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Polymers for EOR Application in High Temperature and High Viscosity Oils: Rock–Fluid Behavior

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Abstract: Viscosity losses and high degradation factors have a drastic impact over hydrolyzed polyacrylamides (HPAM) currently injected, impacting the oil recovery negatively. Previous studies have demonstrated that biopolymers are promising candidates in EOR applications due to high thermochemical stability in harsh environments. However, the dynamic behavior of a biopolymer as scleroglucan through sandstone under specific conditions for a heavy oil field with low salinity and high temperature has not yet been reported. This work presents the rock–fluid evaluation of the scleroglucan (SG at 935 mgL⁻¹) and sulfonated polyacrylamide (ATBS at 2500 mgL⁻¹) to enhance oil recovery in high-temperature for heavy oils (212 °F and total dissolved solid of 3800 mgL⁻¹) in synthetic (0.5 Darcy) and representative rock samples (from 2 to 5 Darcy) for a study case of a Colombian heavy oilfield. Dynamic evaluation at reservoir conditions presents a scenario with stable injectivity after 53.6 PV with a minimal pressure differential (less than 20 psi), inaccessible porous volume (IPV) of 18%, dynamic adsorption of 49 µg/g, and resistance and residual resistance factors of 6.17 and 2.84, respectively. In addition, higher oil displacement efficiency (up to 10%) was obtained with lower concentration (2.7 times) compared to a sulfonated polyacrylamide polymer.

Keywords: enhanced oil recovery (EOR); scleroglucan (SG); sulfonated polyacrylamide (ATBS); RF; RRF; oil displacement

1. Introduction

Most oil mature fields are at an accelerated oil rate production and depletion due to high demand and low global supply of hydrocarbons, where the need to develop and improve the conventional EOR (enhanced oil recovery) techniques with tolerance to adverse conditions of high temperature and salinity (HTHS) is growing [1–3]. Currently, the most used synthetic polymers in injection processes are partially hydrolyzed polyacrylamides (HPAM). HPAM type is a copolymer, obtained by partial hydrolysis of the polyacrylamide. Although these products are highly used in recovery processes due to their acceptable performance, the viscosity of these polymer solutions is susceptible to reservoirs characteristics as high-temperature conditions, salinity, hardness, and high shear stress [4]. Despite the efforts and continuous improvement, synthetic polymers, specifically hydrolyzed polyacrylamides (amide groups) without modification as anionic monomers (replaced by AMPS (2-Acrylamido-2-methylpropane sulfonic acid), ATBS (2-acrylamido-tertbutylsulfonic acid), and NVP (N-Vinylpyrrolidone)) needs to improve the performance in high salinity and high temperature due to disadvantages that limit their application in heavy oil reservoirs [1–3], with high temperatures, hardness (TDS) greater than 5% w/w,

high shear rates ($\dot{\gamma} > 20,000 \text{ s}^{-1}$), and high retention [5–7]. All these factors have been tested with many modified polymers with ATBS and NVP monomers where high tolerance is reached at higher ions and temperatures with higher concentrations [8,9]. Thomas et al. [10], provide some critical features to polymers based on acrylamides for EOR applications at high temperature, high total dissolved solids, lower permeabilities, and high oil viscosities. Temperature and salinity are parameters that involve the addition of sulfonated and NVP monomers to impact the rheological behavior and stability for long periods at reservoir conditions. Gaillard et al. [11], describes the selection and evaluation of synthetic polymers for high temperature and low salinity case where ATBS monomer in polyacrylamide increase the viscosity with a lower concentration and their tolerance to shear and thermal stability in a soft brine. Recently, Seright et al. investigated viable polymers for EOR applications in carbonate reservoirs at high temperature with hard brines. Results showed that ATBS, NVP, and scleroglucan have moderated half-life time (until 17 years) and high polymer retention values ($>200 \mu\text{g/g}$) in carbonates but Scleroglucan showed a plugging effect and viscosity losses ($99 \text{ }^\circ\text{C}$) in the porous medium due to high retention and possible low hydration effect in the preparation of solution [12].

For this reason, there is a need to propose new alternatives and strengthen EOR methods to be applied in reservoirs with adverse conditions and mitigate environmental impacts. Numerous disadvantages presented by synthetic polymers make that biopolymer emerge as an alternative for polymer flooding in EOR processes due to their viscosity capacity and high thermal, mechanical, ionic, and saline tolerance. Different studies have highlighted biopolymers such as xanthan gum (XG), schizophyllan (SPG), hydroxyethyl cellulose (HEC), and scleroglucan (SG), as possible EOR candidates for the excellent properties at high salinity and temperature, high shear stresses, and stability in the presence of various ions [13]. Polysaccharide as Xanthan gum has been widely in many EOR processes with injectivity losses and hydrate problems are reported due to formation damage and plugging caused by impurities and extracellular material from the production process [14,15]. Hydroxyethylcellulose (HEC) biopolymer has shown easily hydratable and high oil incremental with a conventional implementation of a typical HPAM process [15]. Schizophyllan is another polysaccharide with high viscosity potential and stability at high temperatures and salinities. This biopolymer has shown a positive performance of pressure behavior at laboratory and field-scale with incremental oil more than 20% compared with waterflooding [14,16,17]. In addition, Scleroglucan is a neutral biopolymer that has aroused the interest of several researchers mainly in the evaluation of its potential use in improved recovery [18]. Scleroglucan in aqueous phase presents a conformation with a triple helix, semi-rigid rod-like structure [18–20], without the formation of aggregates due to D-glycosidic side groups [21]. Due to its non-ionic nature, the viscosity of the solutions is stable at high ionic forces and temperatures up to $130 \text{ }^\circ\text{C}$ [4,20]. Scleroglucan behavior establishes a scenario with great potential compared to other biopolymers and polyacrylamides in terms of thermal, chemical, mechanical stability, and oil recovery [22]. Recently, the Scleroglucan was evaluated at reservoir conditions ($K = 805 \text{ mD}$, $42 \text{ }^\circ\text{API Oil}$, 8000 ppm TDS , and $82 \text{ }^\circ\text{C}$) [14,23], where dynamic behavior at field-scale showed that scleroglucan is thermally, chemically, and mechanically stable, without injectivity losses. However, some authors have reported that Scleroglucan still presents few corefloods data collections in sandstones (adsorption and propagation behavior) and critical limit factors as temperature ($95 \text{ }^\circ\text{C}$), permeability (200 mD), and high energy during the dissolution to break the aggregates to improve filterability [13]. In addition, Castro et al. [24], evaluated the fluid/fluid behavior of Scleroglucan (SG) and a commercial sulfonated polyacrylamide (ATBS) in synthetic brine where Scleroglucan shows promising properties for EOR applications, including heavy oil reservoirs at high temperature, preserving the viscosity and stability at high salinities ($0\text{--}5\% \text{ w/w}$), ionic strengths (Na^+ , Ca^{2+} , and Mg^{2+}), shear stresses (up to $300,000 \text{ s}^{-1}$), temperatures ($>80 \text{ }^\circ\text{C}$), and wide pH ranges ($3\text{--}10$).

This study compiles the evaluation of the scleroglucan ($\text{SG at } 935 \text{ mgL}^{-1}$) biopolymer with high purity ($>90\%$) compared with a widely used sulfonated polyacrylamide (ATBS at 2500 mgL^{-1}) considering a controlled environment with synthetic brine and rock samples (Berea and representative

plugs) at Sorw conditions (residual oil saturation) for oil efficiency and Sw (water saturation) condition for injectivity test. The objective of this study is to obtain the best injection scenario of a scleroglucan solution in a specific case of Colombian field (212 °F and 3800 mgL⁻¹ TDS) in terms of injectivity, residual factor (RF), residual resistance factor (RRF), and oil displacement efficiency at reservoir conditions.

2. Materials and Methods

2.1. Materials

The polymers employed were a commercial EOR grade scleroglucan (SG, purity > 90%) and a commercial sulfonated polyacrylamide (ATBS-25%) with a molecular weight of 4–5 and 13 million g/mol, respectively. The water used was synthetic brine. For the preparation of the synthetic brine were used 2.9674 g/L NaCl, 0.13 g/L KCl, 0.239 g/L MgCl₂·6H₂O, and 0.583 g/L CaCl₂·2H₂O from Sigma Aldrich (Merck KGaA, Darmstadt, Germany) in type II water (3800 mg/L TDS, ph ≈ 7 and 6.1 mS/cm). The oil used in the wettability restoration was extra-heavy oil (390 cP @ 212 °F and 8 °API) dehydrated (BSW < 3%) and filtered (10, 5, and 2 μm). The porous media used in the dynamic test were a Berea sandstone and representative plugs with dimensions of length and diameter of ~30 cm and ~3.7 cm, respectively.

2.2. Methods

2.2.1. Preparation of Polymer Solutions

Synthetic polymer solutions at a fixed concentration of 2500 mg/L were prepared according to the API-RP-63 [25]. Scleroglucan solutions were prepared following the practices recommended by the supplier [26], considering the agitation, total solubility time, and complete hydration to ensure homogeneity and injection stability. First, stirring the synthetic brine with a propeller-type agitator at 500 rpm to generate a vortex of one-third of total volume, then sprinkle the SG in the vortex shoulder continuously. Second, stir the mixture at 800 rpm for 10 min and heat the solution until it reaches 40 °C. Third, stir the SG solution in an immersion blender (ultra-turrax) at 20,000 rpm for 5 min. Last, filtration test, turbidity, and transmittance measurements are required for biopolymer quality control [24].

2.2.2. Injectivity Tests

For the injectivity tests, samples of high and low permeability were used at 100% water saturation condition. Biopolymer was injected at a concentration of 935 ppm, at a temperature of 212 °F, and confinement and pore pressure of 3100 and 600 Psi, respectively. These tests aim to determine the resistance factor or reduction of mobility (RF) and the residual resistance factor or reduction of permeability (RRF). The protocol consists of plug saturation under vacuum with synthetic brine equivalent to water injection, brine injection at different flow rates (Kabs), polymer injection (RF), and brine injection at the same flow rates (10, 15, and 17 mL/min), recording the pressure differential to determine the reduction of permeability or residual resistance factor (RRF). Y-Error bars including the statistical error (2%) associated to pressure sensor model H2 (low pressure) with a range of 0.1 to 7.2 psi.

2.2.3. Inaccessible Porous Volume (IPV) and Adsorption Test

For polymer adsorption and inaccessible porous volume at residual oil saturation condition (Sorw), the sample is saturated with brine and restored to oil-wettability for 15 days until irreducible water saturation condition (Swirr). Subsequently, brine is injected to calculate the effective permeability to water (Kw) to proceed with the injection of the polymer solution dosed with tracer (5 PV of KSCN) and previously pre-shared (50,000 s⁻¹). The determination of the polymer concentration (polymer-tracer) is

monitored at all times until reaching the plateau zone in the concentration. Then, synthetic brine (5 PV) is injected until the injected solution is displaced, registering polymer and tracer concentration at all times. Finally, a second polymer-tracer slug (5 PV) is injected until the plateau zone is reached again. The determination of the polymer adsorption on the rock is carried out using the method proposed by Zaitoun et al. [27], which relates the polymer concentration in the effluents to the initial concentration injected as a function of the porous volumes injected (C/C_0 vs. PV). Scleroglucan concentration was determined by the colorimetric method using sulfuric acid, acetic acid, and phenol following the Dubois et al. methodology [28]. The procedure consists of add phenol solution and concentrated sulfuric acid in a scleroglucan solution considering a rest and stirring times before measurements. Y-Error bars are including to represent the statistical errors (3%) for data points associated with concentration test measurements with a KSCN standard curve (465 nm and $R^2 = 0.9974$) from 0 to 25 mgL^{-1} and phenol standard curve (490 nm and $R^2 = 0.9890$) from 0 to 80 mgL^{-1} , respectively.

2.2.4. Oil Displacement Tests

Dehydrated and filtered dead oil (BSW < 5%) with a viscosity of 839 cP (20 s^{-1}) at 212 °F was used for the restoration and oil displacement efficiency test. Both polymer solutions were evaluated in high permeability scenarios in concentrations of 2500 mgL^{-1} and 935 mgL^{-1} for ATBS and biopolymer, respectively. These concentrations are based on fluid–fluid studies previously carried out. The first step is the rock saturation and restoration until irreducible water saturation (S_{wirr}) and oil residual water saturation (S_{orw}) condition, monitoring the oil–water volume and differential pressure. Fluid saturation (S_o and S_w) is calculated by distillation extraction using the Dean–Stark method. Subsequently, the previously sheared polymer solution (0.7 PV) is injected and then brine (up to 20 PV), monitoring oil volume and pressure differential at all times. All the dynamic tests (injectivity, IPV, adsorption, and oil displacement test) were performed in a linear system that emulates a producer-injector scenario (Figure 1). For this, a coreflooding equipment in a heating oven was suitable with a confining pneumatic pump, storage, and injection cylinders, a pore pressure subsystem, and a positive displacement pump at flow rate constant. Y-Error bars including the statistical error (2–3%) associated to pressure sensor model H2 (low pressure) with a range of 0.1 to 7.2 psi, H3 (middle–low pressure) with a range of 0.3 to 36 psi, and H5 (high pressure) with a range of 90 to 3625 psi, and further, a percent error (2%) by the water/oil volume and weight effluent measurements by the collector.

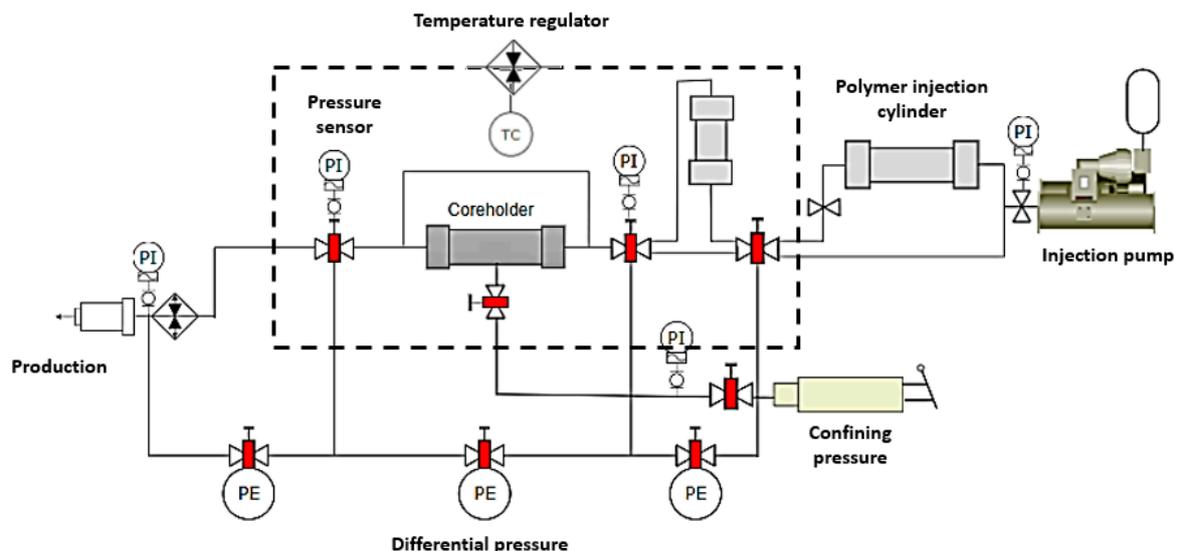


Figure 1. Schematic representation of the coreflooding displacement system for the dynamic evaluation of the polymer solutions in porous media.

3. Results and Discussions

3.1. Injectivity Tests

Biopolymer flow behavior in a porous medium, depending on flow rates at a laboratory scale, presents an increase in pressure differentials with higher flow rates and pore volumes injected. The pressure profiles reflect possible mechanical retention in the pore throats, resulting in slightly permeability reductions when the porous medium is a water saturation ($S_w = 1$). Figure 2 presents the Scleroglucan behavior in a high and low permeability condition with 935 mgL^{-1} of biopolymer. This flow behavior is useful to determine the best scenario of the injection rate of scleroglucan into the reservoir without any associated problems or formation damage by high flow rates and pressure. Scleroglucan presents good injectability in low and high permeability (between 2000 and 4000 mD) at $212 \text{ }^\circ\text{F}$ without differential pressure increase still at rates of up to 17 mL/min (351 ft/day). Additionally, the resistance factor or mobility reduction (RF) and residual resistance factor or permeability reduction (RRF) show the slight porous medium changes after polysaccharide effect and rock–fluid interaction at a high flow rate without sand production. It demonstrated the stability of piston-like behavior and steady flow of rod-like semirigid structure through interconnected porous in a consolidated sandstone with a non-dependence of flow rate (See Table 1) [29].

Table 1. Resistance factor or mobility reduction (RF) and residual resistance factor or permeability reduction (RRF) of biopolymer (Scleroglucan at 935 mgL^{-1}) at $212 \text{ }^\circ\text{F}$ in representative core plugs at water saturation condition ($S_w = 1$).

Gas Permeability (mD) *	Porosity (%)	RF	RRF
4555	20.4	1.3	2
2155	18.8	1.4	1.9

* Correction to core measurement of permeability by Klinkenberg effect.

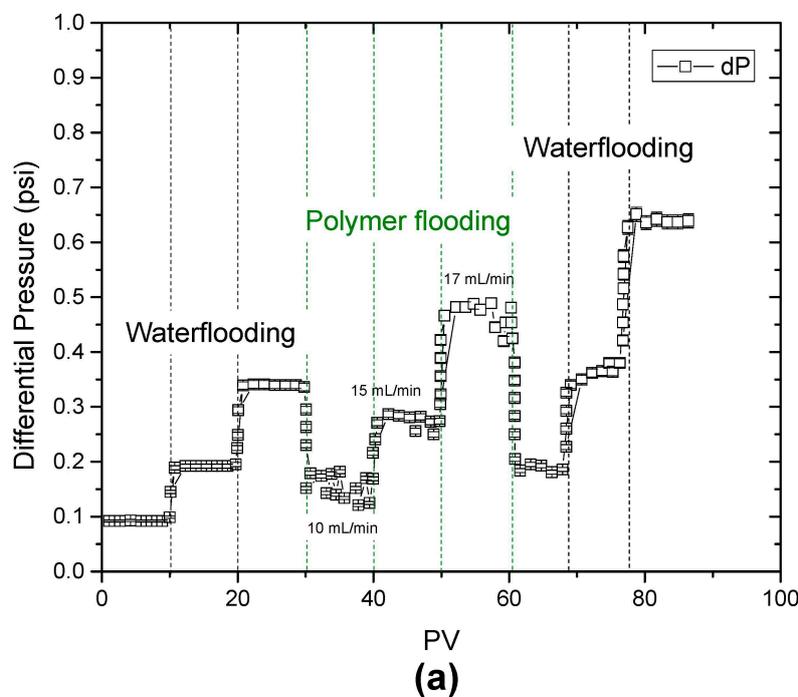


Figure 2. Cont.

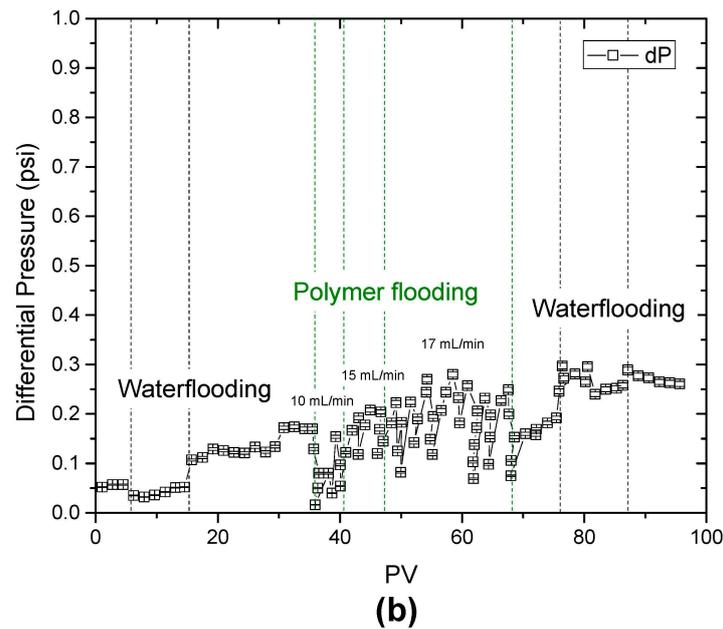


Figure 2. Injectivity test of the Scleroglucan (935 mgL^{-1}) in (a) 2155 mD, and (b) 4555 mD permeability from the representative formation at confining pressure 3100 psi, 212°F and pore pressure of 600 psi. The dotted lines indicate the flow range at 10, 15, and 17 mL/min.

3.2. Adsorption and Inaccessible Porous Volume (IPV) at Sor Condition

Rock–fluid interactions as retention, adsorption, and blockage occur between the polymer molecules and the solid surface when the polymer solution flows through a porous medium, and its effect depends on repulsion and attraction balance [30]. The polymer molecule adsorption on the rock surface is governed by physical adsorption, electrostatic attraction force, Van Der Waals forces, or hydrogen bonds, among other interactions [30,31]. Additionally, polymer adsorption will depend on the components of the aqueous solution (ions, pH, and hardness), the rock nature (wettability and reservoir state), polymer composition, the residence time, solid/liquid ratio, and solid–brine interaction impact on the static and dynamic polymer adsorption [32]. These factors directly influence the polymer’s ability to access and move through connected pores with minimum possible pressure. For IPV or inaccessible pore volume, which indicates the porous volume (fraction of total rock volume) that cannot be accessible by polymer molecules due to steric impediment and hydrodynamic behavior. In extreme cases, the IPV can be between 20 and 30% of the total pore volume depend on the polymer and rock nature [33]. Table 2 presents the adsorption and IPV values of the biopolymer (SG) and the synthetic polymer (ATBS) at 470 and 2000 mgL^{-1} due to adsorption capacity phenomena. Biopolymer behavior does not differ significantly from ATBS in terms of adsorption and IPV, with low adsorptions and inaccessible porous volumes for both cases. Additionally, the adsorption and IPV values are consistent with the structural characteristics and hydrodynamic configuration of scleroglucan, which is lower molecular weight than the synthetic polymer. Its triple helix structure gives it more rigidity or dense steady shape generating low chemical adsorption and hydrodynamic retention [18,22].

Table 2. Adsorption and inaccessible porous volume (IPV) of Scleroglucan (SG) and sulfonated polyacrylamide (ATBS) at Sorw condition.

Sample	Parameters		Rock Properties		Retention	
	mgL^{-1}	μ at $50,000 \text{ s}^{-1}$	Porosity (%)	Density (g/cm^3)	Adsorption ($\mu\text{g/g}$)	IPV (%)
ATBS	2000	41.8	19.67	2.672	10.4	22
SG	470	15	21.93	2.676	15.4	23

Figure 3 presents the polymers flow through a porous medium in the presence of a tracer (KSCN at 30 mgL^{-1}). For ATBS polymer, the first polymer slug slightly advances at the same time to the tracer. Still, both tracer slugs do not break at the same time. This behavior is associated with the low polymer adsorption on the rock surface. In the second polymer slug, cross faster the porous medium first than the tracer due the adsorption sites are saturated, and adsorptive capacity is minimal by the polymer molecules injected into the first slug and IPV effect counteracts its slight delay [34].

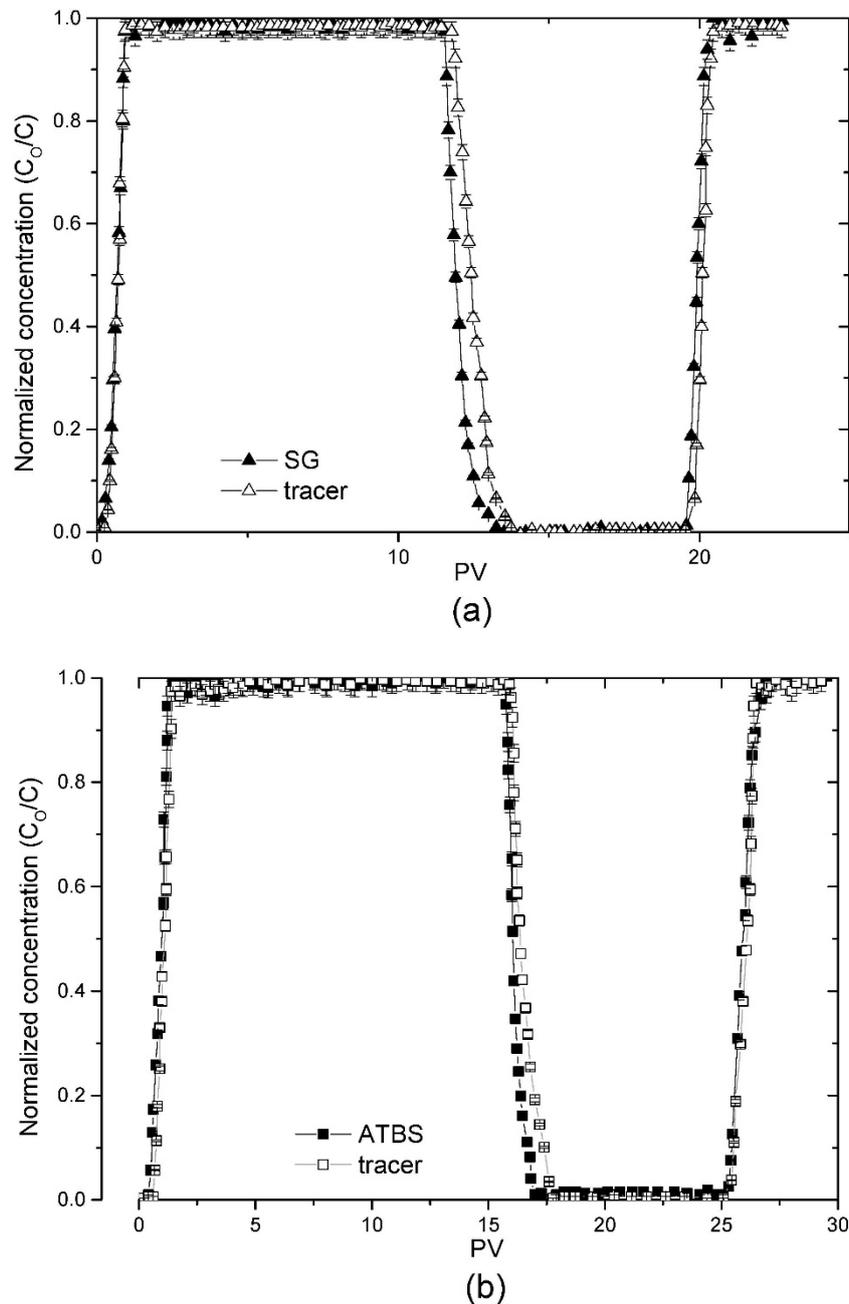


Figure 3. Normalized concentration of polymer and tracer (KSCN at 30 mgL^{-1}) for (a) Scleroglucan (SG at 935 mgL^{-1}) and (b) sulfonated polymer (ATBS at 2000 mgL^{-1}) at Sorw conditions (2500 psi overburden pressure, 500 psi of backpressure and $212 \text{ }^\circ\text{F}$) in a representative core plug.

3.3. Oil Displacement Tests

Figure 4 shows the oil recovery in a Berea core at a controlled environment for the injection of synthetic brine (3800 mgL^{-1} TDS), followed by the biopolymer injection (935 mgL^{-1} SG) at Sorw

conditions. Oil recovery percentages after 20 PV of brine injection (WF) and 53.6 PV of scleroglucan (SG) correspond to 32% and 50%, respectively. The dynamic adsorption of scleroglucan of $49 \mu\text{g/g}$, inaccessible porous volume (IPV) of 18%, resistance factor (RF) of 6.17, and a residual resistance factor (RRF) of 2.84 similar to reported in the literature [18,35]. The pressure behavior during oil displacement is stable, and good injectivity of scleroglucan in the porous medium is presented with an oil recovery percentage higher than 10% to waterflooding (WF). Oil displacement potential can be attributed to the volumetric sweeping by piston-like behavior and the higher resistance factor of scleroglucan. Additionally, its rigid rod-like structure could affect a mechanical entrapment consistent with the adsorption data and observed resistance or “zigzag type” behavior of the pressure differential during its injection. In this case, 20 PV was used to evaluate the potential oil efficiency and the maximum pressure requirement but is not the real scenario in field-scale due to excessive polymer injection that would limit the project technically, operationally, and economically.

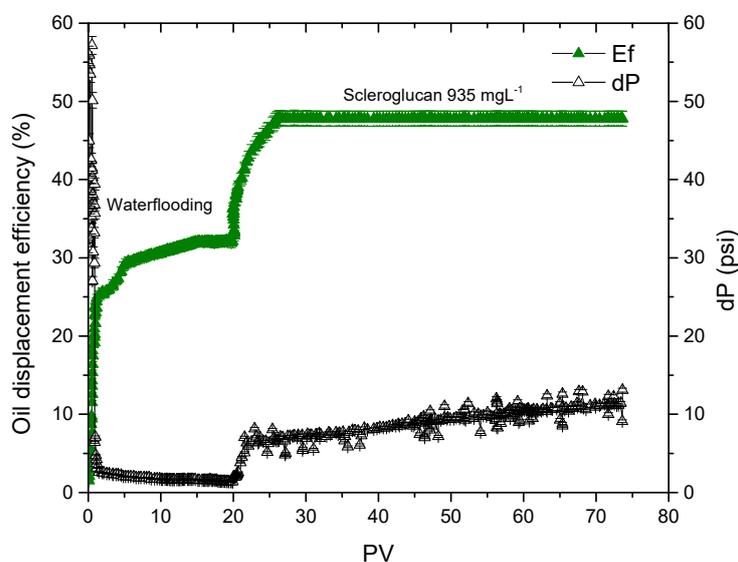


Figure 4. Oil displacement efficiency and differential pressure after waterflooding (3800 mgL^{-1} TDS) and biopolymer flooding (SG, 935 mgL^{-1}). The porous media is composed of Berea Sandstone with porosity (ϕ) and permeability (k) of 22% and 585 mD, respectively. The dimensions of the plug are 6.07 cm in length and 3.73 cm in diameter. Overburden pressure: 1300 psi, Backpressure: 300 psi, and Temperature: 212 °F.

For a representative plug were used 0.7 PV of polymer slug, which represents a typical well injector scenario of polymer flooding project economically viable. The oil efficiency, in this case, was evaluated as a single well injector at a constant rate of 0.24 mL/min (equivalent to 1 ft/day) where waterflooding was in a range between 30 and 32% for both polymers. For both cases, the incremental oil after polymer injection is observed with the significant difference that Scleroglucan has the highest oil recovery with a 2.67 times lower concentration than that of ATBS. The ATBS presented a slightly lower displacement efficiency value due to thermal and mechanical degradation during polymer injection. Figure 5 shows the oil displacement efficiencies for biopolymer (SG) compared with the synthetic polymer (ATBS), evaluated under the same petrophysical and operative conditions. The oil recovery percentage after injection of 10 PV of brine and 0.7 PV of biopolymer followed by 20 VP of water (no more oil is recovery after 1 PV) correspond to 30% and 28%, respectively. Additionally, the differential pressure at the waterflooding endpoints before and after the biopolymer show a residual resistance factor (RRF) of 2.4 and 1.8 for ATBS polymer what is consistent with that reported in the literature for this type of molecule [7,22,34]. Differential pressure behavior during SG injection, determine the stable injectivity of the biopolymer into the formation with an oil incremental significantly higher than that generated by the synthetic polymer. The drastic effect compared with synthetic polymer is immediately finished

the waterflooding (post-biopolymer slug), due to the piston-like effect by the rod-like structure and the hydrodynamic behavior of the scleroglucan molecules penetrating the pore throats as interconnected rods [18,22,23]. In addition, the reduction in the oil/water mobility ratio for ATBS is based on its high molecular weight and pseudo-plasticity, which in turn reduces rock permeability, whereas SG is by high rheological behavior (triple-helix structure and shear-thinning strength), high viscosity (less thermal and chemical degradation), reduction in mobility, and rock permeability.

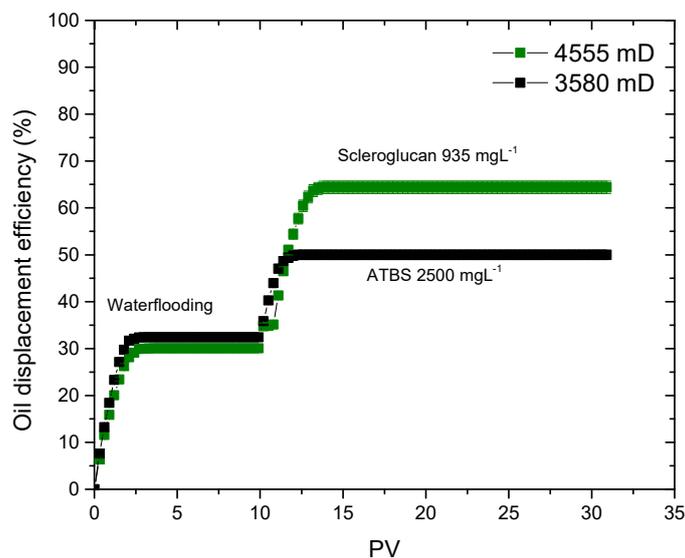


Figure 5. Oil recovery efficiency after waterflooding (3800 mgL^{-1} TDS) and biopolymer flooding (SG, 935 mgL^{-1}) in a representative core plug. The porous media is a composite representative formation with porosity (ϕ) and permeability (k) of 19–21% and 3580–4555 mD, respectively. The dimensions of the composite are 6.6–7.5 cm in length and 3.77–3.79 cm in diameter. Overburden pressure: 3100 psi, Backpressure: 600 psi, and Temperature: 212 °F.

4. Conclusions

Scleroglucan is presented as the best choice for a polymer flooding process due to the high potential to increase the oil recovery efficiency (greater than 10%) with a lower concentration (up to 2.67 times) compared to sulfonated polyacrylamide, which would generate technical, operational, and operational advantages. The oil displacement efficiency by injection of 0.7 VP of biopolymer in environments with high permeability (4000 mD) and medium permeability (2000 mD) reflects a high injectivity advantage and stability of piston-like behavior and steady flow of rod-like semirigid structure through to Berea sandstones with non-dependence of flow rate. Additionally, the adsorption behavior is consistent with the structural and hydrodynamic configuration where SG with a triple helix structure gives it more rigidity or dense steady shape generating low chemical adsorption and hydrodynamic retention compare to sulfonated polyacrylamide.

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