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Utilization of Plant Extract for Treatment of Emulsions in Crude Oil Production

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Abstract:
Emulsion formation causes enormous challenge in the oil and gas industry. Two types of emulsions are common in the oilfield; water in oil and oil in water emulsions. Water in oil emulsion is the most common and thus considered in this work. Emulsions are formed when two immiscible fluids (oil and water) from the reservoir are agitated in the presence of an emulsifying agent during production. Treatment of water in oil emulsion is a costly process and thus, in this work, environmentally friendly demulsifiers are formulated from orange peels and soya bean husks. The orange peels and soya bean husks were first dried under sunlight and ground into fine particles. Thereafter, Soxhlet Extraction technique was used to extract the demulsifiers; orange peel oil (OPO) and soya bean husk oil (SBHO) respectively. The OPO and SBHO were tested on crude oil sample obtained from Niger Delta and results compared with a commercial demulsifier phase treat (PT). Using bottle test method, the OPO, SBHO and PT were tested on the crude oil sample at different concentrations of 0, 200, 400, 600, 800 and 1000ppm's at 500, 1000 and 1500rpm, respectively. The concentrations and revolutions per minute where SBHO, OPO and PT achieved their best separations of crude oil are thus, at 200ppm and 1500rpm it was observed that OPO had 60% crude oil separation. SBHO had 45% crude oil separation at 400-600ppm's using 500rpm. And PT had its best crude oil separation of 87.5% at 500rpm using a concentration of 1000ppm, respectively. It shows that OPO and SBHO performed below the PT, however, with improvements on OPO, it shows a prospect of becoming a usable commercial demulsifier

Keywords: Emulsion, crude oil, orange peel oil, soya bean husk oil

INTRODUCTION

When two non-miscible fluid, like water and hydrocarbon are mixed together, there is lone dispersion of the liquid in the other instead of dissolving in it, this dispersion typically in a medium that is aqueous or in the company of emulsifying agent is an emulsion. The existence of water in oil causes unwanted issues such as: conductivity raise, corrosion, additives leaching so on (Aske,N. 2002). Techniques presently in use in demulsifying crude oil are thermal, electrical, chemical and gravity settling. Demulsification is the parting away the liquid that was dispersed from the liquid it was suspended. Both chemical and mechanical techniques of demulsification are line with Stokes's law. Reason for demulsifying is to break the boundary and constrain the surfactant to go in the direction of the water/oil region, permitting the oil particles and sediments to come together and rise to the outside. Decrease in water phase-viscosity or increase in the diameter of droplets of the oil and a decrease in the density of oil to water also works. There are numerous approaches used in neutralizing emulsion.

Emulsion decomposing; modification or employing air floatation that are dissolved, oxidation or other processes of oxidation are all expensive. Chemically, the emulsion reacts initiating surfactant modification which cannot acts as an emulsifying agent. neutralization of surfactant s that are ionic is the easiest technique applying acid or base ionizer of the salt comprises of calcium or magnesium, such as $CaCl_2$ or $MgSO_4$ sodium soap adds emulsion stability, whose solubility is the smallest in water consequent upon changes in the interfacial film and the-surfactant solubility increases in the bulk phase. the water -phase solubility could be improved by using acetone or alcohol and can help to heave emulsifier from the oil phase. If brine is the aqueous- phase, addition of water will cause separation. Demulsifiers causes Disruption of the ordered emulsifier interface pact of the with demulsifier. They concentrate at the layers because these materials are not very soluble in either phase, Aske, (2002).

Formation of Emulsion

Emulsion could be seen as liquid-dispersion which is completely immiscible in other liquid. In emulsion, the globule regularly exceeds the usual limits for colloids with respect to sizes. Emulsion generally is not present in the wellbore but their existence occurs as production of oil-water progresses with an immense amount of shakeup in the existence of emulsifying agent. When oil/water enters the well bore from the reservoir to the casing through the perforations, relatively huge differential pressure is produced which viciously blend the oil- water that is produced jointly in the company of emulsifying agent so that emulsion is formed Goldzal, *et al* (2000).

Emulsion consists of three phases: the discontinuous phase of thinly separated drop. The continuous phase is the medium that maintains the droplets in suspension. The inter phase is made up of emulsifiers or stabilizers that maintain the emulsion stability, binding the continuous and discontinuous phase collectively and prevent droplets from coming close to each other to band together Poindexter, *et al* (2004). Generally, emulsifiers are surfactants and soaps present either by themselves or as constituents for formation of detergent. Emulsifiers comprises of molecules with hydrophobic and hydrophilic ends. When immiscible liquids are present, the emulsifier travels to the interphase of the continuous/ discontinuous phases to form a defensive covering around the globules of thin phase at the same time as the molecules of the hydrophobic ends migrate or separates into droplets, while the hydrophilic ends stay in the water Sjoglom (2001). Homogenized milk, shaving cream, mayonnaise are some examples of emulsion etc.

Emulsion Properties

Aske (2002). Highlighted the following properties of emulsion:

1. The two liquids that form an emulsion (oil and water) are immiscible liquids.
2. Density/ viscosity of oils that is high generally contains more emulsifiers than lighter oils.
3. API gravity of crude oil that are low will form emulsion that is more stable and has high percentage volume of emulsion than API gravity of crude oil that is high.
4. Crude oil that has high viscosity will by and large make a more stable emulsion than crude oil low viscosity.
5. The color of emulsion must be dark reddish brown

Stability of Emulsion and Factors Affecting It

Stability is generally seen as emulsion resolution and is recognized as a significant water-in-oil emulsions characteristic. a number of emulsions rapidly separates in oil and water phases once detached from surface of the sea, whereas emulsions that are more stable can continue from days to years. Current study shows that the emulsion viscosity is associated with its stability (NRT Science & Technology Committee, 1997). It is dependent on several factors; hence stable emulsion is an emulsion that will not break down without treating. These factors include emulsifying agents, viscosity, specific gravity, water percentage and the age of emulsion.

Process of Demulsification

An amount of universal rules assists in the formation of the fundamental viewpoint on the behavior of emulsion surrounded by commercial demulsifiers (Grace, 1992). To start with, emulsions from hydrocarbon comprises principally of immiscible liquids. Their Separation is influenced by the natural processes, by providing the necessary differential density among the liquid. Next, the rate of gravity settling is function of the surface tension of the droplets which are formed in the inner phase of the emulsion. Bigger droplets have poor surface tension which is dependent on the mass rather than tiny droplets.

Thus, separation rate can be increased by increasing the size of the droplets. Again, if a stabilized emulsion exists in an environment, variations in the conditions of the environmental can influence the stability of the emulsion and hence, separation of the phases will occur. Lastly, when emulsifying agents are present, it gives room for emulsion stability. Immiscible liquids will break up when there are changes or removal of emulsifying agents.

From the overview stated above, it becomes obvious that demulfication has several options. Changes in this vicinity may give rise to emulsion resolution. Demulsification is one of the methods or is a chemical method of treating emulsion in the oil industry.
Other methods include

1. Heating
2. Gravity settling
3. Electrical method
4. Filtration
5. Dilution
6. Centrifugation

These demulsifiers tend to focus on the oil-water interface of the emulsion to separate it into oil and water. They are also called stabilizers. Chemically, they are surfactants which are partially soluble in water and oil. This study describes the effect of various demulsifiers on a crude oil sample using practical techniques. Also, demulsifiers will be compared to each other for evaluation of the performance on each of the crude oil. Processing is the act of purifying or removing impurities, fluids produced from an oil and gas wells normally comprises of mixtures of oil, natural gas, and salt water. They are directed through a manifold system and flow lines to a treating facility which are sometimes installed near the production area.

The first stage in processing the produced stream involves the use of mechanical equipment's called separators.In separation, the fluid stream is separated into their respective phases (oil, gas and water). After separation, each separated stream then undergoes extra processing for proper field treatment. The crude oil on leaving the separator does not always meet the requirements expected for use in refining because it still contains a particular percentage of water; (8% to 10%) that exist as emulsified water. As stated earlier, the presence of this water presents corrosion and scaling tendencies to production equipment's and must be removed.

The water present in the oil and produced solids (e.g., silts, sand, etc.) constitute of what is known as the basic sediments and water (BS&W), a maximum of 1% BS&W, and in some cases less than 0.5% is acceptable, and the limit on salt content of the remaining water in oil is usually in the range of 10 to 15 PTB (Pounds of salt per thousand barrels of oil). Current information has recommended that an equivalent amount of water depart through production of a quantity of 60 million barrels of crude oil per day (Ivanov and Kralehevcky, 1996). Under the production conditions, a proportion of this water can become intimately dispersed throughout the crude oil as small droplets. In crude oil handing the method for removing salt includes the inside mixing of the external crude that comes in with a fresh "wash water" to extract the salts that are soluble in water. In a nutshell, the reason for emulsion treatment is to reduce the salt and BS&W content to appreciable limits, so it could be usedfor refining purposes. (Ivanov and Kralehevcky,1996). Demulsifiers are neutralizers of emulsifying agents. Demulsifier molecules tend to occupy the empty space available for absorption in the emulsion.

Types of Emulsion

Oilfield emulsion is of three types namely.

i. Water-in-oil emulsion
ii. Oil-in-water emulsion
iii. Multiple or complex emulsion

The Emulsion Problem

The systems that favour the natural occurrence of emulsion during hydrocarbon exploitation from the well, are described as unstable thermodynamic systems, co-product with water smear, sediments and salt water of dissimilar saline, and comprises of dual liquid phases (Umar *et al.* 2018). Kokal and Aramco (2005) posited that emulsions from crude oil are acknowledged as a dispersed water globules in the hydrocarbon. They are not welcomed in the production and transportation lines since it has better prospect to produce a composition that is stable if the treatment is not properly done, which could lead to a lot of complications, particularly in course of refining. Various problems could arise at some stage in the exploitation of hydrocarbon from the well to be listed (Zolfaghari *et al*. 2016):

a. The buildup of elevated drop in pressure in flow lines.
b. The high pumping and transportation charges of the combined water–oil through the facilities.
c. The damage of facilities
d. The raise in corrosion and scaling rate
e. The separation equipment tripping in the separating plants for gas/oil. (GOSPs) which restricts the exportation value of the hydrocarbon
f. The low API gravity of the hydrocarbon.
g. The destruction of the catalysts of the processing plant for. downstream
h. The difficulty in advancing the crude oil viscosity (owing to dispersed water drops that are tiny in nature).

Crude Oil Emulsions Classification

Hydrocarbon classification is seen in four major categorises which are SARA fractions which are saturates (waxes), aromatics, resins and asphaltene. This classification depends upon its solubility and polarity in a solvent. Precipitating the crude oil in paraffin solvent is a fundamental means to reduce asphaltenes. In the interim, chromatographic fractionation is used to undo the deasphalted oil (saturates, aromatics and resins). Of the four classes, just saturates alone can simply be differentiated from the other crude-oil in the combination. The deficiency of π-bonds influences them to voluntarily separate the aromatic fractions by using their polarity. The residual oil is including aromatics and hetero-atomic compounds with diverse levels of functionalism, condensation and alkyl substitution (Auflem .2002).

Water in Oil Emulsion Mechanism of Stabilization

The creation of water/oil emulsion was famous in the oil sector oil about 40 years back. (Fingas, 1995). Several works showed that emulsion goes along with several resident solids, surfactants or molecules that function as asphaltenes and resins which adds to the stabilization of emulsion. Amongst the principal research about the water/oil emulsions, according to Goni *et al.* (2015), stability is the main manner in which they are formed. Their studies as well explained that emulsion formation is dependent upon the content of asphaltene and resins as the main fractions. Czarnecki and Moran (2005) and Czarnecki (2009) also posited that asphaltenes and other surfactant material must be present in smaller quantity before an emulsion will stabilize and more studies on the surface interaction were done to find out the molecules that are accountable for high water-in-oil emulsion stability. Surfactant's existences in the interface of the oil–water help to increase small droplets which are important in the formation of emulsion. These surfactants permit the reduction of interfacial tension on the assumption that during demulsification that there are surface free energy changes. Emulsion formation is encouraged by surfactants which produce smaller droplets and assist the stability of the emulsion. Basic information on the emulsifiers will help to proffer pioneering result to make a distinction on stable emulsion formation.

In general, the four major classes (SARA) can be found in hydrocarbon. They differ adequately in adsorptive tendency and solubility, and the applicable techniques are useful in separating them from the hydrocarbon crude oil.

Asphaltenes is usually a fraction of dark brown, black friable substance that sticks, and is a semisolid with no definite melting point, usually foams and swells to deposit residue that is carbonaceous in nature when heated. The subsistence of asphaltenes is recognized to have a significant outcome on both the ability to process and recover hydrocarbon and to solve the issues associated with the stability of emulsion. Certainly, the subsistence of asphaltenes gives raise to low separation rate from the oil medium as a result of solid deposition in the operations for recovery. Formation of coke is caused by separation of phase in processing in addition to asphalt pavement failure by physical structure loss of the asphalt cumulative arrangement (Speight 1992). Therefore, it is important to comprehend the hydrocarbon structure and its stability, by studying the precipitation/flocculation of asphaltene, using solvent/non-solvent mixtures for titration.

Agents which are emulsifiers are accountable for emulsion growth. Griffin (1949) first demonstrated Hydrophilic–lipophilic balances (HLB) and is generally a sufficient and a proficient method to test demulsifier efficiency. The two major dissimilar divisions: hydrophilic head (water liking) and a hydrophobic tail (water disliking) held in the surfactants. (Amphiphilic molecules). The hydrophilic part of the molecules of the surfactant could be positive (cationic), negative (anionic), neutral (non-ionic), or (amphoteric).

However, the hydrophobic part is consisting of one or chains of hydrocarbon, usually carbon atoms ranging from 6 to 22 atoms (Umar *et al.* 2018). Again, Griffin recognized that surfactants that are alkoxylated non-ionic perform better than ionic surfactants.

There was a proposition for the calculation of HLB number from the structure of the chemical that enables the establishment of the surfactants to be employed in water-in-oil or oil-in-water emulsion.

The computation of the HLB number demonstrates that, surfactants with a high HLB number can be exploited for water-in-oil emulsion. On the other hand, surfactants with a smaller HLB number can be exploited for oil-in-water emulsion (Porter 1991).

Table 1: The appearance of water depends on the HLB number (Porter1991)

HLB number	Appearance of adding surfactant on water
1–4	Insoluble
4–7	Poor dispersion unstable
7–9	Stable opaque dispersion
10–13	Hazy solution
13–20	Clear solution

Table 1. Shows the HLB number with an appearance on adding surfactant on water.

Appreciably, the emulsions needed for treatment by separating the oil from the water that is dispersed to meet up the market specifications and transport terms and to reduce the troubles of stable emulsion. In addition, the well-ordered handling of the emulsion could decrease corrosion and the poisoning of catalyst in the facilities used for downstream operations (Kokal and Aramco 2005). The emulsion separating method is essential, and several scholars had anticipated an assortment of approach to achieve the desired handling.

Formation and Stability of Water in Oil Emulsions

An agent that acts like an emulsifier must be there to form a stable water-in-crude oil emulsion (Sjöblom *et al.*, 2002)**.** Such agents consist of particles of clay, extra chemicals or the hydrocarbon components like asphaltenes, waxes, resins and naphthenic acids (Sjöblom *et al.*,2002)**.** The means of emulsification was inadequately implicit till the 1990's (Fingas and Fieldhouse,2003). The fundamental physics of water-in-oil emulsification was implicit in the surfactant engineering, but not in the oil sector (Fingas and Fieldhouse, 2003). For a good number of the emulsions, it is seen that the stability of the emulsion reduces as temperature increases, since at high temperatures there is a corresponding decrease in the continuous phase viscosity with the increased rate of collision of dispersed phase droplets (Cormack, 1999). Emulsions that are Stable could have water content of 20 to 80% which emerges as small droplets but an increase in temperature enhances coalescence and concludes with phase separation Cormack (1999), As a result, emulsion formation and stability mainly a function of the temperature, established conditions and the occurrence of natural substances like asphaltenes, waxes, and resins (Lane, 1995).

Demulsification of Water in Crude Oil Emulsions

The emulsions formed at sea subsequent to oil spillage are basically stable. Demulsification is one of the most difficult tasks to perform in the petroleum sector. demulsifying water in crude oil emulsions entails chemical, thermal, electrical, or a blend of these processes depending on the distinctiveness and properties of the emulsion Mohammed *etal.,(1993***)**. An assortment of techniques of de-emulsification, like use of centrifuge, sedimentation**,** use of heaters use of dispersants and demulsifiers have been studied Kim *et al (,*2002**)**. Among these methods, use of heaters and the use of centrifuge did not get much acceptance owing to the high cost and energy requirements. The awareness that dispersants cannot deal with higher viscosity emulsions gave confident to the study of the possible use of demulsifiers (Cormack, 1999). The addition of chemical demulsifiers in minute quantities can considerably make oil- water separation easy. Poindexter and Lindemuth, (2004). According to Nordvik *et al.* (1996), the key advantages of using demulsifiers are:

1. Fast and less expensive
2. Reduces the crude oil emulsions viscosity
3. Improvement in pump capability
4. Reduction in oil -waste treatment
5. Reduction in the ultimate disposal rate by a factor of10.

Demulsifying emulsions also entail some quantity of chaotic energy (Lane, 1995). The energy situation is not even and depends on the nature of energy induced and the type of demulsifier utilized (Lane, 1995)**.** The main objective of the emulsion breaker/demulsifier is to displace the naturally occurring emulsifying agents from the oil-water interface (Cormack,1999)**.** Nordvik *et* al. (1996) stated that the efficiency of the demulsifier depends upon:

1. Product efficiency (demulsifier)
2. Characteristics of the crude oil
3. Conditions of the environmental
4. Method of Application
5. Application Time

Demulsification of Crude Oil Emulsion

Demulsification is important in the oil sector, painting, coating and treating waste water in environmental technology (kim, 1995)**.** Demulsification has added extra meaning as the employment of single or combination practice for the recovery of in-situ weighty crude-oil is complex as these processes produces viscous emulsions which is a combination of oil- water and mud. Emulsion demulsification forms a fundamental aspect of oil- production. Emulsion destabilizing could be achieved by mechanical, chemical, thermal, or electrical method. Extra practice like adjustment of pH, use of filters, membrane separation and heat handling techniques, may also be employed (Gafonova, 2000). The awareness regarding emulsion characteristics and the means by which they occur for the phase of coalescence of water globule is essential for speedy separation (Ese et *al.,* 1999).

Quality mechanical tools are utilized in destabilizing emulsion like centrifugal separators and so on. Though, this equipment is considerably huge plus costly to set up on offshore-platforms distinctively for conditions of the North-Sea. Therefore, number of equipment should be at the barest minimum to avoid huge financial involvement (Aufluem, 2002). Thermal process is achieved by adding heat to treat emulsion at the refinery/facilities and the emulsion could be resolved with light oil were the main emulsifier is paraffin. A rise in temperature above the melting-point of paraffin in the range of 50-60°C could absolutely weaken the emulsion Grace (1992). Consequently, the temperature that produces the desired result at refinery is 70°C.The use of heat alone is barely makes the emulsion to be resolved.

The method of electricity utilizes electrostatic principle to demulsify produced emulsions and desalting in the refineries. The created electric field upset the elastic skin tendency of each of the droplet, perhaps by the re-orientation of polar molecules. These actions deteriorate the layer of the droplets due to non-concentration of the polar molecules at the surface. Besides, a reciprocated magnetism of particles of neighboring emulsion gets induced charges from the electric field applied Grace, (1992). The attractive and repulsive forces bring charge particles that are opposing each other in a close fashion. As a result, the layer is destabilized, and the droplets engrossed electrically and coalescence occurs.

The main familiar technique of breaking emulsion is the utilization of the mixture heat and chemical which could take care of the agents that causes emulsification (Auflern, 2002). The cost incurred by applying a demulsification plan is moderately small and is completed without shutting down. The rate of separation of W/O emulsion is consequent upon the demulsifier that forms stable emulsion, the temperature, the processing vessel, the concentration, the residence time of the process and the energy at which it mixes.The frequently used technique used to determine relative stability of emulsion for laboratory level is the bottle test. it is an experimental investigation in which different quantity of prospective emulsion breakers are administered a succession of bottles holding secondary samples of emulsion to be demulsified. At some definite time, the degree of separation of phase and interface expression of phase separation is taken into cognizance. Apart from demulsifiers, solvent could be introduced to lessen viscosity. Perhaps a number of diverse bottle test method abound as there are persons who use them regularly. Generally, its entails agitating, stirring up to normalize the emulsion or to blend in the demulsifier to be assessed, and a wait and watch time where the degree of separation of phase is observed with interface clarity and water phase turbidity.The optimization of the amount and kind of chemical employed provides to lower the oil content with in the produced water offshore. The improvement and use of environmentally pleasant chemicals are made feasible via gaining fundamental expertise concerning the techniques concerned to stabilize and break the emulsions. Success of chemical demulsifying techniques based on the following:

1. Ample amount of an appropriately chosen chemical must go into the Emulsion.
2. Transparent systematic addition of the chemical in the emulsion.
3. Adequate warmness is necessary to speed up or cause emulsion resolution.
4. Adequate residence time must subsist in vessels that treat the emulsion to allow demulsified water droplets settlement.

Chemical method is the frequent method used to treat water-in-oil and oil-in-water emulsion and it entails applying chemical additives to speed up demulsification. The stable nature of emulsion is typically influenced by the interface/film and method of surfactant adsorption (Kim, 1995). The techniques applied in chemical method of emulsion breaking of a water-in-crude oil emulsion entails the speeding up of the coalescence in addition to the film splitting procedure. Water droplets that are dispersed move toward one another and compress and forming a thin film of oil that is in continuous phase among them, the external drainage flow of the film can - form slopes in interfacial tension which then counter and delay drainage. The coalescence rate will rely on the dynamics that convey the droplets together, e.g., concentration, and then the force balance that makes the interface stable and disarray.

Demulsifier Performance

Demulsifiers and emulsifiers are extremely alike for the reason that they are surfactant in nature. Hence, the exploit of the emulsion breaker is to "disengage" the significance of the presence of the agents that emulsifies. This disengagement is achieved in three basic steps, which are flocculation, coalescence and solid wetting (Leopold, 1992). Diverse categories of chemical emulsion breakers will give dissimilar results in emulsion breaking practice. The awareness of how emulsion forms and becomes stable, emulsion breaking types, mechanisms of emulsion breaking are extremely vital because it could be helpful in the development of emulsion breaker. As a result, it was examined in the study of the parameters that affects the formation of emulsions that are stable. The parameters that are recognized to influence the performance of demulsifiers are: temperature, ph and solvents/diluents

Oilfield Demulsification

The problems related with the processing emulsion presents an incredible effect, and it has become the key concern in the oil and gas sector. Currently, emulsion-breaking method has been the main interest amid the studies that leads. The overcome the problems related to crude oil emulsions, several factors should be considered to break the emulsion without difficulty such as physical and chemical properties of the crude oil, temperature of the crude oil, space connecting topside and the reservoir, level of disturbance felt among reservoir, separator, turbulent flow, presence of solid that improves the emulsion stabilization. Demulsification is a procedure used for separating emulsion into different component ie oil and water. Fundamentally, the means of demulsification: are biological physical and chemical, the efficacy of these techniques can be seen in their ability to reduce the stability of emulsion and cause separation of phases (Zolfaghari *et al.* 2016). In the petrochemical industry, the separation of the emulsion must be in two phases in order to guarantee the smoothness of the refining process (Abdulredha *et al*. 2018).

Demulsifiers

They are seen as a collection of additives that are applied on water/oil and oil/water emulsion typically at concentrations that low to take apart the water from the crude oil. For the duration of exploitation, the hydrocarbon has a substantial quantity of salty water. There should be salty water removal from the hydrocarbon to evade trouble for the duration of refining, so as to minimize corrosion rate. Abdulredha *et al*. (2018) defined additives as organic subdivision that consists of the hydrophilic and hydrophobic part. Usually, demulsifiers could be characterized into four categories: surfactant non-ionic, ionic, and amphoteric and polymer surfactant. The reason for demulsifiers is to plunge the water to a point that is low in the system where it can regularly be removed. Demulsifiers averts oil-water mixing ability and have structures similar to non-ionic emulsifiers. Demulsifiers' are chemicals which are de-salters and de-oilers, and are regarded to be approximately 40% of the chemicals in the global market. Interest has risen amongst researchers in this area.

Chemical Demulsifiers:

The subsistence of surfactants gives room to chemical additive to be mixed with the demulsifier to help in inhibiting the appearance of emulsion (Feitosa *et al*. 2019). A model that describes the potential of an emulsion breaker to disintegrate the emulsion formed by water-in-oil that has redundant lipophilic surfactants known as asphaltenes exists. Grenoble and Trabelsi (2018) did a work on optimal formulation of demulsifiers on the basis of hydrophilic/lipophilic balance. They opined that the key purpose of a demulsification method is to check the emulsification system by voluntarily adsorbing it at the interfacial phase and waning the asphaltenes or resins film linked with the crude oil to encourage a good interfacial phase destabilization. A number of methods needed to be dealt with. As such, the demulsifier have to aggressive to be adsorbed at the interface to eliminate and disintegrate the asphaltene collection in addition to decreasing the interfacial tension between the crude oil and aqueous phases and thus assist the kinetics of the droplet coalescence (Salager and Forgiarini 2012).

***Demulsification Mechanisms*:**

Various researchers (Biniaz *et al*. 2016.Yang *et al*. 2018; Adewunmi and Kamal 2019;) had established that the emulsion- breaking methods of water/oil emulsion with oil/water emulsions (Martínez-Palou *et al*. 2013; Tao *et al*. 2015). To ably conquer the limitations revealed by the incidence of stabilized emulsion, the chemical, membrane and electrostatic de-emulsifications are the general methods (Behroozi *et al*. 2019). Destabilizing the emulsion formed from crude oil is improved by better temperature, centrifuging, electrical methods, high resonance time and chemical treatment method. Several techniques were formulated for to break emulsion, and many parameters were considered to achieve it, which includes the distribution of droplet size, dosages, and the rate of drainage, the temperature, emulsion viscosity and type of emulsifier/demulsifier (Zolfaghari *et al.* 2016).

Performance Demands on Demulsifiers:

After emulsion-breaking is done, the major thing to look out for is the fundamental demand which is the de-emulsifier performance and its capacity of possessing the characteristics below;

1. Strong interfacial attraction between oil/water with the ability to weaken the layer enclosed by the globules and-or to differ the angle of contact of the solid fraction of the layers interface;
2. Ability to flocculate droplets;
3. Potential to build up coalescence by warm conduit to water's likely attraction to water; and offering reticence of the drainage layer and thinning by induced alterations to the rheology interface (Sjöblom 2001).

The emulsion breaker can influence the interfacial globules layer by dislodgment and owing to its composite nature, changing the continuous-phase solubility and altering interfacial layer viscosity or film drainage supported by adsorption

Chemical Demulsifier as Emulsion Treatment:

Nikkhah et al. (2015) recommended new nanotitania as a tailored demulsifier for emulsion of water-in-oil. A sol–gel technique was made as substitute to synthesis, the nanotitania constituents. They analyzed the nanotitania particles using different techniques. Their outcome demonstrated that the sample that has the highest water separation utilized by the nanotechnology can promote 90% demulsification efficiency and reduced time for water separation.

Feitosa *et al.* (2019) examined additives on the basis of cardanol to evaluate the mechanisms of demulsification. Their results revealed that ethoxylated compounds, at neutral pH, are more appropriate to separate water-in-oil emulsions.

Li *et al*. (2018) examined the dosage and stability analyses, tannic acid phenol amine (TAPA) polyether were used as the demulsifier of water-in-aging- crude-oil (WACO) emulsion They concluded that TAPA could perform as an excellent demulsifier for WACO. Common chemical

Several researchers have used different types of demulsifier formulation to resolve crude oil emulsion. This research attempts to resolve crude oil emulsion using organic based materials for formulation of demulsifiers that are environmentally friendly and economical.

MATERIALS AND METHOD

Materials

Materials used for the research work is summarised in Table 1

Table 1: Materials used as Demulsifiers

Material	Code.	Source	Remark
Soya bean husk oil	SBHO	Soya bean husk	yellowish solvent
Orange peel oil	OPO	Orange peel	brownish solvent
Phase treat	PT	Vendor	colourless solvent

Table 2. IUPAC Name, Molecular Formula and Molecular Weight of Materials Used for experiment

IUPAC NAME	**Molecular Formula**	**Molecular Weight (g/mol)**
2-aminoacetic acid	$C_2H_5NO_2$	75.07
(2-methyl(pheyl) diazeny) naphthalen-2-ol	C $_{17}$NH 14N $_{2}$O	262.3
Phasetreat		

Table 3 Component of Soxhlet extractor and equipment for the experiment

Equipment	**Function**
Aspirator	contains water that goes into the inlet pipe
Condenser	cooling and condensation of the solvent
Extraction chamber	hold samples for extraction
Round bottom flask	contains solvent and anti-bumping
Inlet pipe	takes water from aspirator to condenser
Outlet pipe	takes water from condenser to containment can
Retort stand	holds the Soxhlet set-up
Measuring cylinder	measuring the solvent (N-Hexane)
Beaker	holds extracted oil
Filter paper	holds grinded samples in the extraction chambers
N-Hexane	solvent used for extraction
Anti- Bumping	make the N-Hexane to boil

Method

Extraction of Orange Peel Oil:

5000 kg of orange peel were sourced from Port Harcourt, Rivers State and was exposed to sunlight for drying. The drying process took seven days to properly dry the samples. After drying, the samples were grinded using a grinding machine.50g of the grinded orange peel was wrapped in a filter paper and put into the extraction chamber of the Soxhlet, for effective extraction of the oil, the n-hexane(400ml) was administered through the top of the condenser with the aid of a funnel, the solvent passed through the condenser to the extraction chamber and finally settles at the round bottom flask mixing up with the anti-bumping. After inspecting the setup, the heating mantle (water bath) was put on and setting the mantle to the boiling point of the n-hexane. As the n-hexane begins to boil, it evaporates from the round bottom flask through the extraction chamber which contains the sample and finally the condenser containing the water that cools the system traps the n-hexane and condenses it and it drops as liquid back into the extraction chamber and as the liquid n-hexane increases in volume in the extraction chambers it reaches the siphon point and then siphon back into the round bottom flask, this process continues until the n-hexane in the extraction chamber becomes colourless, which indicates that the oil in the sample has been extracted..This process is repeated until the required volume of the essential oil was obtained from the extraction process.

Plate .1: Fresh and dried orange peel and ground orange peel.

Extraction of Soya Bean Husk:

500 kg of soya bean husk were sourced from Port Harcourt, Rivers State and was exposed to sunlight for drying. The drying process took one day to properly dry the samples. After drying, the samples were ground using a grinding machine.50g of the grinded soya bean husk was wrapped in a filter paper and put into the extraction chamber of the Soxhlet, for effective extraction of the oil, the n-hexane(400ml) was administered through the top of the condenser with the aid of a funnel, the solvent passed through the condenser to the extraction chamber and finally settles at the round bottom flask mixing up with the anti-bumping. After inspecting the setup, the heating mantle (water bath) was put on, and setting the mantle to the boiling point of the n-hexane. As the n-hexane begins to boil, it evaporates from the round bottom flask through the extraction chamber which contains the sample and finally the condenser containing the water that cools the system traps the n-hexane and condenses it and it drops as liquid back into the extraction chamber and as the liquid n-hexane increases in volume in the extraction chambers it reaches the siphon point and then siphon back into the round bottom flask, this process continues until the n-hexane in the extraction chamber becomes colourless, which indicates that the oil in the sample has been extracted.

This process is repeated until the required volume of the essential oil was obtained from the extraction process.

Plate 2: Soya bean husk and ground Soya bean husk.

Plate 3: Soya bean husk oil, orange peel oil and Soxhlet and schematic of Soxhlet extractor

Soya Bean Husk Oil and Orange Peel Orange Physio - Chemical Properties

Free Fatty Acid Determination:

0.125g of samples were measured and transferred into conical flask. 25ml of hot ethanol were also included to the blend, which was heated and stirred gently. Three drops of phenolphthalein indicator were also included into the mixture, which was titrated with NaOH standard solution of 0.04M until a pink colour was obtained.

Free acid content was determined using equation.

$$LipidFFA = \frac{\text{VXFXM}}{\text{10XW}} \quad (1)$$

Where:
V = NaOH volume used
F = equivalent weight of FFA expressed in oleic acid (2.83g)
M = molarity of NaOH
W = weight of NaOH

Acid Value Determination:

25ml diethyl ether was mixed with 25ml of alcohol and 1ml of phenolphthalein solution and was carefully neutralised with 0.1ml sodium hydroxide. 10g of the oil was dissolved in the mixed neutralised solvent and was titrated with aqueous 0.1ml sodium hydroxide and agitating the mixture until a pink colour which persisted for 15second was obtained.

Hence:

$$\text{Acid Value } = \frac{\text{Titre value x } 5.61}{\text{weight of oil}}$$

Saponification Value Determination:

Twenty grams of the extract (oil) was weighed into a conical flask and 25ml of alcohol potassium hydroxide solution was added. A reflux condenser was attached, and the flask was heated in boiling water for 1hour, and it was constantly agitated and 1ml of phenolphthalein solution was added and was titrated and a blank was also done at the same time

$$\text{Saponification Value } = \frac{Blank - titrex\ 28.05}{weihtofoil}. \quad (2)$$

Where:

Blank and titre value are in ml and weight of oil in grams.

Iodine Value Determination:

Wij's Solution:

Eight grams of iodine trichloride was dissolved in 200ml of glacial acetic acid and 9g of iodine was also dissolved in 300ml carbon tetrachloride. The solutions were mixed and diluted to 1000ml with a glacial acetic acid. The extract (oil) was poured into a small beaker and a suitable quantity the sample was weighed by difference into a dry glass Stoppard bottle at about 250ml capacity. The approximate weight in g of the extract to be taken was calculated by dividing 20 by the highest expected iodine value, then10ml of carbon tetrachloride was added to the oil and dissolved.30ml of wijs

A conical flask was used to weigh 0.4 g of the sample with 20ml of chloroform which was added to dissolve the oil. 25ml Wij's solution and 20 ml of 10% KI were subsequently added to the mixture; the flask was shaken and then kept in the dark for a period of 30 minutes at temperature below 30°C. This mixture was later titrated with a 0.1M of $Na_2S_2O_3$ solution until the yellowish colour nearly disappears. Some droplets of 1% starch indicator was added to the mixture. More drops of $Na_2S_2O_3$ were still added to the titration and shaken vigorously until blue coloration disappears.

$$\text{Value of Iodine } = \frac{12.69C\ (V2 - V1)}{M} \quad (3)$$

Where:

C = $Na_2S_2O_3$concentration used

V_1 =$Na_2S_2O_3$volume used for blank titration

V_2 = $Na_2S_2O_3$volume used for determination

M = Sample mass

Peroxide Value Determination:

1gram of the extract (oil) was measured into a clean dry boiling tube and 1gram of powdered potassium iodide was added. A 20ml of solvent mixture (10ml of glacial acetic acid+ 10ml of chloroform) was added to the initial solvent in the clean dry boiling tube. The tube was placed in boiling water and allowed to boil for 30 seconds and vigorously for another 30 seconds. The content was poured quickly into a flask containing 20ml of potassium iodide solution and 0.002M of sodium thiosulphate was titrated using starch. a blank was prepared at the same time.

The peroxide value is calculated thus

Peroxide value =Titre value x 2 in eq/kgmax. (4)

Density And Specific Gravity Determination:

10ml of refined extract was weighed with a 10ml density bottle and recorded.

$$\text{Density} = \frac{\text{Mass of the oil (g)}}{\text{Volume of the oil (cm3)}} \quad (5)$$

$$\text{Specific gravity} = \frac{\text{Density of oil}}{\text{Density of water}} \quad (6)$$

Characterization of Crude Oil:

Specific Gravity (SG):

Crude oil specific gravity was determined using the hydrometer method.

API Gravity:

API gravity is calculated using the relationship

$$\text{API gravity} = \frac{141.5}{\text{SG}} - 131.5 \quad (7)$$

Demulsification of Crude Oil Emulsion:

10ml of the emulsified crude oil was measured into a test tube and the various demulsifiers for this study was added into the crude oil emulsion at varying concentrations in parts per million (ppm). To test the efficacy of the demulsifier a blank sample was prepared in addition. The samples were centrifuged at various revolutions per minute (rpm) for 5minutes and water separation, emulsion separation and crude oil separation were recorded.

RESULTS AND DISCUSSION

Results obtained from the experimental work are presented in the following tables

Table 4 Crude Oil Emulsion doped with varying concentration of SBHO Demulsifier at 500 (rpm)

Conc (ppm)	Velocity (rpm)	Time (mins)	Emulsion (ml)	Water (ml)	Emulsion separated (ml)	crude oil (ml)	BS$ W%	Crude oil%
0	500	5	10	0.5	90	0.5	5	5
200	500	5	10	0.5	6.3	4.2	5	42
400	500	5	10	1	5.8	4.5	10	45
600	500	5	10	1	6.3	4..5	10	45
800	500	5	10	1	6.2	4	10	40
1000	500	5	10	1.5	5.5	3.8	15	38

Table 5. Crude Oil Emulsion doped with varying concentration of OPO at 500 (rpm)

Conc (ppm)	Velocity (rpm)	Time (mins)	Emulsion (ml)	Water (ml)	Emulsion separated (ml)	crude oil (ml)	BS$W %	Crude oil%
0	500	5	10	0.5	9	0.5	5	5
200	500	5	10	1	3.5	5.5	10	55
400	500	5	10	1	3.7	5.3	10	53
600	500	5	10	1.5	3.5	5	15	50
800	500	5	10	1.5	3.7	4.8	15	48
1000	500	5	10	1.5	3.7	4.8	15	48

Table 6 Crude Oil Emulsion doped with varying concentration of Phasetreat Demulsifier at 500 (rpm)

Conc (ppm)	Velocity (rpm)	Time (mins)	Emulsion (ml)	Water (ml)	Emulsion separated (ml)	crude oil (ml)	BS$W %	Crude oil%
0	500	5	10	0.5	90	0.5	5	5
200	500	5	10	1.5	1	7.5	15	75
400	500	5	10	1	0.5	8.5	10	85
600	500	5	10	1	0.5	8.5	10	85
800	500	5	10	1	1	8	10	85
1000	500	5	10	1	0.25	8.75	10	87.5

Table 7. Crude oil separated (%) at 500 rpm

Conc (ppm)	Crude oil PT	crude oil OPO	Crude oil SBHO
0	5	5	5
200	75	55	42
400	85	53	45
600	85	50	45
800	80	48	40
1000	87.5	48	38

Table 8. BS&W (%) And Demulsifiers at 500 rpm

Conc	BS$W% PT	BS$W% OPO	BS$W% SBHO
0	5	5	5
200	15	10	5
400	10	10	10
600	10	15	10
800	10	15	10
1000	10	15	15

From figure 1: the Phasetreat demulsifier performed well, followed by orange peel oil. Soya bean husk oil performed least which were 87.5% of Phasetreat at 1000 ppm, 55% of orange peel oil (OPO) at 200ppm and 45% of Soya bean husk oil (SBHO) at 400 and 600 ppm.

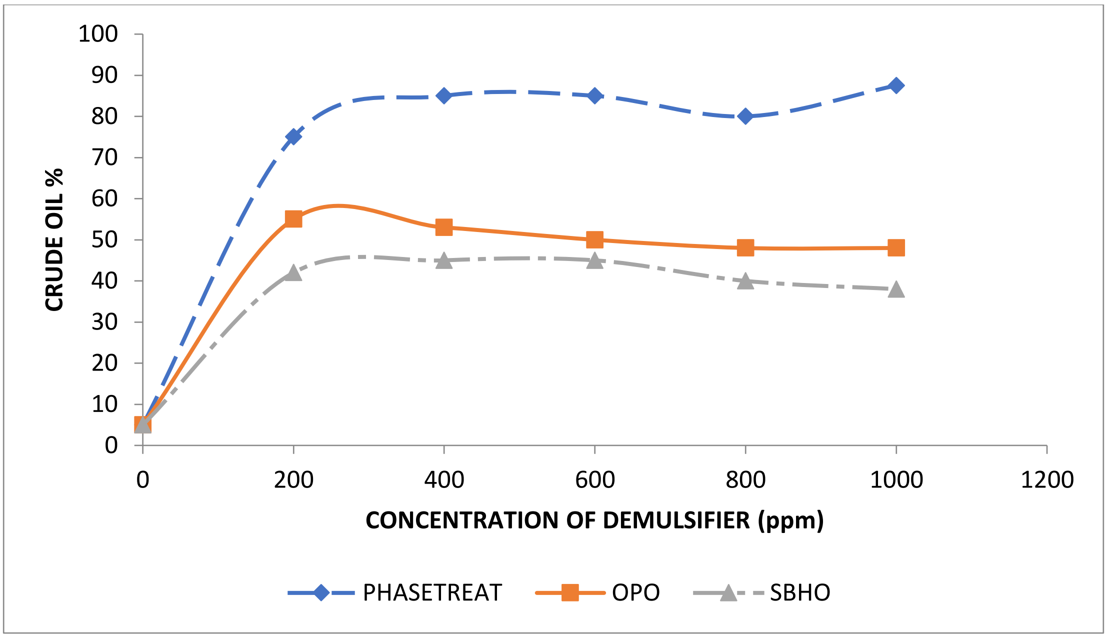

Figure 1 Crude oil (%) VS Concentration of demulsifier at 500 rpm

From Figure 2: the crude oil sample with Soya bean husk oil (SBHO) had the highest BS&W (%) followed by orange peel oil (OPO) It was observed that phase treat had the best separation of basic sediment and water which implied that the sample with the Phasetreat had the best oil separation and SHBO with the least crude oil separation which were 45%, at 1000 ppm 85% at 200 to 1000 ppm and 100% at 1000 ppm respectively

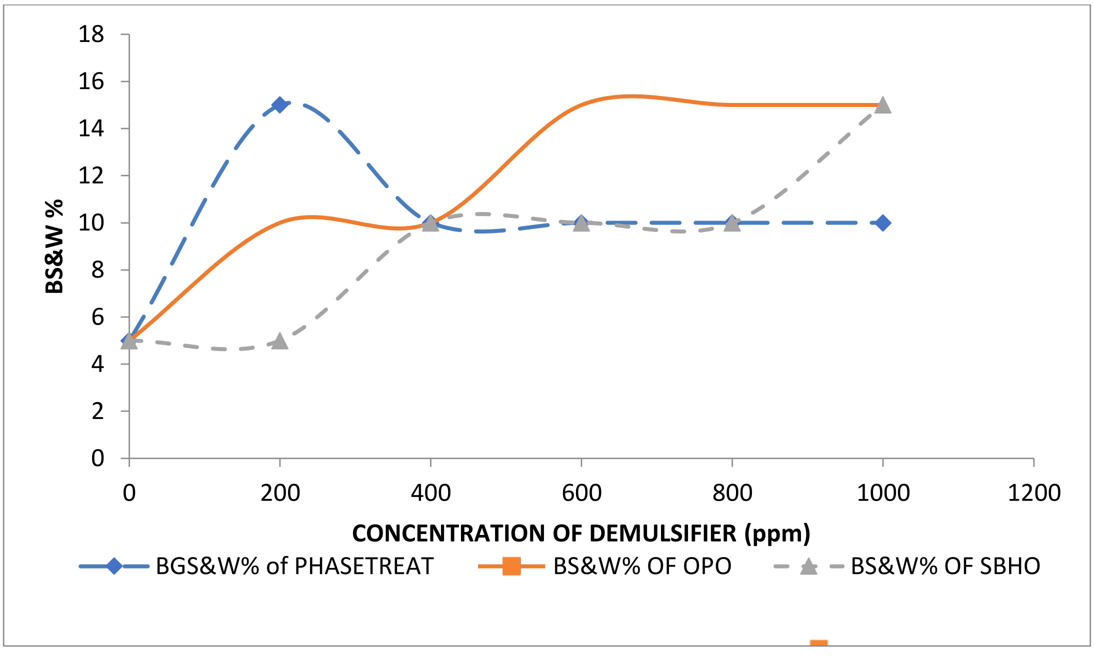

Figure 2: Plot of BS&W (%) VS Concentration of demulsifiers (ppm) at 500 rpm

Table 9: Crude Oil Emulsion doped with varying concentration of SBHO Demulsifier at 1000 (rpm)

Conc (ppm)	Velocity (rpm)	Time (mins)	Emulsion (ml)	Water (ml)	Emulsion separated (ml)	crude oil (ml)	BS$W%	Crude oil%
0	1000	5	10	0.5	9	0.5	5	5
200	1000	5	10	1	5	4	10	40
400	1000	5	10	1	4.8	4..2	10	42
600	1000	5	10	1.5	4.3	4.2	15	42
800	1000	5	10	1.5	4.7	3.8	15	38
1000	1000	5	10	1	5.4	3.6	10	36

Table 10: Crude Oil Emulsion doped with varying concentration of OPO Demulsifier at 1000 (rpm)

Conc (ppm)	Velocity (rpm)	Time (mins)	Emulsion (ml)	Water (ml)	Emulsion separated (ml)	crude oil (ml)	BS$W%	Crude oil%
0	1000	5	10	0.5	90	0.5	5	5
200	1000	5	10	1	3.2	5.8	10	58
400	1000	5	10	1.5	3.2	5.3	15	53
600	1000	5	10	1.5	3.5	5	15	50
800	1000	5	10	2	3	5	20	50
1000	1000	5	10	1.5	3.5	5.,0	15	50

Table 11: Crude Oil Emulsion doped with varying concentration of Phasetreat Demulsifier at 1000 (rpm)

Conc (ppm)	Velocity (rpm)	Time (mins)	Emulsion (ml)	Water (ml)	Emulsion separated (ml)	crude oil (ml)	BS$W%	Crude oil%
0	1000	5	10	0.5	9	0.5	5	5
200	1000	5	10	1.5	1.5	7.5	15	75
400	1000	5	10	1	1	8	10	80
600	1000	5	10	1	1	8	10	80
800	1000	5	10	1	1	8	10	80
1000	1000	5	10	1	1	8	10	80

Table 12: Crude oil (%) of demulsifiers (ppm) at 1000 rpm

Conc	Crude oil (%) SBHO	Crude oil (%) OPO	Crude oil (%) Phase treat
0	5	5	5
200	40	58	75
400	42	53	80
600	42	50	80
800	38	50	80
1000	36	50	80

Table 13: BS&W (% of demulsifiers(ppm) at 1000 (rpm)

Conc	BS$W%SBHO	BS$W% OPO	BS$W% PHASETREAT
0	5	5	5
200	10	10	15
400	10	15	10
600	15	15	10
800	15	20	10
1000	10	15	10

From figure 3. it was observed that Phasetreat performed best in terms of crude oil separation followed by orange peel oil (OPO)and lastly soya bean husk oil (SBHO) was 85% of Phasetreat at 200 ppm, 58% of OPO at 200 ppm and 42% of SBHO at 400ppm to 600 ppm

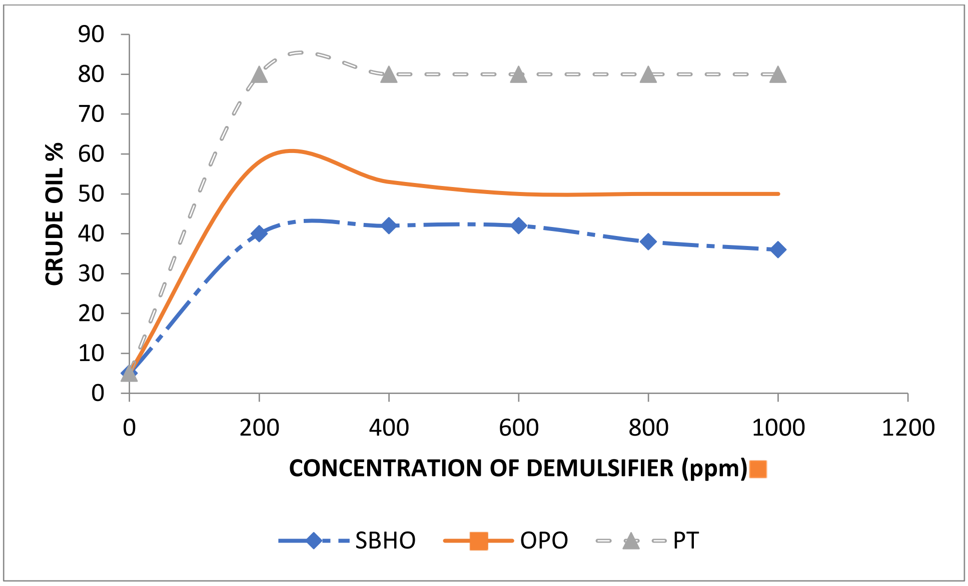

Figure 3: Crude oil separated (%) VS Concentration of demulsifiers (ppm) 1000 RPM

From Figure 4: Phasetreat had a better BS&W (%), followed by orange peel oil (OPO) and then soya bean husk oil (SBHO)

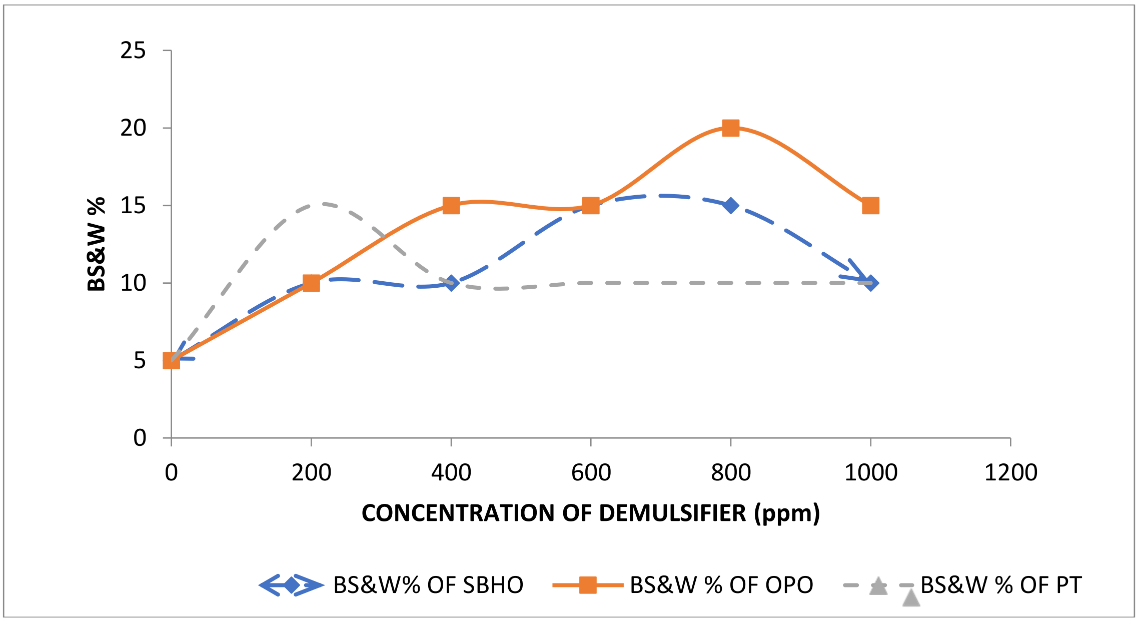

Figure 4 BS&W (%) VS Concentration of demulsifiers (ppm) at 1000 rpm

Table 14: Crude Oil Emulsion doped with varying concentration of soya bean husk oil (SBHO) Demulsifier at 1500 (rpm)

Conc (ppm)	Velocity (rpm)	Time (mins)	Emulsion (ml)	Water (ml)	Emulsion separated (ml)	crude oil (ml)	BS$W%	Crude oil%
0	1500	5	10	0.5	9	0.5	5	5
200	1500	5	10	1.5	5-Apr	4	15	40
400	1500	5	10	1.5	4.5	4	15	40
600	1500	5	10	1.5	4.5	4	15	40
800	1500	5	10	2	4.25	3.75	20	37.5
1000	1500	5	10	1.5	5	3.5	15	35

Table 15 Crude Oil Emulsion doped with varying concentration of OPO at 1500 (rpm)

Conc (ppm)	Velocity (rpm)	Time (mins)	Emulsion (ml)	Water (ml)	Emulsion separated (ml)	crude oil (ml)	BS$W%	Crude oil%
0	1500	5	10	0.5	90	0.5	5	5
200	1500	5	10	1.5	2.5	6	15	60
400	1500	5	10	1.5	3	5..5	15	55
600	1500	5	10	2	3	5	20	50
800	1500	5	10	2	3	5	20	50
1000	1500	5	10	1.5	3.5	5	15	50

Table 16 Crude Oil Emulsion doped with varying concentration of Phasetreat Demulsifier at 1500 (rpm)

Conc (ppm)	Velocity (rpm)	Time (mins)	Emulsion (ml)	Water (ml)	Emulsion separated (ml)	crude oil (ml)	BS$ W%	Crude oil%
0	1500	5	10	0.5	9.0	0.5	5	5
200	1500	5	10	1.5	1	7.5	15	75
400	1500	5	10	1	1	8	10	80
600	1500	5	10	1	1	8	10	80
800	1500	5	10	1.5	1.5	7	15	70
1000	1500	5	10	1.5	1.5	7	15	70

Table 17: Crude oil separated (%) at demulsifier concentration (ppm) at 1500 (rpm

Conc	**Crude SBHO**	**Crude OPO**	**Crude Phase treat**
0	5	5	5
200	40	60	75
400	40	55	80
600	40	50	80
800	37.5	50	70
1000	35	50	70

Table 18: BS&W (%) of demulsifies (ppm) at 1500 rpm

Conc	BS$W% SBHO	BS$W% OPO	BS$W% Phase treat
0	5	5	5
200	15	15	15
400	15	15	10
600	15	20	10
800	20	20	15
1000	15	15	15

From Figure 5: it was observed that Phasetreat performed best in terms of crude oil separation followed by orange peel oil (OPO) and lastly soya bean husk oil (SBHO) which were 80% at 400-600 ppm, 60% at 200ppm and 40% at 200-600 ppm respectively. However, all the plots are in line with the result obtained by Sulaiman, *et al* (2015) and Udonne (2012).

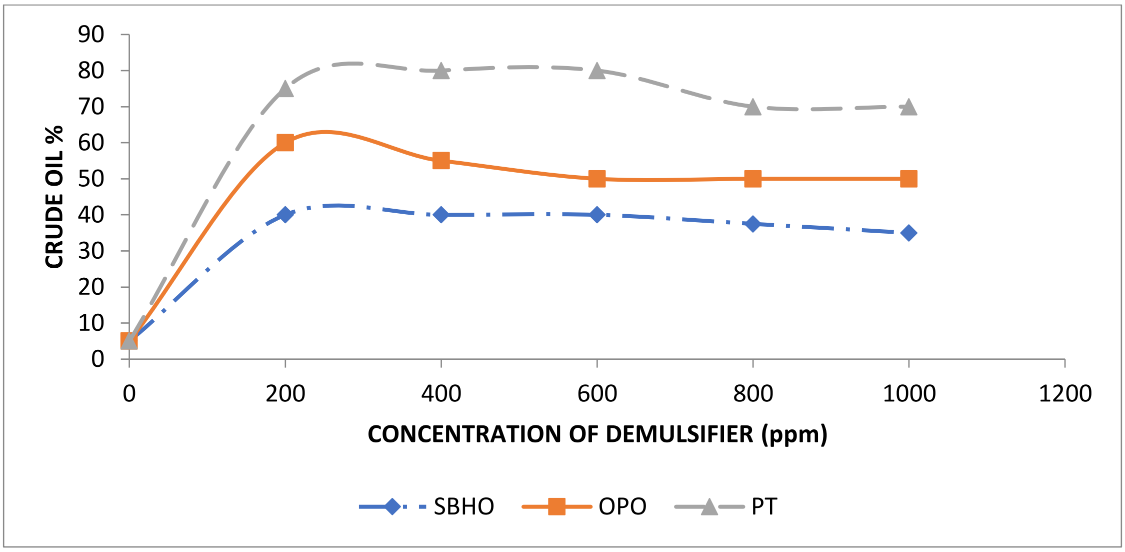

Figure 5 Crude oil separated (%) VS Concentration of demulsifiers (ppm) at 1500 rpm

From Figure 6: Phasetreat had a better BS&W (%) 50% at 400-600ppm followed by orange peel oil (OPO) with 70% at 200 ppm and then soya bean husk oil (SBHO) had 80% at 200-600 pp respectively,

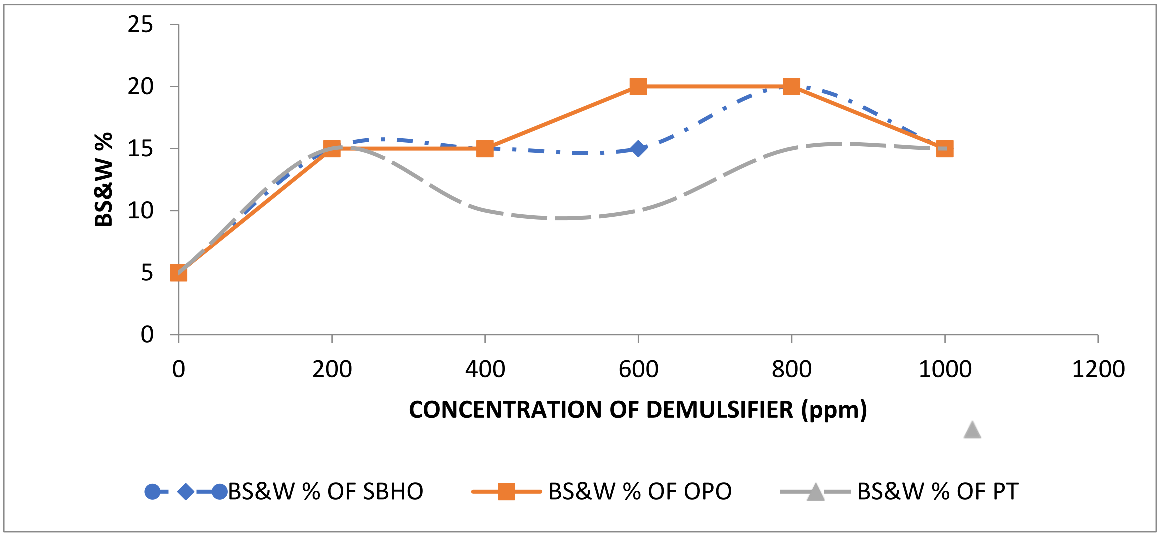

Figure 6:BS&W (%) VS Concentration of demulsifiers (ppm) at 1500 rpm.

CONCLUSION

In this research, utilization of plant extract for treatment of emulsions in crude oil production was successfully investigated by experimental method.

Demulsifiers was formulated from plant extracts (Orange peel and soya bean husk). Treatment of the crude oil emulsion was carried out using the demulsifiers formulated from these plant extracts and the demulsifier obtained from a vendor to resolve the emulsion using the bottle test method. The percentages of crude oil, basic sediment and water and the emulsion separated was obtained at varying concentration in ppm and at various rotation per minutes(rpm). From the results of the test carried out OPO had a better water separation and crude oil separation ability in all the rotation per minute followed soya bean husk oil respectively. For comparative purpose, Phasetreat a conventional demulsifier was used to compare with the formulated demulsifier from plant extracts. At the various rotation per minute (rpm) that is, 500rpm, 1000 rpm and 1500rpm for the various demulsifiers used to resolve the crude oil emulsion, OPO had 60% of crude oil separation from the emulsion at 200 ppm, SBHO had 42% at 400ppm and 600ppm and Phasetreat had 87.5% crude oil separation at 1000 ppm.Finally,Phasetreat performed well at 500 and 1000 rpm and dropped it value at 15000 rpm conversely orange-peel oil and soya bean husk oil showed improvement in their performance from 40 percent and 53 percent at 500-1000 ppm to 60 percent and 42 percent at 1500 rpm. These results were in line with the results obtained by Udonne (2012).

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