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Polymers for Enhanced Oil Recovery Technology

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Abstract

Recently enhance oil recovery (EOR) technology is getting more attention by many countries since energy crises are getting worse and frightened. One of the reasons for this is due to the shortage of current oil resources and difficulties in finding a new oil field. Indonesia is one of the examples, before 2004 Indonesia is a net oil exporting country but after that Indonesia is a net oil importing country. The oil demand in the country is increasing while the oil production capacity is decreasing. In fact, when a new oil reservoir is drilled, the oil amount obtained from it is about 20-40% of the potential and hence there is still 60-80% oil left in the reservoir. Application of EOR technology gives an additional chance to get out more oil from the reservoir, possibly about another 20%. Polymer is the material that plays an important role in the application of EOR technology, especially surfactant and hydrogel polymers. In the technology, surfactant polymer is injected to the reservoir to reduce an interfacial tension between oil and water and is able to wipe out the trapped oil from the reservoir rock and hence increase the oil production. While an injection of hydrogel polymer to the reservoir is to increase a viscosity of fluid containing water so that the fluid is more difficult to flow than the oil, and as a result, the oil production increases. The most common polymer used for this application is polyacrylamide group.

Keywords : EOR; hydrogel; polyacrylamide; acrylic acid; superabsorbent; SAPc.

1. Introduction

Recently enhance oil recovery (EOR) technology is getting more attention by many countries since energy crises are getting worse and frightened. This is also undergone by Indonesia. Before 2004 [1], Indonesia is a net oil exporting country but after that it becomes a net oil importing country. In fact, when a new oil reservoir is drilled, the oil amount obtained from it is about 20-40% of the potential, and hence there is still 60-80% oil left in the reservoir. Application of EOR technology gives an additional chance to

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get out more oil from the reservoir, possibly about another 5-30%. Generally, EOR technology is urgently required especially due to several reasons, i.e. declining oil production since 1995, non-productive primary and secondary recovery, high crude oil price, increasing energy demand, approximately 1.5% per year [2], and significant oil remaining after secondary recovery (~60% of original oil in place, OOIP).

Water flood is commonly used as an economic and effective method in secondary recovery after primary methods have been exhausted. Many of sandstone or carbonate reservoirs have low primary and water flood recovery due to a poor sweep efficiency as the result of bypassed or unswept oil. In general, water flood still leaves 50-70% oil in the formation and it cannot be further removed without the use of chemical, thermal or gas injection processes [2].

Chemical injection or usually known as chemical flooding was, up to 2000's, less common EOR method than thermal and gas but now, huge projects are initiated or revisited. This involves injection of three kinds of chemicals that are alkaline, surfactant and polymer. Each chemical has unique functions and usually isused coincide. Three methods involving these chemicals are polymer, surfactant-polymer (SP) and alkaline-surfactant-polymer flooding (ASP), and surely the most important substance in these methods is polymer.

Polymer flooding is a very mature method with more than 40 years of applications. It has been shown to be effective in recovering unswept oil by improving the mobility ratio. Many examples of technically successful polymer field projects are reported in some literatures. Field practice has shown that polymer flooding can increase recovery of 5-30% of OOIP [3]. The total cost of polymer flooding is actually less than for water flooding due to decreased water production and increased oil production. The efficiency of the process is in the range of 0.7 to 1.75 lb of polymer per bbl of incremental oil production [3].

2. Polymer for Enhanced Oil Recovery

2.1. Principle and mechanism

Polymer is the material that plays an important role in the application of EOR technology, especially for hydrogel polymer. A typical polymer flood project involves mixing and injecting polymer over an extended period of time until about 1/3-1/2 of the reservoir pore volume has been injected. This polymer "slug" is then followed by continued long-term water flooding to drive the polymer slug and the oil bank in front of it toward the production wells. Polymer is injected continuously over a period of years to reach the desired pore volume. When water is injected into a reservoir, it seeks the path of least resistance (usually the layers of highest permeability) to the lower pressure region of the offset producing wells. If the oil in place has a higher viscosity than the injected water, the water will finger through this oil and result in a low sweep efficiency, or bypassed oil. One of the routine screening parameters used for a preliminary analysis of a reservoir is the mobility ratio that represents effects of relative permeability and viscosity of water and oil on fractional flow based on Darcy's Law as below:

$$f_0 = \frac{1}{1+M} = \frac{1}{1+\mu_0 k_w / \mu_w k_0} \quad (1)$$

Addition of polymer into reservoir increases the viscosity of water and reduces relative permeability of water in the reservoir then increases oil recovery due to increase of fractional flow. If the mobility ratio is one or slightly less, the displacement of the oil by the water will be efficient and pistons like [4]. By contrast, if the mobility ratio is greater than one, the more mobile water will finger through the oil and leave behind regions of unswept oil. Based on the principle of mobility ratio, water-soluble polymer can be used to increase the viscosity of the water phase while reducing the permeability of water to the porous rock and thereby creating a more efficient and uniform front to displace oil from the reservoir [5,14].The effect can be obtained at various reservoir conditions with mobile oil saturation is greater than zero. However, significant effect is only obtained at reservoir with a great value of k_o which means a high mobile oil saturation, meanwhile from the oil characteristic aspect, the value will be significant at light oil reservoir so its viscosity is low and its permeability is great.

Ideal properties for mobility control agents can be summarized as follow [6] low cost or high cost-effectiveness, allow high injectivity, effective when mixed with reservoir brines (up to 20% total dissolved solids),resistant to mechanical degradation (up to 1000 $m^3/m^2/d$ flux when entering porous rock), 5 to 10 years stability at reservoir temperature (up to 200 °C), resistant to microbial degradation, low retention (e.g., adsorption) in porous rock, effective in presence of oil or gas, and not sensitive to O_2, H_2S, pH or oilfield chemicals.

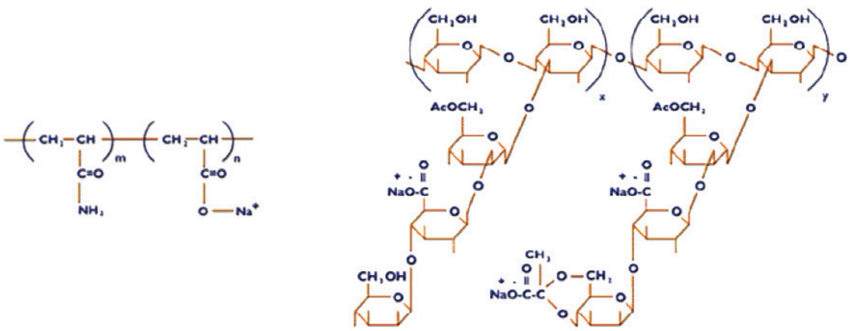
2.2. Recently used polymer

Hydrogel polymers to control the mobility of injected water have been used for many years in EOR applications. These polymers are non-Newtonian (also called pseudoplastic) fluids, because their viscosity is a function of shear rate. They are usually used with surfactants and alkali agents for increasing the sweep efficiency of these tertiary recovery floods. Various research activities have been developing many types of polymers for use in EOR for more than 20 years. Recent inventions that succeed to accommodate the wide variety of conditions encountered in oil fields throughout the world include the following:

Polyacrylamides. A synthetic polymer almost always means polyacrylamides. A variety of these are available from several manufactures. In general, performances of a polyacrylamide will depend on its molecular weight and its degree of hydrolysis [7]. Partially hydrolyzed polyacrylamide (HPAM) is one of the polyacrylamide group, has the shape of straight chain polymer of acrylamide monomers which some of it has been hydrolyzed. The molecule is a flexible chain structure known as a random coil and since it is a polyelectrolyte, it will interact with ions in solution. The structure of polyacrylamide is shown in Figure 1a.

HPAM is the most often used polymer in EOR applications especially because of its relatively low price with good viscosifying properties, and well-known phsycochemical characteristics. The implementation of HPAM is relatively easy and can improve significantly the oil recovery rate under standard reservoir conditions. This polymer is available in various molecular weights up to 30 millions and can be used for temperatures up to 99 °C depending on brine hardness. Meanwhilemodified type such as HPAMAMPS co-polymers and sulphonated polyacrylamide can be used up to 104 and 120 °C. It is produced generally as free flowing powders or as self-inverting emulsions. Some experiences reported that it shows high sensitivity of salinity, presence of oil or surfactant and other chemicals. Precipitation can occur if Ca^{2+} or Mg^{2+} is present in the water.

Xanthan Gum/Biopolymer. Xanthan gum is a polysaccharide or usually called as biopolymer. Its structure is shown in Figure 1b. It is produced by the microbial action of *Xanthomonascampestris* on a substrate of carbohydrate media, with a protein supplement and an inorganic source of nitrogen. The biopolymer is an extracellular slime, which forms on the surface of the cells. The fermented broth is pasteurized to kill the microbes and precipitated from the broth by alcohol, then concentrated. Xanthan gum is well known to have excellent performance in high salinity brine. It is relatively compatible with most surfactants and other injection fluid additives used in tertiary oil recovery formulations.



(a) (b)

Fig. 1. Structure of (a) polyacrylamide (left); (b) xanthan gum (right)

This type usually produced as broth and concentrate form that can be easily diluted to working concentrations without elaborate shear-mixing equipment. The important things are both the forms must be a highly pseudo plastic solutions and are easily pumped. Some experiences reported that xanthan type polymer usually has cellular debris that can cause plugging. Besides, it has significant hydrolytic degradation above 70 °C [5], otherwise some companies tell that now special manufacturing techniques can impart its thermal stability up to 105 °C. Because come from microbial activity, this polymer is usually injected coincide with effective biocide to prevent microbial degradation.

2.3. Needs of new advanced polymer

Many unprofitable projects were the result of inadequate reservoir description or problems with the polymer system being used. In recent years the polymer flooding technology has been field tested extensively and can be classified as proven technology. However, there are limitations with the existing polymer technology such as degradation (thermal, physical, bacterial, and chemical) or polymer rheological. HPAM as the most common used polymer recently also suffers from strict temperature and salinity limitations.

It is important to select the proper polymer for a particular field. Reservoir permeability and oil viscosity are used to determine the optimum molecular weight polymer. Rock composition and polymer adsorption level are used to determine the best anionicity (degree of hydrolysis). The core is originally saturated with 3 wt% NaCl brine and especially in Indonesia the most common reservoir temperature in Indonesia is 160 to 200 °C [5,15]. New generation of polymer has to tolerate high salinity and temperature so there is no practical limit for high salinity reservoir.

2.4. Superabsorbent polymer composite (SAPc) as polymer for EOR

Superabsorbent polymer composites are three-dimensionally crosslinked hydrophilic polymers, reinforced by clay and capable of swelling and retaining possibly huge volumes of water in swollen state [8]. The experiences of using SAPc as plugging agent were conducted in some oilfields in China to meet the need of enhanced oil recovery [9]. After long year operation of water flooding, the water content in crude oil increased which actually decreased the oil output. The higher water content in the crude oil may cause many problems such as increased corrosion, sand production, emulsion formation and disposal, etc. It is an urgent need to reduce the water content in the crude oil. One of the methods to reduce the water content is to adjust the oil-pay in the oil-producing well**.**

As explained earlier that HPAM currently used as polymers for EOR has some drawbacks, especially from their sensitivity to salinity and high temperatures. In his research, Syuhada [10] reported that SAPc as bentonite infiltrated polymer has a greater resistance to mechanical and thermal. In addition, the infiltration of bentonite also makes SAPc less sensitive to other chemicals, particularly surfactants and other minerals contained in water in the reservoir. In research on potato-starch-based SAPc, Li *et al.* [8,11] and Abidin *et al.* [12,13] also reported that SAPc has the ability to absorb high saline water, although its capacity is far below the absorption of fresh water. This suggests that SAPc is absolutely resistant to salinity. These peculiarities are what make SAPc potential for use in the process of flooding.

Swelling mechanism with a huge increase in volume and high absorption capacity in SAPc also theoretically can increase the thickness of the polymer layer attached to the inner wall of the pore of reservoir rock so it would be smaller or even completely covered by a polymer that has been inflated. This clearly will help to enhance oil recovery because the fraction of oil trapped in porous rock becomes much less.

Based on the results of the researches can be concluded that SAPc shows a good mechanical, thermal and rheological properties as compared to the existing polymer. But further advanced study should be done to test the properness as polymer for EOR.

3. Conclusion

There is a big hope that polymer can play an important role in increasing production of oil well to bring out all of us from the current energy crisis since applications of polymer flooding in the enhanced oil recovery (EOR) field has shown some successes to recover more than 20% additional oil from OOIP. HPAM is one of the most common polymers used in the EOR so far, although its properties suffer sharply due to oil salinity and high temperature (more than 70 °C). Superabsorbent polymer composites (SAPc) give a light in overcoming this problem. SAPc has capability of swelling and retaining possibly huge volumes of water in swollen state and its stability in temperature and salinity can be improved such as by copolymerization and reinforcement.

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