EFFECTIVENESS AND EFFICIENCY OF POLYMERS IN ENHANCED OIL RECOVERY OF HIGH WATER CUT RESERVOIRS OF VARYING SALINITIES AND TEMPERATURES VIA RESERVOIR SIMULATIONS

A Thesis

by

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ABSTRACT

The world’s energy demand is increasing and all indications are that oil will be the leading energy supply for the foreseeable future. However, a significant amount of the world’s ‘easy to produce oil’, has been produced. Additionally, some of the remaining oil is rendered immobile due to capillary forces (residual oil) and some oil will be bypassed and remains trapped (bypassed oil) even after a reservoir has undergone secondary recovery. This remaining oil can account for 45- 70% of the original oil in a hydrocarbon reservoir. Therefore, methods to both improve and enhance oil recovery are highly sought. Enhanced oil recovery methods serve to recover such oil through techniques such as: thermal recovery, gas injection, and chemical injection. The latter is the subject of this thesis. Chemical injection involves the use of a surfactant to reduce the surface tension between the oil and the oil bearing rock layer and/ or polymers to increase the viscosity of the injected fluid and thereby improving sweep efficiency and mobility of oil, thus increasing production. In general, the polymers are not effective in removing residual oil and has some associated problems. Conventional polymers have been reported to plug oil reservoirs, biodegrade (biopolymers), or become impuissant in reservoirs with high salinity or high temperatures. Therefore a better solution is needed. This project will evaluate the effectiveness and efficiency of a cassava starch- based polymer with the aim of increasing producibility of residual and bypassed oil, while eliminating negative effects of conventional polymers. Laboratory experiments and computationally efficient models will be employed to simulate the physical performance of the starch- based polymer in reservoir regimes of varying salinities and temperatures. Lastly, a sensitivity analysis will be undertaken to compare the recovery factor, concentration and profitability of starch- based polymer to that of two conventional polymers (Xanthan Gum and Hydrolysed Polyacrylamide (HPAM)).

Through the above methods, it was observed, that when compared to conventional HPAM and Xanthan Gum polymers, the cassava starch- based polymer provides substantive viscosities at low concentration, is more effective in high salinity and high temperature regimes than Xanthan Gum and HPAM but is highly susceptible to biodegradation unless treated with additives. In addition, the oil production capability is comparable to HPAM and Xanthan gum. Residual oil production was inconclusive, pending core flooding experiments.

DEDICATION

For inspiring my creativity, believing in me and encouraging me to do my best- the first time. I dedicate this thesis to my father and mentor, Frederick Paul Garcia, who passed away in April 2016. You were not here physically, but your spirit saw me through.

Trisha – The nobody

CONTRIBUTOR AND FUNDING SOURCES

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This work was supervised by a thesis committee consisting of Dr. Arash Noshadravan, adviser, of the Department of Civil Engineering, Professor Bruce McCarl, Co-Chair, of the Department of Agricultural Economics and Dr. Sara Abedi, committee member, of the Department of Petroleum Engineering.

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NOMENCLATURE

λ	Mobility
M	Mobility Ratio
a	Adsorption Coefficient
B	Formation Volume Factor
Ca	Polymer Adsorption Concentration
Nca	Capillary Number
O	Oil
W	Water
S	Saturation
E_r	Overall Recovery
E_d	Displacement Efficiency
E_v	Vertical Sweep
E_p	Pattern Efficiency
E_s	Macroscopic Sweep
$\dot{m}$	Mass Flux
$\acute{m}$	Source Or Sink Rate
U	Velocity
μ	Viscosity Or Viscosity Multiplier
σ	Surface Tension
θ	Wetting Angle
σ	Interfacial Tension

ρ	Density
φ	Porosity
q	Volumetric Source Term
α	Reservoir Phase
K	Permeability
K_r	Relative Permeability
RRF	Reservoir Reduction Factor
P	Polymer
Rs	Solution Gas- Oil Ratio

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1 INTRODUCTION

The world's energy demand is increasing and according to the BP Energy Outlook (2017), oil will be the leading energy supply for the foreseeable future. The average lifespan of an oil field is 15- 30 years. During that time, several things can happen to deter oil production, including: oil depletion, political instability, oil price instability, technical operations, natural geological phenomena, formation water encroachment etc. As a means of slowing the inevitable oil depletion, reservoirs engineers often employ improved oil recovery (IOR) techniques to attempt to produce oil left behind in the reservoir after primary production. Improved oil recovery is an umbrella term that includes any practice employed to the oil field or well in order to improve oil production, including infill drilling, hydraulic fracturing, enhanced oil recovery methods etc. (glossary.oilfield.slb.com, (2018)). This is particularly done to improve oil sweep efficiency (Sorbie, 1991) by injecting water or gas into oil formations to propel the oil towards the production well. However, oil is still left in the reservoir after secondary production either because it is trapped by capillary forces (residual oil) or it was bypassed (Sorbie, 1991). This unrecovered oil can account for a significant portion (up to 70%) of the total initial oil in the reservoir and as such if recovered can contribute significantly to the total revenue stream of the extracting company. Generally, tertiary or enhanced oil recovery (EOR) methods are utilized to extract this oil. Enhanced oil recovery is a subset of IOR and is defined as a sophisticated technique employed for the purpose of enhancing formation pressure, improve oil displacement or fluid flow in a reservoir; depending on the reservoir temperature, pressure, permeability, porosity, residual oil and water saturation, oil viscosity etc. (glossary.oilfield.slb.com, (2018)).

According to the United States Office of Fossil Energy (2012), three EOR methods have been commercially successful to date. These include: Thermal Recovery, Gas Injection and Chemical Injection. Thermal recovery is used primarily with heavy oils and accounts for more than forty percent of total EOR production. It involves the injection of steam to lower the viscosity of the oil and thus allowing flow to the production well; however, this is restricted in applicability to locations with a natural thermal energy source.

Gas Injection takes two forms depending on the gas used. 1. Carbon Dioxide and natural gas are mixed and injected into unrecovered oil reservoir and they then mix with oil, lowering the viscosity facilitating flow to the production well; 2. Other gases are injected that subsequently expand and in turn pushes oil towards the well. Production using gas injection accounts for sixty percent of the U.S. oil produced via EOR.

One form of chemical injection EOR is polymer EOR, which is the subject of this thesis. It, is the most popular Chemical EOR method and uses conventional polymers, the most widespread of which are, Poly-acrylamide and Xanthan Gum. Alkali-Surfactant Polymer EOR is also utilized, but less so. Polymers are used in conjunction with water to improve oil sweep efficiency. Oil sweep efficiency is defined as the fraction of the reservoir section contacted by the injection fluid. However, some negative effects are associated with them. In particular, Xanthan Gum tends to biodegrade and has been reported to plug formations due to cellulose content, effectively lowering relative permeability to oil and thus reducing the producibility of the oil (Olajire, 2014).

Polyacrylamide becomes impuissant beyond temperatures of sixty degrees Celsius (Olajire, 2014). Hydrolysed Polyacrylamide can withstand temperatures up to a hundred and twenty degrees Celsius (Olajire, 2014) and when these thresholds are exceeded the polymer becomes ineffective. In addition, the effectiveness of the Polyacrylamides is affected by high salinity regimes and as such are not used offshore (Olajire, 2014).

These factors alter the economics of the EOR process and oil field characteristics preclude use in many places, effectively restricting the use of polymers to certain locations. Thus an alternative form of polymer is needed. This thesis investigates an alternative, namely a cassava-based starch polymer. More precisely, the aim of this research is to investigate the effectiveness of a cassava starch- based polymer under alternative temperature and salinity conditions. In doing this, the mobility ratio and susceptibility to biodegradation of the cassava starch- based polymer, as well as the cost of its use and the extent of production enhancement will be investigated.

2 POLYMER EOR OVERVIEW

In polymer flooding EOR applications, polymers are used to improve the movement of oil throughout the reservoir and to the production well. The concept of mobility and mobility ratio explains this phenomenon. Mobility is defined as relative permeability divided by viscosity (Equation 1). Relative permeability is defined as the ratio of the effective permeability or permeability of a particular fluid at a particular saturation to the absolute permeability of that fluid at total saturation (glossary.oilfield.slb.com, (2018)). Viscosity is the property of a fluid that indicates its resistance to flow (glossary.oilfield.slb.com, (2018)). Therefore, mobility is the amount of resistance to flow through a reservoir rock, which a fluid exhibits, at a given saturation of that fluid (Petrowiki.org, (2018)). Seeing that viscosity is in the denominator, intuitively, a fluid with a higher viscosity (a thicker fluid) has a lower mobility. Mobility ratio (M) (Equation 2.) is the ratio of mobility of the displacing fluid (i.e. water or polymer) to the mobility of the fluid to be displaced (i.e. oil). When M is greater than 1, water has a higher Mobility, moves faster and is thus produced faster than the oil. This is undesirable. When M is less than 1, the oil has a higher mobility compared to water, moves faster and is thus produced faster than water. The latter is referred to as favourable mobility ratio and is essential for a higher oil recovery. Ideally, the water viscosity should be more than the oil viscosity for effective waterflooding. In polymer flooding, the water phase is replaced by the polymer phase (Equation 3).

$$\text{Mobility=} \qquad \lambda_{\boldsymbol{\alpha}} = \frac{K_{\alpha}}{\mu_{\alpha}}$$

Equation 3: Phase Mobility

$$\text{Mobility Ratio(M)} = \frac{\frac{K_{\mathbf{w}}}{\mu_{\mathbf{w}}}}{\frac{K_{o}}{\mu_{o}}} = \frac{\lambda_{\mathbf{w}}}{\lambda_{\mathbf{o}}}$$

Equation 1: Oil- water Mobility Ratio

$$\text{Mp} = \frac{\frac{K_{\mathbf{p}}}{\mu_{\mathbf{p}}}}{\frac{K_{o}}{\mu_{o}}} = \frac{\lambda_{\mathbf{p}}}{\lambda_{\mathbf{o}}}$$

Equation 2: Oil- polymer Mobility Ratio

Term definition for equations 1- 3

α– Reservoir phase

O- Oil

W- Water

P- Polymer

M- Mobility ratio

K- Relative Permeability

μ- Viscosity

λ- Mobility

However, conventional polymer EOR only addresses removal of bypassed oil and does not address the oil left behind by capillary forces (residual oil), which is a function of wettability, as in (Equation 4.) (Sorbie, 1991). Wettability is defined as the preference of a solid to be in contact with a particular fluid (phase) over the other due to surface and interfacial forces (Schlumberger, 2017). Wetting phase is described as water- wet, oil- wet or intermediate. Bypassed oil arises because of an unfavourable mobility ratio or because of large- scale heterogeneities such as stratification or channeling in the reservoir (Sorbie, 1991). The unfavourable mobility ratio occurs because the viscosity of water, in a water flood, is significantly lower than that of oil; and is therefore not able to push all the oil towards the production well, leaving some behind as in Figure 1. Therefore polymers are introduced to make the water flood more effective (more viscous) thus displacing the oil.

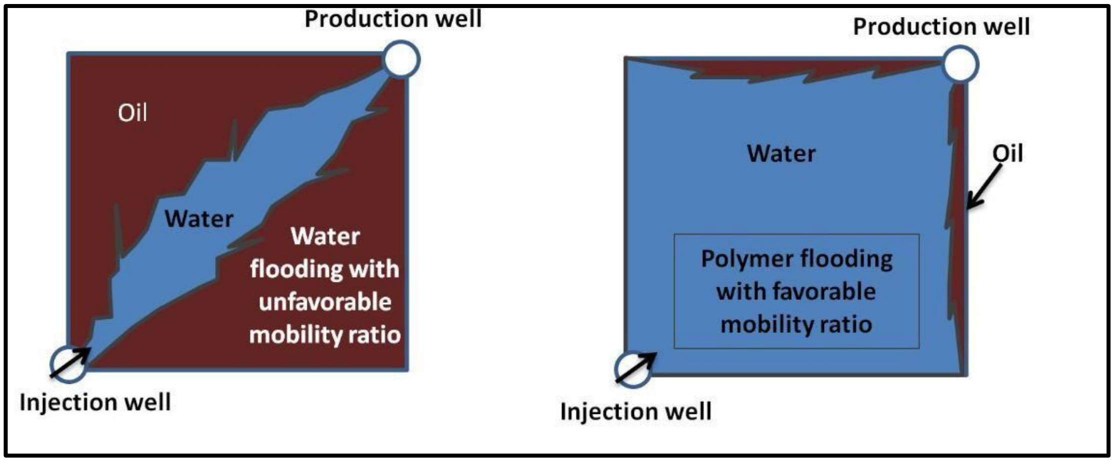


Figure 1: Water Flooding Showing Viscous Fingering (left) and Polymer Flooding Showing Good Reservoir Sweep (right) (Adapted from Zerkalov G. Stanford University).

Equation 4: Capillary Number

$$N_{ca} = \frac{\nu \times \mu}{\sigma \times \cos(\theta)}$$

Term definition for equation 4

N_{ca}- Capillary number
V- Velocity
μ- Viscosity
σ- Surface tension
θ- Wetting angle

Surfactants are generally utilized to lower the surface tension in the reservoir, in order to allow the production of residual oil. Surfactants are defined as a chemical that preferentially adsorbs at an interface, lowering the surface tension or the interfacial tension between fluids or between a fluid and a solid (Schlumberger Oil Field Glossary). Therefore, one of the aims of this project is to create a polymer that is able to significantly improve water flood properties and lower oil to rock surface tension in order to facilitate the production of residual oil as well as bypassed oil.

The concept of residual oil, water/ oil saturations, capillary forces and relative permeability is best illustrated through the relative permeability curve below (Figure 2.). There are several key concepts in the below diagram, however, for our purposes, a water-wet reservoir with an oil and water phase is illustrated, and the relationship between water and residual saturation will be explained.

Firstly, some water is held in a water- wet reservoir, by capillary force. This water is not movable and is referred to as connate water saturation. As a result, the relative permeability to water in this section is zero; as permeability measure the ability of a fluid to flow. However, oil is able to move. In a water flood, water is introduced into the reservoir in order to displace oil i.e. increase the saturation of water and decrease the saturation of oil in the reservoir. This, in essence, reduces the relative permeability to oil and increases that of water. As the saturation of water increases, the saturation of oil decreases, the oil is being displaced and it flows to the production well. However, not all of the oil is able to be produced, because some of it will be held by capillary forces. This is referred to as the residual oil saturation. As a result, the relative permeability to oil in this section is zero. In order to get the oil to move, the capillary force must be increased by decreasing surface tension. The latter is usually the job of surfactant; however the ability of the cassava starch- based polymer, to produce this residual oil will be evaluated.

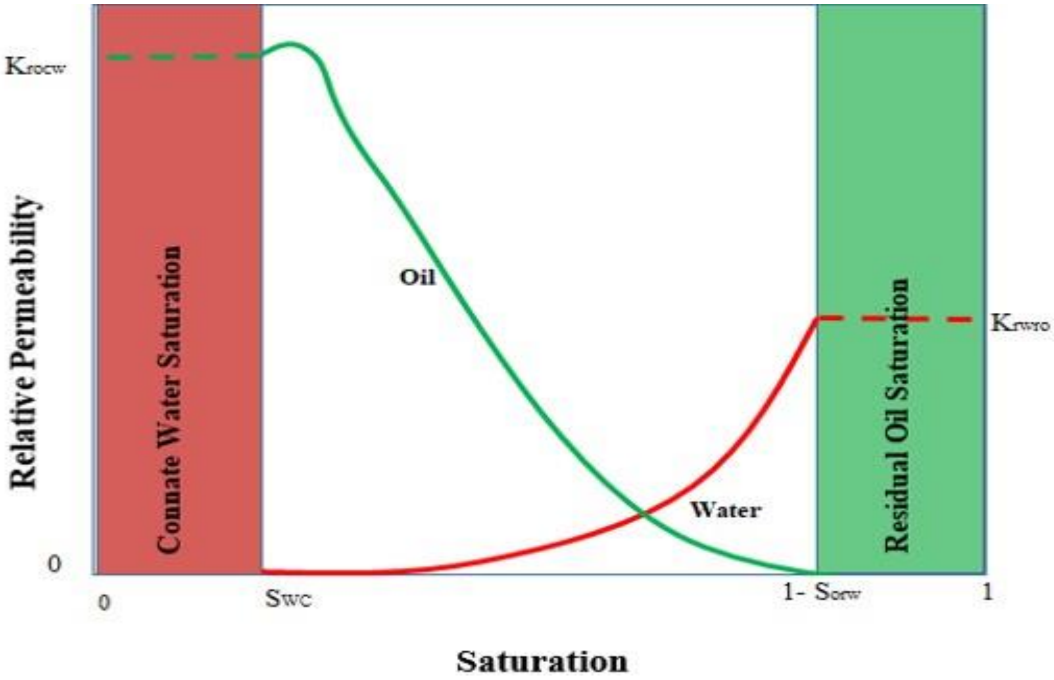


Figure 2: Water - Wet Relative Permeability Curve

Term definitions for Water - Wet Relative Permeability Curve Above

K_{rocw}- Relative permeability to oil at connate water saturation

K_{rwro}- Relative permeability to water at residual oil saturation

S_{wc}- Connate water saturation

S_{orw}- End point of water oil imbibition

3 RESEARCH PROBLEM DESCRIPTION

3.1 Literature Review Search Strategy

Initially, information from professional journals and popular books relating to the broad topic of ‘Polymer enhanced oil recovery” were sought. As this particular polymer is an unconventional one, there is not a wealth of specific information available. Therefore, the literature was reviewed so as to get a general understanding of the intricacies involved and the methodology used to perform polymer enhanced recovery. Including: a) the advantages and disadvantages of using polymers on a whole and that of particular conventionally used polymers; b) the parameters that affect the effectivity of conventional polymers including: shear stress, temperature, and salinity that might also affect that of the starch- based polymer; c) the economics of conventional polymer and d) the chemistry and characteristics of starches that can possibly make it a suitable candidate for polymer EOR. Thereafter, articles addressing starch-based polymer experiments and composition, were sought. These articles were related to the science of polymer EOR, parameters of polymers that can be altered in order to achieve better oil yields, specific threshold within which conventional polymers can operate and polymer EOR simulation models. Lastly, information relating to the productivity and the practicality of using cassava plant were analysed. These resources were primarily obtained from online resources. No date restriction was placed on the articles.

3.1.1 Questions Addressed in the Review

A number of research questions were formulated to act as a guideline to the literature review:

1. Why is there oil left behind after secondary recovery?

2. Why and how does polymer enhanced oil recovery increase production of the oil left behind?
3. What reservoir characteristics and parameters limit the effectiveness of polymer enhanced oil recovery?
4. What are the limitations of conventional polymers?
5. Are starch-based polymers used in enhanced oil recovery?
6. What type of starch- based polymers are currently being used or could be used in EOR?
7. What are some of the positive/ negative effects of using polymers, particularly cassava starch- based polymers?
8. What are the materials needed to create the polymer and are they widely available or easily accessible and economical?
9. How are Cassava-based polymers produced and how would they be introduced through an injection well?
10. What are the costs and benefits of using cassava as the basis for a polymer used in enhanced oil recovery?

3.2 Findings Arising in the Literature

3.2.1 Polymer Effect on Overall Recovery of Incremental Oil via Waterflooding

Starch is generally used as a thickening agent and as sizing material. This same concept is used when considering starch- based polymers for EOR applications, in that, it increases the viscosity of the injecting fluid relative to oil in the reservoir. The concept of mobility speaks to the latter. Standnes, et al. (2014) states that the way in which polymers are improving oil recovery is strongly linked to the concept of mobility ratio, M, which is a function of viscosity and relative permeability. He concluded that increased viscosity can improve recovery by reducing the propensity of the water to flow more than the oil, thereby, reducing viscous fingering and improving microscopic displacement efficiency (to be discussed below). Sorbie (1991) also attributed an increase in sweep efficiency to an increase in viscosity by effectively decreasing the viscous fingering phenomenon.

In the 1993 AAPG Development Geology Reference Manual, Sarem et al. explained waterflooding and introduced the idea of waterflood recovery. He stated that water flooding is an improved oil recovery method that involves injecting water into an oil reservoir for the purpose of maintaining pressure and displacing and producing incremental oil. Additionally, waterflood recovery or overall recovery (E_r) is a product of the displacement efficiency (E_D), invasion or vertical sweep efficiency (E_V) and the pattern efficiency (E_P).

Equation 5: Overall Recovery

$$\mathrm{Er} = \mathrm{E}_D * \mathrm{Ev} * \mathrm{Ep}$$

Term definition for equation 5.

Overall recovery (E_r)- Fraction of initial oil in place recovered

Displacement efficiency (E_D) - Volume of oil displaced divided by the total oil volume

Vertical sweep or invasion efficiency (E_V) - Fraction of vertical reservoir section contacted by the injection fluid

Pattern efficiency (E_P)- pattern swept by the total pattern area

A British Petroleum (2013) paper enhances the formula by adding an economic efficiency factor (E_C). However, the concept remains the same.

Equation 6: Overall Recovery (British Petroleum, 2013)

$$\boldsymbol{Er = ED * ES * EB * EC}$$

Where the term definitions are drawn from British Petroleum (2013) as follows:

- Recovery factor (E_r) – Volume of oil recovered divided by the volume of oil originally in place before applying EOR.
- Microscopic displacement efficiency ($E_{D)}$ – the fraction of oil displaced from the pores by the injected polymer, in those pores which are contacted by it.
- Macroscopic sweep efficiency ((E_S) – The portion of the connected reservoir volume that is swept by the injected fluid (s) as affected by heterogeneity in the rock permeability and gravitational segregation of the fluids.
- Connected volume factor (E_B)- the portion of the total reservoir volume before EOR that is potentially connected to wells
- Economic Efficiency factor ((E_C) - Physical and commercial constraints on the field life

The vertical sweep efficiency ($E_{V)}$ in Equation 5 and the microscopic displacement efficiency (E_D) in Equation 6 are functions of the mobility ratio (M). In waterflooding, the water phase of the mobility ratio can be altered by replacing it with a polymer phase and thereby introducing viscosities which corresponds to that of polymers. The mathematics will be unchanged

3.2.2 Effectiveness of Polymers in Enhanced Oil Recovery

In the book, Polymer- Improved Oil Recovery by Sorbie (1991), two of the above research questions were addressed. Below are the questions and their associated answers:

1. Why is there oil left behind after secondary recovery? Oil is left behind because it is immobilized and trapped by capillary forces (residual oil) or the oil has been bypassed.
2. Are polymers effective in enhanced oil recovery? The suitability of polymers in recovering bypassed oil has been validated. The issue of the effectiveness of polymer EOR on displacing residual oil is still being debated. The effectiveness of polymers to recover bypassed oil is attributed to a mobility ratio (M) that makes the oil more mobile

than that of the polymer and an increase in capillary number (N_C). From Equation 2 it is apparent that in order to decrease the mobility ratio M, the viscosity of the injected fluid has to be increased. A favourable mobility ratio can also be achieved by pore blocking or by lowering the polymer phase permeability. In the latter, the polymer is used to increase the viscosity of the injected fluid and serves to better displace the oil causing it to flow to the production well by blocking pores and lowering the permeability for the polymer, while not affecting that of the oil. Sorbie (1991) further explained that for a two-dimensional heterogeneous reservoir, an M value of approximately 0.1- 0.3 may be suitable. Therefore, this is the range that we will compare the cassava starch- based polymer performance against.

Capillary number, as described in Equation 4, is increased by lowering the interfacial tension, α. This is usually the job of surfactants, and not polymers, through a surfactant sweep. Sorbie (1991) suggests that a capillary number greater than 10^{-6} is sufficient to mobilize residual oil in a reservoir.

3.2.3 Limitations of Current Polymers

Nasr- El-Din and Taylor (1998) highlight the limitations of two conventionally used polymers (Hydrolysed Polyacrylamide (HPAM) and Xanthan Gum biopolymer) for use in EOR. As stated above, polymers are used to increase the viscosity of the injecting fluid in order to increase the amount of oil retrieved from the reservoir and this is done by influencing mobility. The viscosity of HPAMs increases as its molecular weight increases, if other factors remain constant. High molecular weight HPAMs can also be counter-productive because they degrade easily, lowering their viscosity, due to high shear rates experienced near the injection well and at pumps.

HPAM's viscosity also decreases in the high salinity and temperature environments sometimes experienced in a reservoir.

The higher the molecular weight of HPAM, the more easily it is shear degraded (Sorbie, 1991). High molecular weights, however, are required to produce high viscosities, prefferebly at low concentrations. In addition, the viscosity of HPAM decreases rapidly as salinity or hardness increases (Nasr-El-Din et al.,1998). This is due to shielding of ionic groups, which reduces repulsion and causes chain contraction (Nasr-El-Din et al.,1998).

Xanthan Gum based polymers thrive in high salinity environments and are not affected by high shear rates. However, they are very expensive, susceptible to biodegradation, subject to loss of viscosity in high temperature environments and can be difficult to inject because of high cellulose content (Nasr-El-Din et al.,1998).

Historically, conventional polymers have only been known to be effective in displacing oil with viscosities below 150 centipoise (cP). According to Standnes, et al. (2014), polymers are effective in producing oil with viscosities between 150- 1000 cp. Oil with viscosities higher than this can only be removed through use of other EOR techniques.

Collectively the literature shows that, there are several parameters that affect the effectiveness of polymers for the purpose of EOR; particularly salinity, high temperatures and shear rates. Some of these parameters can be adjusted like shear stress, and some parameters such as temperature and reservoir salinity cannot be altered. These latter field characteristics exclude polymer usage from a wide range of locations. Therefore, it is desirable that the proposed cassava starch- based polymer be should able to perform well over wider ranges of such parameters.

3.2.4 Reservoir Wettability

As stated above, there are properties of a reservoir that cannot be altered via engineering practices. Schlumberger (2017) defines wettability as the preference of a solid to be in contact with one fluid rather than another, due to surface and interfacial forces. Wettability does not describe the saturation state: it describes the preference of the solid for wetting by a certain fluid, given the presence of that preferred wetting fluid (Schlumberger, 2017). This is a very critical characteristic of a reservoir under EOR as it determines how or if an injected fluid will be able to displace the oil, and thus affects oil recovery. If for example, the wetting state of a reservoir is oil wet, the surface of the reservoir rock will have an affinity for oil and as such, a water flooding will serve to channel the water through the centre of the rock pore spaces and some oil will remain on the surface of the rock reducing the amount of oil that can be produced. In the oil- wet reservoir, residual oil remains on the surface of the rock due to capillary forces- and this is the residual oil saturation. Most reservoirs have a combination of water- wet and oil- wet sections. In addition, in a water-wet reservoir, the rock shows a strong affinity for water. This causes oil to remain in large pores and thus can snap off and form individual oil ganglion, which is bypassed oil (Sorbie, 1991). Therefore, wettability affects EOR effectiveness.

Consequently, measuring the wetting preference of the reservoir is essential to determining the best polymer flooding approach. Schlumbergers (2017) suggests two methods for computing wetting preference: the imbibition and the capillary- pressure measurement methods. The imbibition method utilizes the Amott- Harvey imbibition test that measures the amount of fluid that is absorbed by a rock either on its own or by force. This is done by placing a rock sample containing oil into a water filled container and observing it over the period of 10 days. When using the capillary- pressure method, the rock sample is placed into a flow cell, and water is forced through the sample. Then, the sample is assumed to be at residual oil saturation where capillary forces are holding the oil fixed to the rock. The above steps are repeated with oil by placing the rock sample into an oil filled tube then later flooding it with oil under pressure. Thereafter, the water and oil imbibition indices are obtained by dividing the quantity of spontaneous imbibition of water or oil to the saturation change of water and oil. The difference between the water and oil values is the Amott-Harvey Index. This will yield a number between positive one (Strongly water- wetting) and negative one (strongly oil- wetting).

3.2.5 Starch- Based Polymers and its Propensity for Enhanced Oil Recovery

As stated by Johnson et al. (2000), starch is one of the most abundant, naturally occurring biodegradable polymers and is made from polysaccharides: amylose and amylopectin. Starch is used for myriads of applications across different industries. In the petroleum industry, a starch derivative is the primary fluid-loss control additive contained in Mixed Metal Oxide drilling fluid (MiSwaco, 2014). MiSwaco (2014) indicates that the added starch has minimal environmental impact. However, there has not been any specific research on cassava-based starch polymers as an additive to a water flooding process used in EOR.

However, there has been research on the properties and characteristics of polymers that make them effective for EOR. What makes an effective polymer? Kjoniksen et al. (2008) defines an effective polymer as one that exhibits: a) high viscosity at low polymer concentrations, b) low interfacial tension with regards to the oil- phase, c) characteristics that increase the viscosity of the water flood improving volumetric sweep efficiency and d) consistent functionality in high salinity and temperature regimes. Raffa, et al. (2016), states that the features of the polymers used in EOR include: very high molecular weight, resistance to mechanical degradation in shear, complete solubility in water; they added, that these polymers should be inexpensive, non- toxic and able to tolerate high salinities and temperatures.

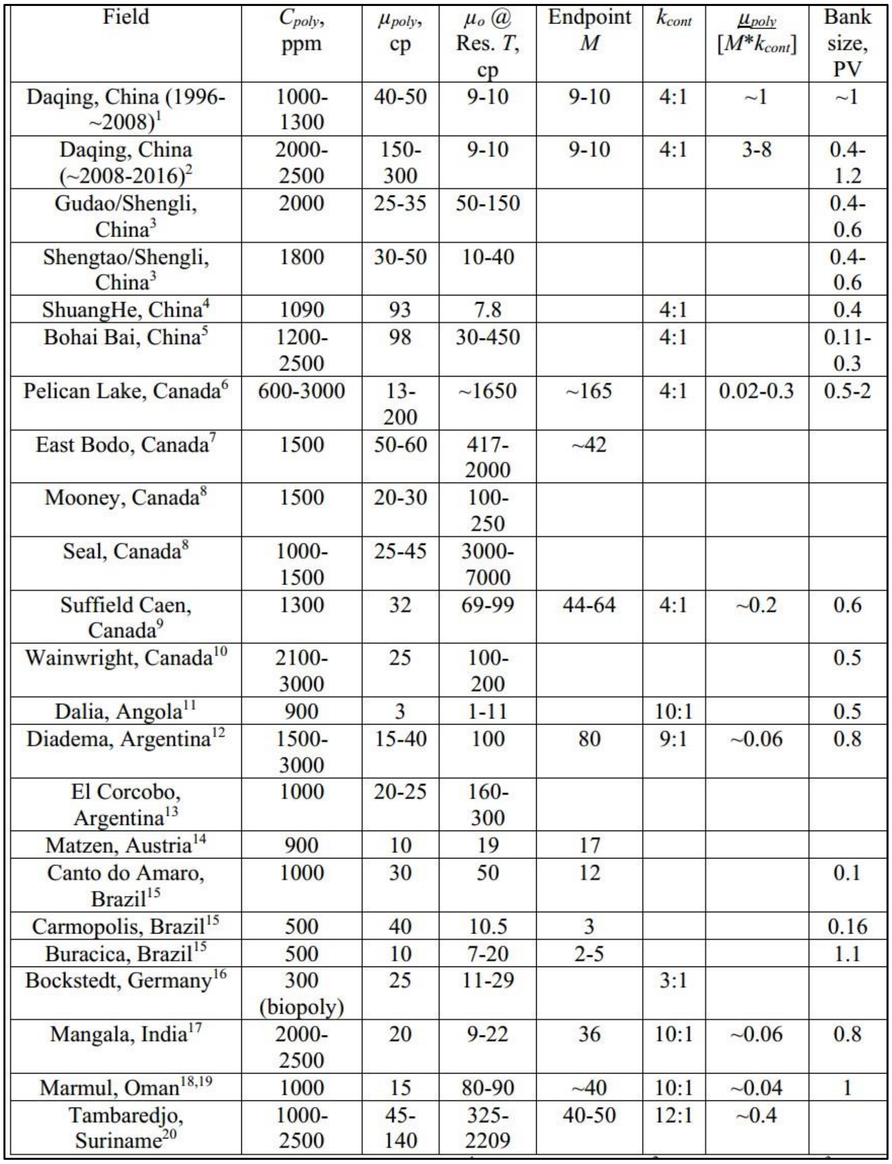
Johnson et al. (2000), states that starch granules exhibit properties that make them react poorly to heat. In particular they have hydrophilic properties and strong intermolecular association via hydrogen bonds due to hydroxyl groups on their granule surface. However, when starch is combined with plasticizers such as water or glycerin then it performs much better under heat. In particular, at temperatures ranging from 90- 180 ^{o}C, and under shear, it readily melts and flows (Johnson et al., 2000). This may be attractive for use in EOR as the thermal stability of starch and its plasticizers is greater than that of the conventional polymers now being used like Xanthan Gum and Polyacrylamide. Those polymers' thermal stabilities are 70- 90 ^{o}C and 90 ^{o}C respectively (Jang et al, 2015). The thermal stability of Polyacrylamide further decreases to 64 ^{o}C when confronted with seawater levels of salinity. Starch also increases the viscosity of its plasticizer. The previously mentioned properties make starch a contender for polymer EOR. The effects of salinity and temperature on this particular polymer will be observed in a laboratory.

3.2.6 Volume and Properties of Polymer in EOR Operations

Sorbie 1992, had established a base case for estimating polymer viscosity as a product of the mobility ratio (M) times the permeability contrast for EOR and estimated the range of polymer mobility ratios to displace a certain viscosity of oil. However, to date, several different approaches have been used with varying rationales. Seright (2017) presented an extensive review of polymers concentrations, viscosities and bank sizes used in industry thus far (Figure 3.). He indicated that for several EOR projects in Canada, they inject 30 centipoise (cp) polymer solutions to displace 1000- 3000 cp oil and in the Daqing oilfield in China, they use 150- 300 cp polymer to displace 10 cp oil.

Seright (2017) concluded that there is no set viscosity, volume of polymer that is injected for EOR purposes, and the basis for the decision is finances. Seright (2017) stated that Wang et al.

(2009) estimates that 20% of the original oil in place in a reservoir can be extracted using 150-300 cp HPAM to displace 10cp oil as opposed to 12% OOIP being displaced by 40 cp HPAM through a polymer flooding mechanism.



Field	C_{poly}, ppm	μ_{poly}, cp	μ_o @ Res. T, cp	Endpoint M	k_{cont}	$\frac{\mu_{poly}}{[M*k_{cont}]}$	Bank size, PV
Daqing, China (1996-~2008)[1]	1000-1300	40-50	9-10	9-10	4:1	~1	~1
Daqing, China (~2008-2016)[2]	2000-2500	150-300	9-10	9-10	4:1	3-8	0.4-1.2
Gudao/Shengli, China[3]	2000	25-35	50-150				0.4-0.6
Shengtao/Shengli, China[3]	1800	30-50	10-40				0.4-0.6
ShuangHe, China[4]	1090	93	7.8		4:1		0.4
Bohai Bai, China[5]	1200-2500	98	30-450		4:1		0.11-0.3
Pelican Lake, Canada[6]	600-3000	13-200	~1650	~165	4:1	0.02-0.3	0.5-2
East Bodo, Canada[7]	1500	50-60	417-2000	~42			
Mooney, Canada[8]	1500	20-30	100-250				
Seal, Canada[8]	1000-1500	25-45	3000-7000				
Suffield Caen, Canada[9]	1300	32	69-99	44-64	4:1	~0.2	0.6
Wainwright, Canada[10]	2100-3000	25	100-200				0.5
Dalia, Angola[11]	900	3	1-11		10:1		0.5
Diadema, Argentina[12]	1500-3000	15-40	100	80	9:1	~0.06	0.8
El Corcobo, Argentina[13]	1000	20-25	160-300				
Matzen, Austria[14]	900	10	19	17			
Canto do Amaro, Brazil[15]	1000	30	50	12			0.1
Carmopolis, Brazil[15]	500	40	10.5	3			0.16
Buracica, Brazil[15]	500	10	7-20	2-5			1.1
Bockstedt, Germany[16]	300 (biopoly)	25	11-29		3:1		
Mangala, India[17]	2000-2500	20	9-22	36	10:1	~0.06	0.8
Marmul, Oman[18,19]	1000	15	80-90	~40	10:1	~0.04	1
Tambaredjo, Suriname[20]	1000-2500	45-140	325-2209	40-50	12:1	~0.4	

Figure 3: Polymer Injection Projects During Recent Years (Adapted from Seright, 2017)

Similarly, Abidin, A. Z (2012) states that “ the ideal properties for mobility control agents can be summarized as follow: 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 m3 /m2 /d flux when entering porous rock), 5 to 10 years stability at reservoir temperature (up to 200 degrees Celsius), resistant to microbial degradation, low retention (e.g., adsorption) in porous rock, effective in presence of oil or gas, and not sensitive to O2, H2S, pH or oilfield chemicals.” Several of these properties will be evaluated in this project. Lastly, Abidin A. Z.(2012) also mentions that “the total cost of polymer flooding is actually less than that of 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.”

4 MOTIVATION FOR RESEARCH

4.1 Objective

This study will examine the feasibility of using the cassava starch-based polymer in enhanced oil recovery. This will be done by comparing the characteristics of this cassava starch-based polymer to conventional polymers with respect to reservoir brine concentrations, temperatures and shear rates and evaluating the relative attractiveness of the cassava starch-based polymer. Secondly, the comparative cost of cassava starch- based polymers will be computed and compared to conventional polymers. To this end, an attempt will be made to identify the total supply chain needed to deliver polymer to the point of mixing and use. This will involve adding the price to produce the volume of polymer needed for EOR on a representative oil field, the starch source, processing costs and transport to the well head. Lastly, the success of any EOR job is the incremental oil it produces; therefore, we will investigate the comparative performance of cassava starch- based polymers versus conventional polymers, in producing oil during EOR activities.

4.2 Hypothesis

Cassava based polymers recover residual and bypassed oil effectively, in an economic manner and perform well in high shear, high salinity and high temperature environments.

4.3 Significance to Industry

One possible outcome of this project is that industry will have a polymer for use in enhanced oil recovery that performs well in high temperature and high salinity environments with shear stability that is economical and environmentally friendly compared to conventional polymers. Another benefit is that a project such as this will provide an alternative market for farmers growing cassava, thus indirectly providing jobs and enhancing incomes.

4.4 Research Strategy

To evaluate the effectiveness of this cassava starch- based polymer, a thorough literature review was conducted to understand the EOR process, define the various parameters of polymers that will be evaluated, and establish how to simulate the properties of the polymer in a reservoir simulator. Laboratory experiments will be done to test and establish the properties of this polymer. Results from laboratory experiments were inputted into an existing reservoir simulator called Matlab Reservoir Simulator that was developed by SINTEF, a company out of Norway and the results analysed. In the simulations, the incremental oil production will be evaluated. In addition, simple cost accounting will be done over the supply chain, from point of cassava production through conversion into a desirable form, through transport to the point where it is mixed for injection inorder to obtain a dollar/ pound value of the cassava starch. Finally, the estimated required volume of polymer needed for an EOR operation will be computed and in turn the amount of cassava needed plus the associated land requirements calculated, then the cassava market will be appraised to determine the availability of that volume of cassava and whether any cassava price increase might occur.

5 RESERVOIR MODEL AND SIMULATION

5.1 The Reservoir Simulation Software

This project utilizes the free open- source: Matlab Reservoir Simulation Toolbox (MRST) developed by the Norwegian company, SINTEF Technology and Society. SINTEF is a multidisciplinary research institute that is active in the fields of industry, technology and the social sciences. As the name implies, the toolbox facilitates reservoir modelling and simulation. It is pre-equipped with different modules that contain tutorials and examples of varying topics. Some topics addressed in the toolbox are: Enhanced Oil Recovery, Carbon Dioxide Storage, Optimization etc. Additionally, it also facilitates prototyping of different reservoirs with user defined parameters while using various computational approaches.

For the purpose of this project, the ‘ad- eor module’ will be utilized. This module focuses on multiphase (oil, water and gas) and compressible flow, with the capability of simulating water flooding and enhanced oil recovery with polymer and surfactant. Lastly, the software provides fully implicit simulations in which all equations and parameters are established within the toolbox. This toolbox allows for the addition of polymer mixing rules, adsorption, velocity dependent viscosity and shear rates and dead pore space (Bao et al., 2017).

5.2 The Reservoir Simulation Model

For the purpose of simulating polymer flow, the ‘Three- Phase 2D Black- Oil model in the MRST software will be utilized. Three fluid components are modeled in the reservoir, namely oil, water and gas in three phases namely oleic, aqueous and gaseous phases respectively. The water phase will eventually be replaced by the polymer. A Black-oil model is defined as a reservoir model consisting of distinct phases (oil, water, gas) i.e. phases that do not mix with each other. In particular, the oil has very little dissolved gas. Bao (2017), explains that in the black oil model, the hydrocarbon phases are not influenced by the polymer phase. The distinction between the phases means that one fluid phase, depending on its characteristics “viscosity” for example, is responsible to push or displace another phase. In this model, the gas phase is optional. The simulation reservoir consists of one injection well completed in the lower section of the reservoir and a production well completed in the upper section of the reservoir (Figure 3). The completion locations of the reservoir are simply for illustration purposes and does not reflect the true configuration. The reservoir itself is 4000m by 200m by 125m (100,000,000m^3 in volume). This reservoir is represented as a 20m by 1m by 5m grid cell reservoir model on a uniform cartesian grid. The rock properties (porosity and permeability) are provided in a matrix within the input deck. It is assumed that permeability in the X and Y direction are the same (Figure 4.).

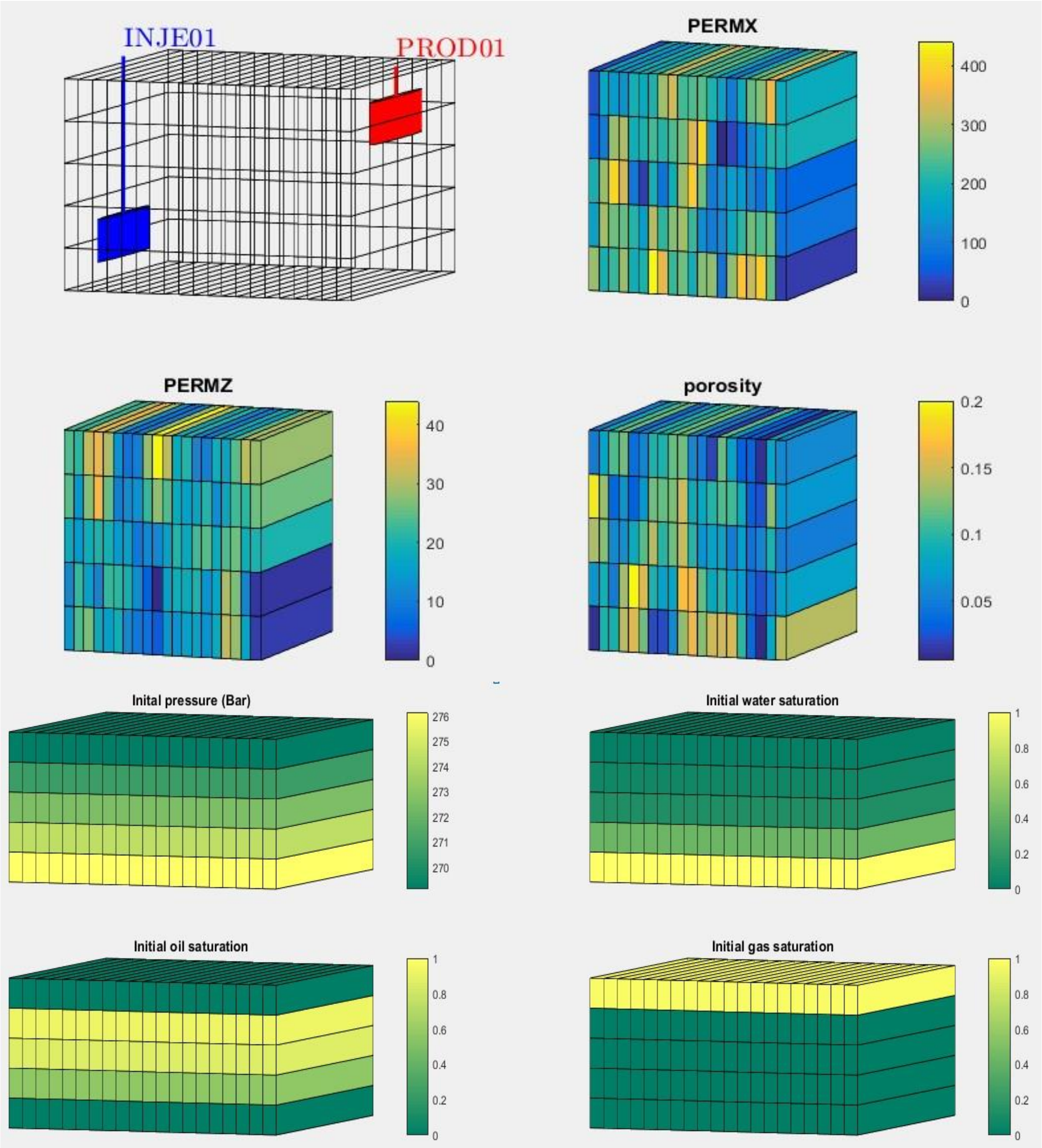


Figure 4: Rock Properties and Initial Conditions (From MRST)

In the simulation, water flooding starts first and commences for 1260 days; this is followed by polymer flooding for 1700 days and finally water flooding resumes

Reservoir parameters	Parameter values	Units
Injection rate	1000	m^3/ day
Bottom hole pressure (injection well)	450	bars
Bottom hole pressure (Production well)	260	bars
Reservoir Depth	4000	M
Reservoir thickness	200	M
Oil density at surface	962	g/mL
Oil viscosity	5	cP
Water viscosity	0.318	cP
Average Porosity	0.2	
Minimum porosity	0.005	
Maximum Porosity	0.02	
Average Permeability	160	
Minimum Permeability	0	
Maximum Permeability	442.02	

Table 1: Reservoir and Model Parameters

This toolbox does not readily offer the option of simulating the variation of viscosity with brine concentration and viscosity variation with temperature. Therefore, the data for these parameters will be obtained from laboratory experiments and the associated results will be incorporated into the model.

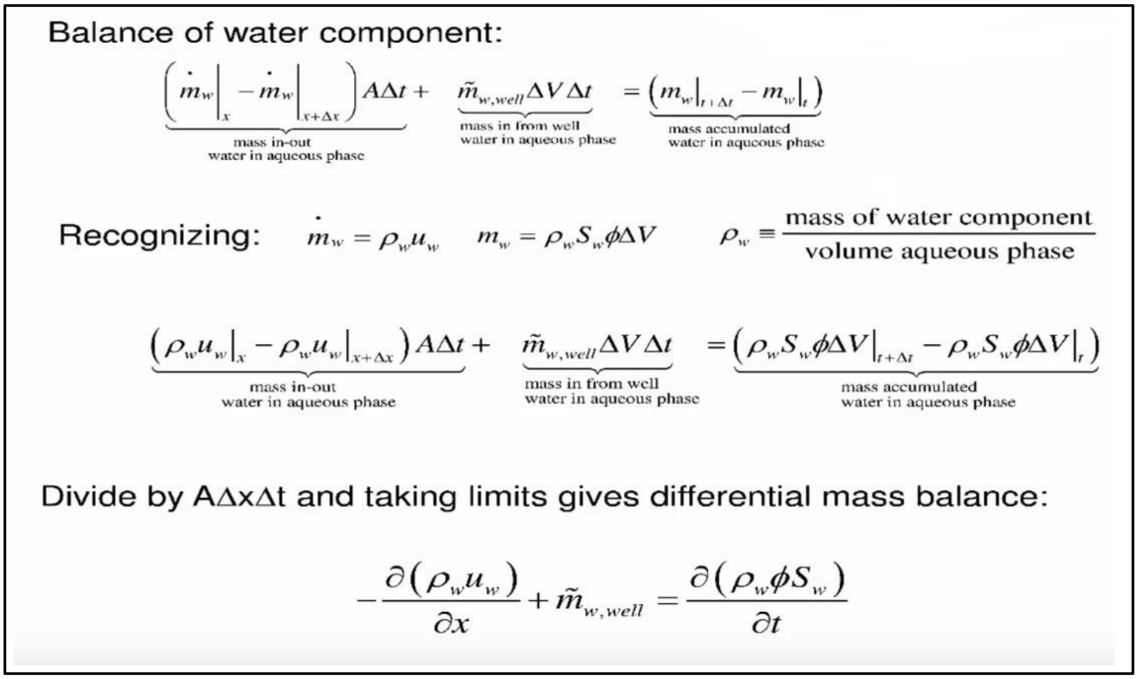
5.2.1 Reservoir Model Equations

Water: $$-\frac{\partial}{\partial \chi}\left(\frac{u_w}{B_w}\right) + q_w = \frac{\partial}{\partial t}\left(\frac{\emptyset S_w}{B_w}\right)$$

Oil: $$-\frac{\partial}{\partial \chi}\left(\frac{u_o}{B_o}\right) + q_o = \frac{\partial}{\partial t}\left(\frac{\emptyset S_o}{B_o}\right)$$

Gas: $$-\frac{\partial}{\partial \chi}\left(\frac{u_g}{B_g} + R_S\frac{u_o}{B_o}\right) + q_g + R_s q_o = \frac{\partial}{\partial t}\left[\emptyset\left(\frac{1}{B_g}S_g + \frac{R_s}{B_o}S_o\right)\right]$$

Figure 5: Three Phase Black Oil Model Mass Balance Equations



Balance of water component:

$$\underbrace{\left(\dot{m}_w\Big|_x - \dot{m}_w\Big|_{x+\Delta x}\right)A\Delta t}_{\substack{\text{mass in-out}\\ \text{water in aqueous phase}}} + \underbrace{\tilde{m}_{w,well}\Delta V\Delta t}_{\substack{\text{mass in from well}\\ \text{water in aqueous phase}}} = \underbrace{\left(m_w\big|_{t+\Delta t} - m_w\big|_t\right)}_{\substack{\text{mass accumulated}\\ \text{water in aqueous phase}}}$$

Recognizing: $\dot{m}_w = \rho_w u_w$ $\quad m_w = \rho_w S_w \phi \Delta V$ $\quad \rho_w \equiv \frac{\text{mass of water component}}{\text{volume aqueous phase}}$

$$\underbrace{\left(\rho_w u_w\big|_x - \rho_w u_w\big|_{x+\Delta x}\right)A\Delta t}_{\substack{\text{mass in-out}\\ \text{water in aqueous phase}}} + \underbrace{\tilde{m}_{w,well}\Delta V\Delta t}_{\substack{\text{mass in from well}\\ \text{water in aqueous phase}}} = \underbrace{\left(\rho_w S_w \phi\Delta V\big|_{t+\Delta t} - \rho_w S_w \phi \Delta V\big|_t\right)}_{\substack{\text{mass accumulated}\\ \text{water in aqueous phase}}}$$

Divide by A∆x∆t and taking limits gives differential mass balance:

$$-\frac{\partial(\rho_w u_w)}{\partial x} + \tilde{m}_{w,well} = \frac{\partial(\rho_w \phi S_w)}{\partial t}$$

Reprinted from [Foster, 2017]

Figure 6: Mass Balance of Water Detailed Equation

Term definitions for Mass Balance Equations

W- water	q- Volumetric source	a- Adsorption coefficient
O- Oil	S- Saturation	r-rock
G- Gas	ø- Porosity	$\dot{m}$- Mass flux
U- Velocity	Rs-Solution gas oil ratio	$\acute{m}$- Source or sink rate
B- Formation Volume Factor	C- Concentration	ρ-Density

5.2.2 The Polymer Model Parameters and Equations (Adapted from Bao, 2017)

$$\partial_t\big(\emptyset\,(1-\ S_{ipv}\big)b_w\,s_wC)+\ \partial_t\ \left(\rho_r C^a\frac{1-\emptyset}{\emptyset}\right)+\nabla.\big(b_wV_pC\big)-\ b_wq_wC=0$$

Figure 7: Polymer Model Equation (Adapted from Bao, 2017)

5.2.3 Polymer Model Parameters

- Inaccessible Pore Space- Describes the portion of the reservoir not accessible to polymer.
- Represented by the scalar **“Sipv”**
- Physical adsorption- represents the attachment of polymer to the rock surface, this will reduce the polymer concentration and introduce a resistance to flow that reduces the effective permeability of water

  $$\rho_r C^a\frac{1-\emptyset}{\emptyset}$$

- Permeability reduction- represents polymer molecules that become lodged in narrow pore throats during polymer flooding

$$R_k\ (c, c_{max}) = 1 + (\text{RRF}-1)\ \frac{c, c_{max})}{c_{max}^{a}}$$

- Effective viscosity –describes the degree of mixing of the polymer in the water

$$u_{p,eff} = u_{fm}\ (C)^{\omega} .\ u_p^{1-\omega}$$

- Shear- modified water viscosity- models the effects of shear on non- Newtonian fluids (polymer)

$$u_{w,sh} = u_{w,eff} \left(\frac{1 + (m_u - 1) m_{sh}}{m_u}\right)$$

Term definition for Polymer Equation

RRF- Reservoir reduction factor	$U_{p,\ eff}$- Effective polymer viscosity
ø- Porosity	U_{fm}- Fully mixed viscosity
ρ_r-rock density	μ- Viscosity multiplier
R_k- Permeability reduction	ω - Mixing parameter
C^a- Polymer adsorption concentration	

5.3 Materials Needed

1. Brine solution of 5%, 10% and 15% Sodium Chloride and Calcium Chloride
2. Calcium Chloride
3. De- ionized water
4. Hot plate
5. Magnetic stirrer
6. Powdered cassava- starch
7. Scale
8. Sodium Chloride
9. Thermometer
10. Viscometer- Three individual types of viscometers were used throughout the project

6 METHODOLOGY

A twofold methodology was utilized. Firstly, laboratory analyses were undertaken to observ the variation of viscosity with: concentration, shear rate, salinity and temperature. Thereafter, the results were inputted into the simulation model, and computational simulations were performed.

6.1 The laboratory Analysis

Experiments were undertaken in order to observe viscosity variation with concentration, shear rate, salinity and temperature:

6.1.1 Viscosity Variation with Concentration

The aim of this section is to observe the variation of polymer concentration with viscosity.

- 4, 5, 6, 8 and 10 grams of powdered starch were chosen for observation of initial viscosity- concentration relationship.
- The various starch concentrations were physically crushed and grinded with pistol and mortar until granulated.
- The various starch concentrations were stirred in 25 ml lukewarm (60 degrees Celsius) de- ionized water to make a thin paste.
- The thin paste was added to 225 ml of water at 100 degrees Celsius and stirred with magnetic stirrers at 300 r.p.m. until solution was thoroughly mixed and translucent.
- The polymers were cooled to 25 degrees Celsius.
- Viscosity measurements were recorded for the individual samples.

6.1.2 Viscosity Variation with Shear Rate

A polymer concentration of 8.64 grams of powdered starch was prepared in 180 mL of de- ionized water and subjected to shear rates of 5, 10, 100, 300, 500, 700, 900, 1000 s^{-1}.

- The powdered starch concentration was physically crushed and grinded with pestle and mortar until granulated
- The powdered starch concentration was stirred in 25 ml lukewarm (60 degrees Celsius) de- ionized water to make a thin paste.
- The thin paste was added to 155 ml of water at 100 degrees Celsius and stirred with magnetic stirrers at 300 r.p.m until solution was thoroughly mixed and translucent.
- The polymers were cooled to 25 degrees Celsius.
- The polymer was added to a viscometer and subjected to the above shear rates.
- Viscosity was plotted against shear rate on a log-log plot for observation.

6.1.3 Viscosity Variation with Salinity

8.64 g/180 ml of powdered polymer was prepared in brine solution of varying compositions (5%, 10% and 15% Sodium Chloride (NaCl) and Calcium Chloride (CaCl) salts) in order to observe the effects of salinity on viscosity.

- 5%, 10% and 15% Sodium Chloride (NaCl) and Calcium Chloride (CaCl) salts were dissolved in 180 ml of de-ionized water until all solids were dissolved.
- 8.64 grams of powdered starch was added to the solutions to observe reactions.
- This mass of starch was physically crushed and grinded with pistol and mortar until granulated.
- The chosen mass of starch was stirred in 25 ml lukewarm (60 degrees Celsius) individual brine solution to make a thin paste.

- The thin paste was added to 155 ml of individual brine solutions at 100 degrees Celsius and stirred with magnetic stirrers at 300 r.p.m until solution was thoroughly mixed and translucent.
- The starch polymers in brine were cooled to 25 degrees Celsius.
- Viscosity measurements were recorded and compared with polymer mixture without salts.

6.1.4 Viscosity Variation with Temperature

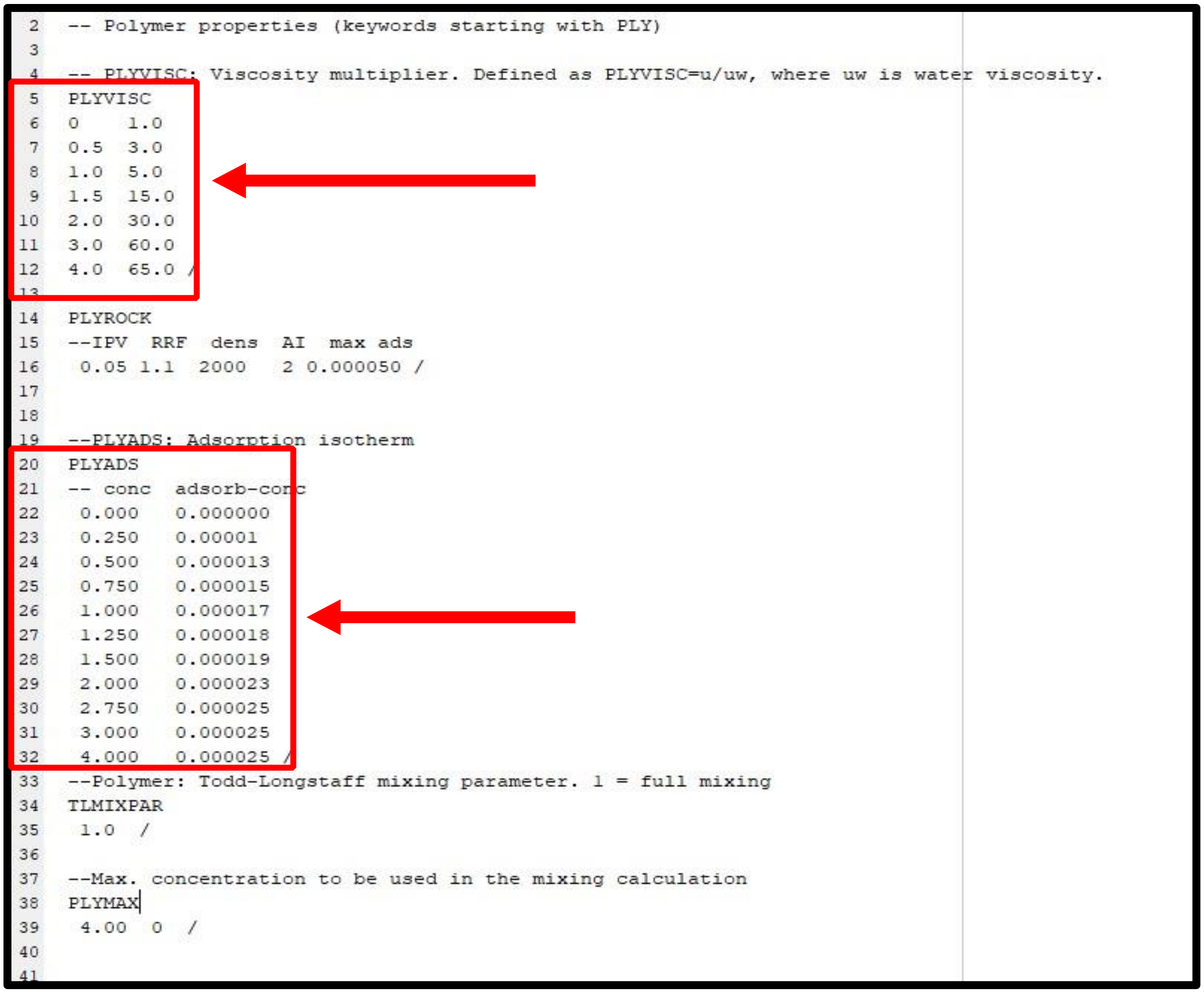
Using the Black Pearl Viscometer, polymer solutions (without salt and with varying concentrations of NaCl and CaCl) were subjected to temperatures of 50, 60, 90, 120 and 148 degrees Celsius and viscosity measurements were observed at various time steps and at a standard shear rate of 7.35 $s^{-1.}$

New samples of polymers without salts and samples with various salt compositions were prepared to observe the effects of temperature.

6.2 Reservoir Simulation

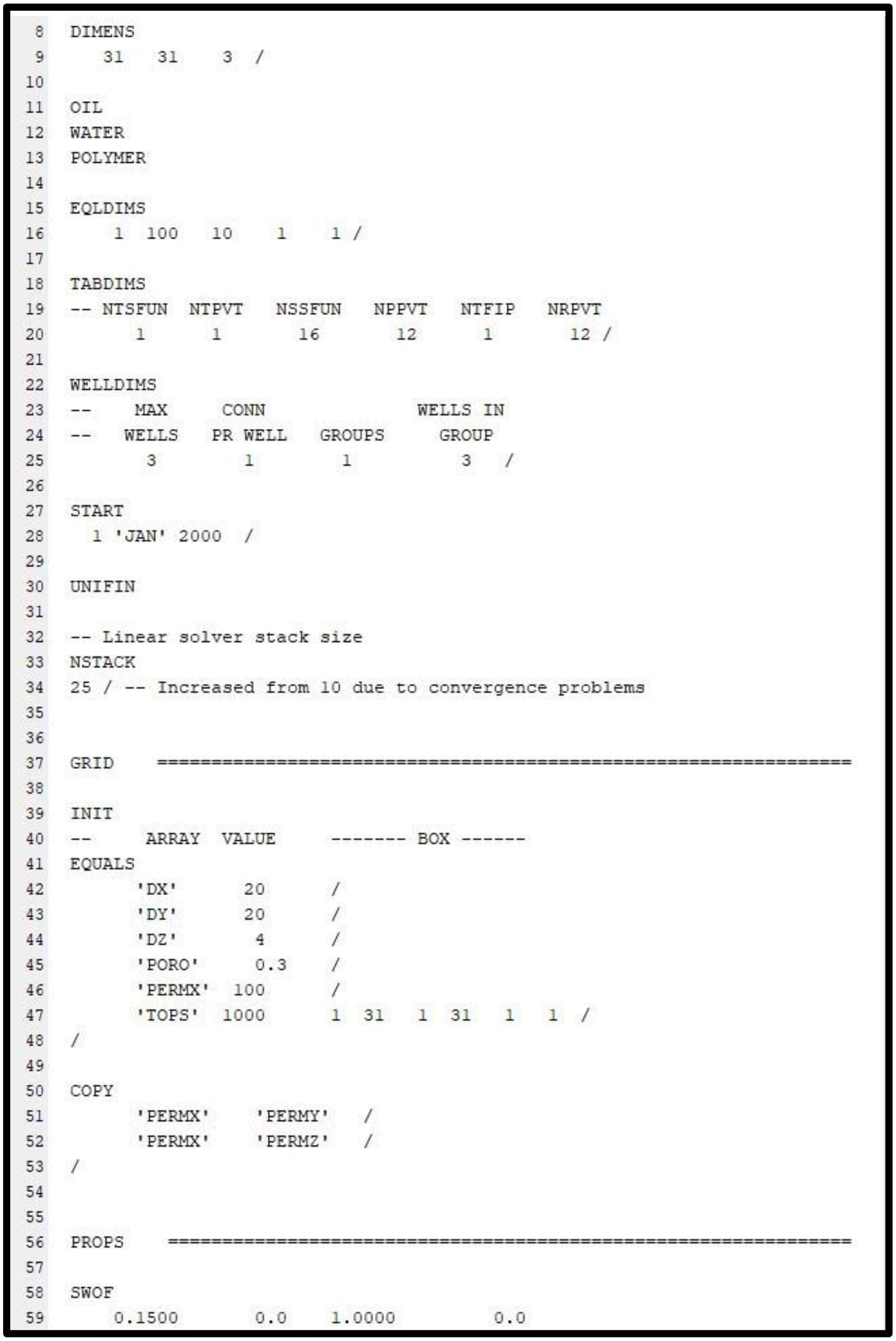
The User defined polymer properties that needed to be inputted into the simulation model are highlighted in Figure 8 below and the reservoir properties are illustrated in Figure 9. The Simulation was performed three times using the following data:

1. Viscosities obtained from solutions without salt, at room temperature and at a shear rate of 7.35 s^{-1}.
2. Viscosities obtained from various salinities were added to the input deck. The shear rate used for this simulation was 7.35 $s^{-1.}$
3. Viscosities obtained from varying temperature with viscosity were used. The shear rate used for this simulation was 7.35 s^{-1}.



```
-- Polymer properties (keywords starting with PLY)

-- PLYVISC: Viscosity multiplier. Defined as PLYVISC=u/uw, where uw is water viscosity.
PLYVISC
0    1.0
0.5  3.0
1.0  5.0
1.5  15.0
2.0  30.0
3.0  60.0
4.0  65.0 /

PLYROCK
--IPV  RRF  dens  AI  max ads
 0.05 1.1  2000   2 0.000050 /


--PLYADS: Adsorption isotherm
PLYADS
-- conc  adsorb-conc
 0.000   0.000000
 0.250   0.00001
 0.500   0.000013
 0.750   0.000015
 1.000   0.000017
 1.250   0.000018
 1.500   0.000019
 2.000   0.000023
 2.750   0.000025
 3.000   0.000025
 4.000   0.000025 /
--Polymer: Todd-Longstaff mixing parameter. 1 = full mixing
TLMIXPAR
 1.0  /

--Max. concentration to be used in the mixing calculation
PLYMAX
 4.00  0  /
```

Figure 8: Matlab Simulation Input Deck Illustrating Polymer Properties



```
DIMENS
   31   31    3  /

OIL
WATER
POLYMER

EQLDIMS
    1  100   10    1    1 /

TABDIMS
-- NTSFUN  NTPVT   NSSFUN   NPPVT   NTFIP   NRPVT
      1      1       16       12       1       12 /

WELLDIMS
--    MAX     CONN              WELLS IN
--   WELLS   PR WELL   GROUPS     GROUP
       3        1        1          3   /

START
  1 'JAN' 2000  /

UNIFIN

-- Linear solver stack size
NSTACK
25 / -- Increased from 10 due to convergence problems


GRID    ================================================================

INIT
--     ARRAY  VALUE     ------- BOX ------
EQUALS
      'DX'      20      /
      'DY'      20      /
      'DZ'       4      /
      'PORO'     0.3    /
      'PERMX'  100      /
      'TOPS'  1000      1  31   1  31   1   1  /
/

COPY
      'PERMX'    'PERMY'   /
      'PERMX'    'PERMZ'   /
/


PROPS    ===============================================================

SWOF
    0.1500       0.0    1.0000         0.0
```

Figure 9: Matlab Reservoir Simulation Input Deck Illustrating Reservoir Properties

7 CASSAVA PLANT OVERVIEW

Cassava, *Manihot esculenta Crantz*, also known as Yucca or Manioc is a tropical plant that thrives in temperatures between 75- 85 ^oF and rainfall conditions averaging 1,000- 1.500 mm per year (Onwueme et al., 1991). This plant is highly susceptible to frost and temperatures below 50 ^oF retards growth (Onwueme et al., 1991). Cassava is very resilient growing in dry and nutrient poor soils. It grows best in light sandy- loam soils, preferably on land that has been ridged and mounded to prevent cuttings from rotting. The plant originated in north- east Brazil. Today over half of the global cassava production and distribution comes from Africa. Cassava comprises approximately 37% of the diet in tropical Africa, 12% in the Americas and 7% in Asia, (United Nations Development Fund for Women (UNIFEM, 1993)). It is primarily processed for human consumption to make traditional products such as gari, cassava bread, cassava rice, cassava beer, tapioca and starch. It is also used in animal feed and in industries as thickening agents and sizing material etc.

Cassava grows as a tuber. The raw product generally consists of 62% water, 20- 25% starch, 12% protein and 1-2% fiber and traces of minerals and fats (Onwueme et al., 1991). Its composition relative to that of a Potato is listed in table 1 (FAO, 2008). There are two varieties of cassava - bitter and sweet cassava. They are so named based on their toxic cyanide- containing glycoside content which ranges between 10- 550 mg/kg (UNIFEM, 1993).

Content	Cassava (%)	Potato (%)	Corn (%)
Water	62	72- 75	15
Starch	20- 25	16- 20	65
Protein	1-2	2- 2.5	13
Fibre	1-2	1- 1.8	7

Table 2: Content Comparison of Cassava, Potato and Corn

7.1 Cassava Planting and Yields

Cassava plants are primarily planted using stem pieces (cuttings). They can also be established using seeds, however this method takes a longer time. Stem pieces are cut from mature plants that average 15- 30 cm in length. The stem pieces must be obtained from disease free plants and stored in a dry, high humidity, well shaded, cool location or planted within forty- eight hours. The stem pieces are planted horizontally, vertically or at an angle of 15^o and the plants mature in 12- 15 months. Stem planting gains the highest commercial yields. The average global yield of cassava is 10 tonnes per hectare while it is 7 tonnes per hectare in Africa and 13 tonnes per hectare in South America (Onwueme et al., 1991). According to the FAO and IFAD (2000), certain cassava cultivars can yield up to 20- 25 tonnes per hectare. In comparison, corn yields average between 12- 13 tons per hectare in the U.S. (University of Illinois, 2017) and potato yields average 16.8 tonnes/ hectare globally (FAO, 2008).

7.2 Cassava Starch

Cassava is the fourth largest source of starch production in the world, after maize, wheat and potato (FAO and IFAD, 2000). Production amounts to 4% of global starch production.

Industrially, cassava starch is extracted by wet milling, sieving and either centrifuging or settling (UINFEM, 1993). The bitter cassava variety contains more starch, so it is mostly used for industrial starch production and making animal feed but not for direct human consumption. The resultant starch is used to produce, cardboard, paper, textile, plywood, glue and alcohol. The starch yield from cassava varies by cultivar. Four to ten tonnes of starch can be produced for every ton of raw cassava, (FAO and IFAD, 2000). Starch made from cassava is odourless and tasteless. According to the FAO and IFAD, (2004) as compared to starch arising from corn and potato, cassava starch solution is smoother, more viscous, provides a neutral pH and requires a lesser temperature to make it viable.

7.3 Worldwide Cassava Use

Cassava is used as a food source mostly in developing countries. In African countries, it is primary produced for local human consumption, and international trade is insignificant. In the U.S., Cassava starch import occurs with volume dependent on shortfalls in the corn starch industry (FAO and IFAD, 2004). In 1997, the U.S. imported approximately 13, 551 metric tonnes of cassava starch and 6,889 metric tonnes in the form of tapioca starch. In the same year, Canada imported 1,771 metric tonnes of cassava starch and 1,043 metric tonnes of tapioca starch (FAO and IFAD, 2004). These figures are quite small compared to the 2.7 million metric tonnes of corn starch produced in the U.S. in the same year. In 1994, cassava supplied less than 2% of the world’s daily calorie intake compared to 20% from wheat and 21% from rice (FAO and IFAD, 2004). Thailand and Indonesia, the largest suppliers of cassava to the international market, supply 80% and 10% of world trade volume respectively (FAO and IFAD, 2004).

7.4 Cassava Starch for Enhanced Oil Recovery

Oil reservoirs exhibit varying temperatures, salinities, brine hardness etc. These characteristics along with porosity, permeability, shear stress and oil viscosity can be deleterious to the effectiveness of a polymer for enhanced oil recovery. Therefore, in assessing a polymer's suitability, field and laboratory evaluations on its performance under such conditions must be undertaken. Data on solubility of the polymer in brine, thermal stability and bulk viscosity with varying starch concentration will be obtained from laboratory experiments carried out using the cassava starch. These characteristics will be used to delineate the effective parameter ranges and limitations of the polymer and will be further inputted into a simulation model.

According to International Starch Trading A/S (1999), several modifications have to be made to traditional starch to make it suitable for oil reservoir injection. Firstly, starch needs to be prepared and supplied in a cold water- soluble form. This makes the reaction of the starch with other additives more uniform and easier to control because polymer viscosity is often adjusted several times during the polymer flooding. Secondly, in the initial preparation of the starch, it needs to be cross-linked with other substances to strengthen and improve resistance to heat, shear and other degrading reservoir characteristics. Addition of biocides is also needed to prevent it from being biodegraded or to extend the time for biodegradation. This time could be in excess of several months. In addition, starch can also be exported in a powdered form with all other ingredients added to it. This is more convenient for offshore purposes.

There is no set ratio for the addition of HPAM or Xanthan Gum to injected water that yields the perfect polymer viscosity for a particular reservoir. Most reservoirs are heterogeneous and thus rock type, porosity, permeability and other characteristics change spontaneously; and polymer concentration is adjusted in the fields to accommodate local characteristics. However, no additives will be mixed with the cassava starch- based polymer.

7.5 Cassava Starch- Based Polymer Economics

The economic feasibility of cassava based polymer will be analysed. Data such as possible cumulative oil recovery (based on the original oil in place), chemical cost per barrel of oil and the polymer efficiency at alternative concentrations will be obtained from simulations. In addition, the oil price, cost to obtain chemicals, taxes imposed and operating costs will also be considered.

8 RESULTS

8.1 Laboratory Analysis Results

Recall from Equation 1, that polymers are added to a water flood in order to provide favourable mobility. Mobility is defined as: relative permeability divided by viscosity. As permeability is a rock property, there is very little that can be done to accurately control it; likewise, the viscosity of oil is defined for a particular reservoir. Therefore, polymer viscosity has to be altered. Mobility ratio, Equation 2, provides a relationship between oil mobility and polymer mobility. As it relates to the viscosity, literature suggests that, ideally, the viscosity of the injected polymer should be greater than that of oil in order for the oil to be displaced by the polymer; therefore, providing a mobility ratio that is less than 1. However, there are reservoir conditions such as salinity, temperature etc. that affect the consistency and functionality of the polymer viscosity. As a result, laboratory experiments were conducted to evaluate the effects of concentration, shear rate, salinity and temperature on polymer viscosity. Polymer functionality is also affected by biodegradation, so this will also be evaluated.

8.1.1 Viscosity Variation with Concentration

Polymers of various concentrations were prepared, and their viscosities were measured at room temperature and at a shear rate of 7.3 1/s (standard shear rate in oil industry). The viscosity/ concentration profile was obtained and compared to that of Xanthan Gum and Hydrolysed Polyacrylamide (HPAM). It can be observed that viscosity is directly proportional to polymer concentration (Figure 10.). This result is consistent with conventional polymers (Figure 11.). However, it is expected that at the same concentration, HPAM should have a higher viscosity because it contains Carboxylate groups that causes chain expansion due to repulsion of the ionic groups as oppose to chain extension and physical entanglement when solvated as in the case with the starch based polymers and Xanthan Gum (Taylor and Nasr-El-Din (1998)). Figure 10., also illustrates that at low polymer concentration, high viscosities can be obtained. The latter is one of the properties of a good polymer. Table 3 illustrates the starch concentration with their associated viscosities.

Concentration(g/250mL)	Viscosity (cP)
8	3,284.92
10	8,959.78
12	10,973.82
15	14,644.77
18	26,470.67
20	33,782.27
22	44,599.37

Table 3: Starch Concentrations and Associated Viscosities

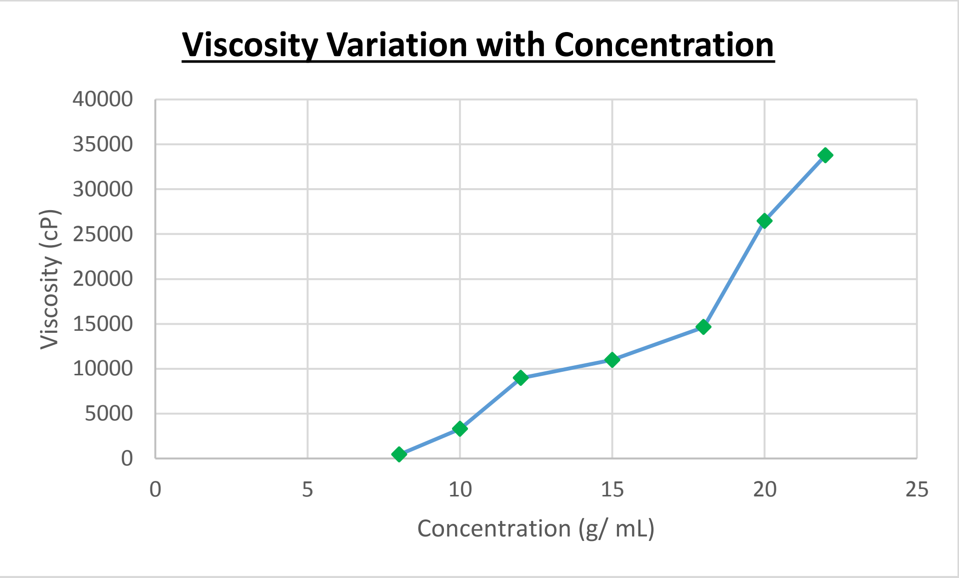
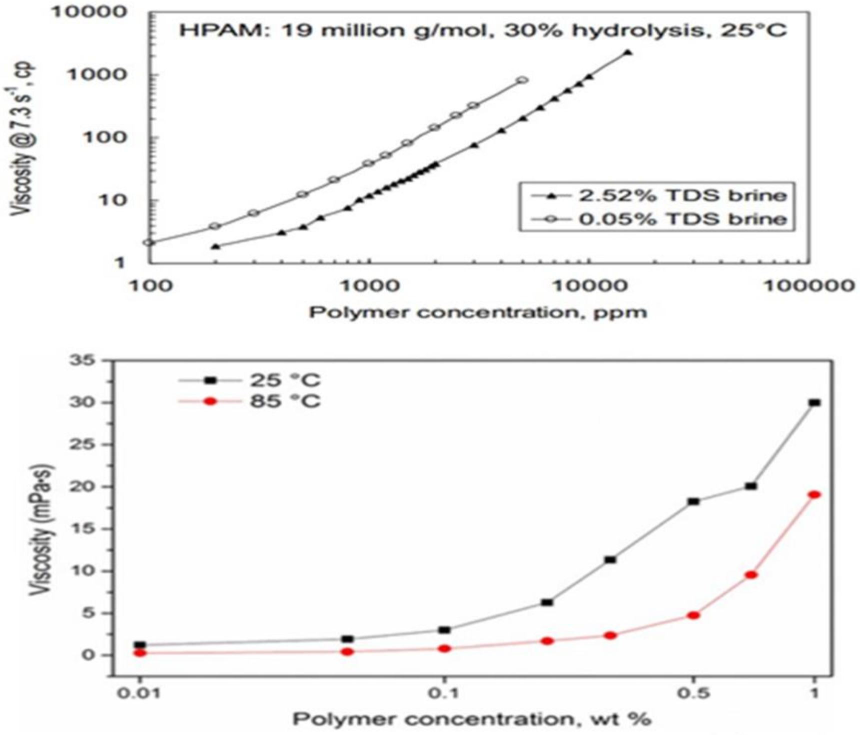


Figure 10: Cassava Starch- Based Polymer Viscosity Variation with Concentration



Hu, Z. et. al. (2017)

Figure 11: HPAM (top) and Xanthan Gum (bottom) Viscosity with Concentration. Adapted from Seright (2017)

8.1.2 Viscosity Variation with Shear

Table 4. depicts the variation of viscosity with shear rates of 5, 10, 100, 300, 500, 700, 900 and 1000 s^{-1} at room temperature with 0% brine. This will be considered the base case. Powdered polymer of 8.64 g was prepared in 180mL of de- ionized water for these observations. The highest shear rates are experienced during injection, and this is typically 7.3 $s^{-1.}$ However, a wide range of shear rates were chosen so as to observe the shear rate values within which the polymer could operate and its potential for use in other applications. Figure 12. Illustrates that the polymer is shear- thinning i.e. viscosity decreases with increase in shear. This means that this cassava starch- based polymer is a non- Newtonian fluid. Both Xanthan Gum and HPAM are non- Newtonian Polymers and the effects of shear rates is illustrated in Figure 13.

As it relates to the Cassava starch- based polymer, there is approximately a 16% decrease in viscosity of the polymer from 5 s^{-1} to about 7.5 s^{-1}. In addition, there is a 93% reduction in viscosity from 5 s^{-1} to 1000 s^{-1}. These results would indicate that in order to obtain a pre-determined viscosity, a more viscous fluid needs to be injected into the well bore to account for the shear thinning effect. This will have a direct implication on price of the polymer injection operation, but in general, most polymers used in the EOR process are shear thinning, so this parameter is also accounted for. Also, the effect of shear thinning on the polymer seems to decrease with increasing shear rates as there is a 4% percent difference between the viscosities at 900 and 1000 s^{-1}.

Shear Rate (1/s)	Viscosity (cP)
5.0048	867.1733
5.0048	895.1467
9.9925	574.4303
9.9925	586.4393
99.9932	206.014
99.9932	193.2132
299.9966	124.8681
299.9966	112.0679
500	92.08
500	91.48
700.0034	78.6568
700.0034	77.2568
900.0068	67.1328
900.0068	66.7328
1000	62.56
1000	60.48

Table 4: Variation of Viscosity with Shear Rate (Base Case)

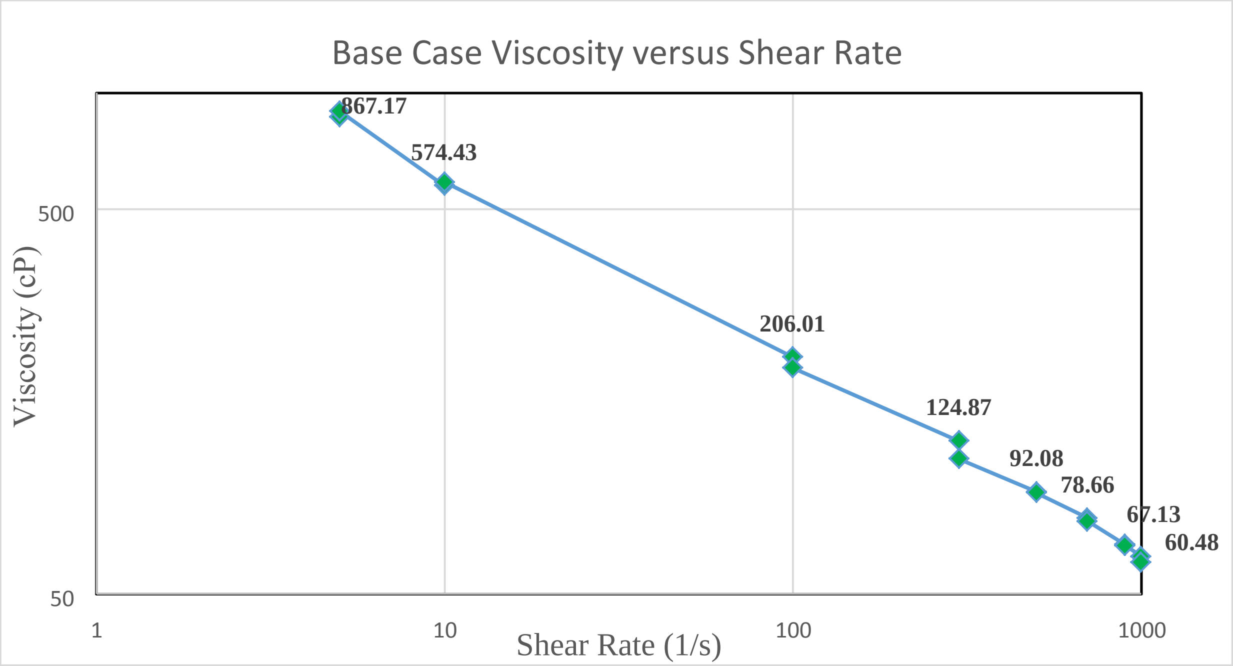
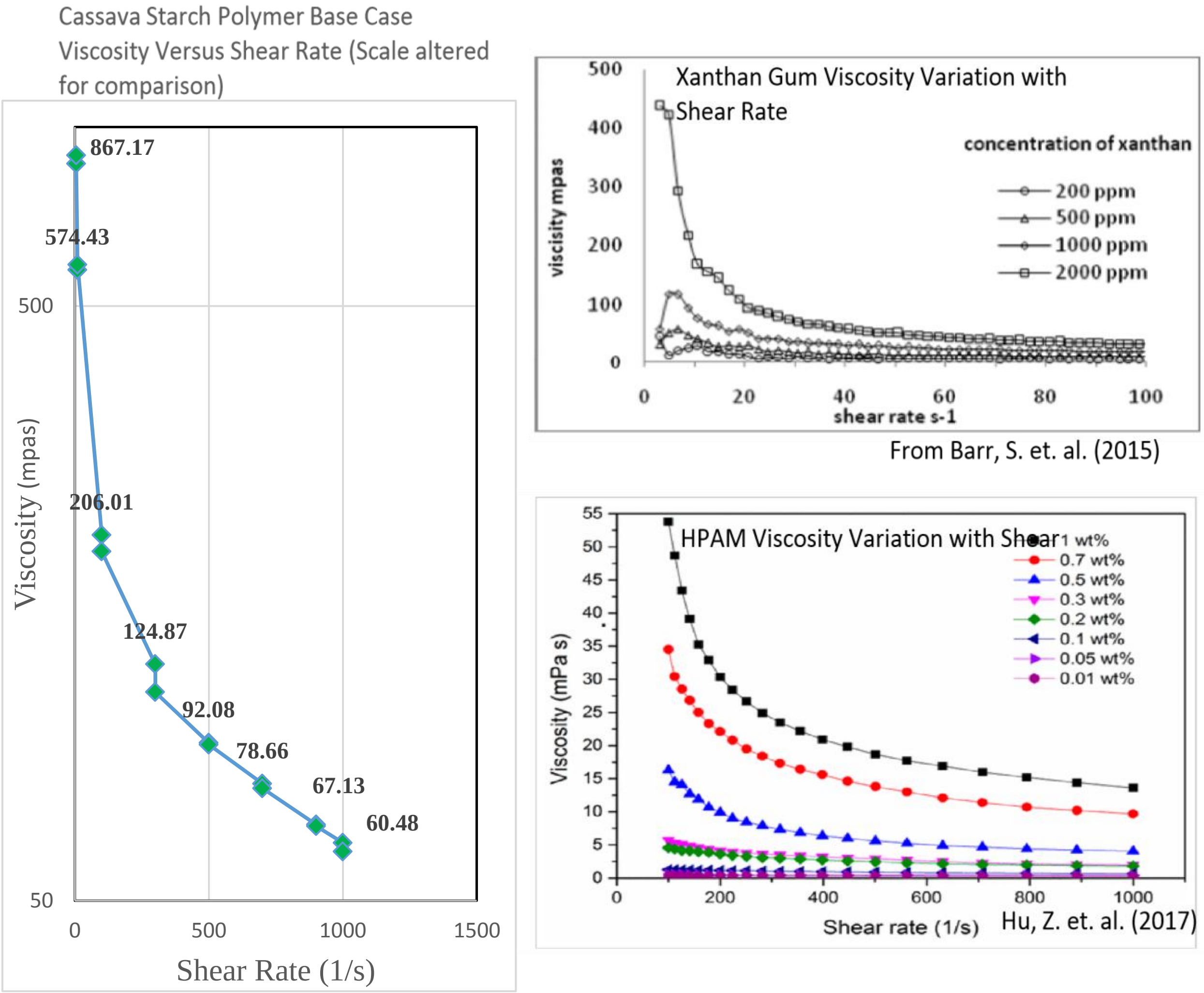


Figure 12: Base Case Viscosity versus Shear Rate of Cassava Starch- Based Polymer



Cassava Starch Polymer Base Case Viscosity Versus Shear Rate (Scale altered for comparison)

Xanthan Gum Viscosity Variation with Shear Rate

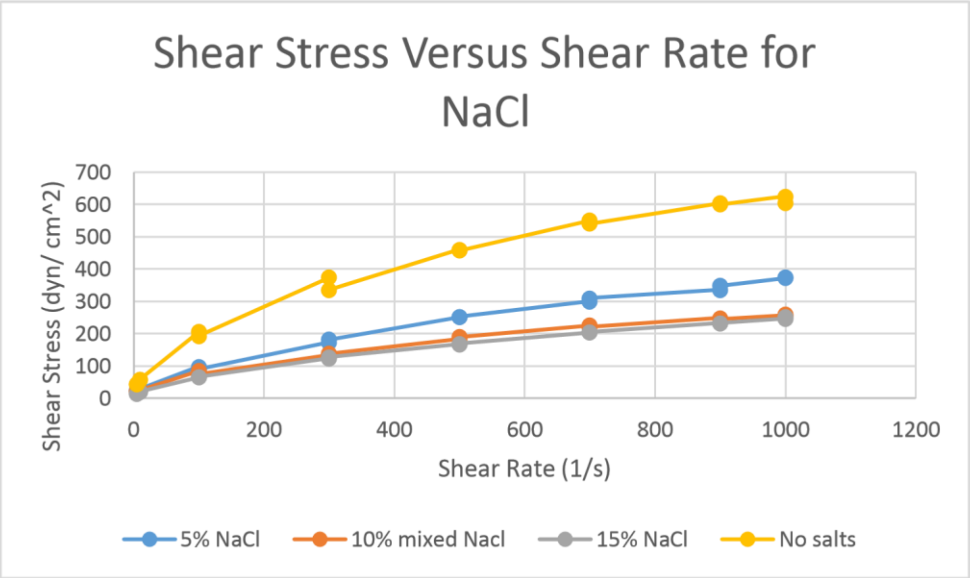
From Barr, S. et. al. (2015)

HPAM Viscosity Variation with Shear

Hu, Z. et. al. (2017)

Figure 13: Viscosity Variation with Shear rates- Comparison of Polymers

The definition of viscosity is Shear Stress (dyn/ cm^2) divided by Shear Rate (1/s). This relationship can be seen in Figure 14. Shear Stress of the Cassava starch- based polymer was plotted against their shear rates at different concentrations of salinity of sodium Chloride Brine and Calcium Chloride Brine. The resulting curves are concaved downwards and this means that viscosity decreases with increasing shear. If the curves were concaved upwards, this would mean that they are shear thickening or Newtonian Fluids.



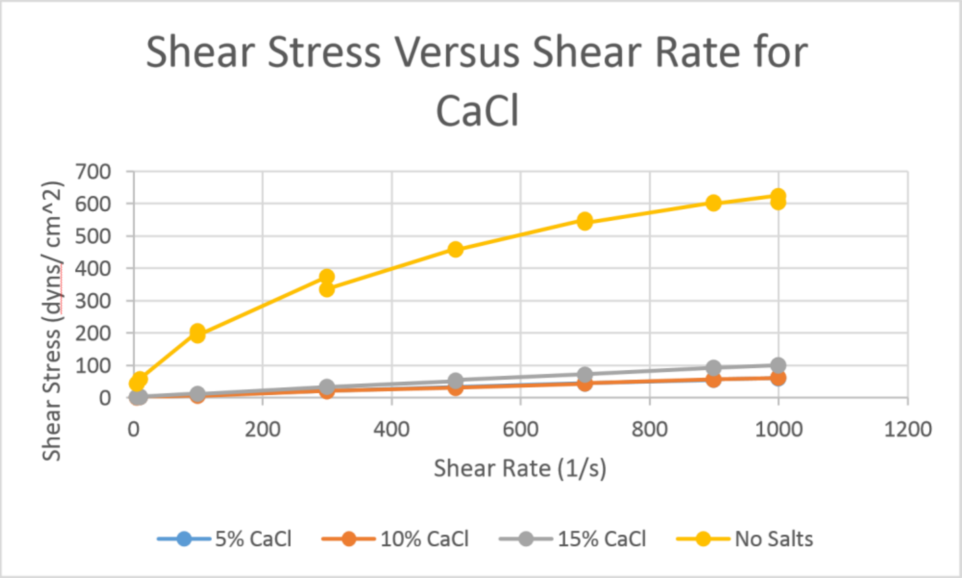


Figure 14: Shear Stress (Dyn/ cm^2) versus Shear Rate (1/s) in NaCl (top)

8.1.3 Viscosity Variation in Sodium Chloride Brine Solution

The aim of this section is to observe the behaviour of the viscosity of the cassava starch- based polymer in Sodium Chloride brine of varying salinities and to compare the results to that of conventional polymers; particularly Polyacrylamide, as the viscosity is known to decrease in high salinity regimes.

Powdered starch of 8.64 g/was added to 180mL of Sodium chloride (NaCl) brine solutions of 5%, 10% and 15 % salinity. The shear rates were varied as in Table 4. to observe the effects of salinity on viscosity at different shear rates. The viscosity variations were observed and the results are shown below:

Shear Rate (1/s)	Sodium Chloride Solution Viscosities (cP)		
	5%	**10%**	**15%**
5.00	1,550.52	1,606.47	2,066.03
5.00	1,554.52	1,630.45	2,289.82
9.99	990.74	1,034.78	1,421.06
9.99	1,004.75	1,066.80	1,451.09
99.99	303.02	299.42	416.83
99.99	296.42	292.02	408.43
300.00	176.40	170.40	242.20
300.00	166.60	156.80	226.47
500.00	131.24	122.72	178.48
500.00	127.16	122.48	169.40
700.00	109.40	104.26	144.57
700.00	108.03	105.86	143.97
700.00	93.91	92.53	124.95
700.00	93.80	93.58	125.22
940.00	86.18	87.82	116.96
1,000.00	86.76	86.22	114.68

Table 5: Shear Rates and Respective Viscosities for 5%, 10% and 15% NaCl Solutions

Viscosity variation with shear rates was observed for different NaCl brine concentrations. The initial viscosity of the polymer in 5% NaCl at a shear rate of 5 s^{-1} was 1,550.52 cP (Figure 15). This shows that viscosity is increasing in the 5% NaCl concentration and represents a 78.8% increase in viscosity when compared to the base case. Shear rates in an EOR project should not go above 10 s^{-1}, therefore when the viscosity values were compared for shear rates between 5 and 10 s^{-1}, there was a 35% decrease in viscosity. This is not a significant loss in viscosity, and it translates to 6,125,000g of polymer. However, in order to get the right mobility, these values still have to be considered. There is a 94% decrease in viscosity from the shear rate of 5 s^{-1} to 1000 s^{-1}. This is comparable to the 93% reduction in viscosity in the base case. These values are expected as the polymer is non- Newtonian.

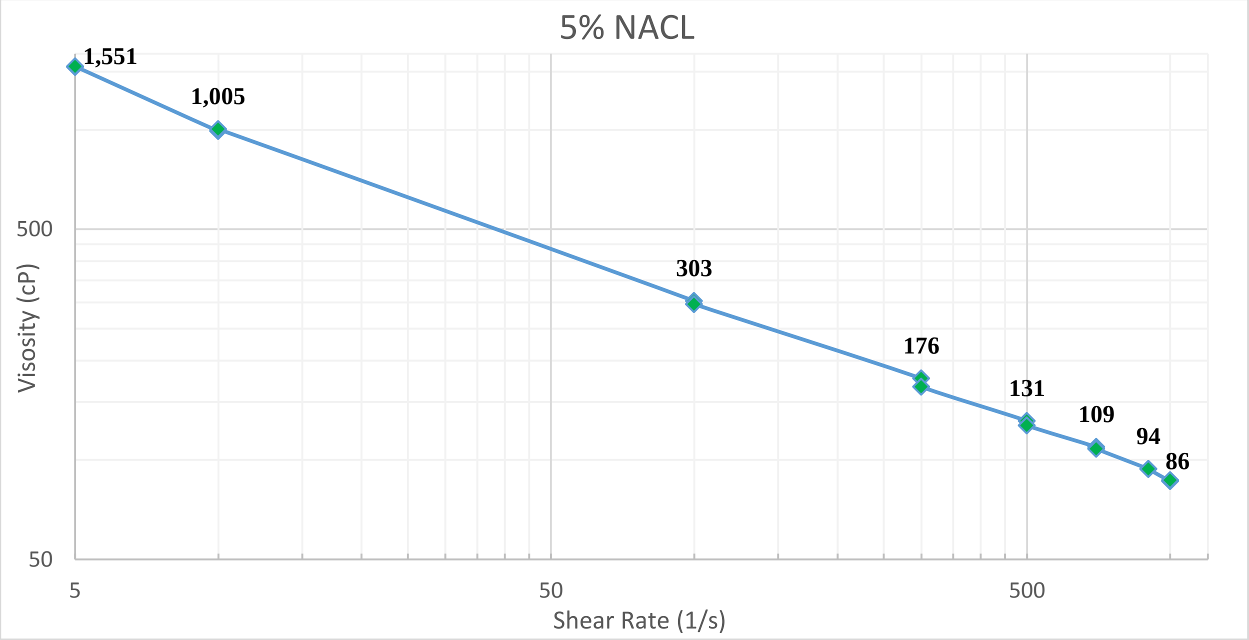


Figure 15: Viscosity Variation in 5% NaCl Concentration

Figure 16. below, illustrates that the initial viscosity of the polymer in 10% NaCl at a shear rate of 5 s^{-1} was 1606.47 cP. This shows that viscosity is increasing in the 10% NaCl concentration

and represents an 85.25% increase in viscosity when compared to the base case. When the viscosity values were compared for shear rates between 5 and 10 s^{-1}, there was a 33.6% decrease in viscosity. This is comparable to the 5% case and it translates to 875,000g polymer. There is a 94.63% decrease in viscosity from the shear rate of 5 s^{-1} to 1000 s^{-1}.

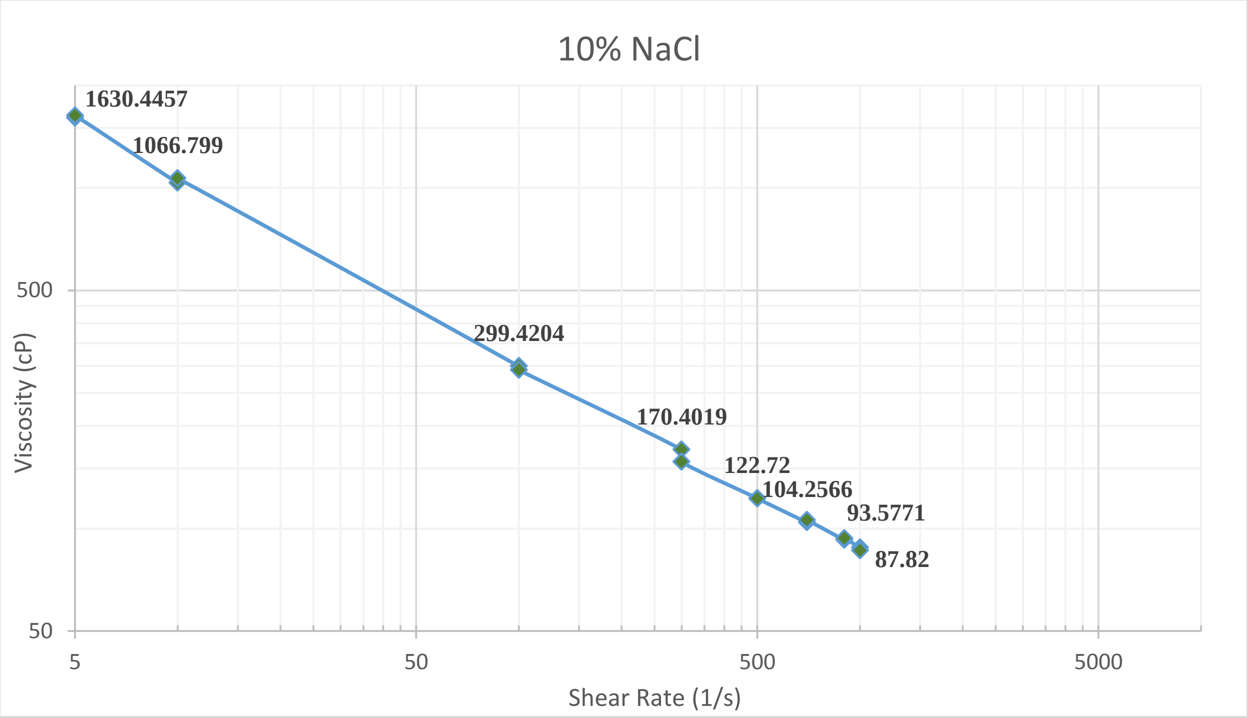


Figure 16: Viscosity Variation in 10% NaCl Concentration

Figure 17. below, illustrates that the initial viscosity of the polymer in 15% NaCl at a shear rate of 5 s^{-1} was 2,066.03 cP. This shows that viscosity is increasing in the 15% NaCl concentration when compared to the 5% and the 10% brines. This represents a 138.25% increase in viscosity when compared to the base case. When the viscosity values were compared for shear rates between 5 and 10 s^{-1}, there was a 29.76% decrease in viscosity. This is comparable to the 5% and

10% case and it translates to 5,208,000 kg of polymer. There is a 94.45% decrease in viscosity from the shear rate of 5 s^{-1} to 1000 s^{-1}.

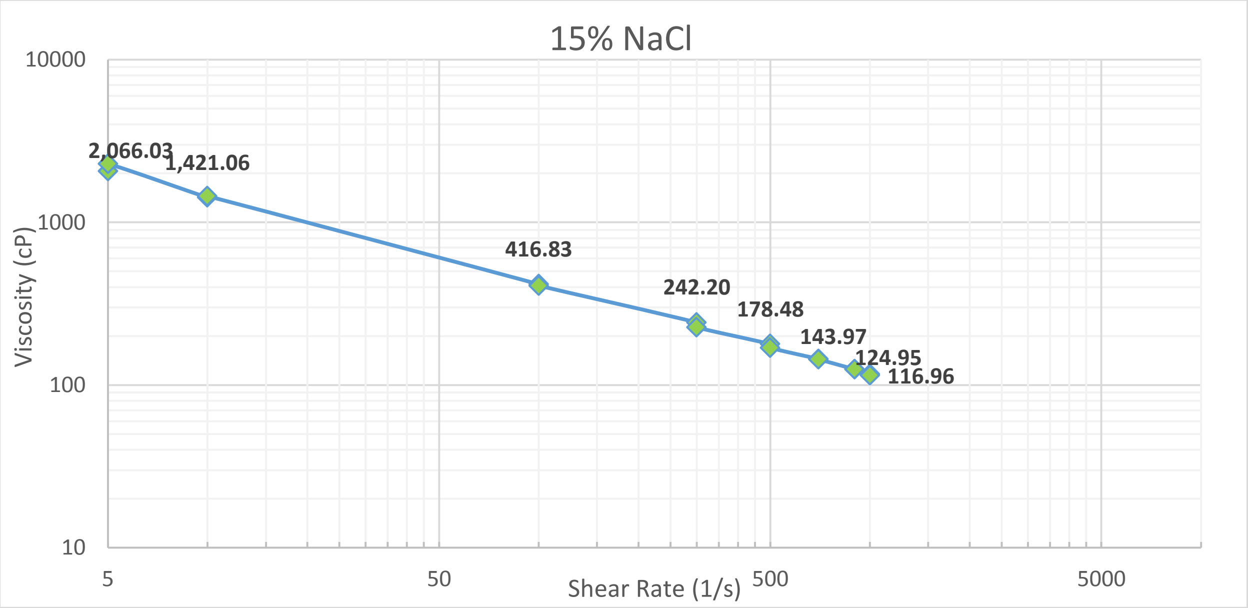


Figure 17: Viscosity Variation in 15% NaCl Concentration

The viscosity of the 15% brine solution is more than that of the base case and the 5% and 10% brine concentrations. Figure 18. below, illustrates the comparison between the different brine compositions and the response of viscosity. The general trend is that for the cassava starch-based polymer, viscosity increases with increasing NaCl concentration.

There does not seem to be a significant difference in the response of viscosity change in the 5%, and 10% NaCl brines. As there was only a 3.6% increase between the initial viscosities of the 5-10% brines and a 0.62% decrease in their final viscosities. However, a greater increase occurred between the 10% and the 15% brine solutions. There was a 28.6% increase between the initial viscosities of the 10% and 15% brines. There was a 32% increase between the final viscosities of the 10% and the 15% brines.

In general, viscosity of the Cassava starch- based polymer increases with increasing Sodium Chloride Concentration. Though NaCl does not affect the Xanthan Gum viscosities in a significant way, the viscosities of the Xanthan gum decrease with increase in NaCl salinity (Figure 19.). Conversely, salinity adversely affects the viscosity of HPAM (Figure 19.)

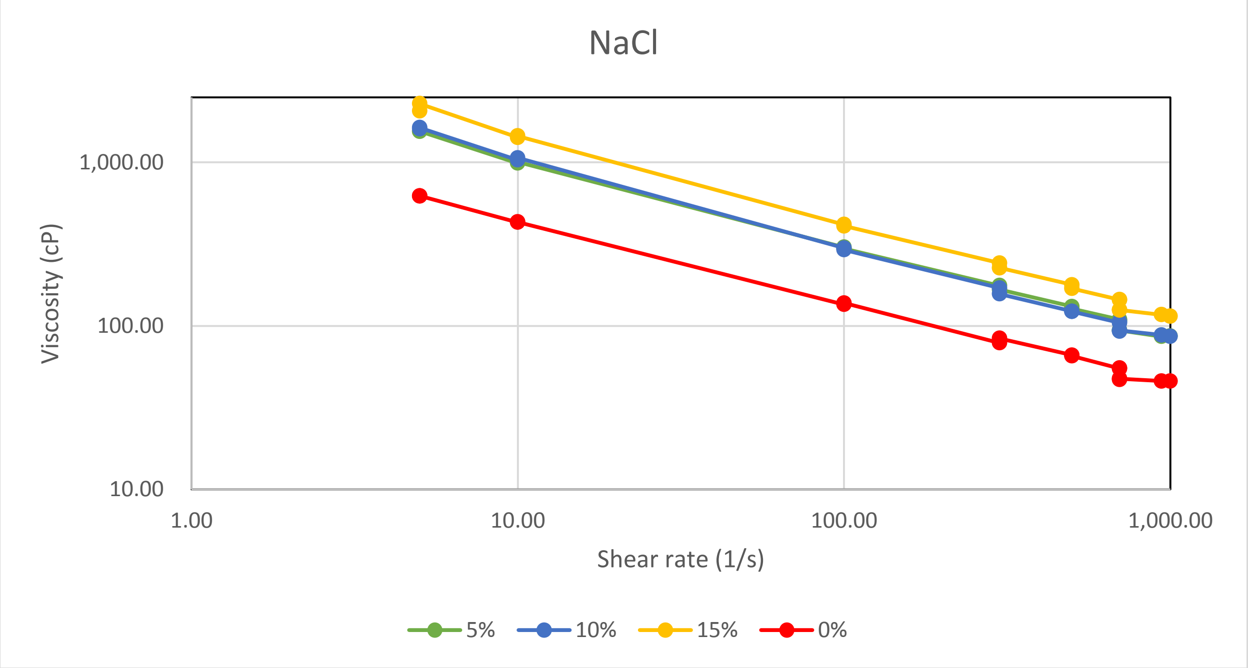
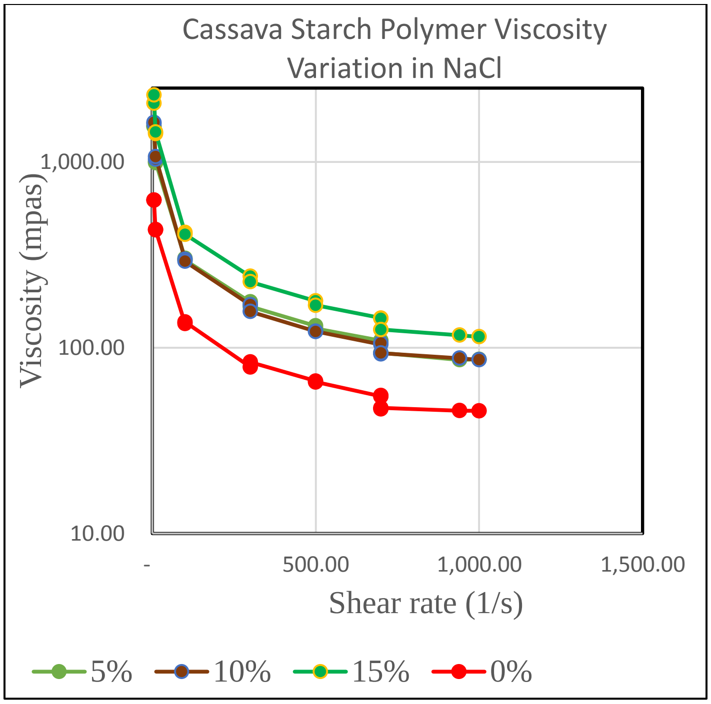
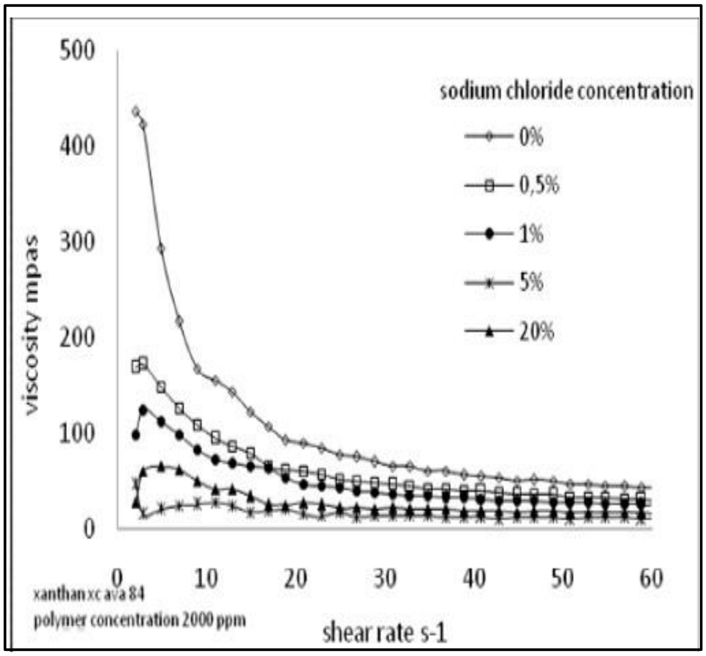


Figure 18: Viscosity Value Comparison between NaCl Brines of Varying Concentrations





Adapted from Barr, S et. Al (2015)

Figure 19: Viscosity Variation Comparison of Cassava- Starch Based Polymer (top) and Xanthan Gum (bottom) with Shear Rates

8.1.4 Viscosity Variation in Calcium Chloride Brine Solution

The aim of this section is to observe the behaviors of the viscosity of the cassava starch- based polymer in Calcium Chloride brine of varying concentration and to compare the results to that of conventional polymers.

Powdered starch of 8.64 g/was added to 180mL of Calcium Chloride (CaCl) brine solutions of 5%, 10% and 15 % salinity. The shear rates were varied as in Table 5. to observe the effects of salinity on viscosity at different shear rates. The viscosity variations were observed and the results are shown below:

Shear Rate (1/s)	Calcium Chloride Solution Viscosities		
	5%	**10%**	**15%**
5.00	263.75	1,019.03	315.70
5.00	355.66	1,090.96	363.65
9.99	218.16	672.50	288.22
9.99	210.16	682.51	294.22
99.99	90.61	198.81	128.01
99.99	88.81	205.01	126.21
300.00	61.73	123.87	87.00
300.00	61.00	123.47	86.67
500.00	50.76	96.36	73.96
500.00	52.00	96.40	74.36
700.00	46.23	81.74	65.34
700.00	45.74	83.43	65.74
700.00	40.22	71.98	65.14
700.00	39.27	72.93	65.14
940.00	37.28	66.24	57.94
1,000.00	37.80	68.18	55.72

Table 6: Shear Rates and Respective Viscosities for 5%, 10% and 15% CaCl Solutions

Shear rates were observed for different brine concentrations. The initial viscosity of the polymer in 5% CaCl at a shear rate of 5 s^{-1} was 355.66 cP (Figure 20 below). This shows that viscosity is decreasing in the 5% CaCl concentration as compared to the base case. This represents a 69.6% decrease in viscosity when compared to the base case. When the viscosity values were compared for shear rates between 5 and 10 s^{-1}, there was a 20.3% decrease in viscosity. This is not a significant loss in viscosity, and it translates to 3,552,500 grams of polymer. There is an 85.6% decrease in viscosity from the shear rate of 5 s^{-1} to 1000 s^{-1}. This is lower than that of the 93% reduction in viscosity in the base case. In general, the viscosity in CaCl brine is lower than that of the base case, however the decrease in viscosity from one shear rate to the next is less pronounced in the CaCl brine.

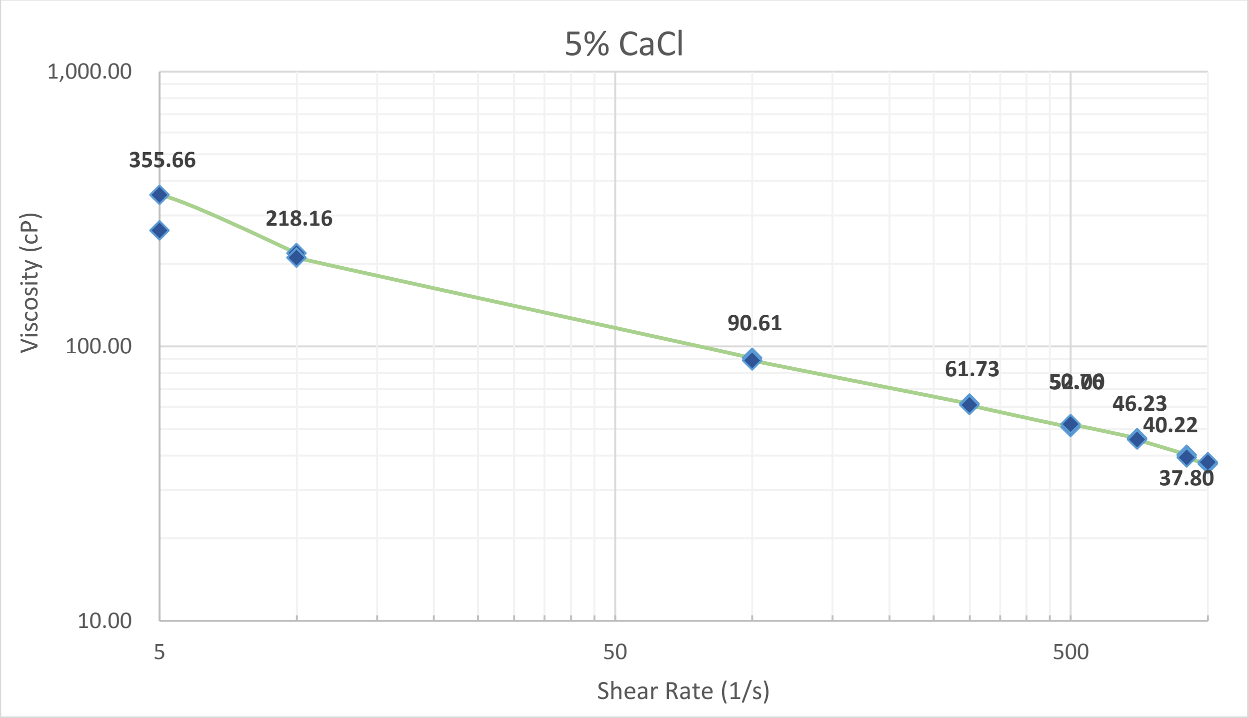


Figure 20: Viscosity Variation in 5% CaCl Concentration

Figure 21., illustrates that the initial viscosity of the polymer in 10% CaCl at a shear rate of 5 s^{-1} was 1,090.96 cP. This shows that viscosity is increasing in the 10% CaCl concentration and represents a 25.81% increase in viscosity when compared to the base case. When the viscosity values were compared for shear rates between 5 s^{-1} and 10 s^{-1}, there was a 34% decrease in viscosity. This is comparable to the 5% case and it translates to 5,950,000 g of polymer. There is a 93.3% decrease in viscosity from the shear rate of 5 s^{-1} to 1000 s^{-1} .

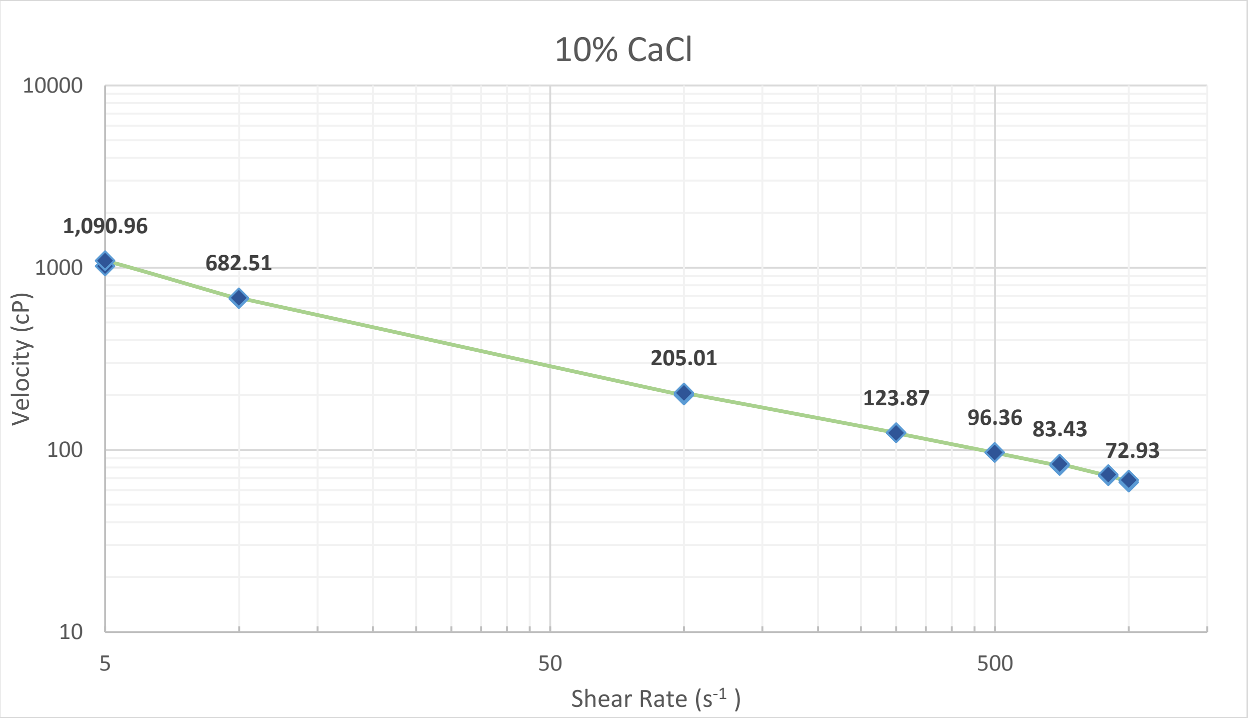


Figure 21: Viscosity Variation in 10% CaCl Concentration

Figure 22. below, illustrates that the initial viscosity of the polymer in 15% CaCl at a shear rate of 5 1/s was 363.65 cP. This shows that viscosity is increasing in the 15% CaCl concentration when compared to the 5% and decreasing as compared to the 10% brines. This represents a 63.6% decrease in viscosity when compared to the base case. When the viscosity values were

compared for shear rates between 5 and 10 s^{-1} there was a 6.8% decrease in viscosity. This translates to 1,190,000 grams pf polymer. There is an 82.35% decrease in viscosity from the shear rate of 5 s^{-1} to 1000 s^{-1}.

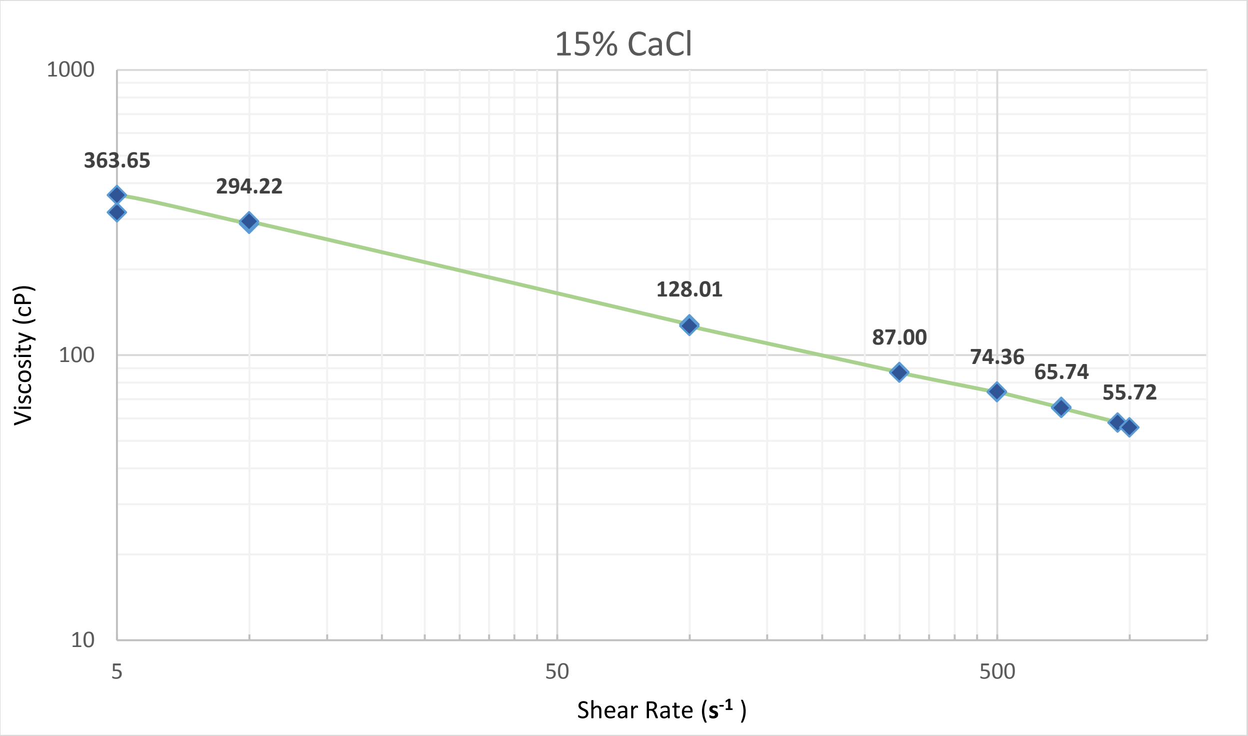


Figure 22: Viscosity Variation in 15% CaCl Concentration

The viscosity of the polymer decreases in both the 5% and the 15% CaCl brine solutions and increases in the 10% brine solution. Figure 23., illustrates the comparison between the different brine compositions and the response of viscosity. It is not clear why the viscosity of the 10% CaCl brine solution increases.

In general, viscosity of the Cassava starch- based polymer is affected by the presence of CaCl brine. When compared to conventional polymers, viscosity generally decreases with increase in

CaCl concentrations more so than it does with NaCl brines. These results are consistent with conventional polymers (Figure 24).

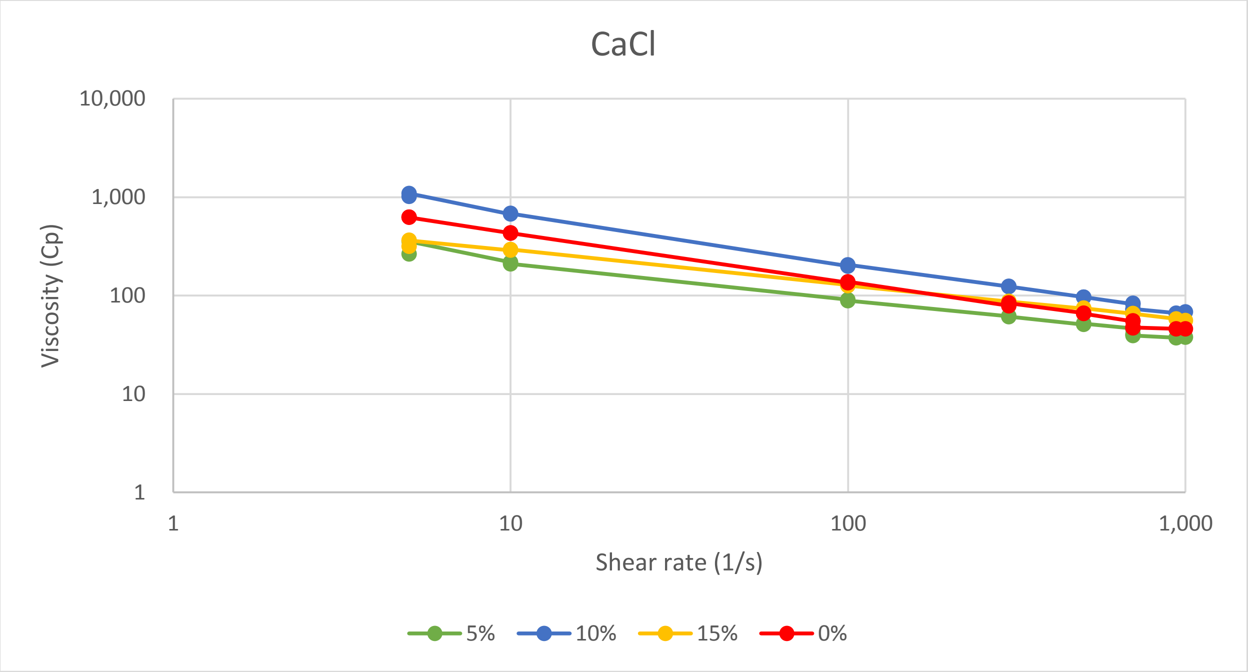
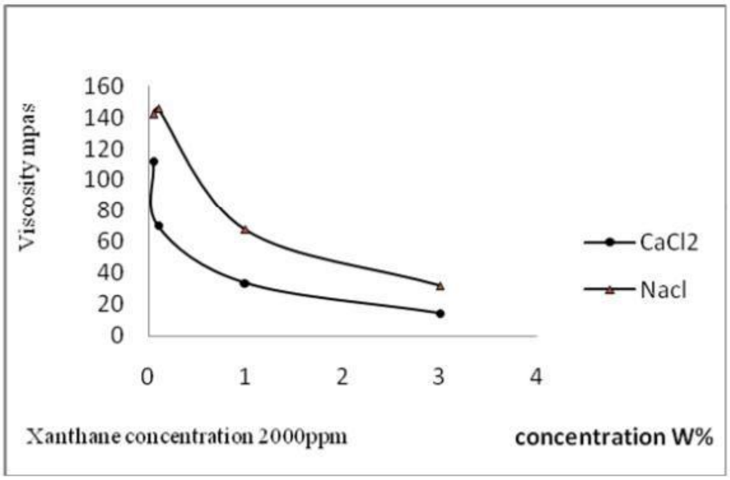


Figure 23: Viscosity Value Comparison between NaCl Brines of Varying Concentrations



From Barr, S. et. al.

Figure 24: Conventional Polymer Viscosity Response to CaCl Brine

8.1.5 Viscosity Variation of Mixed Solution in Sodium Chloride Brine

The variation of viscosity with brine concentrations of Sodium Chloride and Calcium Chloride was also observed for a mixed cassava starch- based polymer solution. Additives were incorporated into the polymer mixture. This is the so called “Mixed Solution” to address the problem of biodegradation. The aim of this section is to observe the behaviors of the viscosity of the mixed cassava starch- based polymer and compared it to the previous results as well as to conventional polymers.

Figure 25., represents the base case of the mixed solution- which means that it does not contain any salts. The initial viscosity of this solution is 143.86 cP. This is lower than all initial viscosities of the previous cases. However it represents the smallest decrease (68.75% decrease) from initial shear rate of 5 s^{-1} to final shear rate of 1000 s^{-1}.

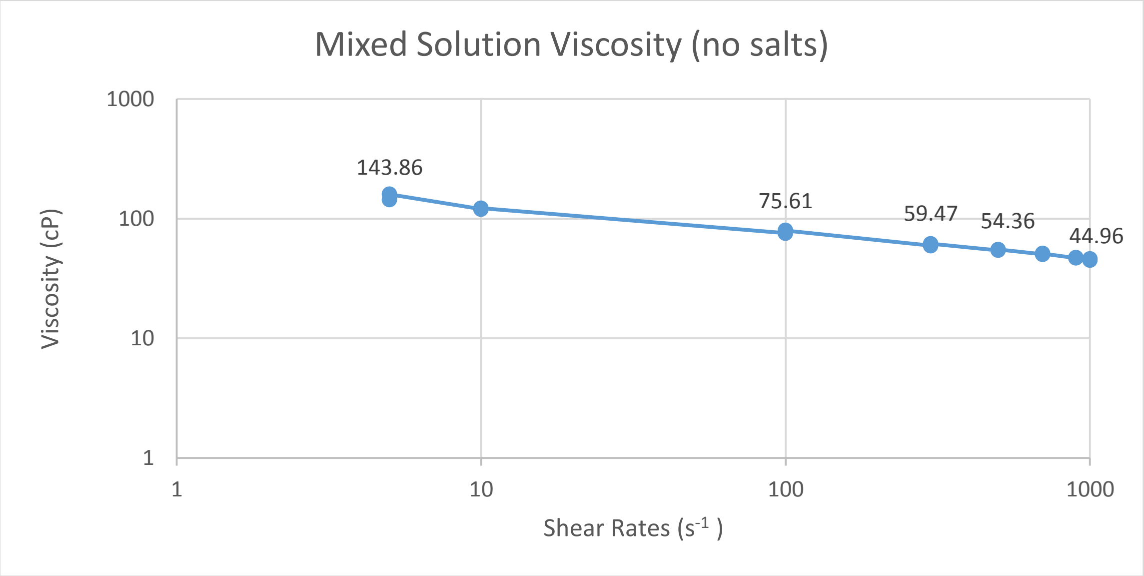


Figure 25: Mixed Solution Viscosity (No Salts)

Viscosity variation with shear rates was observed for the mixed solution with varying concentrations of NaCl brine (Figure 26.). The initial viscosity of the mixed solution in 5% Na*C*l at a shear rate of 5 s^{-1} was 503.5 cP. This shows that viscosity is decreasing in the 5% NaCl concentration and represents a 41.9% decrease in viscosity when compared to the base case. Shear rates between 5 s^{-1} and 10 s^{-1}, were observed to be decreasing by 40.37%. This is a significant loss in viscosity that would have to be accounted for should this combination of additives and polymer be utilized in an EOR application. There is a 92.6% decrease in viscosity from the shear rate of 5 s^{-1} 1/s to 1000 s^{-1}. This is comparable to the 93% reduction in viscosity in the base case.

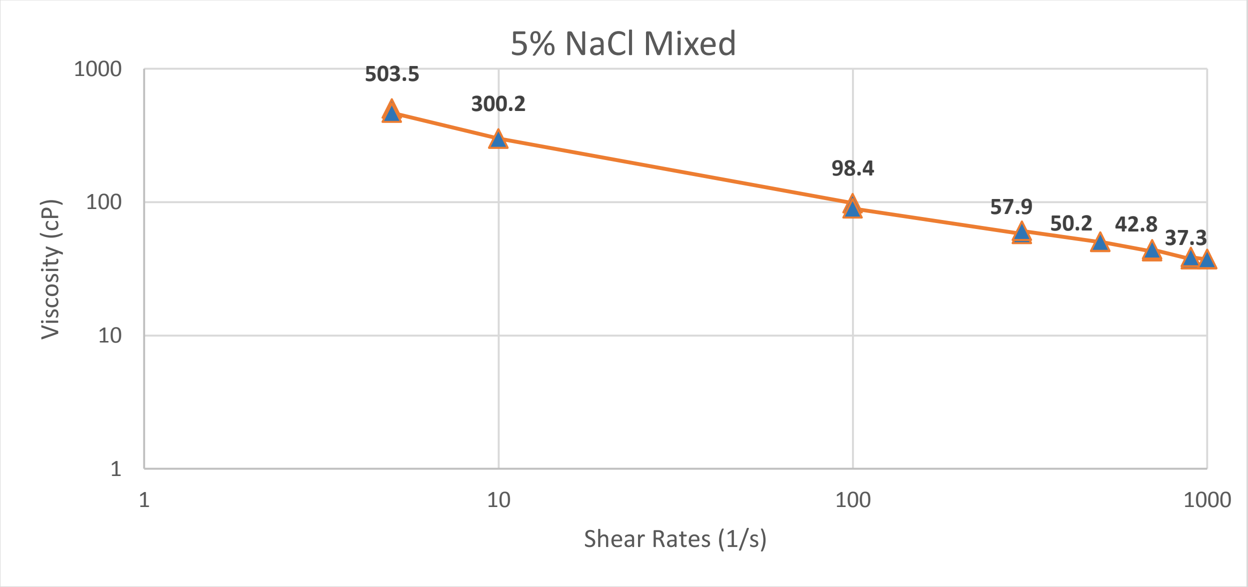


Figure 26: Mixed Solution Viscosity Variation in 5% NaCl Brine

Figure 27. below, illustrates that the initial viscosity of the mixed solution in 10% NaCl at a shear rate of 5 s^{-1} was 435.6 cP. This is shows a 13% decrease from the mixed solution base case, which is not a significant decrease. However, the latter represents a 49.77% decrease from the

polymer base case and a 72% decrease from the 5% NaCl. There was a 41.6% decrease in viscosity between the 5 s^{-1} and 10 s^{-1} shear rates. There is a 94.1% decrease in viscosity from the shear rate of 5 s^{-1} to 1000 s^{-1}. This is comparable with polymer base case.

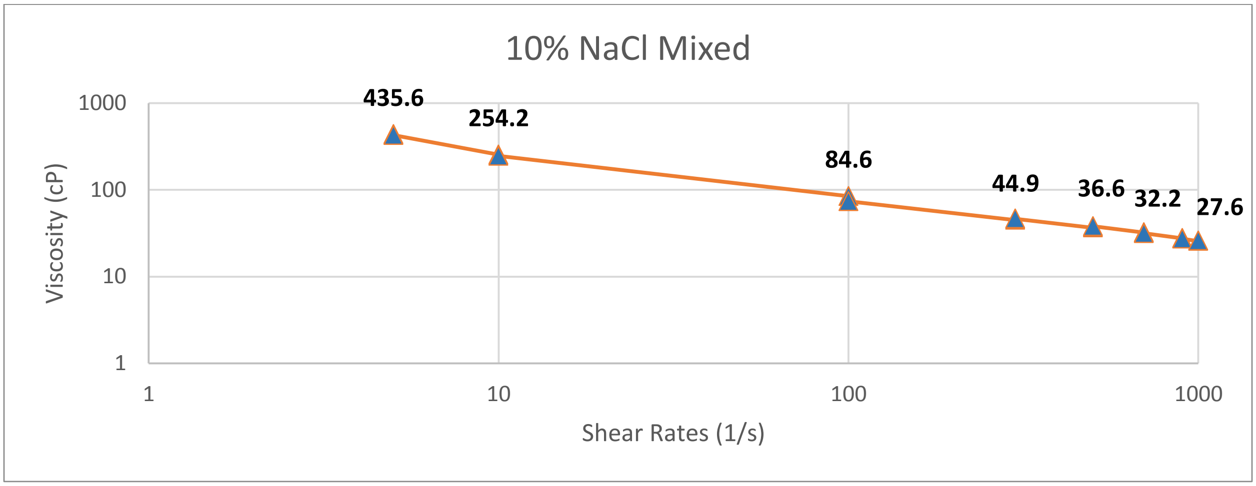


Figure 27: Mixed Solution Viscosity Variation in 10% NaCl Brine

The 15% mixed solution provides a lower viscosity than both the 5% and 10% mixed solutions (Figure 28.). In addition, this is an 85.7% decrease from the polymer solution in the 15% NaCl brine. The viscosity obtained is however 105.56% more than that obtained in the base case. There is a 31.62% decrease in the viscosities experienced between the 5 s^{-1} and the 10 s^{-1} shear rates.

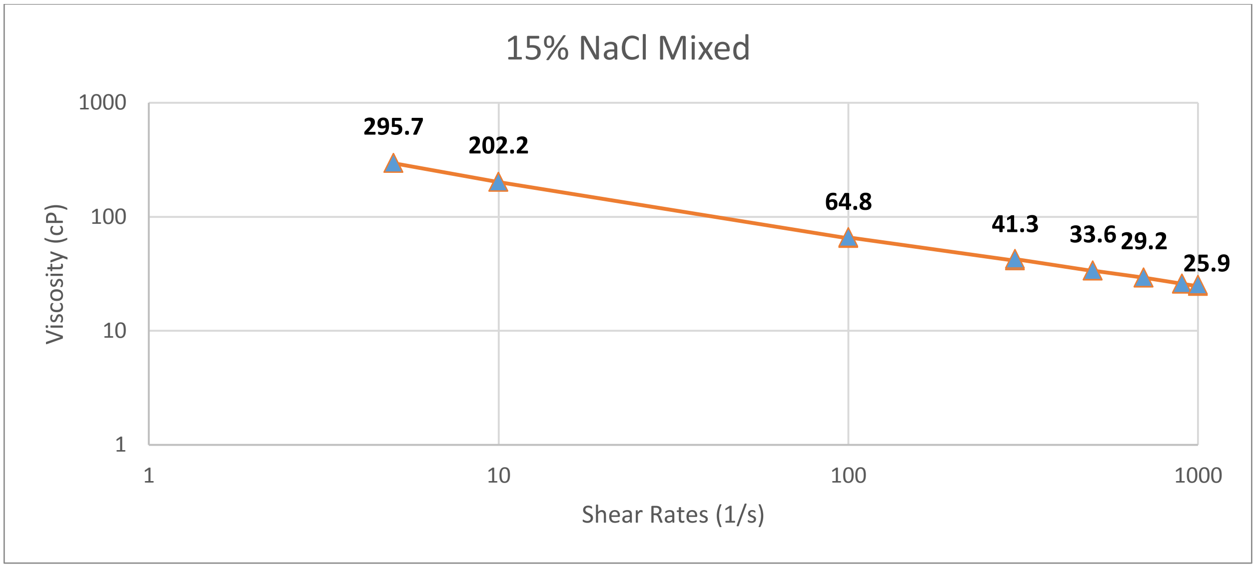


Figure 28: Mixed Solution Viscosity Variation in 15% NaCl Brine

Figure 29., illustrates the comparison of the mixed solutions at different brine compositions and their response of viscosity. The general trend is that viscosity of the mixed solutions decreases with increasing NaCl concentration. There is not a significant variation in viscosity across the three NaCl brine compositions. This is significant, because it proves the functionality of the cassava starch across varying concentrations of salinities.

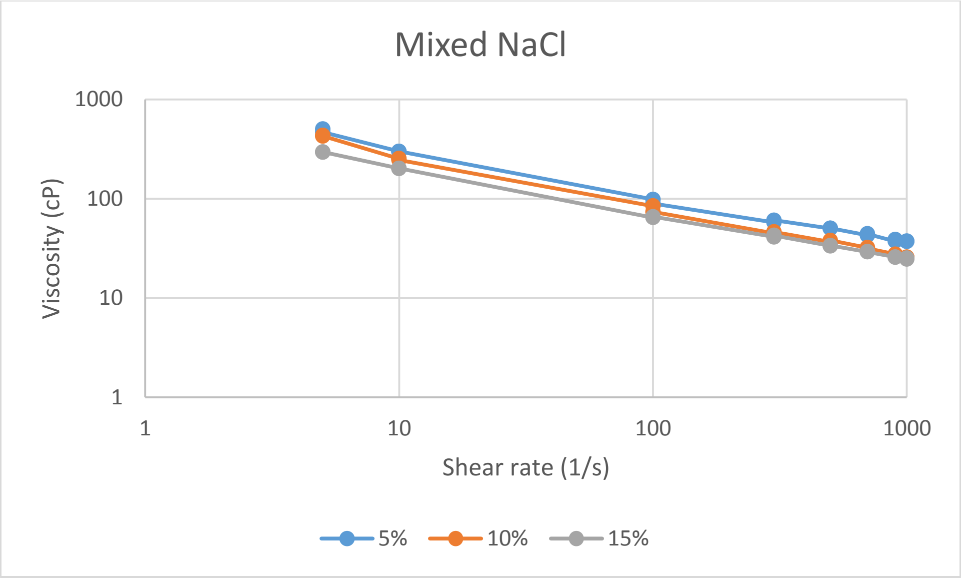


Figure 29: Viscosity Value Comparison of Mixed Solutions in NaCl Brines of Varying Concentrations

8.1.6 Viscosity Variation of Mixed Solution in Calcium Chloride Brine Solution

The results of the mixed solution in Calcium Chloride brine (Figure 30- 34) were not favourable. At the same concentrations as polymer mixtures, the viscosities were up to 98% lower in the case of the 10% CaCl case. Using the mixed solution would result in significant financial ramifications. This trend is noted from 5% to 15% Calcium Chloride.

Shear Rate (s^{-1})	Calcium Chloride Solution Viscosities		
	5%	**10%**	**15%**
5.00	59.94	15.98	47.95
9.99	18.01	18.01	28.02
9.99	14.01	16.01	34.03
99.99	8.00	6.60	12.60
99.99	7.80	6.00	12.20
300.00	7.13	6.87	11.13
300.00	7.33	7.00	11.33
500.00	6.48	6.16	10.36
500.00	6.60	6.40	10.80
700.00	6.34	6.17	10.34
700.00	6.31	6.43	10.31
900.01	6.13	6.24	10.20
900.01	6.24	6.33	10.33
1000.00	6.06	6.16	10.00
1000.00	6.20	6.28	10.20

Table 7: Shear Rates and Respective Viscosities for 5%, 10% and 15% Mixed CaCl Solutions

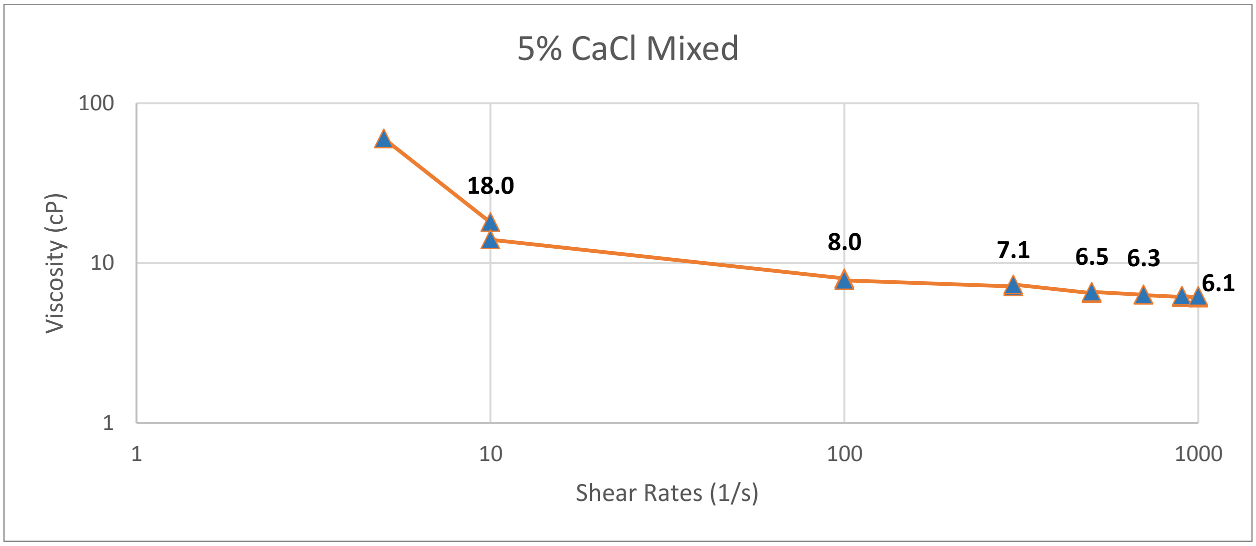


Figure 30: Mixed Solution Viscosity Variation in 5% CaCl Brine

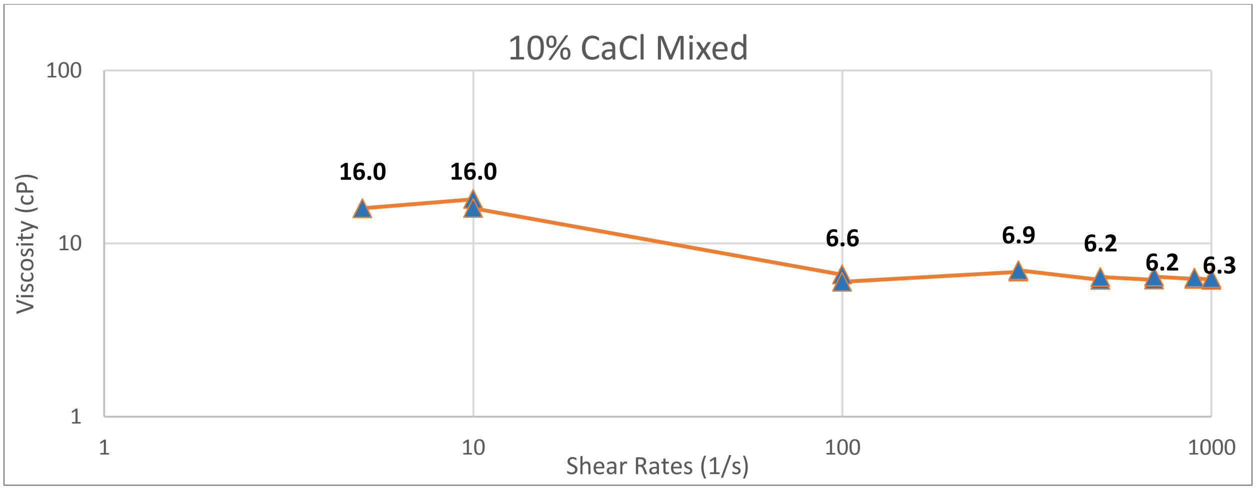


Figure 31: Mixed Solution Viscosity Variation in 10% CaCl Brine

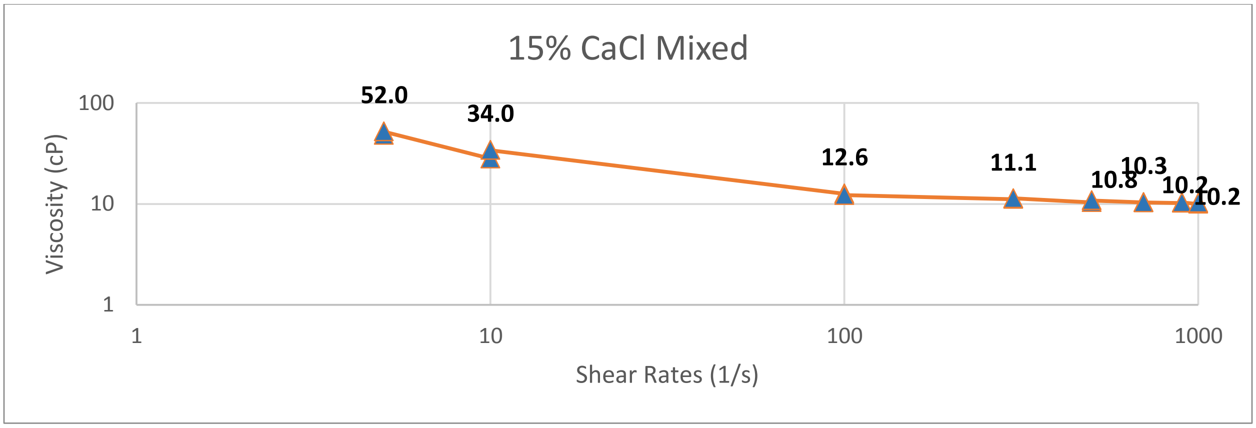


Figure 32: Mixed Solution Viscosity Variation in 15% CaCl Brine

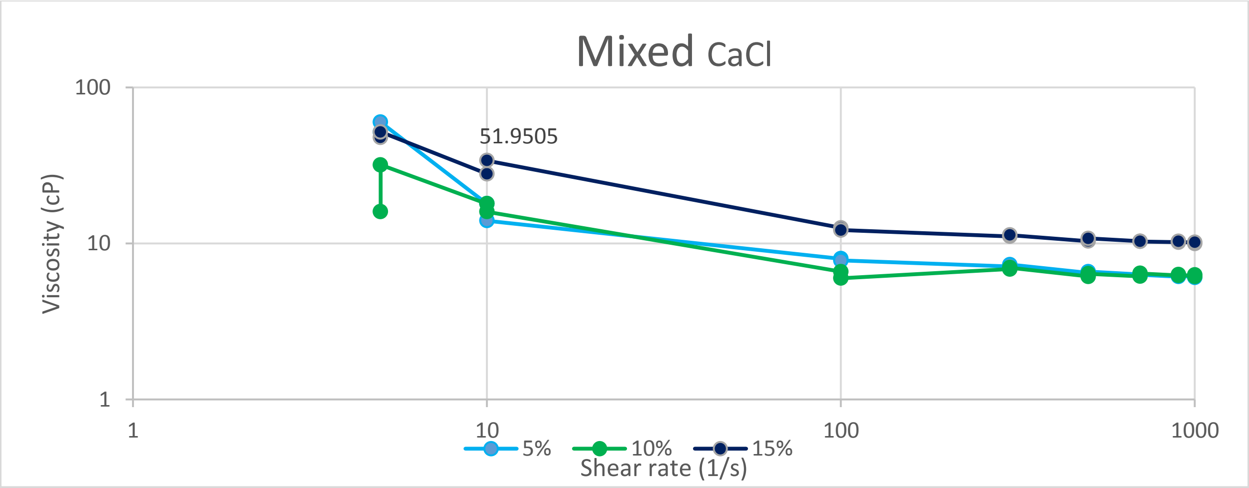
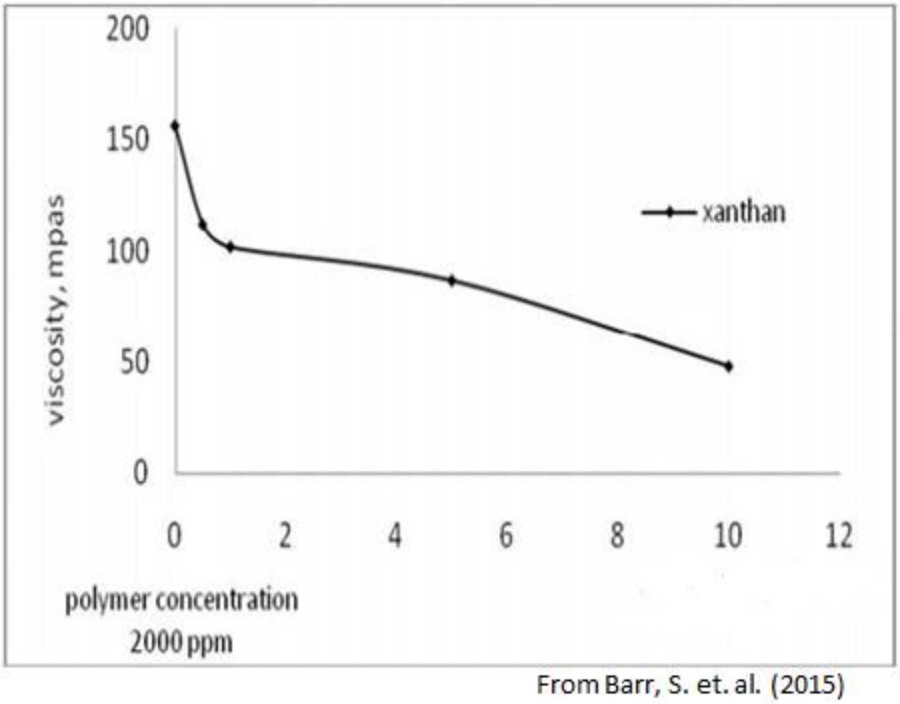


Figure 33: Comparison of Mixed Solution Viscosity Variation in CaCl Brine



From Barr, S. et. al. (2015)

Figure 34: Xanthan Gum Reaction in Mixed Solution

8.1.7 Viscosity Variation with Temperature

Figure 35 illustrates the variation of the Cassava starch- based polymer viscosity with variation in temperature. The trend line shows that there is a gradual decrease in viscosity with variation in temperatures up to 300 ^{o}F. In Figure 36, Xanthan Gum, shows a more pronounced decrease in viscosity with increasing temperature values. In addition, beyond 60 ^{o}c, the HPAM become impuissant and therefore should not be used in such a reservoir.

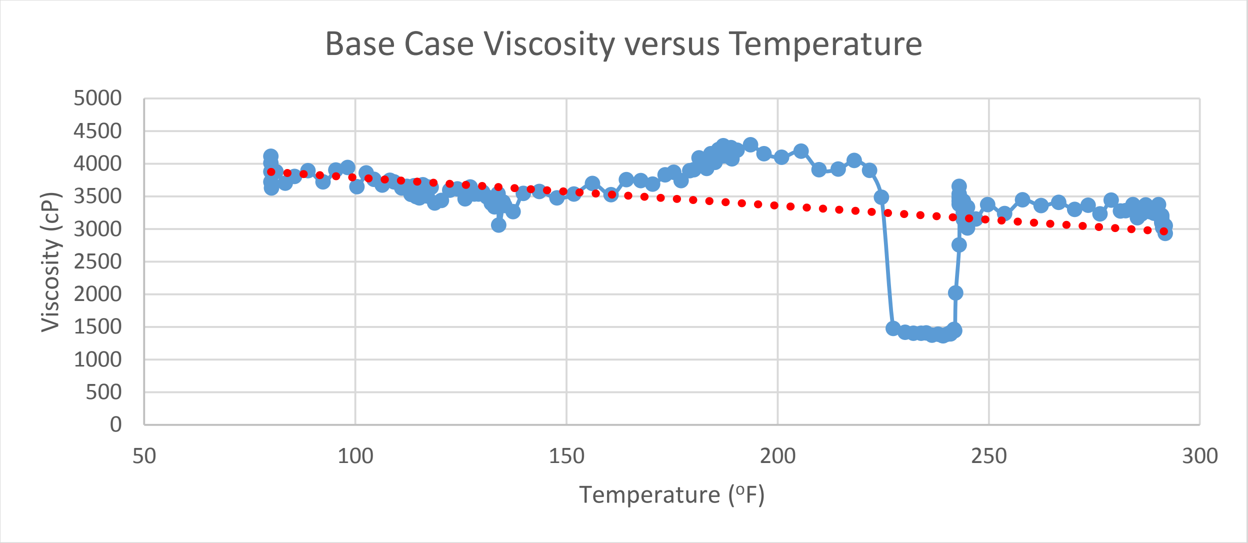
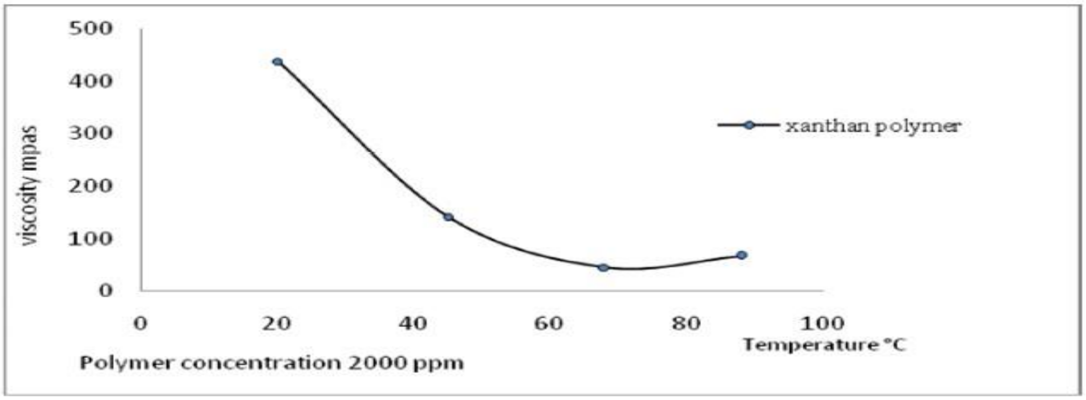
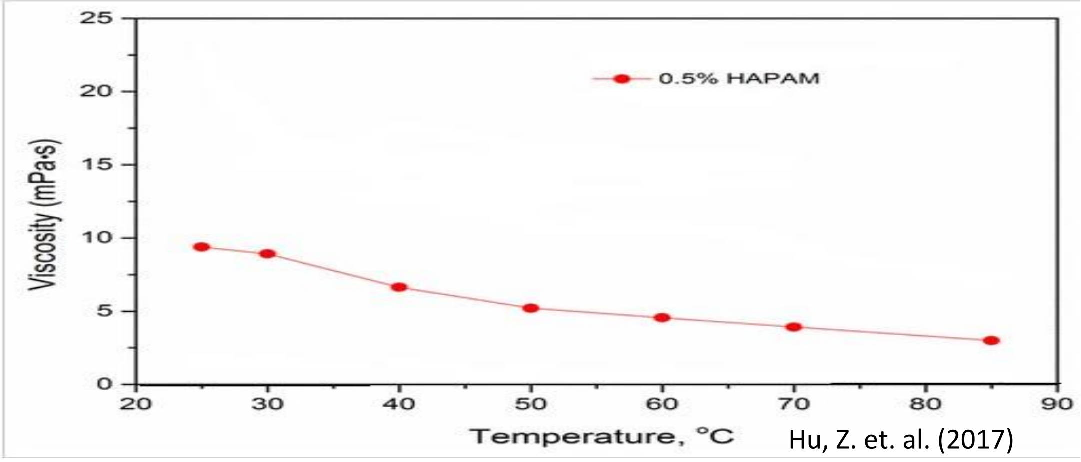


Figure 35: Cassava Starch- Based Polymer Reaction to Temperature Variation



From Barr. S. et. al. (2015)



Hu, Z. et. al. (2017)

Figure 36: Xanthan Gum (top) and HPAM (bottom) Response to Temperature Variation

Figure 37 illustrates the reaction of the Cassava starch- based polymer in 15% NaCl concentration in temperatures beyond 275 ^{o}F. This illustrates that the viscosities of the Cassava starch- based polymer is significantly affected by the presence of high salinity brine and high temperatures more so than the base case. However, as there is only a 41% decrease in viscosity over a wide range of temperatures, this polymer is a viable option in a high salinity, high temperature regime.

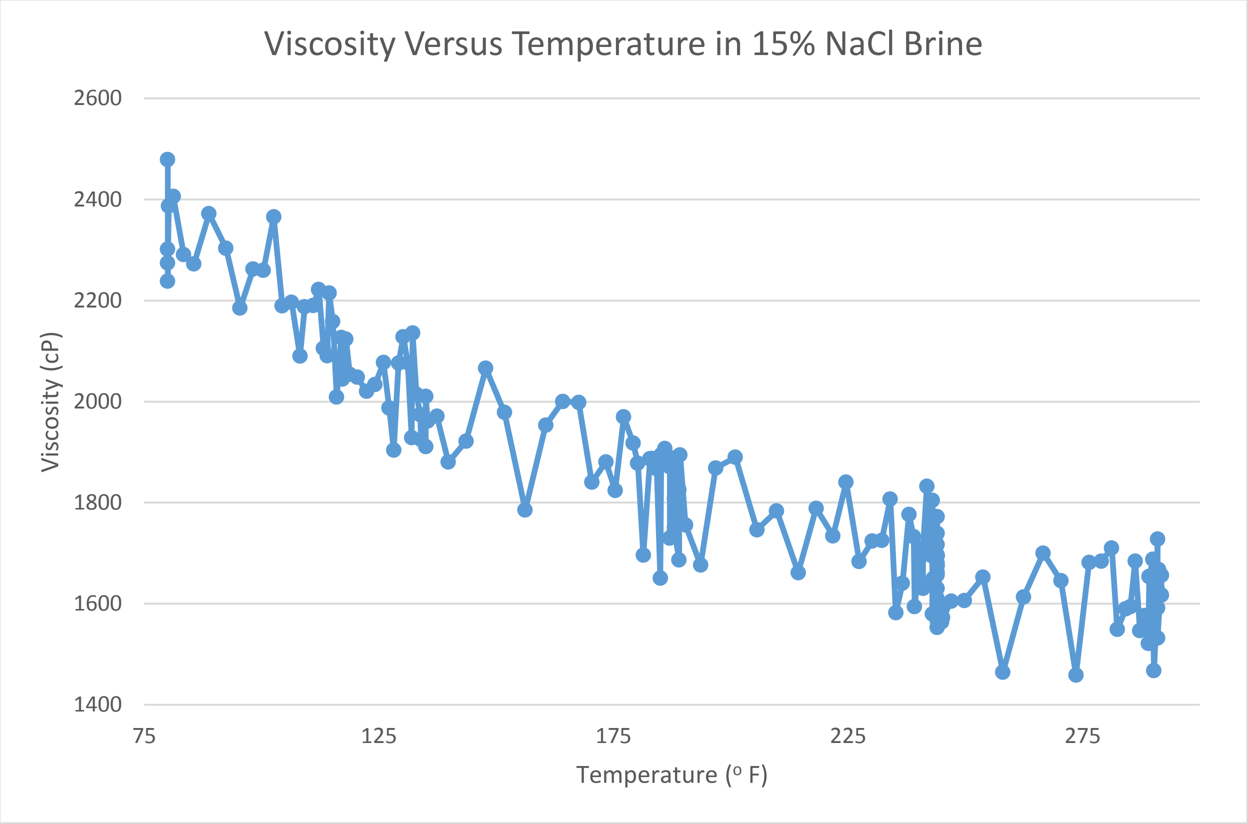


Figure 37: Cassava Starch Reaction to Temperature in High Salinity Brine

8.2 Simulation Results

Hydrolysed Polyacrylamide (HPAM) is the default polymer that was simulated in the simulation model using MRST. Properties of the cassava starch- based polymer will be altered based on established HPAM parameters from the simulator.

The initial condition of the reservoir is such that the water viscosity (0.318 cP) is not sufficient to displace the oil at 4 cP viscosity (Figure 38.). HPAM polymer at varying concentrations were injected into the reservoir, yielding a range of viscosities (Figure 39. (Top A)). The viscosities are expressed as a viscosity multiplier. The viscosity multiplier is a ratio of the viscosity of the polymer to that of water. Other parameters such as polymer adsorption and Shear effect are also illustrated in (Figure 39. (Top B and C)).

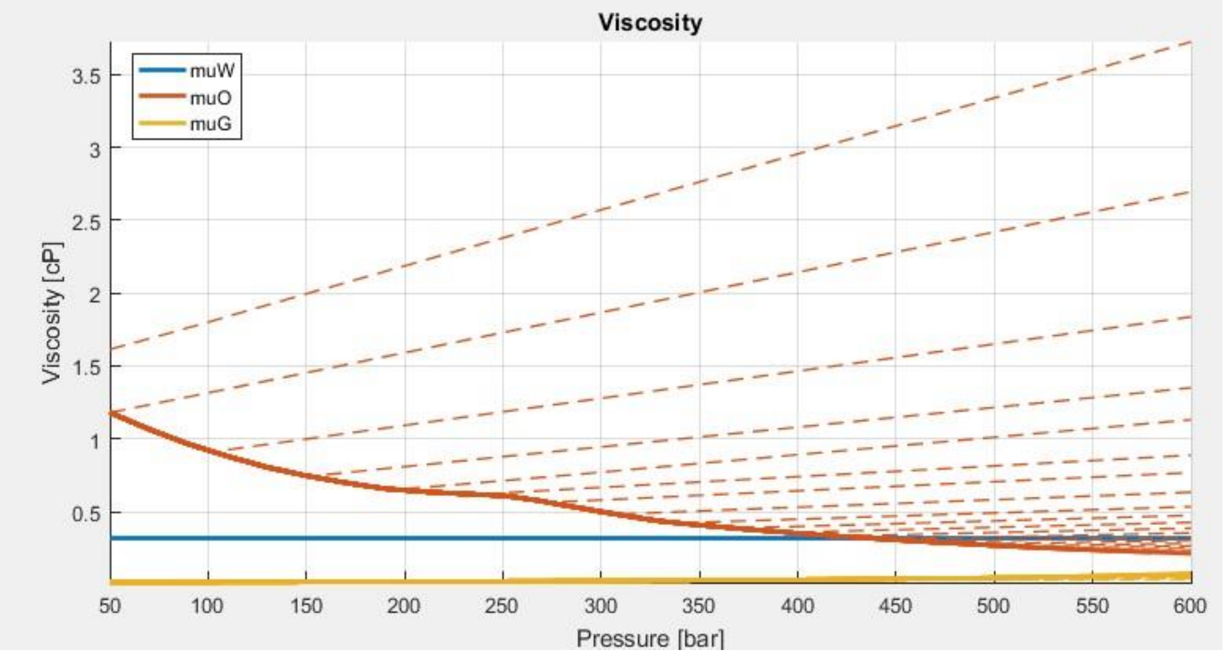


Figure 38: Initial Viscosities of Reservoir Fluid Prior to Polymer Flooding

8.2.1 Polymer Parameter Comparison

Figure 39 compares the polymer viscosity multiplier and the polymer adsorption (from polymer model). The cassava starch provides higher viscosities than the HPAM at concentrations less than 2 Kg/m^3. The HPAM provided approximately two times higher viscosities at concentrations above 2 Kg/m^3. This can be explained by the fact that when solvated, the Carboxylate groups of the HPAM causes chain expansion due to repulsion of the ionic groups (Taylor and Nasr-El-Din (1998)) as oppose to chain extension and physical entanglement that is exhibited by the Cassava Starch- based polymer. However, at greater concentrations, both the cassava starch and the HPAM exhibits similar response to concentration (Figure 40.), which is that as concentration increases, viscosity increases.

The adsorption of the cassava starch records a constant value of approximately 0.0000292 (29.2 x 10^-6) kg/kg, with concentration increase. According to Petrowiki, a desirable adsorption level is 0.00002 kg/kg. Therefore the adsorption level of the starch is comparable to that of the desired level. Due to the levels of adsorption that is exhibited by the cassava starch polymer, it is expected that permeability reduction will be enhanced and as such, the relative permeability to the polymer will be reduced. Reduction of the relative permeability to the polymer will allow the oil to flow faster than the polymer towards the production well Thus, the oil will be produced faster than the polymer.

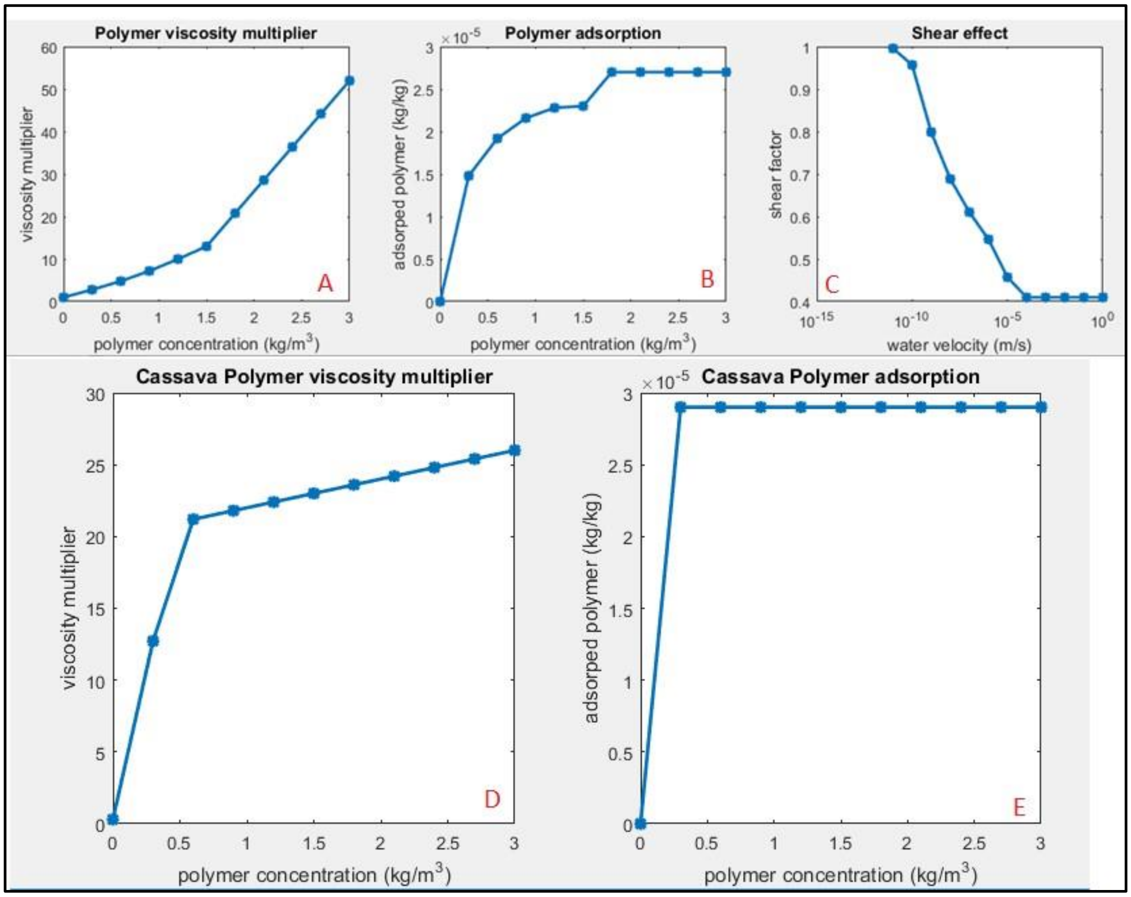


Figure 39: Simulation Results for HPAM (top) and Cassava Polymer (bottom)

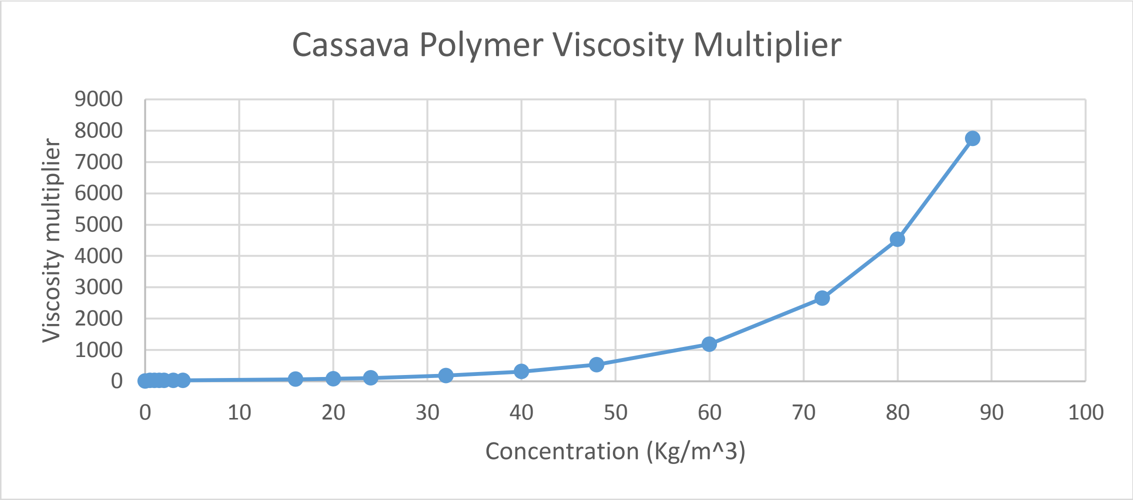


Figure 40: Cassava Polymer Viscosity Multiplier

8.2.2 Oil Production Comparison

Figure 41 depicts the difference in oil production between the base case cassava starch- based polymer and the HPAM with no considerations of Salinity and Temperature. For the first 4000 days, the HPAM produces more oil than the cassava starch- based polymer. After day 4000 and for the remainder of the project, the cassava starch- based polymer produces more oil than the HPAM. There are two reasons why this can possibly happen: 1. Oil production is proportional to the viscosities of the polymer. HPAM exhibits higher viscosity values and will therefore produce more oil in the base case, 2. However, the cassava starch exhibits a constant adsorption value of 29.2 x 10^-6) kg/kg throughout the polymer flooding process, whereas the highest adsorption value exhibited by the HPAM is 27 x 10^-6) kg/kg; this value of adsorption is experienced during the later phase of the project, therefore during this time the cassava will produce more oil.

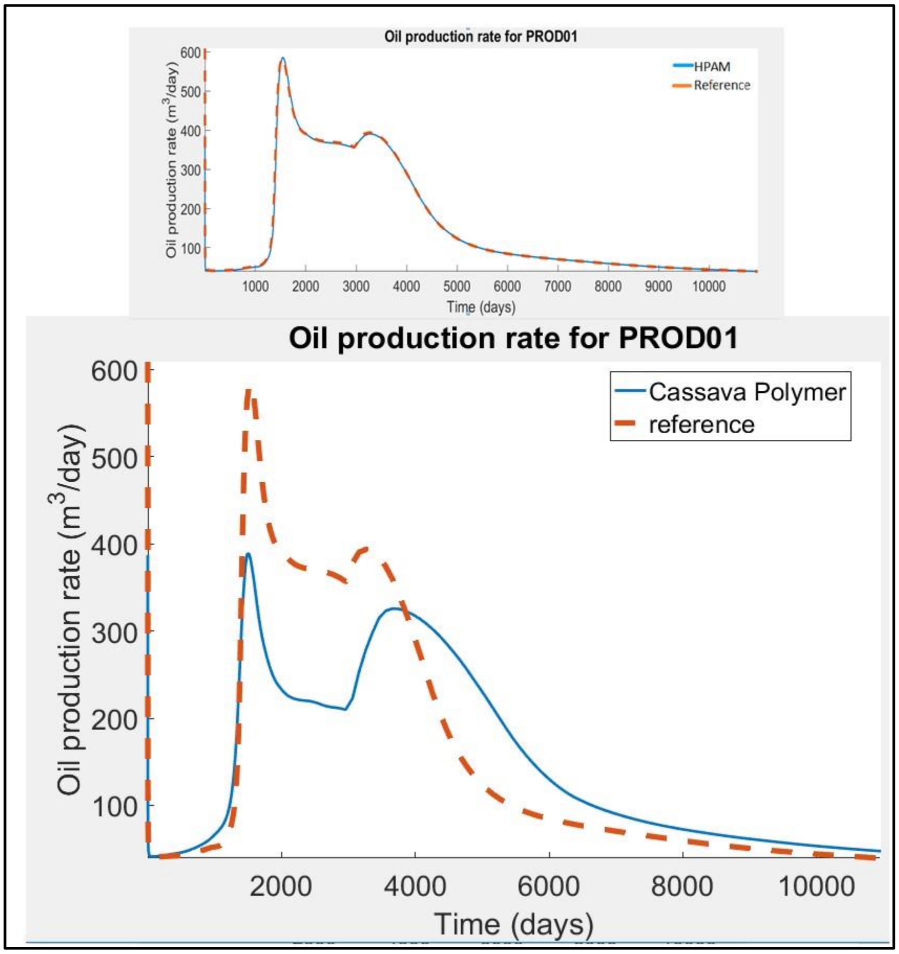


Figure 41: Oil Production Rates for HPAM and Cassava via Simulation

8.2.3 Water Production Comparison

Abidin A. Z.(2012), explains that during a polymer flooding, there is less water production. This has a direct implication on cost because water treatment in oil production accounts for a substantial portion of the budget. Figure 42 illustrates that the water production of the cassava polymer is comparable to that of HPAM for the first 4000 days of the project, and decreases for the duration of the project. This is related to the idea of adsorption and permeability reduction. In a polymer flooding, the polymer blocks some of the pore spaces in the rock and as such, decreased the permeability, this in essence decreases the ability of the formation water to enter into the well bore, and thus there will be less water production. Figure 43 also illustrates the comparison of the oil production with (purple line) and without polymer (yellow line) and shows that there is more oil production with polymer. The water production for the case with (orange Line) and without (blue line) polymer was also observed and verifies that there is less water production with polymer flooding.

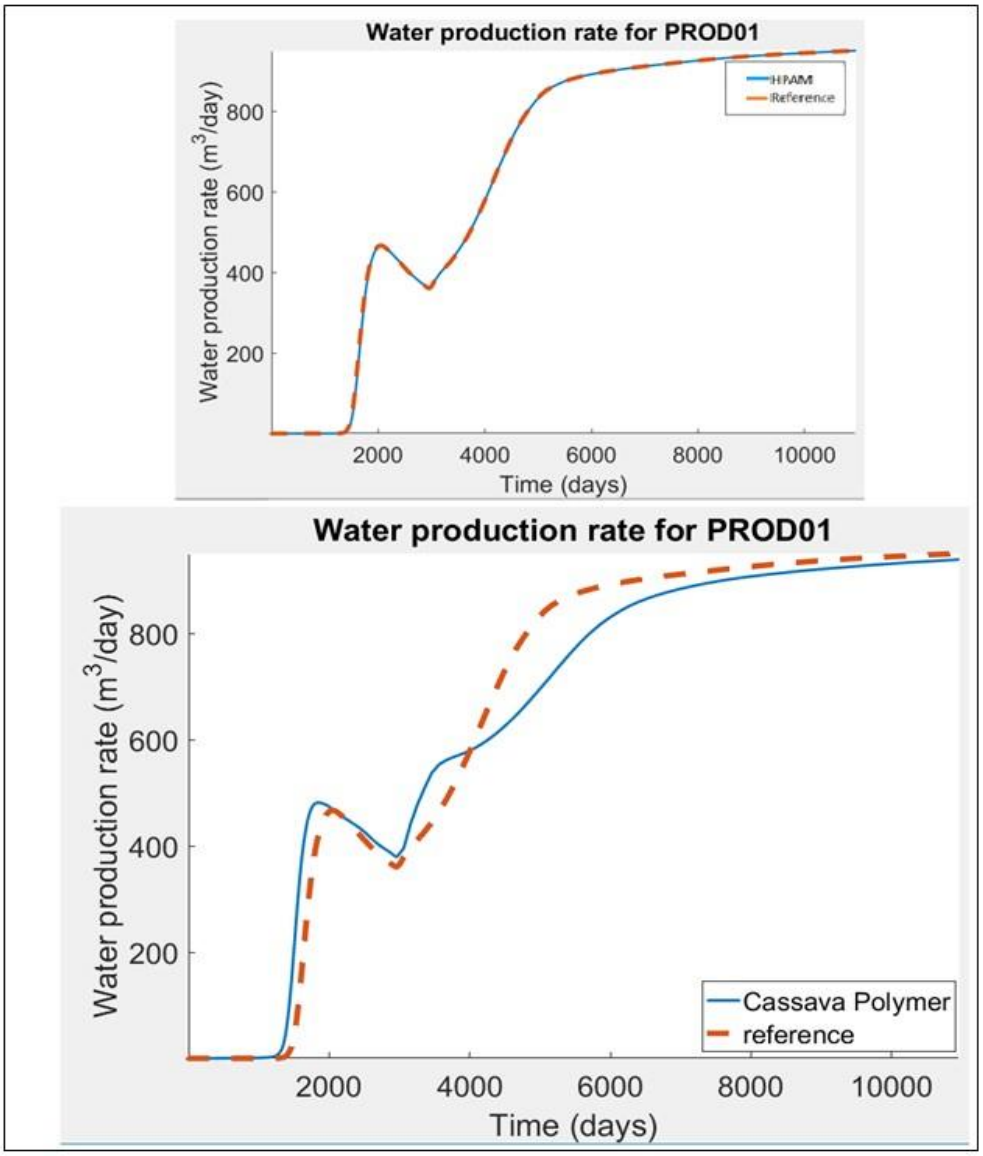


Figure 42: Water Production Comparison between HPAM and Cassava Polymer

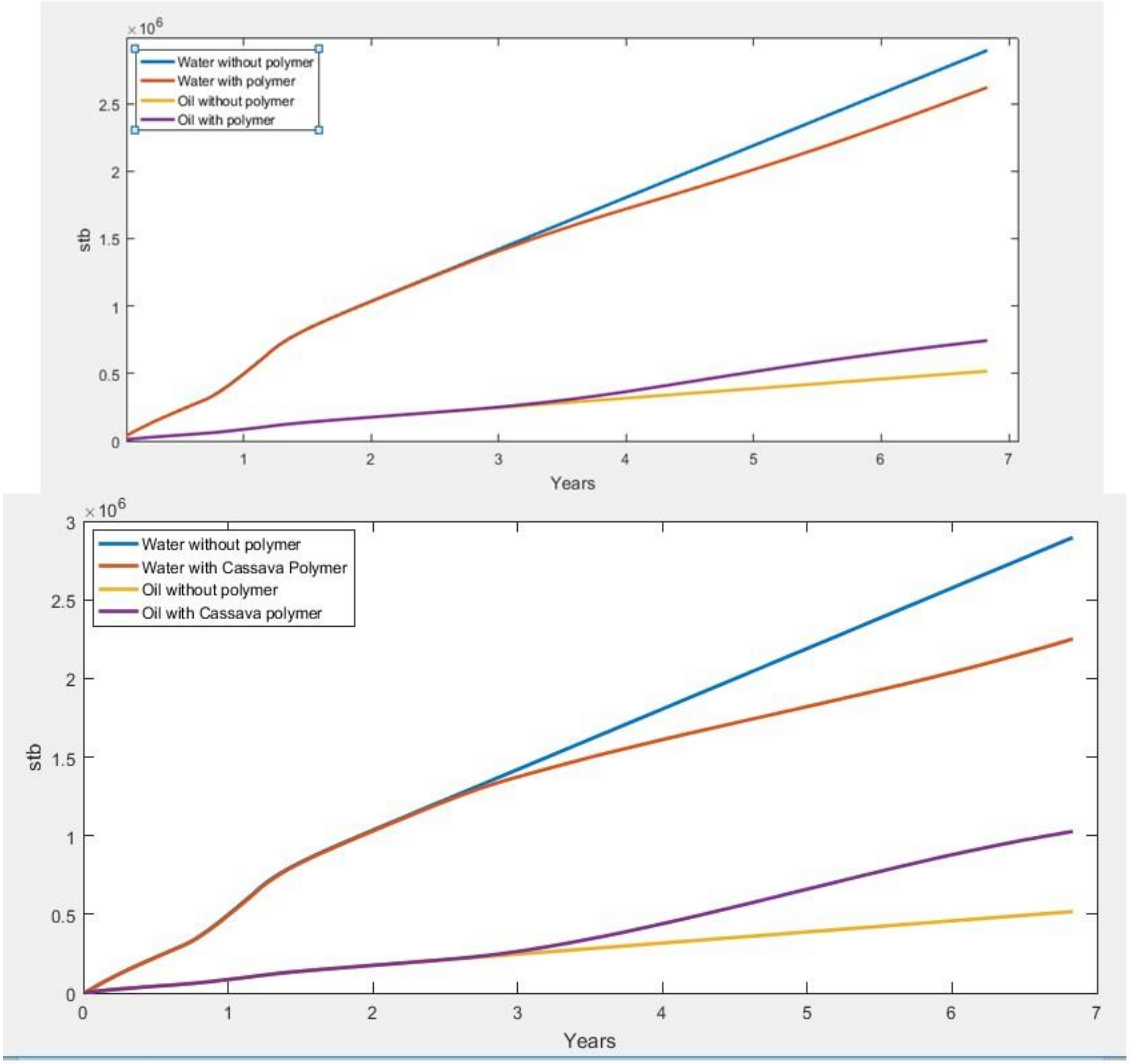


Figure 43: Water Production Comparison With and Without Polymer

A second simulation was carried out to compare the Net Present Value of the HPAM, Xanthan Gum and the Cassava starch- based polymer in a homogeneous Reservoir (Figure 44.). Through this simulation, it was evident that at a price of $1.28 USD, the NPV of the cassava starch- based polymer is comparable to that of the HPAM and higher than that of the Xanthan Gum (Figure 45).

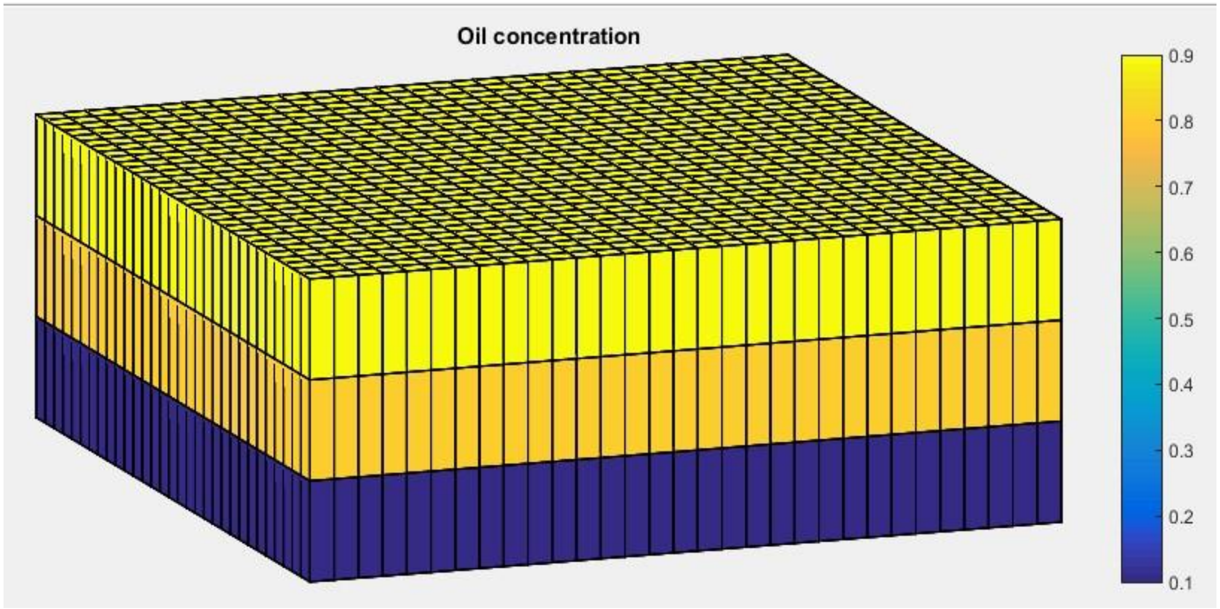


Figure 44: Homogeneous Simulation Reservoir for NPV Comparison

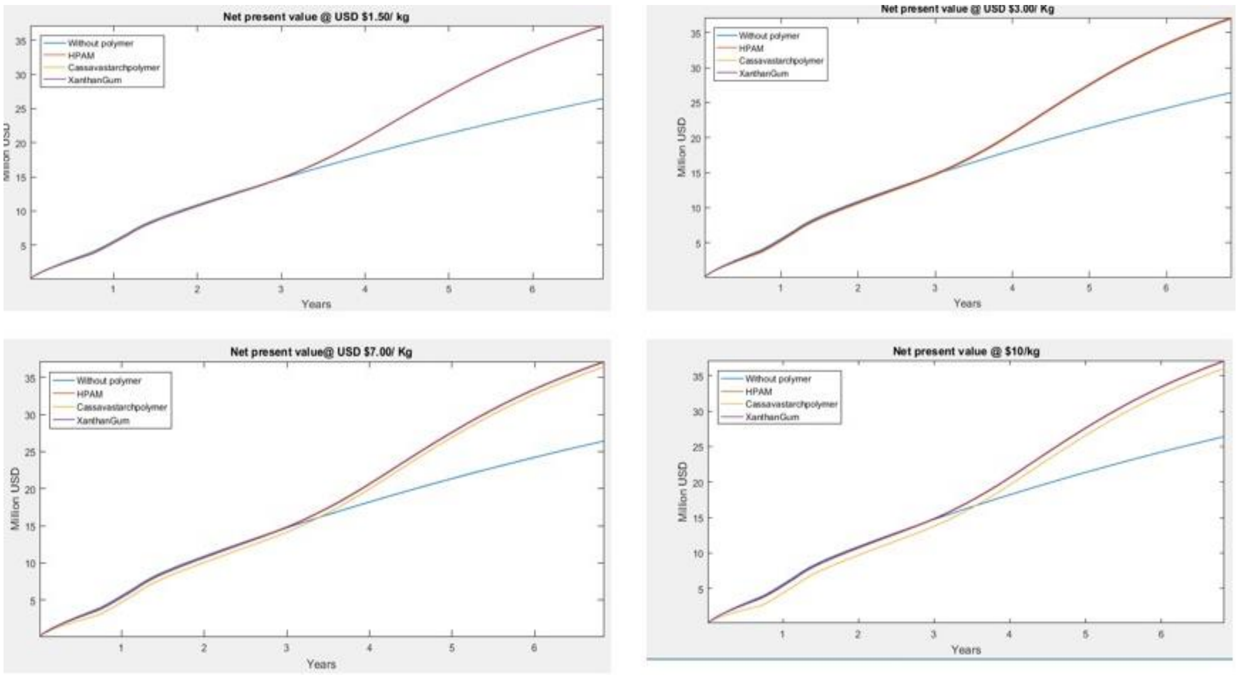


Figure 45: Price Comparison of Polymers

8.3 Sensitivity Analysis

A sensitivity analysis was carried out based on the Bayesian Network concept. Bayesian networks or belief networks model the probability of outcomes representing a state of knowledge. The probabilities that will be modeled are highlighted in Figure 46. In particular, Reservoir salinities, temperatures, permeability and porosity will be model. In addition, the probability of environmental threats and social factors will also be modeled. These factors will be altered and their monetary effect on the industry and the social benefits that they provide will be observed. These values will be compared to that of the conventional polymer HPAM and Xanthan Gum.

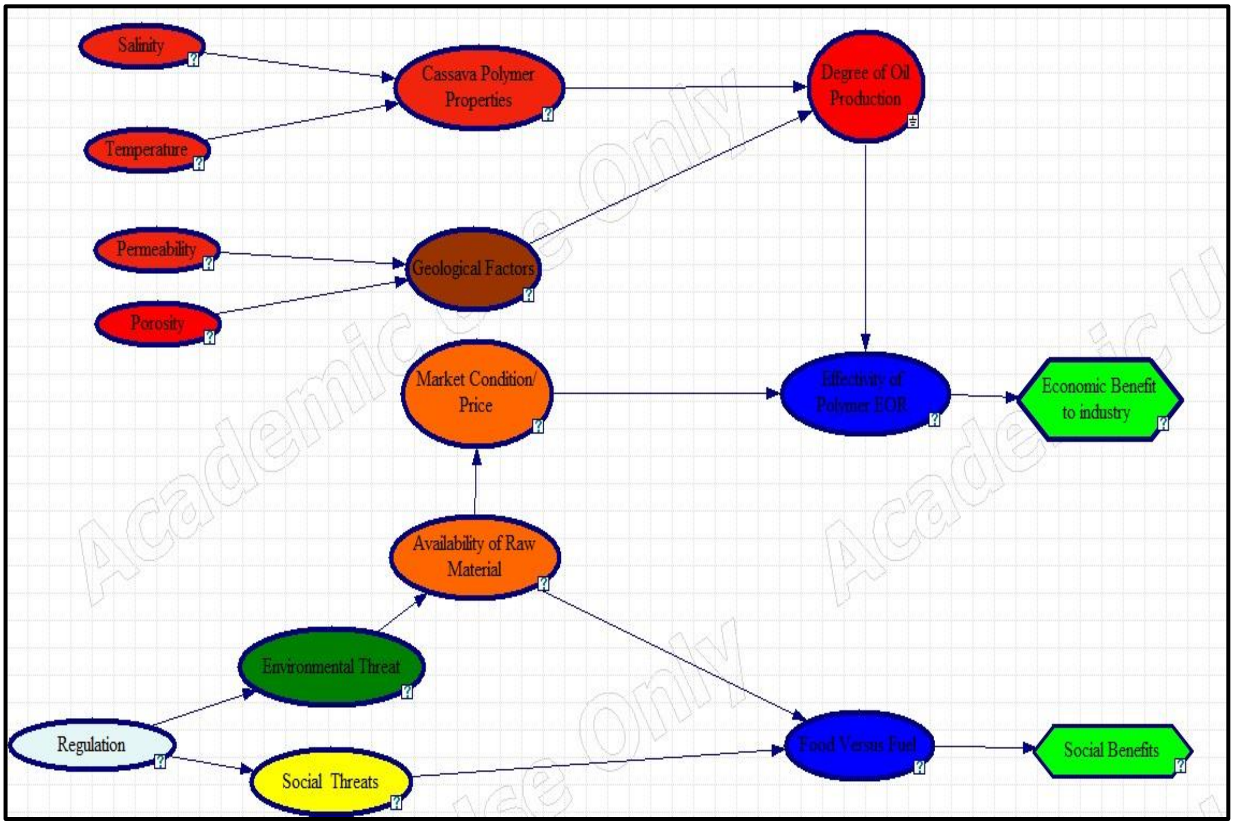


Figure 46: Sensitivity Analysis Using Bayesian Networks

Parameters	**Cost ($/kg)**
Oil Price ($/Stock tank barrels)	74.80
Water production Cost ($/Stock tank barrels)	1
Water injection Cost ($/Stock tank barrels)	0.1
Polymer injection Cost ($/Stock tank barrels)	0.1
Discount factor	0.1
HPAM Cost ($/)	1
Cassava starch- based Polymer ($/)	1.28
Xanthan Gum Cost ($/)	1.87
Mass of polymer (kg)	17,500,000

Table 8: Sensitivity Analysis Parameters

Conversion: 114.42 kg/day= 1 barrel oil/ day

Volume of oil displaced	17,500,000.00
Volume of oil (Barrels)	152,945.29
Price of oil ($/ barrels)	74.8
value of oil for the 1700 days ($/barrels)	11,440,307.64

Table 9: Total Economic Benefit of Oil during Water Flooding

Salinity	High	Medium	Low
Cassava Polymer	$ 5,811,600.00	$ 7,898,960.00	$ 8,341,110.00
HPAM	$5,811,600.00	$ 8,497,040.00	$ 7,933,392.00
Xanthan Gum	$ 4,168,280.00	$ 7,811,100.00	$ 8,925,160.00

Table 10: Economic Benefits with Variation in Salinities

When the values of the salinity was varied based on high, medium and low values of probabilities, the following data in Table 10. was obtained. From the data, it is apparent that Salinity has the highest effect on HPAM, and has similar effects on Xanthan Gum and the least effect on the cassava starch- based Polymer. However, at low salinity, HPAM is more economical.

Temperature	High	Low
Cassava Polymer	$ 8,211,620.00	$ 8,497,040.00
Xanthan Gum	$ 7,271,730.00	$ 7,539,070.00
HPAM	$ 4,129,950.00	$ 8,242,970.00

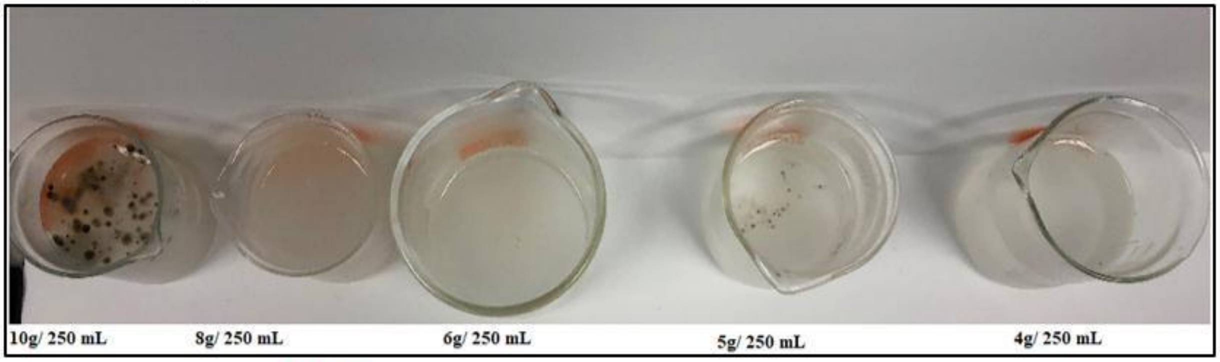
Table 11: Economic Benefits with Variation in Temperature

From Table 11, it is evident that temperature has the highest effect on HPAM and thus at high temperatures, HPAM would yield the lowest economic value. The Cassava Starch- based polymer is least affected by temperature and yields relatively $285,420 less in a high temperature regime.

8.4 Other Considerations

De- ionized water and polymer solutions of varying cassava starch- based polymer concentrations were left unattended and uncovered at a temperature of 25 degrees Celsius for four days to observe their susceptibility to biodegradation. It was observed that the sample with the highest cassava starch- based polymer concentration (10g/250mL) had the highest fungus formation followed by the 5g/250 mL, 4g/ 250mL, 6g/ 250mL and lastly the 8g/ 250 mL. There does not seem to be a consistent correlation between polymer concentration and the amount of biodegradation. Also it is not clear why there was hardly any fungus formation in the 8g/ 250 mL concentration. As this is an undesirable trait of polymers, which is also observed in Xanthan Gum polymers, other compounds were added to the polymer solution (mixed polymer solution). This would be equivalent to the biocides added to the formation during polymer flooding. The mixed polymer solution was left and observed over a period of three weeks and has not experienced any biodegradation (below).

Un- Mixed Polymers after one week



Mixed Polymer after three weeks

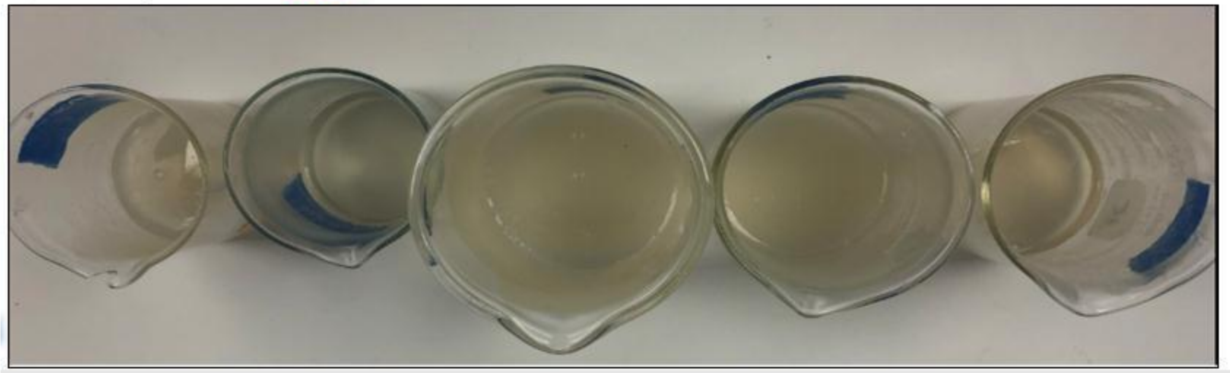


Figure 47: Biodegradation Observation of Varying Polymer Solutions

9 CONCLUSION

9.1 Conclusion of Laboratory Experiments

From the laboratory experiments, it is evident that the Cassava starch- based polymer increases in viscosity with an increase in polymer concentration. This response is better than that of Xanthan Gum; and less so than that of HPAM, because of its chemical make-up which allows for an increase in viscosity with an increase in molecular weight. In addition, The Cassava starch-based polymer shows the best response to temperature than both Hydrolysed Polyacrylamide and Xanthan Gum. At a temperature of approximately 300 degrees Farenheit, the base case Cassava starch- based polymer viscosity decreased by 25%. The responses of the polymers to CaCl brine, is relatively the same, and therefore more polymer would have to be used in order to facilitate a high CaCl brine regime. However, there was a better response from the Cassava starch- based polymer in NaCl brine than both polymers. In the base case, there was an increase in viscosity with increasing NaCl concentrations. The latter was not seen in the conventional polymers. However, the biggest problem remains that the Cassava starch- based polymer is susceptible to biodegradation if not treated with biocides. However, from laboratory observations, minimal amounts of additives can be mixed with the Cassava starch- based polymer to deter bacterial attack.

Therefore, as it relates to the following parameters, the cassava polymer:

- Concentration

Provides high viscosity at low polymer concentrations. This is also the case with both Xanthan Gum and HPAM polymers.

- Shear Rate

Exhibits good resistance to shear rates. Near wellbore injection shear rate of 7.3 s^{-1} has negligible effect on the polymer. In addition, the cassava starch- based polymer is able to withstand shear up to 1000 s^{-1}.

- Salinity

The Cassava starch- based polymer is less affected by Sodium Chloride Brine than it is by Calcium Chloride brine solutions. However, the polymer exhibits better properties in the NaCl brine than both the HPAM and the Xanthan Gum Polymers. However, the response to CaCl brine means that more polymer would have to be utilized to meet a viscosity requirement.

- Temperature

Provides a stable temperature profile in low salinity regimes, however increasing brine solutions affect viscosity.

- Biodegradation

Highly susceptible to biodegradation unless mixed with other substances.

9.2 Conclusion of Model Simulations

When compared to the Simulation outcomes of HPAM, the viscosity, adsorption capability, level of oil production and level of water productions were observed.

The viscosity multiplier values are similar, however high concentrations of approximately 0.0000292 (29.2 x 10^-6) kg/kg, was utilized in this project. The Cassava starch- based polymer exhibits an adsorption value of approximately 0.0000292 (29.2 x 10^-6) kg/kg. This value is within the range of both HPAM and the desired polymer values. This means that it will enhance relative permeability to oil thus increasing oil production.

As it relates to oil production, initially, the HPAM will produce more oil than the Cassava starch-based polymer. However after 4,000 days the cassava starch- based polymer will produce more oil beause: the oil production is proportional to the viscosities of the polymer and the HPAM exhibits higher viscosity values and will therefore produce more oil in the base case, but the cassava starch exhibits a constant adsorption value and will eventually surpass the production of HPAM.

In addition, the HPAM will produce less water than the Cassava starch- based polymer and again after 4,000 days this will change. This is also as a result of adsorption and permeability reduction. With a constant reduction value the water encroachment will decrease.

The net present value of the cassava in a homogeneous reservoir is comparable to that of HPAM at a price of $ 1.28. However the properties of the Cassava starch- based polymer are what will overshadow the use of HPAM. The use of the Cassava starch- based polymer in high salinity regimes are what will affect the profitability of it in general.

9.3 Next Steps

As the ranges of temperatures and salinities used to test the cassava starch- based polymer are similar to those experienced in other oil industry operations, the following can be considered:

- Compare properties of polymer to that of potato starch for use in drilling fluids
- Compare properties of polymer to that of Guar gum for use in fracturing

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