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Original article

Comparative analysis of the performance of hydrophobically associating polymers, xanthan and guar gum as mobility controlling agents in enhanced oil recovery application



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### ABSTRACT

This study aimed to evaluate the performance of hydrophobically associative polymer (HAPAM), xanthan gum, and guar gum in enhanced oil recovery (EOR) processes. Their performances in terms of oil recovery applications were investigated through rheological behavior analysis and core flooding experiments. Rheological studies reveal shear thinning characteristics with HAPAM, posing superior rheological behavior at elevated shear rates for all concentrations tested. Core flooding tests were conducted on different sandstone core samples with similar petrophysical properties to evaluate the EOR performance using the three polymers. Cumulative oil recovered after waterflood implies HAPAM shows better oil recovery capability with 41.1, 62.4 and 63.5 % oil recovered compared to xanthan 32.8, 33.7, and 56.2 % and guar gum with 41.8, 57.1, and 61.2, % using the three concentrations; concentration 1, 2 and 3 (1000, 4000 and 6000 ppm) respectively. The superior performance of HAPAM was also evident in its lesser amount of permeability damage after flooding, with 28.3 %.

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# 1. Introduction

With more than a trillion barrels of oil projected to remain worldwide after primary and secondary recovery, multinational oil firms massively expanded their spending on research and development in the last decade (Li et al., 2017; Wever et al., 2011; Feng et al., 2017). The enhanced oil recovery (EOR) study carried out by oil companies was armed with large budgets when oil prices were high. This has resulted in tremendous improvement in the evolution of new oilfield chemicals in the form of hydrophobically associative polymers, gels and surfactants (Levitt and Pope, 2008; Raffa et al., 2016).

Partially hydrolyzed polyacrylamide (HPAM) and Xanthan were previously used in the polymer flooding process to thicken injected

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water to mobilize capillary trapped water-flooded oil during the secondary recovery method and thus improve the displacement efficiency (Chelaru et al., 1998; Hou, 2007). While they can significantly increase the viscosity of fresh water with relatively low concentrations, HPAM is faced with severe challenges when used in high temperature/salinity oil reservoirs. In such a hostile environment, the loss of efficiency of the HPAM aqueous solution becomes more serious as more amide groups (CO-NH) undergo extensive hydrolysis into carboxylic characters under high temperatures. The hydrolyzed molecules precipitate upon contact with divalent cations, usually contained in brines within oil reservoirs or hard water (François et al., 1997; Kheradmand et al., 1988).

On the other hand, although Xanthan Gum can withstand high salinity conditions, its biodegradability has hindered its sustainable use in EOR operations. Moreover, polymers used in flooding should also be able to withstand long periods of injection and shear. Offshore application of polymer flooding entails the polymer meeting offshore platform requirements beyond the specified oilfield parameters (Gao, 2014). Xanthan gum and hydroxyethyl cellulose (HEC) show good application in the field compared to HPAM / PAM, under high salinity conditions (Kästner et al., 1996). Above all, the need to reduce the challenges of using PAM / HPAM and biodegradable polymers for EOR purposes has necessitated increased research into polyacrylamide chemical derivatives (Gao, 2014; Chen et al., 2013). Researchers have made a substantial effort to produce improved polyacrylamide (PAM). They copolymerized acrylamide with more thermally stable monomers to reduce excessive hydrolysis. It thus increased the thermal stability of the products (Abbas et al., 2020; Wan et al., 2014; Afolabi et al., 2019; Raffa et al., 2016). To some extent, these attempts have paid off in obtaining more excellent retention of polymer viscosity. Nevertheless, thermal degradation was not essentially prevented, but there are still limitations on using HPAM in hostile oil reservoirs (Wang et al., 2010).

Recently, researchers developed an integral derivative of polyacrylamide in the form of Hydrophobically Associating Polyacrylamide (HAPAM). The primary objective for these derivatives was to increase the thickening potential of polyacrylamides under extreme reservoir conditions, including high temperatures and high salinity (Chen et al., 2013; Wever et al., 2013). The enhanced capacity of HAPAM to thicken ensures it has more reduction in Mobility compared to HPAM polymers. This high reduction of Mobility by HAPAM translates into higher incremental oil recovery compared to HPAM polymers (Pancharoen et al., 2010; Guo et al., 2018; Mao et al., 2018). These HAPAMs are synthesized by introducing hydrophobic co-monomers along the backbone of a polymer and these hydrophobic monomers contribute to the polymers' total molecular weight. Numerous studies have been reported on the performance of synthetic water-soluble polymers, HPAM, Xanthan, and guar gum, together with their operational challenges, as mentioned earlier. However, little work has been reported on the performance evaluation of these polymers compared to recently developed chemical derivatives of HPAM (associating polymer, HAPAM) in EOR applications (Bai et al., 2018; Zhang et al., 2017). To address such deficiencies, two conventional polymers, Xanthan and guar gums, were examined in comparison with HAPAM on rheological behaviors, shearing resistance, and core flooding test.

This work evaluated the detailed performance of HAPAM as a mobility-controlling agent for medium oil recovery compared to conventional polymers (Xanthan and Guar Gum polymers). Sandstone core samples from the Niger Delta were used for the polymer flooding tests to provide helpful information on the improved viscosity of water and polymer retention in porous media. Oil displacement studies subsequently offered additional details on the efficacy of this HAPAM in EOR applications under laboratory conditions.

### 2. Materials and experimental methodology

### 2.1. Materials

Xanthan and Guar gums were procured from a local market in Lagos, Nigeria. NaCl with  $\geq$  99% purity and HAPAM were purchased from SNF Fleorger Co. France. All chemicals used were without modification. The crude oil sample used for the rheology/EOR applications and the unconsolidated sandstone core plugs were obtained from an indigenous producing company operating in the Niger Delta region of Nigeria. The crude oil sample exhibits a density of 0.87 g/cm<sup>3</sup>, a viscosity of 14 (cP), and API of 29.3.

# 2.2. Characterization of the polymer

Polymers were characterized using techniques such; as Differential Scanning Calorific, Fourier Transform Infra-red Spectroscopy, Scanning Electron Microscope, and Energy Dispersive X-ray Analysis.

### 2.3. Polymer solution preparation

The overhead stirrer method has been used in the formulation of the polymer solution (Sargent- Weich cone drive variable speed, catalog number 0876445). Equation (1) was used to determine the amount of polymer dissolved in water. Where  $W_{pr}$  = wt. of polymer product,  $W_s$  = wt. of stock solution,  $C_s$  = Conc. of polymer in stock solution,  $A_{pr}$  = activity of polymer product,  $W_{bs}$  = water makeup.

$$W_{pr} = \frac{W_s \times C_s \times 10^{-4}}{A_{pr}} \tag{1}$$

The following equation is used to calculate the amount of water in the polymer solution,

$$W_{bs} = W_s - W_{pr} \tag{2}$$

# 2.4. Rheological analysis

Seven (7) different polymer concentrations were prepared and analyzed for rheological behavior (1000 ppm to 7000 ppm). However, three (3) concentrations representing the lower, highest, and median were used for the core flooding experiments. The viscosities of the polymer solutions were evaluated using Ofite 800 Model viscometer, manufactured by Ofite Testing Equipment Inc. USA, according to API recommended practices 13B-1 and 13B. This allows the evaluation of different polymers based on their rheological properties and also assesses the effects of shear rate and polymer concentration on the polymer viscosity.

### 2.5. Core flooding test

The core flooding procedure was performed using a Reservoir Permeability Tester (RPT) manufactured by Ofite Oilfield Testing Co. The setup is shown in Fig. 1. The experiments were conducted at a laboratory scale using unconsolidated sandstone core plugs (properties described in Table 1), deionized water, polymer solutions, and crude oil sample described in the materials section. The cores were first saturated with water (i.e., 100 percent) and subsequently displaced by crude oil at a rate of 0.5 cc/min until no further water was produced to achieve initial water saturation (S<sub>wi</sub>). Waterflood was first introduced, and percentage recovery was calculated, followed by introducing the different test fluids (polymer solutions). The process discussed above was repeated for the three (3) polymers at different concentrations (1000 ppm, 4000 ppm and 6000 ppm). The saturation profile is presented in Table 2.

### 3. Results and discussion

### 3.1. Rheological performance

The rheological activity of the polymers in solutions was assessed at different concentrations under laboratory conditions (30 °C) to evaluate the polymers' suitability as candidates for polymer flood applications. Fig. 2 presents the variation in viscosity as a function of shear rate under different concentrations for the three polymers. All the polymer solutions exhibit shear-thinning behavior of reducing viscosities with an increase in shear rate, a typical characteristic of pseudo-plastic materials. However, the polymers show increasing viscosity trends with an increase in the number of dissolved solutes (concentration). HAPAM demonstrated superior viscosities and better dependence of viscosity on the shear rate



Fig. 1. Schematic of the core flood experimental using Ofite Reservoir Permeability Tester.

### Table 1

Petrophysical properties and flow conditions.

		Core sample used			
S/N	Parameters	A3	A4	A5	
1	Polymer Type Used	HAPAM	Xanthan Gum	Guar Gum	
2	Core Permeability (mD)	289.9	280.7	309.9	
3	Core Length (cm)	3.4	3.5	2.96	
4	Core Diameter (cm)	3.8	3.8	3.5	
5	Core Bulk Volume (cc)	38.6	39.7	28.5	
6	Core Pore Volume (cc)	7.4	9.0	8.3	
7	Porosity (%)	19	23	29	
8	Flooding Injection Rate (cc/min)	0.5	0.5	0.5	

at different concentrations compared to guar gum and xanthan polymers which are natural polymers. This outstanding rheological behavior could be attributed to the HAPAM structure and composition modification during synthesis (Sarsenbekuly et al., 2017). This behavior is evident in the following techniques; Surface Morphology/Elemental Composition, Fourier Infrared Spectroscopy and Differential Scanning Calorimetry (DSC) for guar gum polymers, xanthan polymers and HAPAM. Please see supplementary sections S1, S2 and S3 for illustrations.

# 3.2. Oil recovery performance

# 3.2.1. HAPAM recovery performance (Hydrophobically associating Polymer)

Four sets of flooding tests per core sample were conducted with each polymer solution and water flood, as discussed under the Core Flooding Test for EOR in the methodology section. Fig. 3a shows the overall flooding result using HAPAM as a recovery agent was successfully conducted on core sample A3 at different concentra-

Table 2						
Core sample S	Saturation	Profile	for	core	sample	s.

tions. The values obtained from the core flooding experiment show some level of incremental oil recovered after each flooding. The different concentrations used for HAPAM were HAPAM, conc. 1,2, and 3 correspond to 1000, 4000 and 6000 ppm. The effectiveness of each concentration was monitored, and the amount of oil recovered with the recovery factor was plotted against the pore volume injected.

For the flooding process, water flooding performance recovered approximately 24.1 % initial oil in place (OOIP) after about 1.6 cc of water had been injected, leaving a vast amount of oil in the core. Sequel to water flooding, HAPAM, conc-1 was then introduced, and it recovered additional oil, up to 17.0 % in trapped recovery. A new concentration of HAPAM, conc.- 2, was introduced when no extra oil was noticed in the effluent. Fig. 3a shows cumulative recovery up to 63.5 % OOIP recovered at the end of injection of conc. 2. HAPAM conc. 3 was chosen based on its rheological performance and tested on core A3. Core sample A3 has similar petrophysical properties to the previous core sample used. To ascertain the recovery potential of HAPAM conc. 3 (6000 ppm),

Samples	Total Pore Volume (cc)	Volume of water expelled (cc)	Total Oil in Place (cc)	Connate Water (cc)	Injection Rate (cc/min)
Core A3	7.4	7.2	7.2	0.2	0.5
Core A3	7.4	7.2	7.2	0.2	0.5
Core A4	9	8.7	8.7	0.3	0.5
Core A4	7.5	7.2	7.2	0.3	0.5
Core A5	8.3	8.0	8.0	0.3	0.5
Core A5	8.1	7.9	7.9	0.2	0.5



Fig. 2. Rheological behavior of the tested enhanced oil recovery polymers at varying concentrations for 30 °C.



Fig. 3. A and b: oil recovery performance after waterflood (a. hapam, b. xanthan gum, c. guar gum).

the water flooding process was performed, followed by injection of HAPAM conc. 3. The results observed at the end of the Water Flooding Process show a recovery of 31.2 % OOIP upon introducing HAPAM conc. 3, an incremental recovery of 31.2 % was noticed, leading to a total recovery of 62.4 % for both water flooding and HAPAM conc. 3.

# 3.2.2. Xanthan gum recovery performance

The second phase of the flooding test involves the introduction of xanthan gum as the test fluid for EOR applications. A similar experimental routine like HAPAM was followed to establish a basis for comparison; the test condition was the same as the HAPAM, and the core petrophysical properties were also the same. From Fig. 3b, it can be deduced that conventional waterflood recovered 24 % of the oil after about 1.2 cc pore volume was injected. This experimental routine is in line with the reported pilot test in the waterflood literature (Afolabi et al., 2019).

Introduction of the three (3) different xanthan gum polymer solutions recovered 8.8, 20.9, and 27.8 % additional oil after water-flood when about 2.5, 3.8, and 3.9 cc pore volume of the polymer

Table 3	
Core sample permeability damage analysis.	

Length (cm)	Diameter (cm)	DifferentialPressure (psi)	Flowrate (cc/min)	Area (cm <sup>3</sup> )	Permeability (mD)	Remarks
3.4	3.8	0.38	0.025	11.34	289.9	Pre-permeability (HAPAM)
3.4	3.8	0.53	0.025	11.34	207.8	Post-Permeability (HAPAM)
					28.3 %	%Impairment
3.5	3.8	0.40	0.025	11.34	280.69	Pre-permeability (Xanthan Gum)
3.5	3.8	0.87	0.025	11.34	239.5	Post-Permeability (Xanthan Gum)
					53.56 %	%Impairment
4.4	3.8	0.46	0.025	11.34	309.9	Pre-permeability (Guar Gum)
4.4	3.8	0.71	0.025	11.34	200.8	Post-Permeability (Guar Gum)
					35.2	%Impairment

solutions were injected for Conc. 1, 2 and 3 respectively. Generally, the xanthan gum recovery performance shows a similar trend to the HAPAM. But in terms of effectiveness, the HAPAM exhibits better performance which is corroborated by the rheological performance results. The better performance of HAPAM as a mobility control agent compared to Xanthan could be explained as HAPAM having better viscosity retention ability than the xanthan gum under shearing conditions (Afolabi et al., 2019) as its solution thickening ability has been enhanced during synthesis. Therefore, resulting in high mobility reduction to water by the HAPAM during flooding test and consequently higher incremental oil recovery compared to Xanthan (Afolabi et al., 2019; Lai et al., Dong, 2013).

### 3.2.3. Guar gum recovery performance

After initial waterflooding, the oil recovery profile for guar gum polymer followed a similar trend with the other two polymers (HAPAM and Xanthan). Supplementary section S4 shows a total 8.4 cc pore volume water, conc. 1, 2 and 3, guar gum polymer solutions flooded into the core A5 at different runs, respectively. At the end of waterflooding, 21.7 % of the initial oil in place was recovered. The oil recovery at this stage was basically a result of the Volumetric Sweep Efficiency technique (Ogunkunle et al., 2020). Furthermore, waterflooding was sustained until no traces of oil were noticed in the effluent. After that, conc. 1 guar gum was introduced, which recovered an additional 22.6 % of trapped oil after injecting 3.6 pore volume conc. 1 solution. The remaining concentration, conc. 2 and 3, recovered an incremental 12.8 and 34.0 % of the residual oil after the waterflood. The guar gum shares a similar performance to HAPAM; however, this was after a considerable amount of guar gum polymer solutions was injected. Specifically, guar gum requires a total of 6.5 cc pore volume polymer solution to recover cumulative 61.2 % oil, while HAPAM needs 5.2 cc pore volume to recover 63.5 % incremental oil.

# 3.3. Permeability impairment

The effect of the overall flooding process on the core samples before and after flooding was evaluated and reported in Table 3. One of the major drawbacks of most mobility buffers (polymers) is the tendency for the polymer to be retained on rock surfaces/pores, thereby reducing the area open to flow and consequentially permeability impairment which results in an additional pressure drop. The amount of retention is directly connected to the permeability impairment level. High permeability impairment after flooding most times implies high polymer retention. From Table 3, it can be observed that HAPAM demonstrates a comparatively low permeability impairment of 28.3 %. In comparison, xanthan gum and guar gum show high polymer retention on a rock surface with about 53.56 % and 35.2 % damage to the rock permeability. The observed low retention with the use of HAPAM can be attributed to the presence of a negatively charged carboxylic group in the polymer structure which leads to repulsion on the surface of the negatively charged sandstone cores; hence, the low polymer retention (Bai et al., 2018; Afolabi et al., 2019). Contrarily, xanthan and guar gums are non-ionic in nature and could quickly form hydrogen bonds upon contact with the sandstone rock surface and get retained, which could lead to high polymer adsorption.

# 3.4. Conclusion

In the present study, the performance of three mobility buffer agents (HAPAM, Xanthan and Guar gum) as mobility control polymers for EOR was evaluated at laboratory conduction (30 °C, no salinity). The polymers were characterized to identify their unique morphology, functional group, and thermal stability potentials as preliminary analysis. The performance in EOR applications was eventually characterized in terms of rheological behavior and oil recovery efficiencies.

The following inferences can be inferred;

- Rheological analysis reveals all tested polymers exhibited pseudo-plastic behavior, with HAPAM proving to have better viscosity characteristics at higher shear rates.
- The flooding tests indicated that the HAPAM is a superior mobility control agent among the three, with incremental oil recovery efficiency of 17.0, 14.2, and 31.2 % for the three concentrations tested.
- A lesser permeability damage effect was also observed with the HAPAM, with a permeability impairment of 28.3 %, confirming the superior oil recovery performances observed
- However, it is recommended that further studies on salinity and temperature effects are required

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jksues.2022.01.003.

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**S1:** Polymer characterization with differential scanning calorimetry (a) Guar gum (b) Xanthan gum (c) HAPAM.



S2: Polymer characterization with scanning electron microscopy SEM/EDX at 200  $\mu$ m (a) Guar gum (b) Xanthan gum (c) HAPAM





# S3: Polymer characterization with FTIR



A sharp peak present at 871.4cm<sup>-1</sup> corresponds to a strong bending behavior of the Alkenes (=C-H) group, respectively. The peak of 931.4cm<sup>-1</sup> represents the stretching behavior of =C-H group, respectively. The sharp peak at 1214.3cm<sup>-1</sup> indicates the vibration of a Carbonyl (C-O) group, respectively. The blunt peak at 1322.8 represents the vibrating behavior of a methyl (C-H) group, respectively. The peak at 2151.4cm<sup>-1</sup> represents the triple bond of the C≡C group, respectively. The peak at 3945.7cm<sup>-1</sup> represents a strong vibration of a hydroxyl (O-H) group, respectively. The absence of an additional peak in the spectrum suggests that the compound is free of elemental contaminants.



In the Figure S3b, the red wavelength represents Guar gum, and the black wavelength represents Xanthan gum. A blunt peak in guar gum present at 651.4cm<sup>-1</sup> represents a vibration of a hydroxyl (O-H) group, respectively. A sharp peak in Guar gum present at 847.1cm<sup>-1</sup> represents the stretching behaviour of a Carbonyl (C-O) group, respectively. The peak present at 908.5cm<sup>-1</sup> corresponds to the behaviour of Alkenes (=C-H) group, respectively. The peak present at 1200.0cm<sup>-1</sup> represent the stretching behaviour of a C-N group. The peak at 2252.8cm<sup>-1</sup> represent a vibration behaviour of a triple bond of C=C group, respectively. The peak at 2605.7cm<sup>-1</sup>, 3595.7cm<sup>-1</sup> and 3885.7cm<sup>-1</sup> represents a stretching vibrating behavior of a hydroxyl (O-H) group, respectively. The blunt peak present at 921.4cm<sup>-1</sup> corresponds to the stretching behavior of a Carbonyl (C-O) group, respectively. The peak at 2990cm<sup>-1</sup> represents a bending behavior of a methyl (C-H) group, respectively. The peak at 3795.7cm<sup>-1</sup> and 3997.2cm<sup>-1</sup> represent a stretching vibration of a methyl (C-H) group, respectively. The absence of an additional peak for each spectrum suggests that the compounds are free of elemental contaminants.



S4: Oil recovery performance after waterflood (a. HAPAM, b. Xanthan gum, c. Guar gum).