Review Article

Bio-based products for water-in-crude oil Emulsification/Demulsification processes: An Update

Abstract

There has been an increase in demand for green demulsifiers that will be as effective as the chemical demulsifiers but without the negative environmental effects. This demand has been partly addressed with the production of some bio-based demulsifiers. It is of importance to know the substances that act as emulsifiers in the production of crude oil and understand the mechanism of emulsification. This paper has reviewed emulsifiers and the mechanism of emulsification as well as bio-based demulsifiers and their mechanisms. This will enhance our knowledge on the type of compounds that can be used in the formation of effective demulsifiers. Innovation of these demulsifiers will enhance crude oil production and in the long run boost profitability and environmental sustainability. Currently, cashew nut shell liquid (CNSL) derivatives are in use for the formulation of effective green demulsifiers for water-in-crude oil emulsions.

Key words: Emulsifiers, Bio-based demulsifiers, mechanism, modification, microbes.

1.0 Introduction

Emulsions generally are dispersion of one liquid matter in another liquid matter of which both are conspicuously immiscible. In human body and in nature, different types of emulsion systems are found. Bile acid is an example of an emulsifier that aids digestion and absorption of fat by the production of finely spread emulsion droplets. (1). The action of combining two liquids substances together in order to compose emulsions is called emulsification while the process of separating them is called demulsification.

The emulsification process is a useful industrial application in homogenization of milk, liquid bimolecular condensates formation and in cutting fluids for metal working.

In contrast, the emergence of water in oil emulsion is a crucial topic in the petroleum section. Actually, water combined with oil can wear away refinery equipment and the water soluble salt can poison catalyst in downstream processing facilities (2) Also water in oil emulsion usually exhibit viscosities that surpass crude oil. This will increase the extracting cost for the transportation of oil in pipeline. Water and oil are generally immiscible. Their miscibility is enhanced by the presence of a surfactant during the process of refining (3).

Emulsions do not show a fixed internal structure like colloids. Inspite of the fact that the words colloid and emulsion are sometimes used vice versa, emulsion ought to be used when both phases, i.e. the dispersed and continuous phase are in their liquid states. (4).

The blends of oil and water are not stable, as oil or water droplets show a tendency to combine with each other. This process is called coalescence (5, 6).

It becomes necessary to introduce an emulsifying agent to stabilize the emulsions. Stabilization can be achieved through homogenization (7)

Emulsifiers have two main functions during the shaking process. They are:

1. To decrease the rate at which water or oil droplets form;
2. To form a coating around the oil droplets to stop coalescence

Crude oil is drawn out from the ground in form of emulsion. Consequently, there is a need for separation. The water content present in the emulsion can create complications for the manufacturing facilities as stated above.

The separation of crude oil emulsion is an important step in the crude oil processing process. The use of a chemical demulsifier is the most common method for breaking up the water in oil emulsion. The use of chemical demulsifiers has a harmful impact on the environment.

Chemical, mechanical, and heat methods are used in the demulsification (separation) process. Chemical demulsifiers are commonly used and have been shown to contain methyl benzene, which has a negative impact on the environment. After further processing, the recovered water from the emulsion will be released into the environment, which has been determined to be poisonous and harmful for marine life. As a result, there's a demand for green demulsifiers.

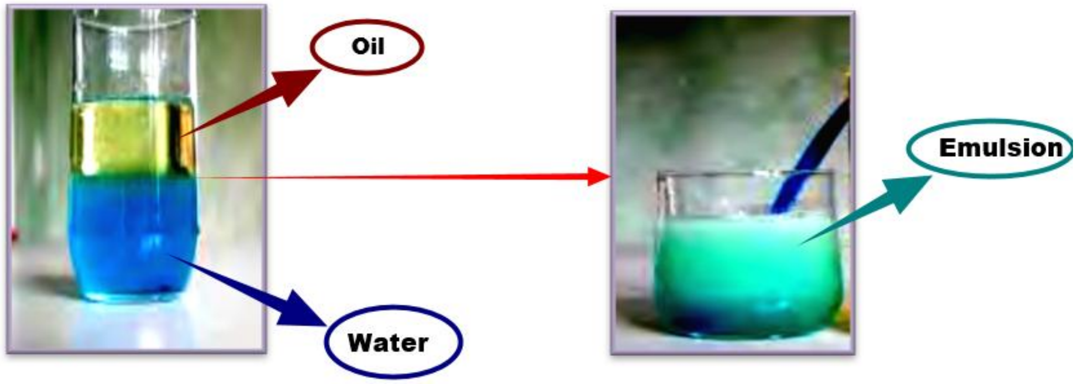

Fig 1: Process of formation of emulsion

1.1 Emulsion Types

There are three basic types of emulsions known in the literature. They are oil-in-water emulsions, water-in-oil emulsions, and polyphasic (2). Every emulsion usually has one continuous phase that suspends droplets of another entity, called the dispersed phase. In the oil-in-water emulsion, the continuous phase is water and the dispersed phase is oil, whereas in the water-in-oil emulsion, the continuous phase is oil and water is the dispersed phase. Polyphasic emulsions contain both of the first two emulsions mentioned above. (2).

1.2 Factors that affect the stability of emulsions.

The term "emulsion stability" can be defined as the ability of an emulsion to maintain its properties over a period of time (8). Nevertheless, the emulsion is thermodynamically unstable, so there is no doubt that it will change the properties of the emulsion. These changes are based on the rate of change in functional characteristics. The slower the change in function, the more stable the emulsion. There are many processes that can slow down or speed up the properties of emulsion (9). These operations include coalescence, flaking, creaming, and Ostwald ripening (10).

1.2.1 Creaming / Sedimentation

The creaming or sedimentation process that occurs in the emulsion can be easily investigated by optical observation (10). In most cases, creaming is characterized by a whitish / yellowish film at the top of the emulsion, and sedimentation occurs when a layer appears at the bottom of the emulsion. The rate at which creaming / precipitation occurs can be determined by quantifying the amount of cream / precipitate in the emulsion and the time it takes to form it. This can be done by placing the emulsion in a measuring cup or test tube and measuring the height of the cream / precipitate every second or minute. (11).

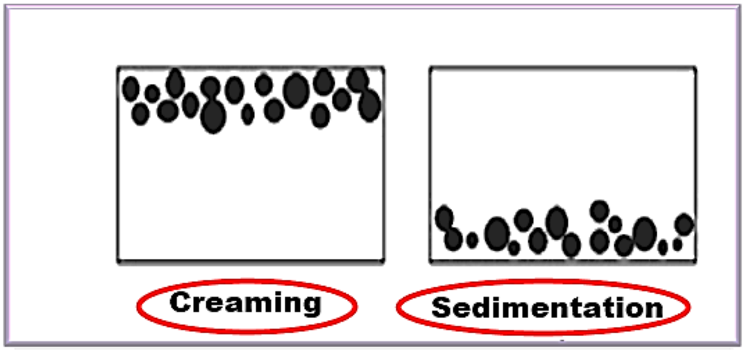

Fig 2: **Creaming and sedimentation of oil emulsion**

1.2.2 Coalescence

Coalescence is defined as the fusion of two or more oil droplets into a single giant droplet. The result is an oil layer on top of the emulsion, which is true for water-in-oil emulsions. (10, 12). When mixed by shaking, water droplets and oil droplets swirl depending on the type of emulsion. The droplets are constantly moving and the collision frequency is very high due to agitation. Collisions can cause coalescence and increase the size of the droplets. Therefore, the presence of an emulsifier in the complex is important to prevent droplet coalescence (7). By adsorbing to the oil-water interface, emulsifier molecules form a layer around the droplet and prevent the droplet from fusing. In addition, the concentration of emulsifier should be high enough to cover the surface of the droplet. If the concentration is too low, the droplet may fuse with adjacent droplets. Another factor that affects droplet size is the time it takes for the emulsifier to adhere to the interface compared to the time between droplet collisions. To minimize coalescence during the emulsification process, it is necessary to ensure that the adsorption time divided by the collision time is much shorter than one.

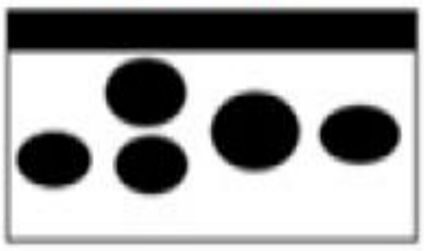

Fig 3 : **Coalescence of oil**

1.2.3 Flocculation

Flocculation is a collection of droplets that retains their physical properties. Coalescence is a collection of fused droplets. Flocculation can be reversible (weak aggregation) or irreversible (heavy aggregation), but coalescence is irreversible (9). Droplet agglomeration antagonizes the stability of the emulsion. This is usually considered an unstable phenomenon. The formation of droplet flocs in the emulsion affects the creaming rate. A good understanding of agglomeration is very important to control the texture and structure of the emulsion (13).

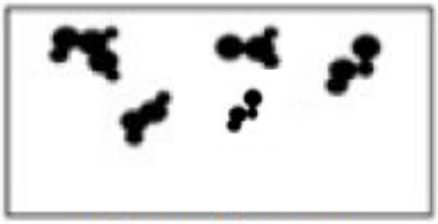

Fig 4: **Flocculation of oil**

1.2.4 Ostwald Ripening

Ostwald ripening in emulsion is the process by which large droplets grow gradually at the expense of small droplets due to the transfer of material in the soluble and dispersed phase (oil) through the continuous phase (water). The solubility of the oil phase increases as the drop radius decreases. Droplet agglomeration and coalescence are the most common causes of emulsion instability, but Ostwald ripening is an important cause of instability in some food emulsion applications, including: Soft drink emulsion (14). There are several ways to control Ostwald ripening. The smaller the droplet size, the higher the solubility of the dispersed phase, and the larger the emulsion droplet, the slower Ostwald ripening. However, coalescence and flocculation are more likely to occur. For emulsions with a narrow droplet size distribution, that is, the difference between the smallest and largest droplets is small. Ostwald ripening is also delayed.

The solubility of oil in water is due to the presence and properties of the emulsifier (11). Ostwald ripening is reduced by using emulsifiers that do not increase oil solubility.

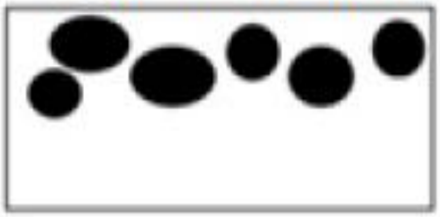

Fig 5 : **Ostwald ripening of oil**

Two or more of these instability phenomena may occur at the same time. It is then important to understand the cause(s) of instability to select suitable components to form stable emulsions. Water-in-oil emulsions are stabilized by a wide range of materials that appear naturally in the heavy crude oil, such as asphaltenes (Biobased surfactants) and clays. To resolve water from the emulsion to meet the pipeline and shipping specifications, the destabilization of emulsion is essential. There are three conditions suitable for the stability of emulsion (9). These are:

1. The liquid involved must be immiscible.
2. Presence of emulsifier
3. Sufficient agitation.

The dispersed water droplets inside the oil field emulsion have films that surround them which help the emulsion to stabilize. The films are believed to be formed by adsorption of high molecular weight polar molecules. These polar molecules exhibit surfactant like behavior. These films increase the interfacial viscosity and thereby increase the stability of the emulsion. Highly viscous interfacial film helps in decreasing the coalescence of water droplets by providing a barrier. The interfacial film is also fortified by the presence of fine solids, further stabilizing the emulsion. The most common emulsifiers found in the petroleum industry include asphaltene, solid paraffin, gum and naphthen (15).

1.3 Thermodynamic and kinetic stability

Thermodynamics provides information on the processes that occur under inert conditions during emulsification or after homogenization. Kinetics provide information about the speed at which these processes occur. A mixture of pure oil and pure water leads to the formation of opaque emulsions. After a certain time, distinct layers of oil and water are visible. This situation is described in one word as coalescence. Coalescence of oil or water droplets taking place in this example is due to thermodynamic instability. The time taken by the droplets to merge is related to kinetics. In order to understand emulsion stabilization mechanisms, it is important to distinguish thermodynamic stability and kinetic stability. Emulsions, especially food emulsions, have been shown to be thermodynamically unstable systems (16). This was shown by considering the free energy of the oil-water system before and after emulsification. During emulsification, the total free energy is positive due to the increased interface area. The formation of food emulsions is thermodynamically disadvantageous. Because emulsions are thermodynamically unstable, kinetic stability is very important in many areas, including food. Emulsions almost certainly decompose, so it is very important to know how long the properties of the emulsion will not change (9). Emulsions exist in a thermodynamically unstable state, but are kinetically stable for months or years. This metastable state (thermodynamic instability and kinetic stability) is due to the fact that the conditions that cause thermodynamic instability occur over a long period of time. After that, the changes in the properties of the emulsion occur very slowly (16).

2.0 Bio-based Products in Stabilization of Emulsions

Emulsifiers are one of the most essential chemicals in emulsion systems because they determine emulsion formation, stability, and physicochemical qualities (17). The development and stability of emulsions has been the subject of current research. These investigations have resulted in a better understanding of how emulsions form and some knowledge of their stability. The polar and asphalt components of the oil have surfactant-like effects on the development of the emulsion. These chemicals have a low HLB (hydrophilic lipophilic balance) and serve as surfactants in the oil, stabilizing water droplets. Aromatic components, particularly BTEX, stabilize polarity and asphaltene in many crude oils (benzene, toluene, ethylbenzene, xylene). Polar compounds, resins, and asphaltene can precipitate if the BTEX is low or depleted due to evaporation. They no longer disintegrate as a result, and can thereby fix water droplets in oil. To generate these emulsions, a significant amount of energy is required if the chemical conditions are correct (17). This emulsification mechanism has been validated by several experiments involving the preparation of "artificial" crude oil and the doping of crude oil. The mechanism is now well understood. Based on this fact, if the pitch, asphaltene, and BTEX contents are known, it is possible to work on predicting the emulsion behavior of crude oil. Studies on emulsion stability have begun, but more work is needed. Emulsion stability can be measured by leaving the prepared emulsion at room temperature for several days. Unstable emulsions decompose quickly, but stable emulsions do not. Most emulsions exhibit this property in a short period of time, whether stable or not. A quick way to determine stability is under development. These studies show that the size of water droplets in an emulsion may be related to stability. Stable emulsions have polydisperse droplets, but unstable emulsions do not. The characteristic red color of the emulsion seems to be related to this polydispersity. Emulsion viscosity correlates with starting oil. However, there is a great deal of variation in this factor. Moisture content is another characteristic of oil. For stable emulsions, it varies between 50-80%. The loss of only about 10% water from a stable emulsion indicates decomposition. However, apparently stable emulsions of some oils can be made when the water content varies from 10 to 80%. The oil deterioration effect is strong. This is related to the BTEX coefficient above. The oil sample must lose enough BTEX to dissolve the asphaltene and resin in the oil before forming the emulsion. Many oils have breakpoints and then form emulsions. This point is relatively sharp with most oils. Very little temporary stable emulsion is formed. An investigation into the energy required to form an emulsion has begun. Some emulsions appear to be more stable when formed at high energy, but most emulsions simply require a "sufficient" amount. The latter is still high compared to other methods such as chemical dispersion (18). Surfactants play two roles in the classical emulsification process. One reduces interfacial tension, promotes droplet deformation and disintegration, and the other reduces droplet coalescence (17). Here, a microfluidic emulsification system is used to completely separate these two processes so that stabilization to coalescence can be studied quantitatively and independently, independent of droplet formation. In addition to the classical effect of stabilization by increasing the detergent concentration, this shows that the dynamics of detergent adsorption at the water-oil interface is an important factor in droplet stabilization. Thus, the microfluidic emulsifier device can be adjusted to improve emulsification while reducing the detergent concentration by increasing the time to first contact of the droplets. Emulsions of oil droplets in water, more commonly water droplets in oil, are common in the manufacture, transportation and refining of petroleum and related products. Emulsions of water in petroleum or petroleum-derived liquids are present in petroleum and can be stabilized by the various surfactants and ingredients that petroleum comes into contact with. These include asphaltene, various types of organic carboxylic acids, inorganic microparticles, and combinations of these three types of materials. When the effect of emulsifier concentration, type of hydrophilic emulsifier, and ratio (weight) of primary emulsion on the stability of water-oil-water emulsion was investigated, milk prepared with 0.5 g of sodium cyanide. The turbidity showed better stability than other compounds. (18). Emulsions made with various types of emulsifiers such as sodium cyanide, cremophore, tween 60, emulsions made from cremophore and tween 60 are small liquids with improved stability compared to sodium cyanide. This means that Cremophor and Tween 60 are superior emulsifiers compared to sodium cyanide. This work was based on a comparison of changes in the ratio of water to oil, and found that the most stable emulsion was an emulsion made from a 50% water-in-oil emulsion. In general, this situation can be very difficult to find in the oil sector. Oil produced by the oil industry does not contain this percentage of water. Temperature changes are also not taken into account.

In the presence of both surfactant and colloidal particles, the balance against coalescence of vegetable oil-in-water “food grade” emulsions has been studied. The results obtained from these studies were compared to the balance of system where only the surfactant or the colloidal particles act as the emulsifier or binder. Prevention of emulsion from creaming was not considered. The types of surfactants selected are;

1. Surfactants that can stabilize oil in water emulsion spontaneously.
2. Surfactants that cannot do same spontaneously. These are water in oil surfactants.

The oil in water surfactant selected were Tween 60 and Sodium Caseinate while monoolein and lecithin were selected as water in oil surfactants.

The findings of this research are as follows: long-term emulsion stability against coalescence was induced by mixed emulsifier complex, notwithstanding the type of surfactant, through a coactive “two-part” process in which both the surfactant and colloidal particles components have specific functions (19). Furthermore, the type of surfactant as well as the concentration is what the emulsion microstructure was proved to depend on. The utilization of oil in water emulsifiers exceeding a particular concentration brought about a removal of particles from the interface, while such a removal was not observed when water in oil emulsifiers were utilized. Further mensuration of interfacial tension and contact angle revealed the surfactant type and concentration are the determinant of the adsorption level of solid particles (19).

The emulsifiers used here prove to be good since it can induce a long-term stability but we should note that it lost its stability at a change in concentration when using oil in water emulsifier. The stability was still retained in the water in oil emulsifier.

Native cellulose has also been used to stabilize emulsion by some researchers. These researchers discovered that native cellulose has not been used in time past because of its insolubility in water. They modified it synthetically to derive cellulose derivatives that are water soluble. These modified celluloses have been widely utilized for diverse applications by the food, cosmetic, pharmaceutical, paint and construction industries. Usually, the synthetically modified celluloses are put to use as rheology modifiers (thickeners) or as emulsifying agents (20). The structural characteristics of cellulose have been examined in the recent decade, with a particular focus on its structural anisotropy (amphiphilicity) and the molecular interactions that rise to its dissolving resistance.

Native cellulose's amphiphilic characteristic is demonstrated by its ability to adsorb at the interface between oil and aqueous solvent solutions, allowing it to stabilize emulsions (20).

The mechanism of stability and application of water-in-oil emulsions including various additives have been examined. The roles of several additives (water and oil soluble types) in stabilizing water in oil emulsions were principally studied and illustrated to acquire new insights into the stability mechanism of emulsion systems. High-Pressure homogenization, Rotor–Stator homogenization, Microchannel emulsification, Membrane emulsification, Microfluidics, and Ultrasound emulsification are some of these methods. (21)

2.1 Mechanism of Stabilization

Emulsifiers prevent droplets from coalescing by generating physical barriers. Emulsifiers are surfactants that have a hydrophilic (water-loving or polar) head group and a hydrophobic (oil-loving or nonpolar) tail group. As a result, both polar and nonpolar molecules attract emulsifiers. Emulsifiers surround the oil droplet in a water emulsion, with their nonpolar tails extending into the oil and their polar head groups towards the water (22). The emulsifier's orientation is inverted in a water-in-oil emulsion: nonpolar tails extend outward into the oil phase, while polar head groups point into the water droplet (23). Emulsifiers reduce the interfacial tension between the oil and water phases in this way, stabilizing the droplets and preventing them from coalescing.

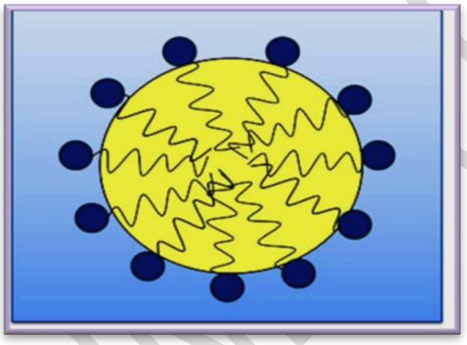

Fig 6 : Oil in water emulsion stability mechanism

Emulsifiers can be cationic (polar head group with a positive charge), anionic (polar head group with a negative charge), or non-ionic (uncharged head group). The positive or negative charges on the outside of the oil droplets electrostatically resist each other when charged emulsifiers cover droplets in an oil in water emulsion, helping to keep the droplets separated (23). The head groups of non-ionic emulsifiers are often big and bulky, pointing away from the oil droplet. These polar head groups collide and tangle with other water droplet head groups, preventing the droplets from joining together sterically. The type of emulsifier employed is determined by the pH of the solution, with cationic emulsifiers being used in low-to-neutral pH solutions and anionic emulsifiers being used in alkaline solutions (22). To improve emulsion stability, non-ionic emulsifiers can be employed alone or in combination with charged emulsifiers.

2.1.1 The choice of an emulsifier

What factors do product formulators consider when selecting an emulsifier for a certain emulsion? Calculating an emulsifier's hydrophilic-lipophilic balance (HLB) or a combination of emulsifiers might be beneficial (24). The emulsifier in an ideal emulsion is equally attracted to the water and oil phases. The emulsifier may lose contact with the phase to which it is less attracted if the balance is tipped in either direction, causing the emulsion to break down (13).

The HLB values of different emulsifiers can be used to forecast their ability to stabilize various types of emulsions. The HLB scale goes from 0 to 20, with 10 indicating an emulsifier that attracts both water and oil equally. Emulsifiers with higher HLB values are more hydrophilic, and thus better at stabilizing oil in water emulsions. Emulsifiers with HLB values less than ten, on the other hand, are more hydrophobic and hence better suitable for water in oil emulsions (25).

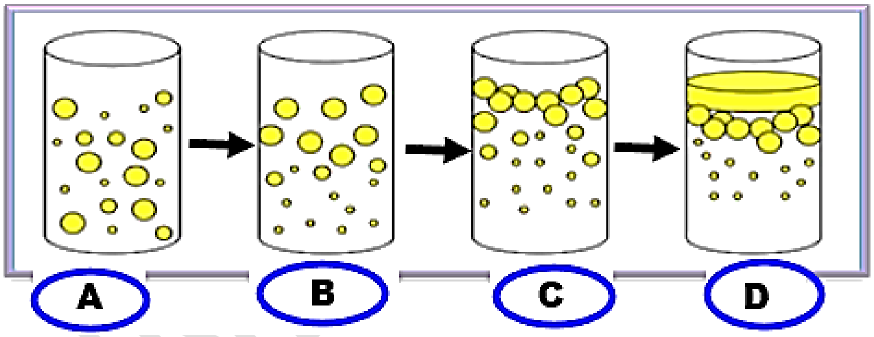

Fig 7 : **Breaking of emulsion steps**

Where [**A**] is a stable emulsion, [**B**] an emulsion has begun to separate, [**C**] an emulsion that is creaming, and [**D**] an emulsion that has broken.

Furthermore, the HLB requirements for various oils vary. Vegetable oil emulsions, for example, require an emulsifier with an HLB of 7–8, but a stable castor oil emulsion requires an HLB of 14. Formulators can substantially improve their chances of establishing a stable emulsion by matching the HLB value of the emulsifier to that of the oil (26).

3.0 Bio-based Products in Demulsification of Emulsion

The separation of generated crude oil from water and basic sediments is the most important aspect of petroleum production since it determines profit. At the same time, it is critical to handle waste water in an effective and environmentally sustainable manner. The separation of water and other foreign elements from the generated crude is the most crucial goal of every oil production facility. One of the most difficult difficulties in today's petroleum sector is breaking this water in oil emulsions (27).

According to a series of research and confidence results, the breakdown of water–in–oil emulsions is still not totally understood, particularly in terms of the effect of added chemical demulsifiers, and more research is needed (28). Hence Demulsifier performance must therefore be improved, both in terms of application and in terms of environmental impact. Recent formulations must be less hazardous and perform at least as well as traditional chemical demulsifiers.

Demulsifiers are used to help separate the water from the water-in-oil emulsion. Synthetic surfactants, which are introduced to water-in-oil emulsions, are used to break down these emulsions. Demulsifiers are used to break emulsions and prevent re-emulsification by destroying the protective coating that the emulsifying agent forms on the surface of water drops. The demulsifying chemical is injected and combined with the emulsion. Following that, water is removed from the oil using sedimentation (29).

3.1 Cashew nut shell liquid and its derivatives

The Cashew Nut Shell Liquid (CNSL) is a useful component of the nut of the Cashew fruit. The oil is found in a soft honeycomb shell, which is the pericarp of the nut, and is dark reddish-brown in color (30). It's a bio-based resin that could be used in a variety of applications as a raw material. The world's population is rapidly growing, and the standard of life is rising, putting a strain on petroleum supplies. As a result of this and other factors, world petroleum reserves are rapidly depleting. As a result, alternative sources of fuel and petrochemical feedstock are required to maintain the level of living and the industrial sector, which is critical to human survival in this decade and beyond (31). Due to its availability and chemical composition, cashew nut shell liquid is a by-product that is used to make "green" products (32, 33, 34).

A by-product of the cashew business, the cashew nut shell is an example of a valuable chemical that can be used as a raw material in the petrochemical sector.

CNSL is essentially a combination of phenolic compounds with varying degrees of unsaturation in the alkyl chain, giving them non-conjugated diene characteristics (35, 36). This distinguishes it from crude oil derivatives as a source of bio-based raw materials. Its primary components (cardanol and anacardic acid) have been used to make adhesives, paints, and plastics (37, 38, 39, 40), as well as antibacterial agents and surfactants (33, 34, 41, 42, 43). In the literature, there are several ways for extracting CNSL. The extraction method utilized affects the efficiency of the oil extracted. The oil content of raw cashew nut shell has been found to be around 20%. The oil bath method leaves around 10% of the oil in the wasted shell as a by-product. Using an expeller extraction procedure, however, more oil can be extracted from the used Cashew Nut Shell.

Table 1 : Compounds that can be extracted from Cashew nut shell liquid

Constituent of CNSL	Method of extraction	Solvent used	Uses of extract	References
Monosaturated cardanol	Soxhlet extraction,	Hexane and methanol	Synthesis of polymers to fabricate adhesives, paints, plastics etc	37, 38, 39, 40.
	super critical CO_2 extraction			
Saturated cardanol	Soxhlet extraction,	Hexane and methanol	It's utilized in resins, coatings, frictional materials, and pigment dispersants for water-based inks in the chemical industry.	44
	super critical CO_2 extraction			
Octacosene	Super critical water	Hexane and methanol	It is used as a solvent and in the synthesis of colloidal quantum dots.	45

Stigmasterol	Super critical water	Hexane and methanol	Sterols are utilized in the production of medications.	46
Monosaturated anacardic acid	Soxhlet extraction,	Hexane and methanol	It is utilized in the manufacturing of cardanol in the chemical industry.	44
β-sitosterol	Soxhlet extraction,	Hexane and methanol	Estrogens, contraceptives, diuretics, and male hormones are all made from β-sitosterol.	46

One of the most prevalent components in cashew nut shell liquid is anacardic acid (47).

Phenolic liquid was recovered from cashew nut shells using acetone and derivatized into anacardic acid-based ethanolamine esters via a one-pot method utilizing Ethanolamine (EA) and Diethanolamine (DEA) in different molar ratios, and evaluated for usage as crude oil emulsion breakers. The physicochemical parameters of the CNSL extract were determined, and FTIR spectral analysis of CNSL and its derivatives validated its chemical alteration. Various crude oil:water mixing ratios of 90:10, 70:30, and 50:50 were utilized to produce laboratory-simulated crude oil emulsions using medium heavy crude and saltwater samples described with ASTM standards. Variations in dosage were used to assess the performance of the anacardic acid-based CNSL extract and derivatives as demulsifiers (10 ppm – 50 ppm), water content (10%, 30%, and 50%), and solvent types (xylene and butanol) by bottle testing at 60°C during a 3-hour period. Under identical settings, the performance of effective demulsifier formulations was compared to that of a commercial demulsifier, Phase Treat-4633 (PT-4633). Water separation increases with demulsifier concentration and emulsion water content, according to the findings, albeit water separation differed among demulsifiers as concentration and water content increased. At 40 ppm and 50 ppm, 50 percent and 60°C, PT-4633 in butanol exhibited effective water separation, with an ideal seperation (100%) seen after 5 minutes (48). Finally, utilizing butanol as a solvent, the examined ethanolamine-CNSL compounds have emulsion breaking capability in a shorter time. This behavior could be attributed to butanol's synergetic function as a solvent; as a result, butanol should be regarded as a solvent substitute for xylene due to its low cost and low toxicity, in contrast to xylene, which is toxic and expensive (48).

3.1.1 Mechanism of Demulsification

Kinetic stability is seen in oilfield emulsions. The development of interfacial coatings that encase the water droplets provides this stability. The interfacial coating must be dissolved and the droplets forced to agglomerate in order to separate this emulsion into oil and water. As a result, fracturing or destabilizing emulsions is directly linked to the elimination of this interfacial coating (2). Temperature, reduced agitation, increased retention time, solid removal, and emulsifying agent control are all factors that facilitate or speed up emulsion breaking.

It takes two steps to separate an emulsion into its component phases. The steps are as follows:

i. Flocculation (aggregation, agglomeration, or coagulation): The flocculation of water droplets is the initial stage in demulsification. The droplets cluster together during flocculation, generating aggregate. The drops are close to each other, even touching at times, but they retain their individuality (i.e., they may not coalesce). Coalescence occurs only if the emulsifier coating enveloping the water droplets is very weak at this stage (2).

ii. Coalescence: The second step in the demulsification process is coalescence. Water droplets fuse or coalesce together to create a bigger drop during coalescence. This is an irreversible process that results in a reduction in the quantity of water droplets and, ultimately, total demulsification (3).

In emulsion breaking, either of these processes can be the rate-determining step.

As a demulsifier, cashew nut shell liquid derivative is a mixture of plant-based fatty acids and oils. The strength of unique micelles helps to speed up separation. Each micelle has a hydrophilic (water-loving) head and a hydrophobic (oil-loving) tail and measures between 1 and 5 nanometers. The hydrophobic tail is drawn to oil and sticks to the droplet, but the hydrophilic head makes the water more slippery. As a result, each micelle collects the oil and rises quickly to the surface to be collected. The micelle will not drop out or settle to the bottom once it has been inserted and mixed into the crude-water combination. Without the use of mechanical separation or procedures, the mixture will remain suspended and aggressively search out oil to bring to the surface.

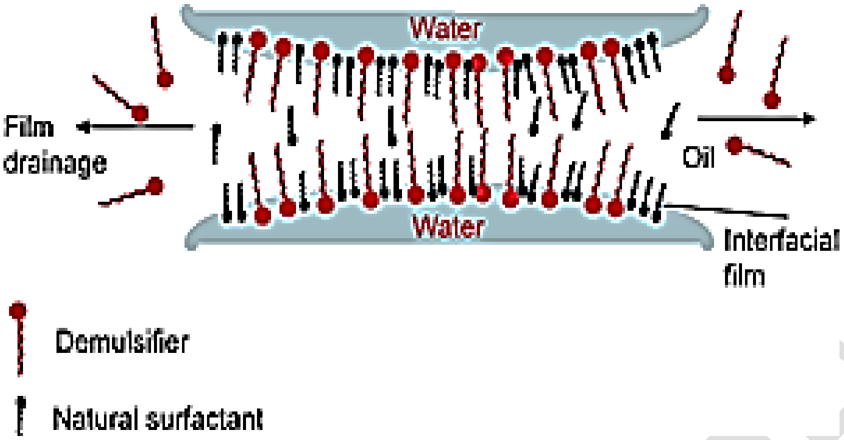

Fig 8 : Mechanism of demulsification

3.2 Microbes in Demulsification of emulsions

The traditional chemical approach of extracting water from crude oil is undesirable from both an economic and environmental standpoint.

Due to the presence of additives with surfactant qualities and water, oil sludge or waste formed during transportation, storage, or refining produces very stable mixes. To separate the leftover oil from the aqueous phase for oil processing, water treatment, and disposal, demulsification is required. Although effective, most chemical demulsifiers are environmental pollutants that do not biodegrade to the necessary levels.

Researchers were able to isolate a strain of Pseudomonas aeruginosa from a site contaminated with refined oil products. This strain was able to demulsify Tween 80–Span 80 stabilized oil-in-water emulsions (kerosene–water) as well as an industrial emulsion. (Daido Dairoll PA-5A) (49). The presence of fatty acids and carbohydrates in the extracellular biodemulsifier was confirmed by GC–MS analysis. Growth on medium containing 1% diesel oil favored the demulsifying activity of cells and culture supernatants. The highest activity was seen for cells and supernatants from 96-hour cultures, and there was a link between culture age, de-emulsification, and cellular hydrophobicity. The addition of up to 60 mg cells or 300 μL supernatant to emulsions improved their activity. The activity was rather stable at 20–40^{0}C and to freezing, but washing the cells with chloroform–methanol–water lowered it by 69 percent (49). This demulsifier could be used in the biotreatment of emulsified oily wastewaters to aid in oil recovery and/or degradation.

Another Microbacterium sp. strain was isolated from oily sludge samples from Siri Island in the south of Iran in 2013, and it produced a powerful, thermally stable microbial demulsifier using glucose as the sole carbon source and yeast extract as a supplement (50). Temperature, inoculum concentration, pH, and culture age were shown to be optimal for microbial demulsifier synthesis at 25°C, 108 CFU/mL, 7 hours, and 24 hours, respectively. For a water-in-crude oil emulsion, the highest demulsification activity and culture broth half-life value were 96.4 percent and 36 hours, respectively, at 80°C in flask. Using cold ethanol, the demulsifier was refined to homogeneity. The water in oil model emulsion had a half-life of 3 hours for 4.33 mg/mL of partially pure microbial demulsifier.

Some researchers looked at the use of microbial biosurfactants as potential bio-based demulsifiers of petroleum derivatives in water emulsions. Biosurfactants crude extracts from yeasts (Candida guilliermondii, Candida lipolytica, and Candida sphaerica) and bacteria (Pseudomonas aeruginosa, Pseudomonas cepacia, and Bacillus sp.) cultivated in industrial residues were investigated for demulsification capacity in crude and pure forms. The best results were found using bacterial biosurfactants, which were able to recover roughly 65 percent of the seawater emulsified with motor oil, compared to only 35–40 percent using yeast products. They also looked at biosurfactants in kerosene emulsions that were oil-in-water and water-in-oil. With all of the biosurfactants studied, there was no correlation between interfacial tension, cell hydrophobicity, and demulsification ratios.

The characteristics of the emulsion and demulsification process were shown in microscopic illustrations of the emulsions in the presence of biosurfactants. The results showed that these agents could be used as demulsifers in marine environments (51).

Biosurfactant de-emulsifiers that are both cost-effective and environmentally friendly have also been developed. Biosurfactant-producing bacteria were isolated from oil-contaminated soil samples from the Nigerian National Petroleum Corporation (NNPC) depot Apata, Ibadan, Oyo State of Nigeria, and used to separate water from crude oil emulsions. Thirty-five of the 41 bacterial strains were then tested using the vapour transfer method for their capacity to de-emulsify hydrocarbon. Pseudomonas sp. AGO1 (50.0 percent), Bacillus sp. DPK1A (50.0

percent), Bacillus subtilis AGO1A (50.0 percent), Pseudomonas aeruginosa DPK3A (55.7 percent), and Bacillus subtilis PMS1B2 (66.0 percent) had the highest de-emulsification activity at 24 hours.

Bacillus subtilis AGO1A (50.0 percent), Pseudomonas aeruginosa DPK3A (60.0 percent), and Bacillus subtilis PMS1B2 (66.7 percent) were found at 48 hours (52). Supplementation of growth medium resulted in higher de-emulsification activities, with Pseudomonas aeruginosa DPK3A demonstrating the maximum de-emulsification activity of 66 percent when grown on growth media supplemented with glucose and yeast extract at 60°C. They compared natural de-emulsifiers to artificial de-emulsifiers. Chemical de-emulsifier produced 63 percent, 60 percent, and 66.2 percent volume of water, while microbial demulsifier produced 66%, 62 percent, and 60% volume of water. This study found that biosurfactant-producing bacteria, particularly Bacillus species isolated from crude oil-contaminated soils, are effective in diesel breakdown and treatment of water-in-crude oil emulsions when cultivated on appropriate medium, lowering costs and reducing pollution (52).

3.2.1 Mechanism of demulsification

The amphipathic properties of biosurfactants allow for a variety of properties such as detergency, emulsification, demulsification, lubrication, foaming, solubilization, and phase dispersion, which can be used in the recovery of hydrocarbon-contaminated water and soil (53), heavy metals (54), and oil spill cleanup (55), among other applications.

Microbial cultures grown on water miscible and/or immiscible substrates create biosurfactants, which are divided into two types: low molecular-mass molecules (lipopeptides, glycolipids, and phospholipids) and high molecular-mass polymers (polymeric and particulate surfactants). The most well-known glycolipids include rhamnolipids, sophorolipids, and trehalolipids, while Surfactin, a lipopeptide, is one of the most effective biosurfactants (55).

Biosurfactants increase the solubility of hydrophilic molecules by reducing surface and interfacial tension. Micelles are molecular aggregations that form at a particular surfactant concentration. The critical micelle concentration (CMC) is the point at which the surface tension is at its lowest stable level (56).

The biodemulsifier is adsorbed to the water–oil interface and reacts with the emulsifier, causing the thin coating on the surface of the droplets in the emulsion to be removed, causing coalescence, which is followed by the droplets settling and the continuous phase being clarified (57).

3.3 Plant extract in Demulsification of Emulsion

Green demulsifiers have been found in green tea extracts and several vegetable oils such as olive and coconut oil. The plant extract was extracted using the soxhlet process, whereas the vegetable oil was made entirely of coconut oil. Gas Chromatography with Mass Spectroscopy was used to determine the composition of the plant extract. Blend demulsifier was made from local materials such as starch, camphor, Calcium Hydroxide ($Ca(OH)_2$), Sodium Hydroxide (NaOH), paraffix wax, liquid soap, and distilled water in order to offer a strong impact of the plant extracts and also as a comparison. Green tea leaf extract, coconut oil, and olive oil were tested in bottles under static and dynamic settings to find the optimum demulsifier. It was found out that Green tea leaf extract and olive oil extracted less water than coconut oil. The coconut oil, sodium hydroxide, and other local elements in the blend demulsifier performed better than the other blend demulsifiers, but not as well as the coconut oil alone (15).

As a suitable green demulsifier, plant extracts such as coconut oil, olive oil, bio-furfural, lemon seed oil, pine oil, cotton seed oil, and papaya extract have been used. Additional studies were conducted to determine the extracts' environmental friendliness. The findings revealed that coconut and cotton seed oils produce the best effects, with cotton seed oil being more cost effective than coconut oil (27).

Bottle test method was used to study the performance of the natural extract and commercial demulsifier on a crude oil sample. Oil was extracted from rice bran using hexane as solvent. Ultrasound-assisted extraction was employed as well as traditional solvent extraction using ethanol. The extract's composition was determined using Gas Chromatography with Mass Spectroscopy. The findings are consistent with the literature. The demulsifier's performance was measured in terms of the percentage of water removed from 100 ml of oil samples. The performance of the chemical and synthetic demulsifiers improved as the volume of demulsifier rose. Under all of the study's experimental circumstances, the extracted demulsifier outperformed the chemical demulsifier. With a volume of 5 mL of extract, a temperature of 70^0C, and a separation period of 60 minutes, the bio-efficiency demulsifier's was maximum. As a result, a water separation efficiency of 85.6 percent was achieved.(58)

3.3.1 Mechanism of Demulsification

There are two types of plant components that can disrupt the emulsion in different ways. The hexane group and octadecenoic acid are the two. Both compositions can react with surfactant to cause the water droplet to flocculate and coalesce.

When the emulsifier is injected into the water in an oil emulsion, the emulsifying agent is displaced as the surface active character, resulting in lower water droplet surface tension and interfacial energy. The water droplets flocculated as they traveled closer each other. The flocculation mechanism resulted in huge droplets coalescing to generate larger droplets. Due to gravity, these coalesced droplets flowed downhill through the oil and eventually collected at the bottom of the treating vessel.

4.0 Conclusion

Emulsion is indeed a great challenge to the oil and gas industry considering the various effects it has to the value and quantity of oil produced. It cannot be avoided owing to the fact that oil is produced alongside water as well as other solid materials such as asphatenes which makes oil and water miscibility possible. Emulsifiers are specific for the oil used in metalworking fluid formulations and can be prepared from hydrolyzed fatty acids of oil incorporated in the formulation (59, 60).

The oil and gas industry have also developed a means to solve their problems with the introduction of chemical demulsifiers. These demulsifiers although effective in its function has side effects which are also of a great concern. This brought about the need of greener demulsifiers.

In this review, emulsification and demulsification using Bio-based products have been reviewed. The three important factors that enhance stability of emulsion are two immiscible liquids, presence of emulsifier and agitation. These three factors are present in the production process of crude oil. Oil and water are immiscible, also the crude oil produced contains organic acids, resins and asphathenes which acts as emulsifier and during the transportation of the oil produced there is usually agitation.

Demulsification is indeed very necessary. This review paper shows that very few works has been done using cashew nut shell liquid but a lot of work has been done using microbes. Comparing the results obtained from cashew nut shell liquid and microbes, we can see that both demulsifiers are very effective. It was also observed that all microbes that were used in the demulsification process were isolated from oil polluted site. This leaves us with a question “does it mean that pollution should be encouraged for us to get microbes that can be modified to demulsifiers?”

Pollution is a great problem and oil polluted site has great effect on the soil as well as man. This should be considered. Researchers are advised to find out if these microbes can be isolated from other sources other than oil polluted sites.

A lot of work is yet to be done using cashew nut shell liquid and other agricultural waste product as demulsifiers. This should also be encouraged among researchers.

Researchers should also go on to convert these products to finished products and make it available to oil industries.

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