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Comparative Analysis of Synthetic and Natural Polymer for Enhanced Oil Recovery

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***Abstract*-**Polymer flooding has proven to be effective in mobilizing residual oil by increasing the viscosity of the displacing fluid, making the displacing fluid more viscous than the displaced fluid. This results in a favourable mobility as the sweep efficiency is increased, thereby contributing to an additional oil recovery of about 20%. Almost all the polymers currently in use are chemically synthesized and imported. However, recent studies have shown that local materials capable of acting as biopolymers have high potentials in enhancing oil recovery. This has attracted more interest due to their low cost, availability and environmentally friendly nature. Therefore, this study was conducted with the aim of comparing the sweep efficiency of certain local polymers and a commonly used synthetic polymer. Three different local biopolymers namely Pectin, Jute leaf (Corchorus) and Terminalia mantaly with synthetic polymer, Polyacrylamide were evaluated in the laboratory at reservoir conditions in the presence of divalent ions. Two synthetic brines with a Total Dissolved Solids (TDS) of 30,000 ppm was prepared in the laboratory to simulate actual formation brine. Aqueous stability test was performed to determine the fluid compatibility with different brines at an increased temperature of about 80 ˚C. Certain rheological properties of the polymers were determined at varying temperature range (30 ˚C - 90 ˚C). Using sandstone core plug, an oil displacement test was conducted to determine the oil recovery factor. Local polymer, Terminalia mantaly resulted in a higher percentage recovery (90%) than Polyacrylamide (81%) at increased temperature of 80 ˚C and in the presence of divalent ions. This study supports the fact that increased temperature and the presence of divalent ions result in mechanical degradation of polymer thereby reducing the sweep efficiency of the polymer. However, local polymer, Terminalia mantaly is less susceptible to these reservoir conditions and if its viscosity is improved upon, it can become a suitable replacement to synthetic polymer, Polyacrylamide during polymer flooding.

Keywords- *Local Polymers, Enhanced Oil Recovery, Divalent Ions*

I. INTRODUCTION

In the light of the global energy demand and a rapidly depleting hydrocarbon reserves, the need to increase oil and gas reserves by improving recovery from existing reserves at a reduced production cost and sustain production from producing fields has become increasingly aggressive. The demand for crude oil is increasing as a significant amount of our energy needs is still satisfied by fossil fuels despite the increasing advocacy for renewable energy. Future predictions for global energy demand indicates that fossil fuels will still contribute a greater percentage to the world's energy mix, with about 52% from hydrocarbon sources energy by 2040 (OPEC Report, 2019). It becomes imperative to ensure that residual or trapped oil are not left abandoned but are recovered from the reservoir in order to improve recovery. Chemical Enhanced Oil Recovery which involves the use of chemicals to enhance oil recovery has proven to be an effective oil recovery method, however, the high cost and negative environmental imprint associated with these chemicals has been a major setback. However, recent laboratory studies has shown the effectiveness of certain local materials in acting as chemical enhanced oil recovery agents. These low cost, non-toxic local materials have been characterised and their displacement efficiency have been determined at ambient conditions. With the recent decline in crude oil prices, oil companies are compelled to have a rethink on their production strategies and optimize their expenses in a bid to reduce production cost and maximize profit. These local materials are considered to be a step in attaining these objectives being that they are more cost-effective and environmentally friendly

II. LITERATURE REVIEW

Polymers are long chained organic molecules with high molecular weight made up of repeating units of monomers that are bonded by a covalent bond (Caenn *et al.*,1989). They are water soluble due to the hydrogen bond between the water molecules and the polar side chain of the polymer. Based on their origin, Polymers are broadly classified into two groups namely; Natural Polymers and Synthetic Polymers. Natural Polymers are mostly gotten from plants and animals sources e.g. Polysaccharides, Proteins and Polyesters while the synthetic polymers are mostly derived from petroleum oil and are man-made e.g. polyethylene. During Chemical Enhanced Oil Recovery operations, the most commonly used polymers are Hydrolyzed polyacrylamides (HPAM) or Polyacrylamide

(PAM) which is a synthetic polymer and Xanthum Gum, a natural or biopolymer (Zerkalov, 2015).

Chemical Enhanced Oil Recovery involves the injection of certain chemicals after secondary oil recovery mechanisms (water flooding) in a bid to increase the capillary number, reduce the value of the interfacial tension between the displacing and displaced fluids, decrease the mobility ratio and improving the sweep and displacement efficiencies. Polymer flooding is a chemical EOR method that has been practiced for over decades wherein polymers are injected into the aqueous phase (water) and injected into the reservoir to increase the viscosity of the water flood. As a viscosifier, water soluble polymers are injected into the brine after the surfactant slug to increase the viscosity of the displacing fluid and decrease the relative permeability of water in the reservoir. This increases oil recovery resulting from an increase in the fractional flow. Water flooding without polymer results in an unfavourable displacement process, known as 'viscous fingering' where the difference in the mobility of the displacing fluid (water) and the displaced fluid (oil) is greater than one (Zerkalov, 2015). During waterflooding, injected water/brine flows through zones of highest permeability of the production well. If such oil reservoirs contain oil with higher viscosity than the injected brine, a situation called unfavourable mobility ratio occurs where the water bypasses through the oil resulting in low sweep efficiency. This effect is detrimental to oil recovery as the displacing fluid quickly reaches the production well without mobilizing or displacing the oil (displaced fluid).

However, the addition of polymers (polymer slug) during tertiary recovery continuously over an extended period to attain the desired pore volume (Abidin *et al.*,2012) will result in a favourable mobility ratio because the polymers increases the viscosity of the displacing fluid, thus, it is able to push the residual oil bank ahead of it oil towards the production well thereby attaining a higher sweep efficiency and a mobility ratio that is less than unity. Their application not only increases the viscosity of the aqueous phase (displacing fluid) but also, improves mobility control, reduces relative water permeability in the formation. In general, polymer solutions behave like pseudoplastic fluids wherein the fluid viscosity is often classified as shear thinning. (Sheng, 2011). Polymer flooding is best used in an oil reservoir with temperature less than 72 degrees Celsius with oil viscosity less than 100 centipoise and in low to moderate salinity reservoirs (Uzoho *et al.*,2015). The most important property of a polymer is its viscosity, since the principal function of a polymer solution is to increase the viscosity of the displacing phase, any factor that affects the viscosity of the polymer will invariably affect its performance or ability to enhance oil recovery. Sheng (2011) reported that HPAM solutions display convincingly higher viscoelasticity than biopolymer solutions at equal concentrations in freshwater but are sensitive to salinity because the addition of salt shields ionic charge and reduces repulsion which then constricts their molecular chain and lowers viscosity. Therefore, their viscosity is lower at salinities above 10000 ppm TDS. He further reported that biopolymers are better polymers than anionic polyacrylamides (PAM) because they are less susceptible to salinity and mechanical shear giving rise to a higher viscous fluid at salinities greater than 10000 ppm compared to polyacrylamides. Sheng (2011) also noted that divalent ions have a higher effect than monovalent ions even at equal concentrations.

Recent studies have shown that these biopolymers can also be sourced from locally grown agricultural products such as *Abelmoschus esculentus, Irvingia gabonensis, Lasianthera africana*, common beans to mention a few. Osuji *et al.*, 2012 ascertained the effectiveness of these local polymers in recovering residual oil and could perform better than the synthetic polymers if improved upon (Ogolo *et al.*,2015). Adebayo *et al.*, (2012) also reported the effectiveness of local polymers (Okro, Ogbono, and Gum Arabic) in improving sweep efficiency with Okro having the best recovery. However, the effectiveness under certain difficult conditions must be evaluated to ascertain its ability to completely replace the synthetic/ foreign polymer chemicals.

This objective of this paper was to compare the tolerance level as well as the sweep efficiency between certain local polymers and synthetic polymer at recovery agents during polymer flooding.

III. METHODOLOGY

Three local biopolymers were used in this experimental study namely: *Corchorus olitorius* (Jute leaf), Pectin and *Terminalia mantaly*. *Corchorus olitorius* is a natural polymer having lipophilic and hydrophilic extract with fibrous roots. This thick, slimy leaf was air dried and pulverised. Resin from *Terminalia mantaly, is* a natural polymer similar to gum Arabic with high concentrations of saponins. It was soaked in distilled water for days and stirred mechanically to form a paste. Pectin is a structural hetero polysaccharide contained in the primary cell wall of terrestrial plants (citrus fruits) where it helps to bind the cells together was commercially obtained. Chemicals used for the formulated brine were purchased from local suppliers. Two types of brines (Hard and Soft Brine) were prepared in the laboratory to simulate actual formation brine. The soft brine contained varying concentrations of sodium chloride and potassium chloride with total dissolved solids of 30,000 ppm and a salinity of 3.0%. The hard brine contained varying concentration of sodium chloride, potassium chloride, calcium and magnesium chloride and a total dissolved solid (TDS) of 30,000 mg/l with 8,000 mg/l being concentrations of the divalent ions: Ca^{2+} and Mg^{2+}. The crude oil used during this study was a medium crude from an oil field in the Niger Delta region of Nigeria. Its physical properties are shown in Table 1:

TABLE I. PHYSICAL PROPERTIES OF CRUDE OIL

Density @ 27°C	$0.92 g/cm^3$
API Gravity	21.1˚
Viscosity	48.64cP @ 31˚C
Colour	Brownish black
pH	6.2

A series of phase behavior test was conducted for the brine-polymer system to ascertain the compatibility of the system under varying concentration in the presence of divalent ions.

Aqueous stability test was performed to determine the fluid compatibility with different brines at various concentrations under an increased temperature of about 100 ˚C. Certain rheological properties of the polymers such as viscosity, gel strength and shear rate were determined at varying temperature range (30 ˚C-100 ˚C) using a viscometer and a rheometer. A core flood set up was used to carry out the oil displacement analysis using a sandstone core plug with an absolute porosity of 27% and a pore volume of 14.02 at reservoir temperature of 80 ˚C.

IV. EXPERIMENTAL PROCEDURES

A. *Aqueous Stability Test*

To analyse fluid-fluid interactions, an aqueous stability test on the three-different polymers and the two brine solutions was performed to determine the presence of any non-homogeneity such as phase separation, cloudiness, and precipitation in the aqueous phase. Varying concentration of the selected polymer (0.1%, 0.5%,1.0%) was mixed in 100 ml of hard and soft brine into test-tubes, sealed to avoid evaporation and visually inspected, cloudy samples containing solids such as precipitates was considered incompatible and failed the screening as only clear, cloudless fluids were selected.

B. *Polymer Rheology Test*

The rheology investigation was carried out on the selected local polymers to determine the viscosity of each polymer solution, the effect of polymer concentration on its viscosity and the effect of temperature on the viscosity of each of the selected polymers.

C. *Procedures for the Rheology Test*

- About 5 grams of each of the selected polymers were used to measure their viscosity at varying temperature ranges.
- Clean the viscometer with water and afterward with alcohol, make a polymer solution with the brine. Using the pipette, drop the amount of polymer solution into the viscometer taking note of the time and temperature.
- The gap size on the rheometer was set to 0.150.
- The computer was set to show a variation from very low shear rate (0.01) to enable the graph shows the Newtonian and Non-Newtonian fluid behaviour.
- A small quantity of polymer solution (enough to fill the required space) was slowly poured on the circular metal plate.
- Once the experiment was run the top metal cone automatically moves down touching the bottom metal plate.
- Each performed test takes between 4 to 7 minutes depending on the shear rate variation.
- Each test was performed at five different temperature ranges, 32 ˚C, 55 ˚C, 70 ˚C, 88 ˚C and 93 ˚C (which is the equivalent of 200 ˚F).

D. *Oil Displacement Test*

Oil displacement analysis was performed to ascertain the recovery factor of these polymer agents on residual oil recovery using sandstone core samples with respect to permeability change, sweep efficiency and incremental oil recovery. The displacement tests consisted of three sequential experiments; Secondary, Tertiary and Chase brine flooding.

E. *Core Flood Procedures*

- Weigh the dried core sample using a measuring scale.
- Using Vernier calipers, measure the diameter and length of the core.
- Determine the density of the brine and then immersed the core sample in the brine and leave in a saturator for 48hours to ensure full saturation.
- Reweigh the core sample and record the difference in weight, calculate the pore volume, bulk volume and porosity.
- Insert the core sample into the core holder in a horizontal position.
- The desired reservoir temperature (80 ˚C) was set manually and allowed to build up into the system. A flow rate of 1 cc/min was used.
- As the reservoir conditions were attained, the experiment began with readings of differential pressure recorded every minute until a steady differential pressure was attained.
- The core flooding experiment began with the displacement of the brine using crude oil. This is usually termed drainage or desaturation process. Oil is used to displace the formation brine at 1.4PV until the first drop of oil is seen. Record the volume of displaced brine which is used as the original-oil-in-place (OOIP).
- Secondary oil recovery or imbibition was performed using hard or soft brine as the displacing fluid at 10 PV to displace crude oil until the first drop of brine is seen and no more oil is recovered. Residual oil saturation was calculated.
- Polymer flooding as a tertiary oil recovery method was used to recover residual oil. A solution of polymer 2 PV was injected continuously into the slug and used as a displacing fluid to enhance oil recovery. The experiment was continued until an oil cut of less than 1% was achieved.

V. RESULTS AND DISCUSSION

Aqueous stability test was conducted on the four selected polymers (three local polymers and one synthetic polymer) in soft brine. This produced clear, compatible solutions devoid of precipitates at reservoir temperature of 100 ˚C as shown in Table 2.

TABLE II. PHASE BEHAVIOUR OF POLYMERS

Polymers	Concentration (%)	Results @ 30˚C	Results @ 100˚C
Corchorus olitorius	0.2, 0.5, 1.0, 1.5	As concentration increased slightly, more particles formed at the base	Compatible solution with coagulated debris formed on top.
Pectin	0.2, 0.5, 1.0, 1.5	Slightly cloudy solution with little debris at the base	An increase in temperature results in clear, cloudless solution with no debris
Terminalia mantaly	0.2, 0.5, 1.0, 1.5	Clear solution over all concentration ranges	Clear solutions over all concentration ranges
Polyacrylamide	0.2,0.5,1.0,1.5	Clear solutions	Clear solutions

However, as the temperature reduced, the debris of *Corchorus olitorius* had coagulated together floating at the top of the solution. Similar compatibility test was carried out on the same polymers in hard brine, this resulted in cloudy solutions especially with the synthetic polymer, Polyacrylamide. This is due to the effect of divalent ions as reported by Sheng (2011). As temperature increased to about 100 degrees celsius, the polyacrylamide solution became slightly less cloudy. Results showed an increase in solubility for all local polymer type as temperature increases. At reservoir temperature of 100 ˚C, all polymer solutions produced clear solutions. The divalent ions had no effect on the compatibility of the local polymers with formation brine while in the case of Polyacrylamide, the effect of divalent ions was minimal. The viscosity of all polymer solutions showed an increase in viscosity as their concentration increased. This is in line with the findings of Sheng (2011) where he noted that the viscosity of the polymer solution is proportional to its concentration where the viscosity tends to increase with a small increase in polymer concentration. The polymer concentration is directly influenced by the number of carbon present in its chain structure therefore a higher molecular chain holds a higher molecular weight in which provides a higher performance. Results from Figure 1 show that synthetic polymer, Polyacrylamide is more viscous than all the local polymers at ambient conditions. Local polymer, *Terminalia mantaly* showed a higher viscosity than the other local polymers with *Corchorus olitorius* having the least viscosity. Figure 2 shows a plot of polymer viscosity as a function of temperature at 500 ppm. As seen in the plots, the viscosity of the synthetic polymer, polyacrylamide reduced gradually as temperature increased while the viscosity of the local polymer solutions increased gradually as temperature increased. This underscores the high tolerance bio polymers have on temperature compared to synthetic polymers. *Terminalia mantaly* maintained a high viscosity cut across all temperature ranges, followed by Pectin.

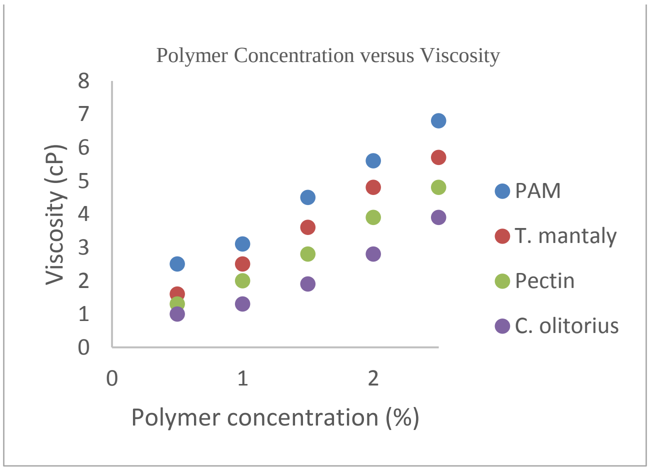

Figure 1. Effect of Polymer Concentration on Polymer Viscosity

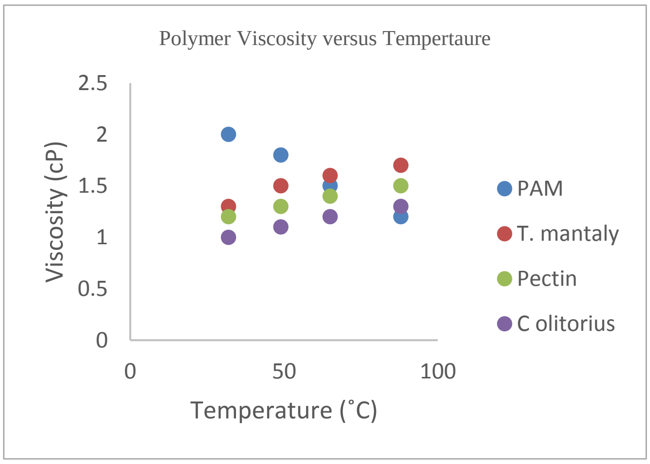

Figure 2. Effect of Temperature on Polymer Viscosity

Based on the results obtained from the compatibility and rheological analysis of the local and synthetic polymers at both ambient and reservoir temperature, two local polymers namely; *Terminalia mantaly* and Pectin as well as synthetic polymer, Polyacrylamide were selected to proceed to the next phase of core flooding analysis.

Sandstone core flooding using the individual polymer agents to enhance oil recovery at reservoir temperature of 80˚C was conducted. Polymer flooding as seen in Figure 3 showed an increase in sweep efficiency as the polymer concentration increased, implying that the higher the concentration, the higher the viscosity, the higher the sweep efficiency of the polymer. *Terminalia mantaly* gave a higher percentage recovery than Polyacrylamide and Pectin. The increase in the percentage oil recovery between 1wt.% and 2 wt.% *Terminalia mantaly* was minimal.

Of the three selected local polymers, *Terminalia mantaly* has a higher tolerance to divalent ions as shown in Figure 4.

Divalent ions had a negative effect on the displacement efficiency of Pectin and Polyacrylamide mainly because the divalent ions shields the repulsive forces of the carboxylic group(-coo-), thus the stretch is reduced and the viscosity of the polymer is reduced. These carboxylic group is supposed to reduce adsorption of polymer to the rock surface (Sheng, 2011).

This implies that presence of divalent ions increases the adsorption of polymer and therefore reduces its concentration and in turn its recoverability.

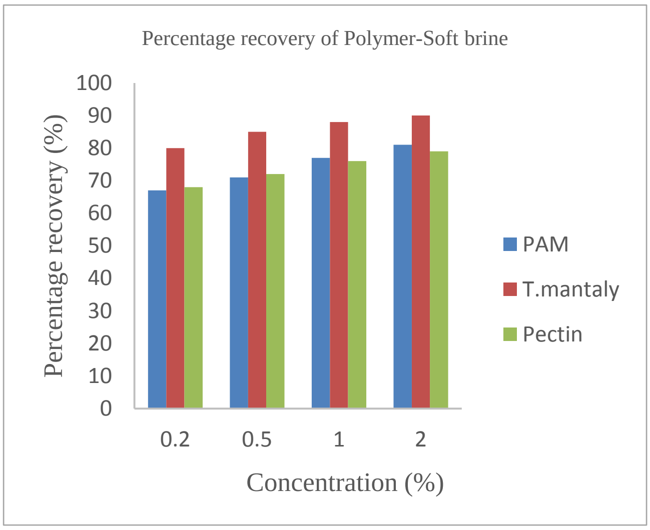

Figure 3. Plot of Polymer-Soft brine versus Percentage recovery

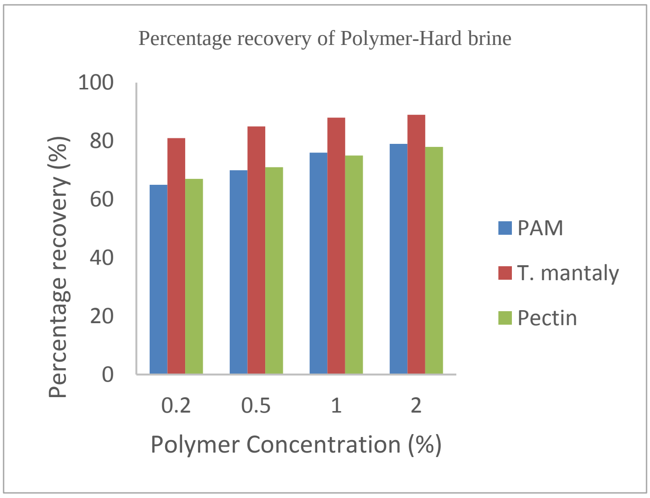

Figure 4. Plot of Polymer-Hard brine versus Percentage recovery.

This study supports the fact that increased temperature and the presence of divalent ions result to mechanical degradation of the polymer solution especially the synthetic polymers, thus reducing the viscosity of the polymer solution thereby reducing its sweep efficiency. However, the local polymer is less susceptible to these reservoir conditions. If its viscosity is improved upon it will serve a good replacement to the synthetic polymer due to its availability, low cost and eco-friendly nature.

CONCLUSIONS

The following conclusions were drawn from this study:

- Results showed that the local and synthetic polymers were compatible with soft brine, while compatibility with hard brine was highly controlled by temperature.
- Rheological analysis of the local and synthetic polymers showed that synthetic polymer, Polyacrylamide is more viscous than the local polymers, however, Terminalia mantaly had a higher viscosity compared to the other local polymers.
- Results obtained from sandstone core flooding showed that the presence of divalent ions in the brine impedes oil recovery resulting in reduced oil recovery.
- Polymer flooding with soft brine gave a higher displacement efficiency compared to hard brine flooding due to the presence of divalent ions.
- Under reservoir conditions of 80˚C, polymer flooding at 2wt.% Polyacrylamide gave a percentage recovery of 81% and 79% in soft and hard brine respectively while local polymer, Terminalia mantaly at 2 wt.% gave a percentage recovery of 90% and 89% in soft and hard brine respectively.
- The results showed that local polymer, Terminalia mantaly performed slightly better than the synthetic Polyacrylamide in soft brine as well as in hard brine under reservoir conditions.

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