Application of Biopolymer in Enhanced Oil Recovery – A Review

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Abstract

The utilization of biopolymer synthesized from organic waste in the processing industry is one of the best waste management techniques. Nevertheless, synthetic polymers are used in enhanced oil and gas recovery, in order to mobilize the trapped oil and gas saturation from the subsurface porous reservoir formations. The injected polymer concentrated saline water is expected to improve the water saturation viscosity, whereby, mobility of the hydrocarbon saturation is enhanced. The costs of the synthetic polymer conventionally used are very high, which attracts biopolymer as the economically best option. However, the chemical characteristics and compatibility of the synthesized biopolymer impose a challenge considering the High Pressure and High Temperature (HPHT) conditions that prevail in the oil and gas reservoirs. The proposed article aims to comprehensively articulate the recent developments and complexities associated with industrial-scale synthesis and injection of biopolymer into oil and gas reservoir formations.

Keywords:

Chitin; Chitosan; Biopolymers; Synthesis and compatibility study; Enhanced Oil Recovery.

1. INTRODUCTION

Rock oil is a Petroleum, which is originated from Latin words petra (rock) and oleum (oil) [1]. It is a mixture of naturally occurring hydrocarbon which may exist in different states depending upon the temperature and pressure conditions. It is generated by the decomposition of burial organism in source rock and then it is migrated to reservoir rock [2]. The role of petroleum industry is to explore and exploit oil from the reservoir. Primary and secondary recovery procedures such as water-flooding and reinjection of produced natural gas can only produce one-third of the original oil in place (OOIP) [3, 4]. However, production can be expanded to 40 to 60% of oil in reservoir by applying the tertiary recovery which is commonly known as Enhanced Oil Recovery (EOR) [5, 6].

In recent years, oil productions are coming from aging fields, the world today, is observing the declination in the rate of oil production from producing regions. Thus, the petroleum industry is facing many difficulties in oil production and conventional techniques may not be able to fulfill the demand of oil [7]. In the years to come, it will be hard to meet this growing demand for oil. Thus, it imparts a big challenge for efficient hydrocarbon recovery. The recovery of oil from reservoirs is a major concern for oil companies and authorities [8].

Enhanced Oil Recovery (EOR) generally refers to higher oil production than that can be obtained through the conventional methods which are normally based on natural pressure differences between reservoir and surface. The purpose of EOR processes is to obtain the recovery of residual oil (i.e. to reduce residual oil saturation) after primary and secondary recovery have been done up to their respective economic limits. EOR is approached to thermal and non-thermal recovery methods.

1.1 Thermal Approach

This method involves the reduction of oil viscosity and thermal expansion by applying the thermal energy and thus, improves the oil mobility. Thermal energy can be supplied by cyclic steam stimulation (CSS), steam flooding, in-situ combustion (ISC), steam-assisted gravity drainage

(SAGD), etc. [9]. Conduction and convection modes of heat transfer are involved in heating the reservoir fluids [10]. In case of reservoir having thin pay-zones, the large amount of heat is lost to the adjacent layers, thus large amounts of heating media (hot water or steam) are required to be injected [11]. The significant decrease in steam rate causes oil cooling, i.e. raises viscosity which in turn decreases oil mobility. Thus, this method can produce only up to the point where the steam rate decreases significantly [12]. Reservoirs at high depth and having thin pay-zones cannot be produced only by applying thermal energy.

1.2 Non-Thermal Approach

Gas injection, chemical injection, microbial injection, nanoparticles, polymer etc. are the different approaches of oil recovery.

1.2.1 Gas Injection

It enhances oil recovery by lowering the interfacial tension between the oil and the fluid that is displacing it. Miscible gas such as Methane, Ethane, Propane, Carbon dioxide, Nitrogen, etc. can be injected depending upon the reservoir conditions [13]. This process is ineffective for heterogeneous formations. Gases provide poor vertical sweep due to very less densities. For the reservoir having pressure less than minimum miscibility pressure of the injected gas, this method cannot be applied. A considerable drawback of miscible gas injection is that produces excess gas [14].

1.2.2 Water Alternating Gas

In this process water and gases are injected alternatively to increase the oil's mobility. As liquid and gas both are involved in this operation, the complexity is very high. If the water is injected in high quantities, then the oil may be trapped in rock pores [15].

1.2.3 Chemical Injection

In these EOR process different chemicals i.e. surfactants, alkaline or polymers are injected in the solution form to improve the oil recovery by imbibition [16]. Based on the chemicals, the process can be classified as surfactant EOR, polymer EOR and alkaline EOR [17]. For the recovery of crude oil which is having medium to high gravity, this method is suitable. It cannot be utilized in high temperature applications owing to its strong dependency on the properties of chemicals and its stability nature. Reservoirs with permeability less than 50 mD, this process cannot be used because of injection problems [18].

1.2.4 Microbial EOR

In this method the residual oil saturation is reduced by injecting the microorganisms in the form of biomass, bio-surfactants, biogases, bio-solvents, etc. (Table 1.) into the oil bearing zones (i.e. reservoirs) [19]. These microbes are produced from the bacteria due to their small sizes allowing high penetration rate. The oil viscosity is reduced by injecting microbes and thus, its flow property gets increased [20].

Table: 1. Microbes and their applications in oil recovery

Product	Microorganism	Application in oil recovery	References
Biomass	Thermococcales, Sulfolobales, Thermotogales, Clostridiales, Cellulosome	Reduce interfacial tension and viscosity, Increase the mobility of oil.	[21, 22]
Bio-surfactants	Bacilli, Pseudomonas, Thiobacillus thiooxidans, Acinetobacter, Microbial cell surface	Maintain activity at harsh environmental conditions, Reduce surface tension, and Provide stable emulsions with large range of hydrocarbons.	[23, 24]
Biogases	Pathogenic bacteria, Swine vesicular disease virus and indicator organisms	Increase pressure, Interfacial tension reduction, viscosity reduction, increase permeability	[25]

Bio-solvents	Dioscorea zingiberensis (DZW), glycerol dehydrogenase (gldh), Clostridium beijerinckii, Clostridium acetobutylicum biomass	Emulsification, Reduces Viscosity	[26]

1.2.5 Nanoparticles injection

These particles are capable of displacing the oil, which is not produced in conventional recovery, by penetrating inside the pore throats because of their very small sizes (in nanometer). The oil is displaced by reducing the required capillary pressure to improve oil mobility which can be attained by dropping IFT between oil and water and altering the rock wettability [27]. Polyacrylamide, colloidal dispersion gels (CDG), polysilicon nanoparticles (PSNP) can be used in this process. Silica, carbon nanotubes, graphene, titanium, alumina, etc. nanoparticles resulted in improved oil recovery [28]. This EOR method ensures good results in laboratory scale but not commercial case because their thermal stabilities at high temperature and pressure are not identical [29].

1.2.6 Polymer injection

The injection of polymer causes reduction in the aqueous phase mobility by enhancing its viscosity and thus, improves the sweep efficiency [30]. Mobility (λ) is the ratio of the fluid permeability to its viscosity, whereas the mobility ratio (M) is the ratio of water mobility to oil mobility (equ.1):

$$M = \frac{\lambda w}{\lambda o} = \frac{kw/\mu w}{ko/\mu o} \qquad \text{equ.(1)}$$

Where k_w, μ_w, k_o, μ_o are water permeability, water viscosity, oil permeability, oil viscosity respectively. M values must be less than 1 for high sweep efficiency. If it is greater than 1 then water shows higher mobility than oil, i.e. oil recovery will be reduced. The injected polymer causes disproportionate permeability reduction (DPR) in heterogeneous reservoir. DPR means reduction in relative permeability of water (k_{rw}) with no reduction in oil relative permeability (k_{ro}). Viscoelasticity is the third considerable characteristics of polymers that improves displacement efficiency at macroscopic as well as at microscopic level [31].

2. BIOPOLYMERS

Biopolymers are polymeric compounds consist of biological monomers. They are derived chemically from biological materials or biosynthesized from living organisms [32]. Gelatin, starch, xanthan gum, scleroglucan, gaur gum, cellulose, collagen, keratin, schizophyllan, welan gum, polysaccharide, scleraglucan, silk, elastin etc. are widely used biomaterials to synthesize biopolymers. Food wastes can be used as raw materials to synthesize biopolymer which makes them economically favorable. Globally, 1.3 billion tonnes food (nearly one third of total food produced) is wasted per annum [33]. Rise in population imparts the increased food wastes generation which is expensive to recover. Thus, the utilization of wastes from food industry is grabbing the attention towards biopolymers. The shells of molluscs (i.e. mussel and olyster), crustacean shells (i.e. crab and prawns), fish scales (i.e. silver and pang scales), Echinodermata (sea cucumber) etc. can also be used to synthesize biopolymers [34, 35]. Biopolymers can also be derived from agricultural wastes such as plants, sugarcane bagasse, mammals' skins, bones, tendons and cartilage, chicken feet and skin, eggshells and microorganisms [36, 37]. They are very flexible and thus, can be altered chemically to achieve desired properties [38]. Their flexibility, biofunctional, nontoxic, sustainability etc. characteristics allow them to showcase their application in oil recovery. It is biodegradable and biocompatible and act as antimicrobial and antioxidant. Their composites possess good hardness along with good tensile and impact strengths as well as good viscoelastic nature thus can be applicable in EOR [39].

3. CHITOSAN SYNTHESIS

Seafood waste materials like shrimp, prawn, lobster shells and fungi and yeast are the raw material to produce natural polysaccharide. Chitin is obtained by the isolation that is approached by demineralization and deprotenization. To remove remaining minerals, the shells are stirred in 4%

hydrochloric acid at room temperature. The shells are deproteinized by using 4% sodium hydroxide at ambient conditions to separate remaining proteins. The reacted products are neutralized by distilled water then dried in hot air oven. Chitin obtained, undergoes deacetylation in presence of 65% NaOH to give Chitosan (Fig.1&2) which then washed thoroughly with distilled water until pH of 6.5-7.5 is reached [36].

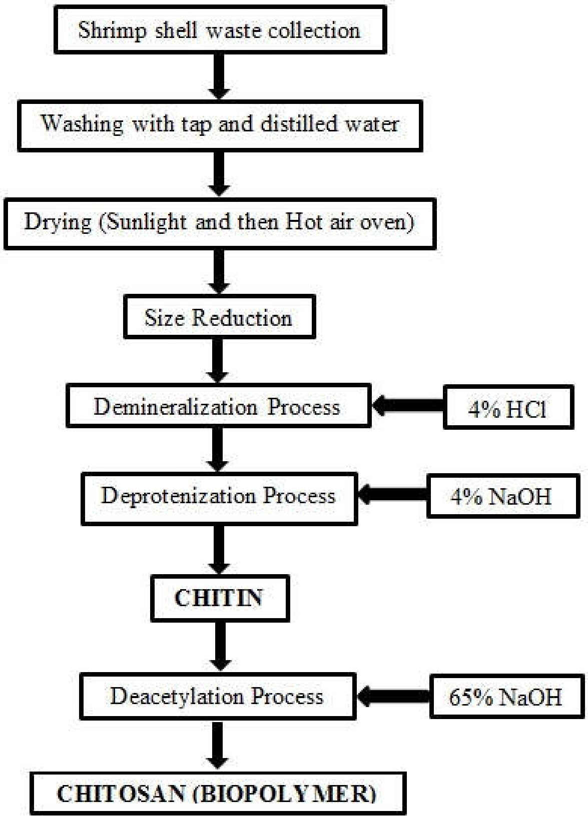

Fig. 1. Biopolymer Synthesis

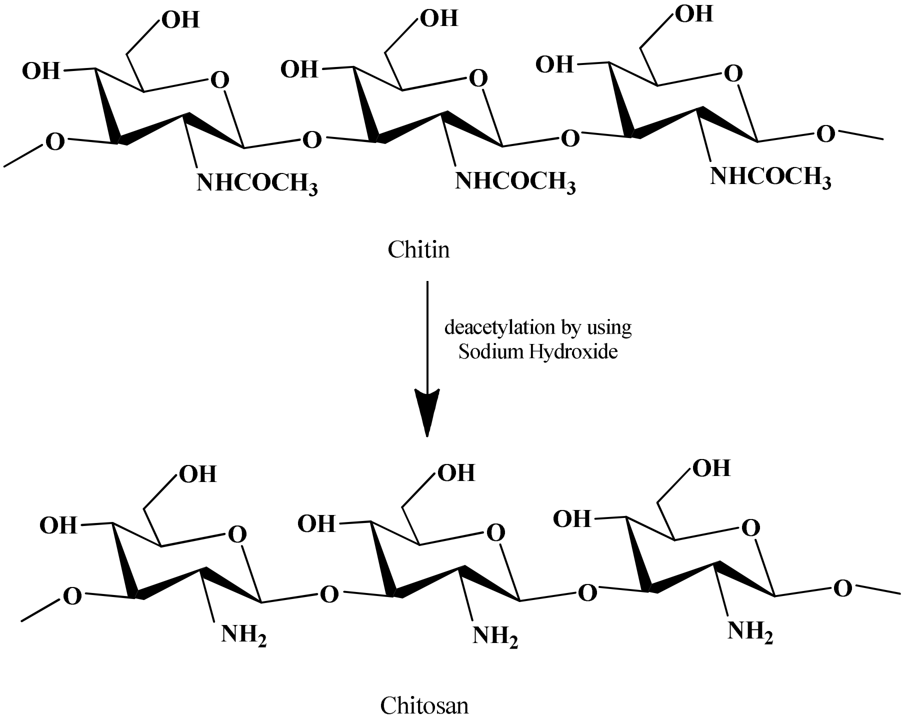

Fig. 2. Conversion of Chitin to Chitosan

4. EVALUATION OF BIOPOLYMER

Biopolymers must first be evaluated for their performance in the oil field before being used as fluid additives of various kinds. The important characteristics tests are filtration, rheological analysis, core flooding test, etc.

1.1 Filtration test

This test helps to understand the fluid's filtration property in the reservoir. Polymer solution undergoes filtration though filter paper at a constant rate. The pressure drop across the filter-paper is measured which gives idea about the components loss from the solution and the flow thorough the filter cake reduction can also be calculated from Darcy's equation [40].

4.2 Rheological analysis

Viscosity of polymeric solutions is measured as a function of shear rate. Dynamic viscoelastic and steady state behavior of fluids are measured by using bingham plastic, power law, Gasson and Herschel-Bulkley model [41].

4.3 Core flooding test

To begin, the core is completely saturated with brine to determine the pore volume, i.e. porosity. Brine, polymer solution and brine in sequence are injected in core. The pressure drop is measured for each fluid injection to calculate resistance factor (RF) and residual resistance factor (RRF). The ratio between pressure decrease in polymer displacing and water flooding is RF, which shows mobility reduction. Permeability is reduced using RRF, which measures the difference between the pressure decrease in flood water after and before polymer injection [42, 43]. They are also tested for solubility, temperature and salt resistance, thickening ability, adsorption, mechanical and long term stability etc. before used for EOR [44].

5. BIOPOLYMER FLOODING STABILITY

Partially hydrolyzed polyacrylamide (HPAM), a copolymer of polyacrylamide (PAM) and polyacrylic acid (PAA) is widely used synthetic polymer in EOR. Hydrophobically associating polymers (consists of acrylamide and hydrophobic), salinity-tolerant polyacrylamide and 2-acrylamide-2-methyl propane-sulfonate (AMPS) are derivatives of polyacrylamide (PMA) and can be used to improve oil recovery [45]. They are unstable in case of high temperature and salinity reservoirs. Thus, the need of compatible polymer for EOR is observed and the attention of petroleum industry is focused towards biopolymers in recent years [46].

During injection, the polymer solution viscosity is affected by many factors such as temperature, salinity, polymer retention, biodegradation, shear rate etc. Biopolymers can withstand higher salinity compared to HPAM and it can be further enhanced by additional chemicals (Table. 2). Addition of 0.1% NaCl or KCl solution shows improvement in xanthan solution stability [47]. Stability of xanthan gum can retain more than 50% of viscosity at 80 ^{0}C for more than five years but at the temperature above 100 ^{0}C. Its structure is impulsively converted into disordered coils [48, 49]. Scleroglucan and Diutan gum work well in high-temperature and high-salinity environments. Oil recovery with diutan gum is believed to be higher than that with xanthan gum at temperature above 100 ^{0}C and higher salinity (Table. 3) [50]. The performance of biopolymer in EOR is affected by oxygen and bacteria. Bacteria cause degradation of biopolymer and bio-plugging, thus damage the formation. Formaldehyde can be used to overcome this problem by retarding the growth of microorganisms [51]. The other problem associated with biopolymer is their loss during oil recovery due to adsorption on the surface and mechanical entrapment. The rate of adsorption depends upon the minerals formation and pH of the fluid. pH maintenance is an option to avoid adsorption. Mechanical entrapment takes place owing to larger molecules passing through smaller channels are trapped and it is controlled by using biopolymers with smaller molecules [43].

Table 2. Characteristics of Polymer and Biopolymer

Polymer	Type	Temp (^{0}C)	Polymer concentration (mg/L)	Salinity (mg/L)	Shear rate (s^{-1})	Viscosity (cP)	Increased Oil recovery (%)	Reference

HPAM	Synthetic	120	3000	38930.076	-	1.2 (from bulk rheology)	10	[52]
Sulfonate copolymer (SPAM)	Synthetic	45	3000	2000	30	15.20 (apparent)	16.7	[12, 53]
Sulfonated polyacrylamide (ATBS)	Synthetic	100	2500	2000	50000	41.8 (apparent)	>10%	[53]
Poly(AM-AA-DMDAA-ACAP)	Synthetic	65	3000	10000	7.34	429.2 (apparent)	16.6	[54]
BD-HMHEC	Synthetic	25	4000	-	6	2040 (apparent)	10.3	[55]
HEC	Synthetic	25	4000	-	6	93 (apparent)	3.6	[55]
Xanthan gum	Biopolymer	50	1750	3908	7	120 (apparent)	28.1	[48, 56]
Welan gum	Biopolymer	50	1750	3908	7	180	35.7	[48, 56]
Scleroglucan (SG)	Biopolymer	100	935	470	50000	15	>10% to water flooding	[53]

Table 3. Comparison of Synthetic and Biopolymer [47, 57]

Comparing Factor	**Synthetic Polymer**		**Biopolymer**		
	HPAM	**AMPS<30 mol%**	**Scleroglucan**	**Schizophyllan**	**Xanthan gum**
Max. Temperature Tolerance (^0C)	60	95	95	120	75-90
Min. permeability limit (mD)	5	5	200	150-300	100
Salinity limit ($ppm \times 10^3$)	0.1 -10	41-230	20-165	30-280	20-220
Bear a shear resistance	Very poor	Very poor	Excellent	Excellent	Very good
Industrial availability	Excellent	Excellent	Poor	Poor	Very good
Logistics and handling	Very good	Excellent	Very poor	Very poor	Very good
Lab experiment result	Excellent	Excellent	Poor	Good	Excellent
Pilot result	Excellent	Very good	Very good	Very good	Excellent
Field result	Excellent	Very good	Very poor	Very poor	Excellent

6. CONCLUSION

Producing oil fields around the world are maturing with minimal recovery factor, on the other hand, discovering major oil reserves are limited. It is evident that, polymer EOR plays a crucial role in improving the microscopic displacement efficiency. Though polymeric method is found to be effective, cost of the polymer and its non-biodegradable behavior impose economic and environmental restrictions. It can be observed from the discussion that, biopolymers, especially chitosan, derived from food waste is a viable and futuristic option for EOR applications. However, site specific investigations on the stability of biopolymers to in-situ conditions as well as its compatibility to resident fluids and the formation, needs to performed, prior to field scale application. In future, EOR with biopolymer can become a great practice in petroleum industry.

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