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.

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1.0 Introduction

The formation of water in oil emulsion is a critical issue in industrial applications such as the petroleum sector. In fact, emulsified water can corrode refinery equipment and the water dissolved salt can poison catalyst in downstream processing facilities (1) Also water in oil emulsion usually exhibit viscosities significantly higher than crude oil. This will increase the pumping 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 (2).

An emulsion is a mixture of two or more liquids that are normally immiscible because of the liquid-liquid phase separation. Emulsions are part of a more general class of two-phase systems of matter called colloids. Although the terms colloid and emulsion are sometimes used interchangeably, emulsion should be used when both phases, dispersed and continuous, are in their liquid states. In an emulsion, one liquid must be the dispersed phase while the other is the continuous phase (3). The dispersed phase is dispersed in the continuous phase. Examples of emulsions include homogenized milk, liquid bimolecular condensates, and some cutting fluids for metal working. When two immiscible liquid is in contact there is a chance for the formation of emulsion.

An emulsion can also be defined as a solution between two immiscible liquids where one liquid is dispersed in other liquid. In an emulsion one liquid is finely dispersed in another liquid (4).

The process of mixing two liquids together in order to prepare emulsions is called emulsification. Mixtures of oil and water are not stable, as oil or water droplets tend to merge with each other. This process is called coalescence (5, 6).

It becomes necessary to introduce a third agent called emulsifier to stabilize the emulsions. Stabilization can be achieved through homogenization (7)

The two main functions of an emulsifier during homogenization are:

1. To decrease the oil-water interfacial tension to facilitate droplet disruption;
2. To form a protective layer around the oil droplets to prevent coalescence

Crude oil is extracted in form of emulsion and hence there is a need for demulsification. The water content present in the emulsion can cause problems for the production facilities as stated above.

The breaking of crude oil emulsion is an important part of crude oil processing. The most commonly used method to break the water in oil emulsion is to use a chemical demulsifier. But chemical demulsifiers have adverse effect on the environment.

There are many methods for demulsification process such as chemical, mechanical and heat. The chemical demulsifiers are majorly used and are found to contain methyl benzene which has adverse environmental effect. The water extracted from the emulsion will be discharged to the environment after further processing, and this has been found out to be toxic and unsafe for marine life. For this reason, there is a need for green demulsifiers.

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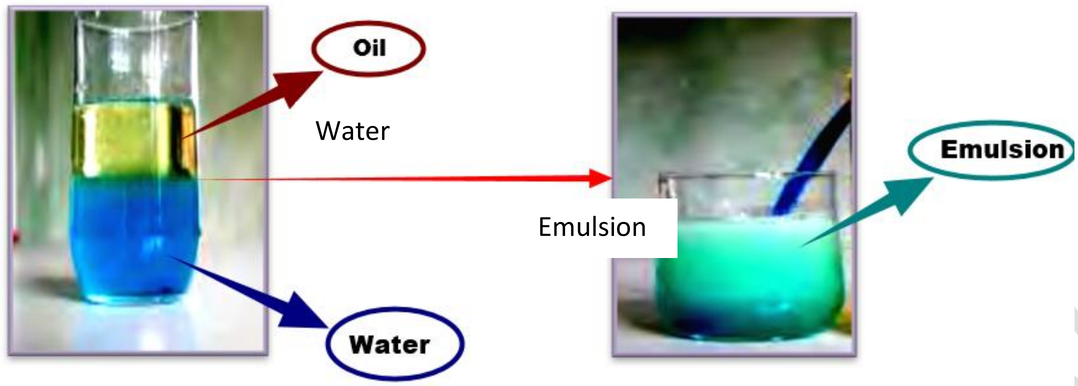

Fig 1: Process of formation of emulsion

1.1 Types of emulsion

There are three basic types of emulsion namely: oil in water emulsion, water in oil emulsion and multiphase (2). In every emulsion there is a continuous phase that suspends the droplets of other element which is called dispersed phase. In oil in water emulsion, the continuous phase is water and dispersed phase is oil, while in water in oil emulsion, oil is the continuous phase while water is the dispersed phase. In multiphase, it consists of water in oil and oil in water simultaneously (2).

1.2 Factors affecting emulsion stability.

The term "emulsion stability" refers to the ability of an emulsion to retain its properties unchanged over a certain period of time (8). However, as emulsions are thermodynamically unstable, changes of emulsion properties will occur. This depends on the rate of property change; the slower the properties change, the more stable the emulsion is. There are many processes that can alter emulsion properties (9). They are coalescence, flocculation, creaming, Ostwald ripening, etc (10).

1.2.1 Creaming/ Sedimentation

Creaming or sedimentation processes occurring in emulsion can be easily assessed by optical observations (10). In most cases, creaming is characterized by a whitish/yellowish layer at the top of emulsion, when a layer appears at the bottom of an emulsion sedimentation occurs. Creaming/sedimentation rate can be determined by measuring the volume of cream/sediment in the emulsion with time. This may be done by placing the emulsion in a calibrated beaker or tube and measuring the height of the cream/sediment every second or minute (11).

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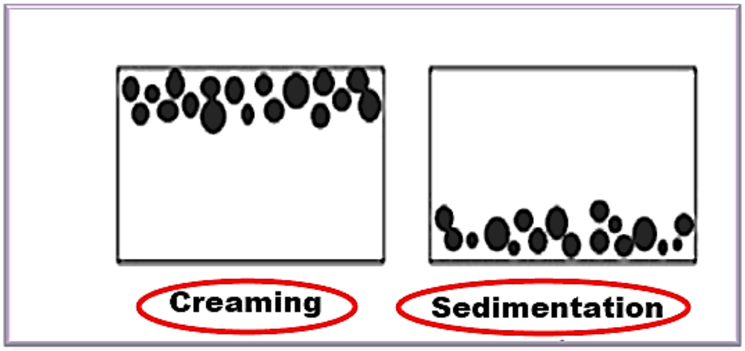

Fig 2: **Creaming and sedimentation of oil emulsion**

1.2.2 Coalescence

Coalescence is the merging of two or more droplets to form a larger single droplet and results in the formation of a layer of oil at the top of emulsion (in the case of oil in water emulsions) (10, 12).

During homogenization, the droplets of water or oil depending on the type of emulsion are disrupted. The droplets are constantly moving and the frequency of collision is very high due to agitation. These collisions may lead to coalescence, increasing then the droplet size. Thus, the presence of emulsifier in the system is necessary to prevent droplets coalescence (7). By adsorbing at the oil-water interface, emulsifier molecules form a layer around the droplets that prevents merging. Also, the concentration of emulsifier must be high enough to cover the droplet surface. In a case where the concentration is too low, droplets are likely to merge with their neighbors. Another factor that affects the droplet size is the time required by the emulsifier to adsorb at the interface compared to the time between droplet collisions. In order to minimize the coalescence during the emulsification process, it is necessary to insure that time of adsorption divided by the time of collision is far less than one.

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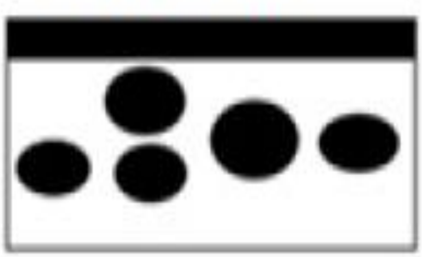

Fig 3 : **Coalescence of oil**

1.2.3 Flocculation

Flocculation is the aggregation of droplets that keep their physical properties; coalescence is the aggregation of droplets that merge together. Flocculation may be reversible (weak flocculation) or irreversible (strong flocculation) while coalescence is irreversible (9).
Droplet flocculation has antagonistic effects on emulsion stability. It is usually considered as an instability phenomenon. The formation of droplets flocs in the emulsion has an influence of the creaming rate.
A good understanding of flocculation is of great importance in order to control the texture and structure of emulsions (13).

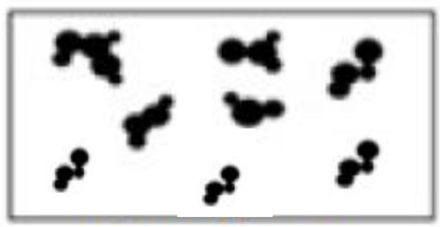

Fig 4: **Flocculation of oil**

1.2.4 Ostwald Ripening

Ostwald ripening in emulsion is a process of gradual growth of the larger droplets at the expense of smaller ones due to mass transport of soluble dispersed phase (oil) through the continuous phase (water). The solubility of the oil phase increases with decreasing droplet radius. Even though droplet flocculation and coalescence are the most common factors of emulsion instability, Ostwald ripening is an important cause of instability in some food emulsion application, like soft drink emulsions (14). There are a few methods to control Ostwald ripening. As the solubility of the dispersed phase increases with decreasing droplet size, Ostwald ripening will be slowed down if the emulsion droplets are bigger. However, coalescence and flocculation are more likely to occur. In emulsions with a narrow droplet size distribution, i.e. the difference between the smallest and the biggest droplets is little; Ostwald ripening will also be retarded.
The solubility of oil in water is due to the presence and the properties of emulsifier (11). By using emulsifiers that do not increase the oil solubility, Ostwald ripening will be reduced.

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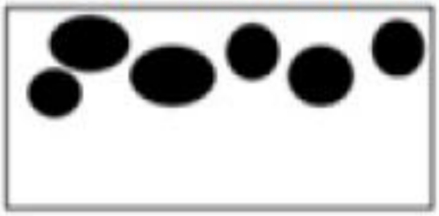

Fig 5 : **Ostwald ripening of oil**

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 (Bio-based 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). They are:

1. Liquids 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 strengthened by the presence of fine solids, further stabilizing the emulsion. In the petroleum industries, the most common emulsifying agents found include asphaltenes, solid paraffin, resinous substances and naphthenes (15).

1.3 Thermodynamic and kinetic stability

Thermodynamics gives information about processes taking place during emulsification or at inert conditions after homogenization. Kinetics gives information about the rate at which these processes occur. The mixture of pure oil and pure water results in the formation of non-transparent 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

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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.

It was shown that emulsions, and particularly food emulsions, are thermodynamically unstable systems (16). This was demonstrated by considering the free energy of the oil-water system before and after emulsification. During emulsification, the overall free energy is positive, due to the increase of interfacial area, i.e. the food emulsion formation is thermodynamically unfavorable.

Since emulsions are thermodynamically unstable, kinetic stability is of great importance in many fields, including food; as emulsions are almost certain to break down, a crucial issue is to know how long emulsion properties remain the same (9). Despite the fact that emulsions exist in a thermodynamically unstable state, some remain kinetically stable for months or years. This metastable state (thermodynamically unstable and kinetically stable), is due to the fact that the condition responsible for thermodynamically instability take place over a long period a time. The changes in emulsion properties occur then very slowly (16).

2.0 Bio-based Products in Stabilization of Emulsions

In an emulsion system, emulsifier is one of the most important substances as it determines the formation, stability and physicochemical properties of emulsions (17).

Studies on the formation and stability of emulsions have been conducted in the past years. These studies have led to a relatively good understanding of why emulsions form and some knowledge about their stability. The formation of emulsions is due to the surfactant-like action of the polar and asphaltene components of oil. These compounds behave like low HLB (hydrophilic-lipophilic balance) surfactants and stabilize water droplets in the oil. The polars and asphaltenes are stabilized in many crude oils by the aromatic components, especially the BTEXs (benzene, toluene, ethylbenzene and xylenes). If the BTEXs are in low quantity or are lost through evaporation, the polars or resins and asphaltenes can precipitate. This means that they are no longer dissolved and thus can stabilize the water-in-oil droplets. A relatively large amount of energy is required to form these emulsions after the chemical conditions are correct (17). This mechanism of emulsion formation has been verified by several experiments including the creation of "artificial" crudes and the doping of crudes. The mechanism has now been

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sufficiently well understood. Due to this fact, work can now proceed on the prediction of emulsion behavior of crudes knowing the content of the resins, asphaltenes and the BTEXs.

Studies of the stability of emulsions have been initiated but further work is still necessary. The stability of emulsions can be measured by leaving prepared emulsions at room temperature for several days. Unstable emulsions will disintegrate rapidly while stable ones will not. Most emulsions are either stable or not and show this characteristic in a short time. Rapid methods for determining stability are under development. These studies show that the droplet size of water in emulsions may be related to stability. A stable emulsion will have poly-disperse droplets, whereas an unstable emulsion will not. The characteristic red colour of an emulsion appears to be related to this poly-dispersability. The viscosity of an emulsion is correlated with the starting oil; however there exists high variation in this factor. The water content is another characteristic of the oil. For stable emulsions, it varies from 50 to 80%. A loss of only about 10% water from a stable emulsion is a sign of break-down. However, apparently stable emulsions of some oils can be made with water contents varying from 10 to 80% water. Breaking down effects on the oil is strong. This relates to the BTEX factor noted above. A sample of oil must lose sufficient BTEX which dissolves the asphaltenes and resins of the oil, before they will form emulsions. There exists a point of break down for many oils after which it will form an emulsion. This point is relatively sharp for most oils. Very few temporary stables emulsions are formed. A study of the energy needed to form an emulsion has begun. It appears that although some emulsions are more stable when formed at high energies, most emulsions simply require a "sufficient" amount; the latter is still high when compared to other processes such as chemical dispersion (18).

In classical emulsification processes, surfactants play two roles: first, they reduce the interfacial tension, facilitating droplet deformation and rupture, and second, they reduce droplet coalescence (17). Here, a microfluidic emulsification system is used to completely uncouple these two processes, allowing stabilization against coalescence to be studied quantitatively and independently of droplet formation. That is demonstrated in addition to the classical effect of stabilization by an increase of surfactant concentration, the dynamics of adsorption of surfactant at the water-oil interface is a key element for droplet stabilization. Microfluidic emulsification devices can therefore be tailored to improve emulsification while decreasing the concentration of surfactant by increasing the time before the droplets first come into contact.

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Emulsions of oil droplets in water but more typically water droplets in oil are common in the production, transportation, and refining of petroleum and related products. Emulsions of water in petroleum or petroleum-derived liquids can be stabilized by a variety of surface-active compounds and components present in petroleum and also with which petroleum comes into contact. These include asphaltenes, carboxylic organic acids of various types, fine inorganic particles, and combinations of these three types of materials.

The effects of emulsifier concentration, type of hydrophilic emulsifier, as well as portions of primary emulsion (weight) on the stability of water-oil-water emulsions have been investigated and it was observed that emulsions prepared with 0.5 gram of sodium cyanide have superior stability over other synthesis conditions (18). Emulsions prepared using different types of emulsifier, such as Sodium cyanide, Cremophor, Tween 60, showed that emulsions made form Cremophor and Tween 60 possess small droplets with enhanced stability when compared with Sodium cyanide.

This means that cremophor and Tween 60 are better emulsifiers compared to Sodium cyanide.

This work was done based on the comparism between change in proportion of water and oil and they discovered that the one with more stability is the emulsion prepared by 50% water in oil emulsion. On a general note it might be quite difficult to find this situation in the oil sector. The oil produced in the oil industry will not have that proportion of water. Also change in temperature was not considered.

The stability against coalescence of vegetable oil-in-water "food grade" emulsions in the presence of both surfactant and colloidal particles have been studied. The results were compared to the stability of system where only the surfactant or the colloidal particles act as the emulsifier. No attempt was made to stop the emulsions from creaming. Two types of surfactants where selected which are;

1. Surfactants that have the ability to stabilise oil in water emulsions on their own.
2. Surfactants that cannot. These are water in oil surfactants.

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

The findings of this research are as follows: the mixed emulsifier systems were shown to induce long-term emulsion stability against coalescence, regardless of the surfactant type, through a synergistic "two-part" mechanism in which both the surfactant and colloidal particles

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components have specific functions (19). Furthermore, the emulsion microstructure was proved to depend on the surfactant's type and concentration: the use of oil in water emulsifiers above a certain concentration induced a displacement of particles from the interface, while such a displacement was not observed using water in oil emulsifiers. Further measurements of interfacial tension and contact angle showed that the level of adsorption of solid particles at the interface depended on the surfactant type and concentration (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 chemically to obtain water-soluble cellulose derivatives. These modified celluloses have been widely used for a range of applications by the food, cosmetic, pharmaceutical, paint and construction industries. In most cases, the modified celluloses are used as rheology modifiers (thickeners) or as emulsifying agents (20) . In the last decade, the structural features of cellulose have been revisited, with particular focus on its structural anisotropy (amphiphilicity) and the molecular interactions leading to its resistance to dissolution.

The amphiphilic behavior of native cellulose is evidenced by its capacity to adsorb at the interface between oil and aqueous solvent solutions, thus being capable of stabilizing emulsions (20).

The stability mechanism and application of water- in- oil emulsions comprising various additives have been reviewed. Several commonly used methods for the preparation of water in oil emulsions, and the roles of different additives (water- and oil- soluble types) in stabilizing water in oil emulsions were mainly discussed and illustrated to gain new insights into the stability mechanism of emulsion systems. These methods include the following: High-Pressure homogenization, Rotor–Stator homogenization, Microchannel emulsification, Membrane emulsification, Microfluidics and Ultrasound emulsification.(21)

2.1 Mechanism of Stabilization

Emulsifiers work by forming physical barriers that keep droplets from coalescing. Types of surfactant, emulsifiers contain both a hydrophilic (water-loving or polar) head group and a hydrophobic (oil-loving or nonpolar) tail. Therefore, emulsifiers are attracted to both polar and

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nonpolar compounds. When added to oil in water emulsion, emulsifiers surround the oil droplet with their nonpolar tails extending into the oil, and their polar head groups facing the water (22). For water in oil emulsion, the emulsifier's orientation is reversed: nonpolar tails extend outward into the oil phase, while polar head groups point into the water droplet (23). In this way, emulsifiers lower the interfacial tension between the oil and water phases, stabilizing the droplets and preventing them from coalescing.

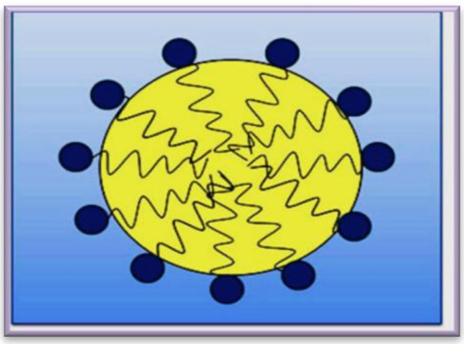

Fig 6 : Oil in water emulsion stability mechanism

Emulsifiers can be cationic (positively charged polar head group), anionic (negatively charged head group), or non-ionic (uncharged head group). When charged emulsifiers coat droplets in oil in water emulsion, the positive or negative charges on the outside of the oil droplets electrostatically repel each other, helping to keep the droplets separated (23). Non-ionic emulsifiers tend to have large, bulky head groups that point away from the oil droplet. These polar head groups clash and tangle with head groups on other water droplets, sterically hindering the droplets from coming together. The type of emulsifier used depends on the application, with cationic emulsifiers typically used in low-to-neutral pH solutions and anionic emulsifiers in alkaline solutions (22). Non-ionic emulsifiers can be used alone or in combination with charged emulsifiers to increase emulsion stability.

2.1.1 The choice of an emulsifier

How do product formulators choose which emulsifier to use for a particular emulsion? Calculating the hydrophilic-lipophilic balance (HLB) of an emulsifier or combination of emulsifiers can help (24). In an ideal emulsion, the emulsifier is equally attracted to the water phase and the oil phase. If the balance is tipped in either direction, the emulsifier may lose contact with the phase to which it is less attracted, causing the emulsion to break down (13).

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Different emulsifiers have different HLB values, which can predict their ability to stabilize various kinds of emulsions. The HLB scale ranges from 0 to 20, with 10 corresponding to an emulsifier that is equally attracted to water and oil. Emulsifiers with HLB values greater than 10 are more hydrophilic and thus better at stabilizing oil in water emulsions. In contrast, emulsifiers with HLB values less than 10 are more hydrophobic and therefore better suited for water i emulsions (25).

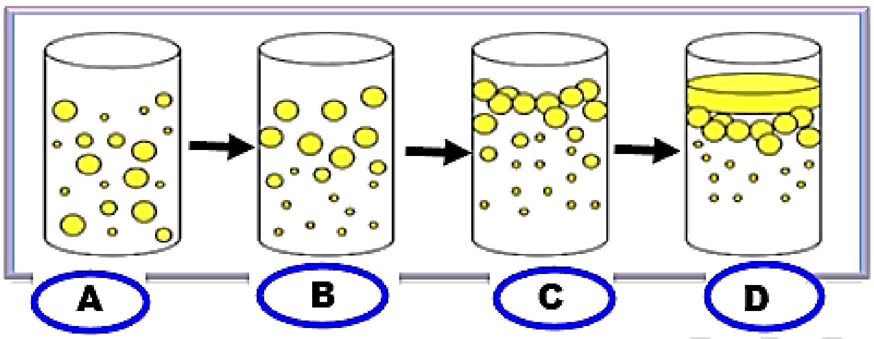

Fig 7 : **Breaking of emulsion steps**

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, different oils have different HLB requirements. For example, vegetable oil emulsions need an emulsifier with an HLB of 7–8, whereas the required HLB value to form a stable castor oil emulsion is 14. By matching the HLB value of the emulsifier with that of the oil, formulators can greatly increase their chances of producing a stable emulsion (26).

3.0 Bio-based Products in Demulsification of Emulsion

Separating produced crude oil from water and basic sediments is the most critical aspect of the petroleum production because the profit depends on doing it efficiently. At the same time, treating waste water in an efficient and environmentally sustainable way is equally important. The most important objective of any oil production facility is the separation of water and other foreign materials from the produced crude. The breaking of this water in oil emulsion constitutes one of the challenging problems in today's petroleum industry (27)**.**

Considering series of research and confidence results, the breaking of water–in-oil emulsions is not yet completely understood, especially as far as the added chemical demulsifiers role is concerned and much investigation still required (28). Hence Demulsifiers performance has to therefore be improved, from the application as well as from the environmental point of view.

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Recently produced formulations must be less toxic and at least as efficient as classical chemical demulsifiers.

In order to properly separate the water from water-in-oil emulsion, demulsifiers are used to enhance the process. The processes involved in the breaking of these emulsions are carried out by using synthetic surfactants which are added to water-in-oil emulsion. The function of the demulsifiers is to break emulsion and prevention of re-emulsification by breaking the protective film which is formed on the surface of water drops, by the emulsifying agent. The demulsifying chemical is injected into emulsion and mixed with it. After that water is removed from oil by sedimentation (29).

3.1 Cashew nut shell liquid and its derivatives

Cashew Nut Shell Liquid (CNSL) is a resourceful component of the Cashew fruits' nut. The oil which is dark reddish-brown in color is found in a soft honeycomb shell, which is the pericarp of the nut (30). It is a Bio-based resin that could serve as a valuable raw material for various applications. Rapid increase in the world population and increase in the standard of living has overstretched petroleum resources. This as well as other factors have resulted in the fast depletion of global petroleum reserves. Therefore, to maintain the standard of living and continuity of industrial sector which is paramount to human survival this decade and beyond, there is a need to find alternative sources of fuel and petrochemical feedstock (31).Cashew nut shell liquid is a by-product, used for fabrication of "green" products, due to its high abundance and its chemical composition (32, 33, 34).

Cashew nut shell, a by-product of the cashew industry, is an embodiment of a useful chemical serving as a raw material for the petrochemical industry.

CNSL is a mixture, essentially, of phenolic compounds, which present several degrees of unsaturation in the alkyl chain, conferring them properties of non-conjugated dienes (35, 36). This makes it an alternative source of Bio-based raw materials different than crude oil derivatives. Its main components (cardanol and Anacardic Acid) have been used in the synthesis of polymers to fabricate adhesives, paints, plastics (37, 38, 39, 40) also antibacterial agents and surfactants (33, 34, 41, 42, 43).

Several methods are available in the literature for the extraction of CNSL. The efficiency of the Oil extracted varies with the method of extraction used. Raw Cashew Nut Shell has been reported to contain over 20% oil. The oil bath process leaves about 10% of the oil as a by-

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product in the spent shell. However, using an expeller extraction process, further quantities of oil may be recovered from the spent 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 is used in the chemical industry in resins, coatings, frictional materials, and surfactants used as pigment dispersants for water-based inks	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 used in the manufacture of pharmaceuticals.	46
Monosaturated anacardic acid	Soxhlet extraction,	Hexane and methanol	It is used in the chemical	44

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			industry for the production of cardanol.	
β-sitosterol	Soxhlet extraction,	Hexane and methanol	β-sitosterol is used to produce estrogens, contraceptives, diuretics, and male hormones	46

Anacardic acid is one of the most abundant compounds in cashew nut shell liquid (47).
Phenolic liquid have been extracted from cashew nut shells using acetone and derivatized using Ethanolamine (EA) and Diethanolamine (DEA) in varying molar ratios via a one-pot process into anacardic acid-based ethanolamine esters and evaluated for use as crude oil emulsion breakers. The CNSL extract was characterized for its physicochemical properties, FTIR spectral analysis for CNSL and the derivatives confirmed its chemical modification. Medium heavy crude and seawater sampled characterized with ASTM standards were used in producing laboratory-simulated crude oil emulsions at varying crude oil: water mixing ratios of 90:10, 70:30 and 50:50. Performance of the anacardic acid-based CNSL extract and derivatives as demulsifiers were evaluated based on variation in dosage (10 ppm – 50 ppm), water content (10%, 30% and 50%), and solvent types (xylene and butanol) at 60℃ within a 3-hr period via bottle testing. The performance of effective demulsifier formulations were compared with a commercial demulsifier, Phase Treat-4633, PT-4633, under similar conditions. Results obtained showed that water separation increases with demulsifier concentration and emulsion water content respectively, though water seperation varied among the demulsifiers as concentration and water content increased. PT-4633 in butanol achieved efficient water separation with an optimal seperation (100%) observed after 5 minutes at 40 ppm and 50 ppm, 50% and 60℃ (48). In conclusion, the evaluated ethanolamine-CNSL products possess emulsion breaking potential using butanol as solvent at shorter times. This behavior may be due to the synergetic effect of butanol as a solvent, thus, butanol should be considered as solvent substitute for xylene due to low cost and toxicity levels, unlike xylene which is toxic and expensive (48).

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3.1.1 Mechanism of Demulsification

Oilfield emulsions possess some kinetic stability. This stability arises from the formation of interfacial films that encapsulate the water droplets. To separate this emulsion into oil and water, the interfacial film must be destroyed and the droplets made to coalesce. Therefore, destabilizing or breaking emulsions is linked directly to the removal of this interfacial film (2). The factors that enhance or speed up emulsion breaking are:

a. Temperature
b. Reduced agitation
c. Increased retention time
d. Solid removal
e. Control of emulsifying agents

The separation of an emulsion into its component phases is a two-step process. The steps are:

i. Flocculation (aggregation, agglomeration, or coagulation): The first step in demulsification is the flocculation of water droplets. During flocculation, the droplets clump together, forming aggregate or "floccs." The droplets are close to each other, even touching at certain points, but do not lose their identity (i.e., they may not coalesce). Coalescence at this stage only takes place if the emulsifier film surrounding the water droplets is very weak (2).

ii. Coalescence: Coalescence is the second step in demulsification. During coalescence, water droplets fuse or coalesce together to form a larger drop. This is an irreversible process that leads to a decrease in the number of water droplets and eventually to complete demulsification (3).

Either of these steps can be the rate-determining step in emulsion breaking.

Cashew nut shell liquid derivative as a demulsifier is a combination of plant based fatty acids and oils. It accelerates separation through the strength of proprietary micelle formulas. Each micelle measures from 1 – 5 nanometers and has a hydrophilic (water loving) head with a hydrophobic (oil loving) tail. The hydrophobic tail is attracted to oil and attaches itself to the oil droplet while the hydrophilic head makes the water more slippery. The result is that each micelle collects the oil and quickly rises to the surface for collection. Once introduced and stirred into the crude-water mixture, the micelle will not drop out or settle at the bottom. The mixture will remain suspended and continue to actively seek out oil to bring to the surface without the need for mechanical separation or processes.

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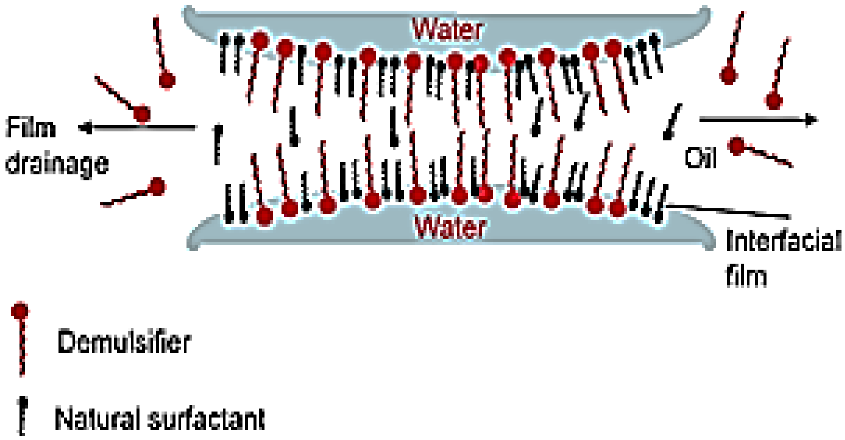

Fig 8 : Mechanism of demulsification

3.2 Microbes in Demulsification of emulsions

Conventional method of removing water from crude oil using chemicals is unfavorable from both the economic and environmental perspectives.

Oil sludge or waste generated in transport, storage or refining forms highly stable mixtures due to the presence and additives with surfactant properties and water forming complex emulsions. Thus, demulsifcation is necessary to separate this residual oil from the aqueous phase for oil processing and water treatment and disposal. Most used chemical demulsifers, although effective, are environmental contaminants and do not meet the desired levels of biodegradation.

Isolation of a strain of Pseudomonas aeruginosa from a site contaminated with refined oil products have been carried out by researchers. This strain exhibited demulsification capabilities against Tween 80–Span 80 stabilized oil-in- water emulsions (kerosene–water), and an industrial emulsion (Daido Dairoll PA-5A) (49). GC–MS analysis confirmed the presence of fatty acids and carbohydrates in the extracellular biodemulsifier. The demulsifying activity of cells and culture supernatants was favored by growth in media containing 1% diesel oil. There was a correlation between culture age, de-emulsification and cellular hydrophobicity, and highest activities were observed for cells and supernatants from 96-hours cultures. Activity increased with addition of up to 60 mg cells or 300 lL supernatant to emulsions. The activity was relatively stable at 20–40 ^{0}C and to freezing, but was reduced by 69% by washing the cells with chloroform–methanol-water (49). This demulsifier has potential for application in biotreatment of emulsified oily wastewaters to promote recovery and/or degradation of oil.

In 2013, another bacterium strain belonging to Microbacterium sp. was isolated from oily sludge samples of Siri Island in the south of Iran and produced a strong, thermo stable microbial

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demulsifier on glucose as a sole carbon source supplemented with yeast extract (50). The optimum values of temperature, inoculum concentration, pH and culture age for microbial demulsifier production were 25°C, 108 CFU/mL, 7 and 24 hours, respectively. The maximum demulsification activity and the half-life value of culture broth measured for a water-in-crude oil emulsion were 96.4% and 36 hour at 80°C in flask. The demulsifier was purified to homogeneity using cold ethanol. For 4.33 mg/mL of partially purified microbial demulsifier, the half-life value for the water in oil model emulsion was 3 hour.

The application of microbial biosurfactants as potential Bio-based demulsifers of petroleum derivatives in water emulsions was investigated by some researchers. Biosurfactants crude extracts, produced by yeasts (Candida guilliermondii, Candida lipolytica and Candida sphaerica) and bacteria (Pseudomonas aeruginosa, Pseudomonas cepacia and Bacillus sp.) grown in industrial residues, were tested for demulsifcation capacity in their crude and pure forms. The best results obtained were for bacterial biosurfactants, which were able to recover about 65% of the seawater emulsifed with motor oil compared to 35–40% only for yeasts products. They also tested biosurfactants with oil-in-water and water-in-oil kerosene model emulsions. No relationship between interfacial tension, cell hydrophobicity and demulsifcation ratios was observed with all the biosurfactants tested. Microscopic illustrations of the emulsions in the presence of the biosurfactants showed the aspects of the emulsion and demulsifcation process. The results obtained demonstrated the potential of these agents as demulsifers in marine environments (51).

Economical and environmentally-friendly biosurfactant de-emulsifiers have also been formulated. Biosurfactant-producing bacteria from oil-contaminated soil samples from Nigerian National Petroleum Corporation (NNPC) depot Apata, Ibadan, Oyo State of Nigeria was isolated and applied on crude oil emulsions for the purpose of separating water-in-crude oil emulsions. Thirty-five of 41 bacterial strains were further screened for ability to de-emulsify hydrocarbon, using vapour transfer method. Highest displayed de-emulsification activities at 24 hours were Pseudomonas sp. AGO1 (50.0%), Bacillus sp. DPK1A (50.0%), Bacillus subtilis AGO1A (50.0%), Pseudomonas aeruginosa DPK3A (55.7%) and Bacillus subtilis PMS1B2 (66.0%); and at 48 hours were, Bacillus subtilis AGO1A (50.0%), Ps. aeruginosa DPK3A (60.0%) and Bacillus subtilis PMS1B2 (66.7%) (52). Higher de-emulsification activities were recorded on supplementation of growth media, with Ps. aeruginosa DPK3A showing the highest de-

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emulsification activity of 66% when grown on growth media supplemented with glucose and yeast extract, at temperature of 60°C. They compared with chemical de-emulsifier. Microbial demulsifier produced 66%, 62% and 60% volume of water, while chemical de-emulsifier produced 63%, 60% and 66.2% volume of water. This study demonstrated that biosurfactant-producing bacteria, especially the Bacillus species isolated from crude oil-contaminated soils, when cultured on appropriate medium is effective in diesel degradation and treatment of water-in-crude oil emulsion; thus, reducing cost and environmental pollution (52).

3.2.1 Mechanism of demulsification

The amphipathic characteristics of biosurfactant allow several properties such as detergency, emulsification, demulsification, lubrication, foaming, solubilization and phase dispersion, which allows application in the recovery of water and soil contaminated by hydrocarbons (53), heavy metals (54), and cleaning of oil spills (55), as well as in other industries.

Biosurfactants are produced by microbial cultures grown on water miscible and/or immiscible substrates and are generally classified into low molecular-mass molecules (lipopeptides, glycolipids and phospholipids) and high molecular-mass polymers (polymeric and particulate surfactants). Rhamnolipids, sophorolipids and trehalolipids are the best known glycolipids, while the lipopeptide Surfactin is one of the most powerful biosurfactant (55).

Biosurfactants reduce surface and interfacial tension, thereby increasing the solubility of hydrophilic molecules. At a given concentration of surfactant, molecular aggregations, denominated micelles are formed. The critical micelle concentration (CMC) is that in which the lowest stable surface tension is reached (56).

In the demulsification process, the biodemulsifier is adsorbed to the water–oil interface and reacts with the emulsifier, resulting in the removal of the thin film from the surface of the droplets in the emulsion, which causes coalescence, followed by the settling of the droplets and clarification of the continuous phase (57).

3.3 Plant extract in Demulsification of Emulsion

Extracts from green tea and some vegetable oil such as the olive and coconut oil have been used as green demulsifiers. The plant extract was obtained using the soxhlet extraction method while the vegetable oil was obtained from 100% coconut oil. The composition of the plant extract was determined using Gas Chromatography with Mass Spectroscopy. In order to provide the

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significant impact of the plant extracts and also as the comparison purpose, blend demulsifier was formulated from local materials such as starch, camphor, Calcium Hydroxide ($Ca(OH)_2$), Sodium Hydroxide (NaOH), paraffix wax, liquid soap and distilled water. Bottle test were conducted under static and dynamic conditions to select the best demulsifier among the green tea leaf extract, coconut oil and olive oil. It was discovered that coconut oil extracted more water than the green tea leaf extract and olive oil. The blend demulsifier containing coconut oil, sodium hydroxide and other local materials performed better than the other blend demulsifiers but not as good as the coconut oil alone (15).

The usage of plant extracts such as coconut oil, olive oil, bio-furfural, lemon seed oil, pine oil, cotton seed oil, and papaya extract as a suitable green demulsifier have been carried out. Further tests was also carried out to determine the eco friendliness of the extracts. The results showed that coconut oil and cotton seed oil gives the best results while cotton seed oil is more economic 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 and conventional solvent extraction with ethanol was also used. Gas Chromatography with Mass Spectroscopy was carried out to ascertain the composition of the extract. Results obtained tally with literature. The performance of the demulsifier was expressed in terms of percentage of water separated from 100 ml of the oil samples. The performance of the chemical demulsifier and synthesized demulsifier increased with increase in volume of demulsifier. The extracted demulsifier performed better than the chemical demulsifier under all the experimental conditions adopted in the study. The highest efficiency of the bio-demulsifier was obtained with a volume of 5 mL of the extract, at a temperature of 70^0 C and separation time of 60 minute. A water separation efficiency of 85.6% was obtained as compared to the chemical demulsifier, which gave an efficiency of 80.2% (58).

3.3.1 Mechanism of Demulsification

There are two main plant compositions that are able to break the emulsion by specific approaches. They are the hexane group and octadecenoic acid. Both compositions can react with surfactant to flocculate and coalesce the water droplet.

Once the emulsifier is injected into the emulsifying agent was displaced by the emulsifier as the surface active character causing lower surface tension and interfacial energy of the water

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droplets. The water droplets moved towards each other and flocculate. The large droplets that resulted from the flocculation process coalesced to form larger droplets. These coalesced droplets moved downward through the oil and finally settled out at the bottom of the treating vessel due to gravity.

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.

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.

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

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