Utilization of Locally Formulated Chemical Demulsifier For Crude Oil Demulsification: A Review

Abstract

Emulsion is a critical problem in the oil and gas industry starting from the production to refining phase, and must be prevented or treated by oilfield operator to ensure that an API standard crude oil. Emulsion could be oil-in-water, water-in-oil and multiple emulsion, and require crude oil, water, emulsifying agent and emulsifying conditions. Several approaches such as mechanical, thermal, electrical and/or chemical approach are used for emulsion management in the oil and gas industry but chemical approach is the most utilized due to its technical, economic and ecological viability nature. The chemical technique of demulsification entails deploying chemical to break the bonds between brine and crude oil, using mechanisms such as flocculation, coalescence and sedimentation. Several demulsifiers exist for demulsification but these chemicals are expensive to developing countries and not ecologically friendly. In these study, a comprehensive review was conducted on the demulsification performance of locally formulated demulsifiers. From the result of the study, comprehensive understanding of emulsion formation concept, mechanism and type is necessary for designing suitable demulsifier.Nicotiana Tabacum recorded 73.33% efficiency, orange peel recorded 60% efficiency, while soya bean husk oil recorded 45% efficiency in demulsification. Camphor, Vegetable Oil, Alum and Liquid Soap were discovered to be key ingredient in the formulation of demulsifier due to their respective roles in local demulsifier. Speed and Temperature increases the demulsification of locally formulated demulsifiers. The demulsifier performance of the locally formulated demulsifiers can be optimized using software.

Keywords: Chemical Demulsification, Crude Oil Production, Agro-Material, Emulsion, Flow Assurance

١. Introduction

Crude Oil by default exists with natural gas and brine water in the pores of the reservoir, and are produced together through the wellbore. While flowing from the wellbore to the surface, these immiscible fluids are temporarily emulsified by continuous mechanism of shear reduction at valves, chokes and wellhead, and pressure(1). Crude oil-in-water emulsion are relatively difficult to manage, and this is due its stabilization through surface-active agents that exists naturally (2,3). The water within the crude oil poses various obstacle in the downstream sector such as damage to the process facilities, corrosion of pipe works, pumps and downstream distillation column, and increased associated cost (4). There are many working and industrial approaches for removing water from emulsions. Emulsion is a critical hurdle in the oil and gas industry, starting from production to refining phase. In most cases, oilfield operator choose to prevent emulsion formation or treat already formed emulsion depending the environmental requirement and cost. This involves approach such as mechanical, thermal, electrical and/or chemical approach (5,6).

١،١. Concept of Emulsion

Emulsion is a colloidal phase formed due to the distribution of an interior phase (dispersed phase) in exterior phase (continuous phase). The exterior phase is been draped by the interior phase, and this is due to its resistance to separation and coalescence, and is stabilized by an emulsifying agent at their interface. Crude oil is a complex hydrocarbon fluid comprising of napthenic acid, resins and asphaltene, with asphaltenes being responsible for the increased stability of water-in-oil-emulsion which is present inproduced crude oil(7).Crude oil is grouped into 4 major fractions using SARA (saturates, aromatics, resins and asphaltenes) analysis based on its polarity and solubility in solvent. Table shows the component of a typical emulsion and their corresponding description.

Table 1: Component of a Typical Emulsion

S/N	**Component**	**Description**	**Reference**
1	Asphaltenes	Dark Brown Amorphous Granular substance Specific Gravity above 1 Represent hexane or pentane in-dissolvable portion of the oil Decomposes at Temperature beyond 300-400^{o}C Influenced by temperature, pressure and oil composition variation	(8,9)
2	Resin	Dark Brown or Black Semi Solids Occupies 2-40%wt of Crude Oil Higher than Asphaltene in composition Polar and Non-Volatile Crude oil component which candissolve in n-heptane, n-pentane and toluene (aromatic solvent) but not soluble in methonal and propanol Comprises of hydrogen carbon, napthenic acid and nitrogen.	(10)
3	Wax	High molecular weight alkanes Melting point (37^{o}C<Melting Point< 100^{o}C) Solid crystalline mixture of normal hydrocarbon (C_{20}-C_{30}) and above. Plays a role in emulsion stability	(11, 12)
4	Finely Divided Solids	Aphaltene precipitates from bitumen The finely sortedparticles wax crystals, sand and clay particles stabilizes emulsions This solids prevent the flattening of the thin film and contributes to the persistent nature of the crude oil	(13)
5	Oil-Field Brine	Increase in salinity yields decrease in droplet-size and improves in solubilizing size of oil-water droplet. At low and high salinity, the mono-layer restricted to set at the flat interface has a likelihood to tilt and enhance tension At morderate concentration, there is less tension and this due to flat monolayer	(14)

١,٢. Types of Emulsion

Emulsion could be dispersion of oil in continuous water phase (oil-in-water) (O-in-W), dispersion of water in continuous oil phase(water-in-oil) (W-in-O)or mixed emulsion, but water-in-oil and oil-in-water are the two major emulsions encountered in the oil and gas industry. The major emulsion types unstable thermodynamically but can be kinetically stable at the same period during their lifespan (15). Based on kinetically stability, emulsion can be grouped into loose, tight and medium emulsion, and vary from each other based on separation rate. For loose emulsion, separation occurs within a few minutes, for medium emulsion, separation occurs within 10minutes, while long separation occurs for tighter emulsion

(1) Oil-in-Water Emulsion**:** For this emulsion type, the oil droplets are dispersed in the water-phase. The mechanism of surfactant stabilization and adsorption within the emulsion is efficient when there is easy solubilization of the surfactant in the continuous phase. For these emulsion type, the oil phase appears as bubbles in the water, and by considering the surfactant's structure (hydrophobic and hydrophilic), the right surfactant type are discovered. However, for water-oil emulsion, water-surfactant substance is more effective.

(2) Multiple Emulsion**:** The shape of multiple emulsion is more complex and comprises of small bubblessuspended within bigger bubbles, which are also suspended within the continuous phase. Multiple emulsion can be water-in-oil-in-water (W-in-O-in-W) and oil-in-water-in-oil (O-in-W-in-O). For W-in-O-in-W emulsion, tiny water bubble are suspended in bigger size oil-bubble which are suspended within the water (continuous phase)(16). The multiple emulsion type can be detected by the type of emulsifying agents involved. The asphaltenes, waxes, resins oil-soluble organic acid and inorganic solids are the surface-active chemical that might be produced with the interfacial film that prevent water bubbles from coalescing. The emulsifying chemicals are fundamental defined by the hydrogen bonding with O, N^- and S^- that makes-up the groups present in the crude oil, as Si-O and Si-OH which also disperses in the water-oil mixture (15). To formulate water-in-oil-emulsion, chemical emulsifying agent preferred is wetted by the oil-phase, and the contact existing between the oil-water-solid layer is > 90°. Despite coming to terms with oil-in-water emulsion formed, the emulsifying agent is desired to wet the water-phase and derivecontact of< 90°. For contact angle closer to 90°, stable emulsion is formed and can be derived (17). These stable emulsion is sometimes categorized between micro-emulsion and macro-emulsion. By considering the size of the droplets, additional type of emulsion referred to as macro-emulsion (dispersed phase diameter > 0.1 µm) is said to be an unstable structure (thermodynamically), and this is due the undesirable contact existing between the oil and water molecules which can continuously break with time (17). Unlike macro-emulsion, micro-emulsion yields a better stability. The micro-emulsion are organically formed when two immiscible oil and water-phase with ultra-low interfacial tension are composed as one. Micro-emulsion records thermodynamic stability and have dispersed phase diameter < 10nm. The small size of these droplets shows micro-emulsion as translucent and clear solution; also, the emulsions will be broken into oil phases and separated waters overtime (18)

(3) Water-in-Oil Emulsion**:** The W-in-O emulsion behavior evaluation is of utmost importance as it exists in the exploration and exploitation of crude oil (19). It is allocated the largest interest during crude production (15), and there is need for these emulsion to be separated into 2 phases for the purpose of achieving crude oil transportation and refinery requirement. Close to 95% of the crude oil globally flows to the surface with W-in-O-emulsion type (20). The W-in-O emulsion could be produced when crude oil mixs with aquifer water (natural brine source), and yields water bubbles dispersed in the oil. The mixing energy needed to generate emulsion is provided at offshore by wave or wind turbulence (21). The W-in-O emulsion is further classified into stable, meso-stable, entrained water and unstable water-in-oil emulsion (22). The analysis of these emulsion types is dependent on their stability influenced by resin content, asphaltene content, fluid density, elasticity, viscosity of the initial oil, rheological features and their physical from more than 400 experimental analysis on oil sample and petroleum products. Of the 4 states, only mesostable and stable W-in-O-emulsion are treated as emulsion. The volume of water in the W-in-O mixture is insignificant in the emulsion grouping(19). The stable water-oil emulsion has the physical look of reddish or brown semi-solid material. The emulsion might be unchanged for within a given period of time. The meso-stable W-in-O emulsion are split into the free oil and water within 1-3 days, and seem to appear as brown or black fluid. The unstable W-in-O emulsion are described as crude oil withinsignificant water volume, and in such case, the water stays within a limited period.

١,٣. Emulsion Formation

The contact between crude oil and water with required mixing presence of emulsifying agents yield crude oil emulsions, these emulsifier and mixing volume requirement are essential during oil emulsion formation (2). The three major criteria required for generation of crude oil emulsion is (i) Two immiscible fluids being in contact, (ii) Presence of Surface Active component, and (iii) Sufficient mixing effect to ensure dispersion of a fluid in another (22). The velocity gradient or pressure gradient needed for production of emulsion is mostly supplied by agitation, which needs sufficient energy. The right surface-active phase can be introduced to lower the energy required to yield given bubble size. The generation of surfactant film within the droplets yields the emulsification process and reduces agitation energy by factor of 10 or > could be attained. W-in-O emulsion will be produced when crude oils are mixed with brine and produced water droplets which disperseswithin the oil as highlighted in Figure 1

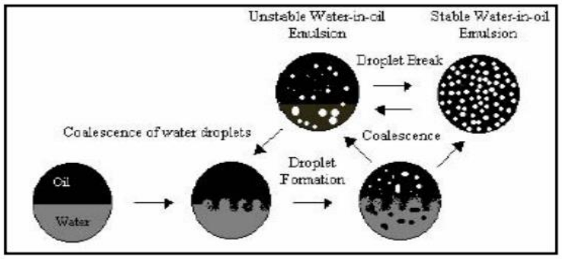

Figure 1: Water-in-Oil Emulsion Formation(21)

١,٤. Emulsion Stability

Stability is widely described as emulsion persistence naturewithin a given system, and has been observed as a vital feature of W-in-Oemulsions. Some emulsion rapidly returns back to individual water and oil phases once taken out from the surface area, whereas a stable emulsions stays for a period of time ranging from days to years. A stable emulsion comprises of a water-phase; emulsifier and oil-phase. The emulsifier (surfactants) exists at the oil interface and speeds up the formation of stabilized W-in-O emulsion. Emulsion stability can be considered in three different scenarios; aggregation, creaming (sedimentation) and coalescence (23) as depicted in Figure 2.

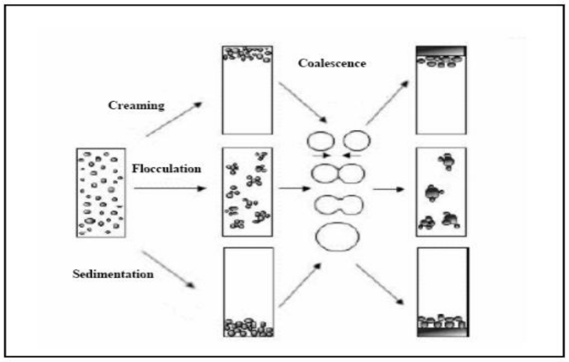

Figure 2: Process taking place in an emulsion to yield emulsion separation and breakdown (7)

The density variation and viscosity of the two immiscible fluids are the two major factors that impacts on the stability of emulsion (24).

(i) **Viscosity:** At high viscosity, the crude oil holds-up more and larger water bubbles in comparison to low viscosity. The introduction of heat, chemicals and diluents can significantly lower these viscosity. This in-turn yields higher water mobility and droplet settling rate resulting to coalescence, collisions and further improves separation rate.

(ii) **Density difference:**The introduction of heat to emulsion, reduces the oil-density at a higher rate than the water-density and thus yielding rapid dropout of the water. This is due to the increase in density variation of the two phases. The removal of water content from light crude oil is easier compared to that of heavy crude oil, and this is as a result of heavy crude oil density being closer to that of water.

Other factors includes percentage water, age of emulsion, control of emulsifying agents and agitation control,

(i) **Percentage Water:** The relative ratio between the crude oil and water in a given system, impacts on emulsion stability. The maximum emulsion stability is detected at low water compositionas the droplet have lesser likelihood of collision with other water bubbles and coalescence happening. The emulsion stability becomes ineffective at increasing percentage of water.

(ii) **Age of Emulsion:** These generally increases emulsion stability. The ratio of emulsifying chemicals in the oil could potential rise due to photolysis, oxidizing action, bacteria action and/or evaporation of lighter hydrocarbon component. This is due to low molecular weight and density hydrocarbons like hexane, butane and pentane present in light ends, and can potentially vaporize significant fraction of xylene overtime. The breaking of the emulsion immediately after its formation reduces the impacts of ageing.

(iii) **Emulsifying Agents:** Emulsifying chemicals or Surfactant plays a vital role in the emulsion production process. The surfactant can be bio-based or chemical engineered. The alteration, neutralization or elimination of this materials prevents or resolves emulsions. The elimination of these reagent might include corrosion inhibition procedures to lower the quantity of iron sulfide, eliminate crude oils that are compatible from crude oil blends or prevent emulsification from occurring. The alteration process includes the introduction of asphaltene dispersant to “tie-up” the polar sites of asphaltene, introduction of paraffin crystal enhancers to prevent the stabilization of emulsion by large paraffin crystals or by increasing the treatment temperature to be above the cloud point temperature of the paraffin crude. The neutralization action of emulsifying chemical by neutralizing polar ion linked with the film of emulsifying agent formed around the emulsified droplets. The neutralization action is conducted by commercial demulsifier or coagulants that support coalescence and accelerate gravity settling rate.

(iv) **Agitation Control:** The emulsion stability could be lowered by eliminating or reducing the agitation of oil-and-water blend. The efficiency of any demulsifier introduced to the treatment system is directly dependent on the optimum contact made with the emulsion. Therefore, the emulsion must be effectively, mixed after the chemical demulsifier has been introduced. The rise in the mild agitation promotes coalescence. Re-emulsification could happen if the emulsion is mixed heavily when broken into water and oil (25)

٢. Concept of Chemical Demulsification

Several demusification approaches such as thermal, mechanical, electrical and chemical exist (29), but chemical demulsifiers are the most utilized for emulsion mitigation, and entails introduction of reagents referred to as demulsifiers. These substances are engineered to counter the stability effect of the emulsifying reagents. Furthermore to mitigate stability impact of emulsifying agents, they move towards the oil-water interface, eliminate or loosen the films and improve coalescence. Optimum emulsion breaking using chemical technique needs selection of proper materials for a given emulsion; right chemical concentration, effective mixing of the selected reagent in the emulsion and reasonable retention time to settle water bubbles in the separator. The chemical approach in most cases, is combined with the heat method to eliminate and neutralize the impact of emulsifying reagents (26)

٢،١. Demulsification Mechanism

The chemical demulsification technique is a dynamic-based process and occurs below non-equilibrium conditions. The process aids in water separation, and reduces viscosity to increase coalescence of water droplets within the emulsion. The stability of emulsion can be attributed to the demulsifier which impacts on the break-down of the film to separate bubbles in an emulsion of oil, water and surfactant. The demulsification process is somewhat complex but can be described as 2-step approach consisting of coalescence and flocculation (2).

(1) Flocculation (Aggregation):This can be expressed as the first motion of demulsifiers on emulsion, and requires bringing together tiny water droplet (27). In a flocculation process, the droplet is close to each other, form aggregates but rarely lose their identity. Coalescence at that stage only happen when there is a weak emulsifier film surrounding the water droplet. The flocculation rate can be influenced by density variation, oil viscosity, water-cut and temperature.

(2) Coalescence:Coalescence is the phenomenon that deals with the rupturing of the films and coming together of the water droplet. This is an irreversible action and is enhanced by an increase flocculation rat, high IFT, high temperature, low viscosities absence of mechanically strong films and water-cuts (28). During coalescence process, extra droplets collectively joins to form a single unit with reduced perfect surface area. Coalescence can be improved by factors such as IFT, flocculation rate, chemical demulsifier, interfacial viscosity, temperature and absence of mechanically strong films.

Other process involved in the demulsification is the Sedimentation. Sedimentation is the process in which droplet of water bubble drops off from emulsion due to its superior density. In the case of inverse process, creaming which is the rise of oil droplet in the water occurs. The creaming and sedimentation utilizes the concept of density variation for their action, and might necessarily break emulsion. There is an accumulation of unresolved emulsion droplet at the oil-water interface in surface equipment, and this leads to the formation of emulsion pad or rag-layer. A pad in the surface facility present several challenges such as increase BS&W in the treated oil, increase residual oil in the treated water, increased equipment upset frequency. Emulsion pads are caused by inefficient demulsifier, low temperature, presence of accumulating solids and other chemicals that derail the demulsifier performance.

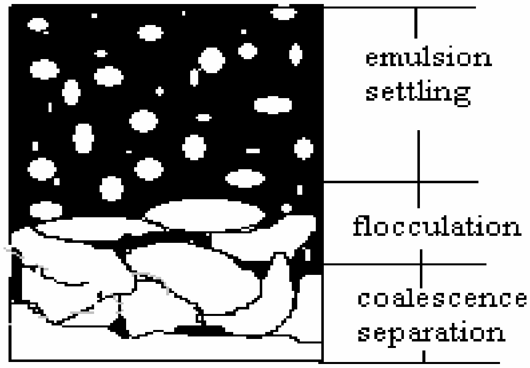

Figure 3: The level of demulsification process of water in oil emulsion(24)

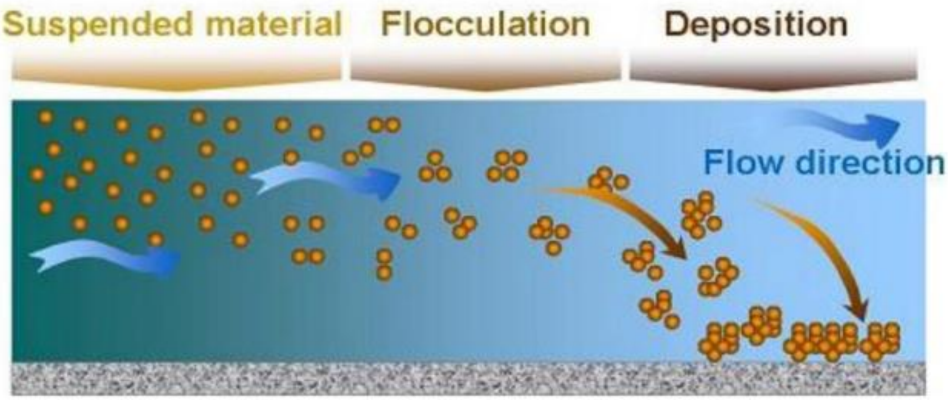

Figure 4: Process of Flocculation (29)

٢,٢. Chemical Demulsifier

Chemical Demulsifiers are molecules that help to separate entrapped water from crude oil at low concentration. They prevent the formation of W-in-O emulsion. The structure of demulsifiers cannot be categorized easily like in the case of emulsifiers. Some demulsifiers have same structure with non-ionic emulsifiers while others are polymers. Demulsifiers are surfactant that vital in breaking the emulsion in a given system (30). Their molecules comprises of the water-loving (hydrophilic) group and water-disliking (hydrophobic) group (31). The hydrophilic group implies that the substance will prefer water-phase than the oil phase while hydrophobic group implies that the substance prefers oil-phase than the water-phase (32-34). The best demulsifiers are the one that improves the destabilization and interfacial mobility of water-oil emulsion and reduces the interfacial shear viscosity. Table 2 depicts the characteristic requirement of demulsifier for optimum quality performance.

Table 2: Feature Requirement of Demulsifiers for Optimum Quality Performance (35)

S/N	Characteristics
1	Ability of the demulsifier to dissolve in the oil-phase
2	The demulsifier should be able to partition into the oil-phase and water-phase
3	The demulsifier concentration in the droplet must be enough to guarantee a high diffusion flux to the interface
4	The demulsifier must be high enough to stop the IFT gradient, thus hastening the film drainage rate to yield coalescence

The nonionic (neutral charged hydrophilic head group), anionic (negatively charged hydrophilic head group) and cationic (positively charged hydrophilic head group) forms the three types of demulsifiers utilized to break crude oil emulsion (36).

(1) Nonionic:These are surfactant with neither positive nor negative hydrophilic head group. These chemicals are not affects by water hardness or pH compared to anionic and cationic demulsifiers. In some cases it is a meritthat they are considered medium to low foaming chemical. It is applicable when a very low foaming surface is required, and its examples includes alkyl phenols, polyalkylene glycols and alkyoxylated amines.

(2) Anionic:This are utilized in virtually all detergent types which are the main component of demulsifiers. This is due to their ease of production and relatively low associated cost. The surfactant active chemicals carried negatively charged hydrophilic head, and have stable and high foaming ability. They are however sensitive to minerals, hard water and pH variations. Common example is the quaternary ammonium compound which is widely utilized in the industry. They comprises of alkybenzene sulfonate (detergent), soaps (fatty acid), lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent) and lignosulfonate (dispersants).

(3) Cationic:These demulsifiers comprises of positively charged hydrophilic head group. The play vital role as antiseptic reagent in cosmetic production as germicides and fungicides. The applied in situation where there are no cheaper alternatives. Common examples is the quaternary ammonium salt such as dimethyl dioctadecyl ammonium chloride.

Figure 5: Basic Structure of a Demulsifier (36)

٢,٢,١. Requirement for Chemical Demulsifier Formulation

Different demulsifiers yields various outcomes in demulsification process. The knowledge of the stability and formation of crude oil emulsion, demulsifier type demulsification mechanism and are very vital considering that it can be utilized in the removal of entrapped water from crude oil emulsion. The parameters that are being discovered to influence demulsifier performance are

(a) Temperature:On a laboratory scale 50-70°C temperature range were considered for demulsification process, and this is similar to the dehydration process similar to an actual refinery process. The internal phase's interfacial viscosity will drop with rise in temperature. This is due to the rate at which film drains, and is increases with increase in temperature. The momentum existing between two water droplet rises before coalescence happens. The two phases of the unmixed fluids are then separated due to the density variation between them (26).

(b) pH**:** The O-in-W emulsion rarely preferred at low pH value ranging from 4-6, while W-in-O emulsion are highly preferred at high pH value ranging from 8-10. The stability of oil-water emulsion produced improved as pH improved from 4-6 but further rise from 6-8 and eventually 10 yielded production of relatively little stable O-in-W emulsion and more stable W-in-O emulsion (37).

(c) Droplet Size distribution**:** The droplet dimension and bubble measurement of every W-in-O or O-in-W emulsion are larger than 100µm and 0.1µm respectively. The minimum droplets size distribution resulted in unrestricted emulsion concentration and viscosity (15). Afterwards, a longer coalescence time for the distributed drops that might either sediment (water bubble) or float (oil droplet). As the average bubble size lowers, the extended retention time reduces the rate at which sizes of droplets separates (15)

(d) Oil and Water Contents**:** Apart from asphaltenes and resins, water and oil contents in W-in-O emulsion are also constraint that can increase emulsion separation and stability. The presence of demulsifier can improve the efficiency of the emulsion separation process by enhancing water content of emulsion and reduce time required to process (6). The concentration of demulsifier is vital for separation of water, and is dependent on the water content proportion (0.3) and volumetric fractions (0.7) (15). Emulsion with higher water content can be easily broken compared to those with lower water composition; this means that high water concentration yields more viscous crude oil. Furthermore, demusification and coalescence rate continues to improve the volume of the dispersed phase; this was due to the entropy increase which yielded an efficient collision between the single phase bubble (38). Contrarily, reducing the oil content from 90%-60% yields little separation in a stabilized O-in-W emulsion, while reducing the oil concentration to 50% can enhance the prompt breakdown of emulsion(2).

(e) Surfactant Molecular Weight**:** The molecular weight of a demulsifier enhances its mobility and diffusion features to yield adsorption kinetics at the interfacial (39). The demulsifiers with bigger molecular weights exhibits lower adsorption kinetic which makes them less active demulsifiers (39). This might be due need for the demulsifier to subdue surfactants which naturally occur within the crude oil. Generally, asphaltene's adsorption kinetics in crude oil is as little as >2-4%wt; thus needs a demulsifier. However, demulsifier is required. A demulsifier with greater molecular weight, provides adsorption interface that interacts with other particles at the interfacial film with mean adsorption kinetics (40).

٢,٢,٢. Chemical Demulsification Performance Evaluation

The performance of a selected demulsifier can be evaluated at both the laboratory and/or field scale level.

(a) **Laboratory Level:** At laboratory level, selected demulsifiers are screened to determine the formulation required to achieve favorable emulsion breaking performance. Some of the techniques utilized on the laboratory techniques include bottle test approach which is a standard method for demulsifier performance (Udourioh et al, 2024)(41).The bottle test is used to derive the water separation volume overtime, the visual nature of the separated water and the associated sludge volume. Other methods includes electric dehydration test, interfacial tension measurement, rheology & viscoelasticity test, microscopy and droplet size distribution

(b) **Field Level:** The field level evaluation is done to validate lab prediction under actual operating conditions. Some of the field scale approaches includes field performance trial (pilot test) which comprises of key indicators such as basic sediment & water, dehydration efficiency(), desalting efficiency, quality of the separated water, chemical dosage, oil recovery and impact analysis on the downstream (Chen et al, 2018)(42). Other methods includes On-line BS&W Analyzer Readings, Heater-Treater Monitoring, Electrostatic Treater/Desalter Monitoring and Water Quality Analysis.

٢,٣. Review of Chemical Demulsifier Formulation

Several demulsifier have been utilized for breaking emulsion by several author globally. Dodd (43) summarized that demulsifier can dissolve in both scenario are efficient in breaking crude oil-based emulsion, as long as little quantity of sulfuric or hydrochloric acid are also introduced, and suggested the use of sulfuric and phenol acid. De Groote (44) postulated that the impact of demulsifying agent, which normally comprises of hydrophilic and hydrophobic group, react with majorly hydrophobic emulsifying reagent an adsorption complex which is hydrophilic or water-wet.

Salager, (12) investigation, showed that the most efficient mechanism for demulsification of a W-in-O or O-in-W emulsion is the removal of the surface active agent from the water-oil phase by restricting oil phase in the micro-emulsion. He also highlighted the chemical and physical phenomena involved in a dehydration process, which can be explained through the simulation the surface active agent which exist naturally in the crude oil and the introduction of chemical demulsifiers to yield extremely unstable emulsion. Sjoblom et al., (45) studied real crude oil emulsion and two synthetic based W-in-O emulsion model system, and made qualitative comparative study in explaining the reaction between demulsifiers and model interfaces. They discovered that the best individual destabilize are fatty alcohols, amine and the highest destabilizing effectiveness is derived with fatty acid-amine blend. From their comparative study between destabilization attributes of the modelled system and true crude oil has distinct differences and obvious similarities. Staiss et al. (46) proposed a new demulsifier comprising of polyester amines. Their merit over conventional demulsifers are more total movement to the interfaces, enhanced emulsion coalescence and breakage, enhanced corrosion inhibition and water quality. FromAamir, (47) study, the blend of sulfonic acid and phenol recorded the best performance as chemical reagent for separating trapped water from crude oil. Al-Shamrani et al., (48) utilized solubilized air flotation approach to separate crude oil from polluted water. They report flocculation and coagulation as very vital pre-treatment methods for solubilized air flotation to enhance the recovery of oil from the process. The utilization of inorganic of certain coagulant such as aluminum sulphate improved the separation technique. Hanapi (49) investigation using the blend of water soluble and oil soluble demulsifier yielded great water separation result. He also observed that the designed demulsifiers to be better than other commercial demulsifier. Nikkhah et al (50) developed a nano-titania as a better chemical demulsifer for the W-in-O emulsion. In their evaluation, a sol–gel approach was carried out as a substitute to design the powder-titania particle. Then, the evaluation continues to evaluate the powdered-titania particles using transmission electron microscopy (TME), particle size analysis (PSA), X-ray difraction (XRD), electrostatic test, standard IP77 and bottle test approach. From their result, nanotechnology promoted water separation upto 90% efficiency and reduced water separation time. In 2016–2019, as reported in the studies conducted by (51), ionic solution can be utilized to separate W-in-O emulsion. In the experimental investigation conducted by Hazrati et al., (52), they proposed liquids with long alkyl chains which is blended with PF6, NTf2 and Cl anions as afunctional demulsifer. The experiment was conducted by observing the interfacial tension (IFT) between the crude oil and water, and within 1-, 2-, 6- and 24-h period, before a bottle-test analysis was conducted. The alky chain length of anion, cation type and IL dosage in three levels were considered to obtain a good behavior of demulsifer. As a result, they achieve water separation effectiveness of 86–95% and IFT value of 0.7–6.26 mN/m. They summarized that the higher demulsification efficiency is obtained at longer alkyl chain length for the ionic liquids, corresponding to higher IFT. Feitosa et al., (53) conducted an investigation on additives based on cardanol to evaluate their demulsifcation mechanisms. The three Brazilian crude oil with 60-240 g/L NaCl of salinity, 30% (v/v) brine cut, at pH value of 3-10 in a constant mixing rate (3200 rpm) were utilized. Four types of chemical reagent (hydrogenation, formaldehyde polycondensation, ethoxylation, and ethoxylation of formaldehyde polycondensation) were utilized to design end-products from cardanol. 1 H NMR and FTIR studies were done to comprehensively describe the reagent. Using bottle tests approach, the experimental study were carried out at temperature 60 °C, and additional 200 ppm of the chemical was tested. Their results indicates that at neutral pH, ethoxylated compounds are more suitable for separatingW-in-O emulsions.Due to the economic and ecological impact of conventional demulsifier to developing countries, several local alternatives have been suggested by several authors.

Udonne (54) carried out a demulsfication of crude oil using sulphuric acid and castor oil. From the result of his experimental study at 500rpm and 1000rpm, sulphuric recovered 1.25% and 2.5% of entrapped water respectively, while castor oil recovered 2.5% and 6.25% respectively. Emuchay et al (55) formulated 3 sets of local demulsifiers (comprising of liquid soap, starch, camphor, calcium hydroxide, paraffin wax, coconut oil and d-limonene) to wit; blend-A, blend-D and blend-E, and compared them with two conventional demulsifiers (EC-2606A and EC-2303A). From the result of their experimental study the local demulsifiers yield the best performance as the separated above 80% water.Francis et al., (56) conducted a comparative demulsification study between conventional demulsifier (separol) and locally-designed demulsifier (mixture from camphor, jatropha oil, paraffin wax, cassava starch, liquid soap), at varying temperature ranges. From their experimental study, the local-designed demulsifier yielded a better performance at all temperature variation as it recovered 2-10ml of water.Amajuonyi, et al., (57) carried out an experimental study on the formulation of demulsifying agents for water in oil emulsion treatment. The study evaluated the effectiveness of two demulsifiers, a locally formulated demulsifier (LFD) and a commercially available imported demulsifier (H_2SO4), in treating water in crude oil emulsion. The material including; alum, cartor oil, starch, liquid soap, camphor and sample of crude oil emulsion used in the study was obtained from an oil field in the Niger Delta region of Nigeria. The centrifugal agitation method was used to determine the most effective demulsifier in breaking the emulsion. The results showed that the LFD was more effective in breaking down the emulsion compared to H_2SO_4. The study concludes that the use of locally formulated demulsifiers can be a cost-effective and efficient alternative to commercial demulsifiers in the oil industry. Falode and Aduroja (58) compared the demulsification performance of commercial demulsifier with locally demulsifier prepared from calotropi procera, jathropha curcas, thevetia ferifolia, terminalia catappa, carica papaya and citrus limonium. From their result gotten through combination of bottle test and response surface methodology, their formulated demulsifier competed favorably with the commercial demulsifier. Victor-Oji et al., (59) compared the demulsification performance of cashew nut shell liquid and a commercial demulsifier. From the result of their study, cashew nut shell liquid competed favorably with the commercial demulsifer can potentially replace it when the economics are favorable. Mepaiyeda et al., (60) compared the demulsification performance of commercial demulsifier with local ionic demulsifier derived from mixing plant extract, coconut oil, starch and liquid soap. From the result of their experimental study, the formulated demulsifiers recorded demulsification performance than the commercially available demulsifiers. Azubuike and Eiroboyi (61) carried out a comparative demulsification study between a commercial demulsifier, sodium dodecyl sulphate (SDS) and locally formulated demulsifer derived from nicotiana tabacum stalk ash and leaf extract. Crude oil emulsion from two oilfield were utilized for the evaluation. From the result of their experimentally study for the first oilfield, the commercial demulsifer yielded the best performance as it recorded 73.33% water separation efficiency while SDS and locally formulated demulsifier recorded 61.67% and 66.67% water separation efficiency respectively. From the result of their experimental study for the second oilfield, the commercial demulsifer yielded the best performance as it recorded 86.67% water separation efficiency while SDS and locally formulation demulsifer recorded 65.83% and 78.33% water separation efficiency respectively. Allen and Amiebibama (62)carried out a demulsification performance evaluation using orange peel oil (OPO), soya bean husk oil (SBHO) and commercial demulsifier phase treat (PT) respectively. From the result of their experimental study at 1000ppm concentration, OPO yielded 60%, SBHO yielded 45% while PT recorded 87.5% crude oil separation respectively. Ndubuisi et al., (63) compared the demulsification performance of locally-formulated demulsifier (comprising of camphor, olive oil, shear butter, starch, distilled water and liquid soap) with conventional demulsifier. From their experimental study, the locally-formulated demulsified performed better than the conventional demulsifier in low temperature-low time system as it recovered 4ml-5.5ml of entrapped water. This demulsification performance of the locally-formulated demulsifier remained fairly constant until 60^{o}C. Okereke et al., (64) conducted a comparative demulsification study between locally formulated demulsifier-1 (CONK1) and locally formulated demulsifier-2 (CONK2). From their experimental study, CONK1 performed better than CONK2 as it recovered 1.0ml to 7.5ml of water, while CONK2 recovered 2.5ml to 5ml of water. Okafor et al., (65) conducted a demulsification performance study using agro-based demulsifier from corn cobs from furnace burner ash (FBA) and microwave ash (MWA), and chemical based demulsifier. From the result of the study, MWA-demulsifier yielded the best demulsification performance as it recorded 72% separation efficiency while the chemical demulsifier and FBA recorded 60% and 39% respectively. Agbabi (66) carried out an experimental assessment on the demulsification performance of jatropha curcas-based demulsifiers. From the results of his study, the locally formulated demulsifiers recovered 72%-100% of trapped water after 480minutes of observation

Table 3: Methodology Utilizes by Previous Authors

S/N	Ref.	Demulsifier	Content	Conc	Temp. Conditions	Speed Conditions
1	**(54)**	Sulphuric Acid	Conventional	1-6 drops 1-6 drops	-	500, 1000 and 1500 RPM
		Castor Oil	Castor Oil		-	
2	**(55)**	Blend-A	Starch, distilled water, limonene, coconut, calcium hydroxide and liquid soap	0.2ml 0.4ml 0.6ml 0.8ml 1.0ml	-	-
		Blend-D	Camphor, Liquid Soap, Distilled Water, Starch and Coconut Oil,			

		Blend-E	Camphor, Coconut Oil, Liquid Soap, Distilled Water, Starch, Petroleum Wax and Calcium Hydroxide			
		EC-2303A	Conventional			
		EC-2606A	Conventional			
3	**(56)**	Local Demulsifier	Jatropha oil, camphor powder, paraffin wax, starch, liquid soap and distilled water	1ml	27°C, 35.6°C, 48.2°C 48.8°C	-
		Separol	Conventional			
4	**(57)**	Local Demulsifier	Alum, Castor Oil, Starch, Liquid Soap, Camphor and Distilled water	0.2ml, 0.4ml, 0.6ml, 0.8ml, 1ml, 1.2ml	85°F	1000 and 1500 RPM
		Sulphuric Acid	Conventional			
5	**(58)**	Local Demulsifier	Calotropis procera, Jathropha curcas, Thevetia ferifolia, Terminalia catappa, carica papaya and Citrus limonium	4g/ml	70°C	-
		W054 Chemical Demulsifier	Conventional			
6	**(59)**	Cashew Nut Shell Extracts	Fluid from Cashew Nut Shell	10ppm, 20ppm, 30ppm, 40ppm, 50ppm	60°C	-
		PhaseTreat (PT) 4633	Conventional			
7	**(60)**	Liquid Formulated Demulsifier	Plant extract, coconut oil, starch and liquid soap	0.034ml 0.102ml	27°C	
		Commercial Demulsifiers	Conventional		27°C	
8	**(61)**	Locally Formulated Demulsifier	Nicotiana Tabacum Leaves Extracts, Seed Oil and Stalk Ash	100ppm 200ppm 300ppm	27°C	
		EO/PO Block Copolymer	Conventional		27°C	
		Sodium Dodecyl Sulphate	Conventional		27°C	
9	**(62)**	Orange Peel Oil	Extract from Orange Peel	0ppm 200ppm	-	500, 1000 and 1500

		Soya Bean Husk Oil	Extract from Soya Bean Husk	400ppm 600ppm 800ppm		RPM
		Phase Treat	Conventional			
10	**(63)**	Locally Formulated Demulsifiers	Camphor powder, Coconut oil, Paraffin wax, Cassava Starch, Liquid Soap.	0.2ml 1ml	20ºC, 40ºC, 60ºC	-
		Imported Demulsifier				
11	**(64)**	Locally Formulated Demulsifier-1	Alum, Castor Oil, Starch, Liquid Soap and Camphor	0.2ml 0.4ml 0.6ml 0.8ml 1.0ml 1.2ml	60ºF	-
		Locally Formulated Demulsifier-2	Alum, Castor, Starch, Liquid Soap, Camphor and Xylene			
12	**(65)**	Furnace Burner Ash based Corn-Cob	Blend of Corn-cobs and Ethanol	5ml	-	-
		Microwave Ash based Corn-Cob	Blend of Corn-cobs and Ethanol			
		Sulphuric Acid	Conventional			
13	**(66)**	Jatropha Curcas-Based	Alum, native soap and camphor	1wt%	-	-

٢,٤. Challenges Associated with Chemical Demulsification Using Local Materials

Demulsifier have recorded impressive performance but the oil and gas industry is continually faced with new challenge. These challenges are grouped into sub-surface and surface based challenges. The sub-surface includes high water-cuts in matured reservoir (67) and well produced by tertiary/enhanced oil recovery (68), while the surface includes the demulsifier and operational based challenges. The operational challenges includes heat required (69) and offshore operating conditions (70), while demulsifier challenges includes sludge formation, biodegradation and quality of the emulsion

(a) **Sludge Formation:**Some of the locally formulated demulsifiers comprises of additives which does not blend homogenous but forms colloidal phase when stirred together, only to return back to separate phase when not stirred. When these demulsifiers are introduced into emulsion, some particles and sediments from the demulsifiers drop to the bottom to form sludge (water-in-oil) comprising of water, hydrocarbons and sediments (71).

(b) **Biodegradation:** The locally formulated demulsifiers are most biodegradable, and decay by action of bacteria and micro-organism. This is really a critical parameter which reduces their ability to effectively compete with conventional materials (72)

(c) **Crude Oil Quality:** The quality of the crude oil poses an obstacle to the performance of the demulsifiers. The quality of the crude oil is tied to the recovery approach utilized to produce it. For crude oil recovery through enhance oil recovery approach, associated reagent such as polymer, surfactant and alkali which aids in its recovery alters its physiochemical property and increases its aphaltene & resin content, and this ultimately leads to the formation of complex stable multiple emulsion (73)

(d) **Nature of the Separated Water:** The nature and quality of the separated water can significantly impact on the choice of demulsifiers to be utilized. The increase in salinity of the separated water negatively impacts on the efficiency of the demulsifiers (74). In the event of separation, the resultant separated water poses an ecological challenge due to the presence of dissolved salts in it.

٢،٥. Probable Solutions to the Challenges

Based on the challenges associated from the locally formulated demulsified, the following research routes are recommended

(a) Comprehensive study of physiochemical properties, asphaltene and resin content properties of the crude oil to be studied.
(b) Comprehensive study of demulsification mechanism for each recovered crude oil to provide theoretical base for the formulation and synthesis of demulsifiers.
(c) The formulation of dual-function demulsifiers suitable for breaking O-in-W emulsion, W-in-O emulsion and complex emulsion
(d) Formulation of demulsifiers with high molecular weight for easy formation of micelle suitable for solubilizing emulsifying agents to break emulsion.
(e) Improve the aromacity and the wettability of the formulated demulsifiers. The aromacity of demulsifier is enhanced by modifying with aromatic compounds and improving the demulsifier’s initiator’s aromacity.
(f) Formulate demulsifiers with more soluble particles and fewer colloidal additives, and the proper operational speed and temperature.
(g) Utilization of chemicals that will be inert to the demulsification performance of the demulsifiers but able to preserve the demulsifer
(h) Simultaneous utilization of chemical demulsification with desalination process (75)
(i) Optimization of demulsifier and desalination performance using algorithms such as response surface methodology (76)

٣. Conclusion

Presented in this study is a review of demulsification and the utilization of locally formulated demulsifiers in the Niger-Delta. The concept of emulsion, demulsification, solutions and locally formulated materials were explored and evaluated.

(1) The comprehensive understanding of emulsion formation concept, mechanism and type is necessary for design of a suitable demulsifiers
(2) Nicotiana Tabacum, Corn cubs, Orange peels, Soybean husk and Moringa Seeds showed promising signs for crude oil demulsification. Camphor powder is a key ingredient in the formulation of crude oil demulsifier. Alum facilitate the settling of sediments, while liquid soap is a binder for the demulsifier to link lipophilic and hydrophilic end.
(3) Formulation of demulsifiers with soluble additives and fewer colloidal is required to reduce sludge formation
(4) Speed and Temperature increases the demulsification of locally formulated demulsifiers
(5) The demulsification performance of the local demulsifier can be further optimized using software such as response surface methodology.

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