant, and polymer injection-controlled viscosity led to acceptable concentration criteria. Snosy *et al*. (2020) has also studied and described flooding and measurement, wettability indication methods, and recorded with the database. Belhaj *et al*. (2020) reported that the concentration of surfactant affects the flooding process, has great effects on offshore oil recovery, and reduction in surfactant concentration would reduce oil-water IFT. Studies found that surfactant concentration influenced the adsorption of ionic and nonionic surfactants onto oil reservoir rocks.

CHARACTERISTICS OF RESERVOIR ROCKS

Shabib-Asl *et al*. (2014) studied wettability alteration on Berea sandstone reservoir rock in laboratory investigation on the effect of low salinity water ion composition. They have classified wettability tables and materials considered. Ayirala *et al*. (2019) have considered that carbonate reservoirs are more complex than sandstones. Rock wettability characteristics, heterogeneities, and complex pore structures are common difficulties to face by the residual oil extractors. In this environment that the oil was trapped in low to ultralow permeability carbonate reservoirs within high fractured rocks. The fractured carbonate rock subjected to different and/or excessive pressure consists of complex wetting surfaces and contributed more complex capillary effects that will affect the oil-wet or mixed wet surfaces.

In this investigation, surfactants have been used and tested in changed wettability from oil-wet/mixed wet to water wet, laboratory and simulation showed that capillary desaturation and residual oil started to mobilize at capillary numbers above $05\text{x}10^{-2}$ showed that surfactant could increase the capillary number, reducing oil-water interfacial tension and altering contact angle. A report from the North Sea team also revealed that reservoir chalk plugs using anionic surfactant solutions of concentration up to 0.05 wt% low surfactant concentration couldn't reduce interfacial tension and noted that wettability alteration contributed to oil recovery. In another report, it was found that cationic surfactants are better performed and more effective in displacing oil from the test core and anionic surfactants couldn't perform this result.

EXPERIMENT RESULT ON BEREA SANDSTONE RESERVOIRS

Sui *et al*. (2020) have carried out active studies on Berea sandstone core test for alkaline-surfactant-polymer flooding, on matured and depicted oils and resulted in favorable sweep and displacement by increased water viscosity, lower oil-water interfacial tension, change reservoir wettability, and produced in-situ surfactant and interacted with active crude oil. The researchers also reminded that ASP flooding salinity affected oil recovery. Liu *et al*. (2010) simulated ASP non-thermal chemical flooding detailed in Table 1.

Li *et al*. (2000) reported an experimental study on the alkaline-surfactant-polymer flood with nature mixed carboxylate that examined effectiveness ASP flooding, phase behaviors, and interfacial tension are important elements and the obtained very high oil recovery of 25.2% as well as 26.8% OOIP. Zhu *et al*. (2013) described the performance of ASP industrial tests in sandstone reservoirs of Daqing, China that with Surfactant (HABS), Alkali (NaOH) combinations achieved a convincing result of 18.2%-18.6%. The Chinese researchers also mentioned Malaysian Petronas' plan to conduct pilot ASP flooding in Dulang Oil Field and met bottleneck of ASP process in high-temperature, high-salinity reservoir conditions. Hasokowati *et al*. (2020) reported surfactant-polymer chemical EOR flooding behaviors of migrating oil in the porous media at boundary condition and final application of Finite difference method that included all variables and spatial derivatives and their experiment results have been tabulated for two types of Berea sandstone reservoir cores with both of different permeability and porosity and achieved high oil recovery EOR results.

Table 1. ASP Simulation design formulated information (Liu *et al.*, 2010).

Initial Oil Saturation	0.3
Formation Brine	2.0% NaCl
Acid Number of Crude Oil	0.2 mg KOH/g
Injection Na_2CO_3 concentration	1.0%
Injection Salinity	2.0% NaCl
Surfactant Concentration	0.2% (Nl blend)
Surfactant Slug Size	0.5 PV
Injection Polymer Concentration (Flopaam 3330S)	5,000 ppm
Injection Solution Viscosity	40 cp
Crude Oil Viscosity	19.7 cp
Polymer Adsorption	20 µg/g
Surfactant Adsorption	0.2 mg/g
Surfactant Retardation Caused by Adsorption β_1*	0.03
Péclet Number	50, 200, 500
Polymer Retardation Caused by Adsorption β_2*	0.01
Optimum Salinity of Pure Soap	0.5% NaCl
Optimum Salinity of Pure Surfactant	5.0% NaCl
IFT Assumption	Wide low IFT region
NX (Gridblock Number)	100
dt_D/dx_D	0.05

Zulkifli *et al*. (2020) reported new surfactants flooding for high-temperature reservoirs application EOR. They have mentioned that two types of surfactants can be used to lower interfacial tension (IFT) and emulsified oil and water and enhance additional oil dispersion of trapped oil in the oil formation strata. It is found that sulfates surfactants can improve surfactant tolerance to high salinities. Certain surfactants such as oleic sulfonates groups and alkyl benzene sulfonates can maintain their stability in high-temperature environments.

Sofla *et al*. (2016) studied and tested a natural surfactant flooding experiment for EOR application. Salinity level achieved surfactant concentration, rock characteristics. Ziziphus Spina-Christi (ZSC) tree plant leaves derived surfactant has been tested for its superb quality in wettability alteration of different rocks including calcite, dolomite, and sandstone. Comparisons with synthetic surfactants at various surfactant concentrations, brine salinities, contact angle measurement on different rock sample slices also have been taken place and satisfactory results claimed. These researchers live oil microemulsion phase behavior test by the application of high pressure in the laboratory environment.

Insights Into Design of Mobility Control and Chemical Oil Recovery and Role Of Chemical Product Design

Farajzadeh *et al*. (2019) methods of mobility control design for EOR. They involved 10 relative fluid mobility of upstream and downstream shock front, and 2) the viscosity displacing agent selected to maintain the balance between total mobility of shock water saturation balanced the minimum mobility across saturation range. These are based on fractured flow analysis of one-dimensional flow. They contended that the water/oil relative permeability curve is devised as the key role template for the design of mobility control in polymer and surfactant and polymers. Polymer adsorption effects have been thoroughly studied. They also found that in their ASP flooding solutions with ultra-low interfacial tension reduction of Windsor III. The polymer viscosity is required to be greater than oil viscosity at low shear rates and noted that for light oils the viscosity of ASP solution is larger than oil viscosity. In lower ultimate oil recovery, the Polymer slug tested was tested the volume of produced oil is greater than ASP injection.

Druetta *et al*. (2019) discussed chemical oil recovery and the role of chemical product design and noted the increased difficulties of recovering the remaining residual original oil in place (OOIP) in tertiary oil extraction programs world while. Each different oil production of tertiary stage posed challenges of unforeseen risk and as well as economic consequences to tackle. As non-thermal chemicals are favorably considered, the right types of chemicals involved are used that should be environment friendly as the most important elements in the chemical injection flooding of ongoing oil production reservoirs of oil fields. Mechanism of surfactants flooding, surfactant screening methods, and processes, understanding the classification of surfactants types such as anionic, cationic, nonionic, zwitterionic in nature, and the right role they play. The product design also posing challenges for the engineers for the successful design of better chemical formulas for different reservoir conditions.

Dilemma of Current Enhanced Oil Recovery Methods

Farajzadeh *et al*. (2021) have reported the current chemical enhanced oil recovery methods and have described the dilemma of the general public favoring more and cleaner energy in near future. Some chemicals are found to cause damage to reservoir rocks that will endanger earth crust stability, hence more environment greener surfactants are considered, and currently, researches are in good progress.

New surfactant Developments

Lu *et al*. (2014) have discussed three new surfactants namely 1) Guerbet alkoxy sulfates, 2) Guerbet alkoxy carboxylates, and 3) Tristyrylphenol alkoxy sulfate surfactants for flooding injection for some real reservoir environments at different rock types. New surfactant retention correlation that could predict retention at various reservoirs has been considered in their studies. They also have achieved laboratory live oil microemulsion phase behavior tests under the high-pressure application.

According to their report, the Guebert reaction is good for commercial consideration and large hydrophobic surfactants could be produced. Anionic surfactants could be derived by adding PO or EO into Guerbet alcohol and followed by surfactants or carboxylation. Guerbet alkoxy carboxylate surfactants are treated as an alternative to sulfate surfactants for high reservoir temperature and that when alkali is not included. They claimed that these are these new surfactants are used with various cosolvents and cosurfactants for the development of high-performance formulation. These formulas are viable to achieve excellent microemulsion behavior and core flooding of oil composition and a wide range of reservoirs.

Pal *et al*. (2018) have reviewed surfactant-assisted chemical EOR and discussed challenges and its future perspectives. They tabulated a long list of laboratories' chemical EOR for carbonate reservoir rocks by using surfactants, alkaline-surfactants and ASP mixed floodings. They claimed that fractured carbonates long drained by water and gas injection could have high residual oil saturation. The authors also mentioned that finding those economical surfactants and alkalis should be thoroughly studied and considered. The softening of seawater and its application with surfactant injection at reservoir conditions could also contribute to economically chemical EOR.

ADVANTAGE AND LIMITATION OF NON-THERMAL CHEMICAL EOR

Manap *et al*. (2011) evaluated AS injection with a pilot test in Angsi offshore oil field well and a satisfactory result was claimed. Southwick *et al*. (2020) have reported success on their AS, SP, and ASP injection and experiment based on Berea outcrop and Berea sandstone oil field rock of offshore oil fields. Selection of surfactant and polymer types and seawater contribution form essential elements.

Bai *et al*. (2017) have studied fractured carbonate chemical flooding by surfactant injection as sandstones do. Surfactant concentration, molecular weight, temperature tolerance, rock, salinity, and slug size are parameters to consider. Russian oil-bearing limestone turned carbonate has been considered. Reservoir injection fluid was HDPG polymer and test in the in-room laboratory. Air injection, thermal and chemical injection methods have been carried out and found that chemical surfactant-polymer flooding is more promising. This test was done in a simulation that simulated similar to real carbonate reservoir conditions. Belhaj *et al*. (2020) have reviewed the effects of surfactant concentration, salinity, temperature, and pH on surfactant adsorption for chemically enhanced oil recovery in great detail.

Massarweh *et al*. (2020) and others reported the surfactant's properties and natural tendencies to influence water-oil interfacial tension and that on rocks. Their in-depth studies have discussed surfactant characteristics, critical micelle concentration, Hydrophile-lipophile-balance (HLB), microemulsion, and the role of the surfactant in oil recovery. They have tabulated a long list of surfactants in reservoir injection review. Reservoir adsorption into reservoir rocks and the types of surfactant application in chemically enhanced oil recovery is also presented in detailed studies. The researchers also tabulated a detailed list of their studies on the effect of salinity, temperature, and pH on surfactant adsorption. A tabulated field case on surfactant-assisted non-thermal chemical enhanced oil recovery performance in different types of reservoir rocks also has been enclosed in their review. Most importantly the researchers in their roundup also included a tabulated list of current research trends on the use of surfactants in chemically enhanced oil recovery as of 2020.

Song *et al*. (2017) have carried out a laboratory flooding study to simulate offshore oilfields EOR using polymer variable concentrations. Song's team has tabulated an oil recovery in their studies at each stage of the scheme depicting polymer injection, core porosity, and the final oil recovery factors obtained. Negin *et al*. (2017) have reported a detailed coverage of the most used surfactants in chemical EOR. They have reviewed and classified these surfactants as anionic, cationic, nonionic, bio-surfactant, and zwitterionic surfactants. They have also listed the advantages and dominant mechanisms of these different types in their round-up. Zhu *et al*. (2013) reported chemical flooding from stromal carbonates starting from core samples preparation, chemicals, fluid, water ionic composition, IFT between crude oil and ASP. The final tabulated chemical formula and results of oil recovery of water flooding have been presented in their paper submitted.

The advantages of non-thermal chemical flooding have been fully described above. However, there is also some severe limitation on some chemical surfactants that are considered causing damages to reservoir formation rocks.

DISCUSSION

Different types of enhanced oil recovery methods and types of alkaline-surfactant-polymers have been considered and found that each type of surfactant injection flooding produced its merits and demerits. Most importantly, all these oil dispersion non-thermal chemicals must be environmentally friendly. In this context, trends also that a green or natural surfactant derived from plants will be explored to improve further in modern-day EOR.

CONCLUSION

It has been found that non-thermal chemical flooding EOR involve in AS, SP, and ASP mixing with reservoir crude oil are good for dispersion of residual oil still trapped in various types of reservoir formation rocks. Both sandstones and carbonates formation are the most common types of oilfield reservoir formation. In real-time, these rocks can be fractured, highly fractured, and/or single or multiphase/later and of homogeneity in nature. Non-thermal chemical EOR has become the most common of modern matured oil well or reservoir residual oil production today and different tent types of chemicals in the form of alkaline, surfactants, and polymers have been researched produced for the disperse oil from trapped reservoir rocks to this date. The characteristics of different types of reservoir rocks have been studied and known in terms of porosity, permeability, viscosity, interfacial tension, and viscosity reduction to enhance smooth oil flow through different reservoir rocks. It has been found that the second critical capillary number at range experiments of AEC, APG, and nature surfactant injection has changed residual oil saturation and driving, lowest second critical capillary numbers, and optimized oil recoveries have improved non-thermal chemical flooding at low permeability reservoir rocks of sandstones and carbonates environment. ASP experiment result of nature mixed carboxylate examined oil recovered by the process of diffusion, adsorption, and desorption found promising (25.2% and 26.8%) in original oil-in-place (OOIP) oil reservoir formation.

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