

Review Article

Development of Polyacrylamide from Waste Agricultural By-Product for Enhanced Oil Recovery Process in Nigerian Oil Industry: Conceptual Review

*¹Adama, K. K., ¹Ikhazuangbe, P.M.O., ²Onyeachu, I. B., ³Aliu, D., ⁴Anani, O. A.

¹Department of Chemical Engineering, Faculty of Engineering, Edo State University Uzairue, Nigeria.
²Department of Industrial Chemistry, Faculty of Science, Edo State University Uzairue, Nigeria.
³Department of Computer Engineering, Faculty of Engineering, Edo State University Uzairue, Nigeria.
⁴Eco-toxicology and Forensic Biology Laboratory, Department of Biological Science, Faculty of Science, Edo State University Uzairue, Nigeria.
*adama.kenneth@edouniversity.edu.ng

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ARTICLE INFORMATION	ABSTRACT			
Article history: Received 07 Jul. 2023 Revised 22 Nov. 2023 Accepted 25 Nov. 2023 Available online 30 Dec. 2023	The use of polymers in enhanced oil recovery process is a form of petroleum biotechnological process for manipulating functions and structures of fossil fuel existing in oil reservoirs for prolonged exploitation. Crude oil production is estimated to be typically 30 - 50 % by both primary and secondary recovery methods. Tertiary recovery of enhanced oil recovery (EOR) methods allows additional 5 – 15 % of the reservoir's residual oil to be recovered. Hence, the need to develop nove			
<i>Keywords</i> : Polyacrylamides Waste agricultural by-product Tertiary oil recovery process Analytical and experimental perspective Synthesis	approaches to improve the efficiency of EOR of oil entrapped in porous media cannot be overemphasized. Polyacrylamides are widely used for various purposes in the petroleum industry but for many years have always been chemically synthesized. The use of biologically synthesized polyacrylamides have gradually gained prominence as a result of their biodegradability, functionality under extreme conditions and other salient properties. However, the use of waste agricultural by-products for synthesizing polyacrylamides for use mainly in the Nigerian oil industry is still very limited due to unverified subsequent contamination of either the underground oil reservoirs or the crude oil product. Analytical and experimental perspective on the use of polyacrylamide derived from waste agricultural by-products for enhanced oil recovery process in the Nigerian oil industry is reviewed in this study.			
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1. INTRODUCTION

Over the last few years, interest in enhanced oil recovery processes have been heightened and this has led to increased interest in the research and development phases to the actual implementation in the oil fields (Fitzpatrick *et al.*, 2000; de Melo *et al.*, 2005; Lino 2005; Yusa *et al.*, 2005; Zhang *et al.*, 2009; Powers *et*

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al., 2017). This renewed interest has been promoted by the current high operating cost and environmental concern, overall worldwide demand, maturation of operational oilfields and relatively fewer deep-waters discoveries (Alvarado and Manrique 2010; Aladasani and Bai 2010; Xu, et al., 2017; Cai et al., 2019; Song et al., 2019; Ali et al., 2020; Ding et al., 2022; Xu et al., 2022; Wang et al., 2022). Thus, optimal crude oil production and recovery has been affected largely by unstable pricing and environmental issues. The overall economics of the process (crude oil production) has affected exploration and exploitation activities in newer oil fields (Kokal and Al-Kaabi 2010; Wei and Xia, 2017; Yao et al., 2020; Wang et al., 2022; Xu et al., 2022; Chen and Liu, 2023; Zhao et al., 2023). Hence, deliberate efforts have been channeled into optimal recovery of crude oils from operation oil wells and oil fields. Traditionally, conventional primary, secondary and tertiary recovery processes have been used. These include the use of inherent pressure by natural drive mechanism, solution gas, gravity drainage, water influx and gas cap drive which are conventional primary recovery processes. The secondary recovery processes include pressure increases, water injection and gas injection. The use of chemical, thermal and solvent methods form the tertiary or enhanced oil recovery process which involves the injection of different materials into existing wells. The primary and secondary processes harness only about 30 - 50 % of overall oil-in-place (OOIP) (Liu et al., 2012). Enhanced or tertiary oil recovery processes account for additional 5 - 15 % of the crude oil reservoir's residual oil (Wang et al., 2023; Suleiman et al., 2021; Wang et al., 2019; Zhai 2016; de Melo et al., 2005; Lino 2005; Yang and Wei, 2004).

Production rates and natural reservoir energy depletion occurs during primary recovery while secondary and tertiary production processes led to addition of more energy to the reservoir fluid system. The major challenges of crude oil recovery in existing production wells include low permeability of some reservoirs, high oil viscosity, poor mobility of the oil, high interfacial tension between water and oil resulting in high capillary forces retaining the oil in the reservoir rock (Li et al., 2023; Zhao et al., 2023; Deng et al., 2022; Ding et al., 2022; Xu et al., 2022; Ali et al., 2020; Cai et al., 2019; Xu et al., 2017). Enhanced crude oil recovery process is usually known as a tertiary recovery process that is applied to mobilize trapped oils in pores held up by viscous and capillary forces. The most common being thermal, chemical and solvent/gases EOR processes. The process is normally applied after primary and secondary recoveries have being exhausted but can also be applied at any stage of a producing filed depending upon the field's performance history. Enhanced oil recovery is needed to maximize recovery after primary and secondary recovery from mature fields which currently operates at 30 - 50 % capacity with a declining production trends and lesser large sized discoveries in order to tap additional oils. In doing so, it boosts the natural energy of the reservoir, interact with the reservoir rock/oil system to create conditions favorable for residual oil recovery in terms of reduction of the interfacial tension between the displacing fluid and oil, increase the capillary number, reduce capillary forces, increase the drive-water viscosity, provide mobility-control, oil swelling, oil viscosity reduction and alteration of the reservoir rock wettability. The ultimate goal of EOR processes is to increase the overall oil displacement efficiency which is a function of microscopic and macroscopic displacement efficiency. It is generally accepted that approximately 30 % of the oil present in a reservoir can be recovered using current enhanced oil recovery technology (Li et al., 2023; Wang et al., 2023; Zhai 2016; Dupius et al., 2011). Similarly, for crude oil production, the recovery percentage by both primary and secondary methods is generally typically in the range of 30 % - 50 % (Tzimas et al., 2005; Brown 2010). However, with tertiary recovery processes or enhanced oil recovery methods, additional 5 -15 % of the reservoir's residual oil can be recovered Wang et al., 2023; Suleiman et al., 2021; Wang et al., 2019; Zhai 2016; Yang and Wei, 2004). Thus, the development of novel approaches to improvement in the efficiency of enhanced crude oil recovery of oil entrapped in porous media is paramount to increase economic profits.

Poor oil recovery in existing production wells may be due to several factors. These includes low permeability of some reservoirs, the high viscosity of the oil which results in poor mobility, high interfacial tension between the water and oil resulting in high capillary forces retaining the oil in the reservoir rock (Wang *et al.*, 2022; Zou *et al.*, 2020; Saberhosseini *et al.*, 2019; Song *et al.*, 2014). Techniques involved in enhanced oil recoveries includes the use of chemicals or physical processes such as pressurization, water-flooding or steaming which are generally unacceptable to most oil reservoirs due to its hazardous nature, cost

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implications and the undesirable levels of residues left behind which is sometimes difficult to dispose of due to environmental concerns (Shamla and Nisha 2014; Amit and Prem 2012; EFSA 2012; Williams 2005; Zhang et al., 2005; Taeymans and Wood 2004; EFSA 2003; Wenzl et al., 2003; Fitzpatrick et al., 2000). A chemical method that has been widely used in oil field applications is polymer flooding (Klaffke et al., 2005; Lineback et al., 2005; Hoeniche et al., 2004). Polymer flooding consist in increasing the viscosity of the oilrecovery drive fluid. It is the simplest and most widely used chemical EOR process for mobility control (Pope 2011). Polymer increases the viscosity of water and this causes a more efficient oil sweeping within the reservoir rock. The polymer lowers the relative permeability to water without substantially changing the oil relative permeability (Pittet et al., 2004); hence favoring the mobility of oil over water. Substantial loss in polymer viscosity due to salinity of reservoir brines is a major problem in the use of polyacrylamides in mobility control applications (Sun et al., 2011; Zhu et al., 2009; Sen 2008; Lazar et al., 2007). Widely used polymers in oil field applications are hydrolyzed polyacrylamides (HPAM) and the biopolymer Xanthan Gum (Prasertsan et al., 2008; Prasertsan et al., 2006; Nemati et al., 2005; Riediker and Stadler 2003). Both are quite expensive and environmentally hazardous, hence regulated by the National Pollutant Discharge Elimination System (NPDES). Other disadvantages include sensitivity of HPAM materials to brine strength of the water phase thereby loosing effectiveness in highly saline environments. However, bio-degradable polyacrylamides are said to have high swelling at low polymer concentration, high efficiency as suspending agents, high pseudo-plasticity, and extreme compatibility with high concentrations of various salts and elevated temperatures when used as components of water-based drilling muds or well completion fluids (Afolabi 2015; Bethke and Bussan 2013; Sen, 2008; Bermdo et al., 2006; Brill et al., 2005). Compatibility with the environment has also led to studies in the evaluation of bio-degradable polyacrylamide's effectiveness in enhanced oil recovery processes (Ali et al., 2020; Prasertsan et al., 2006). The studies evaluated the effects of polymer solutions of different concentrations on viscosity and on the thixotropic properties for different polymer concentrations and on the relative permeability. Chemically-synthesized polyacrylamide material or compounds are not biodegradable and can be toxic to the environment (Zhang et al., 2009; Wenzl et al., 2003; Stadler et al., 2002; Tareke et al., 2002;). HPAM has been reported to be hardly effective in reservoirs with excessive fractures and its use in clayey environment is practically avoided (Lyons and Plisa 2005; Taylor 2003; Shi et al., 2013; Liu et al., 2009; Rabiee 2011). The use of HPAM is mostly limited to reservoir temperatures below certain values due to viscosity loss occasioned by shear degradation and/or increase in salinity and divalent ions (Lyons and Plisa 2005). Taylor and Nasr-El-Din (2007; 2008) reported that HPAM have weak and unstable polymer-solvent interaction bondage and solution viscosity due to hydrophobic polymers cleverage on the polymer backbone. They easily suffer hydrolysis and thermal degradation and most importantly, they are not biodegradable and highly toxic to the environment (Mesias and Morales 2015; Taylor and Nasr-El-Din 2007 & 2008; Exon 2006; David 2003; Friedman 2003).

The use of polymer in enhanced oil recovery is to enhance mobility control as well as improving sweep efficiency of the trapped oils in the reservoir rocks (Fitzpatrick et al., 2000). It improves recovery by reducing the mobility contrast between oil and water and improving the overall sweep efficiency, improve the efficiency of water flood in secondary mode, and improve mobility (Lineback et al., 2005). Water soluble polymers such as polyacrylamides and polyaccharides are effective in improving mobility ratio and reducing permeability contrast (Mottram et al., 2002). In most cases, polymer flooding is applied as a slug process (20 040 % PV) and is driven using brine with polymer concentration usually in the range of 200 – 2000 ppm (Riediker and Stadler 2003). The emerging technological trends in polymer flooding includes the development of temperature and salinity resistant polymer (associative polymers or hydrophobically modified polymers), high-molecular weight polymers, the injection in the reservoir of larger polymer solutions amongst others (Aladasani and Bai 2010; Dupuis et al., 2011; Sheng 2011; Seright et al., 2011; Singhal 2011; Sydansk and Romero-Zeron 2011; Zaitoun et al., 2011). Various chemically synthesized polymers have been investigated for enhanced oil recovery applications but starchy materials such as polysaccharides, polyacrylamides and other water soluble acrylamides-based co-polymers have gained increased industrial attention as potential solutions for EOR (Ali et al., 2020; Prasertsan et al., 2006). Polymer flooding is based on increasing the viscosity of water, decreasing the mobility of water, reduction in permeability and contacting a large volume of the reservoir. However, its limitations include high oil viscosities, higher polymer concentration is required to achieve the desired mobility control; its outcome is better if the project is started before the water-oil ratios becomes excessively high; clays increases polymer adsorption and for conventional flooding, reservoir with excessive fracture must be avoided while lower injectivity than water can adversely affect oil production rate in the early stages of the polymer flood. Some of the problems associated with polymer flooding include acrylamide-type polymers may lose viscosity due to shear degradation or increases in salinity and divalent ions; polymer flooding is limited to reservoir temperatures < 200 °F (93 °C) and xanthan gum polymers are subject to microbial degradation (Lyons and Plisa 2005).

The presence of acrylamide in several starchy foods has been extensively studied (Powers et al., 2017; Ubaoji and Orji 2016; Shamla and Nisha 2014; Amit and Prem 2012; EFSA 2012; Zhang et al., 2009; Hogervorst et al., 2007; Williams 2005; Zhang et al., 2005; Zyzak et al., 2003; Rosen and Hellenas 2002; Tareke et al., 2002; Paulsson et al., 2001; Tareke et al., 2000). Acrylamide is a low molecular weight, polar, low-velocity and hydrophilic molecule $(CH_2 = CH - CO - NH_2)$. It is soluble in water, acetone and ethanol with a melting point of about 84.5 °C and is a colorless and odorless crystalline powder. It is biodegradable and highly mobile in both soil and groundwater (Mesias and Morales 2015; Wyka et al., 2015). Native starches such as potatoes, maize, tapioca seed and wheat starches are powders obtained from plants-wastes containing starches. They can be used as thickening agents, stabilizers, emulsifiers, surfactants, functional additives such as cross-linkers, barrier additives and viscosity modifiers. Polyacrylamides which are modified starches are made by physically, enzymatically or chemically altering the starches to change their inherent properties and structures to suit a particular purpose (Shi et al., 2013; Liu et al., 2009; Rabiee 2011; Taylor 2003; Taylor and Nasr-El-Din 2008; Basaran et al., 2023; Semla et al., 2017; Stadler et al., 2022; Maan et al., 2022; Rosen et al., 2002; Hoenicke et al., 2004). Modified starches do not necessarily mean genetically modified. Modified starches (polyacrylamides) have several inherent properties for application in EOR processes (Lyons and Plisa 2005; Hoenicke and Gatermann 2004; Zhang et al., 2014; Zhang and Lin 2014; Molina-Garcia et al., 2015). Potato tubers contain substantial amount of acrylamide precursor's free asparagine, glucose, and fructose, which explains the high concentrations of acrylamide in potato products. The reaction path involved in acrylamide formation in starchy foods is via the maillard reaction of reducing sugars (Bermudes et al., 2006; Rosen and Hellenas 2002; Mottram et al., 2002). The outcome of these studies led to an increase in the number of researches involving starchy products for the extraction and subsequent polymerization of acrylamides (Zhang et al., 2014; Shamla and Nisha 2014; Amit and Prem 2012; Williams 2005; Hoenicke et al., 2004). Interestingly, several studies have been developed for the analysis of acrylamide in different types of food where acrylamide can be present such as potatoes products, coffee and other starchy products (Maan et al., 2022; Stadler et al., 2022; Semla et al., 2017; Ubaoji and Orji 2016; Molina-Garcia et al., 2015; Troise et al., 2014; Hoenicke et al., 2004; Rosen and Hellenas 2002). Results showed or indicated that acrylamide content in potatoes products is strongly dependent on processing conditions, potato variety, field management, environmental conditions during tuber growth and tuber storage conditions (Mesias and Morales 2015; Bethke and Bussan 2013; Gregory and Mohammed 2006).

2. CHALLENGES IN THE USE OF CHEMICALLY SYNTHESIZED POLYACRYLAMIDES

Presently in oil field applications, hydrolyzed polyacrylamides (HPAM) and Xanthan Gum are the most widely used polymers (Liu *et al.*, 2012; Pope 2011; Lapcin and Pricl 1995). Xanthan Gum is relatively quite expensive though its tolerance to shear and salinity is good. HPAM on the other hand has very poor tolerance to shear and salinity to brine strength of the water phase leading to loss of effectiveness in highly saline environment. It is also very expensive. Its use is mostly in less saline environment. Use of chemically synthesized polymers during conventional flooding operation is hardly effective in reservoirs with excessive fractures and its use in clayey environment is particularly avoided (Deng *et al.*, 2022; Ding *et al.*, 2022; Cai *et al.*, 2019; Xu *et al.*, 2017; Alvarado and Manrique 2010). Applications of these polymers are limited to reservoir temperatures below 200 °F (93 °C) due to viscosity loss occasioned by shear degradation and/or increase in salinity and divalent ions (Marchettini *et al.*, 2013; Romero-Zeron 2012;

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Taylor and Nasr-El-Din 2008; Lyons and Plisa 2005). The synthesized polymers have weak and unstable polymer-solvent interaction bondage and solution viscosity due to the hydrophobic polymer cleavage on the polymer backbone (Taylor and Nasr-El-Din 2007). Most importantly, these synthesized polymers are not biodegradable and are toxic to the environment; hence, highly regulated by the National Pollutant Discharge Elimination System (NPDES). A typical composition of model brine used in core flooding experiments is given in Table 1 (Sun et al., 2011).

Table 1: Composition of model brine ^a used in most core flooding experiments (Sun et al., 2011)									
Constituent	$K^+ + Na^+$	<i>Ca</i> ²⁺	Mg^{2+}	Cl ⁻	SO_{4}^{2-}	HCO_3^-	Total salinity		
Concentration (mg/l)	3945	159	73	6507	19	96	10799		
^a Water type was CaCl ₂ , the viscosity of the brine at 50 °C was 1 mPas, pH was 7.5									

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Table 1 shows the saturated sterile brine of the artificial core after vacuum pumping. This model was used to determine the effective permeability for brine introduction into the reservoir as a tertiary oil recovery procedure. This approach was implemented to overcome one of the main challenges in oil production by water flooding as a tertiary oil recovery method which is high variation of reservoir permeability. The challenges inherent were evaluated by the authors (Sun et al., 2011). Core flooding experiment was conducted by Sun et al., (2011) to understand the effects of polysaccharide produced by transformants applied to selective plugging of high permeability zones. This procedure was conducted at 50 °C which was meant to simulate the actual temperature of the oil reservoirs at the investigated on-site and in-situ location of PetroChina in China.

3. DEVELOPMENTAL BASIS OF STUDY

With increasing current interest in polymer flooding and the prominent role of polyacrylamide as the commonest flooding 'agent', process analysis and development of temperature, salinity resistant and biodegradable polymers with high molecular weight, the potentials of synthesizing polyacrylamide (modified starches) from waste agricultural by-product (potato peels), subsequent characterization techniques that could be applied and possible applications in enhanced oil recovery processes has become very imminent (Marchettini et al., 2013; Liu et al., 2012; Romero-Zeron 2012; Taylor and Nasr-El-Din 2008; Gregory and Mohammed 2006; Lapacin and Pricl 1995). Agricultural wastes that are bio renewable and biodegradable materials can be used to develop polyacrylamides that are cheaper, environmentally friendly and biodegradable from the acrylamide monomer. The developed modified starches (polyacrylamides) can then be used for EOR processes. The developed polyacrylamide would be of relevance to the oil and gas industry in Nigeria in terms of substantial reduction in production cost associated with chemically synthesized polyacrylamides presently in use; reduction in environmental concerns associated with the present oil production activities; improvement in thermal stability in contrast to thermal degradation of present polyacrylamide; application and use in highly saline environment; cheap, renewable, biodegradable and eco-friendly option to the oil industry; increased fractional oil recovery; use of local agricultural waste material for beneficial purpose; reduced water-oil-ratio leading to reduction in material costs; reduction in water treatment processes and handling costs; enhanced efficiency in process operation; use of empirical rheological and simulated models to characterize the actual viscosity and other properties of the developed polyacrylamides and performance testing on EOR processes; and development of local content and expertise in the area of enhanced crude oil recovery and production technique.

Associating polymers cleverage on the incorporation of hydrophobic group on polymer backbone can impact desired properties such as improved polymer-solvent interaction and solution viscosity (Taylor and Nasr-El-Din 2007). For polyacrylamide, significant improvements in properties can be achieved through hydrolysis and copolymerization with other monomers. Since acrylamide-based polymers suffer hydrolysis and thermal degradation, investigations have shown that vinyl copolymers containing 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS) can offer improved stability (Jamshidi and Rabiee 2014). The impact of hydrophobic content of (N-dodecylacrylamide) and surfactant (sodium dodecylsulphate) on the rheological behavior and properties of poly (acrylamide-co-N-dodecylamide) for potential enhanced oil recovery operations have also been studied (Afolabi 2015). The suitability of Gum Arabic for mobility control in enhanced oil recovery was reported by Taiwo and Olafuyi (2015). These studies and other property improvements in polymer flooding has made this study timely (Sydansk and Romero-Zeron 2011; Singhal 2011; Seright *et al.*, 2011).

4. ANALYTICAL PERSPECTIVE

The various analytical studies which include thixotropic, relative permeability, starch rheology, chemical stability, mechanical stability, thermal stability, polymer concentration, size and molecular weight, salinity, viscosity, injectivity, and oil recovery probability would affect the polymer retention and adsorption in the porous media (reservoir rock) and invariably, the reservoir rock permeability (Li et al., 2023; Wang et al., 2023; Xu et al., 2022; Wang et al., 2022; Zou et al., 2020; Cai et al., 2017; Wei and Xia 2017; Zhai, 2016; Guo et al., 2015; Toise et al., 2014; Zhu et al., 2009; Tzimas et al., 2005). These analysis are applicationbased and polymer material-based tests. Reservoir conditions could be simulated with computer software such as STARS, BEST-GEL and so on and would be used to predict future performance of any given reservoir in terms of permeability modification and mobility; oil recovery after polymer flooding and profile modification (Chen and Liu, 2023; Ding et al., 2022; Saberhosseini et al., 2019; Xu et al., 2017). The characterization techniques provides for the quantification and detection of the extract/analyte before and after polymerization by free radical mechanism; thermal analysis of the extract/analyte; morphological study of the sample polymer to evaluate and determine the level of aggregation of the monomer as well as the polymer thereby determining the influence of structural template on the final product, elucidate on the level of uniformity of the analyte in terms of distribution in the polymer matrix; determine the basic functional group and functional monomers of the acrylamide and polyacrylamides as well as the cross-linking agents and initiators and determine with certainty the degree of incorporation or otherwise of the monomer (Deng et al., 2022; Ali et al., 2020; Cai et al., 2019; Xu et al., 2017; Alvarado and Manrique 2010).

5. EXPERIMENTAL PERSPECTIVE

Use of modified starches from waste agricultural by-product of Irish potatoes peels is intended for development and application in enhanced oil recovery process. The acrylamide extract representing the functional monomer (active principle) from the Irish potato peels could be isolated using solvent or water extraction, solid-phase extraction, dispersive solid-phase extraction and super-critical fluid extraction procedures (Toise *et al.*, 2014; Zhu *et al.*, 2009; Prasertsan *et al.*, 2008; Sen, 2008; Prasertsan *et al.*, 2006; Nemati *et al.*, 2005). The acrylamide active principle would be characterized for possible identification, partially hydrolyzed polyacrylamide could be produced via co-hydrolysis under microwave irradiation and post-hydrolysis after conventional heating polymerization. The produced polyacrylamide could then be characterized to determine compatibility. The effect of temperature and salinity on partially hydrolyzed produced polyacrylamide could then be investigated while empirical, rheological and simulated models are then used to characterize the viscosity and other properties of the developed starches and performance analysis (Wang *et al.*, 2023; Li *et al.*, 2023; Yao *et al.*, 2020; Cai *et al.*, 2017; Zhai 2016; Song *et al.*, 2014; Yang and Wei, 2004).

5.1. Polymerization of Acrylamide

The polymerization of acrylamide could be by free-radical process which is a commercially significant approach for synthesizing approximately 50 % of all synthetic polymers (Matyjaszewski and Davis 2002). Free radical polymerization technique possess certain limitations, which include poor control of molecular weight distribution, polymer microstructure and chain end composition. However, various controlled radical polymerization (CRP) procedures have recently been investigated for the production of polyacrylamide with desired properties (Noble and Coote 2013). According to Young and Peter (2011), free-radical polymerization involves initiation, propagation, and termination reactions as expressed in the reaction mechanisms below. This technique is used almost exclusively for polymerization of polymers from monomers of the general structure $CH_2 = CR_1R_2$.

Initiation: This is the first stage in free-radical polymerization. It involves the creation of free radical active center from initiator through hemolysis and its subsequent addition to monomer molecules. These initiators are usually compounds containing persulphates, peroxide (0 - 0) or azo $(-N \equiv N-)$ as shown below.

$$R_1 - 0 - 0 - R_2 \to R_1 - 0 + 0 - R_2 \tag{1}$$

$$R_1 - N = N - R_2 \rightarrow 2R + N \equiv N \tag{2}$$

The free radical generated through either Equations (1) or (2) goes ahead in the next initiation stage to attack bonds in monomer molecule and creating active center.

$$\acute{R} + CH_2 = CHR_2 \rightarrow R - CH_2 - CHR_2 \tag{3}$$

$$\acute{R} + CH_2 = CHR_2 \rightarrow R - CH_2 - CHR_2 - CH_2 \tag{4}$$

Propagation: The second stage involves rapid and sequential growth of polymer chain through monomer addition to active center.

$$\acute{\mathbf{R}} + CH_2 = CHR_2 \rightarrow R - CH_2 - CHR_2 - CH_2 - CHR_2 - CH_2 - CHR_2$$
(5)

$$\acute{\mathbf{R}} + CH_2 = CHR_2 \rightarrow R - CH_2 - CHR_2 - CH_2 - CHR_2 - CHR_2 - CH_2 \tag{6}$$

Termination: At this stage, the destruction of the active center to end propagation occur through either of the following means:

a) Coupling two growing chains to form polymer molecules

$$R - CH_2 + CHR_2 - CH_2 - R \rightarrow R - CH_2 - CHR_2 - CHR_2 - CH_2 - R$$

$$\tag{7}$$

b) Disproportionation termination

$$R - CH_2 + CHR_2 + CHR_2 - CH_2 - R \to R - CH_2 - CH_2R_2 - CHR_2 = CH_2 - R \quad (8)$$

Where R – initiator radical (e.g. sulphate radical from persulphate ion, benzoyloxy radical from benzoyl peroxide and 2-cyanopropyl radicals from azobisisobutyronitrile) and R₂ = pendant group (which is $-CO - NH_2$) in case of acrylamide.

In most polyacrylamide production studies, batch microwave irradiation and conventional solution polymerization procedures could be investigated for comparison (Li et al., 2023; Noble and Coote 2013; Zhu et al., 2009; Sen 2008; Lazar et al., 2007; Tzimas et al., 2005; Matyjaszewski and Davis 2002). Batch microwave irradiation is a one-stage polymerization and alkaline hydrolysis of amide group with crosslinking taking place in a very short period. It has been applied in the production of super absorbent polymers, especially poly sodium acrylate-co-acrylamide. Hydrolysis increases the hydrodynamic volume (high swelling at low polymer concentration) of polyacrylamide by elongating the polymer chain in a partial hydrolysis reaction. Un-hydrolyzed polymer chain may become coiled and less viscous at high salt concentrations and extreme reservoir temperatures. High shear rates around the well bore region of the injection well may impact irreversible shear degradation on the polymer backbone. Thus, chemicallysynthesized polyacrylamides suffer hydrolysis and thermal degradation. Its stability can be improved by the introduction of hydrophobic content and surfactant (Toise et al., 2014; Bermudo et al., 2006). Thus, partial hydrolysis could help to control swelling (hydrodynamics) at low concentrations of the polymer so that the elongation process is terminated at appropriate chain-length. Hence, the modification process. Developing polyacrylamides from potato peels and modifying to compete favorably with chemically synthesized polyacrylamides. Modification process could be in the form of reactive processing, additive compounding, optical modifiers, fillers and reinforcements, stabilizers, surfactants, functional additives, viscosity modifiers, and optimization of formulations using statistical approaches. Conventional heating polymerization is a form of solution polymerization technique had been adopted by Shi et al., (2013) in their study.

6. RESERVOIR SIMULATION

Reservoir conditions are usually simulated using computer model software such as STARS and BEST-GEL to predict the future performance of a given reservoir in terms of permeability modification and mobility, oil recovery after polymer flooding and profile modification (Chen and Liu 2023; Zhao *et al.*, 2023; Wang *et al.*, 2022; Ali *et al.*, 2020; Zou *et al.*, 2020; Yao *et al.*, 2020; Saberhosseini *et al.*, 2019; Song *et al.*, 2019; Xu *et al.*, 2017; Guo *et al.*, 2015; Prasertsan *et al.*, 2008). The simulation process would compare properties of chemically synthesized and developed eco-friendly polyacrylamides with reservoir specific conditions (Wang *et al.*, 2023; Zhang *et al.*, 2021; Cai *et al.*, 2017; Wei and Xia 2017).

7. CONCLUSION AND WAY FORWARD

The usefulness of biodegradable polyacrylamide developed from waste agricultural by-products in enhancing mobility control, improving sweep efficiency of the trapped oils in reservoir rocks during tertiary oil recovery processes have been elucidated in this study. Biodegradable polyacrylamides in many cases have been highlighted to be more effective than chemically synthesized polyacrylamides from the perspective of cost, toxicity level, sensitivity to brine strength, swelling power, and efficiency as suspension agents, plasticity and temperature sensitivity and tolerance.

The utility of polyacrylamides developed from waste agricultural by-products for enhanced oil recovery processes in Nigerian oil industry has not been documented in the Nigerian Oil field at this stage to the best of the authors' knowledge. Preliminary investigations on existing oil fields primary, secondary or tertiary recovery processes carried out to date have shown non utilization of the product or process but with high promise for use and success if implemented. The exact mechanism in the approach for enhanced oil recovery on-site is still hazy and unclear due mainly to lack of controls and insufficient analyses envisaged to on-spot situations. It is generally envisioned that the approach to enhanced oil recovery using agricultural waste by-products for polyacrylamide production in enhanced oil recovery process could be a viable alternative, which, if cautiously investigated and implemented could prove to be an economically feasible method of further enhancing oil recovery in reservoir rocks. Thus, the technologies involved would require the collaborative efforts of devise disciplines to produce field-application-based products for the Nigerian oil industry.

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9. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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